

- Q1.** Give the number of unpaired electrons
(a) La^{3+} ($Z = 57$) (b) Ce^{2+} ($Z = 63$)
- Q2.** Which of the following has maximum unpaired electron $_{22}\text{Ti}^{3\oplus}$, $_{23}\text{V}^{3\oplus}$, $_{26}\text{Fe}^{2\oplus}$.
- Q3.** Write the electronic configurations of the elements with the atomic numbers 70 and 63.
- Q4.** Write the electronic configurations of the elements with the atomic numbers 61 and 91.
- Q5.** Write down the electronic configuration of Tn^{4+} (90), La^{2+} (57).
- Q6.** Write down the electronic configuration of Pm^{3+} (61), Lu^{2+} (71).
- Q7.** Write down the electronic configuration of Cr^{3+} (24), Ce^{4+} (63).
- Q8.** Of the ions CO^{2+} , Sc^{3+} and Cr^{3+} , which ones will give coloured aqueous solutions and how will each of the respond to a magnetic field and why?
- Q9.** Ti^{4+} complexes are diamagnetic or paramagnetic and why?
- Q10.** Use Hund's rule to derive the electronic configuration Ce^{3+} ion and calculate its magnetic moment on the basis of 'spin-only' formula.
- Q11.** Calculate the spin only magnetic moment of M^{2+} ($Z = 27$).
- Q12.** Why does Mn (II) show maximum paramagnetic character amongst the bivalent ions of the first transition series? Calculate the theoretical value of magnetic moment.
- Q13.** What may be stable oxidation state of the transition element with the following d -electron configuration in the ground state of their atoms : $3d^3$, $3d^5$, $3d^8$, and $3d^4$?
- Q14.** Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only?
- Q15.** Which is the most common oxidation state of lanthanides and how is it formed? Give its configuration.
- Q16.** Which of the $3d$ series of the transition metals exhibits the largest number of oxidation states and why?
- Q17.** What are inner transition elements? Decide which of the following atomic numbers are the atomic numbers of the inner transition elements : 29, 59, 74, 95, 102, 104.
- Q18.** Scandium ($Z = 21$) is a transition element but zinc ($Z = 30$) is not. Explain.
- Q19.** Which of the two ferrous or ferric ion has larger magnetic moment and why?
- Q20.** Giving reasons indicate which one of the following would be coloured?
 Cu^+ , VO^{2+} , Sc^{3+} , Ni^{2+} , (At. no. of Cu = 29, V = 23, Sc = 21, Ni = 28)
- Q21.** What is the highest oxidation state of transition elements?

- Q22. Write the highest oxidation state of the element with atomic number 23.
- Q23. A transition element has a configuration $[\text{Ar}]3d^4$ in its +3 oxidation state. What is its atomic number?
- Q24. What are the different oxidation states exhibited by the lanthanoids?
- Q25. What are interstitial compounds? Mention their two important properties.
- Q26. What happens when KMnO_4 is heated? Give chemical equation.
- Q27. Why is KMnO_4 kept in dark bottles?
- Q28. Write the ionic equation representing the oxidising property of acidified KMnO_4 solution.
- Q29. Why does V_2O_5 act as catalyst?
- Q30. Why is $\text{K}_2\text{Cr}_2\text{O}_7$ generally preferred over $\text{Na}_2\text{Cr}_2\text{O}_7$ in volumetric analysis though both are oxidising agents?
- Q31. Which is more basic $\text{La}(\text{OH})_3$ or $\text{Lu}(\text{OH})_3$? Why?
- Q32. Name the oxo metal anions of the first series of the transition metals in which the metal exhibits the oxidation state equal to its group number.
- Q33. Why do Zr and Hf exhibit similar properties?
- Q34. Why is that orange solution of $\text{K}_2\text{Cr}_2\text{O}_7$ turns yellow on adding NaOH to it?
- Q35. To what extent do the electronic configurations decide the stability of oxidation states in the first series of the transition elements? Illustrate your answer with examples.
- Q36. Why is first ionization energy of Cu higher than that of sodium?
- Q37. The first ionization energy of Zn is considerably high than the other members of first transition series.
- Q38. Explain briefly how +2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number?
- Q39. How would you account for the irregular variation of ionisation enthalpies (first and second) in the first series of transition elements?
- Q40. Name a transition element which does not exhibit Variable oxidation states.
- Q41. Fe^{3+} is more stable than Fe^{2+} . Explain.
- Q42. Which metal in the first transition series exhibits +1 oxidation state most frequently and why?
- Q43. Why are Mn^{2+} compounds more stable than Fe^{2+} towards oxidation to their +3 state?
- Q44. The $E^{\ominus 1.0}(\text{M}^{2+} | \text{M})$ value for copper is positive (+0.34V). What is possible reason for this?
- Q45. In the series Se (Z = 21) to Zn (Z = 30), the enthalpy of zinc atomization is the lowest (126 kJ mol^{-1}). Why?
- Q46. Why do transition elements exhibit higher enthalpies of atomization?
- Q47. The electronic configuration of Co^{2+} and Cu^{2+} is d^7 and d^9 respectively, which of these ions is expected to be more paramagnetic?

- Q48. Why is radius of Fe^{2+} less than that of Mn^{2+} ?
- Q49. In the transition series, with an increase in atomic number the atomic radius does not change very much. Why is it so?
- Q50. Why is the third ionization energy of manganese (At. no. = 25) unexpectedly high?
- Q51. Why are transition elements known as *d*-block element?
- Q52. The Chemistry of the actinoid elements is not so smooth as that of the lanthanoids. Justify this statement by giving some examples from the oxidation state of these elements.
- Q53. What are the alloys? Name an important alloy, which contains some of the lanthanoid metals. Mention its uses.
- Q54. Explain why Cu^+ ion is not stable in aqueous solution?
- Q55. Which is a stronger reducing agent Cr^{2+} or Fe^{2+} and why?
- Q56. Copper is regarded as transition metal though it has completely filled *d*-orbitals (d^{10}). Explain.
- Q57. Explain as to why the E^\ominus value for the $\text{Mn}^{3+}/\text{Mn}^{2+}$ with $\text{Fe}^{3+}/\text{Fe}^{2+}$ or $\text{Cr}^{3+}/\text{Cr}^{2+}$.
- Q58. Write the names of three coloured compounds of Ag.
- Q59. Why Zn, Cd and Hg are not regarded as transition element?
- Q60. Why the melting point of transition elements are high?
- Q61. Which transition metal has highest density?
- Q62. Give one example of any compound in which the oxidation state of Ni is zero.
- Q63. What is chromic acid?
- Q64. Name the following:
- Divalent ion of first transition series having maximum magnetic moment.
 - Coloured ion out of Cu^+ or Cu^{2+} .
 - Two ions of first transition series having dipole moment.
- Q65. (a) Of the ions Ag^+ , CO^{2+} and Ti^{4+} , which one will be coloured in aqueous solutions.
(b) If each one of above species is in turn placed in a magnetic field, how will it respond and why?
- Q66. What may be the stable oxidation state of the transition elements with the following *d*-electron configuration the ground state of their atoms?
 $3d^3$, $3d^5$, $3d^8$, and $3d^4$
- Q67. The melting and boiling points of Zn, Cd and Hg are low. Why?
- Q68. What happens when $\text{K}_2\text{Cr}_2\text{O}_7$ is treated with $\text{Pb}(\text{NO}_3)_2$?
- Q69. What happens when potassium dichromate is heated with sodium chloride and conc. H_2SO_4 ?
- Q70. Explain how the colour of $\text{K}_2\text{Cr}_2\text{O}_7$ solution depends on pH of the solution.

- Q71. What is the most common form of chromium in basic solution? What ion forms when a basic solution of chromium is acidified?
- Q72. In moist air, copper corrodes to produce a green layer on its surface. Explain.
- Q73. Why is KMnO_4 solution used to clean surgical instruments in hospitals?
- Q74. How many water molecules are involved in coordination in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$?
- Q75. Actinoid contraction is greater from element to element than lanthanoid contraction. Why?
- Q76. Transition metals of 3d-series do not react readily with dilute acids to liberate hydrogen although they have high negative reduction potential values. Explain.
- Q77. Why the transition elements act as catalysts? Give an examples of the reactions catalysed by them.
- Q78. What is the effect of pH on the colour of the solution of potassium dichromate?
- Q79. Why transition form complexes? What types of bond is present in these compounds?
- Q80. Silver is a transition metal but zinc is not. Why?
- Q81. Chromium is a typical hard metal while mercury is a liquid. Why?
- Q82. The standard reduction potentials of Co^{2+} and Co^{3+} are -0.28 V and 1.8 V respectively. which should be a better oxidising agent in water : Co^{2+} or Co^{3+} ?
- Q83. K_2PtCl_6 is known but Ni compound is not known. State a reason for it.
- Q84. What is the effect of increasing pH on $\text{K}_2\text{Cr}_2\text{O}_7$ solution?
- Q85. Why is that orange solution of $\text{K}_2\text{Cr}_2\text{O}_7$ turns yellow on adding NaOH to it?
- Q86. Write the complete chemical equation for the following: An alkaline solution of KMnO_4 reacts with an potassium iodide.
- Q87. What happens when SO_2 gas is passed through acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution?
- Q88. On the basis of the standard electrode potential values stated for acid solutions, predict whether Ti^{4+} species may be used to oxidise Fe^{II} to Fe^{III} .
- | Reaction | E^-/V |
|--|----------------|
| $\text{Ti}^{\text{IV}} + e^- \longrightarrow \text{Ti}^{3+}$ | : + 0.01 |
| $\text{Fe}^{3+} + e^- \longrightarrow \text{Fe}^{2+}$ | : +0.77 |
- Q89. How is the magnetic moment of a species related to the number of unpaired electrons?
- Q90. Though both Cr^{2+} and Mn^{3+} have d^4 configuration, yet Cr^{2+} is reducing while Mn^{3+} is oxidising. Explain why?
- Q91. Copper is soluble in dil. HNO_3 but not in dil. HCl .
- Q92. Why is $\text{K}_2\text{Cr}_2\text{O}_7$ generally preferred over $\text{Na}_2\text{Cr}_2\text{O}_7$ in volumetric analysis although both are oxidising agents?
- Q93. The properties of lanthanides are fairly similar, while the properties of actinides are considerably different from each other. Explain.

- Q94. Give KMnO_4 oxidising reaction in acidic medium with NO_2^- .
- Q95. Give KMnO_4 oxidising reaction in acidic medium with SO_3^{2-} .
- Q96. Give KMnO_4 oxidising reaction in acidic medium with S^{2-} .
- Q97. Give KMnO_4 oxidising reaction in acidic medium with oxalate ion.
- Q98. Give KMnO_4 oxidising reaction in acidic medium with Fe^{2+} .
- Q99. Give KMnO_4 oxidising reaction in acidic medium with I^- .
- Q100 Which is the last element in the series of the actinoids? Write the electronic configuration of this element. Comment on the possible oxidation state of this element.
- Q101 What is the most common oxidation state exhibited by Scandium, manganese, chromium.
- Q102 CrO_3 is an acid hydride. Explain.
- Q103 What is the most characteristic oxidation state of lanthanoids ?
- Q104 What happens when zinc oxide is dissolved in NaOH ?
- Q105 Give KMnO_4 oxidising reaction in neutral or faintly alkaline solutions with I^- .
- Q106 Give oxidising action of $\text{K}_2\text{Cr}_2\text{O}_7$ in acidic medium with Sn^{2+} .
- Q107 Give oxidising action of $\text{K}_2\text{Cr}_2\text{O}_7$ in acidic medium with Fe^{2+} .
- Q108 Give KMnO_4 oxidising reaction in neutral or faintly alkaline solutions with $\text{S}_2\text{O}_3^{2-}$.
- Q109 Give oxidising action of $\text{K}_2\text{Cr}_2\text{O}_7$ in acidic medium with I^- .
- Q110 Give oxidising action of $\text{K}_2\text{Cr}_2\text{O}_7$ in acidic medium with H_2S .
- Q111 Give preparation reaction of Potassium permanganate, KMnO_4 .
- Q112 Give preparation reaction of Potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$.
- Q113 (a) Write a metal oxide compound for manganese in each of the following oxidation states: +2, +3, +4, +6, +7.
(b) List these metal oxides in the decreasing acidic character.
- Q114 Complete the following reaction equations:
- (a) $\text{Cr}_2\text{O}_7^{2-} + \text{Sn}^{2+} + \text{H}^+ \longrightarrow$
- (b) $\text{MnO}_4^- + \text{Fe}^{2+} + \text{H}^+ \longrightarrow$

- Q115 The sum of first and second ionisation energies and those of third and fourth ionisation energies of nickel and platinum are given below:

	$IE_1 + IE_2$ (kJ mol^{-1})	$IE_3 + IE_4$ (kJ mol^{-1})
Ni	2.49	8.80
Pt	2.66	6.70

Taking these values into account write:

- (a) The most common oxidation state for Ni and Pt and its reason.
- (b) The name of this metal (Ni or Pt) which can form compounds in +4 oxidation state more easily and why?

Q116 Write balanced ionic equation for what happens when:

- Acidified potassium permanganate solution is treated with an oxalate ion in solution.
- An iodide ion is treated with an acidified dichromate ion in solution.

Q117 Draw the structure of chromate and dichromate ions.

Q118 Why are Ni^{2+} compounds thermodynamically more stable than Pt^{2+} compounds, whilst Pt^{4+} compounds are relatively more stable than Ni^{4+} compounds?

Q119 What happens when

- Potassium dichromate reacts with sulphur dioxide in acidic medium?
- Potassium dichromate reacts with Mohr's salt in presence of dil. H_2SO_4 ?

Q120 Complete the following chemical equation:

- $\text{MnO}_4^- (\text{aq}) + \text{S}_2\text{O}_3^{2-} (\text{aq}) + \text{H}_2\text{O}(\text{l}) \longrightarrow$
- $\text{Cr}_2\text{O}_7^{2-} (\text{aq}) + \text{Fe}^{2+} (\text{aq}) + \text{H}^+ (\text{aq}) \longrightarrow$

Q121(a) Of the ions Ag^+ , Co^{2+} and Ti^{4+} which ones will be coloured in aqueous solution?

- If each one of the above ionic species is in turn placed in a magnetic field, how will it respond and why?

Q122 The second and third members in each group of the transition elements have similar atomic radii. Explain.

Q123 The atomic radii of the elements in a transition series do not vary much while they do vary in the case of s and p-block elements. Explain.

Q124 Discuss the chromyl chloride test.

Q125 What is meant by 'disproportion'? Give two examples of disproportion reaction in aqueous solution?

Q126 How is the variability in oxidation states of transition metals different from that of the non-transition metals? Illustrate with examples.

Q127(a) Write the steps involved in the preparation of $\text{K}_2\text{Cr}_2\text{O}_7$ from Na_2CrO_4 .

- What effect does lanthanoid contraction have on the chemistry of the elements which follow lanthanoids?

Q128 Explain why the first ionisation energies of the elements of the first transition series do not vary much with increasing atomic number?

Q129 Predict which of the following will be coloured in aqueous solution Ti^{3+} , V^{3+} , Cu^+ , Sc^{3+} , Mn^{2+} , Fe^{3+} and Co^{2+} . Give reason for each.

Q130(a) Actinide contraction is greater from element to element than lanthanide contraction. Why?

- The outer electronic configuration of two members of the lanthanide series are as follows:



What are their atomic numbers? Predict the oxidation states exhibited by these elements in their compounds.

Q131 How would you account for the following :

- (a) Of the d^4 species, Cr^{2+} is strongly reducing while Mn(III) is strongly oxidising.
- (b) Cobalt (II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised.
- (c) The d^1 configuration is very unstable in ions.

Q132 Which of the following give coloured aqueous solutions: Co^{2+} , Sc^{3+} , Cr^{3+} ? How will each of these respond to magnetic field and why? (Atomic no. Co = 27, Sc = 21 and Cr = 24).

Q133 Why Transition elements form (a) Interstitial compounds (b) Alloys?

Q134 Compare the chemistry of actinoids with that of the lanthanoids with special reference to :

- (a) Electronic configuration
- (b) Oxidation state
- (c) Atomic and ionic sizes

Q135(a) Give balanced chemical equations of two reactions in which KMnO_4 acts as an oxidising agent in the acidic medium.

(b) Give reasons:

- (i) Cr^{2+} is a strong reducing agent whereas Mn^{2+} is not. [Cr = 24, Mn = 25]
- (ii) The transition metal ions such as Cu^+ , Ag^+ and Sc^{3+} are colourless.
- (iii) Chemistry of the actinoids is much more complicated than that of the lanthanoids.

Q136(a) Explain the following

- (i) Transition elements tend to be unreactive with increasing atomic number in the series.
- (ii) d -block elements exhibit more oxidation states than f -block elements.
- (b) A green chromium compound (A) on fusion with alkali gives a yellow compound (B) which on acidification gives an orange coloured compound (C). 'C' on treatment with NH_4Cl gives an orange coloured product (D), which on heating decomposes to give back (A). Identify A, B, C and D. Write equations for reactions.

Q137 Explain:

- (a) Why are Sm^{2+} , Eu^{2+} and Yb^{2+} good reducing agents?
- (b) Can lanthanum ($Z = 57$) exhibit +4 oxidation state?
- (c) Why are +3 oxidation state of gadolinium ($Z = 64$) and lutetium ($Z = 91$) especially stable?
- (d) Why do Zr and Hf exhibit similar properties?

Q138 Explain the following:

- (a) A dark blue precipitate is formed when sodium hydroxide solution is added to copper sulphate solution. The precipitate darkens on heating.
- (b) Cuprous chloride is insoluble in water and dilute HCl but dissolves in concentrated HCl.
- (c) CuS is not precipitated by passing H_2S through copper sulphate solution containing KCN.
- (d) Silver nitrate solution is kept in dark coloured bottles.

Q139 What happens when?

- (a) Silver chloride is treated with aqueous sodium cyanide and the product thus formed is allowed to react with zinc in alkaline medium.
- (b) Zinc oxide is treated with excess of sodium hydroxide solution.
- (c) Ammonium thiocyanate is added to ferric chloride solution.

Q140 Explain the following properties of transition elements

- (a) metallic character, (b) ionization energies.

Q141 Why are the ionization energies of 5d elements greater than those of 3d and 4d elements?

Q142 Give example and suggest reasons for the following features of the transition metal chemistry:

- (a) The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.
(b) A transition metal exhibits highest oxidation state in oxides and fluorides.
(c) The highest oxidation state is exhibited in oxoanions of a metal.

Q143 Give chemical reaction of Lanthanides with water, nitrogen sulphur, oxygen or hydrochloric acid.

Q144 Explain the following giving suitable reason:

- (a) Yellow coloured aqueous solution of sodium chromate changes to orange red when CO_2 under pressure is passed.
(b) Green solution of potassium manganate, K_2MnO_4 , turns purple when CO_2 is circulated.

Q145 What is the equivalent mass of KMnO_4 when it acts as an oxidising agent in acidic medium (molecular mass $\text{KMnO}_4 = 158$)?

Q146 (a) Chromium is a typical hard metal while mercury is a liquid. Explain.

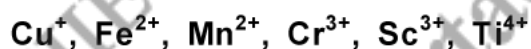
- (b) The melting and boiling points of Zn, Cd and Hg are low. Why?
(c) Though copper, silver and gold have completely filled sets of d-orbitals, yet they are considered as transition metals. Why?

Q147 Assign reason for each of the following:

- (a) Ce^{3+} can be easily oxidised to Ce^{4+} .
(b) E° for $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is more positive than for $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple.
(c) $\text{Lu}(\text{OH})_3$ is a weaker base than $\text{La}(\text{OH})_3$.

Q148 Answer the following;

- (a) Which one of Fe^{2+} and Fe^{3+} ions is more paramagnetic and why?
(b) Which of the following ions are expected to be coloured and why?



- (c) Name the two elements of first transition series which have abnormal electronic configuration and why?
(d) Name the lightest and heaviest elements in terms of density among the transition elements.
(e) How many elements are present in each transition series? Why this number cannot be less or more?

Q149 Explain the following:

- (a) Magnesium oxide is used for lining of steel making furnace.
(b) Cast iron is hard but pure iron is soft in nature.
(c) Fe^{3+} is more stable than Fe^{2+} .
(d) Anhydrous FeCl_3 cannot be obtained by heating hydrated ferric chloride.
(e) The compounds of iron are coloured and paramagnetic.

Q150 What happens when?

- (a) Ferric chloride is added to potassium ferrocyanide.
- (b) Iron reacts with cold dilute nitric acid.
- (c) Potassium ferricyanide is added to ferrous sulphate.
- (d) Excess of potassium iodide is added to mercuric chloride.
- (e) Green vitriol is strongly heated.

Q151 Explain the following:

- (a) Copper is regarded as transition metal though it has completely filled d -orbital (d^{10}).
- (b) Of cobalt and zinc salts, which is attracted in a magnetic field?
- (c) The species $[\text{CuCl}_4]^{2-}$ exist but $[\text{CuI}_4]^{2-}$ does not.
- (d) Copper is largely used in electrical wiring.
- (e) A solution of K_2CO_4 changes colour on being acidified.

Q152 Explain the following:

- (a) Copper (I) salts are not known in aqueous solutions.
- (b) Ferric iodide is very unstable but ferric chloride is not.
- (c) Silver bromide is used in photography.
- (d) Anode mud in copper refining contains silver and gold.
- (e) Silver fluoride is fairly soluble in water while other silver halides are insoluble,

Q153 Explain the following:

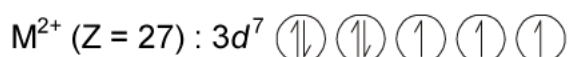
- (a) Mercuric chloride is called corrosive sublimate.
- (b) The colour of mercurous chloride changes from white to black when treated with ammonia solution.
- (c) Excess of carbon is added in the zinc metallurgy.
- (d) Zinc readily liberates hydrogen from cold dilute H_2SO_4 but not from cold concentrated H_2SO_4 .
- (e) The compounds of Zn, Cd and Hg are usually white.

- S1.** (a) ${}_{57}\text{La}^{3+}$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$ unpaired electron = zero
 (b) ${}_{63}\text{Ce}^{2+}$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^7$ unpaired electron = 7
- S2.** ${}_{22}\text{Ti}^{3+}$: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$ unpaired electron - 1
 ${}_{23}\text{V}^{3+}$: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$ unpaired electron - 2
 ${}_{26}\text{Fe}^{2+}$: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ unpaired electron - 4
- S3.** ${}_{70}\text{Z}$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^0$
 ${}_{63}\text{Z}$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^7 5d^0$
- S4.** ${}_{61}\text{Z}$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^4 5d^1$
 ${}_{91}\text{Z}$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^2 6d^1$
- S5.** ${}_{57}\text{La}^{2+}$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 5d^1$
 ${}_{90}\text{Tm}^{4+}$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6$
- S6.** ${}_{61}\text{Pm}^{3+}$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^4$
 ${}_{71}\text{Lu}^{2+}$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^{14} 5d^1$
- S7.** ${}_{24}\text{Cr}^{3+}$: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$
 ${}_{63}\text{Ce}^{4+}$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 5f^5$
- S8.** CO^{2+} and Cr^{3+} will give coloured aqueous solutions because these contain unpaired electrons in outer 3d subshells. CO^{2+} and Cr^{3+} will shown attraction for the magnetic field and will be paramagnetic Sc^{3+} will be repelled by the magnetic field and will be diamagnetic.
- S9.** Diamagnetic, because there is no unpaired electron in Ti^{4+} ($1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^0, 3d^0$).
- S10.** Ce (Z = 58) : $[\text{Xe}]^{54} 4f^1 5d^1 6s^2$
 Ce^{3+} : $4f^1$

No. of unpaired electrons = 1

$$\mu_s = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ B.M.}$$

- S11.** The electronic configuration of M^{2+} (z = 27) is



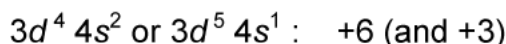
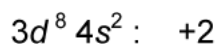
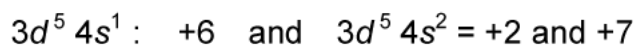
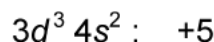
It has 3 unpaired electrons. The spin only magnetic moment is

$$\begin{aligned}\mu_s &= \sqrt{n(n+2)} \\ &= \sqrt{3(3+2)} = \sqrt{15} = 3.87 \text{ BM}\end{aligned}$$

S12. The value of paramagnetic nature depends on the number of unpaired orbitals. Mn (II) possesses maximum number of unpaired orbitals amongst divalent ions of the first transition series and thus, possess maximum value of paramagnetic character.

$$\begin{aligned}\text{Magnetic moment} &= \sqrt{n(n+2)} \\ &= \sqrt{5 \times 7} \quad \text{as } n = 5 \\ &= \sqrt{35} = 5.91 \text{ B.M.}\end{aligned}$$

S13. The stable oxidation states are predicted on the basis that up to Mn, the maximum oxidation states of stability correspond to sum of s and d-electrons. after Mn, there is decrease in the stability of higher oxidation states.



S14. Because oxygen and fluorine have small size and high electronegativity, therefore, they can easily oxidise the metal to its highest oxidation state.

S15. The most common oxidation state of lanthanides is +3. This oxidation state of the lanthanide ions arises due to the loss of two 6s electrons and the one 5d electron, if present from the atom of the elements. If no electron is present in the 5d orbital, then one of electrons from 4f shell is lost. The lanthanides in this state have the general configuration $[\text{Xe}] 4f^{1-14}$.

S16. Mn ($Z = 25$) exhibits the largest number of oxidation states because it has the maximum number of unpaired electrons. Hence, it shows oxidation states from +2 to +7 i.e., +2, +3, +4, +5, +6 and +7.

S17. The inner transition elements are those in which the last electron enters the f-subshell. These include lanthanoids (from atomic number 58–71) and actinoids (from atomic number 90–103). Elements having atomic numbers 59, 95 and 102 are inner transition elements.

S18. Transition elements are those which have partially filled d-subshells in their elementary state or in their commonly occurring oxidation states. Scandium ($Z = 21$) has partially filled d-subshell ($3d^1$) and is therefore, a transition element. On the other hand, zinc ($Z = 30$) has the configuration $3d^{10} 4s^2$. It does not have partially filled d-subshell in its elementary form or in commonly occurring oxidation ionic ($\text{Zn}^{2+} : 3d^{10}$). Therefore, it is not regarded as transition element.

S19. $\text{Fe}^{2+} : [\text{Ar}] 3d^6 : 4$ unpaired electrons

$\text{Fe}^{3+} : [\text{Ar}] 3d^5 : 5$ unpaired electrons

Fe^{3+} has larger magnetic moment because it has more number of unpaired electrons than Fe^{2+} ion.

- S20.** Ni^{2+} because it has incompletely filled d -orbitals.
- S21.** +8 as OsO_4 (Osmanium)
- S22.** The outer electronic configuration will be $3d^3 4s^2$, therefore, the highest oxidation state will be five (equal to the electrons).
- S23.** Atomic No. = (The atomic number of Ar+ d -electrons + oxidation state = $18 + 4 + 3$) = '25'
- S24.** The principal oxidation state of lanthanoids is +3. In addition they exhibit oxidation states of +2 and +4.
- S25.** Those compounds which are formed by elements occupying the voids of transition metals are called interstitial compounds.
- (a) They are non-stoichiometric *i.e.*, their composition is not fixed.
- (b) They have improved properties compared to pure elements *e.g.*, steel does not get rusted whereas iron gets rusted.
- S26.**
$$2\text{KMnO}_4 \xrightarrow{\Delta} \underset{\text{dark pink}}{\text{K}_2\text{MnO}_4} + \underset{\text{green}}{\text{MnO}_2} + \text{O}_2$$
- S27.** KMnO_4 gets decomposed to K_2MnO_4 in presence of light.
- S28.** $\text{MnO}_4^- + 5e^- + 8\text{H}^+ \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$
- S29.** It can form unstable intermediates with the reactants which readily change into products.
- S30.** $\text{Na}_2\text{Cr}_2\text{O}_7$ absorbs moisture from the atmosphere.
- S31.** $\text{La}(\text{OH})_3$ is more basic because of larger size of La than Lu.
- S32.** MnO_4^- : Oxidation state of Mn = +7 (Group No = 7)
 CrO_4^{2-} : Oxidation state of Cr = +6 (Group No = 6)
- S33.** This is because Zr and Hf have similar ionic sizes which is due to lanthanoid contraction.
- S34.** Because dichromate ion convert to coronation.
- $$\underset{\text{(orange)}}{\text{Cr}_2\text{O}_7^{2-}} + 2\text{OH}^- \longrightarrow \underset{\text{(yellow)}}{2\text{CrO}_4^{2-}} + \text{H}_2\text{O}$$
- S35.** In a transition series, the oxidation states which result in half filled and completely filled of d -subshell are more stable. For example, in the first transitions series, electronic configuration of Mn ($Z = 25$) is $[\text{Ar}] 3d^5 4s^2$. It shows oxidation states from +2 to +7 but Mn (II) is most stable because it has stable electronic configuration. Similarly, we can say Zn ($Z = 30$) having electronic configuration $[\text{Ar}] 3d^{10} 4s^2$ exhibits stable +2 oxidation state because of stable completely filled $3d^{10}$ configuration.
- S36.** Cu has d -orbital which is progressively filled and it has poor shielding effect due to which valence electrons are strongly attraction towards nucleus, therefore, it has higher ionization energy.

- S37.** In Zn 3d-subshell contains 10 elements (completely filled), which provides extra stability due to which the value of first ionization energy is higher.
- S38.** as we move in the first row transition elements, the sum of IE_1 and IE_2 increases. as a result reduction potential (E°) becomes less and less negative and hence the stability decreases upto first half of the first row elements.
- S39.** The irregular trends in variation of ionisation enthalpies in the first series of transition elements is because of varying degree of stability of different configurations and atomic size also varying due to screening effect.
- S40.** Scandium ($Z = 21$) does not exhibit variable oxidation states.
- S41.** The electronic configuration of Fe^{2+} and Fe^{3+} ions are:
 $Fe^{2+} : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$
 $Fe^{3+} : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$
- The electronic configuration of Fe^{3+} has half filled subshell and hence it is stable.
- S42.** Copper has electronic configuration $3d^{10} 4s^1$. It can easily lose one ($4s^1$) electron to give stable $3d^{10}$ configuration.
- S43.** Electronic configuration of Mn^{2+} is $[Ar] 3d^5$ which is half filled and hence it is stable. therefore, third ionisation enthalpy is very high *i.e.*, third electron cannot be easily removed. In case of Fe^{2+} , the electronic configuration is $3d^6$. Therefore, Fe^{2+} can easily lose one electron to acquire $3d^5$ stable electronic configuration.
- S44.** The $E^\circ_{(M^{2+}|M)}$ value for copper is positive and this shows that it is least reactive metal among the elements of first transition series. This is because copper has high enthalpy of atomisation and enthalpy of ionization. Therefore, the high energy required to convert $Cu(s)$ to Cu^{2+} is not balanced by its hydration enthalpy.
- S45.** The high enthalpies of atomization of transition elements is due to the participation of electrons ($n - 1$) *d*-orbitals in addition to *ns* electrons in the interatomic metallic bonding. In zinc, no electrons from 3*d*-orbitals are involved in the formation of metallic bonds. On the other hand, in all other metals of 3*d* series electrons from *d*-orbitals are always involved in the formation of metallic bonds.
- S46.** The high enthalpies of atomization are due to large number of unpaired electrons in their atoms. Therefore, they have stronger interatomic interactions and hence, stronger bonding between atoms. Thus, they have high enthalpies of atomization.
- S47.** Co^{2+} is more paramagnetic than Cu^{2+} because Co^{2+} has 3 unpaired electrons whereas Cu^{2+} has 1 unpaired electron.
- S48.** Fe^{2+} has lesser radius than Mn^{2+} because effective nuclear charge is more in Fe^{2+} as compared to Mn^{2+} atomic number of Fe is 26 and Mn is 25.
- S49.** As one proceeds along a transition series, the nuclear charge increases which tends to decrease the size but the addition of electrons in the *d*-subshell increases the screening effect which counter balances the effect of increased nuclear charge.

S50. The bivalent ion Mn^{2+} has configuration $[\text{Ar}] 3d^5$ which is a stable configuration. So the third ionization energy of manganese is unexpectedly high.

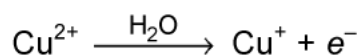
S51. Because the last electron enters in $(n - 1)d$ -orbital of the penultimate shell, having partially filled d orbital in neutral and ionic state. (Zn , Cd , Hg) are not transitional.

S52. Lanthanoids show limited number of oxidation states, such as +2, +3 and +4 (+3 is the principal oxidation state). This is because of large energy gap between $5d$ and $4f$ subshells. On the other hand, actinoids also show principal oxidation state of +3 but show a number of other oxidation states also. For example, uranium ($Z = 92$) exhibits oxidation states of +3, +4, +5, +6, and +7 and neptunium ($Z = 94$) shows oxidation states of +3, +4, +5, +6 and +7. This is because of small energy difference between $5f$ and $6d$ orbitals.

S53. An alloy is a homogeneous mixture of two or more metals or metals and non-metals.

An important alloy of lanthanoid metals is misch metal. It contains about 95% lanthanoid metal and about 5% iron and traces of S, C, Ca or Al. It is used in magnesium based alloy to produce bullets, shells and lighter flints.

S54. Cu^+ is not stable in aqueous solution because of its less negative enthalpy of hydration.



S55. Cr^{2+} is a stronger reducing agent than Fe^{2+} . This is because the configuration of Cr^{2+} changes from d^4 to d^3 Cr^{3+} and d^3 configuration is stable being half filled t_{2g} level.

S56. This is because copper ion, Cu^{2+} has partially filled d -orbitals (d^9).

S57. Mn^{2+} has $3d^5$ electronic configuration. It is stable because half filled configuration of d -subshell. Therefore, Mn has very high third ionization enthalpy for the change from d^5 to d^4 and it is responsible for much more positive E^\ominus value for $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple in comparison to $\text{Cr}^{3+}/\text{Cr}^{2+}$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$ couples.

S58. (a) Silver chromate (Ag_2CrO_4), silver iodide (AgI) and silver oxide (Ag_2O).

S59. Because they have the completely filled d -sub-shell with outer electronic configuration $(n - 1)d^{10}ns^2$.

S60. The melting point of transition elements are high due to the presence of strong intermetallic bonds and covalent bonds, which are formed due to d - d overlapping of unpaired d -electrons.

S61. Osmium.

S62. $[\text{Ni}(\text{CO})_4]$, tetracarbonyl nickel.

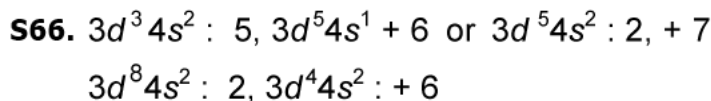
S63. Mixture of $\text{K}_2\text{Cr}_2\text{O}_7$ and conc. H_2SO_4 is known as chromic acid, which is used cleaning of glass apparatus in laboratory.

S64. (a) Mn^{2+}

(b) Cu^+

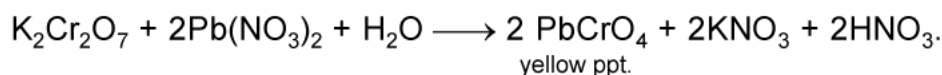
(c) Sc^{3+} , Zn^{2+}

- S65.** (a) Of the ions Ag^+ ($4d^{10}$), Co^{2+} ($3d^7$) and Ti^{4+} ($3s^2 3p^6$), Co^{2+} will be coloured in aqueous solution because it contains unpaired electrons in d -subshell.
- (b) Co^{2+} will be attracted by the magnetic field and is paramagnetic.
 Ag^+ and Ti^{4+} will be repelled by the magnetic field and are diamagnetic.



- S67.** In Zn, Cd and Hg, all the electrons in d -subshell are paired. Hence, the metallic bonds present in them are weak. Therefore, they have low melting and boiling points.

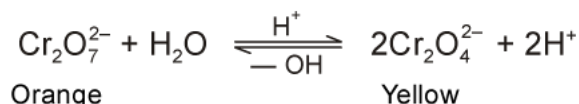
- S68.** Yellow precipitate of PbCrO_4 is formed.



- S69.** It gives orange red vapours of chromyl chloride.



- S70.** In the solution, the following equilibrium exists:

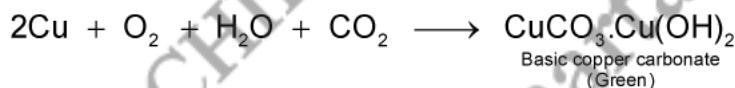


In acidic medium ($\text{pH} < 7$), it exists as $\text{Cr}_2\text{O}_7^{2-}$ ions and hence has orange colour. In basic medium ($\text{pH} > 7$), it exists as CrO_4^{2-} ions and therefore, has yellow colour.

- S71.** In basic solution, the most stable form is chromate ion, CrO_4^{2-} .

In acidic medium, it becomes dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$.

- S72.** In the presence of moist air, a thin film of green basic copper carbonate is formed on its surface and therefore, it corrodes.



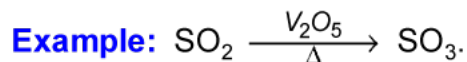
- S73.** Because of the germicidal action of KMnO_4 .

- S74.** Four water molecules are coordinated to Cu^{2+} ion and fifth is attached to anion by hydrogen bonding.

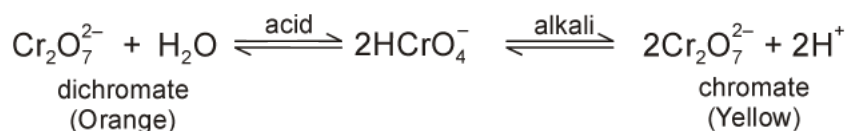
- S75.** This is because of relatively poor shielding by $5f$ electrons in actinoids in comparison with shielding of $4f$ electrons in lanthanoids.

- S76.** Most of the transition metals have the tendency to form a protective layer of their oxides on the surface. This oxide layer is somewhat inert and does not permit the metals to react with dilute acids to liberate hydrogen.

- S77.** (a) Transition metals show variable oxidation states, therefore, they can form intermediate products of different reactant molecules.
- (b) Transition elements are capable to form interstitial compounds due to which they can absorb and activate reacting molecules.



- S78.** At lower pH, the colour of the solution is orange due to the presence of dichromate ions ($\text{Cr}_2\text{O}_7^{2-}$). But in alkaline pH, the colour of the solution changes to yellow due to the conversion of ions to chromate ions.



- S79.** Transition elements form complexes because of the following reasons:

- (a) due to small size and high effective nuclear charge they can attract the electron pairs of ligand molecules;
- (b) they have vacant *d*-orbitals of appropriate energies to accommodate the electron pairs of ligands. *eg.*, $[\text{Fe}(\text{CN})_6]^{4-}$ ($\text{Cu}(\text{NH}_3)_4$)²⁺.

- S80.** According to definition, transition elements are those which have partially filled *d*-subshell in their elementary state or in their one of the oxidation states. Silver ($Z = 47$) can exhibit +2 oxidation state in which it has incompletely filled *d*-subshell ($4d^9$ configuration). Hence, silver is regarded as a transition element.

On the other hand, zinc ($Z = 30$) has the configuration $3d^{10} 4s^2$. It does not have a partially filled *d*-subshell in its elementary form or in its commonly occurring oxidation state ($\text{Zn}^{2+}; 3d^{10}$). Therefore, it is not regarded as a transition element.

- S81.** In chromium, the *M—M* interactions are strong due to the presence of six unpaired electrons in the *3d* and *4s* subshell. On the other hand, in mercury all the electrons in the *5d* and *6s* subshell are paired and therefore, the *M—M* interactions are weak. Therefore, chromium is a typical hard metal while mercury is liquid.

- S82.** Since the standard reduction potential of Co^{3+} is larger than that of Co^{2+} , it suggests that Co^{3+} can be more easily reduced. Therefore, it is a better oxidising agent than Co^{2+} .

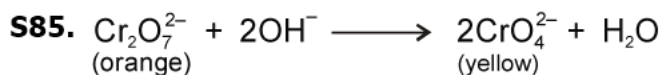
- S83.** This is because Pt^{4+} is more stable than Ni^{4+} as the sum of four ionisation energies of Pt is less than that of Ni.

- S84.** The following equilibrium exists in $\text{K}_2\text{Cr}_2\text{O}_7$ solution.

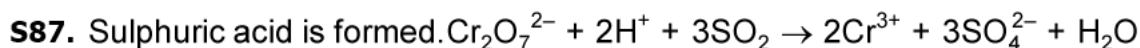
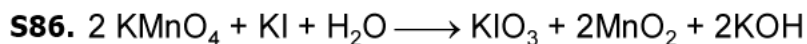


When *pH* is less than 7 (acidic medium), it exists as $\text{Cr}_2\text{O}_7^{2-}$ and has an orange colour.

When *pH* is greater than 7 (basic medium), it exists as CrO_4^{2-} and has a yellow colour.



It is due to formation of chromate ion.



S88. Since $\text{Ti}^{4+} | \text{Ti}^{3+}$ has lower reduction potential than $\text{Fe}^{3+} | \text{Fe}^{2+}$, It cannot be reduced comparison with $\text{Fe}^{3+} | \text{Fe}^{2+}$ ions. Hence, Ti^{4+} cannot oxidize Fe^{2+} to Fe^{3+} .

S89. Magnetic moment, μ_{eff} , can be calculated with the help of following relation,

$$\mu_{\text{eff}} = \sqrt{n(n+2)} \text{ B. M.}$$

Where n is the number of unpaired electrons in the ion or atom and B. M. is Bohr Magnetron (unit of magnetic moment)

If any ion contains two unpaired electron (eg₂₂ Ti^{2+}) the magnetic moment will be 2.76 B.M.

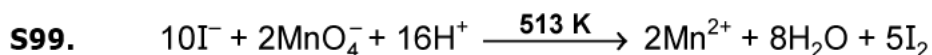
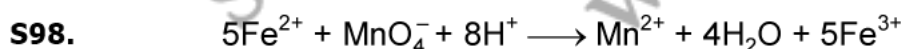
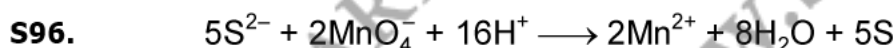
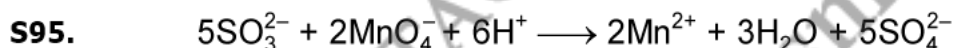
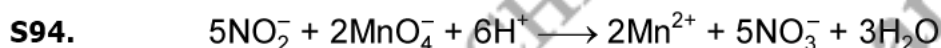
$$\mu_{\text{eff}} = \sqrt{2(2+1)} = 2.76 \text{ B. M.}$$

S90. Cr^{2+} is reducing because its configuration changes from $3d^4$ to $3d^3$. The $3d^3$ configuration is stable because Mn^{2+} on changing to Mn^{3+} becomes stable because of half filled d^5 configuration which has extra stability.

S91. The standard electron potential (E^0) of Cu (0.34) is higher than the E^0 of Hydrogen (zero), hence it can not liberate H_2 from acids, but it dissolves in HNO_3 . Because HNO_3 is a strong oxidising agent and can oxidise copper.

S92. Because $\text{Na}_2\text{Cr}_2\text{O}_7$ is hygroscopic (absorbs moisture), hence it is difficult to prepare its standard solution for volumetric analysis, but because of nonhygroscopic nature of $\text{K}_2\text{Cr}_2\text{O}_7$ its standard solution can be prepared.

S93. In lanthanides the energy difference between $4f$ and $5d$ orbitals is large, therefore, the properties of lanthanides are nearly same. In actinides the energy difference between $5f$ and $6d$ orbitals is small, therefore, the properties of actinides are considerably different from each other.



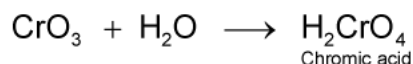
S100 Last actinoid is lawrencium ($Z = 103$)

Electronic configuration : $[\text{Rn}]^{86} 5f^{14} 6d^1 7s^2$

Possible oxidation state : +3

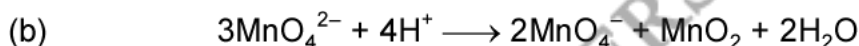
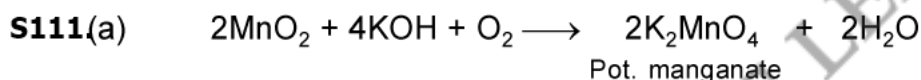
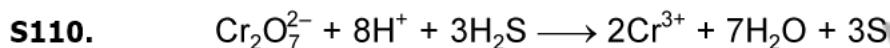
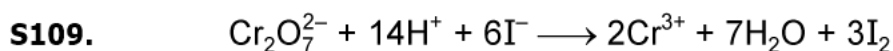
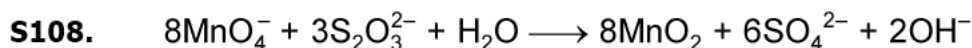
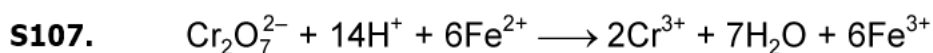
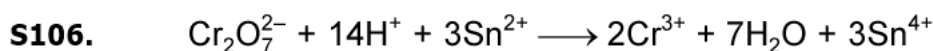
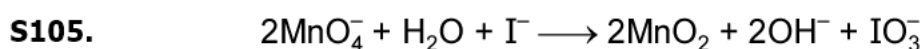
S101.+3

S102. CrO_3 readily dissolves in water to give chromic acid, which acts as strong acid. Therefore, CrO_3 is an acid anhydride.

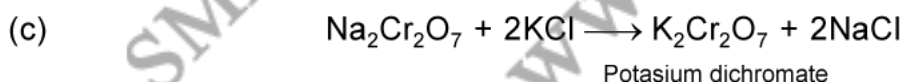
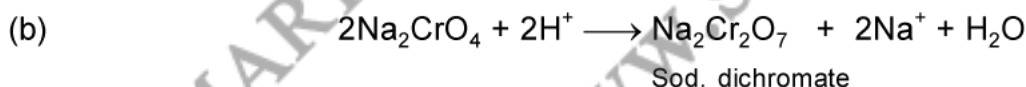
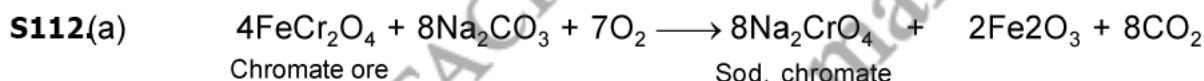


S103.+3

S104. Sodium zincate is formed. $\text{ZnO} + 2\text{NaOH} + \text{H}_2\text{O} \rightarrow \text{Na}_2[\text{Zn}(\text{OH})_4]$

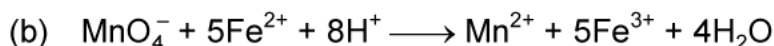
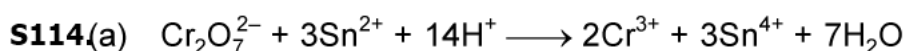


OR



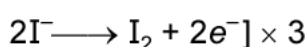
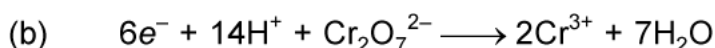
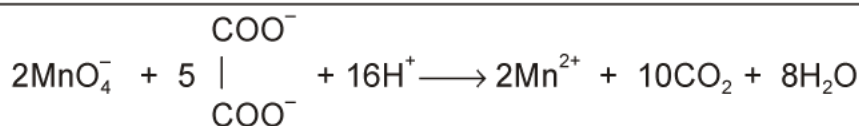
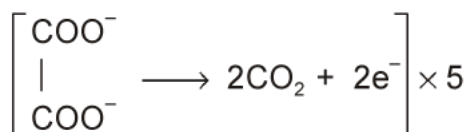
S113(a) MnO , Mn_2O_3 , MnO_2 , MnO_3 , Mn_2O_7

(b) Decreasing order of acidic character: $\text{Mn}_2\text{O}_7 > \text{MnO}_3 > \text{Mn}_2\text{O}_3 > \text{MnO}$

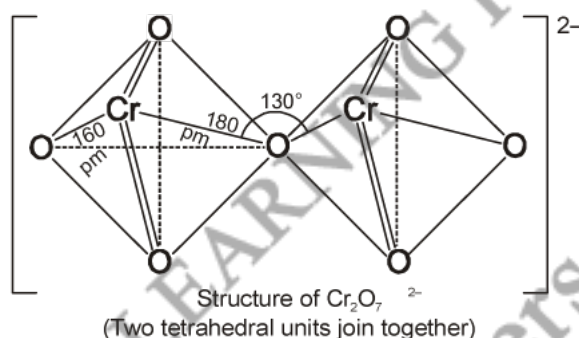
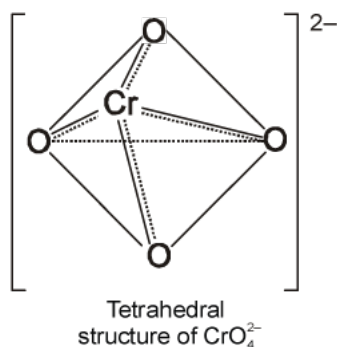


S115(a) Ni shows +2 oxidation state because of lower ($IE_1 + IE_2$). Pt shows +4 oxidation state because extra energy $IE_3 + IE_4$ is balanced by hydration energy.

(b) Pt can form compounds in +4 oxidation state more easily because energy required to remove four electrons is less in case of Pt than Ni.

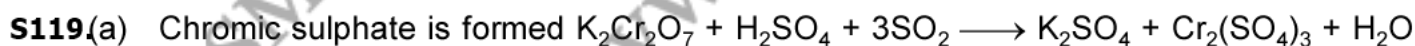


S117.

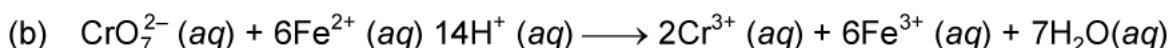
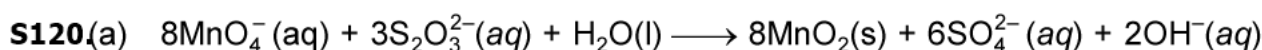


S118. Thermodynamical stability of the compounds can be judged on the basis of the magnitude of ionization energies. The sum of the first two ionization energies of Ni^{2+} is lower than the sum of first two ionization energies of Pt^{2+} , therefore, Ni^{2+} compounds are more stable than Pt^{2+} . On the other hand sum of first four ionization energies of Pt^{4+} is lower than the sum of the first four ionization energies of Ni^{4+} , therefore Pt^{4+} compounds are more stable than Ni^{4+} . The Actual values are gives below:

	Sum of the first two ionization energies (kJ mol^{-1})	Sum of the first four ionization energies (kJ mol^{-1})
Ni	2.49	11.29
Pt	2.66	9.36



(b) Mohr's salt is oxidized to ferric sulphate.



- S121(a)** The ionic species which possesses unpaired electron or electrons in $(n - 1)$ d -subshell will show colour. Of the ions $\text{Ag}^+(4d^{10})$, $\text{Co}^{2+}(3d^7)$ -three unpaired electrons) and $\text{Ti}^{4+}(3d^0)$, Co^{2+} will be coloured as it contains three unpaired electrons and Ag^+ and Ti^{4+} will be colourless.
- (b) When placed in magnetic field, Co^{2+} will be attracted because it is paramagnetic due to unpaired electrons. Ag^+ and Ti^{4+} ions will be repelled by the magnetic field as they are diamagnetic due to presence of paired orbitals.

S122. This is due to lanthanoid contraction by the members of 4f-series which occupy a position between lanthanum ($Z = 57$, a first member of third transition series) and hafnium ($Z = 72$, second member of 3rd transition series).

2 nd transition series	Y	Zr	Nb	Mo
3 rd transition series	La-Lanthanides (58 to 71)	Hf	Ta	W

The pairs of elements such as Zr-Hf, Nb-Ta, Mo-W, etc. possess nearly the same atomic radii and almost the same properties.

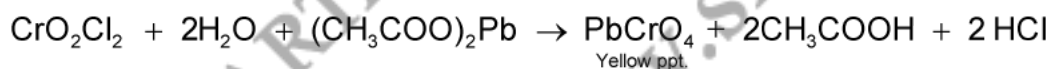
S123. There are operating two effects namely nuclear charge effect and screening effect which oppose each other. Due to increase in nuclear charge from member to member in a transition series, the atomic radii tend to decrease. At the same time, the addition of extra electrons one by one to $(n - 1)$ d -orbitals provides the screening effect.

As the number of d electrons increases, the screening effect increases and this tends to increase size. Due to these opposing tendencies, there is a very small change in the atomic radii in a transition series. In s and p -block elements, the extra electron is added to same s or p -subshell which does not exert screening effect and hence, the atomic radii decreases considerably in a period due to increase in nuclear charge.

S124. Chromyl chloride test is used to detect the presence of chloride ions. When any chloride is heated with solid $\text{K}_2\text{Cr}_2\text{O}_7$ and conc. H_2SO_4 , orange coloured vapours of chromyl chloride are formed.

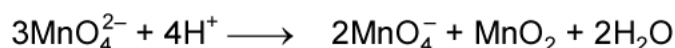


The solution of chromyl chloride gives a yellow precipitate of lead chromate with lead acetate.

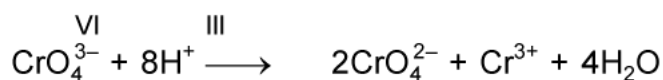


S125. When the oxidation state of an element in a reactant increases in one of the products and decreases in the other product, the phenomenon is called disproportionation.

For example, Mn (VI) in MnO_4^{2-} changes to Mn(VII) in the product MnO_4^- and to Mn (IV) in the product MnO_2 as shown by the reaction:

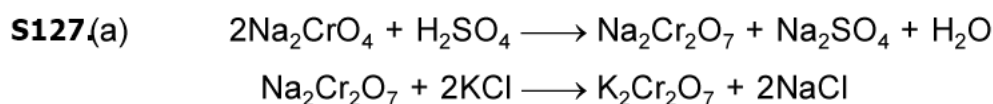


Similarly, Cr (V) undergoes disproportionation in acidic medium as follows:



S126. The variability of oxidation states in transition elements arise because of the participation of $(n-1)$ d -orbitals and ns orbitals. These different oxidation states of transition elements differ by unity. For example, vanadium shows oxidation states of +2, +3, +4 and +5; manganese shows oxidation states of +2, +3, +4, +5, +6 and +7.

On the other hand, some non-transition elements of p -block show variable oxidation states which differ by a unit of two. For example, tin has oxidation states +2 and +4, indium has +1 and +3, etc.



(b) It has the following effects:

- (i) The ionisation energy in $5d$ series is more than that in $3d$ and $4d$ series.
- (ii) There is resemblance between properties of elements $4d$ and $5d$ transition series.

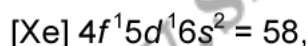
S128. Ionisation enthalpy normally increases with increase in atomic number along a given transition series. However, we find that there is not much variation in ionisation energy (enthalpy) in the first transition series. This can be explained by saying that the removal of an electron alters the relative energies of $4s$ and $3d$ orbitals.

Thus, there is reorganisation energy accompanying ionisation. This results into release of exchange energy which increases as the number of electrons increase in the d -orbitals and also from the transference of electrons into d -orbitals.

S129. The ions which have incompletely filled d -orbitals will be coloured and those with fully filled or empty d -orbitals will be colourless. Ti^{3+} , V^{3+} , Mn^{2+} , Fe^{3+} and Co^{2+} are coloured because they have incompletely filled d -orbitals. Cu^+ and Sc^{3+} are colourless because Cu^+ has $3d^{10}$ completely filled d -orbitals while Sc^{3+} has empty ($3d^0$) d -orbitals.

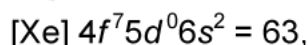
S130(a) This is due to poor shielding by $5f$ electrons in the actinides than that of $4f$ electrons in the lanthanides.

(b) Complete E.C. of 1st element:



i.e., the element is cerium.

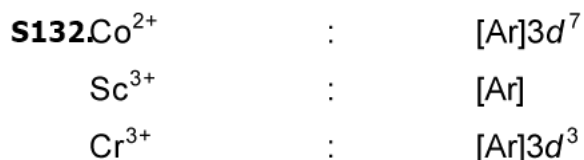
Complete E.C. of 2nd element:



i.e., the element is Europium.

The expected oxidation states of 1st element = +3 and +4 and of 2nd element = +2, +3.

- S131(a)** E values for $\text{Cr}^{3+}/\text{Cr}^{2+}$ is negative (-0.41 V) and for $\text{Mn}^{3+}/\text{Mn}^{2+}$ is positive ($+1.57\text{ V}$). Thus, Cr^{2+} can undergo oxidation and, therefore, is reducing agent. On the other hand, Mn(III) can undergo reduction, and therefore, acts as an oxidizing agent.
- (b) In the presence of complexing agents, cobalt gets oxidised from +2 to +3 state because Co(III) is more than Co(II) .
- (c) after loss of ns electrons, d^1 electron can easily be lost to give a stable configuration. Therefore, the elements having d^1 configuration are either reducing or undergo disproportionation.



Co^{2+} and Cr^{3+} have unpaired electrons in the 3d subshell. Hence, they will give coloured solutions. Co^{2+} and Cr^{3+} will also be attracted by the magnetic field because of the presence of unpaired electrons.

- S133(a)** **Interstitial compounds:** Transition element form large number of interstitial compounds. In these compounds small size atoms like hydrogen, carbon nitrogen, boron, etc., occupy the empty space of metal lattice (interstices). The small entrapped atom in the interstices form the bonds with metals due to which malleability and ductility of the metals decrease, whereas tensile strength increases.

Example: Steel is the interstitial compound of iron and carbon.

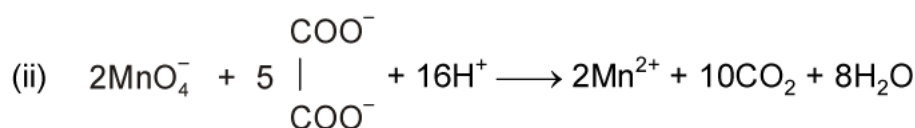
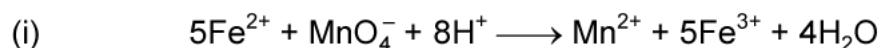
- (b) **Alloys:** Transition elements form alloys with each other because they have almost similar sizes. Due to similar sizes atoms of one metal in the crystal lattice can easily take up the position of the atom of other transition elements. Alloys are more resistant to constituent elements, and usually harder with higher melting point. Example: brass, stainless steel.

- S134(a)** **Electronic configurations:** The general electronic configuration of lanthanoids is $[\text{Xe}]4f^{1-14} 5d^0 6s^2$ whereas that of actinoids is $[\text{Rn}] 5f^{1-14} 6d^0 7s^2$. Thus, lanthanoids involve the filling of 4f-orbitals whereas actinoids involve the filling of 5f-orbitals.

- (b) **Oxidation states:** Lanthanoids have principal oxidation state of +3. In addition, the lanthanoids show limited oxidation states such as +2, +3 and +4 because of large energy gap between 4f and 5d subshells. On the other, actinoids show a large number of oxidation states because of small energy gap between 5f and 6d subshells.

- (c) **Atomic and ionic sizes:** Both lanthanoids and actinoids show decrease in size of their atoms or ions in +3 oxidation state. In lanthanoids, the decrease is called lanthanoid contraction and in actinoids, it is called actinoid contraction.

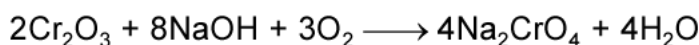
- S135(a)** Oxidation of Fe^{2+} into Fe^{3+} and decomposition of oxalate in the presence of KMnO_4 in acidic medium is explained with the help of following equations.



- (b) (i) Cr^{2+} (d^4) is less stable than Cr^{3+} (d^5), therefore, it is good reducing agent whereas Mn^{2+} is stable due to half filled d -orbitals. It does not change into Mn^{3+} easily therefore, it is not reducing agent.
- (ii) Cu^+ , Ag^+ and Sc^{3+} are colourless because they do not have unpaired electrons.
- (iii) In actinoids, energies of $5f$, $6d$ and $7s$ orbitals are comparable and, therefore, they show large number of oxidation states compared to lanthanoids. That is why their chemistry is more complicated. Secondly, all of them are radioactive and their study becomes difficult. Also there is possibility of frequent electronic transition among $5f$, $6d$ and $7s$ orbitals.

- S136(a)** (i) Reactivity decreases with increase in atomic number of due to decrease in size and increase in ionisation energy.
- (ii) In d -block elements, electrons s -orbital and d -orbital both take part in bond formation. In f -block elements due to poor shielding effect of f -electrons effective nuclear charge increases. Therefore, fewer number of oxidation states are shown.

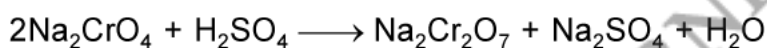
- (b) Compounds A , B , C and D are identified with the help of the following equations



'A'

(yellow)

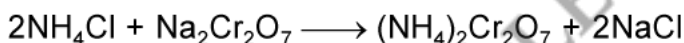
'B'



'B'

(orange)

'C'



(orange)

'D'



Ammonium

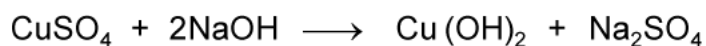
(green)

dichromate

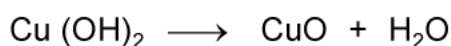
'A'

- S137(a)** The most stable oxidation state of lanthanides is +3. Hence, ions in +2 state tend to change to +3 oxidation state by loss of electron and act as reducing agents.
- (b) La^{3+} has a stable configuration of an inert gas $[(\text{Xe})5d^06s^0]$, i.e., xenon (54–2, 8, 18, 18, 8). To obtain +4 oxidation state, the stable configuration is to be disturbed which is not possible under ordinary conditions and hence La^{4+} does not exist.
- (c) This is because gadolinium in +3 state has half filled $4f$ -subshell ($4f^7$) and lutetium in +3 state has completely filled $4f$ -subshell which are very stable configurations.
- (d) Due to lanthanide contraction, the atomic radii of both Zr and Hf are same. Hence, their properties are similar.

- S138(a)** NaOH reacts with CuSO_4 when dark blue precipitate of $\text{Cu}(\text{OH})_2$ is formed. This precipitate on heating forms CuO which is black in colour. Hence, the colour darkens on heating.

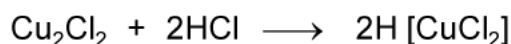


Blue

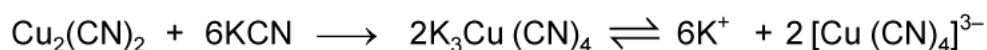
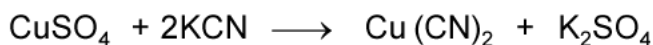


Black

- (b) Cu_2Cl_2 dissolves in conc. HCl due to the formation of a copper complex.



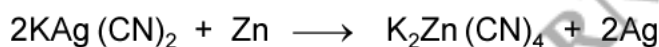
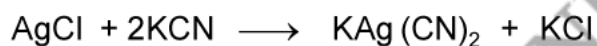
- (c) CuSO_4 forms a complex with KCN.



$\text{K}_3\text{Cu(CN)}_4$ complex does not furnish Cu^{2+} ions. Hence, no precipitate of CuS is formed when H_2S is passed through solution.

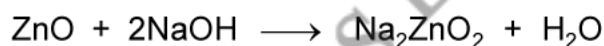
- (d) AgNO_3 is photosensitive. It decomposes in presence of light. To prevent its decomposition, it is kept in coloured bottles as these do not permit light to pass through.

- S139.**(a) AgCl dissolves in KCN forming a complex, potassium argentocyanide. The addition of zinc precipitates silver.

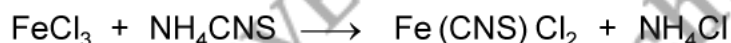


Potassium zincocyanide

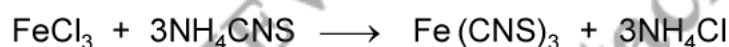
- (b) ZnO dissolves in NaOH forming sodium zincate.



- (c) Deep red coloration due to the formation of a complex is developed.



or



- S140.**(a) **Metallic character:** Since the number of electrons in the outermost shell are two or one and can be removed easily. Therefore, all the transition elements are metals. All three of structures: fcc, hcp and bcc are shown by them. The electrons present in the outermost orbitals form metallic bonds. Due to these metallic bonds they have high melting and boiling points and high thermal and electrical conductivities. All transition metals except Hg, are malleable and ductile.

- (b) **Ionisation energies:** The first ionization energies of transition element lie element the value of ionization energies of s-block and p-block elements. In transition elements last electron goes to $(n - 1)$ d sub-shell which shields the outer ns electrons from the inward pull due to the attraction by the nuclear.

The nuclear charge and shielding effect of $(n - 1)d$ electrons will increase with the increase in atomic number. The ionization energies gradually increase in a particular series of d -block elements. This is due to decrease in size with the increase in atomic numbers which will make the removal of electron difficult. However, shielding effect will also increase with the increase in atomic number which will oppose the decrease in size. Due to these two opposite effects (increased nuclear charge and shielding effect), ionization energies will increase rather slowly in the $3d$ -series.

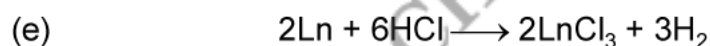
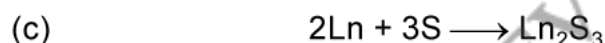
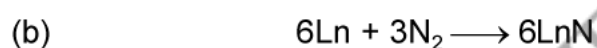
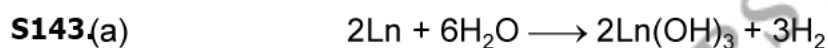
S141. When we move downward in a particular group the atomic number is increased, consequently nuclear charge is also increased. Due to this reason $5d$ elements have greater nuclear charge than $3d$ and $4d$ elements, therefore, the outer electrons are attracted strongly by the nucleus in $5d$ elements.

On the other hand, the shielding effect of $4f$ electrons is very poor due to lanthanide contraction in $5d$ elements, which further increases the attractive forces, hence more energy is required to remove an electron from $5d$ elements than $3d$ and $4d$ elements, where no $4f$ electrons and lanthanide contraction is present.

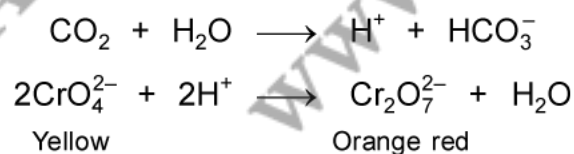
S142.(a) The lower oxide of transition metal having low oxidation state is basic whereas the higher oxide of transition metal having high oxidation state is amphoteric or acidic. For example, MnO(II) is basic while $\text{Mn}_2\text{O}_7(\text{VII})$ is acidic. Similarly, CrO(II) is basic while $\text{Cr}_2\text{O}_3(\text{III})$ is amphoteric.

(b) A transition metal exhibits higher oxidation states in oxides and fluorides because oxygen and fluorine are of small size and high electronegativity and hence can readily oxidise the metals. For example, $\text{OsF}_6[\text{Os(VI)}]$, $\text{V}_2\text{O}_5[\text{V(V)}]$.

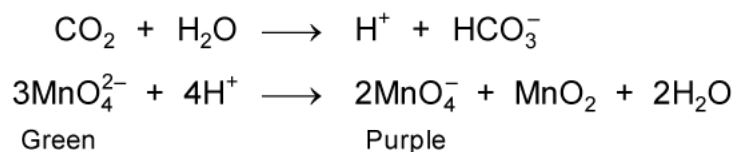
(c) Oxoanions of metals have highest oxidation states. For example, Cr in $\text{Cr}_2\text{O}_7^{2-}$ has an oxidation state of +6 whereas Mn in MnO_4^- has an oxidation state of +7. This is because of high electronegativity of oxygen and is high oxidising property.



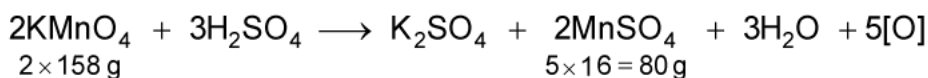
S144.(a) Yellow coloured aqueous solution of sodium chromate changes to orange red on passing CO_2 as H^+ ions are formed which are responsible for conversion of chromate into dichromate.



(b) CO_2 gives H^+ ions which are responsible for conversion of manganate (green) to permanganate (purple).



S145. Oxidising action of KMnO_4 acidic medium is represented as:



$$\text{Eq. mass of KMnO}_4 = \frac{2 \times 158}{80} \times 8 = 31.6$$

or
$$\text{Eq. mass of KMnO}_4 = \frac{\text{Molecular mass}}{\text{Number of electrons gained per molecule}} = \frac{158}{5} = 31.6$$

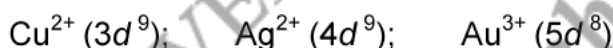


$$\text{Eq. mass of KMnO}_4 = \frac{\text{Molecular mass}}{\text{Change in oxidation state per molecule}} = \frac{158}{5} = 31.6$$

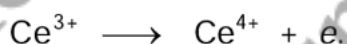
S146(a) In chromium, the interatomic bonding is very strong due to presence of five unpaired electrons in $3d$ -subshell ($3d^5 4s^1$). Therefore, it is a hard metal. In mercury, on the contrary, the $3d$ -subshell is filled to maximum capacity ($5d^{10} 6s^2$), i.e., these electrons are not available for interatomic bonding and thus, bonding is very weak in mercury. Therefore, mercury is a liquid at room temperature.

(b) In Zn, Cd and Hg the $(n-1)$ d -orbitals are filled to their maximum capacity. These d -electrons do not take part in metallic bonding. Thus, metallic bonding is weak in Zn, Cd and Hg. That is why, they have low melting and boiling points.

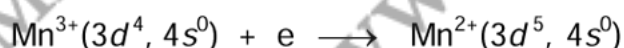
(c) Copper, silver and gold in their common oxidation states have partially filled $(n-1)$ d -orbitals.



S147(a) Ce^{3+} has the configuration $4f^1 5d^0 6s^0$. It can easily lose an electron to acquire more stable configuration ($4f^0 5d^0 6s^0$), i.e., configuration of an inert gas, xenon (2, 8, 18, 18, 8), i.e., Ce^{3+} can be easily oxidised to Ce^{4+} .



(b) E° for $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is more positive than for $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple because Mn^{2+} state is more stable than Mn^{3+} state. Thus, the reduction is spontaneous.



For $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple, $\text{Fe}^{3+} (3d^5, 4s^0)$ is more stable than $\text{Fe}^{2+} (3d^6, 4s^0)$

(c) In the lanthanide series, the size of the M^{3+} ion decreases from La^{3+} to Lu^{3+} . Thus, the covalent nature of $\text{Lu}(\text{OH})_3$ increases (Fajan's rule). Hence, $\text{Lu}(\text{OH})_3$ is weaker than $\text{La}(\text{OH})_3$.

S148(a) Fe^{3+} is more paramagnetic than Fe^{2+} as Fe^{3+} consists five unpaired electrons while Fe^{2+} possesses four unpaired electrons.

- (b) Any ion of transition elements which possesses unpaired d electrons, *i.e.*, $d-d$ transition is possible shows a characteristic colour. $(n-1)d^0$ or $(n-1)d^{10}$ configuration does not involve $d-d$ transition and hence, is colourless.

Fe^{2+} , Mn^{2+} and Cr^{3+} are coloured, while Cu^+ , Sc^{3+} and Ti^{4+} are colourless.

Ion	Configuration	Ion	Configuration
Cu^+	$3d^{10}$ (colourless);	Cr^{3+}	$3d^3$ (coloured)
Fe^{2+}	$3d^6$ (coloured);	Sc^{3+}	$3d^0$ (colourless)
Mn^{2+}	$3d^5$ (coloured);	Ti^{4+}	$3d^0$ (colourless)

- (c) Chromium and copper.

Chromium attains $3d^5, 4s^1$ configuration in which all the d -orbitals are unpaired in order to get extra stability.

Copper attains $3d^{10}, 4s^1$ configuration in which all the d -orbitals are paired in order to get extra stability.

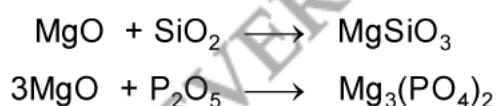
- (d) Lightest element – Scandium;

Heaviest element – Osmium

- (e) Each transition series consists ten elements. This number cannot be 9 or 11 as the maximum capacity of d -orbitals is of 10 electrons which are gradually filled up.

1 st	Tr. series	$3d^{1-10}$	Ten elements
2 nd	Tr. series	$4d^{1-10}$	Ten elements
3 rd	Tr. series	$5d^{1-10}$	Ten elements

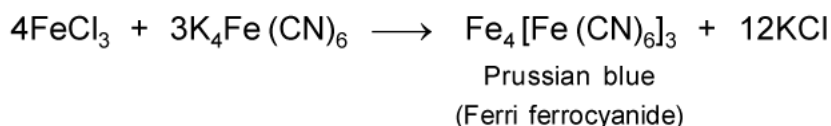
- S149(a)** MgO is basic in nature. It removes acidic impurities present in cast iron used for making steels.



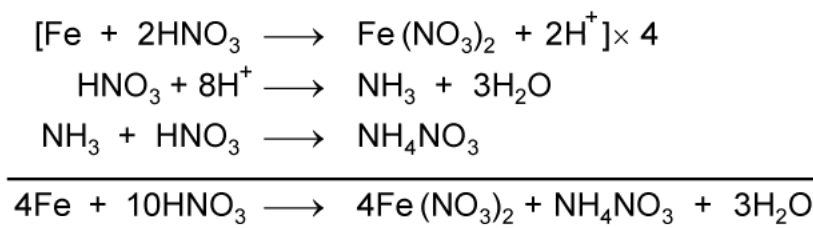
MgO is also a refractory material as it can tolerate very high temperature of the furnace.

- (b) Cast iron consists carbon 2.5 to 5% which is responsible for its hardness.
- (c) Fe^{3+} has the configuration $[\text{Ar}] 3d^5$, *i.e.*, all the five d -orbitals are singly occupied which is a stable configuration in accordance to Hund's rule of maximum multiplicity while the configuration of Fe^{2+} is $[\text{Ar}] 3d^6$ in which one orbital is doubly occupied and rest of the four orbitals are singly occupied. It is not so stable configuration as it is unsymmetrical in nature.
- (d) On heating hydrated ferric chloride, anhydrous ferric chloride is not formed as water of crystallisation reacts to form Fe_2O_3 and HCl .
- (e) Iron compounds either has Fe^{2+} or Fe^{3+} ions and each contains unpaired orbitals which show paramagnetic character. $d-d$ transition is possible. Hence, the compounds are coloured.

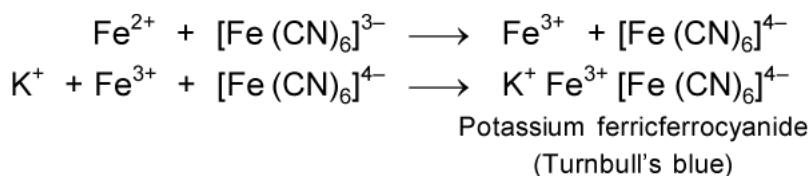
S150.(a) Prussian blue is formed.



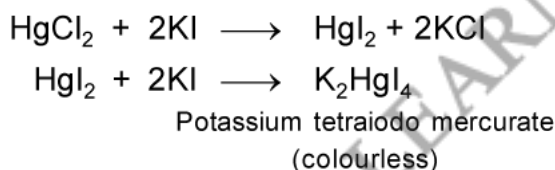
(b) Ammonium nitrate is formed.



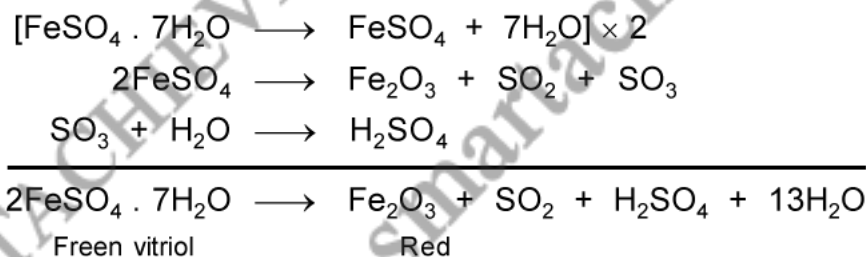
(c) Ferrous ion is first oxidised to ferric ion while ferricyanide ion is reduced to ferrocyanide ion. Then, ferric ions react with ferrocyanide ions to form potassium ferric ferrocyanide (Turnbull's blue).



(d) First scarlet precipitate is formed which then dissolves in excess of potassium iodide forming a complex.



(e) When heated strongly, a mixture of gases consisting SO_2 and SO_3 evolved and a red residue, Fe_2O_3 is formed.



S151.(a) Although copper has $3d^{10}$ configuration yet it can lose one electron from this arrangement. Thus, Cu^{2+} ion has $3d^9$ configuration. So, according to the definition that transition metal cations have partially filled $(n - 1)$ d -subshell, copper is regarded as a transition metal.

(b) Of cobalt and zinc salts, the cobalt salts are attracted in a magnetic field, because cobalt ion containing unpaired electrons is characterised by a permanent magnetic moment. Zn^{2+} ion contains $3d^{10}$ configuration, *i.e.*, no unpaired electrons, so zinc salts are not attracted in magnetic field.

(c) I^- ion is a stronger reducing agent than Cl^- ion. It reduces Cu^{2+} ion. Hence, cupric iodide is converted into cuprous iodide. Thus, the species $[\text{CuI}_4]^{2-}$ does not exist.

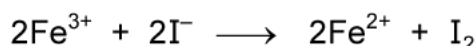
- (d) Copper is a very good conductor of electricity. Moreover, it is not easily affected by the atmosphere.
- (e) On being acidified, the chromate ions dimerise to form dichromate ions which are orange coloured. Thus,



S152(a) Cu (I) salts undergo disproportionation in aqueous solution



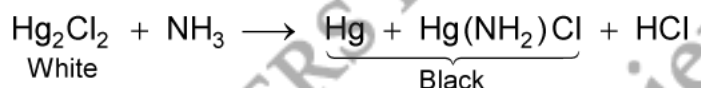
- (b) I^- ion is a stronger reducing agent in comparison to Cl^- ion. Fe^{3+} is easily reduced by iodide ion.



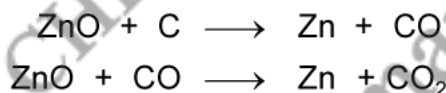
- (c) AgBr is sensitive to light. It is converted into metallic silver grains when light is incident on it.
- (d) Silver and gold are less basic than copper. These are not ionised under the applied voltage and get deposited in the anodic mud.
- (e) The hydration energy of AgF is higher than its lattice energy. Hence, it is soluble in water. The hydration energy values of other halides are smaller than their lattice energy values. Hence, these halides are insoluble in water.

S153(a) HgCl_2 is poisonous (corrosive) in nature. It undergoes sublimation. Due to these properties, it is called corrosive sublimate.

- (b) HgCl_2 reacts with NH_3 to form a mixture of mercury and mercuric amino chloride which is a black substance.



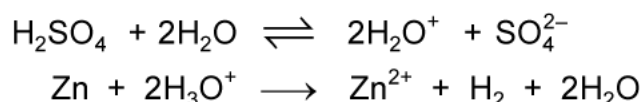
- (c) Carbon has to play a double role,
 - (i) It reduces zinc oxide to zinc.



- (ii) It reduces CO_2 into CO which is used as a fuel



- (d) H_2SO_4 is a covalent compound. Conc. H_2SO_4 does not contain H_3O^+ ions while dilute H_2SO_4 consists H_3O^+ ions which react with zinc to liberate hydrogen.



- (e) In the compounds of zinc metals, M^{2+} ions possess the penultimate *d*-orbitals doubly occupied, *i.e.*, $(n - 1)d^{10}$ configuration. There is no *d-d* transition. Hence, the compounds of zinc metals are colourless.