The d- and f-Block Elements

1. Which one of the following first row transition elements is expected to have the highest third ionization enthalpy ? (2024)

(A) Iron (Z = 26)

(B) Manganese (Z = 25)

(C) Chromium (Z = 24)

(D) Vanadium (Z = 23)

Ans. (B) Manganese (Z = 25)

2. two statements are given - one labelled as Assertion (A) and the other labelled as Reason (R). Select the correct answer to these questions from the codes (A), (B), (C) and (D) as given below. (2024)

(A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

(B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).

(C) Assertion (A) is true, but Reason (R) is false.

(D) Assertion (A) is false, but Reason (R) is true.

Assertion (A) : Separation of Zr and Hf is difficult.

Reason (R) : Zr and Hf have similar radii due to lanthanoid contraction.

Ans. (A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

Previous Years' CBSE Board Questions

4.2 Electronic Configurations of the *d*-Block Elements

VSA (1 mark)

1. Account for the following :
Zn, Cd, Hg are considered as *d*-block elements but not as transition elements. *(1/5, 2020)*

OR

Account for the following :
Zn is not considered as a transition element. *(1/5, AI 2014)* U

SA I (2 marks)

2. What are the transition elements? Write two characteristics of the transition elements. *(Term II, 2021-22C, Delhi 2015)*

4.3 General Properties of the Transition Elements (*d*-Block)

MCQ

3. Which property of transition metals enables them to behave as catalysts?
   (a) High melting point
   (b) High ionisation enthalpy
   (c) Alloy formation
   (d) Variable oxidation states *(2023)*

4. Which of the following is a strong oxidising agent? (At. No. Mn = 25, Zn = 30, Cr = 24, Sc = 21)
   (a) Mn^{3+} (b) Zn^{2+} (c) Cr^{3+} (d) Sc^{3+} *(2021 C)*

5. The incorrect statement about interstitial compounds is
   (a) they are chemically reactive.
   (b) they are very hard.
   (c) they retain metallic conductivity.
   (d) they have high melting point. *(2020)* R

6. Out of the following transition elements, the maximum number of oxidation states are shown by
   (a) Sc (Z = 21) (b) Cr (Z = 24)
   (c) Mn (Z = 25) (d) Fe (Z = 26) *(2020)*

7. **Assertion (A) :** Transition metals have high melting point.
Reason (R) : Transition metals have completely filled *d*-orbitals.
   (a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
   (b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
   (c) Assertion (A) is correct, but Reason (R) is incorrect statement.
   (d) Assertion (A) is incorrect, but Reason (R) is correct statement. *(2020)*

8. **Assertion (A) :** Transition metals have low melting points.
Reason (R) : The involvement of greater number of $(n - 1)d$ and ns electrons in the interatomic metallic bonding.
   (a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
   (b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
   (c) Assertion (A) is correct, but Reason (R) is incorrect statement.
   (d) Assertion (A) is incorrect, but Reason (R) is correct statement. *(2020)* U

VSA (1 mark)

Read the given passage and answer the questions number (9 to 13) that follow :

The *d*-block of the periodic table contains the elements of groups 3-12 and are known as transition elements. In general, the electronic configuration of these elements is $(n - 1)d^{1-10} ns^{1-2}$. The *d*-orbitals of the penultimate energy level in their atoms receive electrons giving rise to three rows of the transition metals *i.e.*, 3*d*, 4*d* and 5*d* series. However, Zn, Cd and Hg are not regarded as transition elements. Transition elements exhibit certain characteristic properties like variable oxidation states, complex formation, formation of coloured ions and alloys, catalytic activity, etc. Transition metals are hard (except Zn, Cd and Hg) and have a high melting point.

9. Why are Zn, Cd and Hg non-transition elements?
10. Which transition metal of 3*d* series does not show variable oxidation states?
11. Why do transition metals and their compounds show catalytic activity?
12. Why are melting points of transition metals high?
13. Why is Cu^{2+} ion coloured while Zn^{2+} ion is colourless in aqueous solution? *(2020)*
14. Out of zinc and tin, whose coating is better to protect iron objects? *(One word, 2020)*
15. Account for the following :
Copper(I) compounds are white whereas copper(II) compounds are coloured. *(1/5, 2020)* Ap
16. Write the formula of an oxoanion of chromium (Cr) in which it shows the oxidation state equal to its group number. *(NCERT, Delhi 2017)*

17. Write the formula of an oxoanion of manganese (Mn) in which it shows the oxidation state equal to its group number. *(Delhi 2017)*

18. How would you account for the following :
Transition metals form coloured compounds? *(1/3, Delhi 2015)*

19. Zn^{2+} salts are white while Cu^{2+} salts are coloured. Why? *(AI 2015)* U

20. Why do transition elements show variable oxidation states? *(Delhi 2014C)*

SA I (2 marks)

21. Calculate the spin-only moment of Co^{2+} ($Z = 27$) by writing the electronic configuration of Co and Co^{2+}. *(2/5, 2020)*

22. Give reason and select one atom/ion which will exhibit asked property :
    - (i) Sc^{3+} or Cr^{3+} (exhibit diamagnetic behaviour)
    - (ii) Cr or Cu (high melting and boiling point)

    (2/5, 2020) An

23. Calculate the number of unpaired electrons in the following gaseous ions :
Mn^{3+} and Cr^{3+} (Atomic number of Cr = 24, Mn = 25)
Which one of them is most stable in aqueous solution and why ? *(2020 C)*

24. Calculate the number of unpaired electrons in the following gaseous ions :
Ti^{3+} and Cr^{3+} (Atomic number of Ti = 22, Cr = 24)
Which one of them is most stable in aqueous solution and why ? *(2020 C)*

25. Give reasons for the following :
    - (i) Transition metals form alloys.
    - (ii) Mn_2O_3 is basic whereas Mn_2O_7 is acidic.

    (2/3, Delhi 2019)

26. Use the data to answer the following and also justify giving reasons :

	Cr	Mn	Fe	Co
$E^\circ_{M^{2+}/M}$	−0.91	−1.18	−0.44	−0.28
$E^\circ_{M^{3+}/M^{2+}}$	−0.41	+1.57	+0.77	+1.97

- (i) Which is a stronger reducing agent in aqueous medium, Cr^{2+} or Fe^{2+} and why?
- (ii) Which is the most stable ion in +2 oxidation state and why? *(AI 2019)*

27. Give reasons :
    - (a) Of the d^4 species, Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidising.
    - (b) The d^1 configuration is very unstable in ions. *(2019 C)*

28. (i) How is the variability in oxidation states of transition metals different from that of the *p*-block elements?
    (ii) Out of Cu^+ and Cu^{2+}, which ion is unstable in aqueous solution and why? *(2/5, Delhi 2017)*

29. Account for the following :
    - (i) Transition metals show variable oxidation states.
    - (ii) Zn, Cd and Hg are soft metals. *(2/5, AI 2017)*

30. Give reasons :
    - (i) Mn shows the highest oxidation state of +7 with oxygen but with fluorine it shows the highest oxidation state of +4.
    - (ii) Transition metals show variable oxidation states.

    (2/3, Delhi 2016) U

31. Account for the following :
    - (i) Transition metals show variable oxidation states.
    - (ii) Cu^+ ion is unstable in aqueous solution.

    (2/3, AI 2015)

32. Why do transition elements show variable oxidation states? In 3*d* series (Sc to Zn), which element shows the maximum number of oxidation states and why? *(Foreign 2015)*

33. How would you account for the following :
    - (i) Highest fluoride of Mn is MnF_4 whereas the highest oxide is Mn_2O_7.
    - (ii) Transition metals and their compounds show catalytic properties. *(2/3, Foreign 2015)*

34. What is meant by 'disproportionation'? Give an example of a disproportionation reaction in aqueous solution. *(NCERT)*
(Delhi 2015C, AI 2015C)

35. Account for the following :
    - (i) Mn^{2+} is more stable than Fe^{2+} towards oxidation to +3 state.
    - (ii) The enthalpy of atomization is lowest for Zn in 3*d* series of the transition elements. *(Delhi 2014)*

36. (i) Write two characteristic of the transition elements.
    (ii) Which of the 3*d*-block elements may not be regarded as the transition elements and why?
    (2/3, Foreign 2014)

37. Assign a reason for each of the following observations :
    - (i) The transition metals (with the exception of Zn, Cd and Hg) are hard and have high melting and boiling points.
    - (ii) The ionisation enthalpies (first and second) in the first series of the transition elements are found to vary irregularly. *(Delhi 2014C)*

38. Assign reasons for the following :
    - (i) Copper(I) ion is not known to exist in aqueous solutions.
    - (ii) Both O_2 and F_2 stabilize high oxidation states of transition metals but the ability of oxygen to do so exceeds that of fluorine. *(AI 2014C)*

39. Give reasons for the following :
   (i) Transition metals exhibit a wide range oxidation states.
   (ii) Cobalt (II) is very stable in aqueous solutions but gets easily oxidised in the presence of strong ligands. *(2/3, AI 2014C)*

40. Assign reasons for the following :
   (i) Cu(I) ion is not known to exist in aqueous solutions. *(NCERT)* U
   (ii) Transition metals are much harder than the alkali metals. *(2/3, AI 2014C)*

41. Assign reasons for the following :
   (i) Transition metals and many of their compounds act as good catalysts.
   (ii) Transition metals generally form coloured compounds. *(AI 2014C)*

SA II (3 marks)

42. Following are the transition metal ions of 3*d* series : Ti^{4+}, V^{2+}, Mn^{3+}, Cr^{3+}
(Atomic numbers : Ti = 22, V = 23, Mn = 25, Cr = 24)
Answer the following :
   (i) Which ion is most stable in aqueous solution and why?
   (ii) Which ion is strong oxidising agent and why?
   (iii) Which ion is colourless and why?
(Term II, 2021-22, 3/5, AI 2017)

43.

	Cr	Mn	Fe	Co	Ni	Cu	Zn
$E^\circ_{M^{2+}/M}$	- 0·91	- 1·18	- 0·44	- 0·28	- 0·25	+ 0·34	- 0·76

From the given E° values of the first row transition elements, answer the following questions :
   (i) Why is $E^\circ_{Mn^{2+}/Mn}$ value highly negative as compared to other elements ?
   (ii) What is the reason for the irregularity in the above E° values ?
   (iii) Why is $E^\circ_{Cu^{2+}/Cu}$ value exceptionally positive ? *(Term II, 2021-22)*

44. Account for the following
   (i) Cu^{2+} salts are coloured while Zn^{2+} salts are white.
   (ii) E° value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+}
   (iii) Transition metals form alloys. *(Term II, 2021-22)*

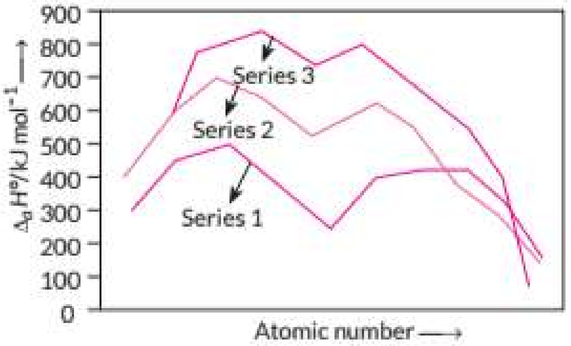
45. (i) Which ion amongst the following is colourless and why?
Ti^{4+}, Cr^{3+}, V^{3+}
(Atomic number of Ti = 22, Cr = 24, V = 23)
   (ii) Why is Mn^{2+} much more resistant than Fe^{2+} towards oxidation?
   (iii) Highest oxidation state of a metal is shown in its oxide or fluoride only. Justify the statement. *(Term II, 2021-22)* Ap

46. (i) Silver atom has completely filled *d*-orbitals in its ground state, it is still considered to be a transition element. Justify the statement.
   (ii) Why are $E^\circ_{M^{2+}/M}$ values of Mn and Zn more negative than expected?
   (iii) Why do transition metals form alloys? *(Term II, 2021-22)* An

47. Give reasons for the following statements :
   (a) Copper does not displace hydrogen from acids. *(NCERT)*
   (b) Transition metals and most of their compounds show paramagnetic behaviour.
   (c) Zn, Cd and Hg are soft metals. *(Term II, 2021-22)*

48. (i) Why are melting points of transition metals high?
   (ii) Why the transition metals generally form coloured compounds ?
   (iii) Why E° value for Mn^{3+}/Mn^{2+} couple is highly positive ? *(Term II, 2021-22)*

49. Answer the following questions on the basis of the figure given below :



   (i) Which element in 3*d* series has lowest enthalpy of atomisation?
   (ii) Why do metals of the second and third series have greater enthalpies of atomisation?
   (iii) Why are enthalpies of atomisation of transition metals quite high? *(Term II, 2021-22)* Ap

50. Define transition metals. Why Zn, Cd and Hg are not called transition metals ? How is the variability in oxidation states of transition metals different from that of *p*-block elements ? *(Term II, 2021-22)*

51. Give reasons for the following statements :
   (a) Transition elements and their compounds act as good catalysts.
   (b) $E^\circ_{(Mn^{2+}/Mn)}$ value is highly negative as compared to other elements.
   (c) Cr^{2+} is a strong reducing agent. *(Term II, 2021-22)*

52. Account for the following :
   (a) Transition elements show variable oxidation states.
   (b) $E^\circ_{Cu^{2+}/Cu}$ value for copper is highly positive.
   (c) Cr^{2+} is a strong reducing agent. *(Term-II, 2021-22C)*

53. Define transition elements. Write two characteristics of transition elements. *(Term-II, 2021-22C)*

54. (a) Why is $E^\circ(Cu^{2+}|Cu)$ exceptionally positive ? Although Cu^+ ion has $3d^{10}$ configuration, yet it is unstable in an aqueous solution. Why? What is the reason for the stability of Cu^{2+} over Cu^+ ion? *(2021C)*

55. Give reasons for the following:
(i) Transition metals form alloys.
(ii) Zinc has lowest enthalpy of atomization.
(iii) Managanese shows higher oxidation state of +4 with fluorine but shows +7 with oxygen. *(2021 C)*

56. Following ions are given :
$Cr^{2+}, Cu^{2+}, Cu^{+}, Fe^{2+}, Fe^{3+}, Mn^{3+}$
Identify the ion which is
(i) a strong reducing agent.
(ii) unstable in aqueous solution.
(iii) a strong oxidising agent.
Give suitable reason in each. *(2020)*

57. Give reasons :
(i) $E°$ value for Mn^{3+}/Mn^{2+} couple is much more positive than that for Fe^{3+}/Fe^{2+}.
(ii) Iron has higher enthalpy of atomization than that of copper.
(iii) Sc^{3+} is colourless in aqueous solution whereas Ti^{3+} is coloured. *(2018)* Ap

58. Account the following :
(i) Transition metals form large number of complex compounds.
(ii) The lowest oxide of transition metal is basic whereas the highest oxide is amphoteric or acidic.
(iii) $E°$ value for the Mn^{3+}/Mn^{2+} couple is highly positive (+1.57 V) as compared to Cr^{3+}/Cr^{2+}. *(3/5, Delhi 2017)*

59. Account for the following :
(i) Mn shows the highest oxidation state of +7 with oxygen but with fluorine, it shows the highest oxidation state of +4.
(ii) Cr^{2+} is a strong reducing agent.
(iii) Cu^{2+} salts are coloured, while Zn^{2+} salts are white. *(3/5, AI 2016)*

60.

$E°_{(M^{2+}/M)}$	Cr	Mn	Fe	Co	Ni	Cu
	−0.91	−1.18	−0.44	−0.28	−0.25	+0.34

From the given data of $E°$ values, answer the following questions :
(i) Why is $E°_{(Cu^{2+}/Cu)}$ value exceptionally positive?
(ii) Why is $E°_{(Mn^{2+}/Mn)}$ value highly negative as compared to other elements?
(iii) Which is a stronger reducing agent Cr^{2+} or Fe^{2+}? Give reason. *(NCERT, 3/5, AI 2015)* An

61. Assign suitable reasons for the following :
(i) The Mn^{2+} compounds are more stable than Fe^{2+} towards oxidation to their +3 state.
(ii) In the 3*d* series from Sc (*Z* = 21) to Zn (*Z* = 30), the enthalpy of atomization of Zn is the lowest.
(iii) Sc^{3+} is colourless in aqueous solution whereas Ti^{3+} is coloured. *(Foreign 2014)*

LA (5 marks)

62. Assign reason for each of the following :
(i) Manganese exhibits the highest oxidation state of +7 among the 3*d* series of transition elements.
(ii) Transition metals and their compounds are generally found to be good catalysts in chemical reactions.
(iii) Cr^{2+} is reducing in nature while with the same *d*-orbital configuration (d^4) Mn^{3+} is an oxidising agent.
(iv) Zn has lowest enthalpy of atomization.
(v) Cu^{+} is unstable in an aqueous solution. *(2023)*

63. The elements of 3*d* transition series are given as
Sc Ti V Cr Mn Fe Co Ni Cu Zn
Answer the following :
(i) Write the element which shows maximum number of oxidation states. Given reason.
(ii) Which element has the highest melting point?
(iii) Which element shows only +3 oxidation state?
(iv) Which element is a strong oxidising agent in +3 oxidation state and why? *(AI 2016)*

4.4 Some Important Compounds of Transition Elements

VSA (1 mark)

64. Account for the following :
Chromates change their colour when kept in an acidic solution. *(1/5, 2020)*

65. Complete the following equation :
$3MnO_4^{2-} + 4H^+ \longrightarrow$
(2020, 2019C 1/3, Foreign 2015)

66. Complete the following equation :
$2MnO_4^- + 6H^+ + 5NO_2^- \longrightarrow$
(2019C, 1/2, Delhi 2015)

67. Orange colour of $Cr_2O_7^{2-}$ ion changes to yellow when treated with an alkali. Why?
(1/5, Delhi 2017) U

68. Complete the following equation :
$MnO_4^- + 8H^+ + 5e^- \longrightarrow$ *(1/5, Delhi 2014)*

69. Complete the following chemical equation:
$SO_2 + MnO_4^- + H_2O \longrightarrow$ *(1/2, AI 2014C)*

SA I (2 marks)

70. How would you account for
(a) The $E°$ value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+} couple or Fe^{3+}/Fe^{2+} couple.
(b) Complete the following equation :
$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow$ *(2023)*

71. Complete the following equations :
(a) $2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow$
(b) $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow$ *(2023)*

72. Write the balanced chemical equations involved in the preparation of $KMnO_4$ from pyrolusite ore (MnO_2). *(2020)*

73. Write the balanced ionic equations showing the oxidising action of acidified dichromate ($Cr_2O_7^{2-}$) solutions with (i) iron (II) ion and (ii) tin (II) ion. *(2020)*

74. How do you prepare :
   (i) K_2MnO_4 from MnO_2?
   (ii) $Na_2Cr_2O_7$ from Na_2CrO_4? *(2020, 2/5, Delhi 2014)*

75. Explain all the steps along with the chemical equation which are used in the preparation of $K_2Cr_2O_7$ from chromite ore. *(2020 C)*

76. When MnO_2 is fused with KOH in the presence of KNO_3 as an oxidizing agent, it gives a dark green compound (*A*). Compound (*A*) disproportionates in acidic solution to give purple compound (*B*). An alkaline solution of compound (*B*) oxidises KI to compound (*C*) whereas an acidified solution of compound (*B*) oxidises KI to (*D*). Identify (*A*), (*B*), (*C*) and (*D*). *(NCERT, Delhi 2019)* An

77. Complete and balance the following chemical equations :
   (i) $Fe^{2+} + MnO_4^- + H^+ \longrightarrow$
   (ii) $MnO_4^- + H_2O + I^- \longrightarrow$ *(2018)* Ap

78. Complete the following equations :
   (i) $2MnO_4^- + 16H^+ + 5S^{2-} \longrightarrow$
   (ii) $KMnO_4 \xrightarrow{\text{Heat}}$ *(2/5, AI 2017)*

79. When chromite ore $FeCr_2O_4$ is fused with NaOH in presence of air, a yellow coloured compound (*A*) is obtained which on acidification with dilute sulphuric acid gives a compound (*B*). Compound (*B*) on reaction with KCl forms an orange coloured crystalline compound (*C*).
   (i) Write the formulae of the compounds (*A*), (*B*) and (*C*).
   (ii) Write one use of compound (*C*). *(Delhi 2016)*

80. Complete the following chemical equations :
   (i) $8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow$
   (ii) $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \longrightarrow$ *(Delhi 2016)*

81. Complete the following equations.
   (i) $2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta}$
   (ii) $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow$ *(2/5, AI 2016)*

82. Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with (i) an iodide (ii) H_2S. *(AI 2015C)*

83. Complete the following equations :
   (i) $Cr_2O_7^{2-} + 2OH^- \longrightarrow$
   (ii) $MnO_4^- + 4H^+ + 3e^- \longrightarrow$ *(AI 2014)*

84. Complete the following equations :
   (i) $2MnO_4^- + 5S^{2-} + 16H^+ \longrightarrow$
   (ii) $Cr_2O_7^{2-} + 2OH^- \longrightarrow$ *(Foreign 2014)*

SA II (3 marks)

85. What is the effect of pH on the solution of $K_2Cr_2O_7$? Also give the structure of chromate and dichromate ion along with the colour of species. *(2020 C)*

86. Explain the method of preparation of sodium dichromate from chromite ore. Give the equation representing oxidation of ferrous salts by dichromate ion. *(AI 2019)*

87. When $FeCr_2O_4$ is fused with Na_2CO_3 in the presence of air it gives a yellow solution of compound (*A*). Compound (*A*) on acidification gives compound (*B*). Compound (*B*) on reaction with KCl forms an orange coloured compound (*C*). An acidified solution of compound (*C*) oxidises Na_2SO_3 to (*D*). Identify (*A*), (*B*), (*C*) and (*D*). *(2019)*

88. Complete the following reactions.
   (i) $MnO_2 + KOH + O_2 \longrightarrow$
   (ii) $I^- + MnO_4^- + H^+ \longrightarrow$
   (iii) $Cr_2O_7^{2-} + Sn^{2+} + H^+ \longrightarrow$ *(AI 2019)*

LA (5 marks)

89. (a) Account for the following :
   (i) Manganese shows maximum number of oxidation states in 3d series.
   (ii) E° value for Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+}.
   (iii) Ti^{4+} is colourless whereas V^{4+} is coloured in an aqueous solution.
   (b) Write the chemical equations for the preparation of $KMnO_4$ from MnO_2. Why does purple colour of acidified permanganate solution decolourise when it oxidises Fe^{2+} to Fe^{3+}? *(2019)*

90. (a) Complete the following chemical reactions :
   (i) $Na_2Cr_2O_7 + KCl \rightarrow$
   (ii) $2MnO_4^- + 5SO_3^{2-} + 6H^+ \rightarrow$
   (b) How does the colour of $Cr_2O_7^{2-}$ change when treated with an alkali? *(2019C)*

4.5 The Lanthanoids

MCQ

91. Lanthanoid contraction is due to increase in
   (a) atomic number
   (b) shielding by 4*f* electrons
   (c) effective nuclear charge
   (d) atomic radius. *(2023)*

92. The most common and stable oxidation state of a Lanthanoid is
   (a) +2 (b) +3
   (c) +4 (d) +6 *(2023)*

93. All the lanthanoids show + 3 as the common oxidation state, yet Ce shows + 4 state because
   (a) it has a tendency to attain noble gas configuration.
   (b) it has a variable ionization enthalpy.
   (c) it has a tendency to gain 1 more electron.
   (d) it has an unpaired electron in 6s. *(2020C)*

VSA **(1 mark)**

94. Give reasons for the following:
Eu^{2+} is a strong reducing agent. *(1/3, Delhi 2019)*

95. Account for the following:
Zr and Hf have almost similar atomic radii.
(1/5, AI 2015) U

96. Name a member of the lanthanoid series which is well known to exhibit +2 oxidation state.
(1/5, Delhi 2014)

97. Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state. *(1/5, AI 2014)*

98. What are the different oxidation states exhibited by the lanthanoids? *(1/3, Foreign 2014)*

SA II **(3 marks)**

99. (a) Write any two consequences of lanthanoid contraction.
(b) Name the element of 3*d* series which exhibits the largest number of oxidation states. Give reason.
(Term II, 2021-22)

100. Account for the following:
(i) Transition elements have higher enthalpies of atomisation.
(ii) Separation of a mixture of Lanthanoid elements is difficult.
(iii) The $E^\circ_{M^{2+}/M}$ value for copper is positive.
(Term II, 2021-22)

101. (i) Which is the most common oxidation state in Lanthanoids?
(ii) Why is there a gradual decrease in the atomic sizes of transition metals in a series with increasing atomic numbers?
(iii) Calculate the number of unpaired electrons in the following gaseous ions:
V^{3+}, Ti^{3+} *(Term II, 2021-22C)*

102. (i) The electronic configuration of Ce is:
$_{58}Ce = [Xe]^{54}\,4f^1\,5d^1\,6s^2$
Calculate the spin only magnetic moment of Ce^{3+} ion.
(ii) Why is copper regarded as a transition element although copper atom has completely filled *d*-orbitals in its ground state?
(iii) Why is Sc^{3+} colourless in aqueous solution whereas Ti^{3+} is coloured? *(Term II, 2021-22C)*

103. What is lanthanoid contraction? What are the consequences of lanthanoid contraction?
(Delhi 2015C)

LA **(5 marks)**

104. (a) (i) Write the number of unpaired electrons in Cr^{3+}. (Atomic number of Cr = 24)
(ii) Complete the reaction mentioning all the products formed:
$Cr_2O_7^{2-} + 3H_2S + 8H^+ \rightarrow$
(b) Account for the following:
(i) Mn^{2+} is more stable than Fe^{2+} towards oxidation to +3 state.
(ii) Copper has exceptionally positive $E^\circ_{M^{2+}/M}$ value.
(iii) Eu^{2+} with electronic configuration $[Xe]\,4f^7\,6s^2$ is a strong reducing agent. *(2023)*

105. (a) Give reasons:
(i) Transition metals and their compounds show catalytic activities.
(ii) Separation of a mixture of Lanthanoid elements is difficult.
(iii) Zn, Cd and Hg are soft and have low melting points.
(b) Write the preparation of the following:
(i) $Na_2Cr_2O_7$ from Na_2CrO_4
(ii) K_2MnO_4 from MnO_2 *(2020)* Ap

4.6 The Actinoids

VSA **(1 mark)**

106. Give reasons:
Actinoids show irregularities in their electronic configurations. *(1/3, 2019, 1/3, Delhi 2016)*

107. How would you account for the following:
Actinoid contraction is greater than lanthanoid contraction? *(2019 C, 1/3, Delhi 2015)*

OR

Assign reasons for the following:
From element to element actinoid contraction is greater than the lanthanoid contraction.
(1/3, AI 2014C)

108. Write one similarity and one difference between the chemistry of lanthanoid and actinoid elements.
(1/5, Delhi 2017) R

109. Chemistry of actinoids is complicated as compared to lanthanoids. Give two reasons. *(1/5, Delhi 2017)*

110. Give reasons for the following:
Actinoids exhibit a greater range of oxidation states than lanthanoids. *(1/3, AI 2014C)*

SA I **(2 marks)**

111. Why do actinoids show a wide range of oxidation states? Write one similarity between the chemistry of lanthanoids and actinoids. *(2/5, AI 2015)*

112. With reference to structural variability and chemical reactivity, write the differences between lanthanoids and actinoids. *(2/5, AI 2014)*

SA II **(3 marks)**

113. Give three points of difference between lanthanoids and actinoids. *(3/5, 2020)*

114. Answer the following:
(a) What is the general electronic configuration of lanthanoids?
(b) What are the common oxidation states of Cerium (At. no. 58)?
(c) Why do actinoids show a wide range of oxidation states? *(2019)*

CBSE Sample Questions

4.2 Electronic Configurations of the d-Block Elements

MCQ

1. Which of the following is the reason for zinc not exhibiting variable oxidation states?
   (a) Inert pair effect
   (b) Completely filled 3*d* subshell
   (c) Completely filled 4*s* subshell
   (d) Common ion effect *(2020-21)*

4.3 General Properties of the Transition Elements (d-Block)

MCQ

2. Which set of ions exhibit specific colours? (Atomic number of Sc = 21, Ti = 22, V=23, Mn = 25, Fe = 26, Ni = 28, Cu = 29 and Zn =30)
   (a) Sc^{3+}, Ti^{4+}, Mn^{3+} (b) Sc^{3+}, Zn^{2+}, Ni^{2+}
   (c) V^{3+}, V^{2+}, Fe^{3+} (d) Ti^{3+}, Ti^{4+}, Ni^{2+}
   (2020-21)

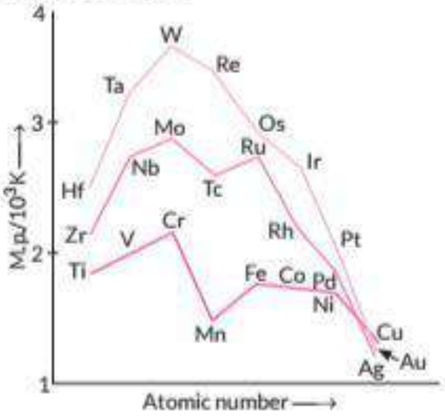
3. Which of the following is a diamagnetic ion? (Atomic numbers of Sc, V, Mn and Cu are 21, 23, 25 and 29 respectively.)
   (a) V^{2+} (b) Sc^{3+}
   (c) Cu^{2+} (d) Mn^{3+}
   (2020-21)

SA II **(3 marks)**

4. (a) Why are fluorides of transition metals more stable in their higher oxidation state as compared to the lower oxidation state?
   (b) Which one of the following would feel attraction when placed in magnetic field: Co^{2+}, Ag^{+}, Ti^{4+}, Zn^{2+}
   (c) It has been observed that first ionisation energy of 5*d* series of transition elements are higher than that of 3*d* and 4*d* series, explain why?

   OR

   On the basis of the figure given below, answer the following questions :



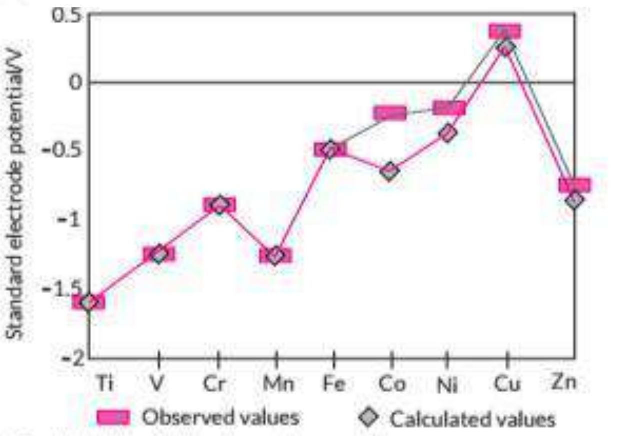
   (a) Why manganese has lower melting point than chromium?
   (b) Why do transition metals of 3*d* series have lower melting points as compared to 4*d* series?
   (c) In the third transition series, identify and name the metal with the highest melting point.
   (Term II, 2021-22) An

5. Account for the following :
   (a) Ti(IV) is more stable than the Ti(II) or Ti(III).
   (b) In case of transition elements, ions of the same charge in a given series show progressive decrease in radius with increasing atomic number.
   (c) Zinc is comparatively a soft metal, iron and chromium are typically hard.
   (Term II, 2021-22)

6. Give reasons for the following :
   (i) Transition elements act as catalysts.
   (ii) It is difficult to obtain oxidation state greater than two for copper.
   (iii) $Cr_2O_7^{2-}$ is a strong oxidising agent in acidic medium whereas WO_3 and MoO_3 are not.

   OR

   Observed and calculated values for the standard electrode potentials of elements from Ti to Zn in the first reactivity series are depicted in the given figure:



   Explain the following observations :
   (i) The general trend towards less negative E° values across the series.
   (ii) The unique behaviour of copper.
   (iii) More negative E° values of Mn and Zn.
   (2020-21) U

4.4 Some Important Compounds of Transition Elements

MCQ

7. $KMnO_4$ is coloured due to
   (a) *d*-*d* transitions

(b) charge transfer from ligand to metal
(c) unpaired electrons in *d* orbital of Mn
(d) charge transfer from metal to ligand.
(Term II, 2021-22)

LA **(5 marks)**

8. Answer the following:
   (a) Why are all copper halides known except that copper iodide?
   (b) Why is the $E^\circ_{(V^{3+}/V^{2+})}$ value for vanadium comparatively low?
   (c) Why HCl should not be used for potassium permanganate titrations?
   (d) Explain the observation, at the end of each period, there is a slight increase in the atomic radius of *d*-block elements.
   (e) What is the effect of pH on dichromate ion solution? *(Term II, 2021-22)*

4.6 The Actinoids

MCQ

9. Given below are two statements labelled as Assertion (A) and Reason (R).
   Assertion (A) : Magnetic moment values of actinides are lesser than the theoretically predicted values.
   Reason (R) : Actinide elements are strongly paramagnetic.
   Select the most appropriate answer from the options given below:
   (a) Both A and R are true and R is the correct explanation of A.
   (b) Both A and R are true but R is not the correct explanation of A.
   (c) A is true but R is false.
   (d) A is false but R is true. *(Term II, 2021-22)*

Detailed SOLUTIONS

Previous Years' CBSE Board Questions

1. Zn, Cd, Hg are considered as *d*-block elements but not as transition elements because they do not have partly filled *d*-orbitals in their atomic state or their common oxidation states (*i.e.*, Zn^{2+}, Cd^{2+}, Hg^{2+}).

Key Points
- The electronic configuration of the elements should be well known.

2. Elements which have incompletely filled *d*-orbitals in their ground state or in any one of their oxidation states are called transition elements.
Characteristics of transition elements :
(i) They show variable oxidation states.
(ii) They exhibit catalytic properties.

3. (d): Due to variable oxidation states of transition metals, they show their catalytic activity.

4. Mn^{3+} is a strong oxidising agent having $E^\circ = +1.57$ V.

5. (a): Interstitial compounds are chemically inert.

6. (c)

Key Points
- In 3*d* series, Mn has maximum number of oxidation state because number of unpaired electrons is maximum in Mn ($3d^5, 4s^2$).

7. (c): Because of strong metallic bonding present in atoms of transition elements, they have high melting points.

8. (d): Transition metals have high melting points because of the involvement of greater number of $(n-1)d$ and *ns* electrons in the interatomic metallic bonding.

9. Zn, Cd and Hg do not have partly filled *d*-orbital in their ground state or common oxidation state.

10. Scandium (Sc) exhibits only (+3) oxidation state.

11. The transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to adsorb the reactant(s) and ability to form complexes. For example; vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation).

12. Strong metallic bonds between the atoms of transition elements are responsible for the high melting points.

13. Zn^{2+} ion has completely filled *d*-subshell and no *d*-*d* transition is possible. So zinc salts are colourless.

Configuration of Cu^{2+} is [Ar] $3d^9$. It has partly filled *d*-subshell and hence it is coloured due to *d*-*d* transition.

14. Zinc

15. Cu(I) compounds have completely filled *d*-orbitals and there are no vacant *d*-orbitals for promotion of electrons whereas Cu(II) compounds have one unpaired electron which is responsible for colour formation.

Concept Applied
- *d*-*d* transition is responsible for the colour formation of transition elements.

16. Oxoanion of chromium in which it shows +6 oxidation state equal to its group number is $Cr_2O_7^{2-}$ (dichromate ion).

17. Formula of oxoanion of manganese is MnO_4^-.
Oxidation state of Mn in this oxoanion = + 7
Group number of Mn is 7.

18. Due to presence of vacant *d*-orbitals and *d*-*d* transitions, compounds of the transition metals are generally coloured.

When an electron from a lower energy *d*-orbital is excited to a higher energy *d*-orbital, the energy of excitation corresponds to the frequency which generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed. The frequency of the light absorbed is determined by the nature of the ligand.

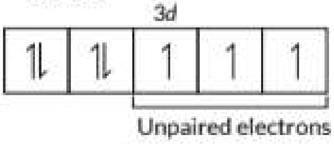
19. Zn^{2+} ion has completely filled *d*-subshell but Cu^{2+} ion has partly filled *d*-subshell.

20. Transition elements can use their *ns* and $(n - 1)$ *d*-orbital electrons for bond formation therefore, they show variable oxidation states. Because, the energy difference between $(n-1)d$ orbital and *ns* orbital is small.

21. **(b):** $Co = [Ar]3d^7 4s^2$

$Co^{2+} = [Ar]3d^7$

$\therefore$



i.e., there are three unpaired electrons ($n = 3$).

Hence, $\mu = \sqrt{n(n+2)}$ B.M.

$= \sqrt{3(3+2)} = 3.87$ B.M.

22. (i) Sc^{3+} has $3d^0$ outer electronic configuration, therefore it is diamagnetic in nature whereas Cr^{3+} has $3d^3$ outer electronic configuration. So, it is paramagnetic due to presence of unpaired electrons.

(ii) Chromium has higher melting and boiling points. In a particular series, the metallic strength increases upto middle with increasing number of unpaired electrons, *i.e.*, upto d^5 configuration. After Cr, the number of unpaired electrons goes on decreasing. Accordingly, the m.pt and b.pt. decrease after middle (Cr) because of increasing pairing of electrons.

23. $Mn^{3+} : 3d^4$

No. of unpaired electrons = 4

$Cr^{3+} : 3d^3$

No. of unpaired electrons = 3

Out of these, Cr^{3+} is most stable in aqueous solution due to half filled t_{2g} level, *i.e.*, t_{2g}^3.

24. $Ti^{3+} : 3d^1$

No of unpaired electrons = 1

$Cr^{3+} : 3d^3$

No. of unpaired electrons = 3

Out of these, Cr^{3+} is most stable in aqueous solution due to half filled t_{2g} level, *i.e.*, t_{2g}^3.

25. (i) Transition metals form alloys because they have similar atomic radii.

(ii) Basic nature of oxides decreases and acidic nature increases with increase in oxidation state of the metal. Oxidation state of Mn in Mn_2O_3 is +3 thus it is basic while in Mn_2O_7 it is +7 thus it is acidic.

26. (i) Cr^{2+} is a stronger reducing agent than Fe^{2+}.

$E^\circ_{Cr^{3+}/Cr^{2+}}$ is negative (–0.41 V) whereas $E^\circ_{Fe^{3+}/Fe^{2+}}$ is positive (+0.77 V). Thus, Cr^{2+} is easily oxidized to Cr^{3+} but Fe^{2+} cannot be easily oxidized to Fe^{3+}. Hence, Cr^{2+} is stronger reducing agent than Fe^{2+}.

(ii) More positive is the value of E°, more feasible will be the reaction.

As $E^\circ_{Co^{3+}/Co^{2+}}$ is maximum, thus Co^{2+} ion is most stable.

27. (a) Cr^{2+} is reducing as its configuration changes from d^4 to d^3 and d^3 has stable half filled t_{2g}^3 configuration. On the other hand change of Mn^{3+} to Mn^{2+} result in half-filled d^5 stable configuration thus Mn^{3+} acts as strong oxidizing agent.

(b) Transition metal ions with d^1 configuration have a tendency to lose this single electron and give ion with a noble gas configuration.

28. (i) Variable oxidation states of transition metals arise due to incomplete filling of *d*-orbitals and it differs from each other by unity *e.g.*, V(V), V(IV), V(III), V(II). In *p*-block elements oxidation states differ generally by a unit of two. *e.g.*, Sn(II), Sn(IV), PCl_3, PCl_5, etc.

(ii) In aqueous solution, Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.

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

Hydration enthalpy of Cu^{2+} is higher than Cu^+ thus Cu^{2+} is more stable in aqueous solution.

29. (i) Transition elements can use their *ns* and $(n - 1)d$ orbital electrons for bond formation therefore, they show variable oxidation states.

For example, Cr has $ns^2(n-1)d^4$ electronic configuration. It utilizes two electrons from its *ns* subshell then its oxidation state = +2. When it utilizes both the electrons, then its oxidation state = +3, +4 or +6.

(ii) In Zn, Cd and Hg, all the electrons in *d*-subshell are paired. Hence, the metallic bonds are weak. That is why they are soft metals with low melting and boiling points.

30. (i) Manganese can form $p\pi - d\pi$ bond with oxygen by utilising 2*p*-orbital of oxygen and 3*d*-orbital of manganese due to which it can show highest oxidation state of +7. While with fluorine it cannot form such $p\pi - d\pi$ bond thus, it can show a maximum of +4 oxidation state.

(ii) Transition elements can use their *ns* and $(n - 1)d$ orbital electrons for bond formation therefore, they show variable oxidation states.

31. (i) Transition elements can use their *ns* and $(n - 1)d$ orbital electrons for bond formation therefore, they show variable oxidation states.

(ii) In aqueous solutions, Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.

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

Cu^{2+} in aqueous solutions is more stable than Cu^+ ion because hydration enthalpy of Cu^{2+} is higher than that of Cu^+. It compensates the second ionisation enthalpy of Cu involved in the formation of Cu^{2+} ions.

32. Transition elements can use their *ns* and (n - 1) *d*-orbital electrons for bond formation therefore, they show variable oxidation states.

Among the 3*d* series, manganese (Mn) exhibits the largest number of oxidation states from +2 to +7 because it has maximum number of unpaired electrons.

Mn - [Ar] $3d^5\,4s^2$

33. (i) Manganese can form $p\pi - d\pi$ bond with oxygen by utilising 2*p*-orbital of oxygen and 3*d*-orbital of manganese due to which it can show highest oxidation state of +7. While with fluorine it cannot form such $p\pi - d\pi$ bond thus, it can show a maximum of +4 oxidation state.

(ii) The transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to adsorb the reactant(s) and ability to form complexes. Vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation) are some of the examples.

34. Disproportionation reaction involves the oxidation and reduction of the same substance. The example of disproportionation reaction in aqueous solution is :

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

35. (i) Electronic configuration of Mn^{2+} is $3d^5$ which is half filled and hence stable. Therefore, third ionization enthalpy is very high, *i.e.*, 3rd electron cannot be lost easily. In case of Fe^{2+}, electronic configuration is $3d^6$. Hence, it can lose one electron easily to give the stable configuration $3d^5$.

(ii) Zinc (Z = 30) has completely filled *d*-orbital ($3d^{10}$), so *d*-orbitals do not take part in interatomic bonding. Hence, metallic bonding is weak.

This is why it has very low enthalpy of atomisation (126 kJ mol^{-1}).

36. (i) Characteristics of transition elements :

(a) They show variable oxidation states.

(b) They exhibit catalytic properties.

(ii) Zn is considered as *d*-block element but not as transition element because it does not have partly filled *d*-orbitals in its atomic state or common oxidation states (*i.e.*, Zn^{2+}).

37. (i) The atoms of transition metals have strong metallic bonds between them due to the involvement of both (n - 1)*d* and *ns* electrons in bonding , thus these have high melting and boiling points.

(ii) Irregular variation of ionisation enthalpies is mainly attributed to varying degree of stability of different 3*d*-configurations (*e.g.*, d^0, d^5, d^{10} are exceptionally stable).

38. (i) In aqueous solution, Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.

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

Hydration enthalpy of Cu^{2+} is higher than Cu^+ that is why Cu^{2+} is more stable in aqueous solution.

(ii) This is due to ability of oxygen to form multiple bonds with metals.

39. (i) Transition elements can use their *ns* and (n - 1) *d*-orbital electrons for bond formation therefore, they show variable oxidation states. Because, the energy difference between (n -1)d orbital and *ns* orbital is small.

(ii) The tendency to form complexes is high for Co(III) as compared to Co(II). Co^{2+} ions are very stable and are difficult to oxidise. Co^{3+} ions are less stable and are reduced by water. In contrast many Co(II) complexes are readily oxidised to Co(III) complexes and Co(III) complexes are very stable, *e.g.*,

$$[Co(NH_3)_6]^{2+} \xrightarrow{\text{Air}} [Co(NH_3)_6]^{3+}$$

This happens because the crystal field stabilisation energy of Co(III) with a $d^6(t_{2g}^6)$ configuration is higher than for Co(II) with a $d^7\ (t_{2g}^6\, e_g^1)$ arrangement.

40. (i) In aqueous solution Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.

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

Hydration enthalpy of Cu^{2+} is higher than Cu^+ that is why Cu^{2+} is more stable in aqueous solution.

(ii) Transition elements have more number of unpaired electron in their valence shells than alkali metals, that is why transition elements make strong metallic bonds, which results in extreme hardness as compared to alkali metals.

41. (i) The transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to adsorb the reactant(s) and ability to form complexes. For example, vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation).

(ii) Due to presence of vacant *d*-orbitals, there is *d-d* transitions in the compounds of the transition metals that is why they are generally coloured.

When an electron from a lower energy *d*-orbital is excited to a higher energy *d*-orbital, the energy of excitation corresponds to the frequency which generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed. The frequency of the light absorbed is determined by the nature of the ligand.

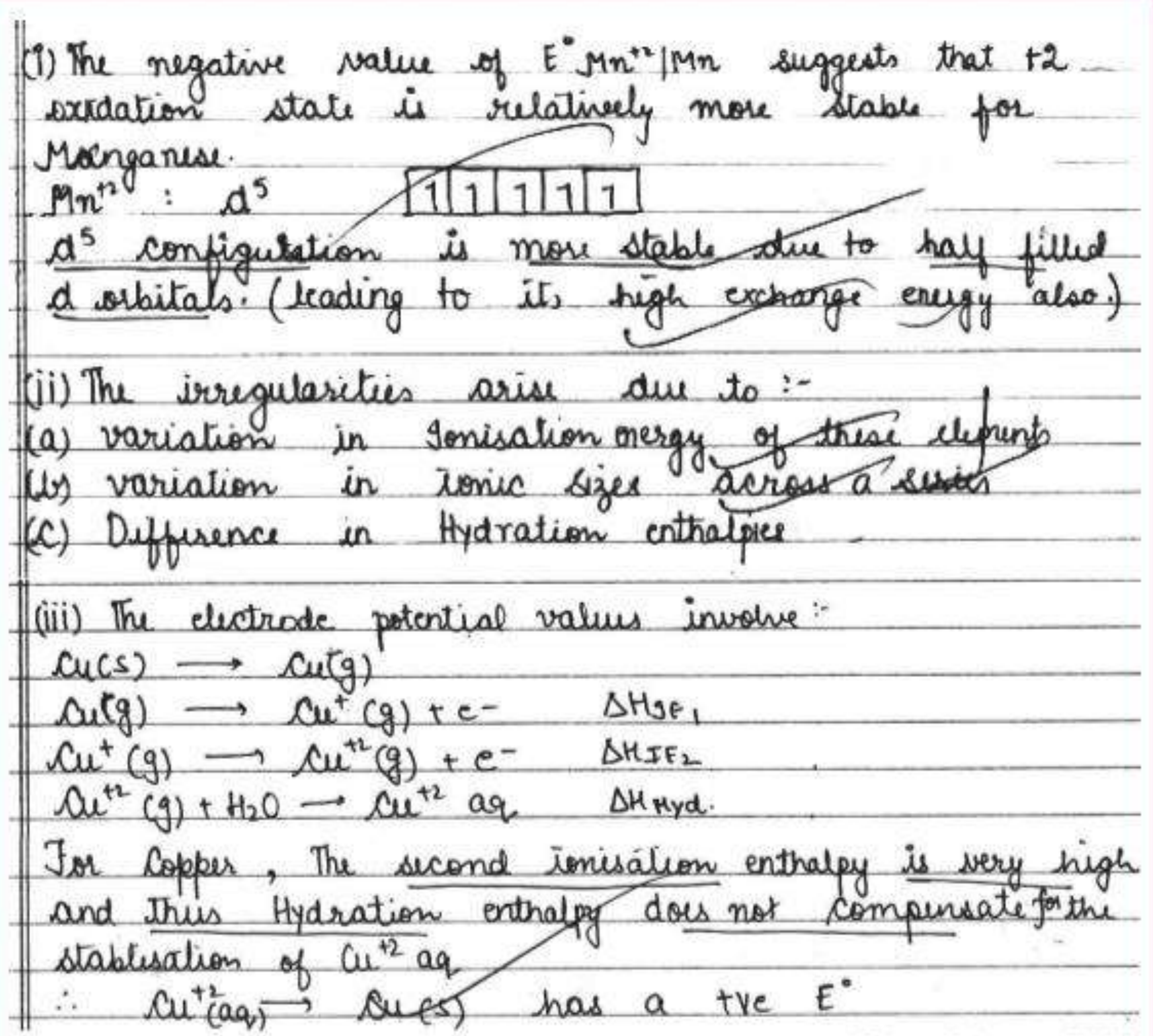
42. (i) Cr^{3+} is most stable, because of stable t_{2g}^3 electronic configuration of Cr^{3+} in aqueous solution.

(ii) Mn^{3+} is the strongest oxidising agent. Mn^{3+} on reduction gives Mn^{2+} which is quite stable due to half filled $3d^5$ electronic configuration.

(iii) Due to absence of unpaired electron in Ti^{4+}, it is a colourless ion.

E.C. of Ti^{4+} = $[Ar]3d^0 4s^0$

43.



(i) The negative value of $E^\circ_{Mn^{+2}|Mn}$ suggests that +2 oxidation state is relatively more stable for Manganese.

Mn^{+2} : d^5 | 1 | 1 | 1 | 1 | 1 |

d^5 configuration is more stable due to half filled d orbitals. (leading to its high exchange energy also.)

(ii) The irregularities arise due to :-

(a) variation in Ionisation energy of these elements

(b) variation in ionic sizes across a series

(c) Difference in Hydration enthalpies

(iii) The electrode potential values involve :-

$Cu(s) \longrightarrow Cu(g)$

$Cu(g) \longrightarrow Cu^+(g) + e^-$ $\quad \Delta H_{IE_1}$

$Cu^+(g) \longrightarrow Cu^{+2}(g) + e^-$ $\quad \Delta H_{IE_2}$

$Cu^{+2}(g) + H_2O \longrightarrow Cu^{+2}\ aq$ $\quad \Delta H_{Hyd.}$

For Copper, The second ionisation enthalpy is very high and Thus Hydration enthalpy does not compensate for the stablisation of Cu^{+2} aq

$\therefore$ $Cu^{+2}_{(aq)} \longrightarrow Cu(s)$ has a +ve E°

[Topper's Answer, 2022]

44. (i) Zn^{2+} ion has completely filled *d*-subshell and no *d-d* transition is possible. So zinc salts are white.

Configuration of Cu^{2+} is [Ar] $3d^9$. It has partly filled *d*-subshell and hence it is coloured due to *d-d* transition.

(ii) E° value of Mn^{3+}/Mn^{2+} is + 1.57 V.

$$Mn^{3+}_{(aq)} + e^- \longrightarrow Mn^{2+}_{(aq)}\ ;\ E^\circ = +1.57\ V$$

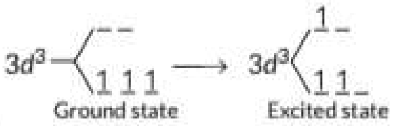
This value is highly positive because Mn^{3+} (d^4) has a very high tendency to get reduced to Mn^{2+} (d^5) which has a stable half - filled electronic configuration.

(iii) Transition metals form alloys because they have similar atomic radii.

45. (i) Colour of transition metal ions is due to the *d-d* transitions. Ions which do not involve in *d-d* transitions are colourless.

Ti^{4+} : $3d^0 4s^0$, No unpaired *d*-electrons, so no *d-d* transition, colourless

Cr^{3+} : $3d^3$, *d-d* transitions occur as shown below :



Hence, Cr^{3+} ion is coloured.

V^{3+} : d^2, *d-d* transition occur as shown below :

Hence, V^{3+} ion is coloured.

In other words, Generally the ions having completely empty *d*-orbitals or no unpaired electron in *d*-orbitals of transition element are colourless.

(ii) $Mn^{2+}(3d^5) \longrightarrow Mn^{3+}(3d^4)$
More stable $\quad$ Less stable

Mn^{2+} is more stable in $3d^5$ state, hence shows resistance towards oxidation.

$Fe^{2+}(3d^6) \longrightarrow Fe^{3+}(3d^5)$
Less stable $\quad$ More stable

Fe^{3+} is more stable hence Fe^{2+} gets oxidised easily to Fe^{3+}.

(iii) Highest oxidation state of transition element is shown with oxides and fluorides, because oxygen and flourine are small in size and have high electronegativity.

46. (i) Silver atom has outer electronic configuration $4d^{10}5s^1$ in its ground state, but silver in +2 oxidation state has electronic configuration $4d^9$. So in +2 oxidation state, silver has incomplete *d*-orbital. Hence, silver is considered as a transition element.

(ii) Mn^{2+} ion has stable half-filled ($3d^5$) electronic configuration whereas Zn^{2+} has completely filled d^{10} configuration. Hence, $E^\circ_{Mn^{2+}/Mn}$ and $E^\circ_{Zn^{2+}/Zn}$ are more negative than expected.

(iii) Transition metals form alloys because they have similar atomic radii.

47. (a) In case of copper, the sum of enthalpy of atomisation and ionisation enthalpy is greater than enthalpy of hydration. That is why $E^\circ_{M^{2+}/M}$ for Cu is positive. So, copper does not displace hydrogen from acids.

(b) Transition metals and most of their compounds contain unpaired electrons in the (n - 1)*d*-orbitals. Hence, they show paramagnetic behaviour.

(c) In Zn, Cd and Hg, all the electrons in *d*-subshell are paired. Hence, the metallic bonds are weak. That is why they are soft metals with low melting and boiling points.

48. (i) The high melting points of transition metals are attributed to the involvement of greater number of (n - 1)*d* electrons in addition to *ns* electrons in the interatomic metallic bonding. In any row, the melting points of these metals rise to a maximum at d^5 except for anomalous values of Mn and Tc and fall regularly as the atomic number increases.

(ii) Due to presence of vacant *d*-orbitals and *d-d* transitions, compounds of the transition metals are generally coloured.

When an electron from a lower energy *d*-orbital is excited to a higher energy *d*-orbital, the energy of excitation corresponds to the frequency which generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed. The frequency of the light absorbed is determined by the nature of the ligand.

(iii) E° value of Mn^{3+}/Mn^{2+} is + 1.57 V.

$$Mn^{3+}_{(aq)} + e^- \longrightarrow Mn^{2+}_{(aq)} \; ; \; E^\circ = +1.57 \text{ V}$$

This value is highly positive because Mn^{3+} (d^4) has a very high tendency to get reduced to Mn^{2+} (d^5) which has a stable half - filled electronic configuration.

49. (i) Enthalpy of atomisation depends on the number of unpaired electrons in the valence shell. Greater the number of valence electrons, stronger is the resultant bonding and higher will be the enthalpy of atomisation. In 3*d* series, zinc has no unpaired electrons in valence shell so, it has lowest enthalpy of atomisation.

(ii) The enthalpies of second and third transition series are high because of the poor shielding of electrons in 4*d* and 5*d* orbitals in comparison to electrons in 3*d* orbital which results in strong metallic bonding.

(iii) Transition metals have high enthalpies of atomisation because of presence of unpaired electrons and poor shielding effect of *d*-orbitals.

50. Elements which have incompletely filled *d*-orbitals in their ground state or in any one of their oxidation states are called transition elements.

Zn, Cd, Hg are considered as *d*-block elements but not as transition elements because they do not have partly filled *d*-orbitals in their atomic state or their common oxidation states (*i.e.*, Zn^{2+}, Cd^{2+}, Hg^{2+}).

Variable oxidation states of transition metals arise due to incomplete filling of *d*-orbitals and it differs from each other by unity *e.g.*, V(V), V(IV), V(III), V(II). In *p*-block elements oxidation states differ generally by a unit of two. *e.g.*, Sn(II), Sn(IV), PCl_3, PCl_5, etc.

51. (a) The transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to adsorb the reactant(s) and ability to form complexes. Vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation) are some of the examples. Catalysis involves the formation of bonds between reactant molecules and atoms at the surface of the catalyst.

(b) Mn^{2+} ion has stable half-filled ($3d^5$) electronic configuration. Its ionisation enthalpy value is lower in comparison to hydration enthalpy. Hence $E^\circ_{Mn^{2+}/Mn}$ is more negative.

(c) Cr^{2+} is a strong reducing agent since its configuration is converted to d^3 from d^4. d^3 has half filled t_{2g} configuration with higher stability.

52. (a) Transition elements can use their *ns* and (n - 1) *d*-orbital electrons for bond formation therefore, they show variable oxidation states. Because, the energy difference between (n -1)*d* orbital and *ns* orbital is small.

(b) Electrode potential (E°) value is the sum of three factors :

(i) Enthalpy of sublimation, $\Delta_{sub}H$ for $Cu_{(s)} \rightarrow Cu_{(g)}$

(ii) Ionisation enthalpy, $\Delta_i H$ for $Cu_{(g)} \rightarrow Cu^{2+}_{(g)}$

(iii) Hydration enthalpy, $\Delta_{hyd}H$ for $Cu^{2+}_{(g)} \rightarrow Cu^{2+}_{(aq)}$

In case of copper the sum of enthalpy of sublimation and ionisation enthalpy is greater than enthalpy of hydration. This is why $E^\circ_{M^{2+}/M}$ for Cu is positive.

(c) Cr^{2+} is reducing since its configuration is converted to d^3 from d^4. d^3 has half filled t_{2g} configuration with higher stability.

53. Elements which have incompletely filled *d*-orbitals in their ground state or in any one of their oxidation states are called transition elements

The following are the characteristics of transition elements :

(a) They show variable oxidation states.

(b) They exhibit catalytic properties.

54. (a) Electrode potential (E°) value is the sum of three factors :

(i) Enthalpy of sublimation $\Delta_{sub}H$ for $Cu_{(s)} \rightarrow Cu_{(g)}$
(ii) Ionisation enthalpy Δ_iH for $Cu_{(g)} \rightarrow Cu^{2+}_{(g)}$
(iii) Hydration enthalpy $\Delta_{hyd}H$ for $Cu^{2+}_{(g)} \rightarrow Cu^{2+}_{(aq)}$

In case of copper the sum of enthalpy of sublimation and ionisation enthalpy is greater than enthalpy of hydration. This is why $E^\circ_{M^{2+}/M}$ for Cu is positive.

(b) In aqueous solutions, Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.

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

Cu^{2+} in aqueous solutions is more stable than Cu^+ ion because hydration enthalpy of Cu^{2+} is higher than that of Cu^+. It compensates the second ionisation enthalpy of Cu involved in the formation of Cu^{2+} ions.

55. (i) Transition metal form alloys because they have similar atomic radii.

(ii) Due to fully filled d-orbital (d^{10}), Zn has weak metallic bond, thus it has lowest enthalpy of atomization.

(iii) Manganese can from $p\pi$-$d\pi$ bond with oxygen by utilising $2p$-orbital of oxygen and $3d$-orbital of manganese due to which it can show highest oxidation state of +7. While with fluorine it cannot form such $p\pi$-$d\pi$ bond thus, it can show a maximum of +4 oxidation state.

56. (i) Cr^{2+} is a strong reducing agent since its configuration is converted to d^3 from d^4. d^3 has half filled t_{2g} configuration with higher stability.

(ii) Cu^+ is unstable in aqueous solution

In aqueous solutions, Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.

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

(iii) Mn^{3+} is a strong oxidising agent because electronic configuration of Mn^{2+} is $3d^5$ which is half filled and hence stable. Therefore, third ionization enthalpy is very high, *i.e.*, 3rd electron cannot be lost easily.

Key Points

- Species tends to act as oxidising and reducing agent to attain most stable oxidation state.

57. (i) From the relation, $\Delta G^\circ = -nFE^\circ$

More positive is the value of E°, reaction will be feasible.

$$\underset{3d^4}{Mn^{3+}} \xrightarrow{+e^-} \underset{\substack{3d^5 \\ \text{More stable} \\ \text{(half filled)}}}{Mn^{2+}} \quad ; \quad \underset{\substack{3d^5 \\ \text{More stable} \\ \text{(half filled)}}}{Fe^{3+}} \xrightarrow{+e^-} \underset{3d^6}{Fe^{2+}}$$

Hence, E°_{value} for Mn^{3+}/Mn^{2+} couple is much more positive than that for Fe^{3+}/Fe^{2+}.

(ii) Greater the number of unpaired electrons, stronger is the metallic bond and therefore, higher is the enthalpy of atomisation. Since, iron has greater number of unpaired electrons than copper hence has higher enthalpy of atomisation.

(iii) Only those ions are coloured which have partially filled d-orbitals facilitating d-d transitions. Sc^{3+} has no unpaired electron but Ti^{3+} has one unpaired electron and hence, Ti^{3+} is coloured.

58. (i) Transition metals form a large number of complex compounds due to following reasons :

- Comparatively smaller size of metal ions.
- High ionic charges.
- Availability of d-orbitals for bond formation.

(ii) Lowest oxidation compounds of transition metals are basic due to their ability to get oxidised to higher oxidation states. Whereas, the higher oxidation state of metal and compounds gets reduced to lower ones and hence are acidic in nature.

e.g., MnO is basic whereas Mn_2O_7 is acidic.

(iii) E° value of Mn^{3+}/Mn^{2+} is + 1.57 V.

$$Mn^{3+}_{(aq)} + e^- \longrightarrow Mn^{2+}_{(aq)} \,;\, E^\circ = +1.57\text{ V}$$

This value is highly positive because Mn^{3+} (d^4) has a very high tendency to get reduced to Mn^{2+} (d^5) which has a stable half - filled electronic configuration.

59. (i) Manganese can form $p\pi$ - $d\pi$ bond with oxygen by utilising $2p$-orbital of oxygen and $3d$-orbital of manganese due to which it can show highest oxidation state of +7. While with fluorine it cannot form such $p\pi$ - $d\pi$ bond thus, it can show a maximum of +4 oxidation state.

(ii) Cr^{2+} is a strong reducing agent since its configuration is converted to d^3 from d^4. d^3 has half filled t_{2g} configuration with higher stability.

(iii) Zn^{2+} ion has completely filled d-subshell and no d-d transition is possible. So zinc salts are white.

Configuration of Cu^{2+} is [Ar] $3d^9$. It has partly filled d-subshell and hence it is coloured due to d-d transition.

60. (i) In case of copper, the sum of enthalpy of atomisation and ionisation enthalpy is greater than enthalpy of hydration. That is why $E^\circ_{M^{2+}/M}$ for Cu is positive.

(ii) Mn^{2+} ion has stable half-filled ($3d^5$) electronic configuration. Its ionisation enthalpy value is lower in comparison to hydration enthalpy. Hence $E^\circ_{Mn^{2+}/Mn}$ is more negative.

(iii) Cr^{2+} is a stronger reducing agent than Fe^{2+}.

$E^\circ_{Cr^{3+}/Cr^{2+}}$ is negative (– 0.41 V) whereas $E^\circ_{Fe^{3+}/Fe^{2+}}$ is positive (+ 0.77 V). Thus Cr^{2+} is easily oxidized to Cr^{3+} but Fe^{2+} cannot be easily oxidized to Fe^{3+}. Hence, Cr^{2+} is stronger reducing agent than Fe^{2+}.

Concept Applied

- $Cu^{2+}_{(aq)}$ is more stable than $Cu^+_{(aq)}$ due to the more negative value of $\Delta_{Hyd}H^\circ$ of Cu^{2+} than Cu^+.

61. (i) Electronic configuration of Mn^{2+} is $3d^5$ which is half filled and hence stable. Therefore, third ionization enthalpy is very high, *i.e.*, 3rd electron cannot be lost easily. In case of Fe^{2+}, electronic configuration is $3d^6$. Hence, it can lose one electron easily to give the stable configuration $3d^5$.

(ii) Zinc (Z = 30) has completely filled d-orbital ($3d^{10}$), so d-orbitals do not take part in interatomic bonding. Hence, metallic bonding is weak.

This is why it has very low enthalpy of atomisation (126 kJ mol^{-1}).

(iii) Only those ions are coloured which have partially filled *d*-orbitals facilitating *d*-*d* transitions.

Sc^{3+} with $3d^0$ configuration is colourless while Ti^{3+} ($3d^1$) is coloured.

62. (i) Manganese can form $p\pi - d\pi$ bond with oxygen by utilising 2*p*-orbital of oxygen and 3*d*-orbital of manganese due to which it can show highest oxidation state of +7, Example - MnO_3F.

(ii) The transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to adsorb the reactant(s) and ability to form complexes. Vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation) are some of the examples. Catalysis involves the formation of bonds between reactant molecules and atoms at the surface of the catalyst.

(iii) Cr^{2+} is reducing as its configuration changes from d^4 to d^3, the later having a half-filled t_{2g} level, on the other hand, the change from Mn^{3+} to Mn^{2+} result in the half-filled (d^5) configuration which has extra stability.

(iv) Zn does not have unpaired electrons due to which metal-metal bonding is weak so Zn has lowest enthalpy of atomisation.

(v) Copper (I) compounds are unstable in aqueous solution and undergo disproportionation.

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

The stability of Cu^{2+}(*aq*) rather than Cu$^+$(*aq*) is due to the much more negative $\Delta_{hyd}H°$ of Cu^{2+}(*aq*) than Cu$^+$(*aq*), which more than compensates for second ionisation enthalpy of Cu.

63. (i) Mn shows maximum no. of oxidation states from +2 to +7 because Mn has maximum number of unpaired electrons in 3*d* sub-shell.

(ii) Cr has maximum melting point, because it has 6 unpaired electrons in the valence shell, hence it has strong interatomic interaction.

(iii) Sc shows only +3 oxidation state because after losing 3 electrons, it has noble gas electronic configuration.

(iv) Mn is strong oxidising agent in +3 oxidation state because change of Mn^{3+} to Mn^{2+} give stable half filled (d^5) electronic configuration,

$E°_{(Mn^{3+}/Mn^{2+})} = 1.5$ V.

64. In aqueous solution,

$$\underset{\substack{\text{Dichromate ion}\\ \text{(Orange red)}}}{Cr_2O_7^{2-}} + H_2O \rightleftharpoons \underset{\substack{\text{Chromate ion}\\ \text{(Yellow)}}}{2CrO_4^{2-}} + 2H^+$$

When an acid is added (*i.e.*, pH of solution decreased), the concentration of H$^+$ ions is increased and the reaction proceeds in the backward direction producing an orange red dichromate solution.

65. $3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$

66. $2MnO_4^- + 6H^+ + 5NO_2^- \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$

67. Orange colour of $Cr_2O_7^{2-}$ ion changes to yellow when an alkali such as NaOH is added because on addition of an alkali, the concentration of H$^+$ ions decreases and hence, the reaction proceeds in the forward direction producing yellow solution containing CrO_4^{2-} ions.

$$\underset{\text{Orange}}{Cr_2O_7^{2-}} + 2OH^- \longrightarrow \underset{\text{Yellow}}{2CrO_4^{2-}} + H_2O$$

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

69. $2MnO_4^- + 5SO_2 + 2H_2O \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$

70. (a) $\Delta G° = -nFE°$

More positive is the *E*° value, reaction will be more feasible.

$$Mn^{3+}_{(aq)} + e^- \longrightarrow Mn^{2+}_{(aq)} \ ; \ E° = +1.57 \text{ V}$$

This value is highly positive because Mn^{3+} (d^4) has a very high tendency to get reduced to Mn^{2+} (d^5) which has a stable half - filled electronic configuration.

$$\underset{\substack{3d^5\\ \text{(More stable)}}}{Fe^{3+}} + e^- \longrightarrow \underset{3d^6}{Fe^{2+}} \ ; \ E° = +0.77 \text{ V}$$

$$Cr^{3+} + e^- \longrightarrow Cr^{2+} \ ; \ E° = -0.41 \text{ V}$$

(b) $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$

71. (a) $2MnO_4^- + 6H^+ + 5NO_2^- \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$

(b) $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

72. Preparation of potassium permanganate : Potassium permanganate is prepared by the fusion of MnO_2 (pyrolusite) with potassium hydroxide and an oxidising agent like KNO_3 to form potassium manganate which disproportionates in a neutral or acidic solution to form permanganate.

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

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

or, $3K_2MnO_4 + 4HCl \rightarrow 2KMnO_4 + MnO_2 + 2H_2O + 4KCl$

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

(ii) $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$.

74. (i) $2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta} 2K_2MnO_4 + 2H_2O$

(ii) Sodium dichromate can be crystallised out from sodium chromate solution by acidifying it with sulphuric acid.

$2Na_2CrO_4 + 2H^+ \longrightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$

75. (i) Yellow solution of Na_2CrO_4 is filtered and acidified with conc. H_2SO_4 acid to give $Na_2Cr_2O_7$.

$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

(ii) Sodium dichromate solution is treated with KCl to give $K_2Cr_2O_7$.

$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

This reaction occurs because potassium dichromate is less soluble than sodium dichromate.

76. (*A*) is K_2MnO_4, (*B*) is $KMnO_4$, (*C*) is KIO_3 and (*D*) is I_2.

$$MnO_2 + 2KOH + KNO_3 \longrightarrow \underset{(A)}{K_2MnO_4} + KNO_2 + H_2O$$

$$3K_2MnO_4 + 2H_2SO_4 \longrightarrow \underset{(B)}{2KMnO_4} + MnO_2 + 2K_2SO_4 + 2H_2O$$

$$2KMnO_4 + H_2O + KI \longrightarrow 2MnO_2 + 2KOH + \underset{(C)}{KIO_3}$$

$$2KMnO_4 + 8H_2SO_4 + 10KI \longrightarrow 6K_2SO_4 + 2MnSO_4 + 8H_2O + 5I_2$$

(D)

77. (i) $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$

(ii) $2MnO_4^- + H_2O + I^- \rightarrow 2OH^- + 2MnO_2 + IO_3^-$

78. (i) $2MnO^-_4 + 16H^+ + 5S^{2-} \longrightarrow 2Mn^{2+} + 8H_2O + 5S$

(ii) $2KMnO_4 \xrightarrow{heat} K_2MnO_4 + MnO_2 + O_2$

79. (i) $4FeCr_2O_4 + 16NaOH + 7O_2 \longrightarrow \underset{(A)}{8Na_2CrO_4} + 2Fe_2O_3 + 8H_2O$

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow \underset{(B)}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$$

$$Na_2Cr_2O_7 + 2KCl \longrightarrow \underset{(C)}{K_2Cr_2O_7} + 2NaCl$$

(ii) Potassium dichromate is used as a powerful oxidising agent in industries and for staining and tanning of leather.

Key Points

- Students must remember the equations involved in the preparation of potassium dichromate.

80. (i) $8MnO_{4\,(aq)}^- + 3S_2O_{3\,(aq)}^{2-} + H_2O_{(l)} \rightarrow 8MnO_{2(aq)} + 6SO_{4\,(aq)}^{2-} + 2OH^-_{(aq)}$

(ii) $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$

81. (i) $2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta} 2K_2MnO_4 + 2H_2O$

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

82. Potassium dichromate is a strong oxidising agent. In the presence of dilute sulphuric acid, one molecule of $K_2Cr_2O_7$ gives 3 atoms of available oxygen.

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

(ii) $K_2Cr_2O_7 + 3H_2S + 4H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3S + K_2SO_4 + 7H_2O$

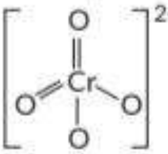
83. (i) $Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$

(ii) $MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O$

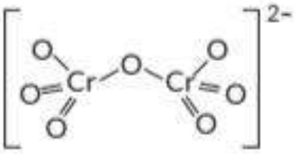
84. (i) $5S^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5S$

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

85. On decreasing pH, *i.e.*, on acidifying, yellow colour of CrO_4^{2-} changes to $Cr_2O_7^{2-}$ (orange) while on increasing pH, *i.e.*, on treating with alkalies, orange colour of $Cr_2O_7^{2-}$ changes to CrO_4^{2-} (Yellow).



Chromate ion (Yellow)



Dichromate ion (Orange)

86. The yellow solution of sodium chromate is acidified with sulphuric acid to give an orange solution of sodium dichromate $Na_2Cr_2O_7$ which is crystallised.

$$\underset{\text{Sodium chromate}}{2Na_2CrO_4} + H_2SO_4 \longrightarrow \underset{\text{Sodium dichromate}}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$$

The solution of sodium dichromate is treated with potassium chloride to obtain potassium dichromate.

$$Na_2Cr_2O_7 + 2KCl \longrightarrow \underset{\text{Potassium dichromate}}{K_2Cr_2O_7} + 2NaCl$$

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

87. $FeCr_2O_4 + Na_2CO_3 \longrightarrow \underset{(A)}{2Na_2CrO_4} + Fe_2O_3 + CO_2$

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow \underset{(B)}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$$

$$Na_2Cr_2O_7 + 2KCl \longrightarrow \underset{(C)}{K_2Cr_2O_7} + 2NaCl$$

$$K_2Cr_2O + H_2SO_4 + Na_2SO_3 \longrightarrow K_2SO_4 + Na_2Cr_2O_7 + H_2O + SO_2$$

88. (i) $2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$

(ii) $2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$

(iii) $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$

89. (a) (i) In 3*d* series, Mn has maximum number of oxidation state because number of unpaired electrons is maximum in Mn ($3d^5, 4s^2$).

(ii) $E°$ value of Mn^{3+}/Mn^{2+} is + 1.57 V.

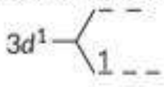
$$Mn^{3+}_{(aq)} + e^- \longrightarrow Mn^{2+}_{(aq)} ; E° = +1.57\text{ V}$$

This value is highly positive because Mn^{3+} (d^4) has a very high tendency to get reduced to Mn^{2+} (d^5) which has a stable half - filled electronic configuration.

(iii) Colour of transition metal ions is due to the *d*-*d* transitions. Ions which do not involve in *d*-*d* transitions are colourless.

Ti^{4+} : $3d^0 4s^0$, no *d*-*d* transition, colourless

V^{4+} : d^1, *d*-*d* transition occur as shown below :



Hence, V^{4+} ion is coloured.

In other words, generally the ions having completely empty *d*-orbitals or no unpaired electron in *d*-orbitals of transition element are colourless.

(b) Preparation of potassium permanganate : Potassium permanganate is prepared by the fusion of MnO_2 (pyrolusite) with potassium hydroxide and an oxidising agent like KNO_3 to form potassium manganate which disproportionates in a neutral or acidic solution to form permanganate.

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

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

or, $3K_2MnO_4 + 4HCl \rightarrow 2KMnO_4 + MnO_2 + 2H_2O + 4KCl$

$$5Fe^{2+} + \underset{\text{(Purple colour)}}{MnO_4^-} + 8H^+ \rightarrow \underset{\text{(Colourless)}}{Mn^{2+}} + 4H_2O + 5Fe^{3+}$$

90. (a) (i) $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

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

(b) Orange colour of $Cr_2O_7^{2-}$ ion changes to yellow when an alkali such as NaOH is added because on addition of an alkali, the concentration of H^+ ions decreases and hence, the reaction proceeds in the forward direction producing yellow solution containing CrO_4^{2-} ions.

$$\underset{\text{Orange}}{Cr_2O_7^{2-}} + 2OH^- \longrightarrow \underset{\text{Yellow}}{2CrO_4^{2-}} + H_2O$$

91. (c): As we move along the lanthanoid series, the nuclear charge increases by one unit at each successive element. The new electron is added into the same subshell *i.e.*, 4*f*. As a result, the attraction of the electrons by the nucleus increases and this tends to decrease the size. Further, as the new electron is added into the *f*-subshell, there is imperfect shielding of one electron by another in this subshell due to the shapes of these *f*-orbitals. This imperfect shielding is unable to counter balance the effect of increased nuclear charge.

92. (b): The most stable and common oxidation state of a lanthanoid is +3. However, some elements show variable oxidation state they try to lose or gain electrons to get +3 states, which makes them strong reducing or oxidising agents respectively.

93. (a): All lanthanoids show +3 as the common oxidation state, yet Ce shows +4 oxidation state due to attainment of noble gas configuration.
Ce^{4+}: $[Xe]4f^0$

94. Eu^{2+} has a strong tendency to lose electrons to attain the more stable +3 oxidation state of lanthanoids hence, it is a strong reducing agent.

95. Due to lanthanoid contraction the elements of 4*d* and 5*d*-series have similar atomic radii *e.g.*, Zr = 145 pm and Hf = 144 pm.

96. Europium (Eu) is well known to exhibit +2 oxidation state due to its half-filled *f* orbital in +2 oxidation state.

97. Lanthanoids showing +4 oxidation state are $_{58}Ce$, $_{59}Pr$, $_{65}Tb$ and $_{66}Dy$.

98. Lanthanum and all the lanthanoids predominantly show +3 oxidation state. However, some of the lanthanoids also show +2 and +4 oxidation states in solution or in solid compounds. This irregularity arises mainly due to attainment of stable empty ($4f^0$), half-filled ($4f^7$) and fully filled ($4f^{14}$) sub shell.

e.g., $Ce^{4+} : 4f^0$, $Eu^{2+} : 4f^7$
$Tb^{4+} : 4f^7$, $Yb^{2+} : 4f^{14}$

99. (a) **Lanthanoid contraction :** The steady decrease in the atomic and ionic radii of lanthanoid elements with increase in atomic number is called lanthanoid contraction.

Consequences of lanthanoid contraction :

(i) Atomic radii of second and third transition series element are almost identical. As a result they occur in nature together and their separation from mixutre different.

(ii) The small difference in atomic radii of lanthanoids is responsible for difference in their basic properties.

(b) Among the 3*d* series, Mn exhibits largest number of oxidation states from +2 to +7 because it has maximum number of unpaired electrons.

100. (i) Because of large number of unpaired electrons in their atoms they have stronger interatomic attraction and hence stronger metallic bonding between atoms resulting in higher enthalpies of atomisation.

(ii) Separation of a mixture of lanthanoids is difficult because they have similar atomic radius due to lanthanoid contraction and similar chemical properties.

(iii) Electrode potential ($E°$) value is the sum of three factors :

1. Enthalpy of sublimation $\Delta_{sub}H$ for $Cu_{(s)} \rightarrow Cu_{(g)}$
2. Ionisation enthalpy $\Delta_i H$ for $Cu_{(g)} \rightarrow Cu^{2+}_{(g)}$
3. Hydration enthalpy $\Delta_{hyd}H$ for $Cu^{2+}_{(g)} \rightarrow Cu^{2+}_{(aq)}$

In case of copper the sum of enthalpy of sublimation and ionisation enthalpy is greater than enthalpy of hydration. This is why $E^\circ_{M^{2+}/M}$ for Cu is positive.

101. (i) +3 is the most common oxidation state in lanthanoids.

(ii) From left to right in a transition series, atomic number increases. Number of protons in the nucleus and number of electrons in the penultimate shell increases. *d*-electrons have very poor shielding power. Thus, effective nuclear charge increases. Nuclear attractive force on the outermost electron increases and hence atomic and ionic radii decreases.

(iii) V(23) : $[Ar]3d^3 4s^2$
V^{3+}: $[Ar]\,3d^2$
No. of unpaired e^- = 2
Ti(22) : $[Ar]3d^2 4s^2$
Ti^{3+} : $[Ar]\,3d^1$
No. of unpaired e^- = 1

102. (i) Ce(58) : $[Xe]4f^1 5d^1 6s^2$
Ce^{3+} : $[Xe]4f^1$

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

(ii) Copper atom has completely filled *d*-orbital ($3d^{10}$) in its ground state.
But in its most common oxidation state of +2 , the configuration is d^9, *i.e.*, the *d*-subshell is incompletely filled. Hence, it is a transition element.

(iii) Only those ions are coloured which have partially filled *d*-orbitals facilitating *d*-*d* transitions. Sc^{3+} has no unpaired electron but Ti^{3+} has one unpaired electron and hence, Ti^{3+} is coloured.

103. **Lanthanoid contraction :** The steady decrease in the atomic and ionic radii of lanthanoid elements with increase in atomic number is called lanthanoid contraction.

Consequences of lanthanoid contraction :

(i) The basic strength of oxides and hydroxides of lanthanoids decrease with increasing atomic number.

(ii) Atomic and ionic sizes of 4*d* transition series elements and 5*d* series elements are similar. *e.g.*, atomic radii of zirconium(Zr) is same as that of hafnium Hf.

104. (a) (i) At. no. of Cr is 24.
Electronic configuration : $[Ar]\,3d^5 4s^1$
Cr^{3+} : $[Ar]3d^3$

No. of unpaired e^- = 3

(ii) $Cr_2O_7^{2-} + 3H_2S + 8H^+ \longrightarrow 2Cr^{3+} + 7H_2O + 3S$

(b) (i) Electronic configuration of Mn^{2+} is $3d^5$ which is half filled and hence stable. Therefore, third ionization enthalpy is very high, *i.e.*, 3rd electron cannot be lost easily. In case of Fe^{2+}, electronic configuration is $3d^6$. Hence, it can lose one electron easily to give the stable configuration $3d^5$.

(ii) In case of copper, the sum of enthalpy of atomisation and ionisation enthalpy is greater than enthalpy of hydration. That is why $E^\circ_{M^{2+}/M}$ for Cu is positive.

(iii) Eu^{2+} has a strong tendency to lose electrons to attain the more stable +3 oxidation state of lanthanoids hence, it is a strong reducing agent.

105. (a) (i) Transition metal and their compounds show catalytic activities due to their ability to adopt multiple oxidation states, ability to absorb the reactant(s) and ability to form complexes.

(ii) Separation of a mixture of lanthanoids is difficult because they have similar atomic radius due to lanthanoid contraction and similar chemical properties.

(iii) In Zn, Cd and Hg, all the electrons in *d*-subshell are paired. Hence, the metallic bonds are weak. That is why they are soft metals with low melting and boiling points.

(b) (i) The yellow solution of sodium chromate is acidified with sulphuric acid to give a orange solution of sodium dichromate $Na_2Cr_2O_7$, which is crystallized.

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

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

106. The irregularities in the electronic configurations of actinoids are due to extra stabilities of the f^0, f^7 and f^{14} orbitals.

107. The actinoid contraction is more than lanthanoid contraction because 5*f*-electrons are more poorly shielded than 4*f*-electrons.

108. Similarity : The elements of both the series are electropositive in nature. They are reactive metals and act as strong reducing agents.

Difference : Lanthanoids except promethium are non-radioactive elements, while all actinoids are radioactive elements.

109. Chemistry of actinoids is more complicated than lanthanoids because

(i) actinoids show greater number of oxidation states due to the comparable energies of 5*f*, 6*d* and 7*s* orbitals.

(ii) most of the actinoids are radioactive and the study of their chemistry in the laboratory is difficult.

110. Actinoids exhibit greater range of oxidation states than lanthanoids. This is because there is less energy difference between 5*f* and 6*d* orbitals in actinoids than the energy difference between 4*f* and 5*d* orbitals in case of lanthanoids.

111. Actinoids exhibit greater range of oxidation states than lanthanoids. This is because there is less energy difference between 5*f* and 6*d* orbitals in actinoids than the energy difference between 4*f* and 5*d* orbitals in case of lanthanoids. Similarity : The elements of both the series are electropositive in nature. They are reactive metals and act as strong reducing agents.

112. **Structure :** All the lanthanoids are silvery white soft metals. Hardness of Lanthanoids increases with increasing atomic number.

The actinoid metals are all silvery in appearance but display a variety of structures. The structural variability is due to irregularities in metallic radii which are greater than that of lanthanoids.

Chemical reactivity : Earlier members of lanthanoid series are quite reactive similar to calcium but with increasing atomic number they behave more like aluminium.

The actinoids are highly reactive in finely divided state.

113. Difference between lanthanoids and actinoids are following :

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

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

(iii) **Chemical reactivity :** First few members of lanthanoids are quite reactive almost like calcium, whereas, actinoids are highly reactive metals especially in the finely divided state. Lanthanoids react with dilute acids to liberate H_2 gas whereas actinoids react with boiling water to give a mixture of oxide and hydride.

Key Points

- In actinoids, neptunium (Np) and plutonium (Pu) show maximum oxidation states upto +3 to +7.

114. (a): General electronic configuration of lanthanoids is $4f^{1-14}5d^{0-1}6s^2$.

(b) Cerium shows +3, +4 oxidation states.

(c) Actinoids exhibit greater range of oxidation states than lanthanoids. This is because there is less energy difference between 5*f* and 6*d* orbitals in actinoids than the energy difference between 4*f* and 5*d* orbitals in case of lanthanoids.

CBSE Sample Questions

1. (b) (1)

2. (c) : V^{3+}, V^{2+}, Fe^{3+} possesses two, three and five unpaired electrons in 3*d*-subshell. Hence, they will give coloured solution. (1)

3. (b): $V^{2+} : 3d^3 \Rightarrow$ No. of unpaired electrons = 3
$\Rightarrow$ paramagnetic
$Sc^{3+} : 3d^0 \Rightarrow$ No. of unpaired electrons is zero
$\Rightarrow$ diamagnetic
$Cu^{2+} : 3d^9 \Rightarrow$ No. of unpaired electron = 1
$\Rightarrow$ paramagnetic
$Mn^{3+} : 3d^4 \Rightarrow$ No. of unpaired electrons = 4 (1)
$\Rightarrow$ paramagnetic

4. (a) The ability of fluorine to stabilise the highest oxidation state is attributed to the higher lattice energy or high bond enthalpy. (1)

(b) Co^{2+} has three unpaired electrons so it would be paramagnetic in nature, hence Co^{2+} ion would be attracted to magnetic field. Rest all ions are diamagnetic in nature. (1)

(c) The transition elements of 5*d* series have intervening 4*f* orbitals. There is greater effective nuclear charge acting on outer valence electrons due to the weak shielding by 4*f* electrons. Hence, first ionisation energy of 5*d* series of transition elements are higher than that of 3*d* and 4*d* series. (1)

OR

(a) Manganese has five unpaired electrons in its *d*-orbital which is completely half filled and having more stability. Hence, these electrons are not free to participate in metallic bonding. So, Mn has less heat of atomization and its melting point is lower than chromium. (1)

(b) The 4*d* and 5*d* transition elements have larger size than that of 3*d* elements. They form strong metal-metal bond which required more energy to break bond. That is why 3*d* series have lower melting point than 4*d* series. (1)

(c) Tungsten (W). (1)

5. (a) Ti is having electronic configuration $[Ar]3d^2 4s^2$ which on loss of four electrons will lead to the formation of Ti^{4+} [Ti(IV)] which is more stable as it acquires nearest noble gas configuration. (1)

(b) In case of transition elements, ions of the same charge in a given series show progressive decrease in radius with increasing atomic number. As the new electron enters in *d*-orbital each time the nuclear charge increases by unity. The shielding effect of a *d* electrons is not that effective, hence the net electrostatic attraction between the nucleus and the outermost electron increases and the ionic radius decreases. (1)

(c) Iron and chromium are having high enthalpy of atomization due to the presence of unpaired electrons, which accounts for their hardness. However, zinc has low enthalpy of atomization as it has no unpaired electron. Hence, zinc is comparatively a soft metal. (1)

6. (i) The transition elements are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to absorb the reactant(s) and ability to form complexes. (1)

(ii) Due to high value of third ionisation enthalpy. (1)

(iii) Mo(VI) and W(VI) are more stable than Cr(VI). (1)

OR

(i) The general trend towards less negative $E°$ values across the series is related to the general increase in the sum of first and second ionization enthalpies. (1)

(ii) Copper has high positive reduction potential ($E°$ value) and this show that copper is least reactive metal. Electrode potential ($E°$) value is the sum of three factors.

(a) Enthalpy of atomisation, $\Delta_a H$ for $Cu_{(s)} \rightarrow Cu_{(g)}$.

(b) Ionisation enthalpy, $\Delta_i H$ for $Cu_{(g)} \rightarrow Cu^{2+}_{(g)}$

(c) Hydration enthalpy, $\Delta_{hyd} H$ for $Cu^{2+}_{(g)} \rightarrow Cu^{2+}_{(aq)}$

In case of copper the sum of enthalpy of atomisation and ionisation enthalpy is is not balanced enthalpy of hydration. This is why $E°_{M^{2+}/M}$ for Cu is positive. (1)

(iii) Mn^{2+} ion and Zn^{2+} ion has stable half-filled($3d^5$) and fully-filled ($3d^{10}$) electronic configuration. Hence $E°_{Mn^{2+}/Mn}$ and $E°_{Zn^{2+}/Zn}$ is more negative. (1)

7. (b): Charge transfer from ligand to metal.

The Mn atom in $KMnO_4$ has +7 oxidation state with electronic configuration $[Ar]3d^0 4s^0$. Since no unpaired electrons are present, *d*-*d* transitions are not possible. The molecule should, therefore, be colourless. But its intense purple colour is due to $L \rightarrow M$ (ligand to metal) charge transfer 2*p*(*L*) of O to 3*d*(*M*) of Mn. (1)

8. (a) Cu^{2+} oxidizes iodide ion to iodine. (1)

(b) The low value for V is due to the stability of V^{2+} having half-filled t_{2g} level. (1)

(c) Permanganate titrations in presence of hydrochloric acid are unsatisfactory since hydrochloric acid is oxidised to chlorine. (1)

(d) The *d* orbital is full with ten electrons and shield the electrons present in the higher *s*-orbital to a greater extent resulting in increase in size. (1)

(e) The chromates and dichromates are inter-convertible in aqueous solution depending upon pH of the solution. Increasing the pH (in basic solution) of dichromate ions a colour change from orange to yellow is observed as dichromate ions change to chromate ions. (1)

9. (b): The magnetic moment is less as the 5*f* electrons of actinides are less effectively shielded which results in quenching of orbital contributions. They are strongly paramagnetic due to presence of unpaired electrons. (1)
