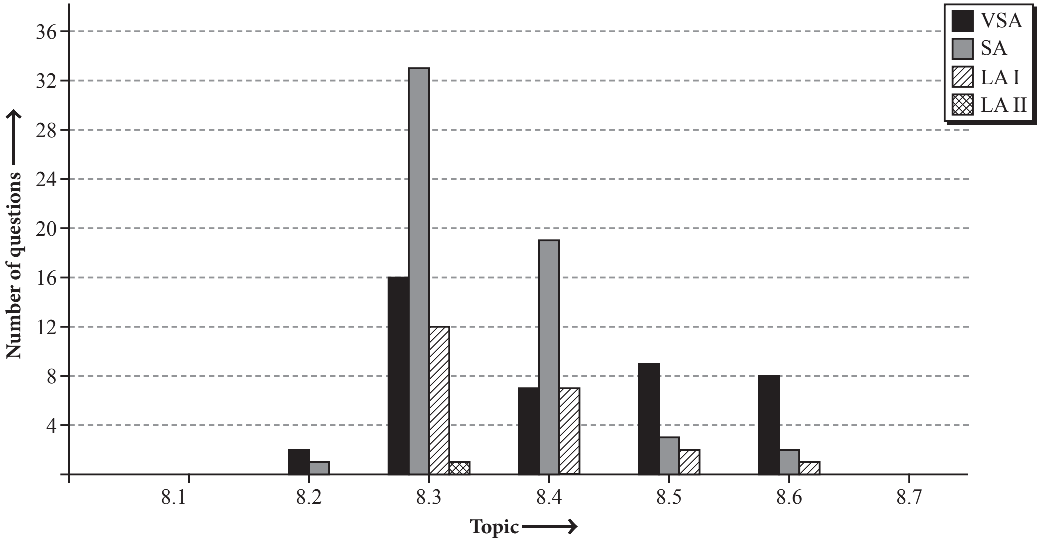
CHAPTER

8

The *d*- and *f*-Block Elements

Topicwise Analysis of Last 10 Years' CBSE Board Questions (2020-2011)



- Maximum total weightage is of *General Properties of the Transition Elements* (*d-Block*).
- Maximum VSA type questions were asked from *General Properties of the Transition Elements* (*d-Block*).
- Maximum SA and LA I type questions were asked from *General Properties of the Transition Elements* (*d-Block*).

QUICK RECAP

TRANSITION ELEMENTS (*d*-BLOCK ELEMENTS)

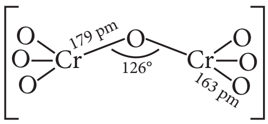
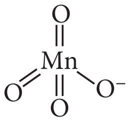
- Elements in which the last electron enters any one of the five *d*-orbitals of their respective penultimate shell are known as *transition elements* or *d-block elements*.
- Their general electronic configuration is $(n-1)d^{1-10}ns^{0-2}$.

Transition series : *d*-block consists of four transition series,
1st Transition series or 3*d* series $_{21}Sc - _{30}Zn$
2nd Transition series or 4*d* series $_{39}Y - _{48}Cd$
3rd Transition series or 5*d* series $_{57}La, _{72}Hf - _{80}Hg$
4th Transition series or 6*d* series $_{89}Ac, _{104}Rf - _{112}Cn$

General characteristics :

Melting and boiling points	High due to strong metallic bonding
Enthalpies of atomisation	High due to strong interatomic interactions
Ionisation enthalpies	Generally increases from left to right in a series
Oxidation states	Variable due to participation of *ns* and $(n-1)d$ electrons
Atomic radii	Decrease from left to right but become constant when pairing of electrons takes place
Complex formation	Form complexes due to high nuclear charge and small size and availability of empty *d*-orbitals to accept lone pair of electrons donated by ligands.
Coloured compounds	Form coloured compounds due to *d-d* transitions
Magnetic properties	Transition metal ions and their compounds are paramagnetic due to presence of unpaired electrons in the $(n-1)d$-orbitals and it is calculated by using the formula, $\mu = \sqrt{n(n+2)}$ where, *n* is the no. of unpaired electrons.
Catalytic behaviour	Due to variable oxidation states and ability to form complexes
Interstitial compounds	Due to empty spaces in their lattices, small atoms can be easily accommodated
Alloy formation	Due to similar atomic sizes

Some important compounds :

Compounds	Preparation	Properties	Uses
Potassium dichromate ($K_2Cr_2O_7$) 	From sodium dichromate (obtained from chromite ore) $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$ $2Na_2CrO_4 + 2H^+ \longrightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$ $Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$	Orange red crystalline solid, oxidising agent having melting point 398°C. **Oxidising agent in acidic medium :** $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ **Oxidises :** I^- to I_2, H_2S to S, Sn^{2+} to Sn^{4+} and Fe^{2+} to Fe^{3+}	In dyeing, photography and leather industry.
Potassium permanganate ($KMnO_4$) 	From potassium manganate (obtained from pyrolusite) $2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$ $2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$	Deep purple crystalline solid, oxidising agent, having melting point 240°C. **Oxidising agent in acidic medium :** $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ **Oxidises :** I^- to I_2, Fe^{2+} to Fe^{3+}, $C_2O_4^{2-}$ to CO_2, S^{2-} to S, SO_3^{2-} to SO_4^{2-}, NO_2^- to NO_3^- **Oxidising agent in faintly alkaline or neutral medium :** $MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$ **Oxidises :** I^- to IO_3^-, $S_2O_3^{2-}$ to SO_4^{2-}, Mn^{2+} to MnO_2	As a disinfectant, germicide, and Baeyer's reagent (alkaline $KMnO_4$).

- Volumetric titrations involving $KMnO_4$ are carried out only in the presence of dil. H_2SO_4 but not in the presence of HCl or HNO_3 because HCl is oxidised to Cl_2 and HNO_3 is itself a strong oxidising agent and partly oxidises the reducing agent. H_2SO_4 does not give any oxygen of its own to oxidise the reducing agent.

INNER TRANSITION ELEMENTS (*f*-BLOCK ELEMENTS)

- **Lanthanoids :** Last electron enters one of the 4*f*-orbitals. Cerium (at. no. 58) to lutetium (at. no. 71).
- **Actinoids :** Last electron enters one of the 5*f*-orbitals. Thorium (at. no. 90) to lawrencium (at. no. 103).

General electronic configuration : $(n-2)f^{1-14}\,(n-1)d^{0-1}\,ns^2$

General characteristics of lanthanoids :

Atomic and ionic radii	Decrease on going from La to Lu.
Oxidation states	Most common oxidation state of lanthanoids is +3. Some elements exhibit +2 and +4 oxidation states due to extra stability of empty, half-filled or fully-filled *f*-subshell, *e.g.*, Ce^{4+} acts as an oxidising agent and gets reduced to Ce^{3+}, Eu^{2+}, Yb^{2+} act as strong reducing agents and get oxidised to Eu^{3+} and Yb^{3+}.
Action of air	All the lanthanoids are silvery white soft metals and tarnish readily in moist air. They burn in oxygen of air and form oxides (Ln_2O_3 type).
Coloured ions	They form coloured trivalent metal ions due to *f*-*f* transitions of unpaired electrons. La^{3+} and Lu^{3+} are colourless ions due to empty ($4f^0$) or fully ($4f^{14}$) orbitals.
Magnetic properties	La^{3+}, Lu^{3+} are diamagnetic while trivalent ions of the rest of lanthanoids are paramagnetic.
Reducing agents	They readily lose electrons and are good reducing agents.
Electropositive character	Highly electropositive because of low ionisation energies.
Alloy formation	They form alloys easily with other metals especially iron.
Tendency to form complexes	Lanthanoids do not have much tendency to form complexes due to low charge density because of their large size. The tendency to form complexes and their stability increases with increasing atomic number.

Lanthanoid contraction : In lanthanoid series, with increasing atomic number, there is progressive decrease in atomic/ionic radii (M^{3+} ions) from La^{3+} to Lu^{3+}.

- **Reason :** Due to addition of new electrons into *f*-subshell and imperfect shielding of one electron by another in the *f*-orbitals, there is greater effect of increased nuclear charge than screening effect hence contraction in size occurs.
- **Consequences :** Their separation is difficult, they have small differences in properties and 4*d* and 5*d* transition series have almost same atomic radii (Zr and Hf have similar properties due to same size).

Uses of lanthanoids : Used in making mischmetal, an alloy of a lanthanoid metal (~ 95%) with iron (~ 5%) and traces of S, C, Ca and Al. It is used to make tracer bullets, shells and lighter flints.

General characteristics of actinoids :

Ionic radii	Like lanthanoids, ionic radii decrease across the series. Actinoid contraction is greater due to poor sheilding effect of the 5*f*-electrons. Further, 5*f*-orbitals extend in space beyond 6*s* and 6*p*-orbitals whereas 4*f*-orbitals are burried deep inside the atom.

Oxidation states	Like lanthanoids, most common oxidation state is +3. They also show oxidation state of +4, +5, +6 and +7, *e.g.*, in Th, Pa, U and Np respectively. They show a large number of oxidation states because of very small energy gap between 5*f*, 6*d* and 7*s* subshells.
Action of air, alkalies and acids	Like lanthanoids they are also silvery white metals, tarnish rapidly in air forming oxide coating and are not attacked by alkalies and are less reactive towards acids.
Coloured ions	Coloured due to *f*-*f* transition except $Ac^{3+}(5f^0)$, $Cm^{3+}(5f^7)$ and $Th^{4+}(5f^0)$ which are colourless.
Magnetic properties	They are strongly paramagnetic.
Density	All actinoids except thorium and americium have high densities.
Melting and boiling points	High melting and boiling points however there is no regular trend with rise in atomic number.
Ionisation energy	They have low ionisation energies than lanthanoides.
Reducing agents	All actinoids are strong reducing agents.
Electropositive character	Highly electropositive metals.

- **Uses of actinoids :** Th is used in atomic reactor and treatment of cancer. U and Pu are used as fuel in nuclear reactor.

- **Differences between lanthanoids and actinoids :**

Lanthanoids	Actinoids
They show +2 and +4 oxidation states in few cases besides +3.	They show higher oxidation states of +4, +5, +6 and +7 besides +3.
Except promethium, they are non-radioactive.	All actinoids are radioactive.
They do not form oxo-cations.	They form oxo-cations like UO_2^{2+}, PuO_2^{2+}, UO_2^{+}, etc.
The compounds of lanthanoids are less basic.	Actinoid compounds are more basic.
They have less tendency of complex formation.	They have greater tendency of complex formation.

Previous Years' CBSE Board Questions

8.2 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)*

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

SA **(2 marks)**

3. What are the transition elements? Write two characteristics of the transition elements. *(Delhi 2015)*

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

VSA **(1 mark)**

Read the given passage and answer the questions number (4 to 8) 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. *(2020)*

4. Why are Zn, Cd and Hg non-transition elements?

5. Which transition metal of 3*d* series does not show variable oxidation states?

6. Why do transition metals and their compounds show catalytic activity?

7. Why are melting points of transition metals high?

8. Why is Cu^{2+} ion coloured while Zn^{2+} ion is colourless in aqueous solution?

9. Out of zinc and tin, whose coating is better to protect iron objects? *(One word, 2020)*

10. 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)*

11. **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)*

12. Account for the following :
Copper(I) compounds are white whereas copper(II) compounds are coloured. *(1/5, 2020)*

13. Write the formula of an oxoanion of chromium (Cr) in which it shows the oxidation state equal to its group number. *(Delhi 2017)*

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

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

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

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

18. Assign reason for the following :
Copper (I) ion is not known in aqueous solution. *(1/2, Delhi 2011)*

19. Explain giving reasons :
Transition metals and their compounds generally exhibit a paramagnetic behaviour. *(1/2, AI 2011)*

SA (2 marks)

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

21. 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)*

22. 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)*

23. 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)*

24. (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)*

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

26. 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)*

27. Account for the following :
(i) Transition metals show variable oxidation states.
(ii) Cu^+ ion is unstable in aqueous solution. *(2/3, AI 2015)*

28. 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)*

29. 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)*

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

31. 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)*

32. (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)*

33. 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)*

34. 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)*

35. 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)

36. Assign reasons for the following :

(i) Cu(I) ion is not known to exist in aqueous solutions.

(ii) Transition metals are much harder than the alkali metals. *(2/3, AI 2014C)*

37. 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)*

38. (i) Which metal in the first transition series (3*d*-series) exhibits +1 oxidation state most frequently and why?

(ii) Which of following cations are coloured in aqueous solutions and why?

Sc^{3+}, V^{3+}, Ti^{4+}, Mn^{2+}

(At. Nos. Sc = 21, V = 23, Ti = 22, Mn = 25)

(Delhi 2013)

39. How would you account for the following?

(i) Transition metals exhibit variable oxidation states.

(ii) Transition metals and their compounds act as catalyst. *(2/3, Delhi 2013)*

40. How would you account for the following?

(i) Many of the transition elements are known to form interstitial compounds.

(ii) The metallic radii of the third (5*d*) series of transition metals are virtually the same as those of the corresponding group member of the second (4*d*) series.

(2/3, Delhi 2012)

41. How would you account for the following?

(i) With the same *d*-orbital configuration (d^4) Cr^{2+} is a reducing agent while Mn^{3+} is an oxidising agent.

(ii) Most of the transition metal ions exhibit characteristic colours in aqueous solutions. *(2/3, Delhi 2012)*

42. How would you account for the following :

(i) The $E^\circ_{M^{2+}/M}$ for copper is positive (+0.34 V). Copper is the only metal in the first series of transition elements showing this behaviour.

(ii) The metallic radii of the third (5*d*) series of transition metals are nearly the same as those of the corresponding members of the second (4*d*) series. *(2/3, AI 2012)*

43. Explain the following observations :

(i) Many of the transition elements are known to form interstitial compounds.

(ii) There is a general increase in density from titanium ($Z = 22$) to copper ($Z = 29$).

(2/3, AI 2012)

44. Explain the following observations.

(i) With the same *d*-orbital configuration (d^4), Cr^{2+} is a reducing agent while Mn^{3+} is an oxidising agent.

(ii) There is hardly any increase in atomic size with increasing atomic numbers in a series of transition metals.

(2/3, AI 2012)

45. Explain the following :

(i) The enthalpies of atomization of transition metals are quite high.

(ii) The transition metals and many of their compounds act as good catalysts.

(Delhi 2012C)

46. Give reason :

(i) Sc (21) is a transition element but Ca (20) is not.

(ii) The Fe^{2+} is much more easily oxidised to Fe^{3+} than Mn^{2+} to Mn^{3+}.

(2/3, AI 2012C)

47. How is the variability in oxidation states of transition elements different from that of non-transition elements? Illustrate with examples. *(2/5, AI 2012C)*

48. Account for the following :

(i) Mn^{2+} compounds are more stable than Fe^{2+} compounds towards oxidation to their +3 state.

(ii) Cr^{2+} is reducing and Mn^{3+} oxidizing when both have d^4 configuration.

(2/5, AI 2012C)

49. Assign reasons for each of the following :

(i) Transition metals generally form coloured compounds.

(ii) Manganese exhibits the highest oxidation state of +7 among the 3rd series of transition elements.

(Delhi 2011)

50. How would you account for the following :

(i) Cr^{2+} is reducing in nature while with the same *d*-orbital configuration (d^4) Mn^{3+} is an oxidising agent.

(ii) In a transition series of metals, the metal which exhibits the greatest number of oxidation states occurs in the middle of the series. *(AI 2011)*

51. State reasons for the following :

(i) Cu (I) ion is not stable in an aqueous solution.

(ii) Unlike Cr^{3+}, Mn^{2+}, Fe^{3+} and the subsequent other V^{2+} ions of the 3*d* series of elements, the 4*d* and the 5*d* series metals generally do not form stable cationic species. *(AI 2011)*

52. Explain giving a suitable reason for each of the following :

(i) Transition metals and their compounds are generally found to be good catalysts.

(ii) Metal-metal bonding is more frequent for the 4*d* and the 5*d* series of transition metals than that for the 3*d* series.

(AI 2011)

LA I (3 marks)

53. 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)*

54. 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)*

55. 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)*

56. 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?

(3/5, AI 2017)

57. 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)*

58.

$E^\circ_{(M^{2+}/M)}$	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 $E^\circ_{(Cu^{2+}/Cu)}$ value exceptionally positive?

(ii) Why is $E^\circ_{(Mn^{2+}/Mn)}$ value highly negative as compared to other elements?

(iii) Which is a stronger reducing agent Cr^{2+} or Fe^{2+}? Give reason. *(3/5, AI 2015)*

59. 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)*

60. Give reasons for the following :
- (i) Mn^{3+} is a good oxidising agent.
- (ii) $E^\circ_{M^{2+}/M}$ values are not regular for first row transition metals (3*d*-series).
- (iii) Although 'F' is more electronegative than 'O', the highest Mn fluoride is MnF_4, whereas the highest oxide is Mn_2O_7. *(3/5, AI 2013)*

61. Give reasons :
- (i) *d*-block elements exhibit more oxidation states than *f*-block elements.
- (ii) The enthalpies of atomization of the transition metals are high.
- (iii) The variation in oxidation states of transition metals is of different type from that of the non-transition metals. *(3/5, AI 2013C)*

62. Explain the following :
- (i) Copper (I) ion is not stable in an aqueous solution.
- (ii) With same (d^4) configuration Cr (II) is reducing whereas Mn (III) is oxidising.
- (iii) Transition metals in general act as good catalysts. *(3/5, Foreign 2011)*

63. How would you account for the following :
- (i) Metal-metal bonding is more extensive in the 4*d* and 5*d* series of transition elements than the 3*d* series.
- (ii) Mn (III) undergoes disproportionation reaction easily.
- (iii) Co (II) is easily oxidised in the presence of strong ligands. *(3/5, Foreign 2011)*

64. Account for the following :
- (i) The transition metals and their compounds act as good catalysts.
- (ii) The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.
- (iii) A transition metal exhibits higher oxidation states in oxides and fluorides. *(3/5, AI 2011C)*

LA II (5 marks)

65. 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)*

8.4 Some Important Compounds of Transition Elements

VSA (1 mark)

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

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

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

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

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

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

72. Give reason :
Orange solution of potassium dichromate turns yellow on adding sodium hydroxide to it. *(1/5, AI 2013C)*

SA (2 marks)

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

74. 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)*

75. 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*). *(Delhi 2019)*

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

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

78. 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)

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

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

81. Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with oxalic acid? Write the ionic equations for the reaction. *(AI 2015C)*

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

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

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

86. Complete the following equations :
(i) $2CrO_4^{2-} + 2H^+ \longrightarrow$
(ii) $KMnO_4 \xrightarrow{\text{Heat}}$ *(AI 2013)*

87. Complete the following chemical equations :
(i) $Cr_2O_7^{2-} + H^+ + I^- \longrightarrow$
(ii) $MnO_4^- + NO_2^- + H^+ \longrightarrow$ *(Delhi 2012)*

88. Complete the following chemical equations :
(i) $MnO^-_{4(aq)} + S_2O^{2-}_{3(aq)} + H_2O_{(l)} \rightarrow$
(ii) $Cr_2O^{2-}_{7(aq)} + Fe^{2+}_{(aq)} + H^+_{(aq)} \rightarrow$ *(AI 2011)*

89. Complete the following reactions in an aqueous medium :
(i) $MnO_4^- + C_2O_4^{2-} + H^+ \rightarrow$
(ii) $Cr_2O_7^{2-} + H_2S + H^+ \rightarrow$
(2/5, Foreign 2011)

90. Complete the following chemical equations :
(i) $Fe^{3+} + I^- \rightarrow$
(ii) $CrO_4^{2-} + H^+ \rightarrow$ *(2/5, Foreign 2011)*

91. Describe the reactions involved in the preparation of $K_2Cr_2O_7$ from chromite ore.
(2/5, AI 2011C)

LA I (3 marks)

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

93. 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)*

94. Complete the following chemical equations :
(i) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow$
(ii) $2CrO_4^{2-} + 2H^+ \rightarrow$
(iii) $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow$
(Delhi 2013)

95. Describe the preparation of potassium permanganate from pyrolusite ore. Write balanced chemical equation for one reaction to show the oxidizing nature of potassium permanganate. *(3/5, AI 2013C)*

96. Describe the preparation of potassium dichromate from chromite ore. What is the effect of change of pH on dichromate ion? *(3/5, AI 2012C)*

97. Describe the preparation of potassium permanganate from pyrolusite ore. What happens when acidified potassium permanganate solution reacts with ferrous sulphate solution? Write balanced chemical equations. *(3/5, AI 2012C)*

98. Complete the following chemical equations :

(i) $MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow$

(ii) $KMnO_4 \xrightarrow{\text{Heated}}$

(iii) $Cr_2O_7^{2-} + H_2S + H^+ \longrightarrow$ *(Delhi 2011)*

8.5 The Lanthanoids

VSA (1 mark)

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

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

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

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

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

104. How would you account for the following :
Zr (Z = 40) and Hf (Z = 72) have almost identical radii. *(1/3, Delhi 2013, 1/5, AI 2013C)*

105. How would you account for the following :
Among lanthanoids, Ln(III) compounds are predominant. However, occasionally in solutions or in solid compounds, +2 and +4 ions are also obtained. *(1/3, AI 2012)*

106. Give reason :

There is a gradual decrease in the size of atoms with increasing atomic number in the series of lanthanoids. *(1/3, Delhi 2012C)*

107. What is meant by 'lanthanoid contraction'? *(AI 2011)*

SA (2 marks)

108. What is lanthanoid contraction? What are its two consequences? *(Delhi 2013C)*

109. What is lanthanoid contraction and what is it due to? Write two consequences of lanthanoid contraction. *(2/5, Delhi 2013C)*

110. What is lanthanoid contraction? Mention its main consequences. *(2/3, Delhi 2012C)*

LA I (3 marks)

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

112. What is lanthanoid contraction? What is its effect on the chemistry of the elements which follow the lanthanoids? *(3/5, AI 2011C)*

8.6 The Actinoids

VSA (1 mark)

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

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

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

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

117. Give reasons for the following :
Actinoids exhibit a greater range of oxidation states than lanthanoids. *(1/3, AI 2014C, Delhi, AI 2012, 1/2, Delhi 2011)*

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

119. How would you account for the following :
Lanthanoids form primarily +3 ions, while the actinoids usually have higher oxidation

states in their compounds, +4 or even +6 being typical. *(1/3, Delhi 2012)*

120. Explain giving reasons :
The chemistry of actinoids is not as smooth as that of lanthanoids. *(1/2, AI 2011)*

SA (2 marks)

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

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

LA I (3 marks)

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

Detailed Solutions

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+}).

2. *Refer to answer 1.*

3. 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.

4. *Refer to answer 1.*

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

6. 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.

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

8. 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.

9. Zinc

10. **(c)**

11. **(c) :** Because of strong metallic bonding present in atoms of transition elements, they have high melting points. Transition elements show variable oxidation states.

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

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

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

15. 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.

16. *Refer to answer 8.*

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

For example, Sc has $ns^2(n-1)\,d^1$ 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.

18. 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.

19. Transition metals and most of their compounds contain unpaired electrons in the $(n-1)d$ orbitals hence show paramagnetic behaviour.

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

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

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.

21. (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) 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.

22. (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 while in Mn_2O_7 is +7.

23. (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°, reaction will be more feasible.

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

24. (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) *Refer to answer 18.*

25. (i) *Refer to answer 17.*

(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.

26. (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) *Refer to answer 17.*

27. (i) *Refer to answer 17.*

(ii) *Refer to answer 18.*

28. *Refer to answer 17.*

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.

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

29. (i) *Refer to answer 26(i).*

(ii) *Refer to answer 6.*

30. Disproportionation reaction involves the oxidation and reduction of the same substance. The examples of disproportionation reaction are :

(i) Aqueous NH_3 when treated with Hg_2Cl_2 (solid) forms mercury aminochloride disproportionatively.

$Hg_2Cl_2 + 2NH_3 \longrightarrow Hg + Hg(NH_2)Cl + NH_4Cl$

(ii) $2Cu^+ \longrightarrow Cu + Cu^{2+}$

31. (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}).

32. (i) *Refer to answer 3.*
(ii) *Refer to answer 1.*

33. (i) As we move along transition metal series from left to right (*i.e.,* Ti to Cu), the atomic radii decrease due to increase in nuclear charge. Hence, the atomic volume decreases. At the same time, atomic mass increases. Hence, the density from titanium (Ti) to copper (Cu) increases. The atoms of transition metals have strong metallic bonds between them, 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).

34. (i) *Refer to answer 18.*

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

35. (i) *Refer to answer 17.*
(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.

36. (i) *Refer to answer 18.*
(ii) This is attributed to the involvement of greater number of electrons from $(n-1)d$ in addition to the *ns* electrons in the interatomic metallic bonding.

37. (i) *Refer to answer 6.*
(ii) *Refer to answer 15.*

38. (i) Copper exhibits +1 oxidation state in its compounds. Electronic configuration of Cu in the ground state is $3d^{10}\,4s^1$. So, Cu can easily lose $4s^1$ electron to give a stable $3d^{10}$ configuration. Thus, it shows +1 oxidation state.

(ii) Only those ions will be coloured which have partially filled *d*-orbitals facilitating *d*-*d* transition. Ions with d^0 and d^{10} will be colourless.

From electronic configuration of the ions, $V^{3+}(3d^2)$ and $Mn^{2+}(3d^5)$, are all coloured. $Ti^{4+}(3d^0)$ and $Sc^{3+}(3d^0)$ are colourless.

39. (i) *Refer to answer 17.*
(ii) *Refer to answer 6.*

40. (i) Transition metals form a large number of interstitial compounds because small atoms of certain non metallic elements (H, B, C, N, etc.) get trapped in voids or vacant spaces of lattices of the transition metals. As a result of filling up of the interstitial spaces such interstitial compounds are hard and rigid.

(ii) This is due to lanthanoid contraction.

41. (i) $E°$ values for the Cr^{3+}/Cr^{2+} and Mn^{3+}/Mn^{2+} couples are

$Cr^{3+}_{(aq)} + e^- \longrightarrow Cr^{2+}_{(aq)}$; $E° = -0.41$ V

$Mn^{3+}_{(aq)} + e^- \longrightarrow Mn^{2+}_{(aq)}$; $E° = +1.551$ V

These $E°$ values indicate that Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidising agent.
(ii) Since, transition elements contain partially filled *d*-subshells, therefore, electrons in these subshells go from lower *d*-subshells to higher *d*-subshells. This is called *d*-*d* transition. This transition takes place by absorbing energy from the visible light. The mixture of the wavelength which is not absorbed is transmitted out. This accounts for the colour of transition elements.

42. (i) 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 greater than enthalpy of hydration.
This is why $E°_{M^{2+}/M}$ for Cu is positive.

(ii) *Refer to answer 40(ii).*

43. (i) *Refer to answer 40(i).*
(ii) As we move along transition metal series from left to right (*i.e.,* Ti to Cu), the atomic radii decrease due to increase in nuclear charge. Hence the atomic volume decreases. At the same time, atomic mass increases. Hence, the density from titanium (Ti) to copper (Cu) increases.

44. (i) *Refer to answer 41(i).*
(ii) 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 counterbalances the effect of increased nuclear charge. As a result, the atomic radii remain practically same after chromium.

45. (i) As transition metals have a large number of unpaired electrons in the *d*-orbitals of their atoms they have strong interatomic attraction or metallic bonds. Hence, they have high enthalpy of atomization.
(ii) *Refer to answer 6.*

46. (i) Sc(21) is a transition element but Ca(20) is not because Sc has incompletely filled 3*d* orbitals.
(ii) *Refer to answer 31(i).*

47. The variability in oxidation states of transition metals is due to the incomplete filling of *d*-orbitals. Their oxidation states differ from each other by unity.

For example, Fe^{3+} and Fe^{2+}, Cu^{2+} and Cu^{+}, etc.
In case of non transition elements the oxidation states normally differ by units of two. For example, Pb^{2+} and Pb^{4+}, Sn^{2+} and Sn^{4+}, etc. It arises due to expansion of octet and inert pair effect.

48. (i) *Refer to answer 31(i).*
(ii) *Refer to answer 41(i).*

49. (i) *Refer to answer 15.*
(ii) As manganese has maximum number of unpaired electrons (5) in 3*d* subshell in addition to 2 electrons in the 4*s* subshell, it can use the 7 electrons for bonding purpose. Thus, it exhibits +7 oxidation state.

50. (i) *Refer to answer 41(i).*
(ii) Middle of the transition series contains greater number of unpaired electrons in $(n-1)d$ and *ns* orbitals.

51. (i) *Refer to answer 18.*
(ii) This is because due to lanthanoid contraction the expected increase in size does not occur hence they have very high value of ionisation enthalpies.

52. (i) *Refer to answer 6.*
(ii) The metals of 4*d* and 5*d*-series have more frequent metal bonding in their compounds than the 3*d*-metals because 4*d* and 5*d*-orbitals are more exposed in space than the 3*d*-orbitals. So the valence electrons are less tightly held and form metal-metal bonding more frequently.

53. (i) 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.
(ii) Cu^{+} is unstable in aqueous solution
In aqueous solutions, Cu^{+} undergoes disproportionation to form a more stable Cu^{2+} ion.

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

(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.

54. (i) From the relation, $\Delta G° = -nFE°$
More positive is the value of $E°$, reaction will be feasible.

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

Hence, $E°_{\text{value}}$ 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.

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

56. (i) Ti^{4+} has highest oxidation state among the given ions. Ti^{4+} has stable inert gas configuration and hence, most stable in aqueous solution.

On the other hand, V^{2+}, Mn^{3+}, Cr^{3+} have unstable electronic configuration and hence, are less stable.

(ii) Due to presence of highest oxidation state of Ti, it acts as the strongest oxidising agent among the given ions.

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

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

57. (i) *Refer to answer 26(i).*

(ii) 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.

(iii) *Refer to answer 8.*

58. (i) *Refer to answer 42(i).*

(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) *Refer to answer 23(i).*

59. (i) *Refer to answer 31(i).*

(ii) *Refer to answer 31(ii).*

(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.

60. (i) Mn^{2+} is more stable due to half filled d^5 configuration and Mn^{3+} easily changes to Mn^{2+} hence, it is a good oxidising agent.

(ii) The $E^\circ_{M^{2+}/M}$ values are not regular which can be explained from the irregular variation of ionisation enthalpes *i.e.*, $IE_1 + IE_2$ and also the sublimation enthalpies which are relatively much less for manganese and vanadium.

(iii) *Refer to answer 26(i).*

61. (i) All transition elements except the first and the last member in each series show a large number of variable oxidation states. This is because difference of energy in the $(n - 1)d$ and ns orbitals is very little.

Hence, electrons from both the energy levels can be used for bond formation.

(ii) *Refer to answer 45(i).*

(iii) *Refer to answer 47.*

62. (i) *Refer to answer 18.*

(ii) *Refer to answer 41(i).*

(iii) *Refer to answer 6.*

63. (i) *Refer to answer 52(ii).*

(ii) Mn^{3+} is less stable and changes to Mn^{2+} which is more stable due to half-filled *d*-orbital configuration. That is why, Mn^{3+} undergoes disproportionation reaction.

(iii) *Refer to answer 35(ii).*

64. (i) *Refer to answer 6.*

(ii) *Refer to answer 55(ii).*

(iii) A transition metal exhibits higher oxidation states in oxides and fluorides because oxygen and fluorine are highly electronegative elements, small in size and strongest oxidising agents. For example, vanadium shows as oxidation state of +5 in V_2O_5. Manganese shows +7 in Mn_2O_7.

65. (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, $E^\circ_{(Mn^{3+}/Mn^{2+})} = 1.5$ V.

66. 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.

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

69. $3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$

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

71. $2MnO_4^- + 5SO_2 + 2H_2O \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$

72. *Refer to answer 67.*

73. 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, $3K_2MnO_4 + 4HCl \rightarrow 2KMnO_4 + MnO_2 + 2H_2O + 4KCl$

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

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

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

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

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

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

$$2KMnO_4 + 8H_2SO_4 + 10KI \longrightarrow 6K_2SO_4 + 2MnSO_4 + 8H_2O + \underset{(D)}{5I_2}$$

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

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

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

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

78. (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.

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

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

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

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

81. *Refer to answer 73.*

Ionic equation for the reaction between oxalic acid and acidified permanganate solution :

$2MnO_4^{2-} + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

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) *Refer to answer 80(ii).*

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

83. (i) *Refer to answer 80(i).*

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

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

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

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

85. (i) $H_2S \longrightarrow 2H^+ + S^{2-}$

$5S^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5S$

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

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

(ii) $2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$

87. (i) *Refer to answer 80(ii).*

(ii) *Refer to answer 68.*

88. (i) *Refer to answer 79(i).*

(ii) $Cr_2O^{2-}_{7(aq)} + 14H^+_{(aq)} + 6Fe^{2+}_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)} + 6Fe^{3+}_{(aq)} + 7H_2O_{(l)}$

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

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

90. (i) $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$

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

91. $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

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

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

Potassium dichromate is converted to chromate if pH is increased.

$$Cr_2O_7^{2-} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} CrO_4^{2-}$$

92. 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 crystallised.

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

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

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

Refer to answer 88 (ii).

93. (i) *Refer to answer 80(i).*

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

(iii) *Refer to answer 79(ii).*

94. (i) *Refer to answer 88(ii).*

(ii) *Refer to answer 90(ii).*

(iii) *Refer to answer 89(i).*

95. *Refer to answer 73.*

Oxidising nature of $KMnO_4$

$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

96. *Refer to answer 91.*

97. *Refer to answer 73.*

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

98. (i) *Refer to answer 89(i).*

(ii) *Refer to answer 86(ii).*

(iii) *Refer to answer 89(ii).*

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

100. 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.

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

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

103. 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., $Ce^{4+} : 4f^0$, $Eu^{2+} : 4f^7$

$Tb^{4+} : 4f^7$, $Yb^{2+} : 4f^{14}$

104. *Refer to answer 100.*

105. *Refer to answer 103.*

106. As the atomic number increases, each succeeding element contains one more electron in the 4*f* orbital and one extra proton in the nucleus. The 4*f* electrons are rather ineffective in screening the outer electrons from the nucleus. As a result, there is gradual increase in the nuclear attraction for the outer electrons. Consequently, the atomic size gradually decreases. This is called lanthanoid contraction.

107. The steady decrease in the atomic and ionic radii (having the same charge) with increase in atomic number across the series from lanthanum to lutetium is known as lanthanoid contraction.

108. Lanthanoid contraction : The steady decrease in the atomic and ionic radii of lanthanoid elements with increase in atomic number is called lanthanoid contraction. It is caused due to imperfect shielding of nuclear charge by 4*f*-electrons.

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.

109. *Refer to answer 108.*

110. *Refer to answer 108.*

111. *Refer to answer 108.*

112. *Refer to answer 108.*

113. 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.

114. 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.

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

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

117. 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.

118. *Refer to answer 116.*

119. *Refer to answer 117.*

120. The chemistry of actinoids is not as smooth as lanthanoid because they show greater number of oxidation states due to comparable energies of 5*f*, 6*d* and 7*s* orbitals.

121. *Refer to answer 117.*
Refer to answer 113.

122. 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.

123. 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, +3 and +4 because of large 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.