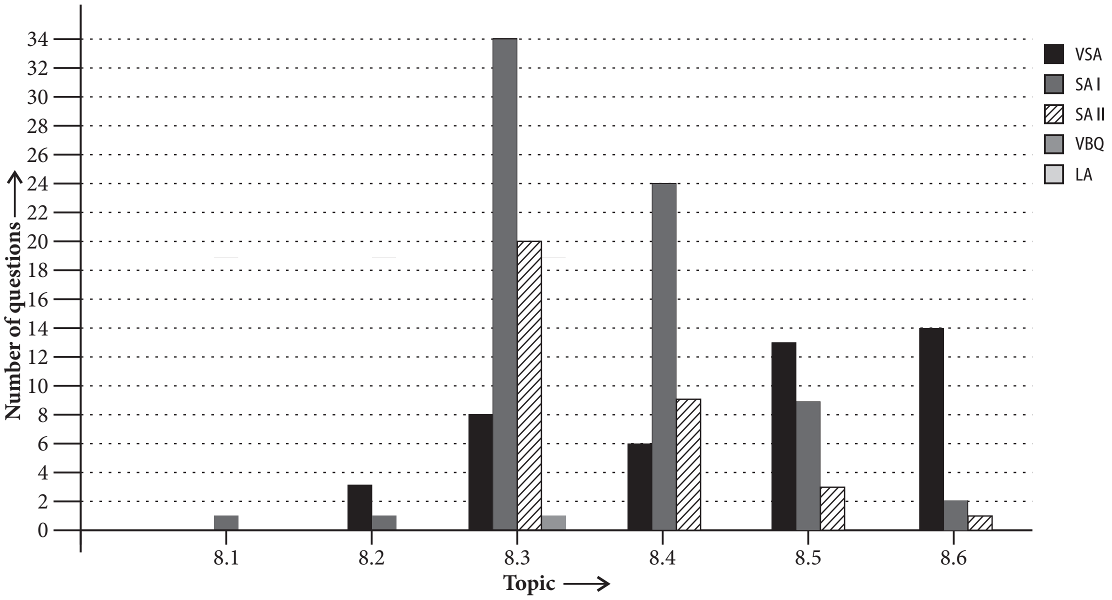
08

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

Topicwise Analysis of Last 10 Years' CBSE Board Questions



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

QUICK RECAP

TRANSITION ELEMENTS (*d*-BLOCK ELEMENTS)

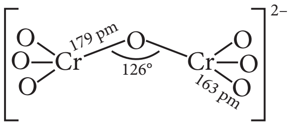
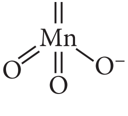
- Elements in which the last electron enters any one of the five *d*-orbitals of their respective penultimate shell are known as *transition elements* or *d-block elements.*
- Their general electronic configuration is $(n-1)d^{1-10}ns^{0-2}$.

- **Transition series :** d-block consists of four transition series,
  1st Transition series or $3d$ series $_{21}Sc - _{30}Zn$
  2nd Transition series or $4d$ series $_{39}Y - _{48}Cd$
  3rd Transition series or $5d$ series $_{57}La$, $_{72}Hf - _{80}Hg$
  4th Transition series or $6d$ 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 accomodated
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) $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$ $Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$	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 4*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 steadily 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 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 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 low transition 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.
- **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 regularly across to 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.
Oxidation states	Like lanthanoids, most common 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	Are 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.
Reducing agents	All actionoids 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

8.1 Position in the Periodic Table

SA I (2 marks)

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

8.2 Electronic Configurations of the *d*-Block Elements

VSA (1 mark)

2. Account for the following :
Zn is not considered as a transition element. *(1/5, AI 2014, 1/2, Delhi 2010)*

3. On what ground can you say that scandium ($Z = 21$) is a transition element but zinc ($Z = 30$) is not? *(1/5, AI 2008C)*

SA I (2 marks)

4. Write down the electronic configuration of
(a) Cr^{3+} (b) Cu^+
(c) Co^{2+} (d) Mn^{2+} *(2/5, AI 2009)*

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

VSA (1 mark)

5. How would you account for the following :
Transition metals form coloured compounds? *(1/3, Delhi 2015, 1/2, 2010)*

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

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

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

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

10. Account for the following :
Compounds of transition elements are often coloured. *(1/2, Delhi 2008C)*

11. Why Cd^{2+} salts are white? *(AI 2007)*

SA I (2 marks)

12. 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)*

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

14. 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)*

15. 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)*

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

17. 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)*

18. (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)*

19. 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)

20. Assign a 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)

21. 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)*

22. 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)*

23. 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)*

24. (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)

25. 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)*

26. 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)*

27. 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)

28. 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)*

29. 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)

30. 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)*

31. 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)

32. 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)*

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

34. 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)*

35. 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)*

36. 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)*

37. 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)*

38. 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)*

39. Explain the following observations :
  (i) Generally there is an increase in density of elements from titanium ($Z = 22$) to copper ($Z = 29$) in the first series of transition elements.
  (ii) Transition elements and their compounds are generally found to be good catalysts in chemical reactions. *(Delhi 2010)*

40. Explain the following observations :
  (i) Among the divalent cations in the first series of transition elements, manganese exhibits the maximum paramagnetism.
  (ii) Cu^+ ion is not known in equeous solutions. *(2/5, Delhi 2010)*

41. Account for the following :
  (i) Cu^+ ions are not stable in aqueous solution.
  (ii) Most of the transition metal ions exhibit paramagnetic behaviour. *(Delhi 2010C)*

42. Account for the following :
  (i) In the series Sc to Zn, the enthalpy of atomisation of zinc is the lowest.
  (ii) The $E°$ value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+}. *(Delhi 2010C)*

43. Account for the following :
  (i) The lowest oxide of a transition metal is basic, the highest is amphoteric/acidic.
  (ii) Cobalt (II) is stable in aqueous solution but in the presence of complexing agents, it is easily oxidised. *(2/5, AI 2010C)*

44. How would you account for the following :
  (i) Many of the transition elements and their compounds can act as good catalysts.
  (ii) The metallic radii of the third (5*d*) series of transition elements are virtually the same as those of the corresponding members of the second series. *(2/3, AI 2009)*

45. How would you account for the following :
  (i) Transition elements have high enthalpies of atomisation.
  (ii) The transition metals and their compounds are found to be good catalysts in many processes? *(AI 2007)*

SA II (3 marks)

46. Account for the following :
  (i) Mn shows the highest oxidation state of +7 with oxygen but with fluorine, if 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)*

47.

$E°_{(M^{2+}/M)}$	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 $E^{\circ}_{(Cu^{2+}/Cu)}$ 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)*

48. What is meant by disproportionation? Give on example of disproportionation reaction in aqueous solutions. *(AI 2015C)*

49. 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)*

50. Give reasons for the following :

(i) Mn^{3+} is a good oxidising agent.

(ii) $E°_{M^{2+}/M}$ 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)*

51. 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)*

52. 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)*

53. 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)*

54. 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)*

55. How would you account for the following :

(i) The atomic radii of the metals of the third (5*d*) series of transition elements are virtually the same as those of the corresponding members of the second (4*d*) series.

(ii) 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.

(iii) The highest oxidation state of a metal is exhibited in its oxide or fluoride. *(Delhi 2010)*

56. How would you account for the following :

(i) The oxidising power of oxoanions are in the order
$VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$

(ii) The third ionization enthalpy of manganese (Z = 25) is exceptionally high.

(iii) Cr^{2+} is a stronger reducing agent than Fe^{2+}. *(3/5, AI 2010)*

57. Give reason for the following :

(i) Transition metals have high enthalpies of atomisation.

(ii) $Fe^{3+}|Fe^{2+}$ redox couple has less positive electrode potential than $Mn^{3+}|Mn^{2+}$ couple.

(iii) Copper (I) has d^{10} configuration, while copper (II) has d^9 configuration, still copper (II) is more stable in aqueous solution than copper (I). *(3/5, Delhi 2010C)*

58. Account for the following :

(i) The enthalpies of atomisation of the transition metals are high.

(ii) The lowest oxide of a transition metal is basic, the highest is amphoteric/acidic.

(iii) Cobalt (II) is stable in aqueous solution but in the presence of complexing agents, it is easily oxidised. *(3/5, AI 2010C)*

59. (a) Name the oxo-metal anion of one of the transition metals in which the metal exhibits the oxidation state equal to the group number.
(b) Account for the following :
  (i) Scandium ($Z = 21$) is regarded as a transition element but zinc ($Z = 30$) is not.
  (ii) $E^\circ(M^{2+}/M)$ value for copper is +ve.
(3/5, AI 2010C)

60. Explain the following observations :
(i) Transition elements are known to form many interstitial compounds.
(ii) With the same *d*-orbital configuration Cr^{2+} ion is reducing while Mn^{3+} ion is oxidising.
(iii) The enthalpies of atomisation of the transition elements are quite high.
(3/5, Delhi 2009)

61. Explain the following observations :
(i) In general the atomic radii of transition elements decrease with atomic number in a given series.
(ii) The $E^\circ_{M^{2+}|M}$ for copper is positive (+0.34 V). It is only metal in the first series of transition elements showing this type of behaviour.
(iii) The E° value for $Mn^{3+}|Mn^{2+}$ couple is much more positive than for $Cr^{3+}|Cr^{2+}$ or $Fe^{3+}|Fe^{2+}$ couple. *(3/5, Delhi 2009)*

62. Explain the following observation :
(i) Cu^+ ion is unstable in aqueous solutions.
(ii) Although Co^{2+} ion appears to be stable, it is easily oxidised to Co^{3+} ion in the presence of a strong ligand.
(iii) The $E^\circ_{Mn^{2+}|Mn}$ value for manganese is much more than expected from the trend for other elements in the series. *(3/5, Delhi 2009)*

63. Give reasons for the following observations :
(i) Cu^+ ion is not stable in aqueous solution.
(ii) Mn(II) ion shows maximum paramagnetic character amongst the bivalent ions of first transition series.
(iii) Scandium (At. no. 21) salts are white.
(3/5, Delhi 2009C)

64. Give reasons for the following observations :
(i) Of the d^4 species, Cr^{2+} is strongly reducing whereas manganese (III) is strongly oxidising.
(ii) The enthalpies of atomisation of the transition metals are quite high.
(iii) Interstitial compounds are well-known for transition metals. *(3/5, AI 2009C)*

65. Assign reasons for the following :
(i) The enthalpies of atomisation of transition elements are high.
(ii) The transition metals and many of their compunds act as good catalyst.
(iii) The E° value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+}.
(3/5, Delhi 2008)

LA (5 marks)

66. 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)

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

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

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

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

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

72. Complete the following chemical equation :
$Cr_2O_{7(aq)}^{2-} + H_2S_{(g)} + H^+_{(aq)} \longrightarrow$ *(1/5, AI 2010)*

SA I (2 marks)

73. 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 a 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)

74. 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)*

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

76. 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)

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

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

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

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

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

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

83. 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, 2/5, AI 2010)

84. 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)*

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

86. Describe the reactions involved in the preparation of $K_2Cr_2O_7$ from chromite ore.
(2/5, AI 2011C, 2/5, Delhi 2009C)

87. How does the acidified potassium permanganate solution react with
(i) iron (II) ions and (ii) oxalic acid?
Write the ionic equations for the reactions.
(2/5, AI 2010C)

88. Complete the following chemical reaction equations :
(i) $MnO^-_{4(aq)} + C_2O^{2-}_{4(aq)} + H^+_{(aq)} \longrightarrow$
(ii) $Cr_2O^{2-}_{7(aq)} + Fe^{2+}_{(aq)} + H^+_{(aq)} \longrightarrow$
(2/5, Delhi 2009)

89. Complete the following chemical reaction equations :
(i) $MnO^-_{4(aq)} + S_2O^{2-}_{3(aq)} + H_2O_{(l)} \longrightarrow$
(ii) $Cr_2O^{2-}_{7(aq)} + H_2S + H^+_{(aq)} \longrightarrow$ *(2/5, Delhi 2009)*

90. Complete the following chemical reaction equations:
(i) $Fe^{2+}_{(aq)} + MnO^-_{4(aq)} + H^+_{(aq)} \longrightarrow$
(ii) $Cr_2O^{2-}_{7(aq)} + I^-_{(aq)} + H^+_{(aq)} \longrightarrow$ *(2/5, Delhi 2009)*

91. (i) Describe how potassium dichromate is prepared from sodium chromate.
(ii) The colour of potassium dichromate solution changes with the change of pH of the solution. Explain how.
(2/5, Delhi 2008, 2/5, AI 2008C)

92. Write complete chemical equations for
(i) Oxidation of Fe^{2+} by $Cr_2O_7^{2-}$ in acidic medium.
(ii) Oxidation of $S_2O_3^{2-}$ by MnO_4^- in neutral aqueous medium. *(AI 2008)*

93. Write the steps involved in the preparation of
(i) $K_2Cr_2O_7$ from Na_2CrO_4
(ii) $KMnO_4$ from K_2MnO_4. *(2/5, Delhi 2007)*

SA II (3 marks)

94. Complete the following chemical equations:
(i) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow$

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

(iii) $3MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow$ *(Delhi 2013)*

95. Lokesh is a social worker. A milkman in the village has been complaining that a factory in his nearby area dumps chemical waste in his field which has become a major cause of decreasing productivity. Lokesh visited that place and found after analyis that the major waste was potassium permanganate which is being absorbed by the soil. He advised the factory people that they should treat potassium permanganate solution before dumping it into the drain.

Comment in brief

(i) About the value/s displayed by Lokesh.

(ii) Write balanced chemical equations for the two reactions showing oxidizing nature of potassium permanganate.

(*VBQ*) *(Delhi 2013C)*

96. 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)*

97. Describe the preparation of potassium dichromate from chromite ore. What is the effect of change of pH on dichromate ion?

(3/5, AI 2012C)

98. 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)*

99. 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)*

100. Describe the preparation of potassium permanganate from pyrolusite ore. Write the ionic equation for the reaction that takes place between acidified $KMnO_4$ solution and iron (II) ions. *(Delhi 2010C)*

101. Describe the oxidising actions of potassium dichromate and write the ionic equations for its reaction with (i) iodide (ii) iron (II) solution (iii) H_2S. *(Delhi 2008)*

102. (i) Describe the commercial preparation of potassium permanganate from pyrolusite ore.

(ii) Write ionic equation to represent the reaction of acidified $KMnO_4$ solution with oxalic acid. *(Delhi 2008C)*

8.5 The Lanthanoids

VSA (1 mark)

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

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

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

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

107. 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,)*

108. 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)*

109. 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)*

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

111. What are different oxidation states exhibited by lanthanoids? *(Delhi 2010)*

112. Explain the following observations :

La^{3+} ($Z = 57$) and Lu^{3+} ($Z = 71$) do not show any colour in solutions. *(1/5, AI 2010)*

113. Give reason for the following :
Among the Lanthanoids, Ce (III) is easily oxidised to Ce (IV). *(1/5, Delhi 2010C)*

114. Give reason for the following :
The second and third transition series elements have almost similar atomic radii.
(1/5, Delhi 2010C)

SA I (2 marks)

115. What is Lanthanoid contraction? What are its two consequences? *(Delhi 2013C)*

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

117. What is lanthanoid contraction? Mention its main consequences. *(2/3, Delhi 2012C, AI 2008C)*

118. Why is europium (II) more stable than cerium (II)? *(AI 2010)*

119. Write the electronic configuration of Ce^{3+} ion, and calculate the magnetic moment on the basis of 'spin-only' formula. [Atomic no. of Ce = 58] *(2/5, AI 2010C)*

120. What is meant by the term lanthanoid contraction? What is it due to and what consequences does it have on the chemistry of elements following lanthanoids in the periodic table? *(2/5, Delhi 2009)*

121. Name an important alloy which contains some of the lanthanoid metals. Mention its two uses. *(2/5, Delhi 2009C)*

122. What is lanthanoid contraction? List any two consequences of lanthanoid contraction. *(2/5, AI 2009C)*

SA II (3 marks)

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

124. What is lanthanoid contraction? What is its effect on the chemistry of the elements which follow the lanthanoids? *(3/5, AI 2011C, 3/5, Delhi 2007)*

8.6 The Actinoids

VSA (1 mark)

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

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

127. Give reasons for the following :
Actinoids exhibit a greater range of oxidation states than lanthanoids. *(1/3, AI 2014C, 1/2, Delhi 2011, 1/5, AI 2008C)*

128. Assign reasons for the following :
From element to element actinoid contraction is greater than the lanthanoid contraction. *(1/3, AI 2014C, 1/5, Delhi 2009, 1/5, Delhi 2008)*

129. 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)*

130. How would you account for the following :
The actinoids exhibit a larger number of oxidation states than the corresponding members in the lanthanoid series. *(1/3, Delhi 2012)*

131. Explain the following observation :
The members of the actinoid series exhibit a larger number of oxidation states than the corresponding members of the lanthanoid series. *(1/3, AI 2012)*

132. Explain the following observation :
Actinoids exhibit a much larger number of oxidation states than the lanthanoids. *(1/3, AI 2012)*

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

134. How would you account for the following :
There is a greater range of oxidation states among the actinoids than among the lanthanoids. *(1/3, AI 2009)*

SA I (2 marks)

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

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

SA II (3 marks)

137. Compare the chemistry of the actinoids with that of lanthanoids with reference to
(i) electronic configuration
(ii) oxidation states
(iii) chemical reactivity. *(Delhi 2010C)*

Detailed Solutions

1. 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.

2. In the electronic configuration of Zn, Cd and Hg the *d*-orbitals are completely filled in the ground state as well as in their common oxidation state. So, they are not regarded as transition metals.

3. On the basis of incompletely filled *d*-orbitals :

Scandium (Z = 21), atom has incompletely filled *d*-orbitals ($3d^1$) in its ground state, so it is regarded as transition element.

On the other hand zinc (Z = 30) atom has completely filled *d*-orbitals ($3d^{10}$) in its ground state as well as most common oxidation state of +2.

4. (a) $Cr^{3+} = {}_{18}[Ar]\ 3d^3$ (b) $Cu^{+} = {}_{18}[Ar]\ 3d^{10}$

(c) $Co^{2+} = {}_{18}[Ar]\ 3d^7$ (d) $Mn^{2+} = {}_{18}[Ar]\ 3d^5$

5. 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.

6. 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.

7. 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.

8. 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.

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

10. *Refer to answer 5.*

11. It has completely filled *d*-orbital (d^{10}).

12. (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 7.*

13. (i) *Refer to answer 7.*

(ii) *Refer to answer 8.*

14. Variation in oxidation state : Transition elements can use their *ns* and $(n-1)d$ orbital electrons for bond formation. Therefore, they show variable oxidation state.

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.

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

Mn – [Ar] $3d^5\ 4s^2$

15. (i) *Refer to answer 12(i).*

(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.

16. Disproportionation reaction involves the oxidation and reduction of the same substance. The two 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) $2Cu^+ \longrightarrow Cu + Cu^{2+}$

17. (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 ($3d^{10}$) 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}).

18. (i) *Refer to answer 1.*
(ii) *Refer to answer 2.*

19. (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.
(ii) Irregular variation of ionisation enthalpies is mainly attributed to varying degree of stability of different $3d$-configurations (*e.g.*, d^0, d^5, d^{10} are exceptionally stable).

20. (i) *Refer to answer 8.*

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

21. (i) *Refer to answer 7.*

(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.

22. (i) *Refer to answer 8.*
(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.

23. (i) *Refer to answer 15(ii).*
(ii) *Refer to answer 5.*

24. (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.

25. (i) *Refer to answer 7.*
(ii) *Refer to answer 15(ii).*

26. (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.

27. (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.
(ii) Since, transition elements contain partially filled 5-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.

28. (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 26(ii).*

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

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

31. (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 15(ii).*

32. (i) Sc(21) is a transition element but Ca(20) is not because of incompletely filled 3*d* orbitals.

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

33. 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.

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

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

35. (i) *Refer to answer 5.*

(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.

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

(ii) Middle of the transition series contains greater number of unpaired electrons in (*n* –1)*d* and *ns* orbitals.

37. (i) *Refer to answer 8.*

(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.

38. (i) *Refer to answer 15(ii).*

(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.

39. (i) *Refer to answer 29(ii).*

(ii) *Refer to answer 15(ii).*

40. (i) This is due to presence of maximum number of unpaired electrons in Mn^{2+} in ($3d^5$).

(ii) *Refer to answer 8.*

41. (i) *Refer to answer 8.*

(ii) *Refer to answer 9.*

42. (i) *Refer to answer 17(ii).*

(ii) 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.

43. (i) 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 acts as acidic in nature.

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

(ii) *Refer to answer 21(ii).*

44. (i) *Refer to answer 15(ii).*

(ii) *Refer to answer 26(ii).*

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

(ii) *Refer to answer 15(ii).*

46. (i) *Refer to answer 12(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 6.*

47. (i) *Refer to answer 28(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) Cr^{2+} is a stronger reducing agent than Fe^{2+}.

Reason 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+}.

48. *Refer to answer 16.*

49. (i) *Refer to answer 17(i).*
(ii) *Refer to answer 17(ii).*

(iii) Only these 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.

50. (i) Mn^{2+} is more stable due to half filled d^5 configuration and Mn^{3+} easily changes to Mn^{2+} hence, it is oxidising.
(ii) The $E^\circ_{M^{2+}/M}$ values are not regular which can be explained from the irregular variation of ionisation enthalpes *i.e.*, $IE_1 + E_2$ and also the sublimation enthalpies which are relatively much less for manganese and vanadium.
(iii) *Refer to answer 12(i).*

51. (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 31(i).*
(iii) *Refer to answer 33.*

52. (i) *Refer to answer 8.*
(ii) *Refer to answer 30(i).*
(iii) *Refer to answer 15(ii).*

53. (i) *Refer to answer 38(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 21(ii).*

54. (i) *Refer to answer 15(ii).*
(ii) *Refer to answer 42(i).*
(iii) *Refer to answer 12(i).*

55. (i) *Refer to answer 26(ii).*
(ii) *Refer to answer 42(ii).*
(iii) *Refer to answer 50(i).*

56. (i) Change in $Cr_2O_7^{2-}$ to Cr(III) is 3 and in MnO_4^- to Mn (II) is 5.
Change in oxidation state is large and the stability of reduced products in V(III) < Cr(III) < Mn(II). This is why oxidising power of $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$.
(ii) Third ionization enthalpy of Mn is very high because the third electron has to be removed from the stable half-filled 3*d*-orbitals [Mn^{2+} ($Z = 25$) $= 3d^5$].
(iii) *Refer to answer 46(iii).*

57. (i) *Refer to answer 31(i).*
(ii) *Refer to answer 17(i).*
(iii) *Refer to answer 8.*

58. (i) *Refer to answer 31(i).*
(ii) *Refer to answer 43(i).*
(iii) *Refer to answer 43(ii).*

59. (a) Manganese shows oxidation state of +7 in its oxometal anion MnO_4^- which is equivalent to its group number 7. Cr in $Cr_2O_7^{2-}$ and CrO_4^{2-} show oxidation state +6 which is equivalent to its group number 6.
(b) (i) *Refer to answer 3.*
(ii) *Refer to answer 28(i).*

60. (i) *Refer to answer 26(i).*
(ii) *Refer to answer 27(i).*
(iii) *Refer to answer 31(i).*

61. (i) The atomic radii of transition elements decrease with the increase in atomic number as the effective nuclear charge increases because shielding effect of *d*-electron is small.
(ii) *Refer to answer 28(i).*
(iii) *Refer to answer 42(ii).*

62. (i) *Refer to answer 8.*
(ii) *Refer to answer 21(ii).*
(iii) *Refer to answer 42(ii).*

63. (i) *Refer to answer 8.*
(ii) *Refer to answer 40(i).*
(iii) *Refer to answer 49(iii).*

64. (i) *Refer to answer 26(i).*
(ii) *Refer to answer 31(i).*
(iii) *Refer to answer 26(i).*

65. (i) *Refer to answer 31(i).*
(ii) *Refer to answer 15(ii).*
(iii) *Refer to answer 42(ii).*

66. (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 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.

67. $2MnO_4^- + 6H^+ + 5NO_2^- \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$

68. $3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$

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

70. $2MnO_4^- + 5SO_2 + 2H_2O \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$

71. When the pH of the solution of potassium dichromate is decreased, the colour of the solution changes from yellow to orange due to the conversion of CrO_4^{2-} ions into $Cr_2O_7^{2-}$ ions.

$$\underset{\text{Yellow}}{2CrO_4^{2-}} + 2H^+ \rightleftharpoons \underset{\text{Orange}}{Cr_2O_7^{2-}} + H_2O$$

72. $Cr_2O_{7(aq)}^{2-} + 3H_2S_{(g)} + 8H^+_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)} + 3S_{(s)}$

73. (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.

74. (i) $8MnO^-_{4\,(aq)} + 3S_2O^{2-}_{3\,(aq)} + H_2O_{(l)} \rightarrow 8MnO_{2(aq)} + 6\,SO^{2-}_{4\,(aq)} + 2OH^-_{(aq)}$

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

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

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

76. 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, $3K_2MnO_4 + 4HCl \rightarrow 2KMnO_4 + MnO_2 + 2H_2O + 4KCl$

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

77. Potassium dichromates are strong oxidising agents.

(i) *Refer to answer 76(ii).*

(ii) *Refer to answer 73.*

78. (i) *Refer to answer 77.*

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

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

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

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

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

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

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

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

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

82. (i) *Refer to answer 76(ii).*

(ii) *Refer to answer 67.*

83. (i) *Refer to answer 74(i).*

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

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

(ii) *Refer to answer 72.*

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

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

86. $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

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

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

Potassium dichromate is converted to chromate if pH is increased.

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

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

(ii) *Refer to answer 84(i).*

88. (i) *Refer to answer 84(i).*

(ii) *Refer to answer 83(ii).*

89. (i) *Refer to answer 74(i).*
(ii) *Refer to answer 72.*

90. (i) $5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$
(ii) *Refer to answer 25(ii).*

91. (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 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.

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

(ii) *Refer to answer 71.*

92. (i) *Refer to answer 88(ii).*
(ii) *Refer to answer 74(i).*

93. (i) *Refer to answer 73(i).*
(ii) The potassium manganate is oxidised to potassium permanganate by oxidation with chlorine.

$$2K_2MnO_{4(aq)} + Cl_{2(g)} \longrightarrow 2KMnO_{4(aq)} + 2KCl_{(aq)}$$

94. (i) *Refer to answer 83(ii).*
(ii) *Refer to answer 81(i).*
(iii) *Refer to answer 84(i).*

95. (i) The values, associated with Lokesh are alertness, care, responsibility and scientific knowledge.

(ii) (a) Oxidation of Oxalate ion into CO_2

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

(b) Oxidation of Nitrite into Nitrate

$$5NO_2^- + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$$

96. *Refer to answer 76.*

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

97. *Refer to answer 91.*

98. *Refer to answer 76.*

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

99. (i) *Refer to answer 84(i).*
(ii) *Refer to answer 81(ii).*
(iii) *Refer to answer 72.*

100. *Refer to answer 98.*

101. (i) *Refer to answer 75(ii).*
(ii) *Refer to answer 83(ii).*
(iii) *Refer to answer 72.*

102. (i) *Refer to answer 77.*
(ii) *Refer to answer 84(i).*

103. 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.

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

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

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

107. *Refer to answer 103.*

108. *Refer to answer 106.*

109. 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.

110. 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.

111. *Refer to answer 106.*

112. Because they have empty 4*f* subshell.

113. Ce(III) has outer configuration $4f^1 5d^0 6s^0$. It easily loses an electron to acquire the configuration $4f^0$ and forms Ce(IV). In fact this is the only (+IV) lanthanoid which exists in solution.

114. *Refer to answer 103.*

115. 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.

116. *Refer to answer 115.*

117. *Refer to answer 115.*

118. Europium (II) has electronic configuration $[Xe]4f^7 5d^0$ while cerium (II) has electronic configuration $[Xe]\ 4f^1\ 5d^1$. In Eu^{2+}, 4*f* subshell is half filled and 5*d*-subshell is empty. Since half filled and completely filled electronic configurations are more stable, Eu^{2+} ions is more stable than Ce^{2+} in which neither 4*f* subshell nor 5*d* subshell is half filled or completely filled.

119. Ce (Z = 58) = $[Xe]^{54}\ 4f^1\ 5d^1\ 6s^2$
$\therefore\ Ce^{3+} = [Xe]^{54}\ 4f^1\ 5d^0\ 6s^0$
Therefore, it has only one unpaired electron. *i.e.,* $n = 1$

$$\therefore\ \mu = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3} = 1.73\text{ BM}$$

120. *Refer to answer 115.*

121. Mischmetal is well known alloy which consists of a lanthanoid metal (about 95%), iron (about 5%) and traces of S, C, Ca, Al etc.
Mischmetal is used in Mg based alloy to produce bullets shells and lighter flint.

122. *Refer to answer 115.*

123. *Refer to answer 115.*

124. *Refer to answer 115.*

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

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

127. 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.

128. The actinoid contraction is more than lanthanoid contraction because of poor shielding by 5*f*-electrons.

129. *Refer to answer 126.*

130. *Refer to answer 126.*

131. *Refer to answer 126.*

132. *Refer to answer 126.*

133. 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.

134. *Refer to answer 126.*

135. *Refer to answer 126.*
Only trends of magnetic properties and colour of lanthanoids are similar to actinoids.

136. 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.

137. (i) **Electronic configuration :** The general electronic configuration of lanthanoids is $[Xe]\ 4f^{1-14}\ 5d^{0-1}\ 6s^2$ where as 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 :** (a) First few members of lanthanoids are quite reactive almost like calcium, where as actinoids are highly reactive metals especialy in the finely divided state.
(b) Lanthanoids react with dilute acids to liberate H_2 gas whereas actinoids react with boiling water to give a mixture of oxide and hydride.