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

Recap Notes

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 $_{21}\text{Sc} - {}_{30}\text{Zn}$

  2nd Transition series or 4*d* series $_{39}\text{Y} - {}_{48}\text{Cd}$

  3rd Transition series or 5*d* series $_{57}\text{La}, {}_{72}\text{Hf} - {}_{80}\text{Hg}$

  4th Transition series or 6*d* series $_{89}\text{Ac}, {}_{104}\text{Rf} - {}_{112}\text{Cn}$
- **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

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).

Practice Time

OBJECTIVE TYPE QUESTIONS

Multiple Choice Questions (MCQs)

1. The correct order of ionic radii of Ce, La, Pm and Yb in +3 oxidation state is

(a) $La^{3+} < Pm^{3+} < Ce^{3+} < Yb^{3+}$

(b) $Yb^{3+} < Pm^{3+} < Ce^{3+} < La^{3+}$

(c) $La^{3+} < Ce^{3+} < Pm^{3+} < Yb^{3+}$

(d) $Yb^{3+} < Ce^{3+} < Pm^{3+} < La^{3+}$

2. $CuSO_4$ is paramagnetic while $ZnSO_4$ is diamagnetic because

(a) Cu^{2+} ion has $3d^9$ configuration while Zn^{2+} ion has $3d^{10}$ configuration

(b) Cu^{2+} ion has $3d^5$ configuration while Zn^{2+} ion has $3d^6$ configuration

(c) Cu^{2+} has half filled orbitals while Zn^{2+} has fully filled orbitals

(d) $CuSO_4$ is blue in colour while $ZnSO_4$ is white.

3. The correct order of number of unpaired electrons is

(a) $Cu^{2+} > Ni^{2+} > Cr^{3+} > Fe^{3+}$

(b) $Ni^{2+} > Cu^{2+} > Fe^{3+} > Cr^{3+}$

(c) $Fe^{3+} > Cr^{3+} > Ni^{2+} > Cu^{2+}$

(d) $Cr^{3+} > Fe^{3+} > Ni^{2+} > Cu^{2+}$

4. Arrange the oxides of manganese according to increasing acidic strength.

(a) $MnO < Mn_3O_4 < Mn_2O_3 < MnO_2 < Mn_2O_7$

(b) $Mn_2O_7 < MnO_2 < Mn_2O_3 < Mn_3O_4 < MnO$

(c) $MnO_2 < Mn_2O_7 < Mn_3O_4 < Mn_2O_3 < MnO$

(d) $Mn_3O_4 < Mn_2O_3 < Mn_2O_7 < MnO_2 < MnO$

5. Which of the following *d*-block element has half-filled penultimate as well as valence subshell?

(a) Cu (b) Au

(c) Ag (d) Cr

6. The correct order of $E_{M^{2+}/M}$ values with negative sign for the four successive elements Cr, Mn, Fe and Co is

(a) Fe > Mn > Cr > Co (b) Cr > Mn > Fe > Co

(c) Mn > Cr > Fe > Co (d) Cr > Fe > Mn > Co

7. The equation

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

represents

(a) reduction (b) disproportionation

(c) oxidation in acidic medium

(d) reduction in acidic medium.

8. Which of the following is not correctly matched with the example given?

(a) An element of first transition series which has highest second ionisation enthalpy – Cu

(b) An element of first transition series with highest third ionisation enthalpy – Zn

(c) An element of first transition series with lowest enthalpy of atomisation – Zn

(d) Last element of third transition series – Cd

9. The magnetic moment of a divalent ion in aqueous solution with atomic number 25 is

(a) 5.9 B.M (b) 2.9 B.M

(c) 6.9 B.M (d) 9.9 B.M.

10. Highest oxidation state of manganese in fluoride is +4 (MnF_4) but highest oxidation state in oxides is +7 (Mn_2O_7) because

(a) fluorine is more electronegative than oxygen

(b) fluorine does not possess *d*-orbitals

(c) fluorine stabilises lower oxidation state

(d) in covalent compounds, fluorine can form single bond only while oxygen forms double bond.

11. Which of the following transition metal ions is colourless?

(a) V^{2+} (b) Cr^{3+}

(c) Zn^{2+} (d) Ti^{3+}

12. $E_{Mn^{3+}/Mn^{2+}}$ is highly positive than that of $E^\circ_{Cr^{3+}/Cr^{2+}}$ or $E^\circ_{Fe^{3+}/Fe^{2+}}$ because

(a) Mn^{2+} (d^5) can be easily oxidised to Mn^{3+}(d^4) due to low ionisation enthalpy

(b) third ionisation enthalpy of Mn is much larger due to stable half filled d^5 electronic configuration of Mn^{2+}

(c) Mn^{3+} is more stable than Mn^{2+} due to higher oxidation state.

(d) second ionisation enthalpy of Mn is higher than third ionisation enthalpy.

13. Interstitial compounds are non-stoichiometric compounds formed by trapping small atoms like C, H or N in crystal lattices of transition metals. Which of the following properties is not shown by these compounds?

(a) They have high melting points, higher than those of pure metals.

(b) They are very hard, some borides are comparable to diamond in hardness.

(c) They are chemically very reactive.

(d) They retain metallic conductivity.

14. Reactivity of transition elements decreases almost regularly from Sc to Cu because of

(a) lanthanoid contraction

(b) regular increase in ionisation enthalpy

(c) regular decrease in ionisation enthalpy

(d) increase in number of oxidation states.

15. For Zn^{2+}, Ni^{2+}, Cu^{2+} and Cr^{2+} which of the following statements is correct?

(a) Only Zn^{2+} is colourless and Ni^{2+}, Cu^{2+} and Cr^{2+} are coloured.

(b) All the ions are coloured.

(c) All the ions are colourless.

(d) Zn^{2+} and Cu^{2+} are colourless while Ni^{2+} and Cr^{2+} are coloured.

16. Which of the following statement concerning lanthanide elements is false?

(a) All lanthanides are highly dense metals.

(b) More characteristic oxidation state of lanthanide elements is +3.

(c) Lanthanides are separated from one another by ion exchange method.

(d) Ionic radii of trivalent lanthanides steadily increases with increase in the atomic number.

17. Which of the following statements is not correct about magnetic behaviour of substances?

(a) Diamagnetic substances are repelled by an applied magnetic field.

(b) Paramagnetic substances are attracted by an applied magnetic field.

(c) Magnetic moment of n unpaired electrons is given by $\mu = \sqrt{n(n-2)}$ B.M.

(d) Magnetic moment increases as the number of unpaired electrons increases.

18. The electronic configuration of Cu(II) is $3d^9$ whereas that of Cu(I) is $3d^{10}$. Which of the following is correct?

(a) Cu(II) is more stable.

(b) Cu(II) is less stable.

(c) Cu(I) and Cu(II) are equally stable.

(d) Stability of Cu(I) and Cu(II) depends on nature of copper salts.

19. Which of the following are basic oxides?

Mn_2O_7, V_2O_3, V_2O_5, CrO, Cr_2O_3

(a) Mn_2O_7 and V_2O_3 (b) V_2O_3 and CrO

(c) CrO and Cr_2O_3 (d) V_2O_5 and V_2O_3

20. Which of the following catalysts is not correctly matched with the reaction?

(a) Vanadium(V) oxide in contact process for oxidation of SO_2 to SO_3.

(b) Finely divided iron in Haber's process in conversion of N_2 and H_2 to NH_3.

(c) $PtCl_2$ catalyses the oxidation of ethyne to ethanal in the Wacker process.

(d) Ni in presence of hydrogen for conversion of vegetable oil to ghee.

21. Which is the non-lanthanide element?

(a) La (b) Lu

(c) Pr (d) Pm

22. Magnetic moment of Ce^{3+} ion on the basis of 'spin-only' formula will be _____ B.M.

(a) 1.232 (b) 1.332

(c) 1.532 (d) 1.732

23. In which of the following pairs of ions, the lower oxidation state in aqueous solution is more stable than the other?

(a) Tl^{+}, Tl^{3+} (b) Cu^{+}, Cu^{2+}

(c) Cr^{2+}, Cr^{3+} (d) V^{2+}, VO^{2+} (V^{4+})

24. Which of the following compounds is expected to be coloured?

(a) Ag_2SO_4 (b) CuF_2

(c) MgF_2 (d) CuCl

25. Consider the following statements with respect to lanthanides :

1. The basic strength of hydroxides of lanthanides increases from $La(OH)_3$ to $Lu(OH)_3$.

2. The lanthanide ions Lu^{3+}, Yb^{2+} and Ce^{4+} are diamagnetic.

Which of the statement(s) given above is/are correct?

(a) 1 only (b) 2 only

(c) Both 1 and 2 (d) Neither 1 nor 2

26. Cu^+ ion is not stable in aqueous solution because

(a) second ionisation enthalpy of copper is less than the first ionisation enthalpy

(b) large value of second ionisation enthalpy of copper is compensated by much more negative hydration energy of $Cu^{2+}_{(aq)}$

(c) hydration energy of $Cu^{+}_{(aq)}$ is much more negative than that of $Cu^{2+}_{(aq)}$

(d) many copper (I) compounds are unstable in aqueous solution and undergo disproportionation reaction.

27. Select the correct option, among Sc(III), Ti(IV), Pd(II) and Cu(II) ions,

(a) all are paramagnetic

(b) all are diamagnetic

(c) Sc(III), Ti(IV) are paramagnetic and Pd(II), Cu(II) are diamagnetic

(d) Sc(III), Ti(IV) are diamagnetic and Pd(II), Cu(II) are paramagnetic.

28. Identify the species in which the metal atom is in +6 oxidation state.

(a) MnO_4^- (b) $Cr(CN)_6^{3-}$

(c) NiF_6^{2-} (d) CrO_2Cl_2

29. Which of the following statements is correct about stability of the complexes of lanthanoids?

(a) Stability of complexes increases as the size of lanthanoid decreases.

(b) Stability of complexes decreases as the size of lanthanoid decreases.

(c) Lanthanoids do not form complexes.

(d) All the complexes of lanthanoids have same stability.

30. Fe^{3+} ion is more stable than Fe^{2+} ion because

(a) more the charge on the atom, more is its stability

(b) configuration of Fe^{2+} is $3d^6$ while Fe^{3+} is $3d^5$

(c) Fe^{2+} has a larger size than Fe^{3+}

(d) Fe^{3+} ions are coloured hence more stable.

31. Transition metals make the most efficient catalysts because of their ability to

(a) adopt multiple oxidation states and to form complexes

(b) form coloured ions

(c) show paramagnetism due to unpaired electrons

(d) form a large number of oxides.

32. General electronic configuration of transition metals is

(a) $(n-1)d^{1\text{-}10}ns^{0\text{-}2}$ (b) $nd^{10}ns^2$

(c) $(n-1)d^{10}ns^2$ (d) $(n-1)d^{1\text{-}5}ns^2$

33. Consider the following statements

I. $La(OH)_3$ is least basic among hydroxides of lanthanides.

II. Zr^{4+} and Hf^{4+} possess almost the same ionic radii.

III. Ce^{4+} can act as an oxidizing agent.

Which of the above is/are true?

(a) I and III (b) II and III

(c) II only (d) I and II

34. Arrange the following in increasing value of magnetic moments.

(i) $[Fe(CN)_6]^{4-}$ (ii) $[Fe(CN)_6]^{3-}$

(iii) $[Cr(NH_3)_6]^{3+}$ (iv) $[Ni(H_2O)_4]^{2+}$

(a) (i) < (ii) < (iii) < (iv)

(b) (i) < (ii) < (iv) < (iii)

(c) (ii) < (iii) < (i) < (iv)

(d) (iii) < (i) < (ii) < (iv)

35. Fe^{3+} compounds are more stable than Fe^{2+} compounds because

(a) Fe^{3+} has smaller size than Fe^{2+}

(b) Fe^{3+} has $3d^5$ configuration (half-filled)

(c) Fe^{3+} has higher oxidation state

(d) Fe^{3+} is paramagnetic in nature.

36. Following order is observed in oxidising power of certain ions:

$VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$

The reason for this increasing order of oxidising power is

(a) increasing stability of the lower species to which they are reduced

(b) increasing stability of the higher species to which they are oxidised

(c) increasing stability of the higher species to which they are reduced

(d) increasing stability of the lower species to which they are oxidised.

37. Which of the following transition metal ions has highest magnetic moment?

(a) Cu^{2+} (b) Ni^{2+}

(c) Co^{2+} (d) Fe^{2+}

38. Which of the following are amphoteric oxides?

(i) Mn_2O_7 (ii) CrO_3
(iii) Cr_2O_3 (iv) CrO
(v) V_2O_5 (vi) V_2O_4
(a) (i) and (iv) (b) (ii) and (iii)
(c) (iii) and (v) (d) (ii) and (vi)

39. Which one of the following is a '*d*-block element'?

(a) Gd (b) Hs
(c) Es (d) Cs

40. Which of the following lanthanide is commonly used?

(a) Lanthanum (b) Nobelium
(c) Thorium (d) Cerium

41. Transition elements form binary compounds with halogens. Which of the following elements will form MF_3 type compounds?

(a) Cr (b) Cu
(c) Ni (d) All of these

42. Although zirconium belongs to 4*d* and hafnium to 5*d*-transition series even they show similar physical and chemical properties because both

(a) belong to *d*-block
(b) have same number of electrons
(c) have similar atomic radius
(d) belongs to the same group of the periodic table.

43. Most of the transition metals exhibit

(i) paramagnetic behaviour
(ii) diamagnetic behaviour
(iii) variable oxidation states
(iv) formation of coloured ions
(a) (ii), (iii) and (iv) (b) (i), (iii) and (iv)
(c) (i), (ii) and (iii) (d) (i), (ii) and (iv)

44. Which of the following has no unpaired electrons but is coloured?

(a) $K_2Cr_2O_7$ (b) K_2MnO_4
(c) $CuSO_4 \cdot 5H_2O$ (d) $MnCl_2$

45. The second and third row elements of transition metals resemble each other much more than they resemble the first row because of

(a) lanthanoid contraction which results in almost same radii of second and third row metals
(b) diagonal relationship between second and third row elements
(c) similar ionisation enthalpy of second and third row elements
(d) similar oxidation states of second and third row metals.

46. Which of the following compounds is not coloured?

(a) $Na_2[CuCl_4]$ (b) $Na_2[CdCl_4]$
(c) $K_4[Fe(CN)]_6]$ (d) $K_3[Fe(CN)_6]$

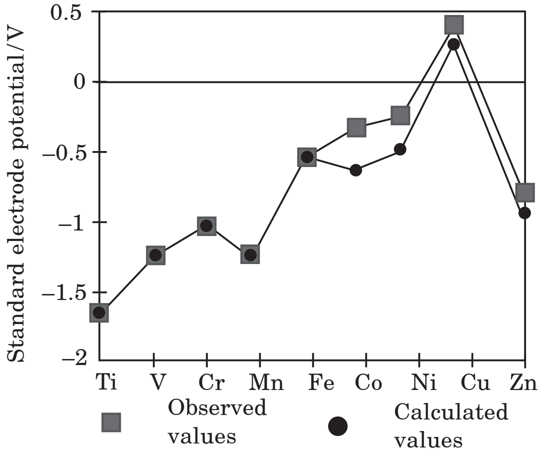
47. The salts of Cu in +1 oxidation state are unstable because

(a) Cu^+ has $3d^{10}$ configuration
(b) Cu^+ disproportionates easily to Cu(0) and Cu^{2+}
(c) Cu^+ disproportionates easily to Cu^{2+} and Cu^{3+}
(d) Cu^+ is easily reduced to Cu^{2+}.

48. Colour of transition metal ions are due to absorption of some wavelength. This results in

(a) *d-s* transition (b) *s-s* transition
(c) *s-d* transition (d) *d-d* transition.

49. The observed values and calculated values of $E°$ of various 3*d*-series elements are shown in the figure.



Which of the following facts cannot be explained on the basis of the given graph?

(a) Inability of Cu to liberate H_2 from acids
(b) Extra stability of $d^5(Mn^{2+})$ and $d^{10}(Zn^{2+})$ configuration
(c) Extra stability of Ni^{2+} due to d^{10} configuration
(d) All of these.

50. For the given reactions :

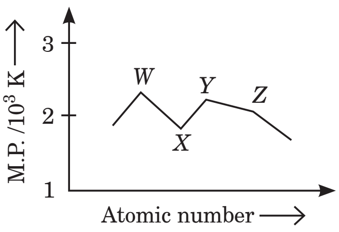
$[Fe(H_2O)_6]^{2+} + NO_3^- + H^+ \longrightarrow X + Y + H_2O$
$[Fe(H_2O)_6]^{2+} + X \longrightarrow Z + H_2O$

The incorrect statement about *X*, *Y* and *Z* is

(a) Magnetic moment of *Y* is 5.9 B.M.
(b) Oxidation state of Fe in *Z* is +1.
(c) Complex *Z* is reddish-brown in colour.
(d) *X* is an acidic oxide of nitrogen.

51. *W*, *X*, *Y* and *Z* are four consecutive members of 3*d*-series.

Trend in their melting point are shown in the given figure.



Correct statement about W, X, Y and Z is

(a) magnetic moment of X in its +2 oxidation state is 2.83 B.M.

(b) W^{3+} ion is green in colour.

(c) Y^{3+} catalyses reaction between iodide and persulphate ions.

(d) stable oxidation states of Z are +1, +2 and +6.

52. Few electrode potential values are given below:

$Cr^{3+}/Cr^{2+} = -0.41$ V

$Cr^{2+}/Cr = -0.90$ V

$Mn^{3+}/Mn^{2+} = +1.57$ V

$Mn^{2+}/Mn = -1.18$ V

On the basis of these values, Krish concluded the following statements:

I. Cr^{2+} is a reducing agent

II. Mn^{3+} is an oxidizing agent

III. both Cr^{2+} and Mn^{3+} exhibit d^4 electronic configuration

IV. when Cr^{2+} is used as a reducing agent, the chromium ion attains d^5 electronic configuration.

The incorrect conclusion made by him is

(a) I (b) II

(c) III (d) IV

53. Find the incorrect analogy for lanthanoids.

(a) Good oxidising agent : Ce^{4+}

(b) Paramagnetic lanthanide ion : Yb^{2+}

(c) Ions that can exist in aqueous solution : Eu^{2+}, Yb^{2+}

(d) Colourless ions : Ce^{3+}, Yb^{3+}

Case Based MCQs

Case I : Read the passage given below and answer the following questions.

The lanthanide series is a unique class of 15 elements with relatively similar chemical properties. They have atomic number ranging from 57 to 71, which corresponds to the filling of the 4f orbitals with 14 electrons. This configuration leads to phenomenon known as lanthanide contraction. The lanthanides are sometimes referred to as the 'rare earth elements', leading to misconception that they are rare. In fact many of the rare earth elements are more common than gold, silver and in some cases, lead. The lanthanides are commonly found in nature as a mixture in a number of monazite ($LnPO_4$) and bastnaesite ($LnCO_3F$) in the +3 oxidation state.

The chemical and physical properties of lanthanides provide the unique features that set them apart from other elements. Lanthanides are most stable in the +3 oxidation state. Yb and Sm though stable in the +3 state, also have accessible +2 oxidation states. The ease of accessibility of both oxidation states is quite important in chemical synthesis and these elements act as Lewis acid in the +3 oxidation state and single electron reductant in the +2 oxidation state.

In the following questions (Q. No. 54-58), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices on the basis of the above passage.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

54. Assertion : The elements scandium and yttrium are called "rare earths".

Reason : Scandium and yttrium are rare on earth's crust.

55. Assertion : Separation of lanthanide elements is difficult.

Reason : They have similar chemical properties.

56. Assertion : There is continuous increase in size among lanthanides.

Reason : Lanthanides show lanthanide contraction.

57. Assertion : Yb^{2+} is more stable than Yb^{3+}.

Reason : Electronic configuration of Yb^{2+} is $[Xe]4f^7$.

58. Assertion : All lanthanides have similar chemical properties.

Reason : Because the lanthanoids differ only in the number of 4*f* - electrons.

Case II : Read the passage given below and answer the following questions from 59 to 63.

The transition elements have incompletely filled *d*-subshells in their ground state or in any of their oxidation states. The transition elements occupy position in between *s*- and *p*-blocks in groups 3-12 of the Periodic table. Starting from fourth period, transition elements consists of four complete series : Sc to Zn, Y to Cd and La, Hf to Hg and Ac, Rf to Cn. In general, the electronic configuration of outer orbitals of these elements is $(n - 1)d^{1-10}\ ns^{0-2}$. The electronic configurations of outer orbitals of Zn, Cd, Hg and Cn are represented by the general formula $(n - 1)d^{10}\ ns^2$. All the transition elements have typical metallic properties such as high tensile strength, ductility, malleability. Except mercury, which is liquid at room temperature, other transition elements have typical metallic structures. The transition metals and their compounds also exhibit catalytic property and paramagnetic behaviour. Transition metal also forms alloys. An alloy is a blend of metals prepared by mixing the components. Alloys may be homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other.

59. Which of the following characteristics of transition metals is associated with higher catalytic activity?

(a) High enthalpy of atomisation
(b) Variable oxidation states
(c) Paramagnetic behaviour
(d) Colour of hydrated ions

60. Transition elements form alloys easily because they have

(a) same atomic number
(b) same electronic configuration
(c) nearly same atomic size
(d) same oxidation states.

61. The electronic configuration of tantalum (Ta) is

(a) $[Xe]4f^0\,5d^1\,6s^2$
(b) $[Xe]4f^{14}\,5d^2\,6s^2$
(c) $[Xe]4f^{14}\,5d^3\,6s^2$
(d) $[Xe]4f^{14}\,5d^4\,6s^2$

62. Which one of the following outer orbital configurations may exhibit the largest number of oxidation states?

(a) $3d^54s^1$
(b) $3d^54s^2$
(c) $3d^24s^2$
(d) $3d^34s^2$

63. The correct statement(s) among the following is/are

(i) all *d*- and *f*-block elements are metals
(ii) all *d*- and *f*-block elements form coloured ions
(iii) all *d*- and *f*-block elements are paramagnetic.

(a) (i) only
(b) (i) and (ii) only
(c) (ii) and (iii) only
(d) (i), (ii) and (iii)

Case III : Read the passage given below and answer the following questions from 64 to 68.

Transition metal oxides are compounds formed by the reaction of metals with oxygen at high temperature. The highest oxidation number in the oxides coincides with the group number. In vanadium, there is a gradual change from the basic V_2O_3 to less basic V_2O_4 and to amphoteric V_2O_5. V_2O_4 dissolves in acids to give VO^{2+} salts. Transition metal oxides are commonly utilized for their catalytic activity and semiconductive properties. Transition metal oxides are also frequently used as pigments in paints and plastic. Most notably titanium dioxide. One of the earliest application of transition metal oxides to chemical industry involved the use of vanadium oxide for catalytic oxidation of sulfur dioxide to sulphuric acid. Since then, many other applications have emerged, which include benzene oxidation to maleic anhydride on vandium oxides; cyclohexane oxidation to adipic acid on cobalt oxides. An important property of the catalyst material used in these processes is the ability of transition metals to change their oxidation state under a given chemical potential of reductants and oxidants.

64. Which oxide of vanadium is most likely to be basic and ionic ?

(a) VO
(b) V_2O_3
(c) VO_2
(d) V_2O_5

65. Vanadyl ion is

(a) VO^{2+}

(b) VO_2^+

(c) V_2O^+

(d) VO_4^{3-}

66. Which of the following statements is false?

(a) With fluorine vanadium can form VF_5.

(b) With chlorine vanadium can form VCl_5.

(c) Vanadium exhibits highest oxidation state in oxohalides $VOCl_3$, $VOBr_3$ and fluoride VF_5.

(d) With iodine vanadium cannot form VI_5 due to oxidising power of V^{5+} and reducing nature of I^-.

67. The oxidation state of vanadium in V_2O_5 is

(a) +5/2

(b) +7

(c) +5

(d) +6

68. Identify the oxidising agent in the following reaction.

$$V_2O_5 + 5Ca \longrightarrow 2V + 5CaO$$

(a) V_2O_5

(b) Ca

(c) V

(d) None of these

Case IV : Read the passage given below and answer the following questions from 69 to 73.

The unique behaviour of Cu, having a positive E accounts for its inability to liberate H_2 from acids. Only oxidising acids (nitric and hot concentrated sulphuric acid) react with Cu, the acids being reduced. The stability of the half-filled (d^5) subshell in Mn^{2+} and the completely filled (d^{10}) configuration in Zn^{2+} are related to their $E^\circ_{(M^{3+}/M^{2+})}$ values. The low value for Sc reflects the stability of Sc^{3+} which has a noble gas configuration. The comparatively high value for Mn shows that $Mn^{2+}(d^5)$ is particularly stable, whereas a comparatively low value for Fe shows the extra stability of $Fe^{3+}(d^5)$. The comparatively low value for V is related to the stability of V^{2+} (half-filled t_{2g} level).

69. Standard reduction electrode potential of Zn^{2+}/Zn is – 0.76 V. This means

(a) ZnO cannot be reduced to Zn by H_2 under standard conditions

(b) Zn cannot liberate H_2 with concentrated acids

(c) Zn is generally the anode in an electrochemical cell

(d) Zn is generally the cathode in an electrochemical cell.

70. E values for the couples Cr^{3+}/Cr^{2+} and Mn^{3+}/Mn^{2+} are –0.41 and +1.51 volts respectively. These values suggest that

(a) Cr^{2+} acts as a reducing agent whereas Mn^{3+} acts as an oxidizing agent

(b) Cr^{2+} is more stable than Cr^{3+} state

(c) Mn^{3+} is more stable than Mn^{2+}

(d) Cr^{2+} acts as an oxidizing agent whereas Mn^{3+} acts as a reducing agent.

71. The reduction potential values of M, N and O are +2.46, –1.13 and –3.13 V respectively. Which of the following order is correct regarding their reducing property?

(a) $O > N > M$

(b) $O > M > N$

(c) $M > N > O$

(d) $M > O > N$

72. Which of the following statements are true?

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

(II) Titanium and copper both in the first series of transition metals exhibits +1 oxidation state most frequently.

(III) Cu^+ ion is stable in aqueous solutions.

(IV) The E value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+} or Fe^{3+}/Fe^{2+}.

(a) (II) and (III)

(b) (I) and (IV)

(c) (I) and (III)

(d) (II) and (IV)

73. The stability of $Cu^{2+}_{(aq)}$ rather than $Cu^{+}_{(aq)}$ is due to

(a) more negative $\Delta_{hyd}H$ of $Cu^{2+}_{(aq)}$

(b) less negative $\Delta_{hyd}H$ of $Cu^{2+}_{(aq)}$

(c) more positive $\Delta_{hyd}H$ of $Cu^{2+}_{(aq)}$

(d) less positive $\Delta_{hyd}H$ of $Cu^{2+}_{(aq)}$.

Case V : Read the passage given below and answer the following questions from 74 to 78.

The *f*-block elements are those in which the differentiating electron enters the $(n-2)f$ orbital. There are two series of *f*-block elements corresponding to filling of 4*f* and 5*f*-orbitals. The series of 4*f*-orbitals is called lanthanides. Lanthanides show different oxidation states depending upon stability of f^0, f^7 and f^{14} configurations, though the most common oxidation states is +3. There is a regular decrease in size of lanthanides ions with increase in atomic number which is known as lanthanide contraction.

74. The atomic numbers of three lanthanide elements X, Y and Z are 65, 68 and 70 respectively, their Ln^{3+} electronic configuration is

(a) $4f^8, 4f^{11}, 4f^{13}$ (b) $4f^{11}, 4f^8, 4f^{13}$

(c) $4f^0, 4f^2, 4f^{11}$ (d) $4f^3, 4f^7, 4f^9$

75. Lanthanide contraction is observed in

(a) Gd (b) At

(c) Xe (d) Te

76. Which of the following is not the configuration of lanthanoid?

(a) $[Xe]4f^{10}6s^2$ (b) $[Xe]4f^1 5d^1 6s^2$

(c) $[Xe]4d^{14}5d^{10}6s^2$ (d) $[Xe]4f^7 5d^1 6s^2$

77. Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state.

(a) Cerium ($Z = 58$)

(b) Europium ($Z = 63$)

(c) Lanthanum ($Z = 57$)

(d) Gadolinium ($Z = 64$)

78. Identify the incorrect statement among the following.

(a) Lanthanoid contraction is the accumulation of successive shrinkages.

(b) The different radii of Zr and Hf is due to consequence of the lanthanoid contraction.

(c) Shielding power of 4*f* electrons is quite weak.

(d) There is a decrease in the radii of the atoms or ions as one proceeds from La to Lu.

Assertion & Reasoning Based MCQs

For question numbers 79-95, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

79. Assertion : Transition metals form substitutional alloys.

Reason : Alloys are made to develop some useful properties which are absent in the constituent elements.

80. Assertion : Reduction potential of Mn (+3 to +2) is more positive than Fe (+3 to +2).

Reason : Ionisation potential of Mn is more than that of Fe.

81. Assertion : Mn^{2+} is more stable than Mn^{3+}.

Reason : Mn^{2+} has half-filled configuration.

82. Assertion : $[Ti(H_2O)_6]^{3+}$ is a coloured ion.

Reason : Ti shows +2, +3, +4 oxidation states.

83. Assertion : Chromium is hard but mercury is soft.

Reason : Chromium is a 3*d* transition element.

84. Assertion : Cu^+ is paramagnetic.

Reason : Cu^+ is less stable than Cu^{2+}.

85. Assertion : Co (IV) is known but Ni (IV) is not.

Reason : Ni (IV) has d^6 electronic configuration.

86. Assertion : Promethium is a man-made element.

Reason : It is radioactive and has been prepared by artificial means.

87. Assertion : Transition metals are good catalysts.

Reason : V_2O_5 or Pt is used in the preparation of H_2SO_4 by Contact process.

88. Assertion : Europium (II) is more stable than cerium (II).

Reason : Cerium salts are used as a catalyst in petroleum cracking.

89. Assertion : When Zn is placed in a magnetic field, it is feebly magnetised in a direction opposite to that of the magnetising field.

Reason : Zn has completely filled atomic orbitals.

90. Assertion : The correct order of oxidising power is : $VO_2^+ < VO < VO^{2+}$.

Reason : The oxidation state of Mn in MnO_4 is +7.

91. Assertion : Transition metals form a large number of interstitial compounds.

Reason : They have high melting point and boiling point.

92. Assertion : Members of 4*d* and 5*d* series of transition elements have nearly same atomic radii.

Reason : Atomic and ionic radii for transition elements are smaller than their corresponding *s*-block elements.

93. Assertion : In transition elements, *ns* orbital is filled up first and (*n* – 1)*d* afterwards, during ionization *ns* electrons are lost prior to (*n* – 1)*d* electrons.

Reason : The effective nuclear charge felt by (*n* – 1)*d* electrons is higher as compared to that by *ns* electrons.

94. Assertion : The maximum oxidation state of chromium in its compounds is +6.

Reason : Chromium has only six electrons in *ns* and (*n* – 1)*d* orbitals.

95. Assertion : Transition metals are poor reducing agents.

Reason : Transition metals form numerous alloys with other metals.

SUBJECTIVE TYPE QUESTIONS

Very Short Answer Type Questions (VSA)

1. Give reasons for the following :

Eu^{2+} is a strong reducing agent.

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

3. Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state.

4. Assign reason for the following :

Copper (I) ion is not known in aqueous solution.

5. Name a member of the lanthanoid series which is well known to exhibit +2 oxidation state.

6. Account for the following :

Zn is not considered as a transition element.

7. How would you account for the following :

Among lanthanoids, La(III) compounds are predominant. However, occasionally in solutions or in solid compounds, +2 and +4 ions are also obtained.

8. Account for the following :

Zr and Hf have almost similar atomic radii.

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

10. Zn^{2+} salts are white while Cu^{2+} salts are coloured. Why?

Short Answer Type Questions (SA-I)

11. Why is europium (II) more stable than cerium (II)?

12. The magnetic moment of a transition metal ion is found to be 3.87 BM. How many number of unpaired electrons are present in it ?

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

	Cr	Mn	Fe	Co
$E_{M^{2+}/M}$	–0.91	–1.18	–0.44	–0.28
$E_{M^{3+}/M^{2+}}$	–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?

14. How would you account for the following :

(i) The $E_{M^{2+}/M}$ 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.

15. 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]

16. (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)

17. 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.

18. What is lanthanoid contraction and what is it due to? Write two consequences of lanthanoid contraction.

19. What is meant by 'disproportionation'? Give an example of a disproportionation reaction in aqueous solution.

20. (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?

Short Answer Type Questions (SA-II)

21. (i) Explain the cause of paramagnetism in lanthanoid ions.

(ii) Nb and Ta exhibit similar properties. Give reason.

(iii) Among the ionic species, Sc^{3+}, Ce^{4+} and Eu^{2+}, which one is a good oxidising agent.

22. 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?

23. Compare qualitatively the first and second ionisation potentials of copper and zinc. Explain the observation.

24. (i) Ce (IV) is a good analytical reagent. Why?

(ii) Account for the following : Copper(I) compounds are white whereas copper(II) compounds are coloured.

25. How do the oxides of transition elements in lower oxidation states differ from those in higher oxidation states and why?

26. 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 Fe^{3+}/Fe^{2+} couple.

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

27. (a) 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.

(b) Name the lanthanoids which show abnormally low value of third ionisation enthalpy.

28. 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) The magnetic moment (B.M.) of Fe^{2+} ion is $\sqrt{24}$.

29. (a) Account the following :

(i) Transition metals form large number of complex compounds.

(ii) $E°$ value for the Mn^{3+}/Mn^{2+} couple is highly positive (+1.57 V) as compared to Cr^{3+}/Cr^{2+}.

(iii) 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)

30. (i) Out of the ions Ag^+, Co^{2+} and Ti^{4+} which will be coloured in aqueous solution?

(ii) If each one of the above ionic species is placed in a magnetic field, how will they respond and why?

31. (a) Explain the following :

The enthalpies of atomization of transition metals are quite high.

(b) 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.

32. (i) Transition metals have very high melting and boiling points. Why?

(ii) In *d*-block element, ionic radii of ions of the same charge decreases progressively with increasing atomic number in a series. Why?

33. (a)

	Cr	Mn	Fe	Co	Ni	Cu
$E_{(M^{2+}/M)}$	–0.91	–1.18	–0.44	–0.28	–0.25	+0.34

From the given data of E values, answer the following questions :

(i) Why is $E_{(Cu^{2+}/Cu)}$ value exceptionally positive?

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

(b) 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)

34. 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) *d*-block elements exhibit more oxidation states than *f*-block elements.

35. 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+}.

Long Answer Type Questions (LA)

36. (a) 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+}.

(b) 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.

37. Compare the general characteristics of the first series of the transition metals with those of the second and third series metals in the respective vertical columns. Give special emphasis on the following points :

(i) electronic configuration

(ii) oxidation states

(iii) ionisation enthalpies and

(iv) atomic sizes.

38. (a) 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?

(v) Why Mn_2O_3 is basic whereas Mn_2O_7 is acidic?

39. (a) Account for the following :

(i) Transition metals show variable oxidation states.

(ii) Zn, Cd and Hg are soft metals.

(b) Give reason :

Iron has higher enthalpy of atomization than that of copper.

(c) What are interstitial compounds? Write their properties.

40. Give reasons for the following :

(i) Silver bromide is used in photography.

(ii) Most transition metal compounds are coloured.

(iii) Zinc and not copper is used for the recovery of metallic silver from complex $[Ag(CN)_2]^-$. Explain.

(iv) The colour of mercurous chloride, Hg_2Cl_2, changes from white to black when treated with ammonia.

(v) The species $[CuCl_4]^{2-}$ exists while $[CuI_4]^{2-}$ does not.

ANSWERS

OBJECTIVE TYPE QUESTIONS

1. (b) : The overall decrease in atomic and ionic radii from La^{3+} to Lu^{3+} is called lanthanoid contraction. Hence, the correct order is

$Yb^{3+} < Pm^{3+} < Ce^{3+} < La^{3+}$

2. (a) : Cu^{2+} has $3d^9$ configuration *i.e.*, one unpaired electron, hence, it is paramagnetic while Zn^{2+} has $3d^{10}$ configuration *i.e.*, all orbitals are filled, hence it is diamagnetic in nature.

3. (c) :
$Fe^{3+} - 3d^5$ No. of unpaired electrons = 5
$Cr^{3+} - 3d^3$ No. of unpaired electrons = 3
$Ni^{2+} - 3d^8$ No. of unpaired electrons = 2
$Cu^{2+} - 3d^9$ No. of unpaired electrons = 1

4. (a) : Acidic strength of oxides of transition metals increases with increase in oxidation number.

$$\overset{+2}{\text{Mn}}\text{O},\ \overset{+8/3}{\text{Mn}_3}\text{O}_4, \overset{+3}{\text{Mn}_2}\text{O}_3, \overset{+4}{\text{Mn}}\text{O}_2, \overset{+7}{\text{Mn}_2}\text{O}_7$$

Hence acidic strength is of the order of

$$\underset{\textit{Basic}}{\text{MnO}} < \text{Mn}_3\text{O}_4 < \underset{\textit{Amphoteric}}{\text{Mn}_2\text{O}_3} < \text{MnO}_2 < \underset{\textit{Acidic}}{\text{Mn}_2\text{O}_7}$$

5. (d) : ${}_{24}Cr \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 \underbrace{4s^1 3d^5}_{\text{half-filled}}$

6. (c) : $E°$ values for M^{2+}/M with negative signs are

Cr = – 0.91 V, Mn = – 1.18 V, Fe = – 0.44 V, Co = – 0.28 V

Thus, the order is Mn > Cr > Fe > Co.

7. (b) : $3\overset{+6}{\text{Mn}}\text{O}_4^{2-} + 4H^+ \longrightarrow 2\overset{+7}{\text{Mn}}\text{O}_4^- + \overset{+4}{\text{Mn}}\text{O}_2 + 2H_2O$ shows disproportionation since the oxidation state of Mn changes from +6 to +7 (MnO_4^-) and +4 (MnO_2).

8. (d) : Hg is the last element of third transition series.

9. (a) : $\mu = \sqrt{n(n+2)}$

Electronic configuration of ion (25) = $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$

No. of unpaired electrons (n) = 5

$\mu = \sqrt{5(5+2)} = \sqrt{35}$ = 5.9 B.M.

10. (d)

11. (c) : $Zn^{2+} \rightarrow 3d^{10}$ has no unpaired electrons to be excited. Hence, it is colourless.

12. (b) : The third ionisation energy of Mn required to change $Mn^{2+}(d^5)$ to $Mn^{3+}(d^4)$ is much larger due to stable half-filled d^5 electronic configuration.

13. (c) : They are not chemically reactive. They are chemically inert.

14. (b) : Reactivity of transition elements decreases almost regularly from Sc to Cu because of regular increase in ionisation enthalpy.

15. (a) : $Zn^{2+}(3d^{10})$ has zero unpaired electron (colourless).

$Ni^{2+}(3d^8)$ has 2 unpaired electrons (coloured).

$Cu^{2+}(3d^9)$ has 1 unpaired electron (coloured).

$Cr^{2+}(3d^4)$ has 4 unpaired electrons (coloured).

16. (d) : Ionic radii of trivalent lanthanides decrease with increase in atomic number.

17. (c) : $\mu = \sqrt{n(n+2)}$ B.M.

18. (a) : Though Cu(I) has $3d^{10}$ stable configuration while Cu(II) has $3d^9$ configuration, yet Cu(II) is more stable due to greater effective nuclear charge of Cu(II) (*i.e.*, to hold 17 electrons instead of 18 in Cu(I)).

19. (b) : In case of transition metal oxides, the oxides with metals in lower oxidation state are basic in nature.

O.S. of Mn in Mn_2O_7 = +7; V in V_2O_3 = +3; V in V_2O_5 = +5; Cr in CrO = +2; Cr in Cr_2O_3 = +3

Thus in V_2O_3, CrO and Cr_2O_3 transition metal ion is in lower oxidation state but Cr_2O_3 is amphoteric in nature. Hence V_2O_3 and CrO are basic in nature.

20. (c) : In the Wacker process, the oxidation of ethyne to ethanal is catalysed by $PdCl_2$.

21. (a) : Lanthanum is a *d*-block element which resembles lanthanides.

22. (d) : The electronic configuration of Ce^{3+} is $4f^1$

Hence, $\mu = \sqrt{n(n+2)} = \sqrt{1(1+2)} = 1.732$ B.M.

23. (a) : Tl^+ is more stable than Tl^{3+} due to inert pair effect. Cu^{2+} is more stable than Cu^+. Cr^{3+} is more stable than Cr^{2+}. V^{4+} in aqueous solution is more stable than V^{2+}.

24. (b) : $Ag_2SO_4 \rightarrow Ag^+ (4d^{10})$ – colourless
$CuF_2 \rightarrow Cu^{2+} (3d^9)$ – coloured
$MgF_2 \rightarrow Mg^{2+}$ (no *d*-electrons) – colourless
$CuCl \rightarrow Cu^+ (3d^{10})$ – colourless

25. (b) : Basic strength decreases from $La(OH)_3$ to $Lu(OH)_3$. Hence, (1) is incorrect.
Ce : [Xe] $4f^1\ 5d^1\ 6s^2$; Ce^{4+} : [Xe] $4f^0$
Yb : [Xe] $4f^{14}\ 6s^2$; Yb^{2+} : [Xe] $4f^{14}$
Lu : [Xe] $4f^{14}\ 5d^1\ 6s^2$; Lu^{3+} : [Xe] $4f^{14}$
The given ions contain no unpaired electrons and therefore, are diamagnetic.

26. (b)

27. (d) : $Sc^{3+} (3d^0)$, $Ti^{4+} (3d^0)$ are diamagnetic while $Pd^{2+} (4d^8)$ and $Cu^{2+} (3d^9)$ are paramagnetic.

28. (d) : In CrO_2Cl_2, O.S. of Cr = +6
MnO_4^-, O.S. of Mn = +7
$Cr(CN)_6^{3-}$, O.S. of Cr = +3
NiF_6^{2-}, O.S. of Ni = +4

29. (a)

30. (b) : $Fe^{2+} - 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$
$Fe^{3+} - 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$
In Fe^{3+}, orbital is half-filled hence provides extra stability.

31. (a) : The transition metals and their compounds are known for their catalytic activity because of their ability to adopt multiple oxidation states and to form complexes.

32. (a) : $(n - 1)d^{1\text{-}10}\ ns^{0-2}$

33. (b) : $La(OH)_3$ is most basic. Hence, (I) is wrong. (II) is correct due to lanthanoid contraction. (III) is correct because Ce^{4+} tends to change to stable Ce^{3+}.

34. (b) : $[Fe(CN)_6]^{4-}$; No. of unpaired electrons = 0
$[Fe(CN)_6]^{3-}$; No. of unpaired electrons = 1
$[Ni(H_2O)_4]^{2+}$; No. of unpaired electrons = 2
$[Cr(NH_3)_6]^{3+}$; No. of unpaired electrons = 3

35. (b) : $3d^5$ configuration is more stable due to singly occupied half-filled orbitals.

36. (a) : The increasing order of oxidising power is due to increasing stability of the lower species to which they are reduced.

37. (d) : More the number of unpaired *d*-electrons, more is the magnetic moment.
$Cu^{2+} - 3d^9$; No. of unpaired electrons = 1
$Ni^{2+} - 3d^8$; No. of unpaired electrons = 2
$Co^{2+} - 3d^7$; No. of unpaired electrons = 3
$Fe^{2+} - 3d^6$; No. of unpaired electrons = 4

38. (c) : Cr_2O_3 and V_2O_5 are amphoteric oxides.

39. (b) : Hs (*Z* = 108) belongs to 6*d* series with electronic configuration – $[Rn]5f^{14}6d^67s^2$.

40. (d) : Ce is most commonly used lanthanoid, nobelium (No) and Th (thorium) are actinoids.

41. (a) : Cr forms CrF_3 whereas Cu and Ni do not form CuF_3 and NiF_3.

42. (c) : Due to lanthanoid contraction, Zr and Hf have nearly equal size.

43. (b) : Due to presence of unpaired electrons in (*n* – 1)*d* orbitals, the most of the transition metal ions and their compounds are paramagnetic. They form coloured ions and show variable oxidation states due to presence of vacant *d*-orbitals.

44. (a) : The electronic configuration of Cr is
${}_{24}Cr \rightarrow [Ar]\ 3d^5\ 4s^1$ (six unpaired electrons)
In $K_2Cr_2O_7$, the oxidation number of Cr = +6. So it has no unpaired electron.

45. (a) : Due to lanthanoid contraction, the atomic radii of second and third row transition elements is almost same. Hence, they resemble each other much more as compared to first row elements.

46. (b) : $Na_2[CuCl_4]$; Cu = +2 or $Cu^{2+} \rightarrow 3d^9$
$Na_2[CdCl_4]$; Cd = +2 or $Cd^{2+} \rightarrow 4d^{10}$
$K_4[Fe(CN)_6]$; Fe = +2 or $Fe^{2+} \rightarrow 3d^6$
$K_3[Fe(CN)_6]$; Fe = +3 or $Fe^{3+} \rightarrow 3d^5$
Since Cd^{2+} has completely filled *d*-subshell hence it is colourless.

47. (b) : Cu^+ ions undergo disproportionation,
$2Cu^+ \rightarrow Cu^{2+} + Cu$

48. (d) : The colour of transition metal ions is due to *d-d* transitions.

49. (c) : Negative value of $E°$ for Ni^{2+}/Ni is related to the highest negative $\Delta H°_{hyd}$.

50. (d) :
$$3[Fe(H_2O)_6]^{2+} + NO_3^- + 4H^+ \longrightarrow \underset{(X)}{NO} + \underset{(Y)}{3[Fe(H_2O)_6]^{3+}} + 2H_2O$$
$$[Fe(H_2O)_6]^{2+} + NO \longrightarrow \underset{\text{Brown }(Z)}{[Fe(H_2O)_5NO]^{2+}} + H_2O$$
In *Y*, Fe^{3+} is present : $[Ar]3d^5$
$\mu = \sqrt{n(n+2)} = 5.9\ \text{B.M.}$
NO is a neutral oxide.

51. (c) : From the melting point trend it is clear that
$W \rightarrow Cr$
$X \rightarrow Mn$
$Y \rightarrow Fe$
$Z \rightarrow Co$

$Mn^{2+} \Rightarrow [Ar]3d^5$

$$\mu = \sqrt{5(5+2)} = 5.9\,B.M.$$

$Cr^{3+} \rightarrow$ Violet

Fe^{3+} catalyses the given reactions :

$2I^- + S_2O_8^{2-} \longrightarrow I_2 + 2SO_4^{2-}$

Co shows +2 and +3 oxidation states.

52. (d) : (a) Cr^{2+} is a reducing agent, it gets oxidised to Cr^{3+} ($3d^3$ or t_{2g}^3, stable half-filled configuration).

(b) Mn^{3+} is an oxidizing agent, it gets reduced to Mn^{2+} ($3d^5$, most stable, half-filled configuration).

(c) Cr (24) : $3d^44s^2$ Mn (25) : $3d^54s^2$

Cr^{2+} : $3d^4$ Mn^{3+} : $3d^4$

Both Cr^{2+} and Mn^{3+} exhibit d^4 electronic configuration.

(d) When Cr^{2+} is used as a reducing agent, the chromium ion attains d^3 electronic configuration.

53. (b) : Ce^{3+} and Yb^{3+} are colourless despite having one unpaired electron.

The lanthanide ions, other than $4f^0$ type (La^{3+} and Ce^{4+}) and the $4f^{14}$ type (Yb^{2+} and Lu^{3+}) are all paramagnetic.

54. (c) : The elements scandium and yttrium are called "rare earths" because they were originally discovered together with lanthanides in rare minerals and isolated as oxides or "earths". Collectively, these metals are also called rare earth elements.

55. (a)

56. (d) : In lanthanide series, with increasing atomic number, there is a progressive decrease in the atomic as well as on radii of trivalent ions form La^{3+} to Lu^{3+}.

57. (c) : Yb^{2+} is more stable than Yb^{3+} because it will acquire stable configuration of completely filled 4*f* subshell after losing 2 electrons. Electronic configuration of Yb^{2+} is $[Xe]4f^{14}$.

58. (a)

59. (b) : The transition metals and their compounds are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states to form complexes.

60. (c) : Because of similar radii and other characteristics of transition metals, alloys are readily formed by these metals.

61. (c)

62. (b) : Greater the number of valence electrons, more will be the number of oxidation states exhibited by the element.

63. (a) : All the *d*-block elements are metals, they exhibit most properties of metals like lustre, malleability, ductility, high density, high melting and boiling point, hardness, conduction of heat and electricity, etc. All the *f*-block elements are also metals but they are not good conductors of heat and electricity.

64. (a) : Oxide of V in lowest oxidation state, *i.e.*, VO is basic and ionic in character.

65. (a) : Vanadyl ion is VO^{2+} where V is in +4 oxidation state.

66. (b) **67. (c)**

68. (a) **69. (a)**

70. (a) : Lesser and negative reduction potential indicates that Cr^{2+} is a reducing agent. Higher and positive reduction potential indicates that Mn^{3+} is a stronger oxidizing agent.

71. (a) : The electrode which has more reduction potential is a good oxidizing agent and has least reducing power.

72. (b) : (I) It is because Mn^{2+} has $3d^5$ electronic configuration which has extra stability.

(II) Not titanium but copper, because with +1 oxidation state an extra stable configuration, $3d^{10}$ results.

(III) It is not stable as it undergoes disproportionation;

$2Cu^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$. The E° value for this is favourable.

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

73. (a) : The stability of $Cu^{2+}_{(aq)}$ rather than $Cu^+_{(aq)}$ is due to the much more negative $\Delta_{Hyd}H^\circ$ of $Cu^{2+}_{(aq)}$ than Cu^+, which more than compensates for the second ionisation enthalpy of Cu.

74. (a) : Terbium (Tb^{3+}) : $4f^8$, Erbium (Er^{3+}) : $4f^{11}$, Ytterbium (Yb) : $4f^{13}$.

75. (a) **76. (c)**

77. (a)

78. (b) : The almost identical radii of Zr (160 pm) and Hf (159 pm), a consequence of lanthanoid contraction.

79. (b) : Transition metals form substitutional alloys since they have nearly the same size, they can substitute one another in the crystal lattice.

80. (c) : $Mn^{2+} = [Ar]3d^5$, $Mn^{3+} = [Ar]3d^4$

$Fe^{2+} = [Ar]3d^6$, $Fe^{3+} = [Ar]3d^5$

Thus, Mn^{2+} has more stable configuration than Mn^{3+} while Fe^{3+} has more stable configuration than Fe^{2+}.

Hence, reduction potential for Mn^{3+}/Mn^{2+} couple is more positive than Fe^{3+}/Fe^{2+}.

As we move across the period, ionisation potential increases, thus, ionisation potential of Fe is more than that of Mn.

81. (a) : A half-filled or fully-filled orbital is more stable than incompletely filled orbital.

Hence Mn^{2+} ($3d^5$) is more stable than Mn^{3+} ($3d^4$).

82. (b) : Ti^{3+} has $[Ar]3d^1$ configuration. Thus, *d–d* transition is possible and thereby it shows colour.

83. (b) : Chromium has maximum number of unpaired *d* electrons while Hg do not have any unpaired *d* electrons. Thus, Cr is hard but Hg is soft metal.

84. (d) : Even though Cu^+ has completely filled 3*d* orbitals, $[Ar]3d^{10}$ the nuclear charge in Cu is not enough to hold a core of 18 electrons in Cu^+ and thus, Cu^+ is unstable in comparison to Cu^{2+}. Cu^+ is diamagnetic in nature.

85. (d) : Both Co and Ni have (IV) oxidation state. Ni (IV) has $3d^6$ electronic configuration.

Metals	**Outer electronic configuration**	**Oxi. states**
Co	$3d^7 4s^2$	+2, +3, +4
Ni	$3d^8 4s^2$	+2, +3, +4

86. (a)

87. (b) : Due to large surface area and variable valencies, transition metals form intermediate activated complexes easily, hence they are used as good catalysts.

88. (b) : The electronic configurations of europium (II) and cerium (II) are Eu^{2+} : [Xe] $4f^7$ and Ce^{2+} : [Xe] $4f^1\ 5d^1$

In Eu^{2+}, *f*-subshell is half-filled thus, it is more stable.

89. (a) : Zinc has all electrons paired $[Ar]3d^{10}4s^2$. So, it is diamagnetic in nature.

90. (d) : The oxidation states of the given compounds are the following,

$VO_2^+ : x + 2(-2) = +1$

$\Rightarrow\ x = +5$

$VO : x - 2 = 0$

$\Rightarrow\ x = +2$

$VO^{2+} : x + 1(-2) = +2$

$\Rightarrow\ x = +4$

The correct order of oxidising power is :

$VO < VO^{2+} < VO_2^+$

In MnO_4^- : $x + 4(-2) = -1$

$\Rightarrow\ x - 8 = -1 \Rightarrow x = -1 + 8 = +7$

91. (b) : Some non-metallic atoms (*e.g.*, H, B, C, N, etc.) are able to fit in the interstitial sites of transition metals lattices to form interstitial compounds.

92. (b) : It is due to lanthanide contraction.

93. (a) **94. (a)**

95. (b) : In actual practice transition metals react with acid very slowly and act as poor reducing agents. This is due to the protection of metal as a result of formation of thin oxide protective film. Further, their poor tendency as reducing agent is due to high ionisation energy, high heat of vapourization and low heat of hydration.

SUBJECTIVE TYPE QUESTIONS

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

2. Formula of oxoanion of manganese is MnO_4^-.

Oxidation state of Mn in this oxoanion = + 7

Group number of Mn is 7.

3. Lanthanoids showing +4 oxidation state are

$_{58}Ce$, $_{59}Pr$, $_{65}Tb$.

4. 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.

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

6. In the electronic configuration of Zn the *d*-orbitals are completely filled in the ground state as well as in its common oxidation state. So, it is not regarded as transition metal.

7. Lanthanum and all the lanthanoids predomi-nantly 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., $Ce^{4+} : 4f^0$, $Eu^{2+} : 4f^7$

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

8. 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.

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

10. 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.

11. 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, so 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.

12. Magnetic moment, μ_{eff} = 3.87 BM corresponds to the number of unpaired electrons, $n = 3$ by applying the formula.

$$\mu_{eff} = \sqrt{n(n+2)}\ \text{BM}$$

For $n = 1$, μ = 1.73 B.M, for $n = 2$, μ = 2.83 BM

For $n = 3$, μ = 3.87 B.M and so on.

13. 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.

14. (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 $E^\circ_{M^{2+}/M}$ for Cu is positive.

(ii) This is due to lanthanoid contraction.

15. Ce (Z = 58) = [Xe] $4f^1\ 5d^1\ 6s^2$

$\therefore$ Ce^{3+} = [Xe] $4f^1\ 5d^0\ 6s^0$

Therefore, it has only one unpaired electron. *i.e.*, $n = 1$

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

16. (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 attain 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.

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

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

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

These E° values indicate that Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidising agent.

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

18. 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).

19. 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) $2Cu^+ \longrightarrow Cu + Cu^{2+}$

20. (i) 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 :

(a) They show variable oxidation states.

(b) They exhibit catalytic properties.

(ii) 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+}).

21. (i) Due to presence of unpaired electrons in *f*-orbital lanthanoid ions are paramagnetic in nature.

(ii) Due to lanthanoid contraction, their sizes are same. Hence, their properties are similar.

(iii) Ce^{4+}. The stable oxidation state of lanthanoids is +3. Ce^{4+} tends to accept an electron to change to +3 state. Hence, it acts as a good oxidising agent.

22. (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+} : $[Ar]3d^0 4s^0$

23. The electronic configuration of Zn and Cu are :

Zn: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$

Cu: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

From the above configuration it is clear that first ionisation energy of Zn is greater than that of Cu (because of $4s^2$ and $4s^1$ configuration of Zn and Cu respectively). More energy is needed to remove an electron from $4s^2$ than from $4s^1$.

The second *I.E.* of Cu is higher than that of Zn because for Cu^+ the configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$ and for Zn^+ the configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$, it is easier to remove $4s^1$ electron of Zn^+ than a 3*d*-electron from $3d^{10}$ (stable configuration).

24. (i) The $E°$ value for Ce^{4+}/Ce^{3+} is 1.74 V which suggests that it can oxidise water. However the reaction rate is very slow and hence Ce (IV) is a good analytical reagent.

(ii) 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.

25. In the lower oxidation state, the transition metal oxides are basic and they are acidic if the metal is in higher oxidation state. The oxides are amphoteric when the metal is in intermediate oxidation state.

For example,

$$\underset{\text{Basic}}{\overset{+3}{Mn_2O_3}} \qquad \underset{\text{Amphoteric}}{\overset{+4}{MnO_2}} \qquad \underset{\text{Acidic}}{\overset{+7}{Mn_2O_7}}$$

In case of lower oxide of a transition metal, the metal atom has a low oxidation state. This means some of the valence electrons of the metal atom are not involved in bonding, hence, these can be used for donation. Thus, these are act as bases.

26. (i) This is due to lanthanoid contraction.

(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.

From the relation, $\Delta G° = -nFE°$

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

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

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

(iii) 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 oxidation state of +4.

27. (a) (i) 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.

(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.

(b) Third ionization enthalpy of lanthanoid is low if it leads to stable empty, half filled or completely filled configuration, as indicated by the abnormally low third ionization enthalpies of La, Gd, and Lu.

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

(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 acts as acidic in nature.

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

(iii) : $Fe^{2+} \Rightarrow 3d^6, \quad \therefore \quad n = 4$

Magnetic moment $= \sqrt{n(n+2)}\ \text{B.M.} = \sqrt{24}\ \text{B.M.}$

29. (a) (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) Because Mn^{2+} is stable due to half filled configuration. Thus Mn^{3+} has high tendency to form Mn^{2+} while Cr^{3+} is more stable than Cr^{2+}.

(iii) 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.

30. (i) The ionic species which possesses unpaired electron or electrons in $(n-1)d$-subshell will show colour. Out of the ions $Ag^+(4d^{10})$, $Co^{2+}(3d^7)$ and $Ti^{4+}(3d^0)$, Co^{2+} will be coloured as it contains three unpaired electrons, Ag^+ and Ti^{4+} will be colourless.

(ii) When placed in magnetic field, Co^{2+} will be attracted because it is paramagnetic due to unpaired electrons. Ag^+ and Ti^{4+} ions will be repelled by the magnetic field as they are diamagnetic.

31. (a) 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.

(b) (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) 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.

32. (i) The high melting and boiling points of transition metals are attributed to the involvement of greater number of electrons from (n – 1) *d*-orbital in addition to the *ns* electrons in the interatomic metallic bonding (*d*-*d* overlap).

(ii) As the atomic number increases the new electron enters the *d*-orbital and expected to increase in atomic size, but due to poor shielding effect of *d*-orbitals the electrostatic attraction between nucleus and outermost orbital increases and hence, the ionic radii decreases.

33. (a) (i) Copper has high energy of atomisation and low energy of hydration.

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

(b) (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.

34. (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 $E_{M^{2+}/M}$ 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) 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.

35. (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) Cr^{2+} is a stronger reducing agent than Fe^{2+}. $E°_{Cr^{3+}/Cr^{2+}}$ is negative (–0.41 V) whereas $E°_{Fe^{3+}/Fe^{2+}}$ 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+}.

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

(ii) 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 $3d^5$.

(b) (i) 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.

(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) 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.

37. (i) Electronic configuration : Electronic configuration of group 3 elements (Sc, Y, La) is [Noble gas] $(n-1)d^1\ ns^2$.

Elements of group 6 (Cr, Mo and W) show exception in electronic configuration. For Cr and Mo [Noble gas] $(n-1)$ $d^5\ ns^1$ and for W it is [Noble gas] $4f^{14}\ 5d^4\ 6s^2$.

Group 11 elements (Cu, Ag and Au) also show exceptional electronic configuration :

Cu : [Ar] $3d^{10}\ 4s^1$, Ag : [Kr]$4d^{10}\ 5s^1$,

Au : [Xe]$4f^{14}\ 5d^{10}\ 6s^1$.

Group - 10 (Ni, Pd and Pt) also show anomalous electronic configuration:

Ni : [Ar] $3d^8\ 4s^2$

Pd : [Kr] $4d^{10}\ 5s^0$

Pt : [Xe] $4f^{14}\ 5d^9\ 6s^1$

(ii) Oxidation states : Elements within the same group show similar oxidation states. Highest number of oxidation states are shown by the elements lying in the middle of the transition series. Minimum oxidation states are shown by the elements lying near to left and far right side of the series. Stability of higher oxidation states increases from first to third series.

(iii) Ionisation enthalpies : Ionisation enthalpies generally decrease down a group. This trend is followed from 3*d* to 4*d*-elements but the ionisation enthalpies either remain same or increase in going from 4*d* to 5*d*-series with the same group. This reverse trend is due to the poor shielding of the nuclear charge by the inner 4*f*-electrons. This increases the Z_{eff} and in turn increases the ionisation enthalpy.

(iv) Atomic size : Due to poor shielding of nuclear charge by 4*f*-electrons, increase in Z_{eff} decreases the size. So, the atomic size increase from 3*d* to 4*d* but decrease or remain almost the same from 4*d* to 5*d*.

38. (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.

(v) 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.

39. (a) (i) 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.

(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.

(b) 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.

(c) When small atoms of non metals like H, C, B, N etc can occupy vacant interstitial spaces in condition metals it give size to interstitial compound like hydrides, carbides. Few properties are as follow

(i) They have high melting points then pure metals.

(ii) They are conductive.

(iii) They are chemically inert.

40. (i) Silver bromide is used in photography because of its sensitivity to sunlight. In light, AgBr reduces to metallic silver.

(ii) The colour of transition metal compound is due to the presence of incompletely filled *d*-orbitals in transition metal ions/atoms, because of this *d-d* transition can occur in them. The colour is due to *d-d* transition for which the energy is absorbed from visible region. The visible colour of a compound is the complementary colour of the absorbed light.

(iii) Zinc is a cheaper and stronger reducing agent as compared to copper.

(iv) Mercurous chloride (white) changes to black on treatment with ammonia because of the formation of finely divided mercury (grey).

(v) Cu^{2+} is reduced to Cu^+ by I^- and thus CuI_2 gets converted to Cu_2I_2. This change cannot be brought about by Cl^-.

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