

Unit

8

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

### I. Multiple Choice Questions (Type-I)

- Electronic configuration of a transition element X in +3 oxidation state is  $[\text{Ar}]3d^5$ . What is its atomic number?
  - 25
  - 26
  - 27
  - 24
- The electronic configuration of Cu(II) is  $3d^9$  whereas that of Cu(I) is  $3d^{10}$ . Which of the following is correct?
  - Cu(II) is more stable
  - Cu(II) is less stable
  - Cu(I) and Cu(II) are equally stable
  - Stability of Cu(I) and Cu(II) depends on nature of copper salts
- Metallic radii of some transition elements are given below. Which of these elements will have highest density?

Element	Fe	Co	Ni	Cu
Metallic radii/pm	126	125	125	128

  - Fe
  - Ni
  - Co
  - Cu

4. Generally transition elements form coloured salts due to the presence of unpaired electrons. Which of the following compounds will be coloured in solid state?
- $\text{Ag}_2\text{SO}_4$
  - $\text{CuF}_2$
  - $\text{ZnF}_2$
  - $\text{Cu}_2\text{Cl}_2$
5. On addition of small amount of  $\text{KMnO}_4$  to concentrated  $\text{H}_2\text{SO}_4$ , a green oily compound is obtained which is highly explosive in nature. Identify the compound from the following.
- $\text{Mn}_2\text{O}_7$
  - $\text{MnO}_2$
  - $\text{MnSO}_4$
  - $\text{Mn}_2\text{O}_3$
6. The magnetic nature of elements depends on the presence of unpaired electrons. Identify the configuration of transition element, which shows highest magnetic moment.
- $3d^7$
  - $3d^5$
  - $3d^8$
  - $3d^2$
7. Which of the following oxidation state is common for all lanthanoids?
- +2
  - +3
  - +4
  - +5
8. Which of the following reactions are disproportionation reactions?
- $\text{Cu}^+ \longrightarrow \text{Cu}^{2+} + \text{Cu}$
  - $3\text{MnO}_4^- + 4\text{H}^+ \longrightarrow 2\text{MnO}_4^- + \text{MnO}_2 + 2\text{H}_2\text{O}$
  - $2\text{KMnO}_4 \longrightarrow \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$
  - $2\text{MnO}_4^- + 3\text{Mn}^{2+} + 2\text{H}_2\text{O} \longrightarrow 5\text{MnO}_2 + 4\text{H}^+$
- a, b
  - a, b, c
  - b, c, d
  - a, d

9. When  $\text{KMnO}_4$  solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after some time because
- $\text{CO}_2$  is formed as the product.
  - Reaction is exothermic.
  - $\text{MnO}_4^-$  catalyses the reaction.
  - $\text{Mn}^{2+}$  acts as autocatalyst.
10. There are 14 elements in actinoid series. Which of the following elements does not belong to this series?
- U
  - Np
  - Tm
  - Fm
11.  $\text{KMnO}_4$  acts as an oxidising agent in acidic medium. The number of moles of  $\text{KMnO}_4$  that will be needed to react with one mole of sulphide ions in acidic solution is
- $\frac{2}{5}$
  - $\frac{3}{5}$
  - $\frac{4}{5}$
  - $\frac{1}{5}$
12. Which of the following is amphoteric oxide?  
 $\text{Mn}_2\text{O}_7, \text{CrO}_3, \text{Cr}_2\text{O}_3, \text{CrO}, \text{V}_2\text{O}_5, \text{V}_2\text{O}_4$
- $\text{V}_2\text{O}_5, \text{Cr}_2\text{O}_3$
  - $\text{Mn}_2\text{O}_7, \text{CrO}_3$
  - $\text{CrO}, \text{V}_2\text{O}_5$
  - $\text{V}_2\text{O}_5, \text{V}_2\text{O}_4$
13. Gadolinium belongs to  $4f$  series. It's atomic number is 64. Which of the following is the correct electronic configuration of gadolinium?
- $[\text{Xe}] 4f^7 5d^1 6s^2$
  - $[\text{Xe}] 4f^6 5d^2 6s^2$
  - $[\text{Xe}] 4f^8 6d^2$
  - $[\text{Xe}] 4f^9 5s^1$

14. Interstitial compounds are formed when small atoms are trapped inside the crystal lattice of metals. Which of the following is not the characteristic property of interstitial compounds?
- They have high melting points in comparison to pure metals.
  - They are very hard.
  - They retain metallic conductivity.
  - They are chemically very reactive.
15. The magnetic moment is associated with its spin angular momentum and orbital angular momentum. Spin only magnetic moment value of  $\text{Cr}^{3+}$  ion is \_\_\_\_\_.
- 2.87 B.M.
  - 3.87 B.M.
  - 3.47 B.M.
  - 3.57 B.M.
16.  $\text{KMnO}_4$  acts as an oxidising agent in alkaline medium. When alkaline  $\text{KMnO}_4$  is treated with KI, iodide ion is oxidised to \_\_\_\_\_.
- $\text{I}_2$
  - $\text{IO}^-$
  - $\text{IO}_3^-$
  - $\text{IO}_4^-$
17. Which of the following statements is **not** correct?
- Copper liberates hydrogen from acids.
  - In its higher oxidation states, manganese forms stable compounds with oxygen and fluorine.
  - $\text{Mn}^{3+}$  and  $\text{Co}^{3+}$  are oxidising agents in aqueous solution.
  - $\text{Ti}^{2+}$  and  $\text{Cr}^{2+}$  are reducing agents in aqueous solution.
18. When acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution is added to  $\text{Sn}^{2+}$  salts then  $\text{Sn}^{2+}$  changes to
- Sn
  - $\text{Sn}^{3+}$
  - $\text{Sn}^{4+}$
  - $\text{Sn}^+$
19. Highest oxidation state of manganese in fluoride is +4 ( $\text{MnF}_4$ ) but highest oxidation state in oxides is +7 ( $\text{Mn}_2\text{O}_7$ ) because \_\_\_\_\_.
- fluorine is more electronegative than oxygen.
  - fluorine does not possess *d*-orbitals.
  - fluorine stabilises lower oxidation state.
  - in covalent compounds fluorine can form single bond only while oxygen forms double bond.

20. Although Zirconium belongs to  $4d$  transition series and Hafnium to  $5d$  transition series even then they show similar physical and chemical properties because\_\_\_\_\_.
- (i) both belong to  $d$ -block.
  - (ii) both have same number of electrons.
  - (iii) both have similar atomic radius.
  - (iv) both belong to the same group of the periodic table.
21. Why is HCl not used to make the medium acidic in oxidation reactions of  $\text{KMnO}_4$  in acidic medium?
- (i) Both HCl and  $\text{KMnO}_4$  act as oxidising agents.
  - (ii)  $\text{KMnO}_4$  oxidises HCl into  $\text{Cl}_2$  which is also an oxidising agent.
  - (iii)  $\text{KMnO}_4$  is a weaker oxidising agent than HCl.
  - (iv)  $\text{KMnO}_4$  acts as a reducing agent in the presence of HCl.

## II. Multiple Choice Questions (Type-II)

**Note :** In the following questions two or more options may be correct.

22. Generally transition elements and their salts are coloured due to the presence of unpaired electrons in metal ions. Which of the following compounds are coloured?
- (i)  $\text{KMnO}_4$
  - (ii)  $\text{Ce}(\text{SO}_4)_2$
  - (iii)  $\text{TiCl}_4$
  - (iv)  $\text{Cu}_2\text{Cl}_2$
23. Transition elements show magnetic moment due to spin and orbital motion of electrons. Which of the following metallic ions have almost same spin only magnetic moment?
- (i)  $\text{Co}^{2+}$
  - (ii)  $\text{Cr}^{2+}$
  - (iii)  $\text{Mn}^{2+}$
  - (iv)  $\text{Cr}^{3+}$
24. In the form of dichromate, Cr (VI) is a strong oxidising agent in acidic medium but Mo (VI) in  $\text{MoO}_3$  and W (VI) in  $\text{WO}_3$  are not because \_\_\_\_\_.
- (i) Cr (VI) is more stable than Mo(VI) and W(VI).
  - (ii) Mo(VI) and W(VI) are more stable than Cr(VI).
  - (iii) Higher oxidation states of heavier members of group-6 of transition series are more stable.
  - (iv) Lower oxidation states of heavier members of group-6 of transition series are more stable.

25. Which of the following actinoids show oxidation states upto +7?
- Am
  - Pu
  - U
  - Np
26. General electronic configuration of actinoids is  $(n-2)f^{1-14}(n-1)d^{0-2}ns^2$ . Which of the following actinoids have one electron in 6d orbital?
- U (Atomic no. 92)
  - Np (Atomic no. 93)
  - Pu (Atomic no. 94)
  - Am (Atomic no. 95)
27. Which of the following lanthanoids show +2 oxidation state besides the characteristic oxidation state +3 of lanthanoids?
- Ce
  - Eu
  - Yb
  - Ho
28. Which of the following ions show higher spin only magnetic moment value?
- Ti<sup>3+</sup>
  - Mn<sup>2+</sup>
  - Fe<sup>2+</sup>
  - Co<sup>3+</sup>
29. Transition elements form binary compounds with halogens. Which of the following elements will form MF<sub>3</sub> type compounds?
- Cr
  - Co
  - Cu
  - Ni
30. Which of the following will **not** act as oxidising agents?
- CrO<sub>3</sub>
  - MoO<sub>3</sub>
  - WO<sub>3</sub>
  - CrO<sub>4</sub><sup>2-</sup>
31. Although +3 is the characteristic oxidation state for lanthanoids but cerium also shows +4 oxidation state because \_\_\_\_\_.
- it has variable ionisation enthalpy
  - it has a tendency to attain noble gas configuration
  - it has a tendency to attain f<sup>0</sup> configuration
  - it resembles Pb<sup>4+</sup>

### III. Short Answer Type

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32. Why does copper not replace hydrogen from acids?
33. Why  $E^\ominus$  values for Mn, Ni and Zn are more negative than expected?
34. Why first ionisation enthalpy of Cr is lower than that of Zn ?
35. Transition elements show high melting points. Why?
36. When  $\text{Cu}^{2+}$  ion is treated with KI, a white precipitate is formed. Explain the reaction with the help of chemical equation.
37. Out of  $\text{Cu}_2\text{Cl}_2$  and  $\text{CuCl}_2$ , which is more stable and why?
38. When a brown compound of manganese (A) is treated with HCl it gives a gas (B). The gas taken in excess, reacts with  $\text{NH}_3$  to give an explosive compound (C). Identify compounds A, B and C.
39. Although fluorine is more electronegative than oxygen, but the ability of oxygen to stabilise higher oxidation states exceeds that of fluorine. Why?
40. Although  $\text{Cr}^{3+}$  and  $\text{Co}^{2+}$  ions have same number of unpaired electrons but the magnetic moment of  $\text{Cr}^{3+}$  is 3.87 B.M. and that of  $\text{Co}^{2+}$  is 4.87 B.M. Why?
41. Ionisation enthalpies of Ce, Pr and Nd are higher than Th, Pa and U. Why?
42. Although Zr belongs to 4d and Hf belongs to 5d transition series but it is quite difficult to separate them. Why?
43. Although +3 oxidation states is the characteristic oxidation state of lanthanoids but cerium shows +4 oxidation state also. Why?
44. Explain why does colour of  $\text{KMnO}_4$  disappear when oxalic acid is added to its solution in acidic medium.
45. When orange solution containing  $\text{Cr}_2\text{O}_7^{2-}$  ion is treated with an alkali, a yellow solution is formed and when  $\text{H}^+$  ions are added to yellow solution, an orange solution is obtained. Explain why does this happen?
46. A solution of  $\text{KMnO}_4$  on reduction yields either a colourless solution or a brown precipitate or a green solution depending on pH of the solution. What different stages of the reduction do these represent and how are they carried out?
47. The second and third rows of transition elements resemble each other much more than they resemble the first row. Explain why?
48.  $E^\ominus$  of Cu is + 0.34V while that of Zn is – 0.76V. Explain.
49. The halides of transition elements become more covalent with increasing oxidation state of the metal. Why?
50. While filling up of electrons in the atomic orbitals, the 4s orbital is filled before the 3d orbital but reverse happens during the ionisation of the atom. Explain why?
51. Reactivity of transition elements decreases almost regularly from Sc to Cu. Explain.

## IV. Matching Type

**Note :** Match the items of Column I and Column II in the following questions.

**52.** Match the catalysts given in Column I with the processes given in Column II.

Column I (Catalyst)	Column II (Process)
(i) Ni in the presence of hydrogen	(a) Ziegler Natta catalyst
(ii) $\text{Cu}_2\text{Cl}_2$	(b) Contact process
(iii) $\text{V}_2\text{O}_5$	(c) Vegetable oil to ghee
(iv) Finely divided iron	(d) Sandmeyer reaction
(v) $\text{TiCl}_4 + \text{Al}(\text{CH}_3)_3$	(e) Haber's Process
	(f) Decomposition of $\text{KClO}_3$

**53.** Match the compounds/elements given in Column I with uses given in Column II.

Column I (Compound/element)	Column II (Use)
(i) Lanthanoid oxide	(a) Production of iron alloy
(ii) Lanthanoid	(b) Television screen
(iii) Misch metal	(c) Petroleum cracking
(iv) Magnesium based alloy is constituent of	(d) Lanthanoid metal + iron
(v) Mixed oxides of lanthanoids are employed	(e) Bullets
	(f) In X-ray screen

**54.** Match the properties given in Column I with the metals given in Column II.

Column I (Property)	Column II (Metal)
(i) An element which can show +8 oxidation state	(a) Mn
(ii) 3d block element that can show upto +7 oxidation state	(b) Cr
(iii) 3d block element with highest melting point	(c) Os
	(d) Fe

**55.** Match the statements given in Column I with the oxidation states given in Column II.

Column I	Column II
(i) Oxidation state of Mn in $\text{MnO}_2$ is	(a) + 2
(ii) Most stable oxidation state of Mn is	(b) + 3
(iii) Most stable oxidation state of Mn in oxides is	(c) + 4
(iv) Characteristic oxidation state of lanthanoids is	(d) + 5
	(e) + 7



56. Match the solutions given in Column I and the colours given in Column II.

Column I (Aqueous solution of salt)	Column II (Colour)
(i) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	(a) Green
(ii) $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$	(b) Light pink
(iii) $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	(c) Blue
(iv) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	(d) Pale green
(v) $\text{Cu}_2\text{Cl}_2$	(e) Pink
	(f) Colourless

57. Match the property given in Column I with the element given in Column II.

Column I (Property)	Column II (Element)
(i) Lanthanoid which shows +4 oxidation state	(a) Pm
(ii) Lanthanoid which can show +2 oxidation state	(b) Ce
(iii) Radioactive lanthanoid	(c) Lu
(iv) Lanthanoid which has $4f^7$ electronic configuration in +3 oxidation state	(d) Eu
(v) Lanthanoid which has $4f^{14}$ electronic configuration in +3 oxidation state	(e) Gd
	(f) Dy

58. Match the properties given in Column I with the metals given in Column II.

Column I (Property)	Column II (Metal)
(i) Element with highest second ionisation enthalpy	(a) Co
(ii) Element with highest third ionisation enthalpy	(b) Cr
(iii) M in $\text{M}(\text{CO})_6$ is	(c) Cu
(iv) Element with highest heat of atomisation	(d) Zn
	(e) Ni

## V. Assertion and Reason Type

**Note :** In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

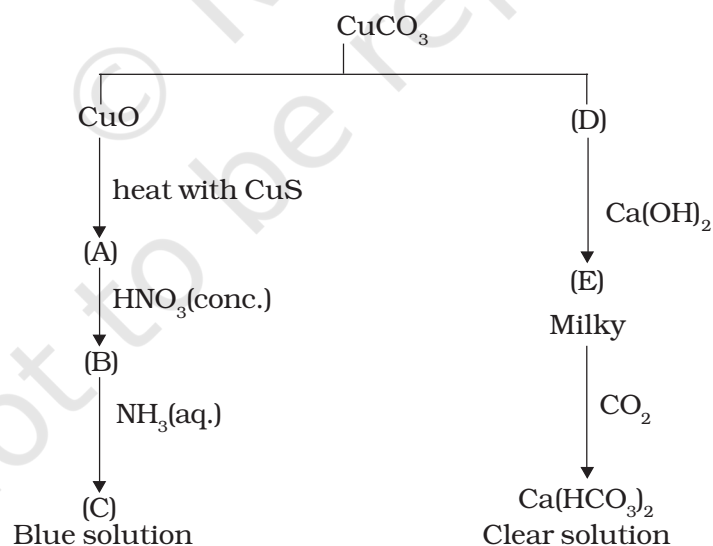
- (i) Both assertion and reason are true, and reason is the correct explanation of the assertion.

- (ii) Both assertion and reason are true but reason is not the correct explanation of assertion.
- (iii) Assertion is not true but reason is true.
- (iv) Both assertion and reason are false.

- 59. Assertion** :  $\text{Cu}^{2+}$  iodide is not known.  
**Reason** :  $\text{Cu}^{2+}$  oxidises  $\text{I}^-$  to iodine.
- 60. Assertion** : Separation of Zr and Hf is difficult.  
**Reason** : Because Zr and Hf lie in the same group of the periodic table.
- 61. Assertion** : Actinoids form relatively less stable complexes as compared to lanthanoids.  
**Reason** : Actinoids can utilise their  $5f$  orbitals along with  $6d$  orbitals in bonding but lanthanoids do not use their  $4f$  orbital for bonding.
- 62. Assertion** : Cu cannot liberate hydrogen from acids.  
**Reason** : Because it has positive electrode potential.
- 63. Assertion** : The highest oxidation state of osmium is +8.  
**Reason** : Osmium is a  $5d$ -block element.

## VI. Long Answer Type

- 64.** Identify A to E and also explain the reactions involved.



- 65.** When a chromite ore (A) is fused with sodium carbonate in free excess of air and the product is dissolved in water, a yellow solution of compound (B) is obtained. After treatment of this yellow solution with sulphuric acid,

compound (C) can be crystallised from the solution. When compound (C) is treated with KCl, orange crystals of compound (D) crystallise out. Identify A to D and also explain the reactions.

- 66.** When an oxide of manganese (A) is fused with KOH in the presence of an oxidising agent and dissolved in water, it gives a dark green solution of compound (B). Compound (B) disproportionates in neutral or acidic solution to give purple compound (C). An alkaline solution of compound (C) oxidises potassium iodide solution to a compound (D) and compound (A) is also formed. Identify compounds A to D and also explain the reactions involved.
- 67.** On the basis of Lanthanoid contraction, explain the following :
- Nature of bonding in  $\text{La}_2\text{O}_3$  and  $\text{Lu}_2\text{O}_3$ .
  - Trends in the stability of oxo salts of lanthanoids from La to Lu.
  - Stability of the complexes of lanthanoids.
  - Radii of 4d and 5d block elements.
  - Trends in acidic character of lanthanoid oxides.
- 68.** (a) Answer the following questions :
- Which element of the first transition series has highest second ionisation enthalpy?
  - Which element of the first transition series has highest third ionisation enthalpy?
  - Which element of the first transition series has lowest enthalpy of atomisation?
- (b) Identify the metal and justify your answer.
- Carbonyl  $\text{M}(\text{CO})_5$
  - $\text{MO}_3\text{F}$
- 69.** Mention the type of compounds formed when small atoms like H, C and N get trapped inside the crystal lattice of transition metals. Also give physical and chemical characteristics of these compounds.
- 70.** (a) Transition metals can act as catalysts because these can change their oxidation state. How does Fe(III) catalyse the reaction between iodide and persulphate ions?
- (b) Mention any three processes where transition metals act as catalysts.
- 71.** A violet compound of manganese (A) decomposes on heating to liberate oxygen and compounds (B) and (C) of manganese are formed. Compound (C) reacts with KOH in the presence of potassium nitrate to give compound (B). On heating compound (C) with conc.  $\text{H}_2\text{SO}_4$  and NaCl, chlorine gas is liberated and a compound (D) of manganese along with other products is formed. Identify compounds A to D and also explain the reactions involved.

## ANSWERS

### I. Multiple Choice Questions (Type-I)

- |          |           |          |           |         |           |
|----------|-----------|----------|-----------|---------|-----------|
| 1. (ii)  | 2. (i)    | 3. (iv)  | 4. (ii)   | 5. (i)  | 6. (ii)   |
| 7. (ii)  | 8. (i)    | 9. (iv)  | 10. (iii) | 11. (i) | 12. (i)   |
| 13. (i)  | 14. (iv)  | 15. (ii) | 16. (iii) | 17. (i) | 18. (iii) |
| 19. (iv) | 20. (iii) | 21. (ii) |           |         |           |

### II. Multiple Choice Questions (Type-II)

- |                 |                 |                 |                |
|-----------------|-----------------|-----------------|----------------|
| 22. (i), (ii)   | 23. (i), (iv)   | 24. (ii), (iii) | 25. (ii), (iv) |
| 26. (i), (ii)   | 27. (ii), (iii) | 28. (ii), (iii) | 29. (i), (ii)  |
| 30. (ii), (iii) | 31. (ii), (iii) |                 |                |

### III. Short Answer Type

32. Cu shows positive  $E^\ominus$  value.
33. **Hint :** Negative  $E^\ominus$  values for  $Mn^{2+}$  and  $Zn^{2+}$  are related to stabilities of half filled and fully filled configuration respectively. But for  $Ni^{2+}$ ,  $E^\ominus$  value is related to the highest negative enthalpy of hydration.
34. Ionisation enthalpy of Cr is lower due to stability of  $d^5$  and the value for Zn is higher because its electron comes out from 4s orbital.
35. The high melting points of transition metals are attributed to the involvement of greater number of electrons in the interatomic metallic bonding from (n-1) d-orbitals in addition to ns electrons
36. **Hint :**  $Cu^{2+}$  gets reduced to  $Cu^+$
- $$2Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 + I_2$$
- (white precipitate)
37. **Hint :**  $CuCl_2$  is more stable than  $Cu_2Cl_2$ . The stability of  $Cu^{2+}$  (aq.) rather than  $Cu^+$ (aq.) is due to the much more negative  $\Delta_{hyd}H^\ominus$  of  $Cu^{2+}$  (aq.) than  $Cu^+$ (aq.).
38. A =  $MnO_2$     B =  $Cl_2$     C =  $NCl_3$
- $$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$
- (A)                          (B)
- $$NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl$$
- (excess)                      (C)
39. **Hint :** It is due to the ability of oxygen to form multiple bonds to metals.
40. **Hint :** Due to symmetrical electronic configuration there is no orbital contribution in  $Cr^{3+}$  ion. However appreciable orbital contribution takes place in  $Co^{2+}$  ion.

41. **Hint :** It is because in the beginning, when 5f orbitals begin to be occupied, they will penetrate less into the inner core of electrons. The 5f electrons will therefore, be more effectively shielded from the nuclear charge than 4f electrons of the corresponding lanthanoids. Therefore outer electrons are less firmly held and they are available for bonding in the actinoids.
42. **Hint :** Due to lanthanoid contraction, they have almost same size (Zr, 160 pm) and (Hf, 159 pm).
43. It is because after losing one more electron Ce acquires stable 4f<sup>0</sup> electronic configuration.
44. KMnO<sub>4</sub> acts as oxidising agent. It oxidises oxalic acid to CO<sub>2</sub> and itself changes to Mn<sup>2+</sup> ion which is colourless.
- $$5\text{C}_2\text{O}_4^{2-} + 2\text{MnO}_4^- + 16\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{CO}_2$$
- (Coloured)  (Colourless)
45. 
$$\text{Cr}_2\text{O}_7^{2-} \xrightleftharpoons[\text{H}^+]{\text{OH}^-} \text{CrO}_4^{2-}$$
- Dichromate  Chromate  
(Orange)  (Yellow)
46. Oxidising behaviour of KMnO<sub>4</sub> depends on pH of the solution.
- In acidic medium (pH < 7)
- $$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$$
- (Colourless)
- In alkaline medium (pH > 7)
- $$\text{MnO}_4^- + \text{e}^- \longrightarrow \text{MnO}_4^{2-}$$
- (Green)
- In neutral medium (pH = 7)
- $$\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \longrightarrow \text{MnO}_2 + 4\text{OH}^-$$
- (Brown precipitate)
47. Due to lanthanoid contraction, the atomic radii of the second and third row transition elements is almost same. So they resemble each other much more as compared to first row elements.
48. **Hint :** High ionisation enthalpy to transform Cu(s) to Cu<sup>2+</sup> (aq) is not balanced by its hydration enthalpy. However, in case of Zn after removal of electrons from 4s-orbital, stable 3d<sup>10</sup> configuration is acquired.
49. As the oxidation state increases, size of the ion of transition element decreases. As per Fajan's rule, as the size of metal ion decreases, covalent character of the bond formed increases.
50. n + 1 rule : For 3d = n + 1 = 5  
4s = n + 1 = 4
- So electron will enter in 4s orbital.
- Ionisation enthalpy is responsible for the ionisation of atom. 4s electrons are loosely held by the nucleus. So electrons are removed from 4s orbital prior to 3d.
51. **Hint :** It is due to regular increase in ionisation enthalpy.

#### IV. Matching Type

52. (i) → (c)      (ii) → (d)      (iii) → (b)      (iv) → (e)      (v) → (a)  
53. (i) → (b)      (ii) → (a)      (iii) → (d)      (iv) → (e)      (v) → (c)  
54. (i) → (c)      (ii) → (a)      (iii) → (b)  
55. (i) → (c)      (ii) → (a)      (iii) → (e)      (iv) → (b)  
56. (i) → (d)      (ii) → (a)      (iii) → (b)      (iv) → (e)      (v) → (f)  
57. (i) → (b)      (ii) → (d)      (iii) → (a)      (iv) → (e)      (v) → (c)  
58. (i) → (c)      (ii) → (d)      (iii) → (b)      (iv) → (a)

#### V. Assertion and Reason Type

59. (i)      60. (ii)      61. (iii)      62. (i)      63. (ii)

#### VI. Long Answer Type

64. A = Cu      B = Cu(NO<sub>3</sub>)<sub>2</sub>      C = [Cu(NH<sub>3</sub>)<sub>4</sub>]      D = CO<sub>2</sub>  
E = CaCO<sub>3</sub>      F = Cu<sub>2</sub>[Fe(CN)<sub>6</sub>]      G = Ca (HCO<sub>3</sub>)<sub>2</sub>  
CuCO<sub>3</sub> → CuO + CO<sub>2</sub>  
CuO + CuS → Cu + SO<sub>2</sub>  
(A)  
Cu + 4HNO<sub>3</sub> (Conc) → Cu (NO<sub>3</sub>)<sub>2</sub> + 2NO + 2H<sub>2</sub>O  
(B)  
Cu<sup>2+</sup> + NH<sub>3</sub> → [Cu(NH<sub>3</sub>)<sub>4</sub>]  
(B)      (C)  
Ca(OH)<sub>2</sub> + CO<sub>2</sub> → CaCO<sub>3</sub> + H<sub>2</sub>O  
(D)      (E)  
CaCO<sub>3</sub> + H<sub>2</sub>O + CO<sub>2</sub> → Ca (HCO<sub>3</sub>)<sub>2</sub>
65. A = FeCr<sub>2</sub>O<sub>4</sub>      B = Na<sub>2</sub>CrO<sub>4</sub>      C = Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>·2H<sub>2</sub>O      D = K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>  
4FeCr<sub>2</sub>O<sub>4</sub> + 8Na<sub>2</sub>CO<sub>3</sub> + 7O<sub>2</sub> → 8Na<sub>2</sub>CrO<sub>4</sub> + 2Fe<sub>2</sub>O<sub>3</sub> + 8CO<sub>2</sub>  
(A)      (B)  
2NaCrO<sub>4</sub> + 2H<sup>+</sup> → Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + 2Na<sup>+</sup> + H<sub>2</sub>O  
Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + 2KCl → K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + 2NaCl  
(C)      (D)
66. A = MnO<sub>2</sub>      (B) K<sub>2</sub>MnO<sub>4</sub>      (C) KMnO<sub>4</sub>      (D) KIO<sub>3</sub>  
2 MnO<sub>2</sub> + 4KOH + O<sub>2</sub> → 2K<sub>2</sub>MnO<sub>4</sub> + 2H<sub>2</sub>O  
(A)      (B)  
3MnO<sub>4</sub><sup>2-</sup> + 4H<sup>+</sup> → 2MnO<sub>4</sub><sup>-</sup> + MnO<sub>2</sub> + 2H<sub>2</sub>O  
(C)  
2MnO<sub>4</sub><sup>-</sup> + H<sub>2</sub>O + KI → 2MnO<sub>2</sub> + 2OH<sup>-</sup> + KIO<sub>3</sub>  
(A)      (D)

67. **Hint :** (i) As the size decreases covalent character increases. Therefore  $\text{La}_2\text{O}_3$  is more ionic and  $\text{Lu}_2\text{O}_3$  is more covalent.  
 (ii) As the size decreases from La to Lu, stability of oxosalts also decreases.  
 (iii) Stability of complexes increases as the size of lanthanoids decreases.  
 (iv) Radii of  $4d$  and  $5d$  block elements will be almost same.  
 (v) Acidic character of oxides increases from La to Lu.
68. (a) (i) Cu, because the electronic configuration of Cu is  $3d^{10}4s^1$ . So second electron needs to be removed from completely filled  $d$ -orbital.  
 (ii) Zn [**Hint :** As above]  
 (iii) Zn [**Hint :** No unpaired electron for metallic bonding]
- (b) (i)  $\text{Fe}(\text{CO})_5$  [**Hint :** EAN rule]  
 (ii)  $\text{MnO}_3\text{F}$  [**Hint :** Mn shows +7 oxidation state;  $d$ -electrons are not involved in bonding.]
69. Interstitial compounds.  
 Characteristic properties :  
 (i) High melting points, higher than those of pure metals.  
 (ii) Very hard.  
 (iii) Retain metallic conductivity.  
 (iv) Chemically inert.
70. (a) Reaction between iodide and persulphate ions is :  

$$2\text{I}^- + \text{S}_2\text{O}_8^{2-} \xrightarrow{\text{Fe(III)}} \text{I}_2 + 2\text{SO}_4^{2-}$$
 Role of Fe (III) ions :  

$$2\text{Fe}^{3+} + 2\text{I}^- \longrightarrow 2\text{Fe}^{2+} + \text{I}_2$$

$$2\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2-} \longrightarrow 2\text{Fe}^{3+} + 2\text{SO}_4^{2-}$$
- (b) (i) Vanadium (V) oxide in contact process for oxidation of  $\text{SO}_2$  to  $\text{SO}_3$ .  
 (ii) Finely divided iron in Haber's process in conversion of  $\text{N}_2$  and  $\text{H}_2$  to  $\text{NH}_3$ .  
 (iii)  $\text{MnO}_2$  in preparation of oxygen from  $\text{KClO}_3$ .
71. A =  $\text{KMnO}_4$       B =  $\text{K}_2\text{MnO}_4$       C =  $\text{MnO}_2$       D =  $\text{MnCl}_2$   

$$\text{KMnO}_4 \xrightarrow{\Delta} \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$$
 (A)                      (B)                      (C)  

$$\text{MnO}_2 + \text{KOH} + \text{O}_2 \longrightarrow 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$$
  

$$\text{MnO}_2 + 4\text{NaCl} + 4\text{H}_2\text{SO}_4 \longrightarrow \text{MnCl}_2 + 2\text{NaHSO}_4 + 2\text{H}_2\text{O} + \text{Cl}_2$$
 (D)