

## 8



# The d- and f- Block Elements

## I. MULTIPLE CHOICE QUESTIONS (TYPE-I)

1. Electronic configuration of a transition element X in +3 oxidation state is  $[Ar]3d^5$ . What is its atomic number?

- (i) 25 (ii) 26  
(iii) 27 (iv) 24

Ans. (ii)

**Explanation:** Electronic configuration of element X =  $[Ar]3d^{5+}$  oxidation state =  $18 + 5 + 3 = 26$ .

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

- (i) Cu(II) is more stable  
(ii) Cu(II) is less stable  
(iii) Cu(I) and Cu(II) are equally stable  
(iv) Stability of Cu(I) and Cu(II) depends on nature of copper salts

Ans. (i)

**Explanation:** 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  $Cu^+$ , which more than compensates for the second ionisation enthalpy of Cu.

3. 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 |

- (i) Fe  
(ii) Ni  
(iii) Co  
(iv) Cu

Ans. (iv)

**Explanation:** On moving across the period in the periodic table the atomic radii of the element decreases towards right that is why density increases towards right in a period.

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?

- (i)  $Ag_2SO_4$  (ii)  $CuF_2$   
(iii)  $ZnF_2$  (iv)  $Cu_2Cl_2$

Ans. (ii)

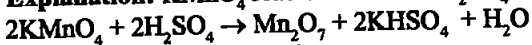
**Explanation:** Here copper is in +2 states in which Cu contains one unpaired electron. Hence it produce colour in solid state.

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:

- (i)  $\text{Mn}_2\text{O}_7$  (ii)  $\text{MnO}_2$   
 (iii)  $\text{MnSO}_4$  (iv)  $\text{Mn}_2\text{O}_3$

Ans. (i)

**Explanation:**  $\text{KMnO}_4$  reacts with conc.  $\text{H}_2\text{SO}_4$  as:



$\text{Mn}_2\text{O}_7$  is highly explosive in nature.

6. The magnetic nature of elements depends on the presence of unpaired electrons. Identify the configuration of transition element, which shows highest magnetic moment.

- (i)  $3d^7$  (ii)  $3d^5$   
 (iii)  $3d^8$  (iv)  $3d^2$

Ans. (ii)

**Explanation:** Greater the no. of unpaired electrons higher will be the magnetic moment.

$\mu = \sqrt{n(n+2)}$  where  $n$  is the number of unpaired electrons and  $\mu$  is the magnetic moment in units of Bohr magneton (BM).

Where  $n$  = no. of unpaired electron

That is why  $3d^5$  has maximum magnetic moment due to maximum no. of unpaired electrons.

7. Which of the following oxidation state is common for all lanthanoids?

- (i) +2 (ii) +3  
 (iii) +4 (iv) +5

Ans. (ii)

**Explanation:** In the lanthanoids, La(II) and Ln(III) compounds are predominant species. However, occasionally +2 and +4 ions in solution or in solid compounds are also obtained. This irregularity (as in ionisation enthalpies) arises mainly from the extra stability of empty, half-filled or filled  $f$  subshell.

8. Which of the following reactions are disproportionation reactions?

- (a)  $\text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{Cu}$   
 (b)  $3\text{MnO}_4^- + 4\text{H}^+ \rightarrow 2\text{MnO}_4^- + \text{MnO}_2 + 2\text{H}_2\text{O}$   
 (c)  $2\text{KMnO}_4 \rightarrow \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$   
 (d)  $2\text{MnO}_4^- + 3\text{Mn}^{2+} + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2 + 4\text{H}^+$   
 (i) (a), (b) (ii) (a), (b), (c)  
 (iii) (b), (c), (d) (iv) (a), (d)

Ans. (i)

**Explanation:** Copper (I) compounds are unstable in aqueous solution and undergo disproportionation.



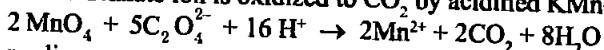
In a disproportionation reaction an element is simultaneously oxidized and reduced.

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

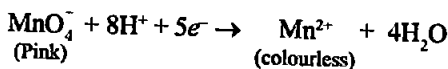
- (i)  $\text{CO}_2$  is formed as the product.
- (ii) Reaction is exothermic.
- (iii)  $\text{MnO}_4^-$  catalyses the reaction.
- (iv)  $\text{Mn}^{2+}$  acts as autocatalyst

Ans. (iv)

**Explanation:** Oxalate ion is oxidized to  $\text{CO}_2$  by acidified  $\text{KMnO}_4$ .



In acid medium



$\text{Mn}^{2+}$  formed in the reaction act as autocatalyst.

10. There are 14 elements in actinoid series. Which of the following elements does not belong to this series?

- (i) U
- (ii) Np
- (iii) Tm
- (iv) Fm

Ans. (iii)

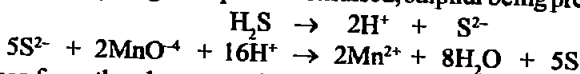
**Explanation:** Tm (thulium) atomic no. = 69 belongs to Lanthanoids (4f) series.

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

- (i)  $\frac{2}{5}$
- (ii)  $\frac{3}{5}$
- (iii)  $\frac{4}{5}$
- (iv)  $\frac{1}{5}$

Ans. (i)

**Explanation:** Hydrogen sulphide is oxidised, sulphur being precipitated:



It is clear from the above reaction that 5 moles of sulphide ions needs 2 moles of permanganate ion therefore one mole of sulphide ion require  $\frac{2}{5}$  moles of permanganate ion.

12. Which of the following is amphoteric oxide?

- (i)  $\text{V}_2\text{O}_3, \text{Cr}_2\text{O}_3$
- (ii)  $\text{Mn}_2\text{O}_7, \text{CrO}_3$
- (iii)  $\text{CrO}, \text{V}_2\text{O}_3$
- (iv)  $\text{V}_2\text{O}_5, \text{V}_2\text{O}_4$

Ans. (i)

**Explanation:** Since they react with acid as well as base.

13. Gadolinium belongs to 4f series. It's atomic number is 64. Which of the following is the correct electronic configuration of gadolinium?

- (i)  $[\text{Xe}] 4f^7 5d^1 6s^2$                       (ii)  $[\text{Xe}] 4f^6 5d^2 6s^2$   
 (iii)  $[\text{Xe}] 4f^8 6d^2$                       (iv)  $[\text{Xe}] 4f^9 5s^1$

Ans. (i)

**Explanation:** Gadolinium belongs to 4f series it has atomic no. = 64. It has extra stability due to half-filled 4f sub shell.

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?

- (i) They have high melting points in comparison to pure metals.  
 (ii) They are very hard.  
 (iii) They retain metallic conductivity.  
 (iv) They are chemically very reactive

Ans. (iv)

**Explanation:** Following are the principal properties of interstitial compounds:

- (i) They have high melting points, higher than those of pure metals.  
 (ii) They are very hard, some borides approach diamond in hardness.  
 (iii) They retain metallic conductivity.  
 (iv) They are chemically inert.

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 \_\_\_\_\_.

- (i) 2.87 B.M.                      (ii) 3.87 B.M.  
 (iii) 3.47 B.M.                      (iv) 3.57 B.M

Ans. (ii)

**Explanation:** Paramagnetism arises from the presence of unpaired electrons, each such electron having a magnetic moment associated with its spin angular momentum and orbital angular momentum. For the compounds of the first series of transition metals, the contribution of the orbital angular momentum is effectively quenched and hence is of no significance. For these, the magnetic moment is determined by the number of unpaired electrons and is calculated by using the 'spin-only' formula.

The magnetic moment  $\mu$  is given by the formula

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

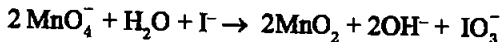
for  $\text{Cr}^{3+} = 3d^3$  the magnetic moment =  $\sqrt{3(3+2)} = \sqrt{15} = 3.87 \text{ BM}$

16.  $\text{KMnO}_3$  acts as an oxidising agent in alkaline medium. When alkaline  $\text{KMnO}_4$  is treated with KI, iodide ion is oxidised to \_\_\_\_\_.

- |                |               |
|----------------|---------------|
| (i) $I_2$      | (ii) $IO^-$   |
| (iii) $IO_3^-$ | (iv) $IO_4^-$ |

Ans. (iii)

**Explanation:** Iodide ion in neutral or faintly alkaline solutions converts iodide to iodate:



17. Which of the following statements is **not** correct?

- (i) Copper liberates hydrogen from acids.
- (ii) In its higher oxidation states, manganese forms stable compounds with oxygen and fluorine.
- (iii)  $Mn^{3+}$  and  $Co^{3+}$  are oxidising agents in aqueous solution.
- (iv)  $Ti^{2+}$  and  $Cr^{2+}$  are reducing agents in aqueous solution.

Ans. (i)

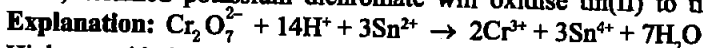
**Explanation:** Cu, having a positive  $E^\ominus = +1.34$  V accounts for its inability to liberate  $H_2$  from acids.

18. When acidified  $K_2Cr_2O_7$  solution is added to  $Sn^{2+}$  salts then  $Sn^{2+}$  changes to

- |                 |                |
|-----------------|----------------|
| (i) Sn          | (ii) $Sn^{3+}$ |
| (iii) $Sn^{4+}$ | (iv) $Sn^+$    |

Ans. (iii)

Thus, acidified potassium dichromate will oxidise tin(II) to tin(IV)



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

- (i) fluorine is more electronegative than oxygen.
- (ii) fluorine does not possess d-orbitals.
- (iii) fluorine stabilises lower oxidation state.
- (iv) in covalent compounds fluorine can form single bond only while oxygen forms double bond.

Ans. (iv)

**Explanation:** Manganese in fluoride is +4 ( $MnF_4$ ) but highest oxidation state in oxides is +7 ( $Mn_2O_7$ ) because in covalent compounds fluorine can form single bond only while oxygen forms double bond. Oxygen has ability to form multiple bonds.

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.

Ans. (iii)

**Explanation:** The almost identical radii of Zr (160 pm) and Hf (159 pm), a consequence of the lanthanoid contraction, account for their occurrence together in nature and for the similar physical and chemical properties.

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.

Ans. (ii)

**Explanation:** Permanganate titrations in presence of hydrochloric acid are unsatisfactory since hydrochloric acid is oxidised to chlorine .

## 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)  $\text{Cu}_2\text{Cl}_2$

Ans. (i) and (ii)

**Explanation:** It is due to charge transfer. In  $\text{MnO}_4^-$  an electron is momentarily transferred from O to the metal, thus momentarily  $\text{O}^{2-}$  is changed to  $\text{O}^-$  and reducing the oxidation state of the metal from Mn (VII) to Mn (VI).

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)  $\text{Cr}^{3+}$

Ans. (i) and (iv)

**Explanation:**  $\text{Co}^{2+} = [\text{Ar}]3d^7$  no. of unpaired electrons = 3

$\text{Cr}^{2+} = [\text{Ar}]3d^4$  no. of unpaired electrons = 4

$\text{Mn}^{2+} = [\text{Ar}]3d^5$  no. of unpaired electrons = 5

$\text{Cr}^{3+} = [\text{Ar}]d^3$  no. of unpaired electrons = 3

We can see that  $\text{Co}^{2+}$  and  $\text{Cr}^{3+}$  have same no. of unpaired electrons i.e. = 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.

Ans. (ii) and (iii)

**Explanation:** In the groups of d-block element higher oxidation states are favourable by heavier element. For example in group 6, Mo(VI) and W(VI) are found to be more stable than Cr(VI). Thus Cr(VI) in the form of dichromate in acidic medium is a strong oxidising agent, whereas  $\text{MoO}_3$  and  $\text{WO}_3$  are not.

25. Which of the following actinoids show oxidation states upto +7?

(i) Am (ii) Pu

(iii) U (iv) Np

Ans. (ii) and (iv)

**Explanation:** Oxidation states of the actinoids are as follows:

(i) Americium ( $Z = 95$ )

Electronic configuration =  $[\text{R}_n]5f^76d^07s^2$

Oxidation states = +3, +4, +5, +6

(ii) Plutonium ( $Z = 94$ )

Electronic configuration =  $[\text{R}_n]5f^66d^07s^2$

Oxidation states = +3, +4, +5, +6, +7

(iii) Uranium ( $Z = 92$ )

Electronic configuration =  $[\text{R}_n]5f^36d^17s^2$

Oxidation states = +3, +4, +5, +6

(iv) Neptunium ( $Z = 93$ )

Electronic configuration =  $[\text{R}_n]5f^46d^17s^2$

Oxidation states = +3, +4, +5, +6, +7

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?

(i) U (Atomic no. 92) (ii) Np (Atomic no. 93)

(iii) Pu (Atomic no. 94) (iv) Am (Atomic no. 95)

Ans. (i) and (ii)

**Explanation:**  $\text{U} \rightarrow 5f^36d^17s^2$

$\text{Np} \rightarrow 5f^46d^17s^2$

27. Which of the following lanthanoids show +2 oxidation state besides the characteristic oxidation state +3 of lanthanoids?

(i) Ce (ii) Eu

(iii) Yb (iv) Ho

Ans. (ii) and (iii)

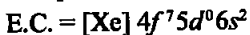
**Explanation:**

(i) Cerium ( $Z = 57$ )

E.C. =  $[\text{Xe}]4f^35d^06s^2$

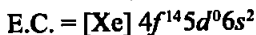
Oxidation states of Ce = +3, +4

(ii) Europium ( $Z = 63$ )



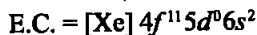
Oxidation states of Eu = +2, +3

(iii) Ytterbium ( $Z = 70$ )



Oxidation states of Yb = +2, +3

(iv) Holmium ( $Z = 67$ )



Oxidation state of Ho = +3

28. Which of the following ions show higher spin only magnetic moment value?

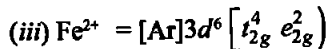
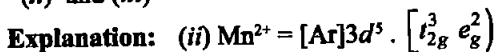
(i)  $\text{Tl}^{3+}$

(ii)  $\text{Mn}^{2+}$

(iii)  $\text{Fe}^{2+}$

(iv)  $\text{Co}^{3+}$

Ans. (ii) and (iii)



According CFT, electron pair up in  $t_{2g}$  and  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  will show higher spin magnetic value.

29. Transition elements form binary compounds with halogens. Which of the following elements will form  $\text{MF}_3$  type compounds?

(i) Cr

(ii) Co

(iii) Cu

(iv) Ni

Ans. (i) and (ii)

Explanation: Only Co and Cr can form halides like  $\text{MF}_3$  beyond Mn no metal has a trihalide except  $\text{FeX}_3$ , and  $\text{CoF}_3$ .

30. Which of the following will not act as oxidising agents?

(i)  $\text{CrO}_3$

(ii)  $\text{MoO}_3$

(iii)  $\text{WO}_3$

(iv)  $\text{CrO}_4^{2-}$

Ans. (ii) and (iii)

Explanation: Higher oxidation states of W and Mo are more stable than is why they will not act as oxidizing agent.

31. Although +3 is the characteristic oxidation state for lanthanoids but cerium also shows +4 oxidation state because \_\_\_\_\_.

(i) it has variable ionisation enthalpy

(ii) it has a tendency to attain noble gas configuration

(iii) it has a tendency to attain  $f^0$  configuration

(iv) it resembles  $\text{Pb}^{4+}$

Ans. (ii) and (iii)



**Explanation:** This irregularity (as in ionisation enthalpies) arises mainly from the extra stability of empty, half-filled or completely filled/subshell. Thus, the formation of Ce(IV) is favoured by its noble gas configuration.

### III. SHORT ANSWER TYPE

32. Why does copper not replace hydrogen from acids?

Ans. The unique behaviour of Cu, having a positive  $E^\ominus = +0.34\text{V}$  accounts for its inability to liberate  $\text{H}_2$  from acids.

33. Why  $E^\ominus$  values for Mn, Ni and Zn are more negative than expected?

Ans. The stability of the half-filled d sub-shell in  $\text{Mn}^{2+}$  and the completely filled  $d^{10}$  configuration in  $\text{Zn}^{2+}$  are related to their  $E^\ominus$  values, whereas for Ni is related to the highest negative  $\Delta_{\text{hyd}}\text{H}$ .

34. Why first ionisation enthalpy of Cr is lower than that of Zn?

Ans. The value of first ionisation enthalpy of Cr is lower because of the absence of any change in the d configuration and the value for Zn is higher because it represents an ionisation from the 4s level.

35. Transition elements show high melting points. Why?

Ans. The high melting points of these metals are attributed to the involvement of greater number of electrons from  $(n-1)d$  in addition to the ns electrons in the interatomic metallic bonding.

36. When  $\text{Cu}^{2+}$  ion is treated with KI, a white precipitate is formed. Explain the reaction with the help of chemical equation.

Ans.  $2\text{Cu}^{2+} + 4\text{I}^- \rightarrow \text{Cu}_2\text{I}_2(\text{s}) + \text{I}_2$

When  $\text{Cu}^{2+}$  reacts with potassium iodide white precipitate of  $\text{Cu}_2\text{I}_2$  is formed.

37. Out of  $\text{Cu}_2\text{Cl}_2$  and  $\text{CuCl}_2$ , which is more stable and why?

Ans.  $\text{CuCl}_2$  is more stable than  $\text{Cu}_2\text{Cl}_2$ . The stability of  $\text{Cu}^{2+}(\text{aq})$  rather than  $\text{Cu}^+(\text{aq})$  is due to the much more negative  $\Delta_{\text{hyd}}\text{H}^\ominus$  of  $\text{Cu}^{2+}(\text{aq})$  than  $\text{Cu}^+$ , which is more than to compensate for the second ionisation enthalpy of Cu.

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.

Ans. 
$$\begin{array}{ccccccc} \text{MnO}_2 & + & 4\text{HCl} & \rightarrow & \text{MnCl}_2 & + & \text{Cl}_2 & + & 2\text{H}_2\text{O} \\ \text{(A)} & & & & & & \text{(B)} & & \\ \text{(Brown compound)} & & & & & & & & \end{array}$$

$$\begin{array}{ccccccc} \text{NH}_3 & + & \text{Cl}_2 & \rightarrow & \text{NCl}_3 & + & 3\text{HCl} \\ & & \text{(Excess)} & & \text{(C)} & & \end{array}$$

$\text{MnO}_2$  is a brown compound of Mn which reacts with HCl to give  $\text{Cl}_2$  gas. This gas forms explosive compound  $\text{NCl}_3$ .

39. Although fluorine is more electronegative than oxygen, but the ability of oxygen to stabilise higher oxidation states exceeds that of fluorine. Why?

**Ans.** The ability of oxygen to stabilise high oxidation states exceeds that of fluorine because oxygen has the ability to form multiple bond with the metal.

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?

**Ans.** Magnetic moment is associated with its spin angular momentum and orbital angular momentum however due to symmetrical electronic configuration there is no orbital motion in  $\text{Cr}^{3+}$ . In  $\text{Co}^{2+}$  appreciable orbital contribution takes place.

41. Ionisation enthalpies of Ce, Pr and Nd are higher than Th, Pa and U. Why?

**Ans.** All the actinoids are believed to have the electronic configuration of  $7s^2$  and variable occupancy of the  $5f$  and  $6d$  subshells. The fourteen electrons are formally added to  $5f$ , though not in thorium ( $Z = 90$ ) but from Pa onwards the  $5f$  orbitals are complete at element 103. Although the  $5f$  orbitals resemble the  $4f$  orbitals (lanthanoids) in their angular part of the wave-function, they are not as buried as  $4f$  orbitals and hence  $5f$  electrons can participate in bonding to a far greater extent that is why ionization enthalpy of lanthanoids Ce, Pr and Nd are higher than Th, Pa and U.

42. Although Zr belongs to  $4d$  and Hf belongs to  $5d$  transition series but it is quite difficult to separate them. Why?

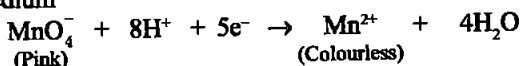
**Ans.** The almost identical radii of Zr (160 pm) and Hf (159 pm), a consequence of the lanthanoid contraction, account for their occurrence together in nature and for the difficulty faced in their separation.

43. Although +3 oxidation states is the characteristic oxidation state of lanthanoids but cerium shows +4 oxidation state also. Why?

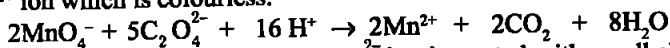
**Ans.** This irregularity (as in ionisation enthalpies) arises mainly from the extra stability of empty, half-filled or completely filled  $f$  subshell. Thus, the formation of Ce(IV) is favoured by its noble gas configuration.

44. Explain why does colour of  $\text{KMnO}_4$  disappear when oxalic acid is added to its solution in acidic medium.

**Ans.** In acidic medium

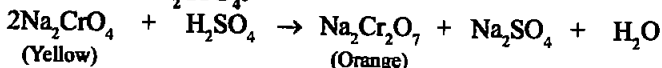


Oxalate ion is oxidized to  $\text{CO}_2$  by acidified  $\text{KMnO}_4$  and itself changes to  $\text{Mn}^{2+}$  ion which is colourless.

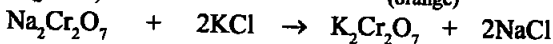
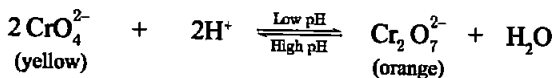


45. When orange solution containing  $\text{Cr}_2\text{O}_7^{2-}$  ion is treated with an alkali, a yellow solution is formed and when  $\text{H}^+$  ions are added to yellow solution, an orange solution is obtained. Explain why does this happen?

**Ans.** Chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution.

**Acidification of  $\text{Na}_2\text{CrO}_4$ :**

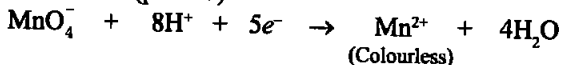
Or



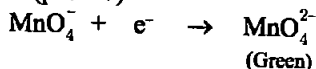
46. A solution of  $\text{KMnO}_4$  on reduction yields either a colourless solution or a brown precipitate or a green solution depending on pH of the solution. What different stages of the reduction do these represent and how are they carried out?

Ans. Oxidising behaviour of  $\text{KMnO}_4$  depends on pH of the solution.

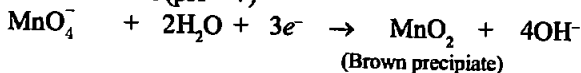
In acidic medium ( $\text{pH} < 7$ )



In alkaline medium ( $\text{pH} > 7$ )



In neutral medium ( $\text{pH} = 7$ )



47. The second and third rows of transition elements resemble each other much more than they resemble the first row. Explain why?

Ans. When atomic sizes of one series are compared with those of the corresponding elements in the other series. The curves show an increase from the first (3d) to the second (4d) series of the elements but the radii of the third (5d) series are virtually the same as those of the corresponding members of the second series. This phenomenon is associated with the intervention of the 4f orbitals which must be filled before the 5d series of elements begin. The filling of 4f before 5d orbital results in a regular decrease in atomic radii called Lanthanoid contraction which essentially compensates for the expected increase in atomic size with increasing atomic number.

48.  $E^\ominus$  of Cu is + 0.34V while that of Zn is - 0.76V. Explain.

Ans. The high energy to transform  $\text{Cu}(s)$  to  $\text{Cu}^{2+}(aq)$  is not balanced by its hydration enthalpy.  $E^\ominus$  for Mn, Ni and Zn are more negative than expected from the trend. The completely filled  $d^{10}$  configuration in  $\text{Zn}^{2+}$  are related to their  $E^\ominus$  values.

49. The halides of transition elements become more covalent with increasing oxidation state of the metal. Why?

Ans. Size of the transition elements decreases as the oxidation states of element increases. Small size favours more covalent character.

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?

Ans. During filling of electrons (n + 1) rule is followed. Hence 4s has lower energy than 3d orbital. After the orbitals are filled 4s go beyond 3d. 4s is farther from nucleus than 3d. Thus the removal of electron from 4s is easier in comparison to 3d.

51. Reactivity of transition elements decreases almost regularly from Sc to Cu. Explain.

Ans. From Sc to Cu ionization enthalpy increases that is why reactivity decreases regularly from Sc to Cu.

#### 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 (Processes)                |
|--|--------------------------------------|
| (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 $\text{KClO}_3$ |

Ans. (i) → (c)                      (ii) → (d)                      (iii) → (b)  
 (iv) → (e)                      (v) → (a)

Explanation: Catalyst → Process

(i) Ni in presence of  $\text{H}_2$  → Vegetable oil to ghee

(ii)  $\text{Cu}_2\text{Cl}_2$  → Sandmeyer reaction

(iii)  $\text{V}_2\text{O}_5$  → Contact process

(iv) Finely divided iron → Haber's process

(v)  $\text{TiCl}_4 + \text{Al}(\text{CH}_3)_3$  → Ziegler Natta catalyst

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 |

- Ans. (i) → (b)                      (ii) → (a)                      (iii) → (d)  
 (iv) → (e)                      (v) → (c)

**Explanation:** Compound /element → use

(i) Lanthanoid oxide → television screen

(ii) Lanthanoid → production of iron alloy

(iii) Misch metal → lanthanoid metal + iron

(iv) Magnesium based alloy → bullets

(v) Mixed oxide of lanthanoids are employed → petroleum cracking

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            |

- Ans. (i) → (c)                      (ii) → (a)                      (iii) → (b)

**Explanation:**

(i) An element can show +8 oxidation states → Os

(ii) 3d block element that can show upto +7 oxidation states → Mn

(iii) 3d block element with highest melting point → Cr

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 $MnO_2$ 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    |

- Ans. (i) → (c)                      (ii) → (a)                      (iii) → (e)  
 (iv) → (b)

**Explanation:**

(i) Oxidation state of Mn in  $MnO_2$  → +4

(ii) Most stable oxidation state of Mn → +2

(iii) Most stable oxidation state of Mn in oxides is → +7

(iv) Characteristic oxidation state of lanthanoid → +3

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

| Column I<br>(Aqueous solution of salt)          | Column II<br>(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        |

Ans. (i)  $\rightarrow$  (d)                      (ii)  $\rightarrow$  (a)                      (iii)  $\rightarrow$  (b)  
(iv)  $\rightarrow$  (e)                      (v)  $\rightarrow$  (f)

**Explanation:**

- (i)  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} \rightarrow$  Pale green  
(ii)  $\text{NiCl}_2 \cdot 4\text{H}_2\text{O} \rightarrow$  Green  
(iii)  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O} \rightarrow$  Light pink  
(iv)  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow$  Pink  
(v)  $\text{Cu}_2\text{Cl}_2 \rightarrow$  Colourless

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

| Column I<br>(Property)  | Column II<br>(Elements) |
|---|-------------------------|
| (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                  |

Ans. (i)  $\rightarrow$  (b)                      (ii)  $\rightarrow$  (d)                      (iii)  $\rightarrow$  (a)  
(iv)  $\rightarrow$  (e)                      (v)  $\rightarrow$  (c)

**Explanation:**

- (i) Lanthanoid shows +4 oxidation state  $\rightarrow$  Cerium (Ce)  
(ii) Lanthanoid shows +2 oxidation state  $\rightarrow$  Europium (Eu)  
(iii) Radioactive lanthanoid  $\rightarrow$  Promethium (Pm)  
(iv) Lanthanoid having  $4f^7$  configuration in +3 states  $\rightarrow$  Gadolinium (Gd)  
(v) Lanthanoid having  $4f^{14}$  configuration in +3 states  $\rightarrow$  Lutetium (Lu)

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 $M(\text{CO})_6$ is                      | (c) Cu            |
| (iv) Element with highest heat of atomisation       | (d) Zn            |
|   | (e) Ni            |

Ans. (i)  $\rightarrow$  (c)                      (ii)  $\rightarrow$  (d)                      (iii)  $\rightarrow$  (b)

(iv)  $\rightarrow$  (a)

**Explanation:**

- (i) Element with highest second ionization enthalpy  $\rightarrow$  Cu  
 (ii) Element with highest third ionization enthalpy  $\rightarrow$  Zn  
 (iii) Metal carbonyl with formula  $M(\text{CO})_6 \rightarrow$  Cr as it forms  $\text{Cr}(\text{CO})_6$   
 (iv) Highest heat of atomisation  $\rightarrow$  Co

#### 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.

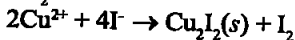
- (i) Both assertion and reason are true, and reason is the correct explanation of the assertion.  
 (ii) Both assertion and reason are true but reason is not the correct explanation of assertion.  
 (iii) Assertion is not true but reason is true.  
 (iv) Both assertion and reason are false.

59. **Assertion :**  $\text{Cu}^{2+}$  iodide is not known.

**Reason :**  $\text{Cu}^{2+}$  oxidises  $\text{I}^-$  to iodine.

Ans. (i)

**Explanation:** All Cu(II) halides are known except the iodide. In this case,  $\text{Cu}^{2+}$  oxidises  $\text{I}^-$  to  $\text{I}_2$ :



60. **Assertion :** Separation of Zr and Hf is difficult.

**Reason :** Because Zr and Hf lie in the same group of the periodic table.

Ans. (ii)

**Explanation:** The almost identical radii of Zr (160 pm) and Hf (159 pm), a consequence of the lanthanoid contraction, account for their occurrence together in nature and for the difficulty faced in their separation.

**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.

**Ans. (iii)**

**Explanation:** The actinoids are highly reactive metals this is because the  $5f$  electrons, will therefore be more effectively shielded from the nuclear charge than the  $4f$  electrons of the corresponding lanthanoids. Because the outer electrons are less firmly held, they are available for bonding in the actinoids.

**62. Assertion :** Cu cannot liberate hydrogen from acids.

**Reason :** Because it has positive electrode potential.

**Ans. (i)**

**Explanation:** Cu having a positive  $E^\ominus$  accounts for its inability to liberate  $H_2$  from acids. Only oxidising acids (nitric and hot concentrated sulphuric acid) react with Cu, as the acids being reduced. The high energy to transform  $Cu(s)$  to  $Cu^{2+}(aq)$  is not balanced by its hydration enthalpy.

**63. Assertion :** The highest oxidation state of osmium is +8.

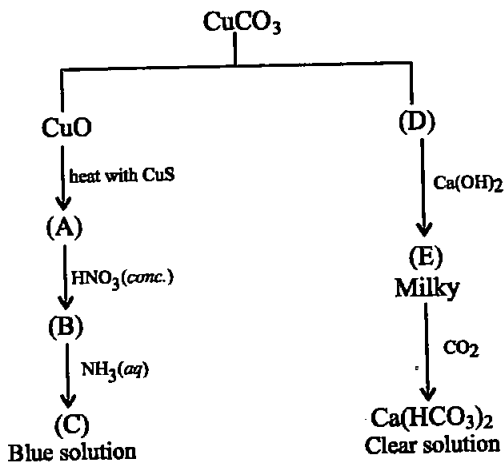
**Reason :** Osmium is a  $5d$ -block element.

**Ans. (ii)**

**Explanation:** By using all the electrons from  $6s$  and  $5d$  with expanded octet osmium can show maximum +8 oxidation states.

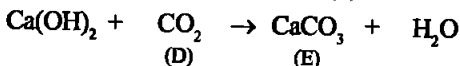
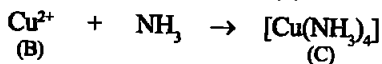
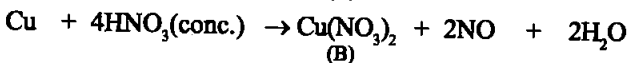
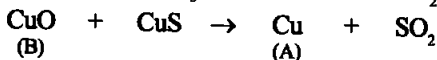
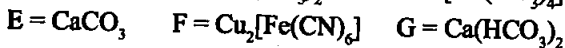
## VI. LONG ANSWER TYPE

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

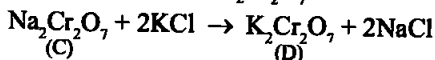
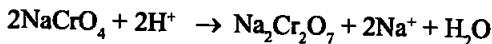
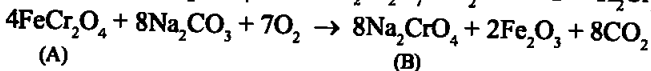
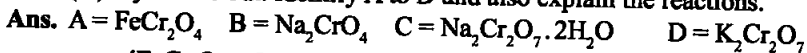




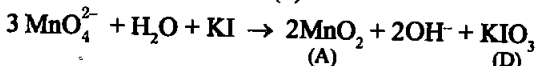
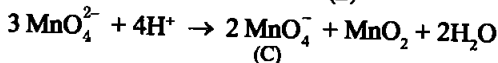
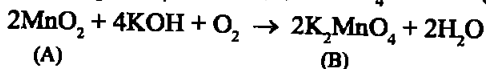
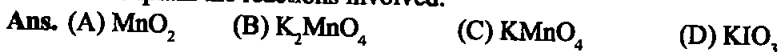
Ans.



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:

(i) Nature of bonding in  $\text{La}_2\text{O}_3$  and  $\text{Lu}_2\text{O}_3$ .

(ii) Trends in the stability of oxo salts of lanthanoids from La to Lu.

- (iii) Stability of the complexes of lanthanoids.
- (iv) Radii of 4d and 5d block elements.
- (v) Trends in acidic character of lanthanoid oxides.

**Ans. Explanation:**

- (i) Because of lanthanoid contraction  $\text{La}_2\text{O}_3$  is more ionic and  $\text{Lu}_2\text{O}_3$  is more covalent.
- (ii) As the size decreases from lanthanum to lutetium the stability of oxosalts decreases.
- (iii) With the decrease in size of Lanthanoids stability of the complex formed by lanthanoids decreases.
- (iv) Radii of 4d and 5d elements will be almost same.
- (v) Acidic character increases from lanthanum to lutetium.

**68. (a) Answer the following questions:**

- (i) Which element of the first transition series has highest second ionisation enthalpy?
- (ii) Which element of the first transition series has highest third ionisation enthalpy?
- (iii) Which element of the first transition series has lowest enthalpy of atomisation?

(b) Identify the metal and justify your answer.

- (i) Carbonyl  $\text{M}(\text{CO})_5$
- (ii)  $\text{MO}_3\text{F}$

- Ans. (a)**
- (i) Exchange the second ionisation enthalpy shows unusually high values for Cr and Cu first transition series where the  $d^5$  and  $d^{10}$  configurations of the  $\text{M}^+$  ions are disrupted, with considerable loss of energy.
  - (ii) The trend in the third ionisation enthalpies is not complicated by the 4s orbital factor and shows the greater difficulty of removing an electron from the  $d^5$  ( $\text{Mn}^{2+}$ ) and  $d^{10}$  ( $\text{Zn}^{2+}$ ) ions.
  - (iii) because of the completely filled 3d sub shell no unpaired electron is left for metallic bonding.
- (b)
- (i) It is  $\text{Fe}(\text{CO})_5$  by EAN rule  
 $\text{EAN} = x + 2 \times 5 = 36$  (Kr is the nearest inert gas)  
 $x = 26$  (atomic no. of the metal) so the metal is iron
  - (ii)  $\text{MO}_3\text{F}$  is  $\text{MnO}_3\text{F}$   
 In  $\text{MO}_3\text{F}$  let us assume  $\text{M} = x$   
 $x + 3 \times (-2) + (-1) = 0$   
 $x = +7$   
 M is in +7 oxidation state so that the given compound is  $\text{MnO}_3\text{F}$

**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.**

**Ans.** Interstitial compounds are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. They are usually non stoichiometric and are neither typically ionic nor covalent.

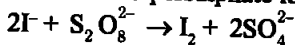
The principal physical and chemical characteristics of these compounds are as follows:

- (i) They have high melting points, higher than those of pure metals.
- (ii) They are very hard, some borides approach diamond in hardness.
- (iii) They retain metallic conductivity.
- (iv) They are chemically inert.

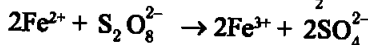
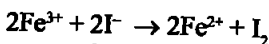
70. (a) Transition metals can act as catalysts because these can change their oxidation state. How does Fe(III) catalyse the reaction between iodide and persulphate ions?

(b) Mention any three processes where transition metals act as catalysts.

**Ans.** (a) The reaction between iodide and persulphate ions.

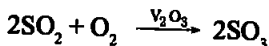
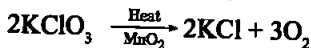


An explanation of this catalytic action can be given as:



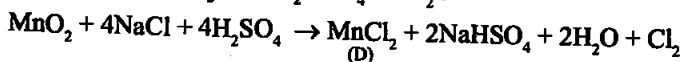
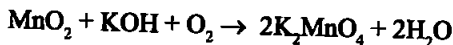
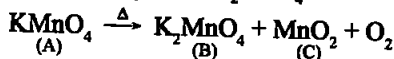
(b)  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

In the above reaction Fe is used as catalyst.



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.

**Ans.** A =  $\text{KMnO}_4$  B =  $\text{K}_2\text{MnO}_4$  C =  $\text{MnO}_2$  D =  $\text{MnCl}_2$



Since, compound (C) on heating with conc.  $\text{H}_2\text{SO}_4$  and NaCl gives  $\text{Cl}_2$  gas. So it is manganese dioxide ( $\text{MnO}_2$ ).

□□□