8

d and *f*-Block Elements

Multiple Choice Questions (MCQs)

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

   (a) 25   (b) 26   (c) 27   (d) 24

Ans. *(b)* Electronic configuration of X^{3+} is $[Ar]3d^5$

It repersents the total number of e^s and oxidation state.

Therefore, atomic number of $X = 18 + 5 + 3 = 26$

Hence, option (b) is correct.

Q. 2 The electronic configuration of Cu(II) is $3d^9$ where as 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

Ans. *(a)* Cu(II) is more stable than Cu(I). As it is known that, Cu(I) has $3d^{10}$ stable configuration while Cu(II) has $3d^9$ configuration. But Cu(II) is more stable due to greater effective nuclear charge of Cu(II) *i.e.,* it hold 17 electrons instead of 18 in Cu(I).

Q. 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

   (a) Fe   (b) Ni   (c) Co   (d) Cu

Ans. *(d)* On moving left to right along period, metallic radius decreases while mass increases. Decrease in metallic radius coupled with increase in atomic mass results in increase in density of metal.

Hence, among the given four choices Cu belongs to right side of Periodic Table in transition metal, and it has highest density (89 g/cm^3).

Q. 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?

    (a) Ag_2SO_4 (b) CuF_2 (c) ZnF_2 (d) Cu_2Cl_2

Ans. *(b)* Transition elements form coloured salt due to the presence of unpaired electrons. In CuF_2, Cu(II) contain one unpaired electron hence, CuF_2 is coloured in solid state.

Q. 5 On addition of small amount of $KMnO_4$ to concentrated H_2SO_4, a green oily compound is obtained which is highly explosive in nature. Identify the compound from the following.

    (a) Mn_2O_7 (b) MnO_2 (c) $MnSO_4$ (d) Mn_2O_3

Ans. *(a)* On addition of $KMnO_4$ to concentrated H_2SO_4, a green oily compound Mn_2O_7 is obtained which is highly explosive in nature.

$$2KMnO_4 + 2H_2SO_4(Conc.) \longrightarrow Mn_2O_7 + 2KHSO_4 + H_2O$$

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

    (a) $3d^7$ (b) $3d^5$ (c) $3d^8$ (d) $3d^2$

💡 **Thinking Process**
This problem is based on calculation of magnetic moment can be done as
Magnetic moment $(\mu) = \sqrt{n(n+2)}$ *BM.*

Ans. *(b)* Greater the number of unpaired electron, higher will be its value of magnetic moment. Since, $3d^5$ has 5 unpaired electrons hence highest magnetic moment.

$$\mu = \sqrt{5(5+2)}$$
$$= \sqrt{35}$$
$$= 5.95\,BM$$

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

   (a) +2   (b) +3   (c) +4   (d) +5

Ans. *(b)* Lanthanoids show common oxidation state of +3. Some of which also show +2 and +4 stable oxidation state alongwith +3 oxidation state. These are shown by those elements which by losing 2 or 4 electrons acquire a stable configuration of f^0, f^7 or f^{14}, *e.g.*, Eu^{2+} is $[Xe]4f^7$, Yb^{2+} is $[Xe]4f^{14}$, Ce^{4+} is $[Xe]4f^0$ and Tb^{4f} is $[Xe]4f^7$.

Q. 8 Which of the following reactions are disproportionation reactions?

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

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

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

    (iv) $2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$

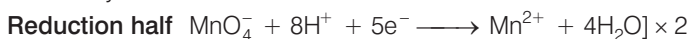   (a) (i)   (b) (i), (ii) and (iii)   (c) (ii), (iii) and (iv)   (d) (i) and (iv)

Ans. (*a*) The reaction in which oxidation as well as reduction, occur upon same atom simultaneously is known as disproportionation reaction.

$$\underset{\text{Reduction}}{\overset{\text{Oxidation}}{Cu^+ \longrightarrow Cu^{2+} + Cu}}$$
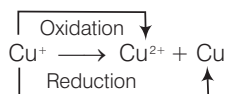
Q. 9 When $KMnO_4$ solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after some time because

    (a) CO_2 is formed as the product   (b) reaction is exothermic

    (c) MnO_4^- catalyses the reaction   (d) Mn^{2+} acts as autocatalyst

Ans. (*d*) When $KMnO_4$ solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after some time because Mn^{2+} acts as autocatalyst.

Reduction half $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$

Oxidation half $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-] \times 5$

Overall equation

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

End point of this reaction Colourless to light pink

Q. 10 There are 14 elements in actinoid series. Which of the following elements does not belong to this series?
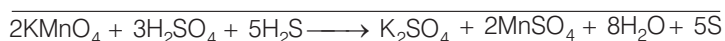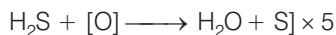
    (a) U   (b) Np   (c) Tm   (d) Fm

Ans. (*c*) Tm $(Z = 69)$ do not belong to actinoid series. The actinoid series is with atomic numbers 90 to 103. Thulium (Tm) with atomic number 69 belongs to lanthanoids ($4f$ series).

Q. 11 $KMnO_4$ acts as an oxidising agent in acidic medium. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphide ions in acidic solution is
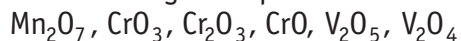
    (a) $\dfrac{2}{5}$ (b) $\dfrac{3}{5}$ (c) $\dfrac{4}{5}$ (d) $\dfrac{1}{5}$

Ans. The reaction of $KMnO_4$ in which it acts as an oxidising agent in acidic medium is

     $2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$

              $H_2S + [O] \longrightarrow H_2O + S] \times 5$

     $\overline{2KMnO_4 + 3H_2SO_4 + 5H_2S \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5S}$

5 moles of S^{2-} ions react with 2 moles of $KMnO_4$. So, 1 mole of S^{2-} ion will react with $\dfrac{2}{5}$ moles of $KMnO_4$.

Q. 12 Which of the following is amphoteric oxide?

     Mn_2O_7, CrO_3, Cr_2O_3, CrO, V_2O_5, V_2O_4

    (a) V_2O_5, Cr_2O_3 (b) Mn_2O_7, CrO_3

    (c) CrO, V_2O_5 (d) V_2O_5, V_2O_4

Ans. (*a*) V_2O_5 and Cr_2O_3 are amphoteric oxide because both react with alkalies as well as acids.

    Note   *In lower oxides, the basic character is predominant while in higher oxides, the acidic character is predominant.*

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

(a) $[Xe]4f^7 5d^1 6s^2$
(b) $[Xe]4f^6 5d^2 6s^2$
(c) $[Xe]4f^8 6d^2$
(d) $[Xe]4f^9 5s^1$

Ans. *(a)* Gadolinium belongs to 4f series and has atomic number 64. The correct electronic configuration of gadolinium is

$$_{64}Gd = {}_{54}[Xe]4f^7 5d^1 6s^2$$

It has extra stability due to half-filled 4f subshell.

Q. 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?

(a) They have high melting points in comparison to pure metals
(b) They are very hard
(c) They retain metallic conductivity
(d) The are chemically very reactive

Ans. *(d)* Interstitial compounds are formed when small atoms are trapped inside the crystal lattice of metals. *Some of their important characteristics are as follows*

(i) They are very hard and rigid.
(ii) They have high melting point which are higher than those of the pure metals.
(iii) They show conductivity like that of the pure metal.
(iv) They acquire chemical inertness.

Q. 15 The magnetic moment is associated with its spin angular momentum and orbital angular momentum. Spin only magnetic moment value of Cr^{3+} ion is

(a) 2.87 BM
(b) 3.87 BM
(c) 3.47 BM
(d) 3.57 BM

Ans. *(b)* The magnetic moment is associated with its spin angular momentum and orbital angular momentum.

Spin only magnetic moment value of Cr^{3+} ion is $3d^3$

Hence, magnetic moment $(\mu) = \sqrt{n(n+2)}$ BM
$$= \sqrt{3(3+2)} = \sqrt{15}$$
$$= 3.87 BM$$

Q. 16 $KMnO_4$ acts as an oxidising agent in alkaline medium. When alkaline $KMnO_4$ is treated with KI, iodide ion is oxidised to ....

(a) I_2
(b) IO^-
(c) IO_3^-
(d) IO_4^-

Ans. *(c)* $KMnO_4$ acts as an oxidising agent in alkaline medium. When alkaline $KMnO_4$ is treated with KI, iodide ion is oxidised to IO_3^-.

Reaction $2KMnO_4 + H_2O + KI \longrightarrow 2MnO_4 + 2KOH + KIO_3$

or, $\qquad\qquad I^- + 6OH^- \longrightarrow IO_3^- + 3H_2O + 6e^-$
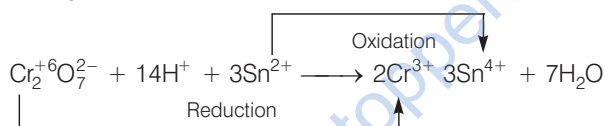
Q. 17 Which of the following statements is not correct?

(a) Copper liberates hydrogen from acids

(b) In its higher oxidation states, manganese forms stable compounds with oxygen and fluorine

(c) Mn^{3+} and Co^{3+} are oxidising agents in aqueous solution

(d) Ti^{2+} and Cr^{2+} are reducing agents in aqueous solution

Ans. *(a)* Copper lies below hydrogen in the electrochemical series and hence does not liberate H_2 from acids. Therefore, option (a) is not correct.

Other three options (b, c, d) are correct.

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

(a) Sn
(b) Sn^{3+}
(c) Sn^{4+}
(d) Sn^+

Ans. *(c)* When acidified $K_2Cr_2O_7$ solution is added to Sn^{2+} salts then Sn^{2+} changes to Sn^{4+}.

The reaction is given below

$$\overset{\text{Reduction}}{\underset{\text{Oxidation}}{Cr_2^{+6}O_7^{2-} + 14H^+ + 3Sn^{2+} \longrightarrow 2Cr^{3+} 3Sn^{4+} + 7H_2O}}$$

Q. 19 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

Ans. *(d)* Highest oxidation state of manganese in fluoride is +4(MnF_4) but highest oxidation state in oxides is +7(Mn_2O_7). The reason is that in covalent compounds fluorine can form single bond while oxygen forms double bond.

Q. 20 Although zirconium belongs to 4d transition series and hafniun to 5d transition series even then they show similar physical and chemical properties because ....

(a) both belong to *d*-block

(b) both have same number of electrons

(c) both have similar atomic radius

(d) both belong to the same group of the Periodic Table

Ans. *(c)* Due to lanthanoide contraction, Zr and Hf possess nearly same atomic and ionic radii *i.e.,* Zr = 160 pm and Hf = 159 pm, Zr^{4+} = 79 pm and Hf^{4+} = 78 pm. Therefore, these two elements show similar properties (physical and chemical properties).

Q. 21 Why is HCl not used to make the medium acidic in oxidation reactions of $KMnO_4$ in acidic medium?

(a) Both HCl and $KMnO_4$ act as oxidising agents

(b) $KMnO_4$ oxidises HCl into Cl_2 which is also an oxidising agent

(c) $KMnO_4$ is a weaker oxidising agent than HCl

(d) $KMnO_4$ acts as a reducing agent in the presence of HCl

Ans. *(b)* HCl is not used to make the medium acidic in oxidation reactions of $KMnO_4$ in acidic medium. The reason is that if HCl is used, the oxygen produced from $KMnO_4$ + HCl is partly utilised in oxidising HCl to Cl, which itself acts as an oxidising agent and partly oxidises the reducing agent.

Multiple Choice Questions (More Than One Options)

Q. 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?

(a) $KMnO_4$ (b) $Ce(SO_4)_2$ (c) $TiCl_4$ (d) Cu_2Cl_2

Ans. *(a, b)*

$KMnO_4$ is coloured due to the charge transfer and not because of the presence of unpaired electrons. Similarly, oxidation state of Ce in $Ce(SO_4)_2$ is +4 with $4f^\circ$ electronic configuration. It is also coloured (yellow) due to charge transfer and not due to $f – f$ transition.

Q. 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?

(a) Co^{2+} (b) Cr^{2+} (c) Mn^{2+} (d) Cr^{3+}

Ans. *(a, d)*

Electronic configuration of Co^{2+} = [Ar] $3d^7$; Number of unpaired electrons = 3

Electronic configuration of Cr^{2+} = [Ar] $3d^4$; Number of unpaired electrons = 4

Electronic configuration of Mn^{2+} = [Ar] $3d^5$; Number of unpaired electrons = 5

Electronic configuration of Cr^{3+} = [Ar] $3d^3$; Number of unpaired electrons = 3

Hence, it is clearly seen that both Co^{2+} and Cr^{3+} have same number of unpaired electrons. *i.e.,* 3.

Q. 24 In the form of dichromate, Cr(VI) is a strong oxidising agent in acidic medium but Mo(VI) in MoO_3 and W(VI) in WO_3 are not because

(a) Cr (VI) is more stable than Mo(VI) and W(VI).

(b) Mo (VI) and W (VI) are more stable than Cr(VI).

(c) Higher oxidation states of heavier members of group-6 of transition series are more stable.

(d) Lower oxidation states of heavier members of group-6 of transition series are more stable.

Ans. *(b, c)*

In *d*-block elements, for heavier elements, the higher oxidation states are more stable. Hence, Mo(VI) and W(VI) are more stable than Cr (VI). Thats why, Cr (VI) in the form of dichromate is a stronger oxidising agent in acidic medium whereas MoO_3 and WO_3 are not.

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

    (a) Am   (b) Pu   (c) U   (d) Np

Ans. *(b, d)*

The oxidation states of the following actinoids are

  (a) Americium $(Z = 95)$; Electronic configuration = $[Rn]5f^7 6d^0 7s^2$
      Oxidation states shown by Am = + 3, + 4, + 5, + 6.

  (b) Plutonium $(Z = 94)$; Electronic configuration = $[Rn] 5f^6 6d^0 7s^2$
      Oxidation states shown by Pu = + 3, + 4, + 5, + 6, + 7.

  (c) Uranium $(Z = 92)$; Electronic configuration = $[Rn] 5f^3 6d^1 7s^2$
      Oxidation states shown by U = + 3, + 4, + 5, + 6.

  (d) Neptunium $(Z = 93)$; Electronic configuration = $[Rn] 5f^4 6d^1 7s^2$
      Oxidation states shown by Np = + 3, + 4, + 5, + 6, + 7.

Q. 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?

    (a) U (Atomic number. 92)   (b) Np (Atomic number. 93)
    (c) Pu (Atomic number. 94)   (d) Am (Atomic number. 95)

Ans. *(a, b)*

General electronic configuration of actinoids is $(n-1)f^{1-14}(n-1)d^{0-2}ns^2$. U and Np each have one electron in 6*d* orbital. (*Also, refer to Q.* 25)

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

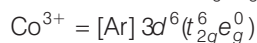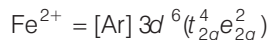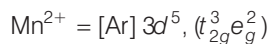   (a) Ce   (b) Eu   (c) Yb   (d) Ho

Ans. *(b, c)*
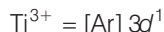
  (a) Cerium $(Z = 57) \Rightarrow$ Electronic configuration = $[Xe]4f^5 5d^0 6s^2$
      Oxidation state of Ce = +3, +4

  (b) Europium $(Z = 63) \Rightarrow$ Electronic configuration = $[Xe]4f^7 5d^0 6s^2$
      Oxidation state of Eu = +2, +3

  (c) Ytterbium $(Z = 70) \Rightarrow$ Electronic configuration = $[Xe]4f^{14} 5d^0 6s^2$
      Oxidation state of Yb = +2, +3

  (d) Holmium $(Z = 67) \Rightarrow$ Electronic configuration = $[Xe]4f^{11} 5d^0 6s^2$
      Oxidation state of Ho = +3

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

    (a) Ti^{3+} (b) Mn^{2+}
    (c) Fe^{2+} (d) Co^{3+}

Ans. *(b, c)*

As,
$$Ti^{3+} = [Ar]\, 3d^1$$
$$Mn^{2+} = [Ar]\, 3d^5,\, (t_{2g}^3 e_g^2)$$
$$Fe^{2+} = [Ar]\, 3d^6 (t_{2g}^4 e_{2g}^2)$$
$$Co^{3+} = [Ar]\, 3d^6 (t_{2g}^6 e_g^0)$$

Crystal field splitting energy (CFSE) is high in Co^{3+}, thus electrons pair up in t_{2g}. Hence, only Fe^{2+} and Mn^{2+} show higher spin magnetic moment value.

Q. 29 Transition elements form binary compounds with halogens. Which of the following elements will form MF_3 type compounds?

    (a) Cr   (b) Co   (c) Cu   (d) Ni

Ans. *(a, b)*

Transition elements such as Cr and Co form binary compounds with halogens, *i.e.,* CrF_3 and CoF_3 whereas Cu and Ni do not form CuF_3 and NiF_3.

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

    (a) CrO_3 (b) MoO_3 (c) WO_3 (d) CrO_4^{2-}

Ans. *(b, c)*

A species can act as oxidising agent only when metal is present in high oxidation state but lower oxidation state show stability. As higher oxidations states of W and Mo are more stable, therefore they will not act as oxidising agents.

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

    (a) it has variable ionisation enthalpy
    (b) it has a tendency to attain noble gas configuration
    (c) it has a tendency to attain f^0 configuration
    (d) it resembles Pb^{4+}

Ans. *(b, c)*

Electronic configuration of $_{58}Ce = {}_{54}[Xe]\, 4f^2 5d^0 6s^2$.

Therefore, electronic configuration of $Ce^{4+} = {}_{54}[Xe]\, 4f^0$.

Thus, it has a tendency to attain noble gas configuration and attain f^0 configuration.

Short Answer Type Questions

Q. 32 Why does copper not replace hydrogen from acids?

Ans. Copper not replace hydrogen from acids because Cu has positive $E°$ value, *i.e.*, less reactive than hydrogen which has electrode potential 0.00V.

Q. 33 Why E^- values for Mn, Ni and Zn are more negative than expected?

Ans. Negative values of Mn^{2+} and Zn^{2+} are related to stabilities of half-filled and completely filled configuration respectively. But for Ni^{2+}, $E°$ value is related to the highest negative enthalpy of hydration.

Hence, E^S values for **Mn**, Ni and Zn are more negative than expected.

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

Ans. Ionisation enthalpy of Cr is less than that of Zn because Cr has stable d^5 configuration. In case of zinc, electron comes out from completely filled 4s-orbital. So, removal of electron from zinc requires more energy as compared to the chromium.

Q. 35 Transition elements show high melting points. Why?

Ans. Transition elements show high melting point, due to involvement of greater number of electrons in the interatomic bonding from $(n-1)d$-orbitals in addition to *ns* electrons in forming metallic bond. Thus, large number of electrons participate forming large number of metallic bond.

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

Ans. When Cu^{2+} ion is treated with KI, it produces Cu_2I_2 white precipitate in the final product.

$$2Cu^{2+} + 4I^- \longrightarrow \underset{\text{(White ppt.)}}{Cu_2I_2} + I_2$$
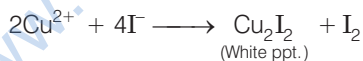
(In this reaction, CuI_2 is formed which being unstable, dissociates into Cu_2I_2 and I_2).

Q. 37 Out of Cu_2Cl_2 and $CuCl_2$, which is more stable and why?
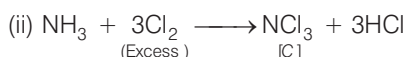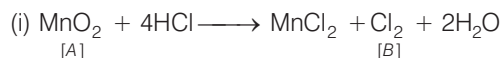
Ans. Among Cu_2Cl_2 and $CuCl_2$, $CuCl_2$ is more stable. Stability of complex can be explained on the basis of stability of oxidation state of copper. Stability of $Cu^{2+}(aq)$ rather than $Cu^+(aq)$ is due to much more negative value of [$\Delta_{hyd}H^S$ of $Cu^{2+}(aq)$]than Cu^+ which more than compensates for the second ionisation enthalpy of Cu.

Q. 38 When a brown compound of manganese (A) is treated with HCl it gives a gas (B). The gas taken in excess, reacts with NH_3 to give an explosive compound (C). Identify compounds A, B and C.

> 💡 **Thinking Process**
> *This problem is based on the properties of MnO_2 and preparation of NCl_3.*

Ans. MnO_2 is the brown compound of Mn which reacts with HCl to give Cl_2 gas. This gas forms an explosive compound NCl_3 when treated with NH_3. Thus, $A = MnO_2$; $B = Cl_2$; $C = NCl_3$ and reactions are as follows

(i) $\underset{[A]}{MnO_2} + 4HCl \longrightarrow MnCl_2 + \underset{[B]}{Cl_2} + 2H_2O$

(ii) $NH_3 + \underset{\text{(Excess)}}{3Cl_2} \longrightarrow \underset{[C]}{NCl_3} + 3HCl$

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

Ans. Oxygen can form multiple bonds with metals, while fluorine can't form multiple bond with metals. Hence, oxygen has more ability to stabilize higher oxidation state rather than fluorine.

Q. 40 Although Cr^{3+} and Co^{2+} ions have same number of unpaired electrons but the magnetic moment of Cr^{3+} is 3.87 BM and that of Co^{2+} is 4.87 BM, Why?

Ans. Magnetic moment of any metal ion can be decided on the basis of spin as well as orbital contribution of electron. Due to symmetrical electronic configuration, there is no orbital contribution in Cr^{3+} ion. However, appreciable orbital contribution takes place in Co^{2+} ion.

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

Ans. Ce, Pr and Nd are lanthanoids and have incomplete 4*f* shell while Th, Pa and U are actinoids and have 5*f* shell incomplete.

In the beginning, when 5*f*-orbitals begin to be occupied, they will penetrate less into the inner core of electrons. The 5*f*-electrons will therefore, be more effectively shielded from the nuclear charge than 4*f* electrons of the corresponding lanthanoids.

Therefore, outer electrons are less firmly held and they are available for bonding in the actinoids.

Q. 42 Although Zr belongs to 4d and Hf belongs to 5d transition series but it is quite difficult to separate them, Why?
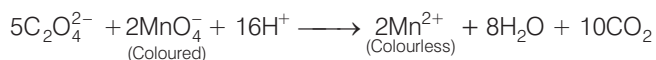
Ans. Separation of Zr and Hf are quite difficult because of lanthanoid contraction. Due to lanthanoid contraction, they have almost same size (Zr = 160 pm and Hf = 159 pm) and thus, similar chemical properties. That's why it is very difficult to separate them by chemical methods.

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

Ans. It is due to the fact that after losing one more electron Ce acquires stable $4f^{\circ}$ electronic configuration. So, Ce shows +4 oxidation state also alongwith +3 oxidation state.

Q. 44 Explain why does colour of $KMnO_4$ disappear when oxalic acid is added to its solution in acidic medium?

Ans. When oxalic acid is added to acidic solution of $KMnO_4$, its colour disappear due to reduction of MnO_4^- ion to Mn^{2+}. Chemical reaction occurring during this neutralisation reaction is as follows

$$5\underset{\text{(Coloured)}}{C_2O_4^{2-}} + 2MnO_4^- + 16H^+ \longrightarrow 2\underset{\text{(Colourless)}}{Mn^{2+}} + 8H_2O + 10CO_2$$

Q. 45 When orange solution containing $Cr_2O_7^{2-}$ ion is treated with an alkali, a yellow solution is formed and when H^+ ions are added to yellow solution, an orange solution is obtained. Explain why does this happen?

Ans. When orange solution containing $Cr_2O_7^{2-}$ ion is treated with an alkali, a yellow solution of CrO_4^{2-} is obtained. On the same way, $Cr_2O_7{}^{2-} \underset{H^+}{\overset{OH^-}{\longrightarrow}} CrO_4{}^{2-}$

$\underset{\substack{\text{Dischromate}\\ \text{(orange)}}}{} \qquad \underset{\substack{\text{Chromate}\\ \text{(yellow)}}}{}$

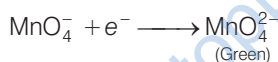when H^+ ions are added to yellow solution, an orange solution is obtained due to interconversion.

Q. 46 A solution of $KMnO_4$ 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 $KMnO_4$ depends on pH of the solution.
In acidic medium (pH < 7)
$$MnO_4^- + 8H^+ + 5e^- \longrightarrow \underset{\text{Colourless}}{Mn^{2+}} + 4H_2O$$
In alkaline medium (pH > 7)
$$MnO_4^- + e^- \longrightarrow \underset{\text{(Green)}}{MnO_4^{2-}}$$
In neutral medium (pH = 7)
$$MnO_4^- + 2H_2O + 3e^- \longrightarrow \underset{\text{(Brown ppt)}}{MnO_2} + 4OH^-$$
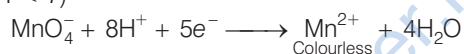
Q. 47 The second and third rows of transition elements resemble each other much more than they resemble the first row. Explain, why?

Ans. 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 and show similar character.

Q. 48 E^s of Cu is +0.34V while that of Zn is −0.76 V. Explain.

Ans. E^s value of Cu is positive because of the fact that sum of sublimation enthalpy and ionisation enthalpy to convert Cu(s) to Cu^{2+} (aq) is so high that it is not compensate by its hydration enthalpy. $E^°$ value for Zn is negative because of the fact that after removal of electrons from 4s orbital, stable $3d^{10}$ configuration is obtained.

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

💡 Thinking Process
This problem is based on concept of Fajan's rule and its application.

Ans. 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.

Therefore, the halide of transition elements become more covalent with increasing oxidation state of the metal.

Q. 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 up of electrons follow $(n+l)$ rule. Here 4s has lower energy than 3d orbital. After the orbitals are filled 4s goes beyond 3d, i.e., 4s is farther from nucleus than 3d. So, electron from 4s is removed earlier than from 3d.

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

Ans. Reactivity of transition elements depends mostly upon their ionisation enthalpies. As we move from left to right in the periodic table (Se to Cu), ionisation enthalpies increase almost regularly.

Hence, their reactivity decreases almost regularly from Se to Cu.

Matching The Columns

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

Column I (Catalyst)		Column II (Process)	
A.	Ni in the presence of hydrogen	1.	Ziegler-Natta catalyst
B.	Cu_2Cl_2	2.	Contact process
C.	V_2O_5	3.	Vegetable oil to ghee
D.	Finely divided iron	4.	Sandmeyer reaction
E.	$TiCl_4 + Al(CH_3)_3$	5.	Haber's process
		6.	Decomposition of $KClO_3$

Ans. **A.** → (3)   **B.** → (4)   **C.** → (2)   **D.** → (5)   **E.** → (1)

Catalyst		Process
A.	Ni in the presence of hydrogen	Vegetable oil to ghee
B.	Cu_2Cl_2	Sandmeyer reaction
C.	V_2O_5	Contact process $SO_2 \xrightarrow{V_2O_5} SO_3$
D.	Finely divided iron	Haber's process $N_2 + 3H_2 \xrightarrow{Fe} 2NH_3$
E.	$TiCl_4 + Al(CH_3)_3$	Ziegler-Natta catalyst

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

	Column I (Compound/element)		Column II (Use)
A.	Lanthanoid oxide	1.	Production of iron alloy
B.	Lanthanoid	2.	Television screen
C.	Misch metall	3.	Petroleum cracking
D.	Magnesium based alloy is constituent of	4.	Lanthanoid metal + iron
E.	Mixed oxides of lanthanoids are employed	5.	Bullets
		6.	X-ray screen

Ans. A. $\rightarrow$ (2)   B. $\rightarrow$ (1)   C. $\rightarrow$ (4)   D. $\rightarrow$ (5)   E. $\rightarrow$ (3)

	Compound /Element	Use
A.	Lanthanoid oxide	Television screen
B.	Lanthanoid	Production of iron alloy
C.	Misch metall	Lanthanoid metal + iron
D.	Magnesium based alloy is constitute of	Bullets
E	Mixed oxides of lanthanoids are employed	Petroleum cracking

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

	Column I (Property)		Column II (Metal)
A.	An element which can show +8 oxidation state	1.	Mn
B.	3d block element that can show upto +7 oxidation state	2.	Cr
C.	3d block element with highest melting point	3.	Os
		4.	Fe

Ans. A. $\rightarrow$ (3)   B. $\rightarrow$ (1)   C. $\rightarrow$ (2)

A. Osmium is an element which can show +8 oxidation state.

B. 3d block element that can show upto +7 oxidation state is manganese.

C. 3d block element with highest melting point is chromium.

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

	Column I		Column II
A.	Oxidation state of Mn in MnO_2 is	1.	+2
B.	Most stable oxidation state of Mn is	2.	+3
C.	Most stable oxidation state of Mn in oxides is	3.	+4
D.	Characteristic oxidation state of lanthanoids is	4.	+5
		5.	+7

Ans. A. → (3)   B. → (1)   C. → (5)   D. → (2)

    A. Oxidation state of Mn in MnO_2 is $+4$.

    B. Most stable oxidation state of Mn is $+2$.

    C. Most stable oxidation state of Mn in oxides is $+7$.

    D. Characteristic oxidation state of lanthanoids is $+3$.

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

Column I (Aqueous solution of salt)		Column II (Colour)	
A.	$FeSO_4 \cdot 7H_2O$	1.	Green
B.	$NiCl_2 \cdot 4H_2O$	2.	Light pink
C.	$MnCl_2 \cdot 4H_2O$	3.	Blue
D.	$CoCl_2 \cdot 6H_2O$	4.	Pale green
E.	Cu_2Cl_2	5.	Pink
		6.	Colourless

Ans. A. → (4)   B. → (1)   C. → (2)   D. → (5)   E. → (6)

	Aqueous solution of salt	Colour
A.	$FeSO_4 \cdot 7H_2O$	Pale green
B.	$NiCl_2 \cdot 4H_2O$	Green
C.	$MnCl_2 \cdot 4H_2O$	Light pink
D.	$CoCl_2 \cdot 6H_2O$	Pink
E.	Cu_2Cl_2	Colourless

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

Column I (Property)		Column II (Element)	
A.	Lanthanoid which shows $+4$ oxidation state	1.	Pm
B.	Lanthanoid which can show $+2$ oxidation state	2.	Ce
C.	Radioactive lanthanoid	3.	Lu
D.	Lanthanoid which has $4f^7$ electronic configuration in $+3$ oxidation state	4.	Eu
E.	Lanthanoid which has $4f^{14}$ electronic configuration in $+3$ oxidation state	5.	Gd
		6.	Dy

Ans. A. → (2)   B. → (4)   C. → (1)   D. → (5)   E. → (3)

    A. Lanthanoid which shows $+4$ oxidation state is cerium.

        $_{58}Ce = [Xe]4f^2 5d^0 6s^2$; Oxidation state $= +3, +4$

    B. Lanthanoid which can show $+2$ oxidation state is europium.

        $_{63}Eu = [Xe]4f^7 5d^0 6s^2$; Oxidation state $= +2, +3$

C. Radioactive lanthanoid is promethium. It is the only synthetic (man-made) radioactive lanthanoid.

D. Lanthnoid which has $4f^7$ electronic configuration in $+3$ oxidation state is gadolinium.
$_{64}Gd = [Xe]4f^7 5d^1 6s^2$; Oxidation state $= +3$

E. Lanthanoid which has $4f^{14}$ electronic configuration in $+3$ oxidation state is lutetium
$_{71}Lu = [Xe]4f^{14} 5d^1 6s^2$; Oxidation state $= +3$

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

Column I (Property)		Column II (Metal)	
A.	Element with highest second ionisation enthalpy	1.	Co
B.	Element with highest third ionisation enthalpy	2.	Cr
C.	M in $M(CO)_6$ is	3.	Cu
D.	Element with highest heat of atomisation	4.	Zn
		5.	Ni

Ans. **A.** $\rightarrow (3)$ **B.** $\rightarrow (4)$ **C.** $\rightarrow (2)$ **D.** $\rightarrow (1)$

A. $Cu^+ = 3d^{10}$ which is very stable configuration due to full-filled orbitals. Hence, removal of second electron requires very high energy.

B. $Zn^{2+} = 3d^{10}$ which is very stable configuration. Hence, removal of third electron requires very high energy.

C. Metal carbonyl with formula $M(CO)_6$ is $Cr(CO)_6$.

D. Nickel is the element with highest heat of atomisation.

Assertion and Reason

In the following questions a statement of assertion (A) followed by a statement of reason (R) is given. Choose the correct answer out of the following choices.

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

(b) Both assertion and reason are true but reason is not the correct explanation of assertion.

(c) Assertion is not true but reason is true.

(d) Both assertion and reason are false.

Q. 59 Assertion (A) Cu^{2+} iodide is not known.
Reason (R) Cu^{2+} oxidises I^- to iodine.

Ans. *(a)* Assertion and reason both are correct and reason is the correct explanation of assertion.

Copper (II) iodide (CuI_2) is not known because Cu^{2+} oxidises I^- to Iodine.

Q. 60 Assertion (A) Separation of Zr and Hf is difficult.

Reason (R) Because Zr and Hf lie in the same group of the Periodic Table.

Ans. *(b)* Assertion and reason are true but reason is not correct explanation of assertion.

Separation of Zr and Hf is difficult; it is not because of they lie in the same group of Periodic Table. This is due to lanthanoid contraction which causes almost similar radii of both of them.

Q. 61 Assertion (A) Actinoids form relatively less stable complexes as compared to lanthanoids.

Reason (R) Actinoids can utilise their 5f orbitals alongwith 6d orbitals in bonding but lanthanoids do not use their 4f orbital for bonding.

Ans. *(c)* Assertion is not true but reason is true.

Actinoids form relatively more stable complexes as compared to lanthanoids because of actinoids can utilise their 5f orbitals along with 6d orbitals in bonding but lanthanoids do not use their 4f orbitals for bonding.

Q. 62 Assertion (A) Cu cannot liberate hydrogen from acids.

Reason (R) Because it has positive electrode potential.

Ans. *(a)* Assertion and reason both are correct and reason is correct explanation of assertion.

Cu can not liberate hydrogen from acids because it has positive electrode potential. Metals having negative value of electrode potential liberate H_2 gas.

Q. 63 Assertion (A) The highest oxidation state of osmium is +8 .
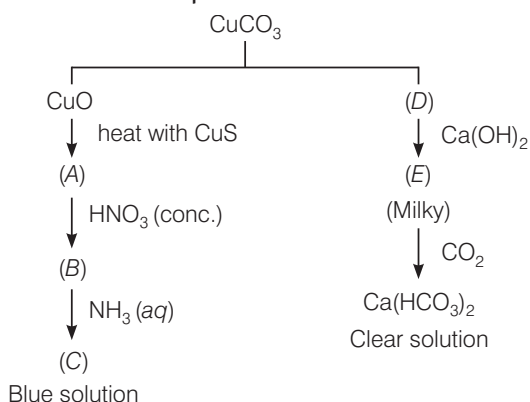
Reason (R) Osmium is a 5d-block element.

Ans. *(b)* Assertion and reason both are correct but reason is not the correct explanation of assertion.

The highest oxidation state of osmium is +8 due to its ability to expand their octet by using its all 8 electrons (2 from 6s and 6 from 5d).
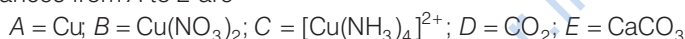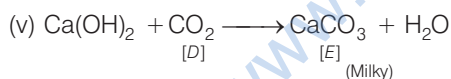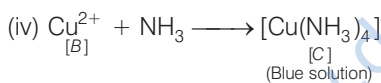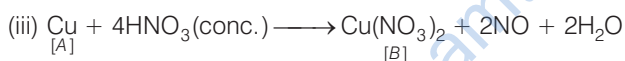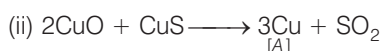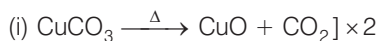
Long Answer Type Questions

Q. 64 Identify A to E and also explain the reaction involved.

Ans. The substances from A to E are

$$A = Cu; \ B = Cu(NO_3)_2; \ C = [Cu(NH_3)_4]^{2+}; \ D = CO_2; \ E = CaCO_3$$

Reactions:

(i) $CuCO_3 \xrightarrow{\Delta} CuO + CO_2] \times 2$

(ii) $2CuO + CuS \longrightarrow \underset{[A]}{3Cu} + SO_2$

(iii) $\underset{[A]}{Cu} + 4HNO_3(conc.) \longrightarrow \underset{[B]}{Cu(NO_3)_2} + 2NO + 2H_2O$

(iv) $\underset{[B]}{Cu^{2+}} + NH_3 \longrightarrow \underset{\underset{(Blue\ solution)}{[C]}}{[Cu(NH_3)_4]}$

(v) $\underset{[D]}{Ca(OH)_2} + CO_2 \longrightarrow \underset{\underset{(Milky)}{[E]}}{CaCO_3} + H_2O$
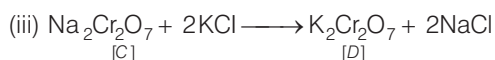
(vi) $CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$
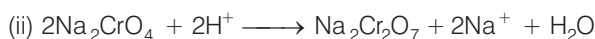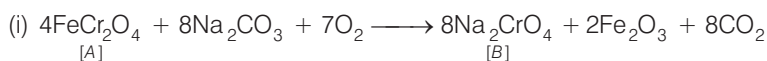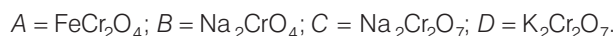
Q. 65 When a chromite ore (A) is fused with sodium carbonate in free excess of air and the product is dissolved in water, a yellow solution of compound (B) is obtained. After treatment of this yellow solution with sulphuric acid, compound (C) can be crystallised from the solution. When compound (C) is treated with KCl, orange crystals of compound (D) crystallise out. Identify A to D and also explain the reactions.

Ans. $K_2Cr_2O_7$ is an orange compound. It is formed when $Na_2Cr_2O_7$ reacts with KCl. In acidic medium, yellow coloured CrO_4^{2-} (chromate ion) changes into dichromate.

The given process is the preparation method of potassium dichromate from chromite ore.

$$A = FeCr_2O_4; \ B = Na_2CrO_4; \ C = Na_2Cr_2O_7; \ D = K_2Cr_2O_7.$$

(i) $\underset{[A]}{4FeCr_2O_4} + 8Na_2CO_3 + 7O_2 \longrightarrow \underset{[B]}{8Na_2CrO_4} + 2Fe_2O_3 + 8CO_2$

(ii) $2Na_2CrO_4 + 2H^+ \longrightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$

(iii) $\underset{[C]}{Na_2Cr_2O_7} + 2KCl \longrightarrow \underset{[D]}{K_2Cr_2O_7} + 2NaCl$
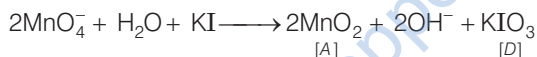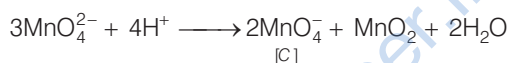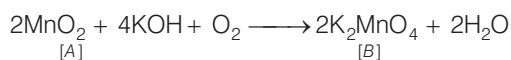
Q. 66 When an oxide of manganese (A) is fused with KOH in the presence of an oxidising agent and dissolved in water, it gives a dark green solution of compound (B). Compound (B) disproportionates in neutral or acidic solution to give purple compound (C). An alkaline solution of compound (C) oxidises potassium iodide solution to a compound (D) and compound (A) is also formed. Identify compounds A to D and also explain the reactions involved.

> 💡 **Thinking Process**
> *This problem based on the concept of preparation and properties of potassium permanganate.*

Ans. It is the method of preparation of potassium permanganate (purple).

Thus, $(A) = MnO_2$ $(B) = K_2MnO_4$
$(C) = KMnO_4$ $(D) = KIO_3$

$$\underset{[A]}{2MnO_2} + 4KOH + O_2 \longrightarrow \underset{[B]}{2K_2MnO_4} + 2H_2O$$

$$3MnO_4^{2-} + 4H^+ \longrightarrow \underset{[C]}{2MnO_4^-} + MnO_2 + 2H_2O$$

$$2MnO_4^- + H_2O + KI \longrightarrow \underset{[A]}{2MnO_2} + 2OH^- + \underset{[D]}{KIO_3}$$

Q. 67 On the basis of lanthanoid contraction, explain the following:
   (i) Nature of bonding in La_2O_3 and Lu_2O_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. (i) As the size decreases covalent character increases. Therefore, La_2O_3 is more ionic and Lu_2O_3 is more covalent.
  (ii) As the size decreases from La to Lu, stability of oxo salts 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.

Q. 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 $M(CO)_5$
       (ii) MO_3F

Ans. **(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 which is very difficult.

(ii) Zinc, because of electronic configuration of $Zn = 3d^{10}4s^2$ and $Zn^{2+} = 3d^{10}$ which is fully filled and hence is very stable. Removal of third electron requires very high energy.

(iii) Zinc, because of it has completely filled $3d$ subshell and no unpaired electron is available for metallic bonding.

(b) **(i)** Carbonyl $M(CO)_5$ is $Fe(CO)_5$

According to EAN rule, the effective number of a metal in a metal carbonyl is equal to the atomic number of nearest inert gas EAN is calculated as

$$EAN = \text{number of electrons in metal} + 2 \times (CO)$$
$$= \text{atomic number of nearest inert gas}$$

In $M(CO)_5 = x + 2 \times (5) = 36$ (Kr is the nearest inert gas)

$$x = 26 \text{ (atomic number of metal)}$$

So, the metal is Fe(iron).

(ii) MO_3F is MnO_3F.

In MO_3F

Let us assume that oxidation state of M is x

$$x + 3 \times (-2) + (-1) = 0$$

or, $x = +7$ *i.e.*, M is in $+7$ oxidation state of $+7$. Hence, the given compound is MnO_3F.

Q. 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.
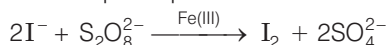
Ans. When small atoms like H, C and N get trapped inside the crystal lattice of transition metals.

(a) Such compounds are called interstitial compounds.

(b) Their characteristic properties are;

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

(ii) They are very hard.

(iii) They retain metallic conductivity.

(iv) They are chemically inert.

Q. 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)** Reaction between iodide and persulphate ions is

$$2I^- + S_2O_8^{2-} \xrightarrow{\text{Fe(III)}} I_2 + 2SO_4^{2-}$$

Role of Fe(III) ions $\qquad 2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$

$$2Fe^{2+} + S_2O_8^{2-} \longrightarrow 2Fe^{3+} + 2SO_4^{2-}$$

(b) (i) Vanadium (V) oxide used in contact process for oxidation of SO_2 to SO_3.

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

(iii) MnO_2 in preparation of oxygen from $KClO_3$.

Q. 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. H_2SO_4 and NaCl, chlorine gas is liberated and a compound (D) of manganese alongwith other products is formed. Identify compounds A to D and also explain the reactions involved.

💡 Thinking Process

This problem is based on preparation and properties of $KMnO_4$, K_2MnO_4 and MnO_2.

Ans. Since, compound (C) on treating with conc. H_2SO_4 and NaCl gives Cl_2 gas, so it is manganese dioxide (MnO_2). It is obtained alongwith MnO_4^{2-} when $KMnO_4$ (violet) is heated.

Thus, $(A) = KMnO_4$ $(B) = K_2MnO_4$

$(C) = MnO_2$ $(D) = MnCl_2$

$$\underset{[A]}{KMnO_4} \xrightarrow{\Delta} \underset{[B]}{K_2MnO_4} + \underset{[C]}{MnO_2} + O_2$$

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$

$$MnO_2 + 4NaCl + 4H_2SO_4 \longrightarrow \underset{[D]}{MnCl_2} + 4NaHSO_4 + 2H_2O + Cl_2$$