Question Bank on d and f block elements

Question 1- Explain:

(i) Generally, there is an increase in the density of elements from titanium (Z = 22) to copper (Z = 29) in the first series of transition elements.

(ii) Transition elements and their compounds are generally found to be good catalysts in chemical reactions. Also, they generally form coloured compounds.
(iii) Metal-metal bonding is more frequent for the 4d and the 5d series of transition metals than that for the 3d series.

Answer: (i) From titanium (Z = 22) to copper (Z = 29) in the first series of transition elements, the atomic size of elements decreases and mass increases. Therefore, there is an increase in the density of these elements.
(ii) Transition elements and their compounds are generally found to be good catalysts in chemical reactions because of the presence of unpaired electrons in their incomplete d^- orbitals and variable oxidation states. Transition elements generally form coloured compounds as they undergo d-d transition by absorption of energy from visible regions and then the emitted light shows complementary colours.
(iii) It is because they have their electrons of the outermost shell at a greater distance from the nucleus, in comparison to atoms of 3d transition metals.

Question 2- Account for the following:
(i) Copper (I) ion is not known in aqueous solution.
(ii) Actinoids exhibit a greater range of oxidation states than lanthanoids.
(iii) Manganese exhibits the highest oxidation state of +7 among the 3d series of transition elements.
(iv) The enthalpies of atomization of transition metals are quite high.
Answer: i) $Cu^{2+}_{(aq)}$ is much more stable than $Cu^{+}_{(aq)}$ because second ionization enthalpy of copper is large but Δ_{hyd} (hydration enthalpy) for $Cu^{2+}_{(aq)}$ is much more negative than that for $Cu^{2+}_{(aq)}$ and hence it more than compensates for the second ionization enthalpy of copper. Therefore, many copper (I) compounds undergo disproportionation as follows :
$2Cu+ \rightarrow Cu^{2++} Cu$
(ii) Actinoids exhibit a greater range of oxidation states than lanthanides as there is a very small energy gap between 5f, 6d and 7s subshells. Therefore, all the electrons can take part in bonding and shows variable oxidation states.
(iii) All the oxidation states are exhibited from +2 to +7 by Mn and no other element of this series shows this highest state of oxidation.

(iv) The enthalpies of atomization of transition metals are quite high due to a large number of unpaired electrons in their atoms. They have stronger interatomic interaction.

Question 4- (a) Which metal in the first transition series (3d series) exhibits +1 oxidation state most frequency and why?
(b) Which of the following cations are coloured in aqueous solutions and why?
SC^{3+}, V^{3+}, Ti_4^+, Mn^{2+}.
(At. nos. Sc = 21, V = 23, Ti = 22, Mn = 25)
Answer: (a) Copper exhibits + 1 oxidation state more frequently because of its electronic configuration $3d_{104}s_1$. It can easily lose $4s_1$ electrons to give a stable $3d_{10}$ configuration.
(b) $SC^{3+} = 4S_0\ 3d^{3+}$ = no unpaired electron
$V^{3+} = 3d_2\ 4s_0$ = 2 unpaired electron
$Ti_4^+ = 3d_0\ 4s_0$ = no unpaired electron
$Mn^{2+} = 3d_5\ 4s_0$ = 5 unpaired electron
Thus V^{3+} and Mn^{2+} are coloured in their aqueous solution due to the presence of unpaired electrons.
Question 5- What is Lanthanoid contraction? State its consequences.
Answer: The overall decrease in atomic and ionic radii with an increasing atomic number is known as lanthanoid contraction. From La^{+3} to Lu^{+3} in lanthanoid series, the size of ion decreases and this decrease is known as lanthanoid contraction. It arises due to imperfect shielding of one 4f electron by another present in the same subshell.
Consequences of lanthanoid contraction are :
(i) Similarity: Due to lanthanoid contraction, the size of elements which follow (Hf – Hg) is almost similar to the size of the elements of previous row (Zr – Cd) and are difficult to separate.
(ii) Basicity difference: Due to lanthanoid contraction, the size decreases from La^{+3} to Lu^{+3}. Thus, the covalent character increases. Hence, the basic character of hydroxides also decreases. Thus, $La(OH)_3$ is most basic while $Lu(OH)_3$ is the least basic.
Question 6- Give reasons:
(i) The highest oxidation state of a transition metal is usually exhibited in its oxide.
(ii) Co^{2+} is easily oxidised in the presence of a strong ligand.
(iii) Actinoids show a wide range of oxidation states.
(iv) The silver atom has completely filled d-orbitals ($4d_{10}$) in its ground state, yet it is regarded as a transition element.
(v) E° value for Mn^{3+}/Mn^{2+} couple is much more positive than Cr^{3+}/Cr^{2+}.
Answer: (i) The highest oxidation state of a transition metal is usually exhibited in its oxide because of high electronegativity, smaller size and lower ionization energy.
(ii) Co^{2+} is easily oxidised in the presence of a strong ligand as it has higher crystal field energy. This energy pairs the electrons to give inner orbital complexes (d_2sp_3).

(iii) Actinoids show a wide range of oxidation states as they have comparable energies of 5f, 6d and 7s orbitals.
(iv) The silver atom has completely filled d-orbitals ($4d_{10}$) in its ground state, yet it is regarded as a transition element as it has incomplete d-orbital ($4d_9$) in its +2 oxidation state.
(v) The large positive E° value for Mn^{3+}/Mn^{2+} indicates that Mn^{2+} is much more stable than Mn^{3+} due to stable half-filled configuration ($3d^5$). Therefore, the 3rd ionisation energy of Mn will be very high and Mn^{3+} is unstable and can be easily reduced to Mn^{2+}. E° value for Cr^{3+} / Cr^{2+} is positive but small. It means that Cr^{3+} can also be reduced to Cr^{2+} but less easily.

Why is zinc not regarded as a transition element?
Answer:
It is because neither Zn nor Zn^{+2}

ions have incompletely filled d-orbitals.

Question 2:
Copper atom has completely filled d-orbitals in its ground state but it is a transition element. Why?
Answer:
It is because Cu^{+2}

has $3d_9$, incompletely filled d-orbitals, therefore, it is a transition metal.

Question 3:
Zn^{+2} salts are white while Cu^{+2} salts are coloured. Why?
Answer:
Zn^{+2} salts are white because it does not have unpaired electron, whereas Cu^{+2} salts are coloured because it has unpaired electron and undergoes d-d transition by absorbing light from visible region and radiate blue colour.

Short Answer Type Questions [I] [2 Marks]

Question 4:
Why do transition elements show variable oxidation states? How is the variability in oxidation states of d-block different from that of the p-block elements?
Answer:
It is due to similar energy of (n – 1)d and ns orbitals, electrons from both can be lost. In p-block, lower oxidation state is more stable due to inert pair effect, whereas in ehblock elements higher oxidation states are more stable. In d-block, oxidation states differ by one, whereas in p-block, it differs by two.

Question 5:
(i) Why do actinoids show wide range of oxidation states?

(ii) Why is actinoid contraction greater than lanthanoid contraction?

Answer:

(i) It is because 5f, 6d and 7s have comparable energy.

(ii) 5f orbitals have poor shielding effect than 4f orbitals, therefore, effective nuclear charge is more in actinoids than lanthanoids.

Question 6:

What are the transition elements? Write two characteristics of the transition elements.

Answer:

Those elements which either themselves or their ions have incompletely filled

Characteristics:

(i) They show variable oxidation state.

(ii) They form coloured ions.

Question 7:

Write one similarity and one difference between the chemistry of lanthanoids and that of actinoids.

Answer:

Similarity:

Lanthanoids show lanthanoid contraction like actinoids contraction.

Dissimilarity:

Lanthanoids show mostly +3 oxidation state. Few show +2 and +4, whereas Actinoids show +3, +4, +5, +6 and +7 oxidation states.

Question 8:

Why dp transition elements show variable oxidation states? In 3d series (Sc to Zn), which element shows the maximum number of oxidation states and why?

Answer:

Transition elements show variable oxidation states because electrons from both s and d orbitals take part in bond formation. In 3d series, 'Mn' shows maximum number of oxidation states because it has maximum number of electrons in s as well as in d orbitals which can take part in bond formation.

Short Answer Type Questions [II] [3 Marks]

Question 9:

(i) E° value for the Mn^{+3}/Mn^{+2} couple is positive (+1.5 V) whereas that of Cr^{+3}/Cr^{+2} is negative (-0.4 V). Why? '

(ii) Transition metals form coloured compounds. Why?

(iii) Complete the following equation:

Answer:

(i) Mn^{+2} is more stable than Mn^{+3} due to half filled d-orbitals ($3d^5$), whereas Cr^{+3} is more stable than Cr^{+2} due to half filled orbitals.

(ii) It is due to presence of unpaired electrons which undergo d-d transition by absorbing light from visible region and radiate complementary colour.

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

Question 10:
(i) MnO is basic whereas Mn_2O_7 is acidic in nature. Why?
(ii) Transition metals form alloys. Why?
(iii) Complete the following equation:
$2MnO_4^- + 4KOH + O_2 \longrightarrow$
Answer:
(i) In MnO, Mn has +2 oxidation state, whereas in Mn_2O_7, Mn has + 7 oxidation state. Higher the oxidation state, more will be acidic nature, e.g. Mn_2O_7. Lower the oxidation state, more will be basic nature, e.g. MnO.
(ii) It is due to similar atomic size, they can replace one another in metallic bond.
(iii) $2MnO_4^- + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$

Question 11:
(a) How would you account for the following:
(i) Actinoid contraction is greater than lanthanoid contraction.
(ii) Transition metals form coloured compounds.
(b) Complete the following equation:
$2\ MnO_4^- + 6H^+ + 5NO_2^- \longrightarrow$
Answer:
(a) (i) Refer Ans. to Q.5 (ii).
(ii) Refer Ans. to Q.9 (ii).
(b) $2\ MnO_4^- + 6H^+ + 5NO_2^- \longrightarrow 2Mn^{2+} + 3H_2O + 5NO_3$

Question 12:
(a) Account for the following:
(i) Cu^+ is unstable in an aqueous solution.
(ii) Transition metals form complex compounds
(b) Complete the following equation:
$Cr_2O_2^- + 8H^+ + 3NO_2^- \longrightarrow$
Answer:
(a) (i) It is because hydration energy of Cu^{2+} overcomes 2nd ionisation enthalpy, that is why Cu^+ changes to Cu^{2+} and Cu.
$2Cu^+ \longrightarrow Cu^{2+} + Cu$
(ii) It is due to their small size, high charge and availability of vacant d-orbitals

(b) $6e^- + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$ ...(i)

$[H_2O + NO_2^- \longrightarrow NO_3^- + 2H^+ + 2e^-] \times 3$ ...(ii)

$8H^+ + Cr_2O_7^{2-} + 3NO_2^- \longrightarrow 2Cr^{3+} + 4H_2O + 3NO_3^-$

[Adding (i) and (ii)]

Question 13:
(a) How would you account for the following:
(i) Highest fluoride of Mn is MnF_4 whereas the highest oxide is Mn_2O_2
(ii) Transition metals and their compounds show catalytic properties.
(b) Complete the following equation:
$3MnO_4^- + 4H^+ \longrightarrow$
Answer:

(a) (i) Oxygen can form double bond, therefore, it can form Mn_{207}, whereas 'F' cannot form double bonds, so, it can form MnF_4.
(ii) Transition metals show variable oxidation states, therefore, they and their compounds act as catalyst.
(b) $3MnO_4^- + 4H^+ \longrightarrow MnO_2 + 2MnO_4^- + 2H_2O$

Long Answer Type Questions [5 Marks]

Question 14:
(a) A blackish brown solid 'A' when forced with alkali metal hydroxide in presence of air, produces a dark green coloured compound 'B', which on electrolytic oxidation in alkaline medium gives a dark purple coloured compound 'C'. Identify A, B, C and write the reactions involved. What happens when an acid solution of green coloured compound (B) is allowed to stand for some time.
(b) (i) Calculate the spin magnetic moment of M^{2+}(aq) ion. Atomic number (Z) = 27.
(ii) Chromium is typical hard metal while mercury in liquid, explain.

Answer:

(a) $\underset{\text{'A' (blackish brown solid)}}{2MnO_2} + 4KOH + O_2 \longrightarrow \underset{\text{'B' (green)}}{K_2MnO_4} + 2H_2O$

$\underset{\text{'B'}}{2K_2MnO_4} + H_2O + (O) \xrightarrow{\text{Electrolysis}} \underset{\substack{\text{(Purple)}\\ \text{'C'}}}{2KMnO_4} + 2KOH$

or $\underset{\substack{\text{Green}\\ \text{'B'}}}{3MnO_4^{2-}} + 4H^+ \longrightarrow \underset{\substack{\text{Purple}\\ \text{'C'}}}{2MnO_4^-} + MnO_2 + 2H_2O$

(b) (i) M(27) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^7$

M^{2+}(aq): [Ar] $4s^0\ 3d^7$ | ↑↓ | ↑↓ | ↑ | ↑ | ↑ |

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

$\mu = \sqrt{3 \times 5} = \sqrt{15} = 3.87$ BM.

(ii) Cr is typically hard metal due to presence of large number of unpaired electrons, metal-metal interaction is strong whereas mercury does not have unpaired electrons and has large size, therefore, forms weak metallic bond.

Question 15:
Account for the following:
(a) (i) EU^{2+} is strong reducing agent
(ii) Transition metals form coloured compounds
(iii) Zn has lowest enthalpy of atomisation.
(b) Complete the following equations:
(i) $KMn0_4$(heat) ——-> (ii) $Cr_20_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow$

Answer:
(a) (i) It is because Eu^{3+} is more stable.
(ii) Refer Ans. to Q.9 (ii).
(iii) It is due to weak metallic bonds due to completely filled d-orbitals.

(b) (i) $2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$
(ii) $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$

Question 16:
Account for the following:
(a) (i) Transition elements form interstitial compounds.
(ii) $Mn^{s+}(3d^4)$ is strongly oxidising, whereas $Cr^{2+}(3d^4)$ is strongly reducing.
(iii) Transition metals have high melting points.
(b) What is misch metal? Write its one use.
Answer:
(a) (i) Small size atoms B, C, H can occupy voids present in transition metals.
(ii) Mn^{3+} gains one electron to form Mn^{2+} since 3dD is more stable, whereas Cr^{2+} loses one electron for $Cr^{3+}(i_3p$ which is more stable, so, it acts as reducing agent.
(iii) It is due to involvement of unpaired ((-electrons to form strong metallic bond.
(b) It contains 95% lanthanoid metal, 5% iron and traces of S, C, Ca and Al.
Use: Its magnesium based alloy is used to produce bullets, shells, flints.

Very Short Answer Type Questions [1 Mark]

Question 17:
Actinoid contraction is greater from element to element than lanthanoid contraction. Why?
Answer:
Refer Ans. to Q. 5 (ii).

Short Answer Type Questions [I] [2 Marks]

Question 18:
Complete the following equations:
(i) $2MnO_4^- + 5S^{2-} + 16H^+ \longrightarrow$
(ii) $Cr_2O_7^{2-} + 2\ OH^- \longrightarrow$
Answer:
(i) $2MnO_4^- + 5S^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 5S + 8H_2O$
(ii) $Cr_2O_7^{2-} + 2\ OH^- \longrightarrow 2CrO_4^{2-} + H_2O$

Question 19:
Complete the following equations:
(i) $2MnO_4^- + 5\ NO_2^- + 6H^+ \longrightarrow$
(ii) $Cr_2O_7^{2-} + 14\ H^+ + 6e^- \longrightarrow$
Answer:
(i) $2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$
(ii) $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

Question 20:

Complete the following equations:

(i) $2MnO_4^- + 5SO_3^{2-} + 6H^+ \longrightarrow$

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

Answer:

(i) $2MnO_4^- + 5SO_3^{2-} + 6H^+ \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$

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

Question 21:

Describe the general trends in the following properties of first series 3d of transition elements:

(i) number of oxidation states exhibited (ii) formation of oxometal ions.

Answer:

(i) The tendency to show number of oxidation states increases from Sc to Mn and then decreases because number of unpaired electrons increases till Mn, then decreases.

(ii) Tendency to form oxometal ions increases from Sc to Cr and then decreases due to increase in unpaired electrons and ability to form multiple bonds with oxygen.

Short Answer Type Questions [II] [3 Marks]

Question 22:

(a) What are the different oxidation states exhibited by the lanthanoids?

(b) Write two characteristics of the transition elements.

(c) Which of the 3d-block elements may not be regarded as the transition elements and why?

Answer:

(a) Lanthanoids, mostly show +3 oxidation state but some of them show +2 and +4 oxidation states also due to the stability of electronic configuration ($4f^\circ$, $4f_7$ and $4f_{14}$), e.g. Eu shows +2, whereas Ce shows +4 oxidation state.

(b) (i) They show variable oxidation states.

(ii) They form coloured compounds.

(c) Zn may not be regarded as transition metal because neither 'Zn' nor Zn^{2+} ions have incompletely filled d-orbital.

Question 23:

Assign suitable reasons for the following:

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

(b) In the 3d series from Sc (Z = 21) to Zn (Z = 30), the enthalpy of atomization of Zn is the lowest.

(c) Sc^{3+} is colourless in aqueous solution, whereas Ti^{3+} is coloured.

Answer:

(a) Mn^{2+} has $3d_5$ (stable electronic configuration), therefore, it does not get oxidised to Mn^{3+}, whereas Fe^{2+} has $3d_6$ which readily changes to Fe^{3+} ($3d_5$), which has stable electronic configuration.

(b) Zinc does not have unpaired electrons and larger in size, therefore, it has weak

metallic bonds. That is why it has least enthalpy of atomisation.
(c) Sc^{3+} is colourless as it does not have unpaired electron and cannot undergo d-d transition, whereas Ti^{3+} is coloured due to presence of unpaired electrons and undergoes d-d transition by absorbing light from visible region and radiate complementary colour.

Long Answer Type Questions [5 Marks]

Question 24:
(a) How do you prepare:
(i)K_2Mn_{04} from Mn_{02}?
(ii) Na_2Cr_{207} from Na_2Cr_{04}?
(b) Account for the following:
(i) Mn^{2+} is more stable than Fe^{2+} towards oxidation to +3 state.
(ii) The enthalpy of atomization is lowest for Zn in 3 d series of the transition elements.
(iii) Actinoid elements show wide range of oxidation states.
Answer:
(a) (i) $2Mn_{02} + 4KOH + 0_2 \longrightarrow 2K_2Mn_{04} + 2H_{20}$
(ii) $2Na_2Cr_{04} + H_2S_{04}(conc.) \longrightarrow Na_2Cr_{207} + Na_2S_{04} + H_{20}$
(b) (i) Refer Ans. to Q.23 (a).
(ii) Refer Ans. to Q.23 (b).
(iii) Refer Ans. to 0.5 (i).

Question 25:
(i) Name the element of 3d transition series which shows maximum number of oxidation states. Why does it show so?
(ii) Which transition metal of 3d series has positive $E°(M^{2+}/M)$ value and why?
(iii) Out of Cr^{3+} and Mn^{3+}, which is a stronger oxidizing agent and why?
(iv) Name a member of the lanthanoid series which is well known to exhibit + 2 oxidation state.
(v) Complete the following equation:
$MnO_4^- + 8H^+ + 5e^- \longrightarrow$
Answer:
(i) Mn because it has five unpaired electrons and 2 electrons in s-orbital which can take part in bond formation, therefore, it shows maximum number of oxidation states.
(ii) $E°CU_9{}^+/CU$ has +ve value due to high ionisation enthalpies and sublimation energies and lower hydration energy.
(iii) Mn^{3+} is stronger oxidising agent because it can gain electrons to become Mn^{2+} which is more stable due to $3d_5$ (half filled d-orbitals), whereas Cr^{3+} is stable due to f_3 (half filled orbitals).
(iv) Europium shows +2 oxidation state. Ytterbium (Yb) also shows +2 oxidation state.
(v) $Mn_{04} + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_{20}$.

Question 26:
(a) Complete the following equations:
(i) $Cr_{207}{}^{2-} + 20H^- \longrightarrow$
(ii) $Mn_{04}{}^- + 4H^+ + 3e^- \longrightarrow$ ‘

(b) Account for the following:
(i) Zn is not considered as a transition element.
(ii) Transition metals form a large number of complexes.
(iii) The E° value for the Mn^{3+}/Mn_2 + couple is much more positive than that for Cr^{3+}/Cr^{2+} couple.

Answer:

(a) (i) $Cr_{207}^{2-} + 20H^- \longrightarrow 2CrO_4^- + H_2O$
(ii) $MnO^- + 4H^+ + 3e^- \longrightarrow Mn_{02}{}^+ 2H_{20}$
(b) (i) Refer Ans. to Q.l.
(ii) It is due to small size, higher charge and presence of vacant d-orbitals of suitable energy.
(iii) Refer Ans. to Q.9 (i).

Question 27:

(i) With reference to structural variability and chemical reactivity, write the Differen ces between lanthanoids and actinoids.
(ii) Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state.
(iii) Complete the following equation:
$Mn_{04}^- + 8H^+ + 5e^- \longrightarrow$
(iv) Out of Mn^{3+} and Cr^{3+}, which is more paramagnetic and why?
(Atomic nos.: Mn = 25, Cr = 24)

Answer:

(i)

Lanthanoids	Actinoids
(i) They show +3 oxidation state mostly along with +2 and +4 by few elements. (ii) These are less reactive due to high I.E.	(i) They show +3, +4, +5, +6 and +7 oxidation states. (ii) They are more reactive due to low I.E. (Ionisation enthalpy)

(ii) Ce shows +4 oxidation state.
(iii) $MnO^- + 8H_4 + 5e^- \longrightarrow Mn^{2+} + 4H_{20}$
(iv) Mn^{3+} ($3d_4$) has 4.unpaired electrons, therefore, it is more paramagnetic than Cr^{3+}) which has three unpaired electrons.

Short Answer Type Questions [I] [2 Marks]

Question 28:

(a) Which metal in the first transition series (3d series) exhibits +1 oxidation state most frequently and why?
(b) Which of the following cations are coloured in aqueous solutions and why?
Sc^{3+}, V^{3+}, Ti_4^+, Mn^{2+}
(At. Nos. Sc = 21, V = 23, Ti = 22, Mn = 25)

Answer:

(a) Copper exhibits +1 oxidation state frequently due to stable electronic configuration.
(b) V^{3+} and Mn^{2+} are coloured, due to the presence of unpaired electrons, they can

undergo d-d transitions. Others are colourless due to the absence of unpaired electrons and cannot undergo d-d transitions.

Short Answer Type Questions [II] [3 Marks]

Question 29:

How would you account for the following?
(i) Transition metals exhibit variable oxidation states.
(ii) Zr (Z = 40) and Hf (Z = 72) have almost identical radii.
(iii) Transition metals and their compounds act as catalyst.

Answer:

It is because electrons from (n – 1)d and ns take part in bond formation.
(ii) It is due to lanthanoid contraction which is due to poor shielding effect off-electrons, due to which effective nuclear charge increases, therefore, Zr and Hf have almost identical radii.
(iii) It is because they show variable oxidation states and form unstable intermediates which readily change into products.

Question 30:

Complete the following chemical equations:

(*i*) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow$

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

(*iii*) $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow$

Answer:

(*i*) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

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

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

Long Answer Type Questions [5 Marks]

Question 31:

(*a*) Give reasons for the following:

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

(*ii*) $E^\circ_{M^{2+}/M}$ **values are not regular for first row transition metals (3*d* series).**

(*iii*) Although 'F' is more electronegative than 'O', the highest Mn fluoride is MnF_4, whereas the highest oxide is Mn_2O_7.

(*b*) Complete the following equations:

(*i*) $2CrO_4^{2-} + 2H^+ \longrightarrow$ **(*ii*)** $KMnO_4 \xrightarrow{\text{heat}}$ **[AI]**

Answer:

(a) (i) It is because Mn^{3+} can gain one electron to form Mn^{2+} which is stable due to half-filled *d*-orbitals ($3d^5$).

(ii) It is due to irregular variations of ionisation enthalpies ($\Delta_i H_1 + \Delta_i H_2$) and sublimation enthalpies in 3*d* transition series.

(iii) It is because oxygen can form multiple bonds with 'Mn', whereas 'F' cannot.

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

(ii) $2KMnO_4 \xrightarrow{\text{heat}} K_2MnO_4 + MnO_2 + O_2$

Question 32:

(a) Why do transition elements show variable oxidation states?

(i) Name the element showing maximum number of oxidation states among the first series of transition metals from Sc (Z = 21) to Zn (Z = 30).

(ii) Name the element which shows only +3 oxidation state.

(b) What is lanthanoid contraction? Name an important alloy which contains some of the lanthanoid metals.

Answer:

(a) Refer Ans. to Q.29 (i).

(i) 'Mn' shows maximum number of oxidation states; +2, +3, +4, +6, +7.

(ii) Sc shows only +3 oxidation state.

(b) The decrease in atomic and ionic size with increase in atomic number is called lanthanoid contraction. Misch metal is an important alloy which contains some of the lanthanoid metals.

Question 33:

Assign reasons for the following:

(i) In the series Sc (Z = 21) to Zn (Z = 30), the enthalpy of atomisation of Zn is the lowest.

(ii) Zr and Hf have almost identical radii.

(iii)Transition metals show variable oxidation states.

(iv) The value for copper is positive (+ 0.34 V).

(v) Cr^{2+} is a very good reducing agent.

Answer:

(i) It is due to weak metallic bond due to absence of unpaired electrons.

(ii) It is due to lanthanoid contraction.

(iii) Refer Ans. to Q.29 (i).

(iv) It is because of high ionisation enthalpy of Cu which is not compensated by hydration energy.

(v) It is because Cr^{2+} loses an electron to form Cr^{3+} which is more stable as i_2g orbitals are half-filled, i.e. more stable.

Question 34:

Describe the preparation of KMn_{04} from pyrolusite ore (MnO_4). How does the acidified permanganate solution react with the following:

(i) Fe^{2+} ions

(ii) Oxalic acid ($C_2H_20_4$)

Write the ionic equations for the reactions involved.

Answer:

Potassium permanganate is prepared by fusion of Mn_{02} with alkali metal hydroxide (KOH) in presence of 0_2 or oxidising agent like KNO_3. It produces dark green K_2Mn_{04} which undergoes oxidation as well as reduction in neutral or acidic solution to give permanganate.

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

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

Alternative Method:

$$MnO_2 \xrightarrow[\text{in the presence of } O_2 \text{ or } KNO_3]{\text{fused with KOH}} \underset{\text{(manganate ion)}}{MnO_4^{2-}}$$

$$\underset{\text{(Green)}}{MnO_4^{2-}} \xrightarrow{\text{electrolysis}} \underset{\text{(Purple)}}{MnO_4^-} + e^-$$

(*i*) Fe^{2+} ion gets oxidised to Fe^{3+} ion when it reacts with acidified $KMnO_4$.

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

(*ii*) Oxalic acid will get oxidised to CO_2 and H_2O by reacting with acidified $KMnO_4$.

$$5\begin{vmatrix} COOH \\ COOH \end{vmatrix} + 2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

or

$$5\begin{vmatrix} COO^- \\ COO^- \end{vmatrix} + 2MnO_4^- + 16H^+ \longrightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

Short Answer Type Questions [I] [2 Marks]

Question 35:

Complete the following chemical equations:

(*i*) $Cr_2O_7^{2-} + H^+ + I^- \longrightarrow$

(*ii*) $MnO_4^- + NO_2^- + H^+ \longrightarrow$

Answer:

(i) $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ ...(i)

$[2I^- \longrightarrow I_2 + 2e^-] \times 3$ ...(ii)

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

(ii) $[5e^- + 8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$ ...(i)$] \times 2$

$[H_2O + NO_2^- \longrightarrow NO_3^- + 2H^+ + 2e^-] \times 5$ ...(ii)

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

Adding (i) and (ii)

Short Answer Type Questions [II] [3 Marks]

Question 36:

How would you account for the following?
(i) Many of the transition elements are known to form interstitial compounds,
(ii) The metallic radii of the third (5d) series of transition metals are virtually the same as those of the corresponding group members of the second (4d) series.
(iii) Lanthanoids form primarily +3 ions, while the actinoids usually have higher oxidation states in their compounds, +4 or even +6 being typical.

Answer:

(i) Small size atoms, such as B, C and H can occupy voids present in transition metals.
(ii) It is due to lanthanoid contraction.
(iii) It is because lanthanoid lose 2 electrons from 6s orbitals and one from 5d – or 4/ orbitals and are stable in +3 oxidation state. Actinoids can lose electrons from 7s, 6d and 5/ orbitals easily due to comparable energies and show higher oxidation states +4 and +6.

Question 37:

How would you account for the following?
(i) With the same d-orbital configuration (d_4) Cr^{2+} is a reducing agent while Mn^{3+} is an oxidising agent. .
(ii) The actinoids exhibit a large number of oxidation states than the corresponding members in the lanthanoid series.
(iii) Most of the transition metal ions exhibit characteristic colours in aqueous solutions

Answer:

(i) Refer Ans. to Q.16 (a) (ii).
(ii) It is because 5f, 6d and Is have comparable energy.
(iii) Refer Ans. to Q.9 (ii).

Question 38:
Explain the following observations giving an appropriate reason for each:
(i) The enthalpies of atomization of transition elements are quite high.
(ii) There occurs much more frequent metal-metal bonding in compounds of heavy transition metals (i.e. 3rd series).
(iii) Mn^{2+} is much more resistant than Fe^{2+} towards oxidation.
Answer:
(i) It is because of strong metallic bonds due to large number of unpaired electrons in d-orbitals.
(ii) It is due to presence of unpaired electrons which participate in metal-metal bonding in 5d series (3rd series).
(iii) Refer Ans. to Q.23 (a).

Question 39:
How would you account for the following:
(i) Among lanthanoids, Ln(III) compounds are predominant. However, occasionally in solutions or in solid compounds, +2 and +4 ions are also obtained.
(ii) The $E°M^{2+}/M$ for copper is positive (0.34V). Copper is the only metal in the first series of transition elements showing this behaviour.
(iii) The metallic radii of the third (5d) series of transition metals are nearly the same as those of the corresponding members of the second series.
Answer:
(i) It is because after losing 2 electrons and 4 electrons, they acquire stable configuration, i.e. $f°, f_7, f_{14}$.
(ii) $E°CU^{2+}/CU$ ·ias +ve value due to high ionisation enthalpies and sublimation energies and lower hydration energy.
(iii) It is due to lanthanoid contraction.

Question 40:
Explain the following observations:
(i) Many of the transition elements are known to form interstitial compounds.
(ii) There is a general increase in density from titanium (Z = 22) to copper (Z = 29).
(iii) The members of the actinoid series exhibit a larger number of oxidation states than the corresponding members of the lanthanoid series.
Answer:
(i) Refer Ans. to Q.16 (a) (i).
(ii) It is due to increase in atomic mass and decrease in atomic size, therefore, density increases from Ti(22) to Cu(29).
(iii) It is because 5f, 6d and 7s have comparable energy.

Question 41:
Explain each of the following observations:
(i) With the same d-orbital configuration (d_4), Cr^{2+} is a reducing agent while Mn^{3+} is an oxidising agent.
(ii) Actinoids exhibit a much larger number of oxidation states than the lanthanoids.
(iii) There is hardly any increase in atomic size with increasing atomic numbers in a series of transition metals.
Answer:
(i) Refer Ans. to Q.16 (a) (ii).

(ii) It is due to 5f electrons which are more effectively shielded than 4f electrons therefore, outer electrons are less firmly held and available for bonding in actinoids and they show a wide range of oxidation states.
(iii) It is due to lanthanoid contraction, effective nuclear charge does not decrease, therefore, atomic size does not increase appreciably in the series of transition metals

Long Answer Type Questions [5 Marks]

Question 42:
(a) Complete and balance the following chemical equations:
(i) $Cr_2O_7^{2-} + I^- + H^+ \longrightarrow$
(ii) $MnO_4^- + SO^{2-} + H^+ \longrightarrow$
(b) Explain the following observations:
(i) Transition elements and their compounds are known to act as catalysts.
(ii) The higher oxidation states are usually exhibited by the members in the middle of a series of transition elements.
(iii) The metal-metal bonding is more frequently found with the second and third series of transition elements.

Answer:
(a) (i) Refer Ans. to Q.35 (i).

(ii) $[5e^- + 8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O \quad ...(i)] \times 2$

$[H_2O + SO_3^{2-} \longrightarrow SO_4^{2-} + 2H^+ + 2e^- \quad ...(ii)] \times 5$

$6H^+ + 2MnO_4^- + 5SO_3^{2-} \longrightarrow 5SO_4^{2-} + 3H_2O + 2Mn^{2+}$

Adding (i) and (ii)

(b) (i) Refer Ans. to Q.29 (iii).
(ii) It is due to large number of unpaired electrons in the middle of series of transition metals.
(iii) It is due to poor shield effect ofd, and f-orbitals, more unpaired electrons can take part in metal-metal bonds.

Question 43:
(a) Calculate the number of unpaired electrons in the following gaseous state ions: Mn^{2+}, Cr^{3+}, V^{3+} and Fe^{2+}
which one of these in the most stable in aqueous solutions?
(At. nos. V = 23, Cr = 24, Mn = 25, Fe = 26)
(b) Explain the following observations:
(i) The transition metal ions are usually coloured in aqueous solutions.
(ii) Cu(I) is not stable in an aqueous solution.
(iii) The highest oxidation state of a transition metal is exhibited in its oxide or fluoride.

Answer:

(a) $Mn^{2+}(25)$: [Ar] $4s^0\ 3d^5$ ↑ ↑ ↑ ↑ ↑ 5 unpaired electrons

$Cr^{3+}(24)$: [Ar] $4s^0\ 3d^3$ ↑ ↑ ↑ 3 unpaired electrons

$V^{3+}(23)$: [Ar] $4s^0\ 3d^2$ ↑ ↑ 2 unpaired electrons

$Fe^{2+}(26)$: [Ar] $4s^0\ 3d^6$ ↑↓ ↑ ↑ ↑ ↑ 4 unpaired electrons

(b) (i) Refer Ans. to Q.9 (ii).
(ii) It is because Cu^{2+} is more stable because hydration energy overcomes 2nd ionisation energy.
(iii) It is because oxygen and fluorine are strong oxidising agents, highly electronegative, small size and can provide energy for formation of transition metal ion in higher oxidation state.

Very Short Answer Type Questions [1 Mark]

Question 44:
What is meant by 'lanthanoid contraction'?
Answer:
The decrease in size with the increase in atomic number among lanthanoids is called lanthanoid contraction.

Short Answer Type Questions [I] [2 Mark]

Question 45:
Assign reasons for the following:
(i) Copper (I) ion is not known in aqueous solution.
(ii) Actinoids exhibit greater range of oxidation states than lanthanoids.
Answer:
(i) Refer Ans. to Q.43 (b) (ii).
(ii) Refer Ans. to Q.41 (ii).

Question 46:
Assign reasons for each of the following:
(i) Transition metals generally form coloured compounds.
(ii) Manganese exhibits the highest oxidation state of $^{+7}$ among the 3d series of transition elements
Answer:
(i) Refer Ans. to Q.9 (ii).
(ii) Mn has electronic configuration (Ar) $4s_2\ 3d_5$ and all the electrons in 's' as well as 'd' orbitals can take part in bond formation, therefore, it shows + 7 highest oxidation state.

Question 47:
How would you account for the following:
(i) Cr^{2+} is reducing in nature while with the same d-orbital configuration (d_4) Mn^{3+} is an oxidising agent.
(ii) In a transition series of metals, the metal which exhibits the greatest number of oxidation states occurs in the middle of the series.

Answer:
(i) It is because Cr^{2+} loses electron to become Cr^{3+} which is more stable due to half filled t_2g orbitals, whereas Mn^{3+} will gain electrons to become Mn^{2+} which is more stable due to half filled d-orbitals.
(ii) It is due to large number of unpaired electrons in d-orbitals in middle of the series.

Question 48:
Complete the following chemical equations:

(i) $MnO_4^-(aq) + S_2O_3^{2-}(aq) + H_2O(l) \longrightarrow$

(ii) $Cr_2O_7^{2-}(aq) + Fe^{2+}(aq) + H^+(aq) \longrightarrow$

Answer:

(i) $8MnO_4^-(aq) + 3S_2O_3^{2-}(aq) + H_2O(l) \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$

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

Question 49:
State reasons for the following:
(i) Cu (I) ion is not stable in an aqueous solution.
(ii) Unlike Cr^{3+}, Mn^{2+}, Fe^{3+} and the subsequent other M^{2+} ions of the 3d series of elements, the 4d and the 5d series metals generally do not form stable cationic species.
Answer:
(i) It is because Cu^{2+} is more stable because hydration energy overcomes 2nd ionisation energy.
(ii) It is because energy required to remove electron is more due to greater effective nuclear charge which is due to lanthanoid contraction.

Question 50:
Explain giving reasons:
(i) Transition metals and their compounds generally exhibit a paramagnetic behaviour.
(ii) The chemistry of actinoids is not so smooth as that of lanthanoids.
Answer:
(i) It is because of presence of unpaired electrons in d-orbitals of transition metal.
(ii) It is because all of them are radioactive and some of them have short half life, therefore, the chemistry of actinoids is not smooth.

Question 51:
Explain giving a suitable reason for each of the following:
(i) Transition metals and their compounds are generally found to be good catalysts.
(ii) Metal-metal bonding is more frequent for the 4d and the 5d series of transition metals than that for the 3d series.
Answer:
(i) It is because they show variable oxidation states and have vacant rf-orbitals forming unstable intermediates which readily change into products.
(ii) It is due to poor shielding effect of 4f orbitals, more unpaired electrons take part in metallic bond formation.

Short Answer Type Questions [II] [3 Marks]

Question 52:

Complete the following chemical equations:

(i) $MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow$

(ii) $KMnO_4 \xrightarrow{\text{heated}}$

(iii) $Cr_2O_7^{2-} + H_2S + H^+ \longrightarrow$

Answer:

(i) Refer Ans. to Q.30 (iii)

(ii) Refer Ans. to Q.15 (b) (i)

(iii) $[Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ ...(i)

$[H_2S \longrightarrow 2H^+ + S + 2e^-] \times 3$ ...(ii)

$Cr_2O_7^{2-} + 8H^+ + 3H_2S \longrightarrow 2Cr^{3+} + 7H_2O + 3S$

Adding (i) and (ii)

Long Answer Type Questions [5 Marks]

Question 53:

(a) Complete the following reactions in an aqueous medium:

(i) $Mn_{04}^- + C_{207}^{2-} + H^+$ ——->

(ii) $Cr_{20}^{2-} + H_2S + H^+$ ———->

(b) How would you account for the following:

(i) Metal-metal bonding is more extensive in the 4d and 5d series of transition elements than the 3d series.

(ii) Mn(III) undergoes disproportionation reaction easily.

(iii) Co (II) is easily oxidised in the presence of strong ligands

Answer:

(a) (i) Refer Ans. to Q.30 (iii)

(ii) Refer Ans. to Q.52 (iii)

(b) (i) Refer Ans. to Q.51 (ii)

(ii) It is unstable, therefore, undergoes disproportionation.

(iii) Strong ligands provide energy which overcomes 3rd ionisation enthalpy of Co(II) and it gets oxidised to Co^{3+} to form more stable complex.

Question 54:

(a) Complete the following chemical equations:

(i) $Fe^{3+} + I^-$ ——->

(ii) $CrO_4^- + H^+$ ——->

(b) Explain the following:

(i) Copper (I) ion is not stable in an aqueous solution.

(ii) With same (d_4) configuration Cr(II) is reducing, whereas Mn(III) is oxidising.

(iii) Transition metals in general act as good catalysts.

Answer:

(a) (i) $2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$

(ii) $\underset{\text{(yellow)}}{2CrO_4^{2-}} + H^+ \rightleftharpoons \underset{\text{(orange)}}{Cr_2O_7^{2-}} + H_2O$

(b) (i) Refer Ans. to Q.43 (b) (ii)
(ii) Refer Ans. to Q.47 (i)
(iii) Refer Ans. to Q.51 (i)

Short Answer Type Questions [I] [2 Marks]

Question 55:
Explain the following observations:
(i) Generally there is an increase in density of elements from titanium (Z = 22) to copper (Z = 29) in the first series of transition elements.
(ii) Transition elements and their compounds are generally found to be good catalysts in chemical reactions.
Answer:
(i) It is because atomic mass increases more than atomic volume, therefore, density increases from titanium (Z = 22) to copper (Z = 29).
(ii) It is because they show variable oxidation states and have vacant d-orbitals forming unstable intermediates which readily change into products.

Question 56:
Explain the following observations:
(i) Transition elements generally form coloured compounds.
(ii) Zinc is not regarded as a transition element
Answer:
(i) It is due to presence of unpaired electrons in (i-orbitals therefore, they undergo d-d transitions by absorbing light from visible region and radiate complementary colour.
(ii) It is because neither Zn nor Zn^{2+} ions have incompletely filled d-orbitals.

Question 57:
Describe the preparation of
(i) Potassium dichromate from sodium chromate and
(ii) KMn_{04} from K_2MnO_4
Answer:
(i) Sodium chromate gets oxidised to sodium dichromate with the help of concentrated H_2SO_4. On treatment with KCl, we get $K_2Cr_2O_7$.

$$2Na_2CrO_4 + \underset{\text{(Conc.)}}{H_2SO_4} \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

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

(ii) On electrolysis, K_2MnO_4 gets oxidised to $KMnO_4$.

$$MnO_4^{2-} \xrightarrow[\text{at anode}]{\text{electrolysis}} MnO_4^- + e^-$$

Question 58:
Give reasons for the following observations:

(i) Mn(II) ion shows maximum paramagnetic character amongst the bivalent ions of first transition series.
(ii) Scandium (At. no. 21) salts are white.

Answer:

(i) It is due to presence of five unpaired electrons.
(ii)Sc^{3+} does not have unpaired electrons, therefore, cannot undergo d-d transition by absorbing light from visible region. Therefore, its salts are white.

Short Answer Type Questions [II] [3 Marks]

Question 59:

How would you account for the following?
(i) The atomic radii of the metals of the third (5d) series of transition elements are virtually the same as those of the corresponding members of the second (4d) series.
(ii) The E° value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+} couple or Fe^{3+}/Fe^{2+} couple.
(iii) The highest oxidation state of a metal is exhibited in its oxide or fluoride.

Answer:

(i) It is due to lanthanoid contraction which is due to poor shielding effect of f-electrons.
(ii) It is because Mn^{2+} is more stable than Mn^{3+} due to stable half filled 3d° configuration:
(iii) It is because oxygen and fluorine are strong oxidising agents, highly electronegative, small size and can provide energy for formation of transition metal ion in higher oxidation state

Question 60:

Explain the following:
(i) The transition elements have great tendency for complex formation,
(ii) There is a gradual decrease in the atomic sizes of transition elements in tt series with increasing atomic numbers.
(iii) Lanthanum and Lutetium do not show colouration in solutions.
(At. No. : La = 57, Lu = 71)

Answer:

(i) It is due to presence of vacant d-orbitals of suitable energy, smaller size of cations and higher charge.
(ii) It is due to increase in effective nuclear charge gradually because unpaired electrons increase in the beginning and then decrease. There is repulsion between paired electrons.
(iii) It is due to absence of unpaired electrons, they do not absorb light from visible region and do not radiate colour.

Question 61:

Explain the following observations:
(i) The enthalpies of atomisation of transition metals are quite high.
(ii) There is a close similarity in physical and chemical properties of the 4d and 5d series of the transition elements, much more than expected on the basis of usual family relationship.
(iii) The members in the actinoid series exhibit larger number of oxidation states than

the corresponding members in the lanthanoid series.

Answer:

(i) Refer Ans. to Q.38 (i).

(ii) It is due to lanthanoid contraction, the ionic size of 4d and 5d transition series in similar.

(iii) Refer Ans. to Q.41 (ii).

Long Answer Type Questions [5 Marks]

Question 62:

(a) Complete the following chemical equations:

(i) $MnO_4^- (aq) + S_2O_3^{2-} (aq) + H_2O (l) \longrightarrow$

(ii) $Cr_2O_7^{2-} (aq) + Fe^{2+} (aq) + H^+ (aq) \longrightarrow$

(b) Explain the following observations:

(i) La^{3+} (Z = 57) and La^{3+}(Z = 71) do not show any colour in solutions:

(ii) Among the divalent cations in the first series of transition elements, manganese exhibits the maximum paramagnetism.

(iii) Cu^+ ion is not known in aqueous solutions.

Answer:

(a) (i) $8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$

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

(b) (i) It is because they do not have unpaired electrons and cannot undergo f-f transitions.

(ii) It is due to maximum number of unpaired electrons(s).

(iii) Refer Ans. to Q. 12 (a) (i).

Question 63:

(a) Describe the following characteristics of the first series of the transition metals and their trends in the series (Sc to Zn):

(i) Atomic radii (ii) Oxidation states (iii) Ionisation enthalpies

(b) Name an important alloy which contains some of the lanthanoid metals. Mention its two uses.

Answer:

(a) (i) Atomic and covalent radii: The atomic radii decrease' from Sc to Cr because number of unpaired electrons increases, therefore, effective nuclear charge increases. The atomic size of Fe, Co, Ni is almost same because pairing of electrons takes place in rf-orbitals causing repulsion and effective nuclear charge does not increase appreciably. Cu and Zn have bigger size because repulsion between paired electrons increases. Ionic radii of bivalent cations decrease from Sc to Cu due to increase in number of protons.

(ii) Oxidation state: Transition metals show variable oxidation states due to tendency of 'd' as well as 's' electrons to take part in bond formation. The highest oxidation state is equal to the total number of electrons in 's' as well as of-orbitals.

The maximum oxidation state shown by the elements of first transition series increases from Sc to Mn and then decreases to Zn. Sc shows maximum + 3 and Mn shows + 7, V(+ 5), Gr(+ 6), Fe(+ 3), Ni(+ 2), Co(+ 3), Cu(+ 2) and Zn(+ 2) oxidation state.

(iii) Ionisation enthalpies: There is slight and irregular variation in ionisation energies of transition metals due to irregular variation of atomic size. The I.E. of 5d transition series is higher than M and 4d transition series because of lanthanoid contraction, so, effective nuclear charge increases.
(b) Misch metal is an alloy which contains some of the lanthanoid metals. It contains 45% lanthanoid metals and iron (—5%) and traces of S, C, Ca and Al.
Misch metal is used in Mg-based alloy to produce bullets, shell and lighter flint.
Addition of 3% misch metal to magnesium increases its strength and used in making jet engine parts.

Question 64:
(a) Write the electronic configuration of Ce^{3+} ion, and calculate the magnetic moment on the basis of 'spin-only' formula. [Atomic No. of Ce = 58]
(b) Account for the following:
(i) Thf enthalpies of atomisation of the transition metals are high.
(ii) The lowest oxide of a transition metal is basic, the highest is amphoteric/ acidic.
(iii) Cobalt (II) is stable in aqueous solution but in the presence of complexing agents, it is easily oxidised.

Answer:
(a) $Ce(58) : [Xe]4f^1 5d^1 6s^2$

$Ce^{3+}(58) : [Xe]4f^1$

Spin only formula

$$\text{Magnetic moment} = \sqrt{4S(S+1)} = \sqrt{4 \times \frac{1}{2}\left(\frac{1}{2}+1\right)} = \sqrt{2 \times \frac{3}{2}} = \sqrt{3}$$
$$= 1.732 \text{ B.M.}$$

where 'S' is spin quantum number, Ce^{3+} has one unpaired electron which has spin quantum number equal to 1/2.

(b) (i) It is because of strong metallic bonds due to large number of unpaired electrons in d-orbitals.
(ii) It is because transition metals in lowest oxidation state are more metallic and in higher oxidation state are least metallic, therefore, oxides in lower oxidation state are basic, whereas in higher oxidation state are amphoteric/acidic.
(iii) Strong oxidising agents provide energy for loss of one more electron from Co^{2+}.

Question 65:

(a) Complete the following chemical equations:

(i) $Cr_2O_7^{2-}(aq) + H_2S(g) + H^+(aq) \longrightarrow$

(ii) $Cu^{2+}(aq) + I^-(aq) \longrightarrow$

(b) How would you account for the following:

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

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

(iii) Cr^{2+} is a stronger reducing agent than Fe^{2+}. **[Foreign]**

Answer:

(a) (i) $Cr_2O_7^{2-}(aq) + 3H_2S(g) + 8H^+(aq) \longrightarrow 2Cr^{3+} + 3S + 7H_2O$

(ii) $2Cu^{2+}(aq) + 2I^-(aq) \longrightarrow 2Cu^+(aq) + I_2(s)$

(b) (i) It is because V in lower oxidation state is less stable than Cr which is less stable than Mn. That is why MnO_4^- is best oxidising agent and VO_2^+ is least.

(ii) Mn (25) has electronic configuration $[Ar]4s^23d^5$. Electronic configuration of Mn^{2+} is $[Ar]4s^03d^5$. After losing 2 electrons, it has half filled *d*-orbital, which is more stable, that is why Mn^{2+} has exceptionally high third ionization energy, *i.e.* the energy required to remove third electron is very high.

(iii) It is because in Cr^{3+}, d^3 (half filled t_{2g} orbitals) is more stable in aqueous solution than Fe^{3+} (d^5) *i.e.*, Cr^{3+} is more stable than Fe^{3+}.

Short Answer Type Questions [I] [2 Marks]

Question 66:

Complete the following chemical reaction equations:

(i) $MnO_4^-(aq) + C_2O_4^{2-}(aq) + H^+(aq) \longrightarrow$

(ii) $Cr_2O_7^{2-}(aq) + Fe^{2+}(aq) + H^+(aq) \longrightarrow$

Answer:

(i) Refer Ans. to Q.30 (iii).

(ii) Refer Ans. to Q.30 (i).

Question 67:

Complete the following chemical equations:

(i) $Cr_2O_7^{2-}(aq) + C_2O_4^{2-}(aq) + H^+(aq) \longrightarrow$

(ii) $MnO_4^-(aq) + Fe^{2+}(aq) + H^+(aq) \longrightarrow$

Answer:

(i) $Cr_2O_7^{2-} + 3C_2O_4^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O + 6CO_2$

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

Question 68:

State reasons for the following observations:

(i) The enthalpies of atomisation of transition elements are quite high.

(ii) There is a greater horizontal similarity in the properties of the transition elements than of the main group elements.

Answer:

(i) It is due to smaller size of transition metals and strong metallic bonds due to presence of large number of unpaired electrons.

(ii) It is due to similarity in atomic and ionic size, there is more horizontal similarity. Secondly, in transition elements, incoming electron goes to inner shell (d-orbitals), whereas in main group elements, the incoming electron goes to outermost shell.

Short Answer Type Questions [II] [3 Marks]

Question 69:
How would you account for the following:
(i) Many of the transition elements and their compounds can act as good catalysis.
(ii) The metallic radii of the third (5d) series of transition elements are virtually the same as those of the corresponding members of the second series.
(iii) There is a greater range of oxidation states among the actinoids than among the lanthanoids.
Answer:
(i) Refer Ans. to Q.29 (ii).
(ii) Refer Ans. to Q.36 (ii).
(iii) Refer Ans. to Q.40 (iii).

Question 70:
Explain the following observations:
(i) With the same d-orbital configuration (d_4), Cr^{2+} ion is a reducing agent while Mn^{3+} ion is an oxidising agent.
(ii) Cu^{+} ion is not stable in aqueous solutions.
(iii) Among the 3d series of transition elements, the largest number of oxidation states are exhibited by manganese.
Answer:
(i) Refer Ans. to Q. 16 (a) (ii).
(ii) Refer Ans. to Q.12 (a) (i).
(iii) It is so because manganese (Mn) has five unpaired electrons and 2 electrons in s orbital which can take part in bond formation. Hence, it shows maximum number of oxidation states.

Long Answer Type Questions [5 Marks]

Question 71:
(a) Complete the following chemical reaction equations:
(i) Mn_{04}^{-} (aq) + C_{204}^{2-} (aq) + H^{+} (aq) ——->
(ii) $Cr_2O_7^{-}$(aq) + Fe^{2+} (aq) + H^{+}(aq) ——->
(b) Explain the following observations about the transition/inner transition elements: –
(i) There is in general an increase in density of element from titanium ‘ (Z = 22) to copper (Z = 29).
(ii) There occurs much more frequent metal-metal bonding in compounds of heavy transition elements (3rd series).
(iii) The members in the actinoid series exhibit a larger number of oxidation states than the corresponding members in the lanthanoid series.
Answer:
(a) (i) Refer Ans. to Q.30 (iii).
(ii) Refer Ans. to Q.30 (i).
(b) (i) Refer Ans. to Q.55 (i).
(ii) Refer Ans. to Q.38 (ii).
(iii) Refer Ans. to Q.41 (ii).

Question 72:

(a) Complete the following chemical equations for reactions:

(i) Mn_{04}^{-} (aq) + $S_2O_3^{2-}$(aq) + H_{20}(l) ——->

(ii) $Cr_2O_7^{-}$(aq) + H_2S(g) + H^+(ag) ———>

(b) Give an explanation for each of the following observations:

(i) The gradual decrease in size (actinoid contraction) from element to element is greater among the actinoids than that among the lanthanoids (lanthanoid contraction).

(ii) The greatest number of oxidation states are exhibited by the members in the middle of a transition series.

(iii) With the same d-orbital configuration (d_4), Cr^{2+} ion is a reducing agent but Mn^{3+} ion is an oxidising agent.

Answer:

(a) (i) Refer Ans. to Q.62 (a) (i).

(ii) Refer Ans. to Q.65 (a) (i).

(b) (i) Refer Ans. to Q.5 (ii).

(ii) Refer Ans. to Q.47 (ii).

(iii) Refer Ans. to Q.16 (a) (ii).

Question 73:

(a) Complete the following chemical reaction equations:

(i) $Cr_2O_7^{2-}(aq) + I^-(aq) + H^+(aq) \longrightarrow$

(ii) $MnO_4^-(aq) + Fe^{2+}(aq) + H^+(aq) \longrightarrow$

(b) Explain the following observations:

(i) In general, the atomic radii of transition elements decrease with increasing atomic number in a given series.

(ii) The $E^\circ_{M^{2+}/M}$ for copper is positive (+ 0.34 V). It is the only metal in the first series of transition elements showing this type of behaviour.

(iii) The E° value for Mn^{3+}/Mn^{2+} couple is much more positive than for Cr^{3+}/Cr^{2+} or Fe^{3+}/Fe^{2+} couple. **[Delhi]**

Answer:

(a) (i) Refer Ans. to Q.35 (i).

(ii) Refer Ans. to Q.67 (ii).

(b) (i) Refer Ans. to Q.60 (ii).

(ii) Refer Ans. to Q.39 (ii).

(iii) Refer Ans. to Q.59 (ii).

Question 74:

(a) What is meant by the term lanthanoid contraction? What is it due to and what consequences does it have on the chemistry of elements following lanthanoids in the periodic table?

(b) Explain the following observations:

(i) Cu^+ ion is unstable in aqueous solutions.

(ii) Although Co^{2+} ion appears to be stable, it is easily oxidised to Co^{3+} ion in the presence of a strong ligand.

(iii) The $E_{Mn^{2+}/Mn}$ value for manganese is much more than expected from the trend for other elements in the series.

Answer:

(a) The decrease in atomic and ionic size with increase in atomic number is called lanthanoid contraction. It is due to poor shielding effect of 4f electron due to which effective nuclear charge increases.

Consequences:

• The lanthanoids have similar ionic size and resemble with each other closely in their properties.

• Their separation becomes difficult.

(b) (i) Refer Ans. to Q. 12 (a) (i).

(ii) Strong ligand provides energy which overcomes third ionisation energy to form Co^{3+} ion which forms more stable complex than Co^{2+}.

(iii) It is due to low sublimation energy, low and ionisation enthalpy and high hydration energy.

Question 75:

Differentiate between Lanthanide's an Actinides

Answer:

Lanthanides		Actinides	
i)	Binding energies of 4f electrons are higher.	i)	Binding energies of 5f electrons are lower.
ii)	Maximum oxidation satate exhibited by lanthanides is +4 e.g. Ce^{4+}	ii)	Due to lower binding energies they show higher oxidation states such as +4, +5 and +6. Uranium exhibits +6 oxidation state in UF_6 and UO_2Cl_2
iii)	4f electrons have greater shielding effect.	iii)	5f electrons have poor shielding effect.
iv)	Most of their ions are colourless.	iv)	Most of their ions are coloured U^{3+} (red), U^{4+} (green) and UO_2^{2+} (yellow)
v)	They are paramagnetic but magnetic properties can be easily explained.	v)	They are also paramagnetic but their magnetic properties are very difficult to interpret.
vi)	They do not form complexes easily.	vi)	They have much greater tendency to form complexes.
vii)	Except promethium, they are non-radioactive.	vii)	All of them are radioactive.
viii)	Their compounds are less basic.	viii)	Their compounds are more basic.
ix)	They do not form oxocations.	ix)	They form oxocations such as UO_2^{2+}, UO^{+}, NpO_2^{+}, PuO_2^{+}.

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Note:

This topic is inclusive of all the topics including reduced syllabus for the academic year 2020-2021

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