IMPORTANT QUESTIONS CLASS – 12 CHEMISTRY CHAPTER – 4 THE d AND f-BLOCK ELEMENTS

Question 1.
Explain the following:
(i) Out of Sc^{3+}, Co^{2+}, and Cr^{3+} ions, only Sc^{3+} is colorless in aqueous solutions. (Atomic no.: Co = 27; Sc = 21 and Cr = 24)
(iI) The $E^{\circ}Cu^{2+}/Cu$ for copper metal is positive (+0.34), unlike the remaining members of the first transition series
(iiI) $La(OH)_3$ is more basic than $Lu(OH)_3$. (CBSE Sample paper 2018)
Answer:
(i) Co^{2+}: $[Ar]3d^7$, Sc^{3+}: $[Ar]3d^{\circ}$
Cr^{3+}: $[Ar]3d^3$
Co^{2+} and Cr^{3+} have unpaired electrons. Thus, they are colored in an aqueous solution.
Sc^{3+} has no unpaired electron. Thus it is colorless.
(ii) Metal copper has a high enthalpy of atomization and enthalpy of ionization. Therefore the high energy required to convert Cu(s) to Cu^{2+}(aq) is not balanced by its hydration enthalpy.
(iii) Due to lanthanoid contraction the size of lanthanoid ion decreases regularly with the increase in atomic size. Thus covalent character between lanthanoid ion and OH' increases from La^{3+} to Lu^{3+}. Thus the basic character of hydroxides decreases from $La(OH)_3$ to $Lu(OH)_3$

Question 2.
(a) Complete the following chemical reactions:
(i) $2MnO_4^- + 5\ NO_2^- + 6\ H^+ \rightarrow$
(ii) $3MnO_4^{2-} + 4\ H^+ \rightarrow$
Answer:
(i) $5NO_2 - + 2MnO4^- + 6H+ \rightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$
(ii) $3MnO_4^{2-} + 4H+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$

(b) Name a member of the lanthanoid series which shows a +4 oxidation state. (CBSE 2019C)
Answer:
Cerium / Ce

Question 3.
Give reasons:
(i) E° value for Mn^{3+}/Mn^{2+} couple is much more positive than that for Fe^{3+}/Fe^{2+}.
Answer:
The comparatively high value for Mn shows that $Mn^{2+}(d^5)$ is particularly stable/Much larger third ionization energy of Mn (where the required change is from d^5 to d^4).

(ii) Iron has a higher enthalpy of atomization than copper.
Answer:
Due to the higher number of unpaired electrons.

(iii) Sc^{3+} is colorless in an aqueous solution whereas Ti^{3+} is colored. (CBSE 2018)
Answer:
The absence of unpaired d-electron in Sc^{3+} whereas in Ti^{3+} there is one unpaired electron or Ti^{3+} shows the d-d transition.

Question 4.
(i) Complete the following chemical equations for reactions:
(a) MnO_4^- (aq) + S_2O_32- (aq) + H_2O (I) →
(b) $Cr_2O_7^-$ (aq) + H_2S(g) + H^+(aq) →
Answer:
(a) $8MnO_4^-$ (aq) + $3S_2O_32-$ (aq) + H_2O (l) → $8MnO_2$ (s) + $6SO_42-$ (aq) + 2OH- (aq)
(b) $Cr_2O_7^{2-}$ (aq) + $3H_2S$(g) + $8H^+$ (aq) → $2Cr^{3+}$(aq) + 3S(s) + $7H_2O$

(ii) Give an explanation for each of the following observations:
(a) The gradual decrease in size (actinoid contraction) from element to element is greater among the actinoids than that among the lanthanoids (lanthanoid contraction).
Answer:
(a) This is because of relatively poor shielding by 5f electrons in actinoids in comparison with shielding of 4f electrons in lanthanoids.

(b) The greatest number of oxidation states are exhibited by the members in the middle of a transition series.
Answer:
This is because, in the middle of the transition series, the maximum number of electrons are available for sharing with others. The small number of oxidation states at the extreme left side is due to a lesser number of electrons to lose or share. On the other hand, at the extreme right-hand side, due to a large number of electrons, only a few orbitals are available in which the electrons can share with others for higher valence.

(c) With the same d-orbital configuration (d^4) Cr^{2+} ion is a reducing agent but the Mn^{3+} ion is an oxidizing agent. (CBSE Delhi 2009)
Answer:
Cr^{2+} is reducing as its configuration changes from d^4 to d^3, the latter having a half-filled t_{2g} level. On the other hand, the change from Mn^{3+} to Mn^{2+} results in the half-filled (d^5) configuration which has extra stability.

Question 5.
(i) Complete the following chemical reaction equations:
(a) Fe^{2+} (aq) + $MnO^{-}4$ (aq) + H^{+} (aq) →
(b) $Cr_2O_7^{2-}$ (aq) + I^{-} (aq) + H^{+} (aq) →
Answer:
(a) 5Fe2+ (aq) + MnO4- (aq) + 8H+ (aq) → Mn^{2+} (aq) + $5Fe^{3+}$ (aq) + $4H_2O$(l)
(b) $Cr_2O_7^{2-}$ (aq) + $6I^{-}$ (aq) + 14H+ (aq) → $2Cr^{3+}$(aq) + $3I_2$ (s) + $7H_2O$(l)

(ii) Explain the following observations:
(a) Transition elements are known to form many interstitial compounds.
Answer:
Transition metals form interstitial compounds. Transition metals have a unique character to form interstitial compounds with small non-metallic elements such as hydrogen, boron, carbon, and nitrogen. The small atoms of these non-metallic elements (H, B, C, N, etc.) fit into the vacant spaces of the lattices of the transition metal atoms. As a result of the filling up of the interstitial spaces, the transition metals become rigid and hard.

These interstitial compounds have similar chemical properties as the parent metals but have different physical properties, particularly, density, hardness, and conductivity. For example, steel and cast iron are hard because of the formation of interstitial compounds with carbon. These interstitial compounds have a variable composition and cannot be expressed by a simple formula. Therefore, these are called nonstoichiometric compounds.

(b) With the same d^4 d-orbital configuration Cr^{2+} ion is reducing while the Mn^{3+} ion is oxidizing.
Answer:
Cr^{2+} is reducing as its configuration changes from d^4 to d^3, the latter having a half-filled t_{2g} level. On the other hand, the change from Mn^{3+} to Mn^{2+} results in the half-filled (d^5) configuration which has extra stability.

(c) The enthalpies of atomization of the transition elements are quite high. (CBSE Delhi 2009)
Answer:

The transition metals have strong interactions of electrons in the outermost orbitals and therefore, have high melting and boiling points. These suggest that the atoms of these elements are held together by strong forces and have high enthalpy of atomization.

Question 6.
(i) Complete the following chemical equations:
(a) MnO_4^- (aq) + $S_2O_3^{2-}$ (aq) + H_2O(l) →
(b) $Cr_2O_7^{2-}$ (aq) + Fe^{2+} (aq) + H^+ (aq) →
Answer:
(a) $8MnO_4^- + 3S_2O_3^{2-} + H_2O \rightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$
(b) $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

(ii) Explain the following observations:
(a) La3+ (Z = 57) and Lu3+ (Z = 71) do not show any colour in solutions.
Answer:
In La3+ there are no f-electrons and in Lu^{3+} the 4f sub-shell is complete (4/14). Therefore, there are no unpaired electrons and consequently, d-d transitions are not possible. Hence, La^{3+} and LU^{3+} do not show any color in solutions.

(b) Among the divalent cations in the first series of transition elements, manganese exhibits the maximum paramagnetism.
Answer:
Among the divalent cations in the first
transition series, Mn (Z = 25) exhibits the maximum paramagnetism because it has the maximum number of unpaired electrons ($3d^5$): five unpaired electrons.

(c) Cu^+ ion is not known in aqueous solutions. (CBSE 2010)
Answer:
In an aqueous solution, Cu^+ undergoes disproportionation changing to Cu^{2+} ion.
$2Cu^+ \rightarrow Cu^{2+} + Cu$

Question 7.
(i) Give reasons for the following:
(a) Mn^{3+} is a good oxidizing agent.
(b) $E°M^{2+}/M$ values are not regular for first-row transition metals (3d series).
(c) Although 'F' is more electronegative than 'O', the highest Mn fluoride is MnF4, whereas the highest oxide is Mn207.
(ii) Complete the following equations:
(a) $2CrO_4^{2-} + 2H^+ \rightarrow$
(b) $KMnO_4$

$\xrightarrow{\text{Heat}}$

OR

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

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

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

(ii) What is lanthanoid contraction? Name an important alloy that contains some of the lanthanoid metals. (CBSE2013)

Answer:

(i) (a) Mn^{3+} ($3d^4$) on changing to Mn^{2+} ($3d^5$) becomes stable, half-filled configuration has extra stability. Therefore, Mn^{3+} can be easily reduced and acts as a good oxidizing agent.

(b) $E°(M^{2+}/M)$ values are not regular in the first transition series metals because of irregular variation of ionization enthalpies ($IE_1 + IE_2$) and the sublimation energies.

(c) Among transition elements, the bonds formed in +2 and +3 oxidation states are mostly ionic. The compounds formed in higher oxidation states are generally formed by sharing of d-electrons. Therefore, Mn can form MnO4- which has multiple bonds also, while fluorine cannot form multiple bonds.

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

(b) $2KMnO_4 \xrightarrow{Heat} K_2MnO_4 + MnO_2 + O_2$

OR

(i) (a) The transition elements show variable oxidation states because their atoms can lose a different number of electrons. This is due to the participation of inner (n -1). d-electrons in addition to outer ns electrons because the energies of the ns and (n – 1) d-subshells are almost equal.

(b) Manganese

(c) Scandium

(ii) The steady decrease in atomic and ionic sizes of lanthanide elements with increasing atomic numbers is called lanthanide contraction. In the lanthanoids, there is a regular decrease in the size of atoms and ions with an increase in atomic number. For example, the ionic radii decrease from Ce^{3+} (111 pm) to Lu^{3+} (93 pm).

Cause of lanthanoid contraction. As we move through the lanthanoid series, 4f-electrons are being added, one at each step. The mutual shielding effect of electrons is very little, even smaller than that of d-electrons. This is due to the shape of f-orbitals. The nuclear charge, however, increases by one at each step. Hence, the inward pull experienced by the 4f-

electrons increases. This causes a reduction in the size of the entire 4f shell. The sum of the successive reductions gives the total lanthanoid contraction. The important alloy is mischmetal.

Question 8.
(i) How do you prepare:
(a) K_2MnO_4 from MnO_2?
(b) $Na_2Cr_2O_7$ from Na_2CrO_4?
(ii) Account for the following:
(a) Mn^{2+} is more stable than Fe^{2+} towards oxidation to +3 state.
(b) The enthalpy of atomization is lowest for Zn in the 3d series of the transition elements.
(c) Actinoid elements show a wide range of oxidation states.
OR
(a) Name the element of 3d transition series which shows a maximum number of oxidation states. Why does it show so?
(b) Which transition metal of 3d series has a positive $E^{\circ}(M^{2+}/M)$ value and why?
(c) Out of Cr^{3+} and Mn^{3+}, which is a stronger oxidizing agent and why?
(d) Name a member of the lanthanoid series which is well known to exhibit a +2 oxidation state.
(e) Complete the following equation:
$MnO_4^- + 8H^+ + 5e^- \rightarrow$ (CBSE Delhi 2014)
Answer:
(i) (a) When MnO_2 is fused with caustic potash (KOH) or potassium carbonate in the presence of air, a green mass of potassium manganate is formed.

$$2MnO_2 + 4KOH + O_2 \xrightarrow{\text{Heat}} 4\ 2K_2MnO_4 + 2H_2O$$

Or

$$2MnO_2 + 2K_2CO_2 + O_2 \rightarrow 2K_2MnO_4 + 2CO_2.$$

(b) Na2Cr04 is acidified with dilute sulphuric acid to get $Na_2Cr_2O_7$.

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

(ii) (a) Electronic configuration of Mn^{2+} is [Ar]Bd^5 which is half-filled and hence is stable. Therefore, the third ionization enthalpy is very high, i.e. the third electron cannot be easily removed. In the case of Fe^{2+}, the electronic configuration is $3d^6$. Therefore, Fe^{2+} can easily lose one electron to acquire a $3d^5$ stable configuration. Thus, Mn^{2+} is more stable than Fe^{2+} towards oxidation to + 3 states.

(b) The high enthalpies of atomization of transition elements are due to the participation of electrons (n – 1) d-orbitals in addition to ns electrons in the interatomic metallic bonding. In the case of zinc, no electrons from 3d-orbitals are involved in the formation of metallic

bonds. On the other hand, in all other metals of 3d series electrons from d-orbitals are always involved in the formation of metallic bonds.

(c) Lanthanoids show a limited number of oxidation states, such as +2, +3, and +4 (+3 is the principal oxidation state). This is because of the large energy gap between 5d and 4/ subshells. On the other hand, actinoids also show a principal oxidation state of +3 but show a number of other oxidation states also. For example, uranium (Z = 92) exhibits oxidation states of +3, +4, +5 and +6 and neptunium (Z = 94) shows oxidation states of +3, +4, +5, +6 and +7. This is because of the small energy difference between 5f and 6d orbitals.
OR
(a) Manganese (Z = 25) shows the largest number of oxidation states because it has the maximum number of unpaired electrons. It shows oxidation states from +2 to +7, i.e. +2, +3, +4, +5, +6 and +7.

(b) The $E^{\circ}(M^{2+}|M)$ value for copper is positive and this shows that it is the least reactive metal among the elements of the first transition series. This is because copper has a high enthalpy of atomization and enthalpy of ionization. Therefore, the high energy required to convert Cu(s) to $Cu^{2+}(aq)$ is not balanced by its hydration enthalpy.

(c) Mn^{3+} is a stronger oxidizing agent than Cr^{3+} because $Mn^{3+}(3d^4)$ changes to stable half-filled ($3d^5$) configuration while in the case of Cr^{3+} ($3d^5$) is stable (half-filled) and it cannot be readily changed to Cr^{2+} ($3d^4$).

(d) Europium.

(e) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$.

Question 9.
(a) Account for the following:
(i) Manganese shows the maximum number of oxidation states in 3d series.
(ii) E° value for Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+}.
(iii) Ti^{4+} is colorless whereas V^{4+} is colored in an aqueous solution.
(b) Write the chemical equations for the preparation of KMn04 from Mn02. Why does the purple color of acidified permanganate solution decolorize when it oxidizes Fe^{2+} to Fe^{3+}?
OR
(a) Write one difference between transition elements and p-block elements with reference to variability of oxidation states.
(b) Why do transition metals exhibit higher enthalpies of atomization?
(c) Name an element of the lanthanoid series which is well known to show a +4 oxidation state. Is it a strong oxidizing agent or a reducing agent?
(d) What is lanthanoid contraction? Write its one consequence.

(e) Write the ionic equation showing the oxidation of Fe(ll) salt by acidified dichromate solution. (CBSE Al 2019)

Answer:

(a) (i) Manganese has the electronic configuration: $3d^5\ 4s^2$. It has a maximum number of unpaired electrons and hence shows maximum oxidation states.

(ii) Mn^{2+} has $3d^5$ electronic configuration. It is stable because of the half-filled configuration. Therefore, Mn3 easily gets reduced to Mn^{2+}. Thus, $E^{\circ}(M^{3+}/Mn^{2+})$ is positive. On the other hand, Cr^{3+} is more stable in the +3 oxidation state due to stable t2g3 configuration.

(iii) Ti^{4+} $(3d^{\circ})$ does not have any d-electrons. Therefore, there are no d-d transitions whereas V^{4+}, $(3d^1)$ has one electron in d-subshell and d-d transitions are possible and hence it is colored.

(b) $2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$

$3K_2MnO_4 + 4HCL \rightarrow 2KMnO + MnO_2 + 2H_2O$

When acidified $KMnO_4$ oxidizes Fe2+ to Fe3+ its purple color gets decolorized due to the formation of Mn2+ from

MnO_4– ion.

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

Or

(a) Transition elements, in general, show variable oxidation states which differ by 1 unit, whereas p-block elements show variable oxidation states which differ by 2 units.

(b) Transition eLements have unpaired d-electron and therefore have strong metallic bonding between atoms. Hence, they have high enthalpies of atomization.

(c) Cerium. It is a strong oxidizing agent.

(d) The regular decrease In atomic and ionic radii of the Lanthanides with increasing atomic number is catted Lanthanoid contraction.

Consequence: 5d series elements have almost the same size as the 4d series.

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

Question 10.

(i) Account for the following:

(a) Mn shows the highest oxidation state of +7 with oxygen but with fluorine, it shows the highest oxidation state of +4.

(b) Zirconium and Hafnium exhibit similar properties.

(c) Transition metals act as catalysts.

(ii) Complete the following equations:

(a) $2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta}$

(b) $Cr_2O_7^{2-} + 14H^+ + 6I^-$

Or

The elements of 3d transition series are given as:

Sc Ti V Cr Mn Fe Co Ni Cu Zn

Answer the following:

(a) Write the element which is not regarded as a transition element. Give reason.

(b) Which element has the highest m.p.?

(c) Write the element which can show an oxidation state of +1.

(d) Which element is a strong oxidizing agent in the +3 oxidation state and why? (CBSE 2016)

Answer:

(i) (a) Manganese shows the highest oxidation state of +7 with oxygen but +4 with fluorine. This is because oxygen has a tendency to form multiple bonds and hence stabilize the high oxidation state.

(b) Due to lanthanoid contraction, Zr and Hf show similar properties.

(c) The transition metals act as catalysts. This is due to their ability to show multiple oxidation states.

(ii) (a) $2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$

(b) $Cr_2O_7^{2-} + 14H+ + 6I^- \rightarrow 2Cr^{3+} + 7H_2O + 3I_2$

Or

(a) Zn because of not having partially filled d-orbitals in its ground state or ionic state.

(b) Chromium, Cr

(c) Copper, Cu

(d) Mn, because Mn^{2+} has extra stability due to half-filled d-subshell.

Mn: [Ar] $3d^5\ 4s^2$; Mn^{2+}: [Ar]$3d^5$

Mn^{3+} has four electrons ($3d^4$) in 3d subshell and requires only one electron to get a half-filled 3d subshell and therefore, acts as a strong oxidizing agent.