CH-8 d- and f- Block Elements

Ques 1. Why do transition elements show variable oxidation states?

Ans 1. (ns) and (n -1) d orbital electrons have very less energy difference.

Ques 2. Generally, there is an increase in density of elements from titanium (Z = 22) to copper (Z = 29) in the first series of transition elements. Justify.

Ans 2. From titanium to copper the atomic size of elements decreases and mass increases as a result of which density increases.

Ques 3. Transition elements generally form coloured compounds. Why?

Ans 3. Because of presence of unpaired d electrons, which undergoes d-d transition.

Ques 4. Which metal in the first transition series (3d series) exhibits +1 oxidation state most frequency and why?

Ans 4. Copper exhibits + 1 oxidation state more frequently i.e., Cu^{+1} because of its electronic configuration $3d^{10}4s^1$. It can easily lose $4s^1$ electron to give stable $3d^{10}$ configuration.

Ques 5. Name a member of the lanthanoid series which is well known to exhibit +2 oxidation state.

Ans 5. Europium (Eu)

Ques 6. Out of Cr^{3+} and Mn^{3+} which is a stronger oxidizing agent and why?

Ans 6. Mn^{3+} is a stronger oxidising agent because it forms stable d^5 configuration in Mn^{2+} by accepting an electron thus acting as an oxidising agent.

Ques 7. The enthalpies of atomization of transition metals are quite high.

Ans 7. In transition elements, there are large number of unpaired electrons in their atoms, thus they have a stronger metallic bonding between the atoms. Due to this they have high enthalpies of atomization.

Ques 8. Why is enthalpy of atomization lowest for Zn in 3d series of transition elements?

Ans 8. Enthalpy of atomization is related to number of unpaired electrons. Higher the number of unpaired electrons, higher will be metallic bonding thus more enthalpy of atomization. Since Zn does not have any unpaired electron so it has the lowest enthalpy of atomization.

Ques 9. The transition metals (with the exception of Zn, Cd and Hg) are hard and have high melting and boiling points. Give reason.

Ans 9. Because of stronger metallic bonding and high enthalpies of atomization.

Ques 10. Cu^+ is colourless and Cu^{2+} is colour. Why?

Ans 10. Cu^+ is d^{10} configuration thus all the d orbitals are filled and hence no possibility of d-d transition. Thus Cu^+ is colourless.

Cu^{2+} is d^9 configuration thus d-d transition is possible due to presence of an unpaired electron in it. Thus, it is coloured.

Ques 11. Zn does not show variable oxidation state. Justify.

Ans 11. As Zinc has fully filled d^{10} configuration thus it does not have any vacant d orbital and hence does not show variable oxidation state.

Ques 12. Cadmium salts are white. Give reason.

Ans 12. Cd in its ground as well as excited state has $4d^{10}$ configuration thus all the d orbitals are filled and hence no possibility of d-d transition. Thus cadmium salts are white.

Ques 13. Zr(Z=40) and Hf(Z=72) have almost identical radii.

Ans 13. Due to lanthanoid contraction.

Ques 14. $E^o_{M^{2+}|M}$ for copper is positive.

Ans 14. The enthalpy of atomisation is very high for Cu but its hydration energy is very low. The high energy to convert Cu (s) to Cu^{2+} (aq) is not balanced by its hydration enthalpy. Thus for this conversion E^o value is positive.

Ques 15. Which of the following cations are coloured in aqueous solutions and why?

Sc^{3+} , V^{3+} , Ti^{4+} , Mn^{2+}

Ans 15. V^{3+} and Mn^{2+} are coloured because of d-d transition.

Sc^{3+} and Ti^{4+} are d^0 configuration thus no d-d transition and hence colourless.

Ques 16. Name two elements which show only +3 oxidation state.

Ans 16. Sc and La

Ques 17. (i) What is lanthanoid contraction?
(ii) Name an alloy which contains some of the lanthanoid elements.

Ans 17. (i) The regular decrease in the size of the atoms and ions in lanthanoid series with increase in atomic number is known as Lanthanoid Contraction.
(ii) Misch metal

Ques 18. Name the transition element which shows maximum number of oxidation states in the first transition series.

Ans 18. Mn

Ques 19. Many of the transition elements are known to form interstitial compounds.

Ans 19. Because the atomic sizes of transition metals are big enough to accommodate small atoms like carbon, hydrogen etc. in the voids of their lattice.

Ques 20. Although 'F' is more electronegative than 'O', the highest fluoride of Mn is MnF_4 while the highest oxide is Mn_2O_7. Give reason.

Ans 20. Since Oxygen can form multiple bonds with the metals whereas Fluorine forms only single bonds thus metal shows highest Oxidation state with Oxygen and not Fluorine . Therefore the highest fluoride of Mn is MnF_4 in which O.S. of Mn is +4 while the highest oxide is Mn_2O_7 in which O.S. of Mn is +7 .

Ques 21. Why lanthanoids form primarily +3 ions while the actinoids usually have higher oxidation states in their compounds.

Ans 21. In actinoids there is less energy difference in the 5*f*, 6*d* and 7*s* orbitals as compared to 4*f*, 5*d* and 6*s* orbitals in case of lanthanoids. This means that more electrons are available for bonding in actinoids as compared to the members of lanthanoid family. Thus, actinoids show variable oxidation state and lanthanoids do not.

Ques 22. Metal-metal bonding is more extensive in the 4d and 5d series of transition elements than the 3d series. Explain.

Ans 22. Down the group in the transition metals, the atomic size increases. Therefore, electrons in elements belonging to 4d and 5d series are less loosely held by the nucleus as compared to the elements present in 3d series but in the same group. Thus these electrons are readily available for metal-metal bonding in 4d and 5d series as compared to 3d series thus metal-metal bonding is more extensive in 4d and 5d series.

Ques 23. How will you account for the fact that Cr^{2+} is reducing in nature while with the same d-configuration (d^4), Mn^{3+} is an oxidizing agent?

Ans 23. Cr^{2+} $(3d^4) \rightarrow Cr^{3+}$ $(3d^3) + e^-$

Cr^{2+} acts as a reducing agent due to greater stability of Cr^{3+} with exactly half filled t_{2g} orbitals.

On the other hand the change from Mn^{3+} to Mn^{2+} results in half filled d^5 configuration which has extra stability thus it behaves as an oxidising agent.

Ques 24. Explain why Zn, Cd and Hg are generally not regarded as transition elements.

Ans 24. Zn, Cd and Hg are not regarded as transition elements because they have filled d^{10} configuration in both ground and excited states. They differ in many characteristics as compared to rest of the elements belonging to the same period; but being the end elements they have been retained in the d-block.

Ques 25. Explain why is Ce^{4+} ion a strong oxidizing agent.

Ans 25. Ce^{4+} has noble configuration of Xe (Z=54) but it has a strong urge to change to +3 oxidation state which is the most common oxidation state of lanthanoids. Therefore, it acts as a strong oxidising agent.

Ques 26. Transition elements and their compounds are generally found to be good catalysts in chemical reactions. Discuss.

Ans 26. Transition elements can adopt variable oxidation state to form complexes. These intermediate compounds will provide a new path will lower activation energy. Further they get decomposed on reaction with the other reactant regenerating the catalyst.

Ques 27. Why is Cu^+ ion not known in aqueous solutions?

Ans 27. Cu(I) compounds involving Cu^+ ions are unstable in aq. medium and undergo disproportionation because of very low hydration enthalpy of Cu^+.

$2Cu^+ \rightarrow Cu^{2+} + Cu$

Ques 28. Why is $La(OH)_3$ more basic than $Lu(OH)_3$?

Ans 28. $La(OH)_3$ is more basic than $Lu(OH)_3$ because the latter has more covalent character than former (Lu is smaller than La due to lanthanoid contraction and according to fazan's rule smaller cation means more covalent character). Thus the release of OH- from $Lu(OH)_3$ is more difficult and is therefore less basic than $La(OH)_3$.

Ques 29. The elements of 3d transition series are given as:
Se Ti V Cr Mn Fe Co Ni Cu Zn
Answer the following:
(i) Write the element which shows maximum number of oxidation states. Give reason.
(ii) Which element has the highest m.p.?
(iii) Which element shows only +3 oxidation state?
(iv) Which element is a strong oxidizing agent in +3 oxidation state and why?

Ans 29. (i) Mn shows, maximum number of oxidation states upto +7. It has the maximum number of unpaired electrons.
(ii) Cr has the highest melting point.
(iii) Sc shows only +3 oxidation state.
(iv) Mn is a strong oxidizing agent in +3 oxidation state because after reduction it attains +2 oxidation state in which it has the most stable half-filled (d^5) configuration.