8.21. How would you account for the following:
(i) Of the d^4 species, Cr^{2+} is strongly reducing while manganese (III) is strongly oxidizing.
(ii) Cobalt (II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised.
(iii) The d^1 configuration is very unstable in ions.
Sol:
(i) E° value for Cr^{3+}/Cr^{2+} is negative (-0.41 V) whereas E° values for $Mn^{3+}/Mn^{2+}$is positive (+1.57 V). Hence, Cr^{2+} ion can easily undergo oxidation to give Cr^{3+} ion and, therefore, act as strong reducing agent whereas Mn^{3+} can easily undergo' reduction to give Mn^{2+} and hence act as an oxidizing agent.
(ii) Co (III) has .greater tendency to form coordination complexes than Co (II). Hence, in the presence of ligands, Co (II) changes to Co (III), i.e., is easily oxidized.
(iii) The ions with dx configuration have the tendency to lose the only electron present in d-subshell to acquire stable d° configuration. Hence, they are unstable and undergo oxidation or disproportionation.

8.22. What is meant by disproportionation? Give two examples of disproportionation reaction in aqueous solution
Sol: Disproportionation reactions are those in which the same substance undergoes oxidation as well as reduction, i.e., oxidation number of an element increases as well as decreases to form two different products.

$$3\,\overset{VI}{Mn}O_4^{2-} + 4H^+ \longrightarrow 2\,\overset{VII}{Mn}O_4^- + \overset{IV}{Mn}O_2 + 2H_2O$$

$$2Cu^{+1} \rightarrow Cu^{+2} + Cu$$

8.23. Which metal in the first series of transition metals exhibits + 1 oxidation state most frequently and why?
Sol: Cu has electronic configuration 3 d^{10} $4s^1$. It can easily lose $4s^1$ electron to acquire the stable $3d^{10}$ configuration. Hence, it shows + 1 oxidation state.

8.24. Calculate the number of unpaired electrons in the following gaseous ions : Mn^{3+}, Cr^{3+}, V^{3+} and Ti^{3+}. Which one of these is the most stable in aqueous solution.
Sol:
Mn^{3+} = $3d^1$ = 4 unpaired electrons,
Cr^{3+} = $3d^3$ = 3 electrons,
V^{3+} = $3d^2$ = 2 electrons,
Ti^{3+}=$3d^1$ = I electron.
Out of these, Cr^{3+} is most stable in aqueous solution because of half-filled t_{2g} level.

8.25. Give examples and suggest reasons for the following features of the transition metal chemistry:
(i) The lowest oxide of transition metal is basic the highest is amphoteric/ acidic.

(ii) A transition metal exhibits highest oxidation state ih oxides and fluorides.
(iii) The highest oxidation state is exhibited in oxoanions of a metal.
Sol:
(i) The lower oxide of transition metal is basic because the metal atom has low oxidation state whereas higher once are acidic due to high oxidation state. For example, MnO is basic whereas Mn_2O_7 is acidic. Oxides in lower oxidation state are ionic hence basic. Oxides in higher oxidation state are covalent hence acidic
(ii) A transition metal exhibits higher oxidation states in oxides and fluorides because oxygen and fluorine are highly electronegative elements, small in size and strongest oxidising agents. For example, osmium shows an oxidation states of + 6 in O_5F_6 and vanadium shows an oxidation states of + 5 in V_2O_5.
(iii) Oxo metal anions have highest oxidation state, e.g., Cr in $Cr_2O_7^{2-}$ has an. oxidation state of + 6 whereas Mn in MnO_4^- has an oxidation state of +7. This is again due to the combination of the metal with oxygen, which is highly electronegative and oxidizing agent.

8.26. Indicate the steps in the preparation of:
(i) $K_2Cr_2O_7$ from chromite ore
(ii) $KMnO_4$ from pyrolusite ore.
Sol:

(i) $$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$
$$2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$$
$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

(ii) $$2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta} 2K_2MnO_4 + 2H_2O$$

$$\underset{\text{Manganate ion}}{MnO_4^{2-}} \xrightarrow[\text{reduction}]{\text{Electrolytic}} \underset{\text{permanganate ion}}{MnO_4^-} + e^-$$

8.27. What are alloys? Name an important alloy which contains some of the lanthanoid metals. Mention its uses.
Sol: An alloy is a homogeneous mixture of two or more metals and non-metals. An important alloy containing lanthanoid metals is misch metal which contains 95% lanthanoid metals (Ce, La and Nd) and 5% iron along with traces of S, C, Ca and Al. It is used in making parts of jet engines.

8.28. What are inner transition elements? Decide which of the following atomic numbers are the atomic numbers of the inner transition elements: 29, 59, 74, 95, 102, 104.
Sol: The f-block elements in which the. last electron enters into f-sub shell-are called inner-transition elements. These include lanthanoids (Z=58 to 71) and actinoids (Z=90 to 103). Thus, the elements with atomic numbers 59,95 and 102 are the? inner transition elements.

8.29. The chemistry of the actinoid elements is not so smooth as that of the lanthanoids. Justify this statement by giving some examples from the oxidation state of these elements.
Sol: Lanthanoids show limited number of oxidation state, viz, +2, +3 and +4 (out of which +3 is most common). This is because of large energy gap between 4f 5d and 6s subshells. The dominant

oxidation state of actinoids is also +3 but they show a number of other oxidation states also. For example, uranium (Z=92) and plutonium (Z - 94), show +3, +4, +5 and +6, neptunium (Z = 94) shows +3, +4, +5 and +7, etc. This is because of the small energy difference between. 5f, 6d and 7s orbitals of the actinoids.

8.30. Which is the last element in the series of the actinoids? Write the electronic configuration of this element. Comment on the possible oxidation state of this element
Sol: Last actinoid=Lawrencium (Z = 103)
Electronic configuration = $[Rn]^{86}$ $5f^{14}$ $6d^{1}$ $7s^{2}$ Possible oxidation state = +3.

*********** END **********