

**Q 8.1:**

**Write down the electronic configuration of:**

(i)  $\text{Cr}^{3+}$  (ii)  $\text{Pm}^{3+}$  (iii)  $\text{Cu}^+$  (iv)  $\text{Ce}^{4+}$  (v)  $\text{Co}^{2+}$  (vi)  $\text{Lu}^{2+}$  (vii)  $\text{Mn}^{2+}$  (viii)  $\text{Th}^{4+}$

**Ans :**

(i)  $\text{Cr}^{3+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$

Or,  $[\text{Ar}]^{18} 3d^3$

(ii)  $\text{Pm}^{3+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^4$

Or,  $[\text{Xe}]^{54} 3d^3$

(iii)  $\text{Cu}^+$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$

Or,  $[\text{Ar}]^{18} 3d^{10}$

(iv)  $\text{Ce}^{4+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$

Or,  $[\text{Xe}]^{54}$

(v)  $\text{Co}^{2+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$

Or,  $[\text{Ar}]^{18} 3d^7$

(vi)  $\text{Lu}^{2+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^{14} 5d^1$

Or,  $[\text{Xe}]^{54} 2f^{14} 3d^3$

(vii)  $\text{Mn}^{2+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

Or,  $[\text{Ar}]^{18} 3d^5$

(viii)  $\text{Th}^{4+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6$

Or,  $[\text{Rn}]^{86} 2+$

**Q 8.2:**

**Why are  $\text{Mn}^{2+}$  compounds more stable than Fe towards oxidation to their +3 state?**

**Ans :**

Electronic configuration:  $\text{Fe}^{2+}$  is  $[\text{Ar}]^{18} 3d^6$ .

$\text{Mn}^{2+}$  is  $[\text{Ar}]^{18} 3d^5$ .

We know that half and completely filled orbitals are more stable. Hence, Mn with (+2) state has a stable  $d^5$  configuration, which is why  $\text{Mn}^{2+}$  shows resistance to oxidation to  $\text{Mn}^{3+}$ . We know that,  $\text{Fe}^{2+}$  has  $3d^6$  configuration and by losing one electron, its configuration changes to a more stable  $3d^5$  configuration. Therefore,  $\text{Fe}^{2+}$  easily gets oxidized to  $\text{Fe}^{3+}$  oxidation state.

**Q 8.3:**

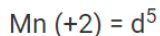
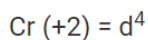
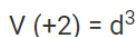
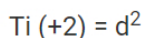
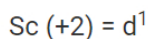
**Explain briefly how +2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number?**

**Ans :**

In the table below, the oxidation states of the first half of the first row of transition metals are displayed.

|                        | Sc | Ti | V  | Cr | Mn |
|------------------------|----|----|----|----|----|
|                        |    | +2 | +2 | +2 | +2 |
|                        |    | +3 | +3 | +3 | +3 |
|                        |    | +4 | +4 | +4 | +4 |
|                        |    | +5 | +5 | +6 |    |
|                        |    | +6 | +7 |    |    |
| <b>Oxidation state</b> |    |    |    |    |    |

We can see that except, Sc all other metals have a +2 oxidation state. As moving in the increasing order of atomic number from 21 to 25, that is from Sc to Mn, the number of electrons in 3d orbitals increases from 1 to 5.



+2 oxidation state is attained by the loss of the two 4s electrons by these metals. Since the number of d electrons in (+2) state also increases from Ti(+2) to Mn(+2), the stability of +2 state increases (as d-orbital is becoming more and more half-filled). Mn (+2) has  $d^5$  electrons (that is half-filled d shell, which is highly stable).

**Q 8.4:**

**To what extent do the electronic configurations decide the stability of oxidation states in the first series of the transition elements? Illustrate your answer with examples.**

**Ans :**

The oxidation states with the maximum number (+2 to +7) are exhibited by the elements of Mn oxidation states that are in the first half of the transition series. With the increase in atomic number, the stability of +2 oxidation state increases. Once more electrons are filled in the d-orbital, this happens to a great extent. The +2 oxidation state is not shown by the Sc. Its electronic configuration is  $4s^2 3d^1$ . It loses all the three electrons to form  $\text{Sc}^{3+}$ , +3 oxidation state of Sc is very stable as by losing all three electrons, it attains stable noble gas configuration, [Ar]. Ti (+4) and V(+5) are very stable for the same reason. For Mn, +2 oxidation state is very stable as after losing two electrons, its d-orbital is exactly half-filled,  $[\text{Ar}] 3d^5$ .

**Q 8.5:**

**What may be the stable oxidation state of the transition element with the following d electron configurations in the ground state of their atoms:  $3d^3$ ,  $3d^5$ ,  $3d^8$  and  $3d^4$ ?**

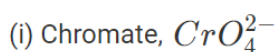
**Ans :**

|       | Electronic configuration in ground state | Stable oxidation states                           |
|-------|------------------------------------------|---------------------------------------------------|
| (i)   | $3d^3$ (Vanadium)                        | +2, +3, +4 and +5                                 |
| (ii)  | $3d^5$ (Chromium)                        | +3, +4, +6                                        |
| (iii) | $3d^5$ (Manganese)                       | +2, +4, +6, +7                                    |
| (iv)  | $3d^8$ (Cobalt)                          | +2, +3                                            |
| (v)   | $3d^4$                                   | There is no $3d^4$ configuration in ground state. |

**Q 8.6:**

**Name the oxometal anions of the first series of the transition metals in which the metal exhibits the oxidation state equal to its group number.**

**Ans :**



Oxidation state of Cr is + 6.



Oxidation state of Mn is + 7.

(iii) Vanadate,  $VO_3^-$

Oxidation state of V is + 5.

**Q 8.7:**

**What is lanthanoid contraction? What are the consequences of lanthanoid contraction?**

**Ans:**

On moving along the lanthanoid series, the atomic number gradually increases by one. With the increase in atomic number, the number of protons and electrons present in the atom also increases by one. The effective nuclear charge increases as electrons are being added to the same shell. Owing to the proton addition being pronounced more above the interelectronic repulsions resulting from electron addition, nuclear attraction increase happens. Also, with the increase in the atomic number, the number of electrons in the 4f orbital also increases. The 4f electrons have poor shielding effect. Therefore, the effective nuclear charge experienced by the outer electrons increases. Consequently, the attraction of the nucleus for the outermost electrons increases. This results in a steady decrease in the size of lanthanoids with an increase in the atomic number. This is termed as lanthanoid contraction.

Consequences of lanthanoid contraction

- (i) It is due to lanthanide contraction that there is variation in the basic strength of lanthanide hydroxides. (Basic strength decreases from  $La(OH)_3$  to  $Lu(OH)_3$ .)
- (ii) There is a similarity in the properties of second and third transition series.
- (iii) Separation of lanthanoids is possible due to lanthanide contraction

**Q 8.8:**

**What are the characteristics of the transition elements and why are they called transition elements? Which of the d-block elements may not be regarded as the transition elements?**

**Ans:**

Transition elements are those elements in which the atoms or ions (in stable oxidation state) contain partially filled d-orbital. These elements are found in the d-block and show a transition of properties between s-block and p-block. Hence, these are called transition elements.

Elements such as Cd, Hg and Zn cannot be called as transition elements because they have completely filled d-sub shell.

**Question 8.9:**

**In what way is the electronic configuration of the transition elements different from that of the non transition elements?**

**Ans :**

Transition metals have a partially filled d-orbital. Hence, the electronic configuration of transition elements is  $(n - 1)d^{1-10} ns^{0-2}$ .

The non-transition elements either do not have a d-orbital or have a fully filled d-orbital.

Therefore, the electronic configuration of non-transition elements is  $ns^{1-2}$  or  $ns^2 np^{1-6}$ .

**Q 8.10:**

**What are the different oxidation states exhibited by the lanthanoids?**

**Ans :**

In the case of lanthanoids, +3 oxidation state is most common.

That is,  $Ln(III)$  compounds are predominant.

However, +2 and +4 oxidation states can also be found in the solution or in solid compounds.

**Q 8.11:**

**Explain giving reasons:**

- (i) Transition metals and many of their compounds show paramagnetic behavior.
- (ii) The enthalpies of atomisation of the transition metals are high.
- (iii) The transition metals generally form coloured compounds.
- (iv) Transition metals and their many compounds act as good catalyst.

**Ans :**

(i) The catalytic activity of the transition elements can be explained by two basic facts.

(a) Transition metals provide a suitable surface for the reactions to occur.

(b) Owing to their ability to show variable oxidation states and form complexes, transition metals form unstable intermediate compounds. Thus, they provide a new path with lower activation energy,  $E_a$ , for the reaction.

(ii) Most of the complexes of transition metals are coloured. This is because of the absorption of radiation from visible light region to promote an electron from one of the d-orbitals to another. In the presence of ligands, the d-orbitals split up into two sets of orbitals having different energies. Therefore, the transition of electrons can take place from one set to another. The energy required for these transitions is quite small and falls in the visible region of radiation. The ions of transition metals absorb the radiation of a particular wavelength and the rest is reflected, imparting colour to the solution.

(iii) Transition elements have high effective nuclear charge and a large number of valence electrons. Therefore, they form very strong metallic bonds. As a result, the enthalpy of atomization of transition metals is high.

(iv) Transition metals show paramagnetic behaviour. Paramagnetism arises due to the presence of unpaired electrons with each electron having a magnetic moment associated with its spin angular momentum and orbital angular momentum. However, in the first transition series, the orbital angular momentum is quenched. Therefore, the resulting paramagnetism is only because of the unpaired electron.

**Q 8.12:**

**What are interstitial compounds? Why are such compounds well known for transition metals?**

**Ans :**

Transition metals are large in size and they also contain lots of interstitial sites.

These interstitial sites can be used to trap atoms of other elements (that have small atomic size), such as H, C, N. The compounds resulting are called interstitial compounds.

**Q 8.13:**

**How is the variability in oxidation states of transition metals different from that of the non transition metals? Illustrate with examples.**

**Ans :**

In the case of transition elements, the oxidation state can vary from +1 to the highest oxidation state by removing all its valence electrons. Also, in transition elements, the oxidation states differ by 1 ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ;  $\text{Cu}^+$  and  $\text{Cu}^{2+}$ ). In non-transition elements, the oxidation states differ by 2, for example, +2 and +4 or +3 and +5, etc.

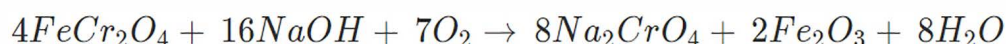
**Q 8.14:**

**Describe the preparation of potassium dichromate from iron chromite ore. What is the effect of increasing pH on a solution of potassium dichromate?**

**Ans :**

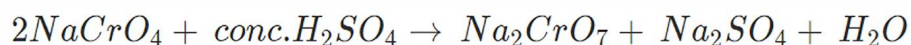
From iron chromite ore, Potassium dichromate is prepared as in the following steps.

Step (1): Preparation of sodium chromate

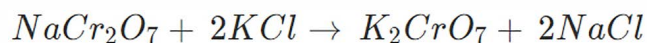




Step (2): Conversion of sodium chromate into sodium dichromate



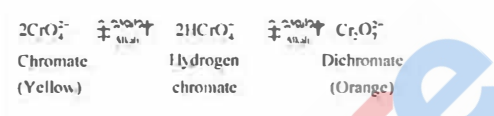
Step (3): Conversion of sodium dichromate to potassium dichromate



Potassium chloride being less soluble than sodium chloride is obtained in the form of orange coloured crystals and can be removed by filtration.

The dichromate ion ( $\text{Cr}_2\text{O}_7^{2-}$ ) exists in equilibrium with chromate ( $\text{CrO}_4^{2-}$ ) ion at pH 4.

However, by changing the pH, they can be inter converted.



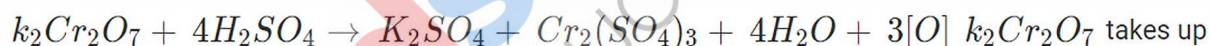
**Q 8.15:**

**Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with:**

**(i) iodide (ii) iron(II) solution and (iii) H<sub>2</sub>S**

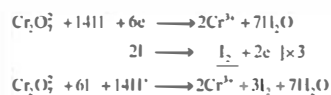
**Ans :**

$\text{K}_2\text{Cr}_2\text{O}_7$  acts as a very strong oxidising agent in the acidic medium.

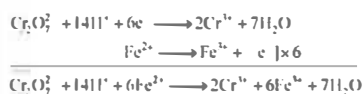


electrons to get reduced and acts as an oxidizing agent. The reaction of  $\text{K}_2\text{Cr}_2\text{O}_7$  with H<sub>2</sub>S, iron (II) solution and other iodide are given below.

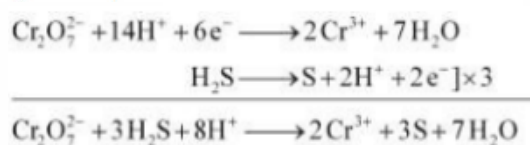
(i)  $\text{K}_2\text{Cr}_2\text{O}_7$  oxidizes iodide to iodine.



(ii)  $\text{K}_2\text{Cr}_2\text{O}_7$  oxidizes iron (II) solution to iron (III) solution i.e., ferrous ions to ferric ions.



(iii)  $\text{K}_2\text{Cr}_2\text{O}_7$  oxidizes H<sub>2</sub>S to sulphur.



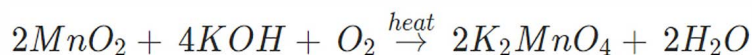
Q 8.16:

Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with

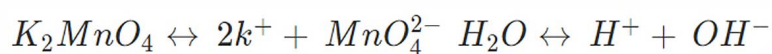
(i) iron(II) ions (ii) SO<sub>2</sub> and (iii) oxalic acid?  
Write the ionic equations for the reactions.

Ans :

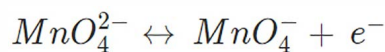
Potassium permanganate can be prepared from pyrolusite (MnO<sub>2</sub>). The ore is fused with KOH in the presence of either atmospheric oxygen or an oxidising agent, such as KNO<sub>3</sub> or KClO<sub>4</sub>, to give K<sub>2</sub>MnO<sub>4</sub>.



The green mass can be extracted with water and then oxidized either electrolytically or by passing chlorine/ozone into the solution. Electrolytic oxidation



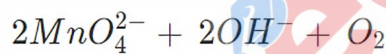
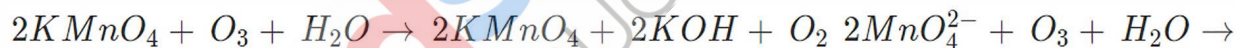
At anode, manganate ions are oxidized to permanganate ions.



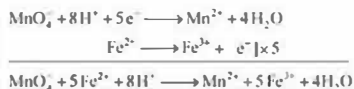
Oxidation by chlorine



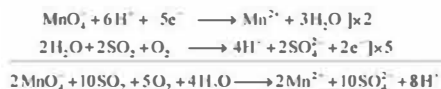
Oxidation by ozone



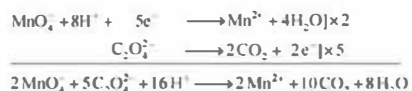
(i) Acidified KMnO<sub>4</sub> solution oxidizes Fe (II) ions to Fe (III) ions i.e., ferrous ions to ferric ions.



(ii). Acidified potassium permanganate oxidizes SO<sub>2</sub> to sulphuric acid.



(iii) Acidified potassium permanganate oxidizes oxalic acid to carbon dioxide



Q 8.17:

For M<sup>2+</sup>/M and M<sup>3+</sup>/M<sup>2+</sup> systems the EV values for some metals are as follows:

Cr<sup>2+</sup>/Cr -0.9V Cr<sup>3+</sup>/Cr<sup>2+</sup> -0.4 V

Mn<sup>2+</sup>/Mn -1.2V Mn<sup>3+</sup>/Mn<sup>2+</sup> +1.5 V

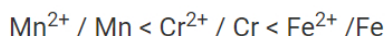
Fe<sup>2+</sup>/Fe -0.4V Fe<sup>3+</sup>/Fe<sup>2+</sup> +0.8 V

Use this data to comment upon:

- the stability of  $\text{Fe}^{3+}$  in acid solution as compared to that of  $\text{Cr}^{3+}$  or  $\text{Mn}^{3+}$  and
- the ease with which iron can be oxidised as compared to a similar process for either chromium or manganese metal.

Ans :

(i) The reduction potentials for the given pairs increase in the following order.



So, the oxidation of Fe to  $\text{Fe}^{2+}$  is not as easy as the oxidation of Cr to  $\text{Cr}^{2+}$  and the oxidation of Mn to  $\text{Mn}^{2+}$ . Thus, these metals can be arranged in the increasing order of their ability to get oxidised as:  $\text{Fe} < \text{Cr} < \text{Mn}$

(ii) The  $E^\ominus$  value for  $\text{Fe}^{3+}/\text{Fe}^{2+}$  is higher than that for  $\text{Cr}^{3+}/\text{Cr}^{2+}$  and lower than that for  $\text{Mn}^{3+}/\text{Mn}^{2+}$ . So,

the reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  is easier than the reduction of  $\text{Mn}^{3+}$  to  $\text{Mn}^{2+}$ , but not as easy as the reduction of  $\text{Cr}^{3+}$  to  $\text{Cr}^{2+}$ . Hence,  $\text{Fe}^{3+}$  is more stable than  $\text{Mn}^{3+}$ , but less stable than  $\text{Cr}^{3+}$ . These metal ions can be arranged in the increasing order of their stability as:  $\text{Mn}^{3+} < \text{Fe}^{3+} < \text{Cr}^{3+}$

**Q 8.18:**

Predict which of the following will be coloured in aqueous solution?  $\text{Ti}^{3+}$ ,  $\text{V}^{3+}$ ,  $\text{Cu}^+$ ,  $\text{Sc}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Co}^{2+}$ . Give reasons for each.

Ans :

Ions with electrons in d-orbital will be the only ones that will be coloured and the ions with empty d-orbital will be colourless.

| Element | Atomic Number | Ionic State      | Electronic configuration in ionic State |
|---------|---------------|------------------|-----------------------------------------|
| Ti      | 22            | $\text{Ti}^{3+}$ | $[\text{Ar}] 3d^1$                      |
| V       | 23            | $\text{V}^{3+}$  | $[\text{Ar}] 3d^2$                      |
| Cu      | 29            | $\text{Cu}^+$    | $[\text{Ar}] 3d^{10}$                   |
| Sc      | 21            | $\text{Sc}^{3+}$ | $[\text{Ar}]$                           |
| Mn      | 25            | $\text{Mn}^{2+}$ | $[\text{Ar}] 3d^5$                      |
| Fe      | 26            | $\text{Fe}^{3+}$ | $[\text{Ar}] 3d^5$                      |
| Co      | 27            | $\text{Co}^{2+}$ | $[\text{Ar}] 3d^7$                      |

All other ions, except  $\text{Sc}^{3+}$ , will be coloured in aqueous solution because of d-d transitions. Not  $\text{Sc}^{3+}$  as it has an empty d-orbital.

**Q 8.19:**

Compare the stability of +2 oxidation state for the elements of the first transition series.

Ans:

|    |    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|----|
| Sc |    |    | +3 |    |    |    |    |
| Ti | +1 | +2 | +3 | +4 |    |    |    |
| V  | +1 | +2 | +3 | +4 | +5 |    |    |
| Cr | +1 | +2 | +3 | +4 | +5 | +6 |    |
| Mn | +1 | +2 | +3 | +4 | +5 | +6 | +7 |
| Fe | +1 | +2 | +3 | +4 | +5 | +6 |    |
| Co | +1 | +2 | +3 | +4 | +5 |    |    |
| Ni | +1 | +2 | +3 | +4 |    |    |    |
| Cu | +1 | +2 | +3 |    |    |    |    |
| Zn |    | +2 |    |    |    |    |    |

From the table above:

Mn shows maximum number of oxidation states, changing between +2 to +7.

The number of oxidation states increases as we move on from Sc to Mn.

On moving from Mn to Zn, the number of oxidation states decreases due to a decrease in the number of available unpaired electrons.

The relative stability of the +2 oxidation state increases on moving from top to bottom. This is because on moving to bottom from the top, it becomes more and more difficult to remove the third electron from the d-orbital.

**Question 8.20:**

**Compare the chemistry of actinoids with that of the lanthanoids with special reference to:**

**(i) electronic configuration (iii) oxidation state**

**(ii) atomic and ionic sizes and (iv) chemical reactivity.**

**Ans :**

(i) Electronic configuration

The general electronic configuration for lanthanoids is  $[\text{Xe}]^{54} 4f^{0-14} 5d^{0-1} 6s^2$  and that for actinoids is  $[\text{Rn}]^{86} 5f^{1-14} 6d^{0-1} 7s^2$ . Unlike 4f orbitals, 5f orbitals are not deeply buried and participate in bonding to a greater extent.

(ii) Atomic and Ionic sizes :

Similar to lanthanoids, actinoids also exhibit actinoid contraction (overall decrease in atomic and ionic radii). The contraction is greater due to the poor shielding effect of 5f orbitals.

(iii) Oxidation states :

The principal oxidation state of lanthanoids is (+3). However, sometimes we also encounter oxidation states of + 2 and + 4. This is because of extra stability of fully-filled and half-filled orbitals. Actinoids exhibit a greater range of oxidation states. This is because the 5f, 6d, and 7s levels are of comparable energies. Again, (+3) is the principal oxidation state for actinoids. Actinoids such as lanthanoids have more compounds in +3 state than in +4 state.

(iv) Chemical reactivity:

In the lanthanide series, the earlier members of the series are more reactive. They have reactivity that is comparable to Ca. With an increase in the atomic number, the lanthanides start behaving similar to Al. Actinoids, on the other hand, are highly reactive metals, especially when they are finely divided. When they are added to boiling water, they give a mixture of oxide and hydride. Actinoids combine with most of the non-metals at moderate temperatures. Alkalies have no action on these actinoids. In case of acids, they are slightly affected by nitric acid (because of the formation of a protective oxide layer).

**Question 8.21:**

**How would you account for the following:**

**(i) Of the d4 species,  $\text{Cr}^{2+}$  is strongly reducing while manganese(III) is strongly oxidising.**

**(ii) Cobalt(II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised.**

**(iii) The d1 configuration is very unstable in ions**

**Ans:**

(i)  $\text{Cr}^{2+}$  is strongly reducing in nature. It has a  $d^4$  configuration. While acting as a reducing agent, it gets oxidized to  $\text{Cr}^{3+}$  (electronic configuration,  $d^3$ ). This  $d^3$  configuration can be written as configuration, which is a more stable configuration. In the case of  $\text{Mn}^{3+}$  ( $d^4$ ), it acts as an oxidizing agent and gets reduced to  $\text{Mn}^{2+}$  ( $d^5$ ). This has an exactly half-filled d-orbital and is highly stable.

(ii)  $\text{Co(II)}$  is stable in aqueous solutions. However, in the presence of strong field complexing reagents, it is oxidized to  $\text{Co(III)}$ . Although the 3rd ionization energy for Co is high, but the higher amount of crystal field stabilization energy (CFSE) released in the presence of strong field ligands overcomes this ionization energy.



(iii) The ions in  $d^1$  configuration tend to lose one more electron to get into stable  $d^0$  configuration. Also, the hydration or lattice energy is more than sufficient to remove the only electron present in the d-orbital of these ions. Therefore, they act as reducing agents.

**Q 8.22:**

**What is meant by 'disproportionation'? Give two examples of disproportionation reaction in aqueous solution.**

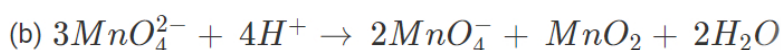
**Ans :**

It is found that sometimes a relatively less stable oxidation state undergoes an oxidation-reduction reaction in which it is simultaneously oxidised and reduced. This is called disproportionation.

For example,



Cr(V) is oxidized to Cr(VI) and reduced to Cr(III).



Mn (VI) is oxidized to Mn (VII) and reduced to Mn (IV).

**Question 8.23:**

**Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why?**

**Ans:**

In the first series of transition metals, Cu exhibits +1 oxidation state very frequently. We know Cu has an electronic configuration of  $[Ar] 3d^{10}$ , that is, the completely filled d-orbital makes it highly stable.

**Question 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?**

**Ans:**

|       | Gaseous ions         | Number of unpaired electrons |
|-------|----------------------|------------------------------|
| (i)   | $Mn^{2+}, [Ar] 3d^5$ | 4                            |
| (ii)  | $Cr^{3+}, [Ar] 3d^3$ | 3                            |
| (iii) | $V^{3+}, [Ar] 3d^2$  | 2                            |
| (iv)  | $Ti^{3+}, [Ar] 3d^1$ | 1                            |

$Cr^{3+}$  is the most stable in aqueous solutions owing to a  $t_{2g}^3$  configuration.

**Question 8.25:**

**Give examples and suggest reasons for the following features of the transition metal chemistry:**

- The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.
- A transition metal exhibits highest oxidation state in oxides and fluorides.
- The highest oxidation state is exhibited in oxoanions of a metal.

**Ans:**

(i) In the case of a lower oxide of a transition metal, the metal atom has a low oxidation state. This means that some of the valence electrons of the metal atom are not involved in bonding. As a result, it can donate electrons and behave as a base. On the other hand, in the case of a higher oxide of a transition metal, the metal atom has a high oxidation state. This means that the valence electrons are involved in bonding and so, they are unavailable. There is also a high effective nuclear charge. As a result, it can



accept electrons and behave as an acid.

For example,  $Mn^{II}O$  is basic and  $Mn_2^{VII}O_7$  is acidic.

(ii) Oxygen and fluorine act as strong oxidising agents because of their high electronegativities and small sizes. Hence, they bring out the highest oxidation states from the transition metals. In other words, a transition metal exhibits higher oxidation states in oxides and fluorides.

For example, in  $OsF_6$  and  $V_2O_5$ , the oxidation states of Os and V are +6 and +5 respectively.

(iii) Oxygen is a strong oxidising agent due to its high electronegativity and small size. So, oxo-anions of a metal have the highest oxidation state. For example, in , the oxidation state of Mn is +7.

#### Q 8.26:

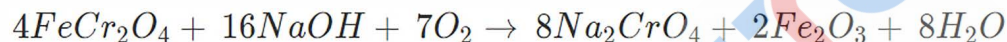
**Indicate the steps in the preparation of:**

**(i)  $K_2Cr_2O_7$  from chromite ore. (ii)  $KMnO_4$  from pyrolusite ore.**

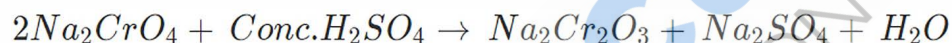
**Ans:**

(i) Potassium dichromate (  $K_2Cr_2O_7$  ) is prepared from chromite ore ( $FeCr_2O_4$ ) in the following steps.

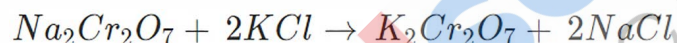
Step (1): Preparation of sodium chromate



Step (2): Conversion of sodium chromate into sodium dichromate



Step(3): Conversion of sodium dichromate to potassium dichromate



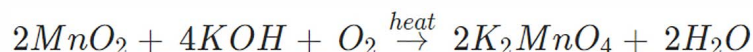
Potassium chloride being less soluble than sodium chloride is obtained in the form of orange coloured crystals and can be removed by filtration.

The dichromate ion  $Cr_2O_7^{2-}$  exists in equilibrium with chromate ion  $CrO_4^{2-}$  at pH 4.

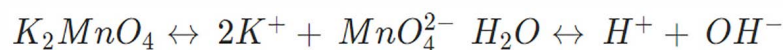
However, by changing the pH, they can be interconverted.



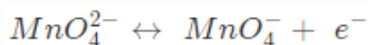
(ii) Potassium permanganate (  $KMnO_4$  ) can be prepared from pyrolusite ( $MnO_2$ ). The ore is fused with KOH in the presence of either atmospheric oxygen or an oxidising agent, such as  $KNO_3$  or  $KClO_4$ , to give  $K_2MnO_4$ .



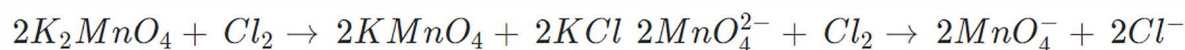
The green mass can be extracted with water and then oxidized either electrolytically or by passing chlorine/ozone into the solution. Electrolytic oxidation



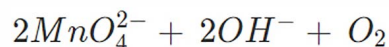
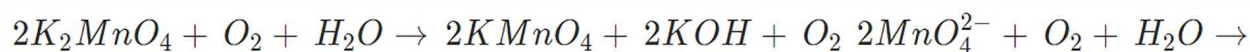
At anode, manganate ions are oxidized to permanganate ions.



Oxidation by chlorine



Oxidation by ozone



**Question 8.27:**

**What are alloys? Name an important alloy which contains some of the lanthanoid metals. Mention its uses.**

**Ans :**

An alloy is a solid solution of two or more elements in a metallic matrix. It can be a partial solid solution or a complete solid solution. Alloys generally are created as they have varied properties compared to their constituent elements. An important alloy of lanthanoids is Mischmetal. It contains lanthanoids (94–95%), iron (5%), and traces of Al, Ca, Si, C, S.

Uses

- (a) It is used in tracer bullets and shells.
- (b) Mischmetal is used in cigarettes and gas lighters.
- (c) It is used in flame-throwing tanks.

**Question 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.**

**Ans :**

Inner transition metals : elements in which the last electron enters the f-orbital.

The elements in which the 4f and the 5f orbitals are progressively filled are called f-block elements.

From the given atomic numbers, the inner transition elements are the ones with atomic numbers 59, 95, and 102.

**Q 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.**

**Ans :**

Lanthanoids project 3 oxidation states (+2, +3, +4). From these, +3 state is the most common.

Lanthanoids display a limited number of oxidation states because the energy difference between 4f, 5d, and 6s orbital's is quite large. While, the energy difference between 5f, 6d, and 7s orbital's is very less. Hence, actinoids display a large number of oxidation states.

For example, neptunium displays +3, +4, +5, and +7 while uranium and plutonium display +3, +4, +5, and +6 oxidation states. The most common oxidation state in case of actinoids is also +3.

**Q 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.**

**Ans :**

In the actinoid series, the last element is lawrencium, Lr. The atomic number of the element is 103 and its electronic configuration is  $[Rn] 5f^{14} 6d^1 7s^2$ . The most common oxidation state displayed by it is +3; because after losing 3 electrons it attains stable  $f^{14}$  configuration.

**Q 8.31:**

**Use Hund's rule to derive the electronic configuration of  $Ce^{3+}$  ion, and calculate its magnetic moment on the basis of 'spin-only' formula.**

**Ans :**



Magnetic moment can be calculated as:

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

Where,

n = number of unpaired electrons

In Ce, n = 2

$$\nu = \sqrt{2(2+2)} = \sqrt{2 \times 4} = \sqrt{2 \times 4} = 2\sqrt{2}$$

$$= 2.828 \text{ BM}$$

**Q 8.32:**

**Name the members of the lanthanoid series which exhibit +4 oxidation states and those which exhibit +2 oxidation states. Try to correlate this type of behaviour with the electronic configurations of these elements.**

**Ans :**

| +2      | +4      |
|---------|---------|
| Nd(60)  | Ce (58) |
| Sm(62)  | Pr (59) |
| Eu (63) | Nd (60) |
| Tm(69)  | Tb (65) |
| Yb (70) | Dy (66) |

In the parenthesis are the atomic numbers of the elements are given.

Tb after forming  $Tb^{4+}$  attains a stable electronic configuration of  $[Xe] 4f^7$ .

Yb after forming  $Yb^{2+}$  attains a stable electronic configuration of  $[Xe] 4f^{14}$ .

Eu after forming  $Eu^{2+}$  attains a stable electronic configuration of  $[Xe] 4f^7$ .

Ce after forming  $Ce^{4+}$  attains a stable electronic configuration of  $[Xe]$ .

**Q 8.33:**

**Compare the chemistry of the actinoids with that of lanthanoids with reference to:**

**(i) electronic configuration (ii) oxidation states and (iii) chemical reactivity**

**Ans :**

Chemical reactivity

In the lanthanide series, the earlier members of the series are more reactive. They have reactivity that is comparable to Ca. With an increase in the atomic number, the lanthanides start behaving similar to Al. Actinoids, on the other hand, are highly reactive metals, especially when they are finely divided. When they are added to boiling water, they give a mixture of oxide and hydride. Actinoids combine with most of the

non-metals at moderate temperatures. Alkalies have no action on these actinoids. In the case of acids, they are slightly affected by nitric acid (because of the formation of a protective oxide layer).

### Electronic configuration

The general electronic configuration for lanthanoids is  $[\text{Xe}]5d^{0-1} 4f^{0-14} 6s^2$  and that for actinoids is  $[\text{Rn}]5d^{0-1} 5f^{0-14} 7s^2$ . Unlike 4f orbitals, 5f orbitals are not deeply buried and participate in bonding to a greater extent.

### Oxidation states

The principal oxidation state of lanthanoids is (+3). However, sometimes we also encounter oxidation states of +2 and +4. This is because of the extra stability of fully-filled and half-filled orbitals. Actinoids exhibit a greater range of oxidation states. This is because the 5f, 6d, and 7s levels are of comparable energies. Again, (+3) is the principal oxidation state for actinoids. Actinoids such as lanthanoids have more compounds in +3 state than in +4 state.

### **Q 8.34 :**

**Write the electronic configurations of the elements with the atomic numbers 61, 91, 101, and 109.**

**Ans :**

| Atomic number | Electronic configuration       |
|---------------|--------------------------------|
| 61            | $[\text{Xe}]5d^1 4f^9 6s^2$    |
| 91            | $[\text{Rn}]5d^1 5f^9 7s^2$    |
| 101           | $[\text{Rn}]5d^1 5f^{13} 7s^2$ |
| 109           | $[\text{Rn}]5d^1 5f^{14} 7s^2$ |

### **Q 8.35:**

**Compare the general characteristics of the first series of the transition metals with those of the second and third series metals in the respective vertical columns. Give special emphasis on the following points:**

**(i) electronic configurations (ii) oxidation states (iii) ionisation enthalpies and (iv) atomic sizes**

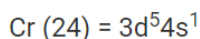
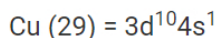
**Ans :**

(i) In the 1st, 2nd and 3rd transition series,

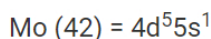
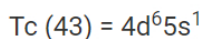
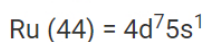
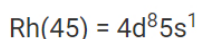
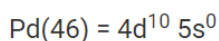
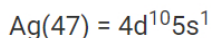
the 3d, 4d, and 5d orbitals are respectively filled. We know that elements in the same vertical column generally have similar electronic configurations.

In the first transition series,

two elements show unusual electronic configurations:

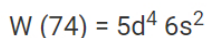
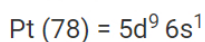
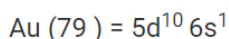


Similarly, there are exceptions in the second transition series. These are:





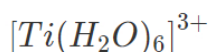
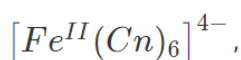
There are some exceptions in the third transition series as well. These are:



As a result of these exceptions, it happens many times that the electronic configurations of the elements present in the same group are dissimilar.

(ii) In each of the three transition series the number of oxidation states shown by the elements is the maximum in the middle and the minimum at the extreme ends. However, +2 and +3 oxidation states are quite stable for all elements present in the first transition series. All metals present in the first transition series form stable compounds in the +2 and +3 oxidation states. The stability of the +2 and +3 oxidation states decreases in the second and the third transition series, wherein higher oxidation states are more important.

Some stable complexes are :



The issue is that no such complexes are known for the second and third transition series such as Mo, W, Rh, In. They form complexes in which their oxidation states are high.

For example:  $\text{WCl}_6$ ,  $\text{ReF}_7$ ,  $\text{RuO}_4$ , etc.

(iii) In each of the three transition series, the first ionisation enthalpy increases from left to right. However, there are some exceptions. The first ionisation enthalpies of the third transition series are higher than those of the first and second transition series. This occurs due to the poor shielding effect of 4f electrons in the third transition series. Certain elements in the second transition series have higher first ionisation enthalpies than elements corresponding to the same vertical column in the first transition series. There are also elements in the 2nd transition series whose first ionisation enthalpies are lower than those of the elements corresponding to the same vertical column in the 1<sup>st</sup> transition series.

(iv) Atomic size generally decreases from left to right across a period. Now, among the three transition series, atomic sizes of the elements in the second transition series are greater than those of the elements corresponding to the same vertical column in the first transition series. However, the atomic sizes of the elements in the third transition series are virtually the same as those of the corresponding members in the second transition series. This is due to lanthanoid contraction.

#### Q 8.36:

**Write down the number of 3d electrons in each of the following ions:**

**Ti<sup>2+</sup>, V<sup>2+</sup>, Cr<sup>3+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup>.**

**Indicate how would you expect the five 3d orbitals to be occupied for these hydrated ions (octahedral).**

**Ans :**

| Metal ion        | Number of d-electrons | Filling of d-orbitals |
|------------------|-----------------------|-----------------------|
| Cu <sup>2+</sup> | 9                     | $t_{2g}^6 e_g^3$      |
| Ni <sup>2+</sup> | 8                     | $t_{2g}^6 e_g^2$      |



|                              |   |                  |
|------------------------------|---|------------------|
| CO <sub>2</sub> <sup>+</sup> | 7 | $t_{2g}^5 e_g^2$ |
| Fe <sup>3+</sup>             | 5 | $t_{2g}^3 e_g^2$ |
| Fe <sup>2+</sup>             | 6 | $t_{2g}^4 e_g^2$ |
| Mn <sup>2+</sup>             | 5 | $t_{2g}^3 e_g^2$ |
| Cr <sup>3+</sup>             | 3 | $t_{2g}^3$       |
| V <sup>2+</sup>              | 3 | $t_{2g}^3$       |
| Ti <sup>2+</sup>             | 2 | $t_{2g}^2$       |

**Q 8.37:**

**Comment on the statement that elements of the first transition series possess many properties different from those of heavier transition elements.**

**Ans :**

In many ways, the properties of elements of heavier transition elements differ from those of the first transition series.

- The elements of the first transition series form low-spin or high-spin complexes depending upon the strength of the ligand field. However, the heavier transition elements form only low-spin complexes, irrespective of the strength of the ligand field.
- The enthalpies of atomisation of the elements in the first transition series are lower than those of the corresponding elements in the second and third transition series.
- The melting and boiling points of the first transition series are lower than those of the heavier transition elements. This is because of the occurrence of stronger metallic bonding (M-M bonding).
- For heavier elements, the higher oxidation states are more common whereas for first transition series elements the +2 and +3 oxidation states are more common.
- The atomic sizes of the elements of the first transition series are smaller than those of the heavier elements (elements of 2nd and 3rd transition series). However, the atomic sizes of the elements in the third transition series are virtually the same as those of the corresponding members in the second transition series. This is due to lanthanoid contraction.

**Q 8.38:**

**What can be inferred from the magnetic moment values of the following complex species?**

**Example            Magnetic Moment (BM)**

**K<sub>4</sub>[Mn(CN)<sub>6</sub>]    2.2**

**[Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>    5.3**

**K<sub>2</sub>[MnCl<sub>4</sub>]        5.9**

**Ans :**

Magnetic moment (  $\nu = \sqrt{n(n+2)}$  )

For value n = 1,  $\nu = \sqrt{1(1+2)} = \sqrt{3} = 1.732$

For value  $n = 2$ ,  $\nu = \sqrt{2(2 + 2)} = \sqrt{8} = 2.83$

For value  $n = 3$ ,  $\nu = \sqrt{3(3 + 2)} = \sqrt{15} = 3.87$

For value  $n = 4$ ,  $\nu = \sqrt{4(4 + 2)} = \sqrt{24} = 4.899$

For value  $n = 5$ ,  $\nu = \sqrt{5(5 + 2)} = \sqrt{35} = 5.92$

$$K_2[MnCl_4] \quad \sqrt{n(n + 2)} = 2.2$$

What we could see from the calculation above is that  $n=5$  would be the closest value given to the term. Here the +2 oxidation state in the complex is Mn. This would mean that in the d-orbital, the Mn has 5 electrons.

Hence, we can say that  $Cl^-$  is a weak field ligand and does not cause the pairing of electrons.

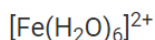
$$K_4[Mn(CN)_6] \quad \sqrt{n(n + 2)} = 2.2$$

For in transition **metals**, the magnetic moment is calculated from the spin-only formula.

Therefore,

We can see from the above calculation that the given value is closest to  $n = 1$ . Also, in this complex, Mn is in the +2 oxidation state. This means that Mn has 5 electrons in the d-orbital.

Hence, we can say that  $CN^-$  is a strong field ligand that causes the pairing of electrons.



$$\sqrt{n(n + 2)} = 5.3$$

Thus the calculation given above proves that the closest value to  $n=4$ . In addition to this, the +2 oxidation state in this complex is none other than Fe. The d-orbital for Fe would have 6 electrons.