

Chapter 8

The d- and f- Block Elements

1 Marks Questions

1. Zinc, cadmium and mercury are not considered as transition metals. Why?

Ans. Zinc, cadmium and mercury have fully filled d^{10} configuration. Therefore they are not considered as transition metal.

2. Write the general configuration of d- block elements.

Ans. General electronic configuration of d- block elements is $(n-1)d^{1-10}ns^{1-2}$.

3. What are the factors that decide the ionization potential?

Ans. The ionization potential values are governed by various ionization enthalpy values, bond enthalpy values and hydration enthalpy values.

4. What are interstitial compounds. Give two examples

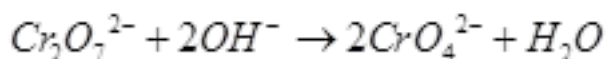
Ans. Compounds formed by trapping small atoms like H, C, or N inside the crystal lattices of metals eg. TiC, Mn_4N etc.

5. What is the ore of $K_2Cr_2O_7$ and $KMnO_4$?

Ans. Potassium dichromate \rightarrow chromite ore ($FeCr_2O_4$) Potassium Permanganate \rightarrow MnO_2 pyrolusite.

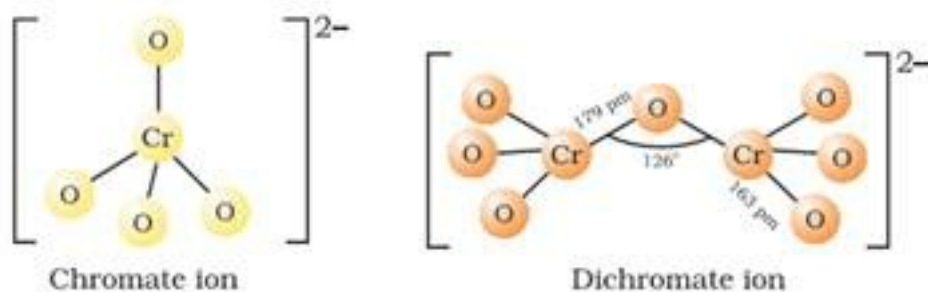
6. What is the effect of adding a base to potassium dichromate?

Ans. When a base is added to orange coloured potassium dichromate its colour changes to yellow due to formation of potassium chromate.



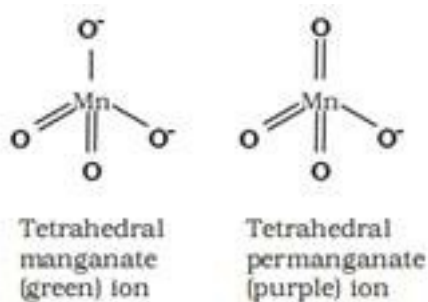
7. Draw the structure of chromate and dichromate ions?

Ans.

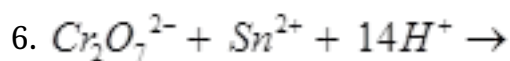
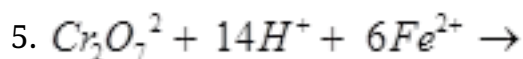
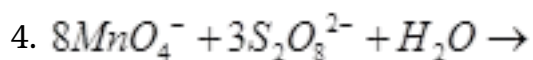
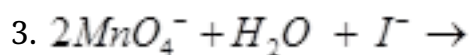
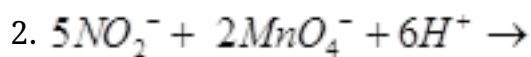
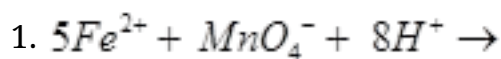


8. Draw the structure of manganate and permanganate ions?

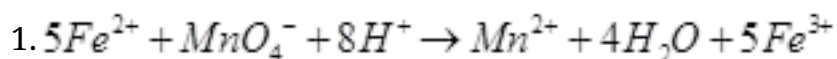
Ans.

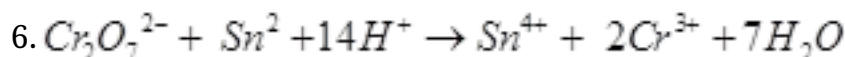
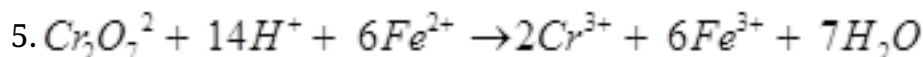
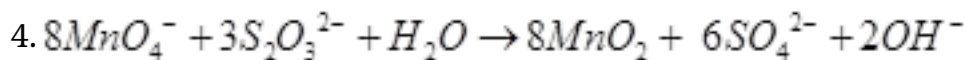
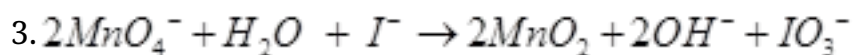
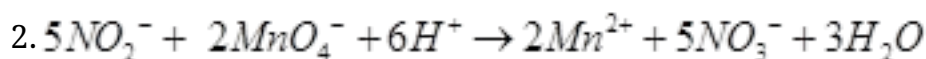


9. Complete and balance:-



Ans.





10. Name the two series of f-block.

Ans. The two series are-

i) 4f series or Lanthanoids ii) 5f series or actinoids.

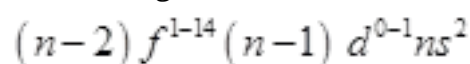
11. The chemistry of actinoids is more complicated than lanthanoids. Why?

Ans. The complications in the actinoid series is due to

i) Existence of a wide range of oxidation states. ii) Their radioactivity.

12. What is the general valence configuration of f-block elements?

Ans. The general electronic configuration of f-block elements is



13. What is the most common oxidation state of lanthanoids and actinoids?

Ans. The common oxidation states of

(1) 4f series is +3

(2) 5f series is +3, +4, +5, +6 & +7

14. Actinoid contraction is more than lanthanoid contraction. Give reason.

Ans. The actinoid contraction is more than Lanthanoid contraction as the shielding

Power of 5f orbitals is poorer than 4f orbitals.

15. What is the composition of mischmetall? Give its one use.

Ans. Mischmetall is an alloy of a Lanthanoid metal and iron and traces of S, C, Ca &

Al. It is used in Magnesium based alloy to produce bullets, shell and lighter Flint.

16. Actinoids show larger number of oxidation states than lanthanoids. Why?

Ans. Actinoids can show many oxidation states as in actinoids 5f orbitals are filled which are not as buried as Lanthnoids and can also participate in bonding to a greater extent besides 6d and 7s electrons.

2 Marks Questions

1. Give an explanation for the catalytic properties shown by transition metals.

Ans. Catalytic properties shown by transition metals can be explained due to

- (i) Presence of variable valency and ability of elements to form complexes.
- (ii) Surface of metals where the reaction can occur.

2. Write some characteristics of interstitial compounds.

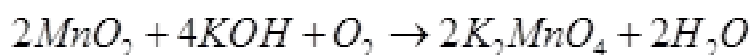
Ans. Some characteristics of interstitial compounds are

- (i) They have high melting points.
- (ii) They are very hard.
- (iii) They retain metallic lusture.
- (iv) They are chemically inert.

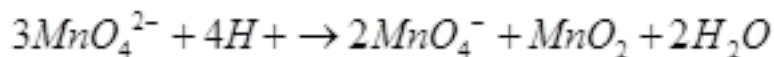
3. Describe the steps of preparation of $KMnO_4$?

Ans. Potassium Permanganate is prepared in two steps:

Step 1: Fusion of MnO_2 with KOH and oxidizing agent to give dark green K_2MnO_4 .



Step 2: Disproportionation of manganate ions to give permanganate ions.



4. Give some of the uses of $KMnO_4$?

Ans. Uses of potassium permanganate –

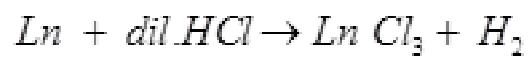
- (a) As an oxidizing agent.
- (b) For bleaching of wool, cotton & silk.
- (c) For decolourisation of oils.

5. What happens when

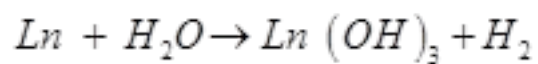
(a) A lanthanoid reacts with dil- acid

(b) A lanthanoid reacts with water.

Ans. (i) When a Lanthanoid reacts with dil- acid, it liberate hydrogen gas.



(ii) When a Lanthanoid reacts with water, it forms hydroxide.



3 Marks Questions

1. Transition metals generally form coloured ions. Why? Which of the following will be colored? Sc^{3+} , V^{2+} , Mn^{2+} , Cu^{+} , Ni^{2+} .

Ans. Transition metals form coloured ions due to d-d transition. Coloured ions will be those which have unpaired electrons.

Sc^{3+}	$3d^0$	Colourless
V^{2+}	$3d^3$	Coloured
Mn^{2+}	$3d^5$	Coloured
Cu^{+}	$3d^{10}$	Colourless
Ni^{2+}	$3d^8$	Coloured.

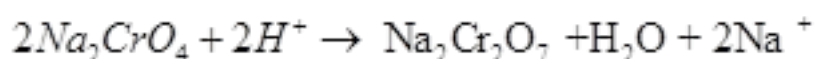
2. Explain the steps of preparation of potassium dichromate?

Ans. Preparation of potassium dichromate takes place in three steps.

Step 1: Fusion of chromite ore with sodium or potassium carbonate in free excess of air.



Step 2: Conversion of Sodium Chromate to Sodium Dichromate by acidifying it.



Step 3: Conversion of sodium dichromate to potassium dichromate by reaching it with KCl.



3. What is the lanthanoid contraction? What are its causes and consequences?

Ans. Lanthanoid contractions – The cumulative effect of the regular decrease in size or radii of Lanthanoid with increase in atomic number is called Lanthanoid contraction.

Causes - The shape of f orbitals is diffused. They have poor shielding effect due to which the effective nuclear charge increase with increase in atomic number. This causes a decrease in atomic radii

Consequences – Due to Lanthanoid contraction-

1. Radii of the members of the third transition series is similar to those of second transition series.
2. It becomes difficult to separate Lanthanoids.

5 Marks Questions

1. Give reasons-

- (i) Transition metals have high melting points.
- (ii) Second and third transition series have similar radii.
- (iii) Second ionization is difficult from Cu and Cr whereas it is easy for Zn.
- (iv) Most of the transition elements are paramagnetic.
- (v) Transition elements form alloys.

Ans.(i) In transition metals besides ns electrons, $(n-1)d$ electrons can also participate in bonding making stronger metallic bonds. This increases their melting points.

(ii) Due to lanthanoid contraction, there is a decrease in size of 5d series. This makes their sizes same as sizes of elements of 4d series.

(iii) In Cr the electronic configuration is $3d^5 4s^1$ and for Cu, it is $3d^{10} 4s^1$. In these after first ionization, which removes the electron from 4s, second ionization requires disturbance in half filled or fully filled configuration which requires high enthalpy whereas the configuration of Zn is $3d^{10} 4s^2$. Here after second ionization, the configuration of Zn is completely filled. Therefore second ionization is easier for Zn but difficult for Cr and Cu.

(iv) Para magnetism in transition elements arises due to presence of one or more unpaired electrons in atomic orbitals.

(v) Due to similarity in their sizes, transition metals can take each others position in their crystal lattice. Therefore they are able to form alloys.

2. Silver atom has completely filled d orbitals ($4d^{10}$) in its ground state. How can you say that it is a transition element?

Ans. Ag has a completely filled $4d$ orbital ($4d^{10} 5s^1$) in its ground state. Now, silver displays two oxidation states (+1 and +2). In the +1 oxidation state, an electron is removed from the s -orbital. However, in the +2 oxidation state, an electron is removed from the d -orbital. Thus, the d -orbital now becomes incomplete ($4d^9$). Hence, it is a transition element.

3. In the series Sc (Z = 21) to Zn (Z = 30), the enthalpy of atomization of zinc is the lowest, i.e., 126kJ mol^{-1} . Why?

Ans. The extent of metallic bonding an element undergoes decides the enthalpy of atomization. The more extensive the metallic bonding of an element, the more will be its enthalpy of atomization. In all transition metals (except Zn, electronic configuration: $3d^{10} 4s^2$), there are some unpaired electrons that account for their stronger metallic bonding. Due to the absence of these unpaired electrons, the inter-atomic electronic bonding is the weakest in Zn and as a result, it has the least enthalpy of atomization.

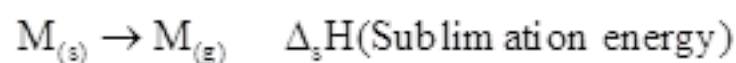
4. Which of the 3d series of the transition metals exhibits the largest number of oxidation states and why?

Ans. Mn (Z = 25) = $3d^5 4s^2$ Mn has the maximum number of unpaired electrons present in the d-subshell (5 electrons). Hence, Mn exhibits the largest number of oxidation states, ranging from +2 to +7.

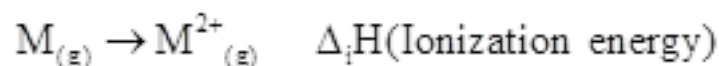
5. The $E^\ominus(M^{2+} / M)$ value for copper is positive (+0.34V). What is possibly the reason for this? (Hint: consider its high $\Delta_s H^\ominus$ and low $\Delta_{\text{hyd}} H^\ominus$)

Ans. The $E^\ominus(M^{2+} / M)$ value of a metal depends on the energy changes involved in the following:

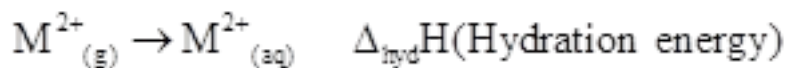
1. Sublimation: The energy required for converting one mole of an atom from the solid state to the gaseous state.



2. Ionization: The energy required to take out electrons from one mole of atoms in the gaseous state.



3. Hydration: The energy released when one mole of ions are hydrated.



Now, copper has a high energy of atomization and low hydration energy. Hence, the $E^\ominus(M^{2+}/M)$ value for copper is positive.

6. How would you account for the irregular variation of ionization enthalpies (first and second) in the first series of the transition elements?

Ans. Ionization enthalpies are found to increase in the given series due to a continuous filling of the inner d -orbitals. The irregular variations of ionization enthalpies can be attributed to the extra stability of configurations such as d^0 , d^5 , d^{10} . Since these states are exceptionally stable, their ionization enthalpies are very high.

In case of first ionization energy, Cr has low ionization energy. This is because after losing one electron, it attains the stable configuration ($3d^5$). On the other hand, Zn has exceptionally high first ionization energy as an electron has to be removed from stable and fully-filled orbitals ($3d^{10} 4s^2$).

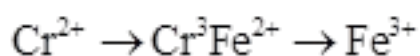
Second ionization energies are higher than the first since it becomes difficult to remove an electron when an electron has already been taken out. Also, elements like Cr and Cu have exceptionally high second ionization energies as after losing the first electron, they have attained the stable configuration ($Cr^+ : 3d^5$ and $Cu^+ : 3d^{10}$). Hence, taking out one electron more from this stable configuration will require a lot of energy.

7. Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only?

Ans. Both oxide and fluoride ions are highly electronegative and have a very small size. Due to these properties, they are able to oxidize the metal to its highest oxidation state.

8. Which is a stronger reducing agent Cr^{2+} or Fe^{2+} and why?

Ans. The following reactions are involved when Cr^{2+} and Fe^{2+} act as reducing agents.



The $E^\ominus_{Cr^{3+}/Cr^{2+}}$ value is - 0.41 V and $E^\ominus_{Fe^{3+}/Fe^{2+}}$ is +0.77 V. This means that Cr^{2+} can be easily oxidized to Cr^{3+} , but Fe^{2+} does not get oxidized to Fe^{3+} easily. Therefore, Cr^{2+} is a better reducing agent than Fe^{2+} .

9. Calculate the 'spin only' magnetic moment of $M_{(aq)}^{2+}$ ion ($Z = 27$).

Ans. $Z = 27$



Therefore, $M^{2+} = [Ar]3d^7$



i.e., 3 unpaired electrons

Therefore, $n = 3$

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

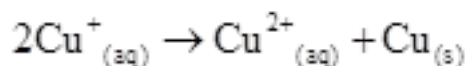
$$= \sqrt{3(3+2)} = \mu$$

$$= \sqrt{15} = \mu$$

$$\mu \approx 4BM$$

10. Explain why Cu^+ ion is not stable in aqueous solutions?

Ans. In an aqueous medium, Cu^{2+} is more stable than Cu^+ . This is because although energy is required to remove one electron from Cu^+ to Cu^{2+} , high hydration energy of Cu^{2+} compensates for it. Therefore, Cu^+ ion in an aqueous solution is unstable. It disproportionates to give Cu^{2+} and Cu.



11. Actinoid contraction is greater from element to element than lanthanoid contraction. Why?

Ans. In actinoids, 5f orbitals are filled. These 5f orbitals have a poorer shielding effect than 4f orbitals (in lanthanoids). Thus, the effective nuclear charge experienced by electrons in valence shells in case of actinoids is much more than that experienced by lanthanoids. Hence, the size contraction in actinoids is greater as compared to that in lanthanoids.

12. Write down the electronic configuration of:

(i) Cr^{3+} + (iii) Cu^+ (v) Co^{2+} (vii) Mn^{2+}

(ii) Pm^{3+} (iv) Ce^{4+} (vi) Lu^{2+} (viii) 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, $[\text{Ar}]^{18} d^7$

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

13. Why are Mn^{2+} compounds more stable than Fe^{2+} towards oxidation to their +3 state?

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

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

It is known that half-filled and fully-filled orbitals are more stable. Therefore, Mn in (+2) state has a stable d^5 configuration. This is the reason Mn^{2+} shows resistance to oxidation to Mn^{3+} . Also, Fe^{2+} has

$3d^6$ configuration and by losing one electron, its configuration changes to a more stable $3d^5$ configuration. Therefore, Fe^{2+} easily gets oxidized to Fe^{+3} oxidation state.

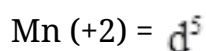
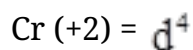
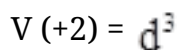
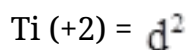
14. Explain briefly how +2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number?

Ans. The oxidation states displayed by the first half of the first row of transition metals are given in the table below.

	Sc	Ti	V	Cr	Mn
Oxidation state		+ 2	+ 2	+ 2	+ 2
	+3	+ 3	+ 3	+ 3	+ 3
		+ 4	+ 4	+ 4	+ 4
			+ 5	+ 5	+ 6
				+ 6	+ 7

It can be easily observed that except Sc, all others metals display +2 oxidation state. Also, on moving from Sc to Mn, the atomic number increases from 21 to 25. This means the number of electrons in the 3d-orbital also increases from 1 to 5.

Sc (+2) = d^1



+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).

15. 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 elements in the first-half of the transition series exhibit many oxidation states with Mn exhibiting maximum number of oxidation states (+2 to +7). The stability of +2 oxidation state increases with the increase in atomic number. This happens as more electrons are getting filled in the *d*-orbital. However, Sc does not show +2 oxidation state. Its electronic configuration is $4s^2 3d^1$. It loses all the three electrons to form 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, $[Ar]3d^5$.

16. 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.

17. 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.(i) Vanadate, VO_3^-

Oxidation state of V is + 5.

(ii) Chromate, CrO_4^{2-}

Oxidation state of Cr is + 6.

(iii) Permanganate, MnO_4^-

Oxidation state of Mn is + 7.

18. What is lanthanoid contraction? What are the consequences of lanthanoid contraction?

Ans.As we move along the lanthanoid series, the atomic number increases gradually by one. This means that the number of electrons and protons present in an atom also increases by one. As electrons are being added to the same shell, the effective nuclear charge increases. This happens because the increase in nuclear attraction due to the addition of proton is more pronounced than the increase in the interelectronic repulsions due to the addition of electron. Also, with the increase in 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 the increase in the atomic number. This is termed as lanthanoid contraction.

Consequences of lanthanoid contraction

(i) There is similarity in the properties of second and third transition series.

(ii) Separation of lanthanoids is possible due to lanthanide contraction.

(iii) It is due to lanthanide contraction that there is variation in the basic strength of lanthanide hydroxides. (Basic strength decreases from $\text{La}(\text{OH})_3$ to $\text{Lu}(\text{OH})_3$)

19. 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 lie in the d -block and show a transition of properties between s -block and p -block. Therefore, these are called transition elements.

Elements such as Zn, Cd, and Hg cannot be classified as transition elements because these have completely filled d -subshell.

20. 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. Therefore, 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^2np^{1-6} .

21. What are the different oxidation states exhibited by the lanthanoids?

Ans. In the lanthanide series, +3 oxidation state is most common i.e., Ln(III) compounds are predominant. However, +2 and +4 oxidation states can also be found in the solution or in solid compounds.

22. Explain giving reasons:

(i) Transition metals and many of their compounds show paramagnetic behaviour.

(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) 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.

(ii) 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.

(iii) 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.

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

(a) 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.

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

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

Ans. Transition metals are large in size and contain lots of interstitial sites. Transition elements can trap atoms of other elements (that have small atomic size), such as H, C, N, in

the interstitial sites of their crystal lattices. The resulting compounds are called interstitial compounds.

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

Ans. In 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 (Fe^{2+} and Fe^{3+} ; Cu^+ and Cu^{2+}). In non-transition elements, the oxidation states differ by 2, for example, +2 and +4 or +3 and +5, etc.

25. Describe the preparation of potassium dichromate from iron chromite ore.

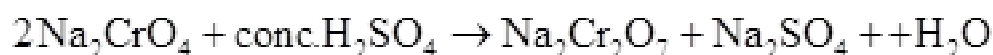
What is the effect of increasing pH on a solution of potassium dichromate?

Ans. Potassium dichromate 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

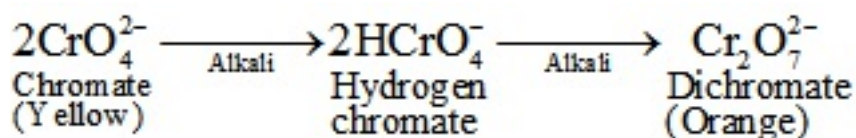


Step(3): Conversion of sodium dichromate to potassium dichromate



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

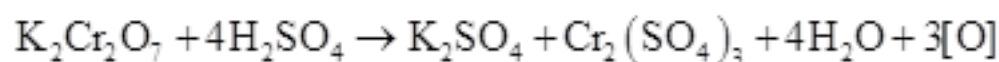
The dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) exists in equilibrium with chromate (CrO_4^{2-}) ion at pH 4. However, by changing the pH, they can be interconverted.



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

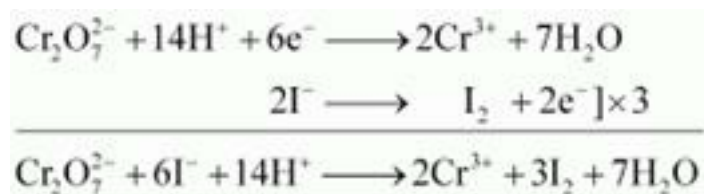
(i) iodide (ii) iron(II) solution and (iii) H_2S

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

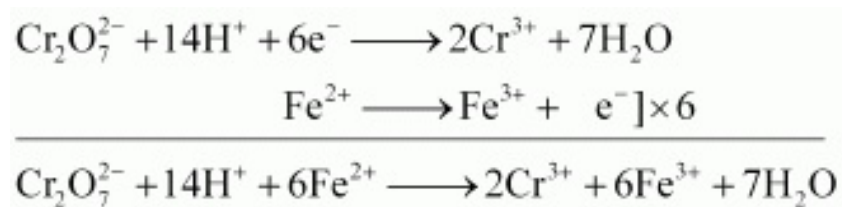


$\text{K}_2\text{Cr}_2\text{O}_7$ takes up electrons to get reduced and acts as an oxidising agent. The reaction of $\text{K}_2\text{Cr}_2\text{O}_7$ with other iodide, iron (II) solution, and H_2S are given below.

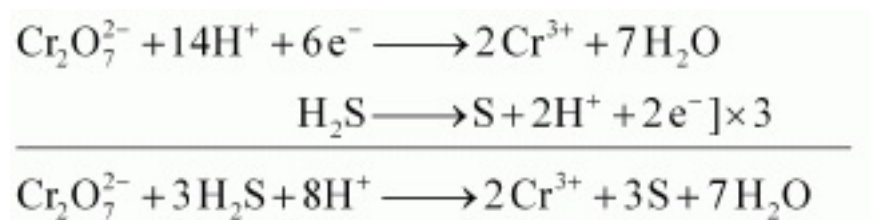
(i) $\text{K}_2\text{Cr}_2\text{O}_7$ oxidizes iodide to iodine.



(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.

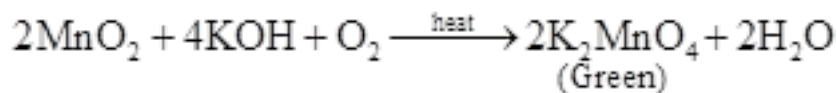


(iii) $\text{K}_2\text{Cr}_2\text{O}_7$ oxidizes H_2S to sulphur.



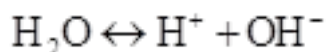
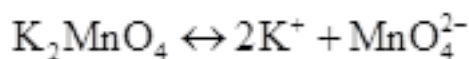
27. Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with (i) iron (II) ions (ii) SO_2 and (iii) oxalic acid? Write the ionic equations for the reactions.

Ans. Potassium permanganate 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 .

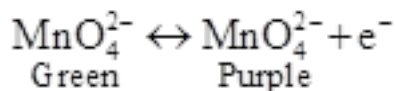


The green mass can be extracted with water and then oxidized either electrolytically or by passing chlorine/ozone into the solution.

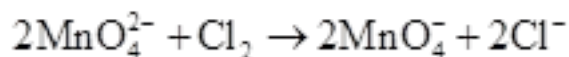
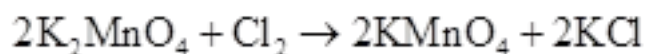
Electrolytic oxidation



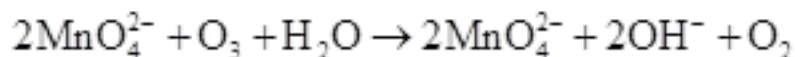
At anode, manganate ions are oxidized to permanganate ions.



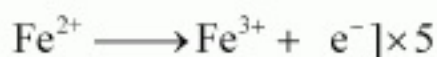
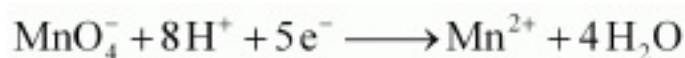
Oxidation by chlorine



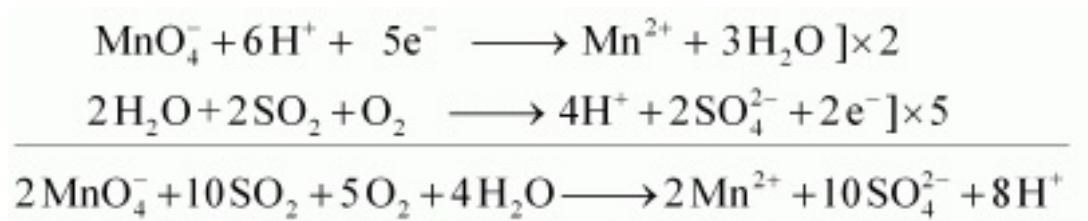
Oxidation by ozone



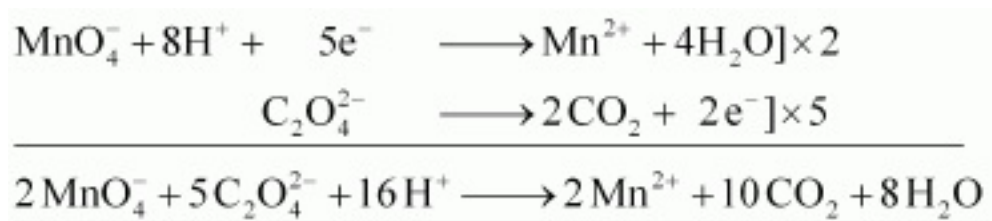
(i) Acidified KMnO_4 solution oxidizes Fe (II) ions to Fe (III) ions i.e., ferrous ions to ferric ions.



(ii) Acidified potassium permanganate oxidizes SO_2 to sulphuric acid.



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



28. For M^{2+} / M and $\text{M}^{3+} / \text{M}^{2+}$ systems, the E^\ominus values for some metals are as follows:

$$\text{Cr}^{2+} / \text{Cr} - 0.9\text{V}$$

$$\text{Cr}^{3+} / \text{Cr}^{2+} - 0.4\text{V}$$

$$\text{Mn}^{2+} / \text{Mn} - 1.2\text{V}$$

$$\text{Mn}^{3+} / \text{Mn}^{2+} + 1.5\text{V}$$

$$\text{Fe}^{2+} / \text{Fe} - 0.4\text{V}$$

$$\text{Fe}^{3+} / \text{Fe}^{2+} + 0.8\text{V}$$

Use this data to comment upon:

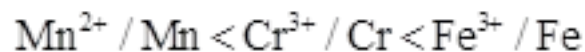
(i) The stability of Fe^{3+} in acid solution as compared to that of Cr^{3+} or Mn^{3+} and

(ii) The ease with which iron can be oxidised as compared to a similar process for either chromium or manganese metal.

Ans.(i) 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 Fe^{3+} to Fe^{2+} is easier than the reduction of

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

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



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

29. Predict which of the following will be coloured in aqueous solution?

Ti^{3+} , V^{3+} , Cu^+ , Sc^{3+} , Mn^{2+} , Fe^{3+} and Co^{2+} . Give reasons for each.

Ans. Only the ions that have electrons in *d*-orbital and in which d-d transition is possible will be coloured. The ions in which *d*-orbitals are empty or completely filled will be colourless as no d-d transition is possible in those configurations.

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

From the above table, it can be easily observed that only Sc^{3+} has an empty *d*-orbital and Cu^+ has completely filled *d*-orbitals. All other ions, except Sc^{3+} and Cu^+ , will be coloured in aqueous solution because of *d* - *d* transitions.

30. 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				

From the above table, it is evident that the maximum number of oxidation states is shown by Mn, varying from +2 to +7. The number of oxidation states increases on moving 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 from top to bottom, it becomes more and more difficult to remove the third electron from the *d*-orbital.

31. 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) 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 5*f*, 6*d*, and 7*s* 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.

(iii) 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 5*f* orbitals.

(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).

32. How would you account for the following:

(i) Of the d^4 species, 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 d^1 configuration is very unstable in ions.

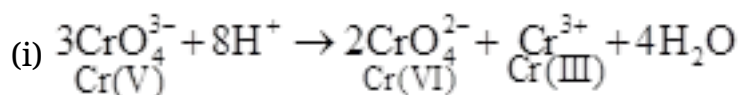
Ans.(i) Cr^{2+} is strongly reducing in nature. It has a d^4 configuration. While acting as a reducing agent, it gets oxidized to Cr^{3+} (electronic configuration, d^3). This d^3 configuration can be written as t_{2g}^3 configuration, which is a more stable configuration. In the case of $Mn^{3+} (d^4)$,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

half-filled d -orbital and is highly stable.

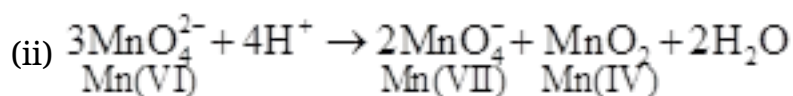
(ii) Co(II) is stable in aqueous solutions. However, in the presence of strong field complexing reagents, it is oxidized to Co (III). Although the 3rd ionization energy for Co is high, but the higher amount of crystal field stabilization energy (CFSE) released in the presence of strong field ligands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

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



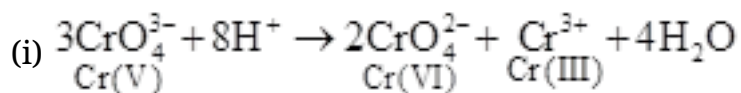
Cr(V) is oxidized to Cr(VI) and reduced to Cr(III).



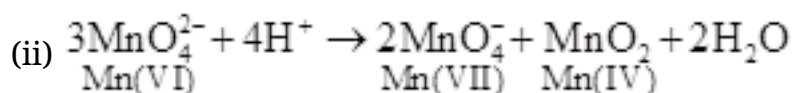
Mn (VI) is oxidized to Mn (VII) and reduced to Mn (IV).

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).

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

Ans. In the first transition series, Cu exhibits +1 oxidation state very frequently. It is because Cu (+1) has an electronic configuration of $[\text{Ar}]3d^{10}$. The completely filled d -orbital makes it highly stable.

35. 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
1	$\text{Mn}^{3+}, [\text{Ar}]3d^4$	4
2	$\text{Cr}^{3+}, [\text{Ar}]3d^3$	3
3	$\text{V}^{3+}, [\text{Ar}]3d^2$	2
4	$\text{Ti}^{3+}, [\text{Ar}]3d^1$	1

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

36. 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 in oxides and fluorides.

(iii) 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, $\text{Mn}^{\text{II}}\text{O}$ is basic and $\text{Mn}_2^{\text{VII}}\text{O}_7$ 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 MnO_4^- , the oxidation state of Mn is +7.

37. Indicate the steps in the preparation of:

(i) $\text{K}_2\text{Cr}_2\text{O}_7$ from chromite ore.

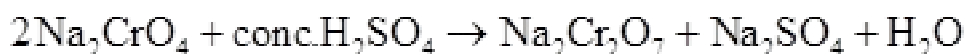
(ii) KMnO_4 from pyrolusite ore.

Ans.(i) Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) 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

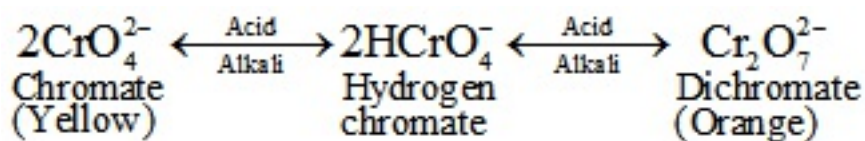


Step(3): Conversion of sodium dichromate to potassium dichromate

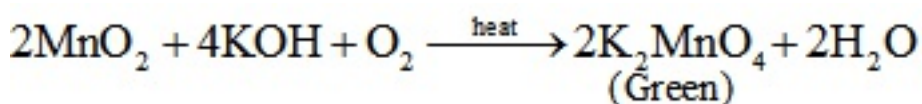


Potassium chloride being less soluble than sodium chloride is obtained in the form of orange coloured crystals and can be removed by filtration.

The dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) exists in equilibrium with chromate (CrO_4^{2-}) ion at pH 4. However, by changing the pH, they can be interconverted.

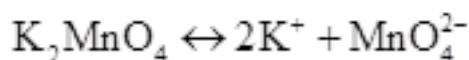


(ii) Potassium permanganate (KMnO_4) can be prepared from pyrolusite (MnO_2). The ore is fused with KOH in the presence of either atmospheric oxygen or an oxidising agent, such as KNO_3 or KClO_4 to give K_2MnO_4 .

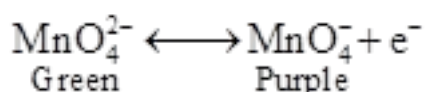


The green mass can be extracted with water and then oxidized either electrolytically or by passing chlorine/ozone into the solution.

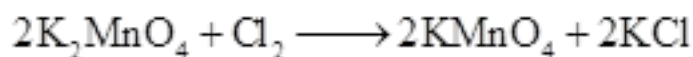
Electrolytic oxidation



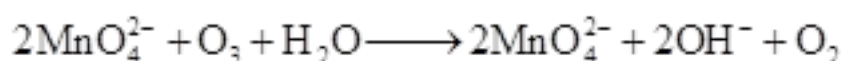
At anode, manganate ions are oxidized to permanganate ions.



Oxidation by chlorine



Oxidation by ozone



38. 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 either be a partial solid solution or a complete solid solution. Alloys are usually found to possess different physical properties than those of the component elements.

An important alloy of lanthanoids is Mischmetal. It contains lanthanoids (94-95%), iron (5%), and traces of S, C, Si, Ca, and Al.

Uses

(1) Mischmetal is used in cigarettes and gas lighters.

(2) It is used in flame throwing tanks.

(3) It is used in tracer bullets and shells.

39. 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 are those 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. Among the given atomic numbers, the atomic numbers of the inner transition elements are 59, 95, and 102.

40. 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 primarily show three oxidation states (+2, +3, +4). Among these oxidation states, +3 state is the most common. Lanthanoids display a limited number of oxidation states because the energy difference between $4f$, $5d$, and $6s$ orbitals is quite large. On the other hand, the energy difference between $5f$, $6d$, and $7s$ orbitals is very less. Hence, actinoids display a large number of oxidation states. For example, uranium and plutonium display +3, +4, +5, and +6 oxidation states while neptunium displays +3, +4, +5, and +7. The most common oxidation state in case of actinoids is also +3.

41. 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. The last element in the actinoid series is lawrencium, Lr. Its atomic number is 103 and its electronic configuration is $[Rn]5f^{14}6d^17s^2$. The most common oxidation state displayed by it is +3; because after losing 3 electrons it attains stable f^{14} configuration.