

**Question 8.1:**

Write down the electronic configuration of:

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

**(ii)**  $\text{Pm}^{3+}$  **(iv)**  $\text{Ce}^{4+}$  **(vi)**  $\text{Lu}^{2+}$  **(viii)**  $\text{Th}^{4+}$

Answer

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

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

**Question 8.2:**

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

Answer

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

Electronic configuration of  $\text{Fe}^{2+}$  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  $\text{Mn}^{2+}$  shows resistance to oxidation to  $\text{Mn}^{3+}$ . Also,  $\text{Fe}^{2+}$  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.

**Question 8.3:**

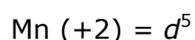
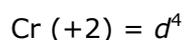
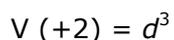
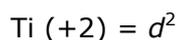
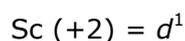
Explain briefly how +2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number?

Answer

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  |
|------------------------|----|-----|-----|-----|-----|
|                        |    | + 2 | + 2 | + 2 | + 2 |
|                        | +3 | + 3 | + 3 | + 3 | + 3 |
| <b>Oxidation state</b> |    | + 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.



+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).

**Question 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.

Answer

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]  $3d^5$ .

**Question 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  $3d^4$ ?

Answer

|       | 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. |

**Question 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.

Answer

(i) Vanadate,  $\text{VO}_3^-$

Oxidation state of V is + 5.

(ii) Chromate,  $\text{CrO}_4^{2-}$

Oxidation state of Cr is + 6.

(iii) Permanganate,  $\text{MnO}_4^-$

Oxidation state of Mn is + 7.

#### Question 8.7:

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

Answer

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  $\text{Lu}(\text{OH})_3$ .)

**Question 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?

Answer

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.

**Question 8.9:**

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

Answer

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  $ns^2 np^{1-6}$ .

**Question 8.10:**

What are the different oxidation states exhibited by the lanthanoids?

Answer

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.

**Question 8.11:**

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.

Answer

(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.

#### Question 8.12:

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

Answer

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.

**Question 8.13:**

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

Answer

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 ( $\text{Fe}^{2+}$  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.

**Question 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?

Answer

Potassium dichromate is prepared from chromite ore ( $\text{FeCr}_2\text{O}_4$ ) in the following steps.

**Step (1):** Preparation of sodium chromate



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

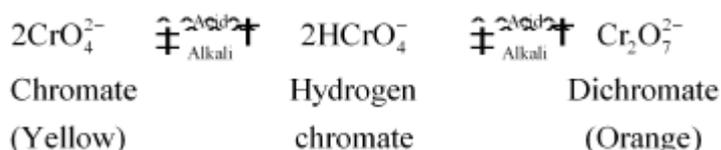


**Step(3):** Conversion of sodium dichromate to potassium dichromate



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 ( $\text{CrO}_4^{2-}$ ) ion at pH 4. However, by changing the pH, they can be interconverted.

**Question 8.15:**

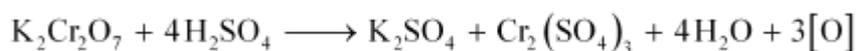


Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with:

(i) iodide (ii) iron(II) solution and (iii)  $\text{H}_2\text{S}$

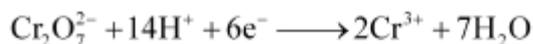
Answer

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

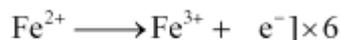
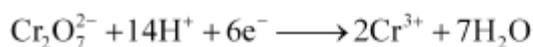


$\text{K}_2\text{Cr}_2\text{O}_7$  takes up electrons to get reduced and acts as an oxidising agent. The reaction of  $\text{K}_2\text{Cr}_2\text{O}_7$  with other iodide, iron (II) solution, and  $\text{H}_2\text{S}$  are given below.

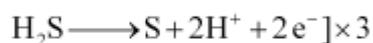
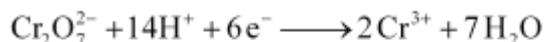
(i)  $\text{K}_2\text{Cr}_2\text{O}_7$  oxidizes iodide to iodine.



(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  $\text{H}_2\text{S}$  to sulphur.



#### Question 8.16:

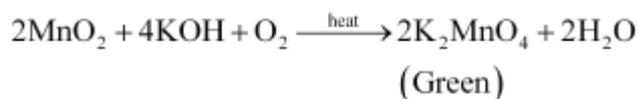
Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with (i) iron(II) ions (ii)  $\text{SO}_2$  and (iii) oxalic acid?

Write the ionic equations for the reactions.

Answer

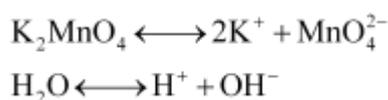


Potassium permanganate can be prepared from pyrolusite ( $\text{MnO}_2$ ). The ore is fused with KOH in the presence of either atmospheric oxygen or an oxidising agent, such as  $\text{KNO}_3$  or  $\text{KClO}_4$ , to give  $\text{K}_2\text{MnO}_4$ .

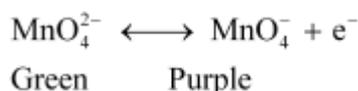


The green mass can be extracted with water and then oxidized either electrolytically or by passing chlorine/ozone into the solution.

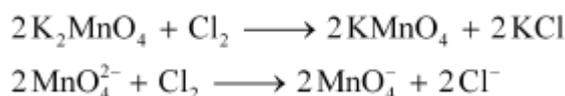
Electrolytic oxidation



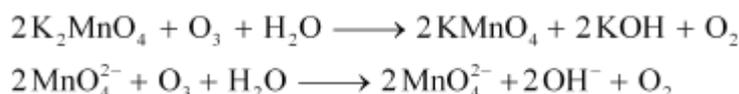
At anode, manganate ions are oxidized to permanganate ions.



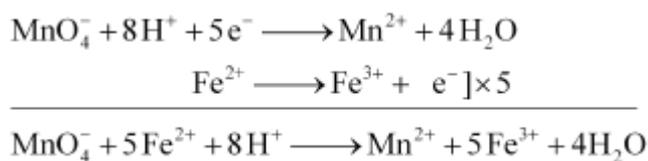
Oxidation by chlorine



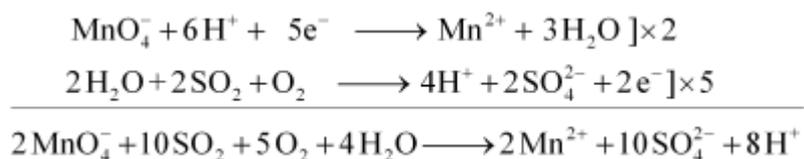
Oxidation by ozone



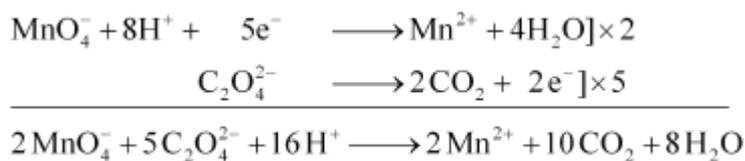
**(i)** Acidified  $\text{KMnO}_4$  solution oxidizes Fe (II) ions to Fe (III) ions i.e., ferrous ions to ferric ions.



**(ii)** Acidified potassium permanganate oxidizes  $\text{SO}_2$  to sulphuric acid.



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

**Question 8.17:**

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

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

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

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

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

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

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

Use this data to comment upon:

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

Answer

(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  $\text{Fe}^{3+}$  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:  $\text{Mn}^{3+} < \text{Fe}^{3+} < \text{Cr}^{3+}$

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

$$\text{Mn}^{2+}/\text{Mn} < \text{Cr}^{2+}/\text{Cr} < \text{Fe}^{2+}/\text{Fe}$$

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:  $\text{Fe} < \text{Cr} < \text{Mn}$

**Question 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.



Answer

Only the ions that have electrons in *d*-orbital will be coloured. The ions in which *d*-orbital is empty will be colourless.

| Element | Atomic Number | Ionic State      | Electronic configuration in ionic state |
|---------|---------------|------------------|---|
| Ti      | 22            | Ti <sup>3+</sup> | [Ar] 3d <sup>1</sup>                    |
| V       | 23            | V <sup>3+</sup>  | [Ar] 3d <sup>2</sup>                    |
| Cu      | 29            | Cu <sup>+</sup>  | [Ar] 3d <sup>10</sup>                   |
| Sc      | 21            | Sc <sup>3+</sup> | [Ar]                                    |
| Mn      | 25            | Mn <sup>2+</sup> | [Ar] 3d <sup>5</sup>                    |
| Fe      | 26            | Fe <sup>3+</sup> | [Ar] 3d <sup>5</sup>                    |
| Co      | 27            | Co <sup>2+</sup> | [Ar] 3d <sup>7</sup>                    |

From the above table, it can be easily observed that only Sc<sup>3+</sup> has an empty *d*-orbital. All other ions, except Sc<sup>3+</sup>, will be coloured in aqueous solution because of *d*–*d* transitions.

**Question 8.19:**

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

Answer

|    |    |           |           |           |           |    |           |
|----|----|-----------|-----------|-----------|-----------|----|-----------|
| Sc |    |           | +3        |           |           |    |           |
| Ti | +1 | +2        | <b>+3</b> | <b>+4</b> |           |    |           |
| V  | +1 | +2        | +3        | <b>+4</b> | <b>+5</b> |    |           |
| Cr | +1 | +2        | <b>+3</b> | +4        | +5        | +6 |           |
| Mn | +1 | <b>+2</b> | +3        | +4        | +5        | +6 | <b>+7</b> |



|    |    |           |           |    |    |    |  |
|----|----|-----------|-----------|----|----|----|--|
| Fe | +1 | <b>+2</b> | <b>+3</b> | +4 | +5 | +6 |  |
| Co | +1 | <b>+2</b> | <b>+3</b> | +4 | +5 |    |  |
| Ni | +1 | <b>+2</b> | +3        | +4 |    |    |  |
| Cu | +1 | <b>+2</b> | +3        |    |    |    |  |
| Zn |    | <b>+2</b> |           |    |    |    |  |

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.

**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.

Answer

**(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 4*f* orbitals, 5*f* 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  $5f$  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).

### Question 8.21:

How would you account for the following:

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

Answer

(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  $t_{2g}^3$  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) Co(II) is stable in aqueous solutions. However, in the presence of strong field complexing reagents, it is oxidized to Co (III). Although the 3<sup>rd</sup> 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.

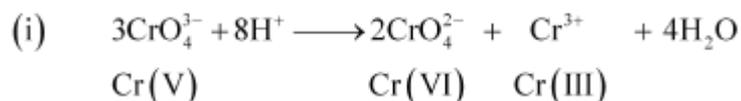
**Question 8.22:**

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

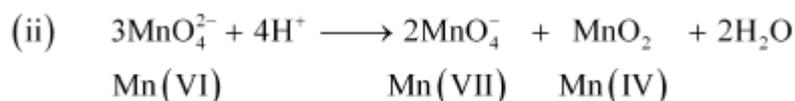
Answer

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?

Answer

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.

**Question 8.24:**

Calculate the number of unpaired electrons in the following gaseous ions:  $\text{Mn}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{V}^{3+}$  and  $\text{Ti}^{3+}$ . Which one of these is the most stable in aqueous solution?

Answer



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

$\text{Cr}^{3+}$  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:

- (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.

Answer

(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  $\text{OsF}_6$  and  $\text{V}_2\text{O}_5$ , 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  $\text{MnO}_4^-$ , the oxidation state of Mn is +7.

### Question 8.26:

Indicate the steps in the preparation of:

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

(ii)  $\text{KMnO}_4$  from pyrolusite ore.

Answer

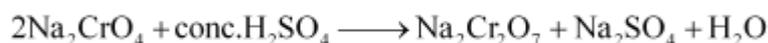
(i)

Potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) is prepared from chromite ore ( $\text{FeCr}_2\text{O}_4$ ) in the following steps.

**Step (1):** Preparation of sodium chromate



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

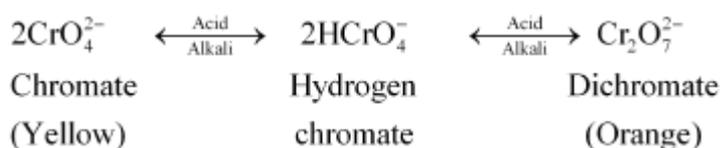


**Step(3):** Conversion of sodium dichromate to potassium dichromate



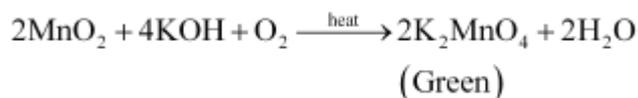
Potassium chloride being less soluble than sodium chloride is obtained in the form of orange coloured crystals and can be removed by filtration.

The dichromate ion ( $\text{Cr}_2\text{O}_7^{2-}$ ) exists in equilibrium with chromate ( $\text{CrO}_4^{2-}$ ) ion at pH 4. However, by changing the pH, they can be interconverted.



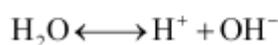
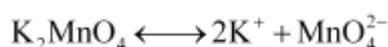
(ii)

Potassium permanganate ( $\text{KMnO}_4$ ) can be prepared from pyrolusite ( $\text{MnO}_2$ ). The ore is fused with KOH in the presence of either atmospheric oxygen or an oxidising agent, such as  $\text{KNO}_3$  or  $\text{KClO}_4$ , to give  $\text{K}_2\text{MnO}_4$ .



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.



Green                  Purple

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.

Answer

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.

**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.

Answer

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.

**Question 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.

Answer

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.

**Question 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.

Answer

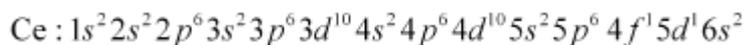
The last element in the actinoid series is lawrencium, Lr. Its atomic number is 103 and its electronic configuration is  $[Rn]5f^{14}6d^17s^2$ . The most common oxidation state displayed by it is +3; because after losing 3 electrons it attains stable  $f^4$  configuration.

**Question 8.31:**



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

Answer



Magnetic moment can be calculated as:

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

Where,

$n$  = number of unpaired electrons

In Ce,  $n = 2$

$$\begin{aligned}\text{Therefore, } \mu &= \sqrt{2(2+2)} \\ &= \sqrt{2 \times 4} \\ &= \sqrt{8} \\ &= 2\sqrt{2} \\ &= 2.828 \text{ BM}\end{aligned}$$

**Question 8.32:**

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

Answer

The lanthanides that exhibit +2 and +4 states are shown in the given table. The atomic numbers of the elements are given in the parenthesis.

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



|         |         |
|---------|---------|
| Yb (70) | Dy (66) |
|---------|---------|

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

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

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

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

### Question 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.

Answer

#### 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.

#### 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.

#### 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 8.34:**

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

Answer

| Atomic number | Electronic configuration             |
|---------------|--------------------------------------|
| 61            | $[\text{Xe}]^{54} 4f^5 5d^0 6s^2$    |
| 91            | $[\text{Rn}]^{86} 5f^2 6d^1 7s^2$    |
| 101           | $[\text{Rn}]^{86} 5f^{13} 5d^0 7s^2$ |
| 109           | $[\text{Rn}]^{86} 5f^{14} 6d^7 7s^2$ |

**Question 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:

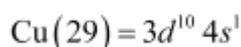
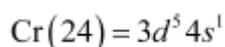
- (i) electronic configurations,
- (ii) oxidation states,
- (iii) ionisation enthalpies, and
- (iv) atomic sizes.

Answer

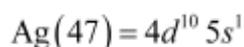
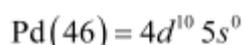
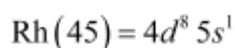
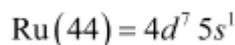
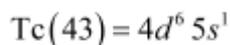
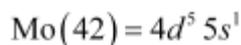
(i) In the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> transition series, the 3d, 4d and 5d orbitals are respectively filled.

We know that elements in the same vertical column generally have similar electronic configurations.

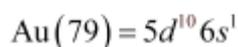
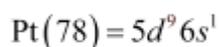
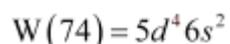
In the first transition series, two elements show unusual electronic configurations:



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.

For example  $[\text{Fe}^{\text{II}}(\text{Cn})_6]^{4-}$ ,  $[\text{Co}^{\text{III}}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  are stable complexes, but 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 2<sup>nd</sup> 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.

**Question 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).

Answer

| Metal ion        | Number of <i>d</i> -electrons | Filling of <i>d</i> -orbitals |
|------------------|-------------------------------|-------------------------------|
| Ti <sup>2+</sup> | 2                             | $t_{2g}^2$                    |
| V <sup>2+</sup>  | 3                             | $t_{2g}^3$                    |
| Cr <sup>3+</sup> | 3                             | $t_{2g}^3$                    |
| Mn <sup>2+</sup> | 5                             | $t_{2g}^3 e_g^2$              |
| Fe <sup>2+</sup> | 6                             | $t_{2g}^4 e_g^2$              |
| Fe <sup>3+</sup> | 5                             | $t_{2g}^3 e_g^2$              |
| CO <sup>2+</sup> | 7                             | $t_{2g}^5 e_g^2$              |
| Ni <sup>2+</sup> | 8                             | $t_{2g}^6 e_g^2$              |



|                  |   |                  |
|------------------|---|------------------|
| $\text{Cu}^{2+}$ | 9 | $t_{2g}^6 e_g^3$ |
|------------------|---|------------------|

**Question 8.37:**

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

Answer

The properties of the elements of the first transition series differ from those of the heavier transition elements in many ways.

**(i)** The atomic sizes of the elements of the first transition series are smaller than those of the heavier elements (elements of 2<sup>nd</sup> and 3<sup>rd</sup> 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.

**(ii)** +2 and +3 oxidation states are more common for elements in the first transition series, while higher oxidation states are more common for the heavier elements.

**(iii)** 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.

**(iv)** 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).

**(v)** 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.

**Question 8.38:**

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

**Example Magnetic Moment (BM)**

$\text{K}_4[\text{Mn}(\text{CN})_6]$  2.2

$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  5.3

$\text{K}_2[\text{MnCl}_4]$  5.9

Answer



Magnetic moment ( $\mu$ ) is given as  $\mu = \sqrt{n(n+2)}$ .

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

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

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

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

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

**(i)  $K_4[Mn(CN)_6]$**

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

$$\sqrt{n(n+2)} = 2.2$$

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.

**(ii)  $[Fe(H_2O)_6]^{2+}$**

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

We can see from the above calculation that the given value is closest to  $n = 4$ . Also, in this complex, Fe is in the +2 oxidation state. This means that Fe has 6 electrons in the  $d$ -orbital.

Hence, we can say that  $H_2O$  is a weak field ligand and does not cause the pairing of electrons.

**(iii)  $K_2[MnCl_4]$**

$$\sqrt{n(n+2)} = 5.9$$

We can see from the above calculation that the given value is closest to  $n = 5$ . 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  $\text{Cl}^-$  is a weak field ligand and does not cause the pairing of electrons.

Text solution

**Question 8.1:**

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

Answer

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.

**Question 8.2:**

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

Answer

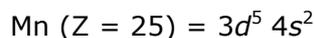
The extent of metallic bonding an element undergoes decides the enthalpy of atomization. The more extensive the metallic bonding of an element, the more will be its enthalpy of atomization. In all transition metals (except Zn, electronic configuration:  $3d^{10} 4s^2$ ), there are some unpaired electrons 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.

**Question 8.3:**



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

Answer



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.

#### Question 8.4:

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

Answer

The  $E^\ominus(\text{M}^{2+}/\text{M})$  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  $E^\ominus(\text{M}^{2+}/\text{M})$  value for copper is positive.

#### Question 8.5:

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

Answer

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 ( $\text{Cr}^+$ :  $3d^5$  and  $\text{Cu}^+$ :  $3d^{10}$ ). Hence, taking out one electron more from this stable configuration will require a lot of energy.

**Question 8.6:**

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

Answer

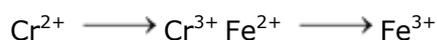
Both oxide and fluoride ions are highly electronegative and have a very small size. Due to these properties, they are able to oxidize the metal to its highest oxidation state.

**Question 8.7:**

Which is a stronger reducing agent  $\text{Cr}^{2+}$  or  $\text{Fe}^{2+}$  and why?

Answer

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



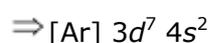
The  $E^\circ_{\text{Cr}^{3+}/\text{Cr}^{2+}}$  value is  $-0.41$  V and  $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}}$  is  $+0.77$  V. This means that  $\text{Cr}^{2+}$  can be easily oxidized to  $\text{Cr}^{3+}$ , but  $\text{Fe}^{2+}$  does not get oxidized to  $\text{Fe}^{3+}$  easily. Therefore, 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

**Question 8.8:**

Calculate the 'spin only' magnetic moment of  $\text{M}^{2+}_{(aq)}$  ion ( $Z = 27$ ).

Answer

$$Z = 27$$





$$\therefore M^{2+} = [\text{Ar}] 3d^7$$



i.e., 3 unpaired electrons

$$\therefore n = 3$$

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

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

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

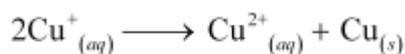
$$\mu \approx 4 \text{ BM}$$

### Question 8.9:

Explain why  $\text{Cu}^+$  ion is not stable in aqueous solutions?

Answer

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



### Question 8.10:

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

Answer

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.

## Chapter:-8 The d-and f-Block Elements

5 Marks Chapter

### **POINTS TO BE REMEMBERED: ---**

The elements of periodic table belonging to group 3 to 12 are known as d-Block elements.

The general electronic configuration of these elements is  $(n-1)d^{1-10} ns^{1-2}$

d-Block elements are collectively known as Transition Elements because properties of these elements vary in between s-Block and p-Block elements.

A transition element should have partially filled  $(n-1)d$  orbital in its atomic or any of the ionic state.

Group 12 elements i.e. Zn, Cd, Hg have completely filled  $(n-1)d$ -orbital in atomic & ionic state & thus these elements are considered as Typical Transition Elements.

All these elements are metals. They are less electropositive than s-block elements & more electropositive than p-block elements.

The atomic radii decreases from group 3 to 6 (i.e. Sc to Cr) because of increase in effective nuclear charge gradually.

The atomic radii of group 7,8 9 &10 elements (i.e. Fe,Co,Ni) is almost same because pairing of electrons take place in  $(n-1)d$  orbital causing repulsion i.e. shielding of  $(n-1)d$  orbital.

Group 11 &12 elements i.e. Cu & Zn have bigger size due to strong shielding of completely filled  $(n-1)d$  orbital.

Density of the transition metals from Sc to Cu increases due to high atomic mass and small atomic volume.

The transition elements show variable oxidation state due to small energy difference between  $(n-1)d$  &  $ns$  orbital as a result both  $(n-1)d$  &  $ns$  electrons take part in bond formation.

The highest oxidation state of an element is equal to number of unpaired electrons present in  $(n-1)d$  &  $ns$  orbital.

Transition elements have high enthalpy of atomization/ sublimation Because of large number of unpaired electrons in their atoms, they have stronger interatomic interaction and hence strong metallic bonding is present between atoms.

Most of transition elements are paramagnetic due to presence of unpaired electrons in (n-1) d orbital.

Most of transition elements are used as catalyst. It is due to (i) partially filled (n-1) d orbital (ii) Variable oxidation state (iii) Ability to change oxidation state frequently.

Most of transition elements form coloured compounds due to presence of unpaired electrons in (n-1) d orbital & thus they can undergo d-d transition.

Most of transition elements form complex compounds due to (i) small size (ii) high charge (iii) presence of vacant d-orbital of suitable energy.

Transition elements have lower value of Reduction Potential due to high ionization potential, high heat of sublimation & low enthalpy of hydration.

Transition elements form interstitial compounds because size of interstitial voids is similar to size of non- metals C, N, O, H.

Transition elements form alloys due to similar ionic radii.

The oxides of transition metals in lower oxidation state are BASIC, intermediate oxidation state are AMPHOTERIC, highest oxidation state are ACIDIC.

### **LANTHANOIDS: ---**

1. The 14 elements after Lanthanum having atomic number 58 to 71 are collectively known as Lanthanoids.
2. The general electronic configuration of these elements is  $[\text{Xe}] 4f^{1-14}, 5d^{0-1}, 6s^2$ .
3. Most common oxidation state of these elements is +3, but Ce shows +4, Eu +2, because they acquire stable configuration.
4. The size of Lanthanoids and its trivalent ion decreases from La to Lu due to poor shielding of 4f electrons. It is known as lanthanoids contraction.

### **ACTINOIDS:--**

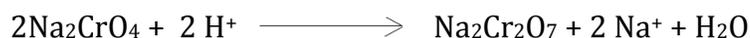
1. The 14 elements after Actinium having atomic number 90 to 113 are collectively known as Actinoids.
2. The general electronic configuration of these elements is  $[\text{Rn}] 5f^{1-14}, 6d^{0-1}, 7s^2$ .
3. The size of actinoids and its trivalent ion decreases from Ac to Lw due to poor shielding of 5f electrons. It is known as actinoids contraction.
4. The elements after U (92) are man made known as transuranic elements.

### **POTASSIUM DICHROMATE:--**

**Preparation:** - It takes place in three steps-

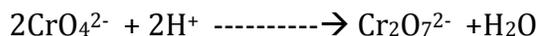
- (i) Conversion of chromite ore to sodium chromate.
- (ii) Conversion of sodium chromate to sodium dichromate.
- (iii) Conversion of sodium dichromate to potassium dichromate

Following reaction take place:--

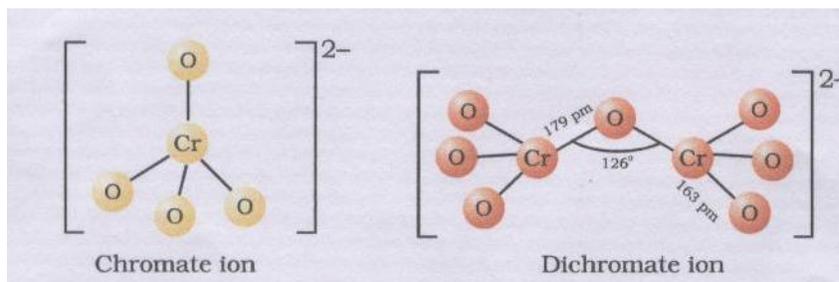
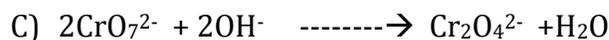


The chromates and dichromates are interconvertible in aqueous solution depending upon Ph of the solution.

A) In Acedic medium(PH<7)



B) In basic medium (PH >7)



### POTASSIUM PERMANGNATE:--

#### Preparation: --

It takes place in two steps:-

- (i) Conversion of pyrolusite ore into potassium magnate
- (ii) Conversion of potassium magnate to potassium permanganate

Following reactions take place:-



### QUESTION ANSWERS

#### (TWO MARK QUESTIONS)

Q.1-Explain briefly how +2 oxidation state becomes more and more stable in the first half of the first row transition elements with increasing atomic number.

A.1-In  $\text{M}^{2+}$  ions, 3d-orbitals get occupied gradually as the atomic number increases. Since, the number of empty d-orbitals decreases, the stability of cations increases from  $\text{Sc}^{2+}$  to  $\text{Mn}^{2+}$ .  $\text{Mn}^{2+}$  is most stable as all d-orbitals are singly occupied.

Q.2- Explain why transition elements have many irregularities in their electronic configurations?

A.2-In the transition elements, there is a little difference in the energy of (n-1) d-orbitals and ns-orbitals. Thus, incoming electron can occupy either of shell. Hence, transition elements exhibit many irregularities in their electronic configurations.

Q.3-What are different oxidation states exhibited by Lanthanides?

A.3-The common stable oxidation state of lanthanides is +3. However some members also show oxidation states of +2 & +4.

Q.4-How is the variability in oxidation states of transition metals different from that of the non-transition metals? Illustrate with examples.

A.4-The transition elements use its (n-1)d, ns and np orbital and the successive oxidation states differ by unity. For example, Mn shows all the oxidation states from +2 to +7. On

other hand non transition elements use its ns, np and nd orbitals and the successive oxidation states differ by two units e.g. Sn<sup>2+</sup>, Sn<sup>4+</sup> etc.

Q.5- Why do transition elements show variable oxidation states?

A.5- The transition elements show variable oxidation state due to small energy difference between (n-1) d & ns orbital as a result both (n-1)d & ns electrons take part in bond formation.

Q.6-Why are Mn<sup>2+</sup> compounds more stable than Fe<sup>2+</sup> compounds towards oxidation to +3 state?

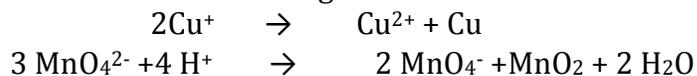
A.6-The electronic configuration of Mn<sup>2+</sup> is [Ar] 3d<sup>5</sup>, i.e. all five d-orbitals are singly occupied. Thus this is stable electronic configuration and further loss of electron requires high energy. On other hand side the electronic configuration of Fe<sup>2+</sup> is [Ar] 3d<sup>6</sup>, i.e. Loss of one electron requires low energy.

Q.7-To what extent do the electronic configuration decide the stability of oxidation state in the first series of the transition elements? Illustrate your answer with an example.

A.7-In a transition series, the oxidation state which lead to exactly half filled or completely filled orbitals are more stable.e.g. the electronic configuration of Fe is [Ar] 3d<sup>6</sup> 4s<sup>2</sup>. It shows various oxidation state but Fe(III) is more stable than Fe(II).

Q.8-What is meant by disproportionation? Give two examples.

A.8-Those reactions in which same substance undergoes oxidation as well as reduction are called disproportionation reactions.e.g.



Q.9- Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why?

A.9- Copper with configuration [Ar] 3d<sup>10</sup> 4s<sup>1</sup> exhibits +1 oxidation state. Copper loses 4s<sup>1</sup> electron easily and achieved a stable configuration 3d<sup>10</sup> by forming Cu<sup>+</sup>.

Q.10- What are inner transition elements?

A.10- The f-block elements in which the last electron accommodated on (n-2) f-subshell are called inner transition elements. These include atomic numbers 58 to 71 and from 90 to 103.

Q.11- The paramagnetic character in 3d-transition series elements increases upto Mn and then decreases. Explain why?

A.11- In the 3d-transition series as we move from Sc (21) to Mn (25) the number of unpaired electrons increases and hence paramagnetic character increases. After Mn, the pairing of electrons in the d-orbital starts and the number of unpaired electrons decreases and hence, paramagnetic character decreases.

Q.12- Comment on the statement that elements of the first transition series possess many properties different from those of heavier transition metal

A.12-The following points justify that the given statement is true:-

(i) Ionization enthalpies of heavier transition elements are higher than the elements of 3d series. Consequently, heavier transition elements are less reactive in comparison to 3d-elements.

(ii) Melting points of heavier transition elements are higher than 3d-elements.

(iii) Higher oxidation states of heavier transition elements are stable whereas lower oxidation states are stable in 3d-elements.

Q.13-What are transition elements? Which d-block elements are not regarded as transition elements and why?

A.13- An element which has partially filled (n-1) d orbital is known as transition elements. Group 12 elements i.e. Zn, Cd, Hg have completely filled (n-1) d-orbital in atomic & ionic state & thus these elements are not considered as Transition Elements.

Q.14-What are interstitial compounds? Why are such compounds well known for transition metal?

A.14- Compounds of transition metal with relatively smaller non-metals are known as interstitial compounds. These compounds are well known for transition metals because size of C, N, O, and B is similar to size of interstitial voids of transition metal

Q.15-For the first row of transition metals the  $E^0$  values are:-

| $E^0$ values | V     | Cr    | Mn    | Fe    | Co    | Ni    | Cu    |
|--------------|-------|-------|-------|-------|-------|-------|-------|
| $M^{2+}/M$   | -1.18 | -0.91 | -1.18 | -0.44 | -0.28 | -0.25 | +0.34 |

Explain the irregularity in the above values.

A.15-The  $E^0$  ( $M^{2+}/M$ ) values are not regular which can be explained from the irregular variation of ionization energy and sublimation energy of Mn due to half-filled orbitals.

**(THREE MARK QUESTIONS)**

Q.1- Decide giving reason which one of the following pairs exhibits the property indicated:

- (i)  $Sc^{3+}$  or  $Cr^{3+}$  exhibits paramagnetism
- (ii) V or Mn exhibits more number of oxidation states
- (iii)  $V^{4+}$  or  $V^{5+}$  exhibits colour

A.1- (i)  $Sc=[Ar] 3d^1 4s^2$ ;  $Sc^{3+}=[Ar]$ ; it has no unpaired electron so diamagnetic  
 $Cr=[Ar] 3d^5 4s^1$ ;  $Cr^{3+}=[Ar] 3d^3$ ; it has three unpaired electrons paramagnetic  
 (ii)  $V=[Ar] 3d^3 4s^2$   $Mn=[Ar] 3d^5 4s^2$  Thus V exhibit oxidation states of +2, +3, +4, +5

Whereas Mn exhibit oxidation states of +2 to +7.

(iii)  $V^{4+}=[Ar] 3d^1 \rightarrow$  coloured  $V^{5+}=[Ar] \rightarrow$  colourless

Q.2-(a) Describe the general trends in the following properties of the first series of the transition elements:-

- (i) Stability of +2-oxidation state
- (ii) Formation of oxometal ions

(b) Write steps involved in the preparation of  $KMnO_4$  from  $K_2MnO_4$

A.2- (a) i-The elements of first transition series show decreasing tendency to form divalent cation as we move left to right in the series. This trend is due to general increase in the first and second ionization energy. The greater stability of  $Mn^{2+}$  is due to half filled  $d^5$  configuration and that of zinc is due to  $d^{10}$  configuration.

(ii) All metal except Sc form oxide of type MO which are basic. The highest oxidation number in all oxide, coincide with the group number and is attain in  $Sc_2O_3$  to  $Mn_2O_7$ . Formation of oxoanions is due to high electro negativity and small size of oxygen atom.

2-(b) It takes place in two steps:-

- (iii) Conversion of pyrolusite ore into potassium manganate.
- (iv) Conversion of potassium manganate to potassium permanganate.

Following reactions take place:-



Q.3-(a) Write the steps involve in the preparation of  $K_2Cr_2O_7$  from chromite ore.

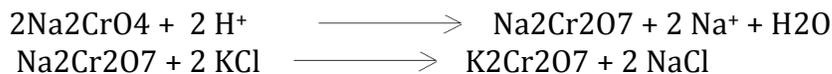
(b) What is the effect of pH on dichromate ion solution?

A.3-(a):- It takes place in three steps-

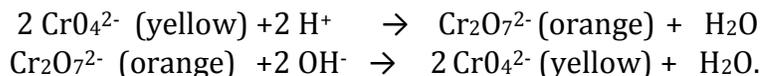
- (iv) Conversion of chromite ore to sodium chromate.
- (v) Conversion of sodium chromate to sodium dichromate.
- (vi) Conversion of sodium dichromate to potassium dichromate

Following reactions take place:-





(b) Dichromate ion is orange in acidic solution (pH < 7) and turns yellow in basic solution. It is due to interconversion of dichromate ion to chromate ion. Following reactions take place:-



Q.4- (a) What is lanthanide contraction? What effect does it have on the chemistry of the elements, which follow lanthanoids?

(b) The chemistry of actinoid elements is not so much smooth as that of lanthanoids. Justify these statements by giving some examples from the oxidation state of these elements.

A.4- (a) The size of Lanthanoids and its trivalent ion decreases from La to Lu. It is known as lanthanoids contraction.

Cause: - It is due to poor shielding of 4f electrons.

Consequences of lanthanide contraction: - (i) Basic strength of hydroxide decreases from  $\text{La}(\text{OH})_3$  to  $\text{Lu}(\text{OH})_3$ . (ii) Because of similar chemical properties lanthanides are difficult to separate.

(b) Lanthanoids show limited number of oxidation states i.e. +2, +3, +4 (out of which +3 is most common). This is because of a large energy gap between 4f, 5d and 6s subshell. The dominant oxidation state of actinides is also +3 but they show a number of other oxidation state also e.g. +4, +5, and +7. This is due to small energy difference between 5f, 6d and 7s orbitals.

Q.5- 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) Of the  $d^4$  species,  $\text{Cr}^{2+}$  is strongly reducing while manganese(III) is strongly oxidizing.

A.5-(i) The oxide of transition metals in lower oxidation states are generally basic while those in the higher oxidation states are acidic. Acidic character increases with increase in oxidation state is due to decrease in size of metal ion and increase in charge density. e.g.  $\text{MnO}$  (basic),  $\text{Mn}_3\text{O}_4$  (amphoteric),  $\text{Mn}_2\text{O}_7$  (acidic).

(ii) A transition metal exhibits higher oxidation states in oxides and fluorides because oxygen and fluorine are the most electronegative elements and thus easily can unpair electrons of metal atom.

(iii) Because oxidizing and reducing property depends on  $E^0$  value. Since  $E^0$  value of  $\text{Cr}^{3+}/\text{Cr}^{2+}$  is negative while that of  $\text{Mn}^{3+}/\text{Mn}^{2+}$  is positive, as a result  $\text{Cr}(\text{II})$  act as reducing agent and  $\text{Mn}(\text{III})$  is strong oxidizing.

Q.6- For  $\text{M}^{2+}/\text{M}$  and  $\text{M}^{3+}/\text{M}^{2+}$  systems, the  $E^0$  values for some metals are as follows:

|                            |       |                                 |       |
|----------------------------|-------|---------------------------------|-------|
| $\text{Cr}^{2+}/\text{Cr}$ | -0.9V | $\text{Cr}^{3+}/\text{Cr}^{2+}$ | -0.4V |
| $\text{Mn}^{2+}/\text{Mn}$ | -1.2V | $\text{Mn}^{3+}/\text{Mn}^{2+}$ | +1.5V |
| $\text{Fe}^{2+}/\text{Fe}$ | -0.4V | $\text{Fe}^{3+}/\text{Fe}^{2+}$ | +0.8V |

Use this data to comment upon :-

(i) the stability of  $\text{Fe}^{3+}$  in acid solution as compared to  $\text{Cr}^{3+}$  or  $\text{Mn}^{3+}$  and

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

A.6- (i)  $E^0$  for  $\text{Cr}^{3+}/\text{Cr}^{2+}$  is -0.4V i.e. negative, this means  $\text{Cr}^{3+}$  ions in the solution cannot be reduced to  $\text{Cr}^{2+}$  easily i.e.  $\text{Cr}^{3+}$  is stable. As  $\text{Mn}^{3+}/\text{Mn}^{2+}$  is +1.5V i.e. positive means  $\text{Mn}^{3+}$  can

easily reduced to  $Mn^{2+}$  ions in comparison to  $Fe^{3+}$  ions. Thus relatively stability of these ions is:-



(ii) The oxidation potentials for the given pairs will be +0.9V, +1.2V and 0.4V. Thus, the order of their getting oxidized will be in the order  $Mn > Cr > Fe$ .

Q.7-Account for the following statements:

(i) Cobalt (II) is stable in aqueous solution but in the presence of strong ligands and air, it can be oxidized to Co (III).

(ii) The  $d^1$  configuration is very unstable in ions.

(iii) One among the lanthanides, Ce (III) can be easily oxidized to Ce (IV).

A.7- (i) Strong ligands force cobalt (II) to lose one more electron from 3d-subshell and thereby induced  $d^2sp^3$  hybridisation.

(ii) The ion with  $d^1$  configuration try to lose the only electron in order to acquire inert gas configuration.

(iii) The configuration of Ce is  $[Xe] 4f^1, 5d^1, 6s^2$ . There is no much difference between the energy of 4f, 5d and 6s orbitals and thus, Ce can utilize electrons present in these orbitals and hence oxidation state of +4.

Q.8- Compare the chemistry of actinides with that of the lanthanoids with special reference to:

(i) electronic configuration

(iii) oxidation state

(ii) atomic and ionic sizes and

(iv) chemical reactivity

A.8-

### Comparison of Lanthanoids and Actinides

| Properties               | Lanthanoids  | Actinides   |
|--------------------------|--|---|
| Electronic configuration | $[Xe] 4f^{1-14}, 5d^{0-1}, 6s^2$   | $[Rn] 5f^{1-14}, 6d^{0-1}, 7s^2$  |
| Atomic/ionic sizes       | Size decreases from La to Lu, and size is more than actinides.   | Size decreases from Ac to Lw, and size is smaller than lanthanoids due to poorer shielding of 5f electrons                              |
| Oxidation states         | Common oxidation is +3 where other oxidation states are +2, +4. It is due to a large energy gap between 4f, 5d and 6s subshell | Common oxidation is +3 where other oxidation states are +2, +4, +5 and +7 due to small energy difference between 5f, 6d and 7s orbitals |
| Chemical reactivity      | The earlier member quite reactive but with increasing atomic number they behave like aluminum.                                 | The actinides highly reactive, especially in finely divided.  |
| Complex formation        | Less tendency to form complex due to less charge density.  | More tendency to form complex due to high charge density.   |

Q.9-(a) What is actinides contraction? What effect does it have on the chemistry of the elements, which follow actinides?

(b) Name an important alloy, which contains some of the lanthanide metals. Mention its uses.

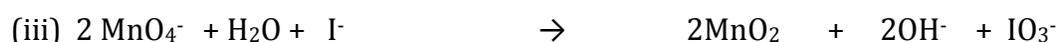
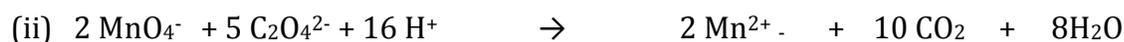
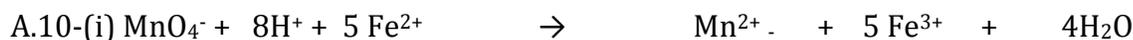
A.9- (a) The size of actinoid and its trivalent ion decreases from Ac to Lw. It is known as actinides contraction.

Cause: - It is due to poor shielding of 5f electrons.

Consequences of actinides contraction: - (i) Basic strength of hydroxide decreases from  $\text{Ac}(\text{OH})_3$  To  $\text{Lw}(\text{OH})_3$ . (ii) Because of similar chemical properties l actinides are difficult to separate.

(b) An important alloy containing lanthanoid metals is mischmetal, which contains 95% lanthanide metal and 5% Fe along with traces of S, C, Ca and Al. It is used in Mg-based alloy to produce bullets, shells and lighter flint.

Q.10- Complete following reactions:-



### (FIVE MARK QUESTIONS)

Q.1-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.

(v) Transition metals have a strong tendency to form complexes.

A.1- (i) Transition metals and many of their compounds show paramagnetic behaviour due to presence of unpaired electrons in (n-1) d orbital.

(ii) The enthalpies of atomisation of the transition metals are high Because of large number of unpaired electrons in their atoms, they have stronger interatomic interaction and hence strong metallic bonding is present between atoms.

(iii) The transition metals generally form coloured compounds due to presence of unpaired electrons in (n-1) d orbital & thus they can undergo d-d transition.

(iv) Transition metals and their many compounds act as good catalyst It is due to (i) partially filled (n-1) d orbital (ii) Variable oxidation state (iii) Ability to change oxidation state frequently.

(v) Transition metals have a strong tendency to form complexes Most of transition elements form complex compounds due to (i) small size (ii) high charge (iii) presence of vacant d-orbital of suitable energy.

Q.2- Give reasons for the following:-

(i) Fe has higher melting point than Cu.

(ii)  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is coloured while  $[\text{Sc}(\text{H}_2\text{O})_6]$  is colourless.

(iii) The 4d and 5d series of transition metals have more frequent metal-metal bonding in

their compound than do the 3d metals.

(iv) Transition metals some time exhibit very low oxidation state such as +1 and 0.

(v) Hg is not considered a transition metal.

A.2-(i) This is because Fe ( $3d^6, 4s^1$ ) has four unpaired electrons in 3d-subshell. While Cu ( $3d^{10}, 4s^1$ ) only one unpaired electron in 4s shell. Hence metallic bonding is stronger in Fe than those in Cu.

(ii) The oxidation state of Ti in  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is +3 and its configuration is  $[\text{Ar}] 3d^1$  i.e one unpaired electron and hence it is coloured. Whereas the oxidation state of Sc in  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$  is +3 and its configuration is  $[\text{Ar}] 3d^0$  i.e no unpaired electron and hence it is colourless.

(iii) In the same group of d-block elements, the 4d and 5d transition elements are larger size than that of 3d elements. Hence, the valence electrons are less tightly held and form metal-metal bond more frequently.

(iv) +1 oxidation state is shown by elements like Cu because after loss of one electron, it acquire stable configuration. Zero oxidation state is shown in metal carbonyl, because  $\pi$  - electrons donated by CO are accepted into the empty orbital.

(v) The characteristic properties of transition metal are due to partially filled d-orbitals. Hg has completely filled d-orbital, as a result it doesn't show properties of transition metals and hence is not considered as transition metal.

Q.3-(a) write electronic configuration of element having atomic number 101.

(b) Which element show maximum oxidation state in 3d transition series?

(c) What is mischmetal?

(d) Explain why  $\text{Cu}^+$  ion is not stable in aqueous solution?

(e) Name the transition metal which is well known to exhibit +4 oxidation state?

A.3-(a)  $[\text{Rn}] 5f^{13}, 6d^0, 7s^2$ .

(b) Mn, Which shows +7 oxidation state in  $\text{KMnO}_4$ .

(c) It is an important alloy, which contains 95% lanthanide metal and 5% Fe along with traces of S, C, Ca and Al. It is used in Mg-based alloy to produce bullets, shells and lighter flint.

(d) Water is a good complexing agent and thus Cu forms complex by losing one more electron from 3d orbital.

(e) Cerium (Z=58)

Q.4-(a) Write the preparation of potassium dichromate from iron chromite. What happens when potassium dichromate reacts with (i) Hydrogen sulphide (ii)  $\text{FeSO}_4$ ?

(b) Why do Zr and Hf exhibit almost similar properties?

(c) Why is  $\text{La}(\text{OH})_3$  stronger base than  $\text{Lu}(\text{OH})_3$ .

A.4- (a) Preparation:- It takes place in three steps-

(i) Conversion of chromite ore to sodium chromate.

(ii) Conversion of sodium chromate to sodium dichromate.

(iii) Conversion of sodium dichromate to potassium dichromate

Following reaction takes place:-



Reactions: - (i)  $\text{Cr}_2\text{O}_7^{2-} + 8 \text{H}^+ + 3 \text{H}_2\text{S} \rightarrow 2\text{Cr}^{3+} + 7 \text{H}_2\text{O} + 3\text{S}$

(ii)  $\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6 \text{Fe}^{2+} \rightarrow 2\text{Cr}^{3+} + 7 \text{H}_2\text{O} + 6 \text{Fe}^{3+}$ .

(b) Because both have similar ionic size

(c) Due to lanthanoid contraction size of  $\text{La}^{3+}$  is smaller than  $\text{Lu}^{3+}$  as a result Lu-O bond will stronger than La-O bond.

Q.5- Give reasons for the following:-

(i) Transition metals have high enthalpy of hydration.

(ii) Zn, Cd and Hg are not regarded as transition metal.

(iii) d block elements exhibit a large number of oxidation state than f block elements.

(iv) The second and third members in each group of transition element have similar atomic radii.

(v)  $K_2 [PtCl_6]$  is well known compound whereas the corresponding Ni compound is not known.

A.5-(i) Transition metal ions are smaller and have higher charge, therefore have high enthalpy of hydration.

(ii) Group 12 elements i.e. Zn, Cd, Hg have completely filled (n-1) d-orbital in atomic & ionic state & thus these elements are not considered as transition elements.

(iii) The difference in the energy of (n-1) d orbital and ns orbital is very small and thus both sub-shells are used for bond formation. Whereas in f block elements (n-2)f orbitals lie underneath and hence are not available for bond formation.

(iv) The second and third members in each group of transition element have similar atomic radii due to lanthanoid contraction. It arises due to poor shielding of d and f electron.

(v) The oxidation state of Pt is +4 which is stable for Pt. The +4 oxidation state for Ni is very difficult to achieve because the sum of first four ionization energies is very high. Hence, the corresponding Ni(II) compound is known.

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**Reasoning:**

Q1 Why are transition metals called d block elements?

Q2 What causes exceptional electronic configuration of Cr and Cu?

Q3 Why are  $Mn^{2+}$  salts more stable than  $Fe^{2+}$  while  $Fe^{3+}$  salts are more stable than  $Mn^{3+}$ ?

Q4 Transition metals are hard; possess high densities and high enthalpies of atomization.

Q5 Metallic character decreases along the period.

Q6 Melting Points and Boiling points first increases and then decrease gradually.

Q7 Transition metals have high mp and bps.

Q8. Transition metals have higher I.E. than s- block metals.

Q9 In third and second transition series atomic radii are almost similar.

Q10 Ionization enthalpies in general increase along the period.

Q11 Transition metals can also form acidic oxides.

Q12 First I.E of Mn is exceptionally high (717KJ/mol)

Q13 First I.E of Zn is high (906KJ/mol). Why?

Q14 2<sup>nd</sup> I.E of Cu is higher than Zn. Why?

Q15 2<sup>nd</sup> I.E of Cr is higher than Mn. Why?

Q16 1<sup>st</sup> I.E decreases from Mn to Ni.

Q17 3<sup>rd</sup> I.E is exceptionally high (3260KJ/mol) for Mn.

Q18 Comment on the formation and existence of  $Zn^{3+}$  ion.

Q19 Zn, Cd, and Hg have fully filled d-orbital. Are they transition metals?

Q20 Ionization enthalpies of the 5d elements are quite higher.

Q21 Transition metals show variable oxidation states.

Q22 Higher O.S increases along the period reaches a maximum value than decreases.

Q23 Transition elements in their lower oxidation state form ionic compounds. Why?

Q24 Transition elements also form some compounds with zero oxidation state.

Q25 Transition metals form complexes.

Q26 Transition metals form coloured complexes.

Q27  $Sc^{3+}$ ,  $Ti^{4+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$  salts are white and diamagnetic.

Q28 Transition metals show paramagnetic properties.

Q29 Transition metals show catalytic properties.

## **CHAPTER- 9: CO-ORDINATION COMPOUNDS**

**3 Marks Chapter**

The compounds which contain dative bonds between metal atom and surrounding species is called

co-ordination compounds .

The branch of inorganic chemistry which deals with the study of preparation properties of coordination

compound is called co-ordination chemistry.



### **POINTS TO REMEMBER:**

#### **1. Coordination compounds**

Coordination compounds are compounds in which a central metal atom or ion is linked to a number of ions or neutral molecules by coordinate bonds

or which contain complex ions. Examples-  $K_4[Fe(CN)_6]$ ;  $[Cu(NH_3)_4]SO_4$ ;  $Ni(CO)_4$

#### **2. The main postulates of Werner's theory of coordination compounds**

(i) In coordination compounds metals show two types of linkages or valences- Primary and

Secondary.

ii) The primary valences are ionisable and are satisfied by negative ions.

iii) The secondary valences are non-ionisable and are satisfied by neutral molecules or negative ions. The secondary valence is equal to the C.N. and is fixed for a metal.

iv) The ions or groups bound by secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.

#### **3. Difference between a double salt and a complex**

Both double salts as well as complexes are formed by the combination of