

## Chapter-8

### The d & f block elements

### Class-XII

### Subject-Chemistry

8.1 Write down the electronic configuration of:

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

#### Answer 8.1

- i.  $\text{Cr}^{3+}$ : -  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$
- ii.  $\text{Pm}^{3+}$ : -  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^4$
- iii.  $\text{Cu}^{+}$ : -  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$
- iv.  $\text{Ce}^{4+}$ : -  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$
- v.  $\text{Co}^{2+}$ : -  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$
- vi.  $\text{Lu}^{2+}$ : -  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^{14} 5d^1$
- vii.  $\text{Mn}^{2+}$ : -  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$
- viii.  $\text{Th}^{4+}$ : -  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6$

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

#### Answer 8.2

We know that, half-filled and fully-filled orbitals are more stable.

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

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

Thus,  $\text{Mn}^{2+}$  is stable because of  $d^5$  configuration. But,  $\text{Fe}^{2+}$  has  $d^6$  configuration which is less stable than  $\text{Mn}^{2+}$ . Hence, by losing one electron, its configuration changes to a more stable state. Therefore,  $\text{Mn}^{2+}$  shows resistance to oxidation to  $\text{Mn}^{3+}$  but  $\text{Fe}^{2+}$  easily gets oxidized to  $\text{Fe}^{3+}$  oxidation state.

### 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 8.3

In the first row transition elements, except Sc, all others metals display +2 oxidation state. On moving from Sc to Mn, the atomic number increases. Thus, the number of electrons in the 3d-orbital also increases.

Sc (+2) = $d^1$
Ti (+2) = $d^2$
V (+2) = $d^3$
Cr (+2) = $d^4$
Mn (+2) = $d^5$

Elements attain +2 oxidation state by losing two 4s electrons. Stability of +2 states in the first series increases till first half as by losing 2 electrons, these elements acquire stable oxidation state.

### 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 8.4

Transition elements show many oxidation states like Mn exhibiting maximum number of oxidation states (+2 to +7). The stability of +2 oxidation state increases with the increase in atomic number because more electrons are getting filled in the d-orbital.

If we observe Scandium, it does not show +2 oxidation state as its electronic configuration is  $4s^2 3d^1$ . Thus, by losing all three electrons, it attains stable noble gas configuration and becomes more stable. Similarly, Ti (+4) and V (+5) are very stable. In case of Mn, +2 oxidation state is very stable.

**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 8.5**

Electronic configuration in ground state	Stable oxidation states
$3d^3$ (Vanadium)	+2, +3, +4 and +5
$3d^5$ (Chromium)	+3, +4, +6
$3d^5$ (Manganese)	+2, +4, +6, +7
$3d^8$ (Cobalt)	+2, +3
$3d^4$	No $3d^4$ configuration in ground state

**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 8.6**

a) Vanadate,  $VO_3^-$

Oxidation state of V is + 5

b) Chromate,  $CrO_4^{2-}$

Oxidation state of Cr is + 6

c) Permanganate,  $MnO_4^-$

Oxidation state of Mn is + 7

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

### Answer 8.7

Lanthanoid contraction: -

On moving along the lanthanoid series, atomic number increases. It means that the number of electrons and protons present in an atom also increases by one. Here, electrons are adding into the same shell because of which the effective nuclear charge increases.

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.

Because of increase in number of electrons in the  $4f$  orbital, shielding effect of  $4f$  electrons is not that much effective as it should be. Thus, the effective nuclear charge experienced by the outer electrons increases. Consequently, the electrostatic force of attraction of nucleus for the outermost electrons increases. This results in a steady decrease in the size of lanthanoids. This is known as lanthanoid contraction.

### Consequences of lanthanoid contraction

- a) Separation of lanthanoids is possible because of this.
- b) Similarity in the properties of second and third transition series.
- c) Because of this, there is variation in the basic strength of lanthanide hydroxides. (Basic strength decreases from  $\text{La}(\text{OH})_3$  to  $\text{Lu}(\text{OH})_3$ ).

## 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 8.8

Characteristics of the transition elements: -

- a) **Electronic Configuration:** - The general electronic configuration of d-block elements is  $ns^2(n-1)d^{1-10}$ .
- b) **Metallic Character:** - All the d-block elements have valence electrons in their outermost shell and thus all are metals. All are hard, ductile and malleable solids.
- c) **Atomic and Ionic Radii:** - The Atomic and Ionic Radii of transition elements are smaller than their corresponding s-block elements and are greater than their corresponding p-block elements.
- d) **Boiling and Melting points:** - All the transition elements have high M.P. and B.P., as compared to s-block elements due to their strong metallic bonding. However Zn, Cd, Hg have relatively low values of M.P. and B.P. Due to their completely filled d-orbitals.
- e) **Ionisation Energy:** - The Ionisation energy of d-block elements lies in between the of s-block and p-block elements. Thus they are more electropositive than p-block elements and less electropositive than s-block elements.
- f) **Oxidation state:** - The Transition elements show variable oxidation state in their compounds. For e.g.: -  
Ti : +2, +3, +4  
Cr : +1, +2, +3, +4, +5, +6  
Mn : +2, +3, +4, +6, +7  
Fe : +2, +3  
Cu : +1, +2
- g) **General Chemical Reactivity:** - The d-block elements are less reactive as compared to s-block elements due to their high ionisation energy.
- h) **Conductivity:** - All the Transition elements are good conductors of heat and electricity.

In transition elements, atoms or 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.

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

## Answer 8.9

Electronic configuration of transition elements: -  $(n-1)d^{1-10} ns^{0-2}$

Electronic configuration of non-transition elements: -  $ns^{1-2}$  or  $ns^2 np^{1-6}$

Transition metals have a partially filled  $d$ -orbital whereas the non-transition elements do not have  $d$ -orbitals.

## 8.10 What are the different oxidation states exhibited by the lanthanoids?

### Answer 8.10

+3 oxidation state is most common in the lanthanide series. However, +2 and +4 oxidation states are also present in the solution or in solid compounds.

## 8.11 Explain giving reasons:

- Transition metals and many of their compounds show paramagnetic behaviour.
- The enthalpies of atomisation of the transition metals are high.
- The transition metals generally form coloured compounds.
- Transition metals and their many compounds act as good catalyst.

### Answer 8.10

- Paramagnetic behaviour arises because of unpaired electrons. Transition elements contain unpaired valence electrons in its  $d$ -orbital. Thus, they exhibit paramagnetic behaviour.
- Because of high effective nuclear charge and a large number of valence electrons, transition elements form very strong metallic bonds. As a result, the enthalpy of atomization of transition metals is high.
- In transition elements, absorption of radiation to promote an electron from one of the  $d$ -orbitals to another falls into visible region. 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 on following facts: -Ability to show multiple 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.

Transition metals also provide a suitable surface for the occurrence of reaction.

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

### Answer 8.12

**Interstitial compounds: -**

Because of large size, transition metals contain lots of interstitial sites. Thus, they can trap atoms of other elements of smaller size, such as H, C, N, in the interstitial sites of their crystal lattices. The resulting compounds formed are called interstitial compounds.

Interstitial compounds are well known because of their interstitial sites.

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

### Answer 8.13

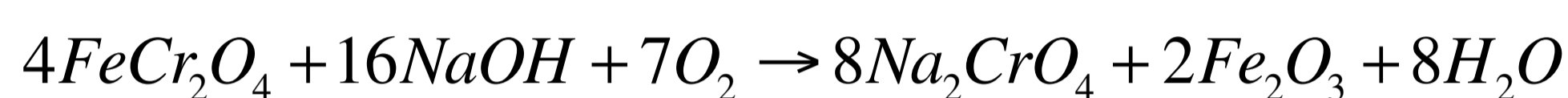
Because of presence of d-orbital electrons, transition elements show multiple oxidation state as compared to non-transition elements. The oxidation state can vary from +1 to the highest oxidation state by removing all its valence electrons. In transition elements, the oxidation states differ by 1 ( $\text{Fe}^{2+}$  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.

**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?**

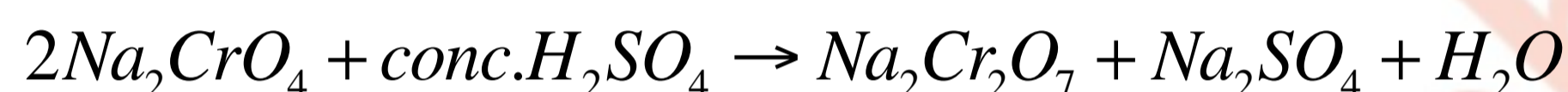
### Answer 8.14

Preparation of Potassium dichromate from chromite ore: -

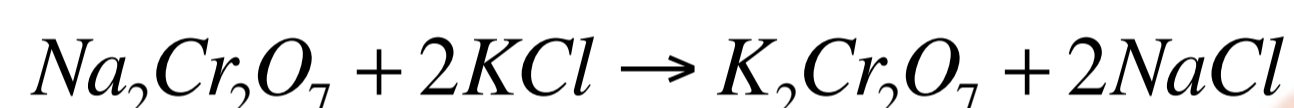
Step 1: Preparation of sodium chromate



Step 2: Conversion of sodium chromate into sodium dichromate

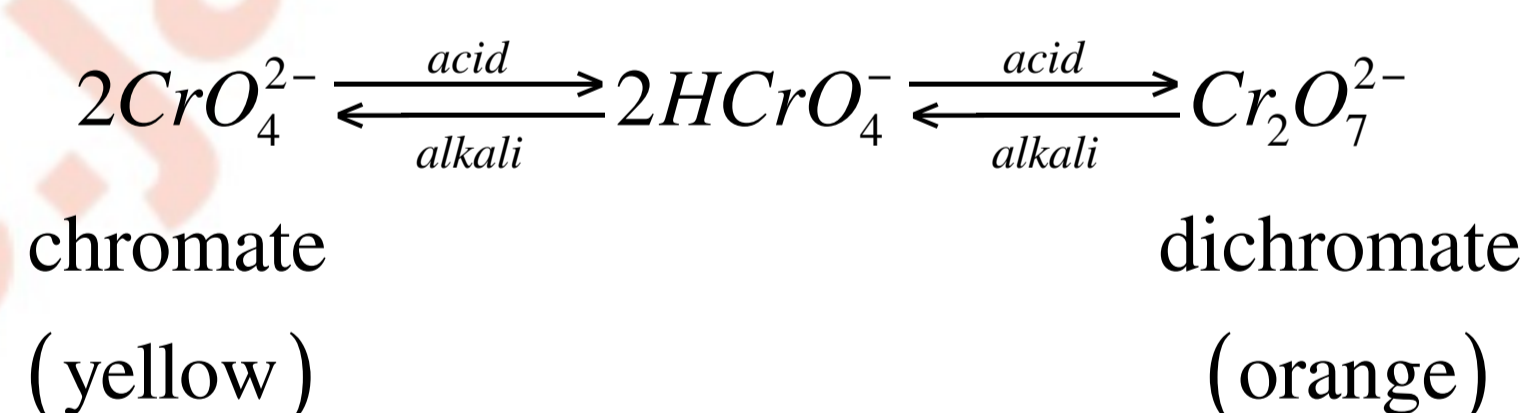


Step 3: Conversion of sodium dichromate to potassium dichromate



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 exists in equilibrium with chromate ion at pH 4. On changing the pH, they can be inter-converted.

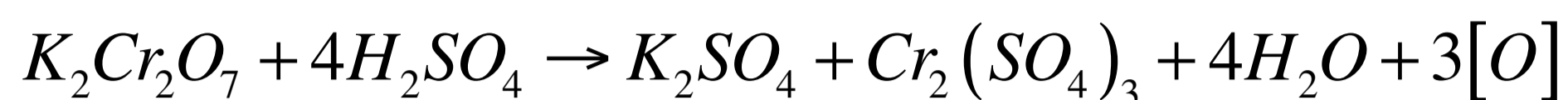


**8.15 Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with:**

- iodide
- iron(II) solution and
- $\text{H}_2\text{S}$

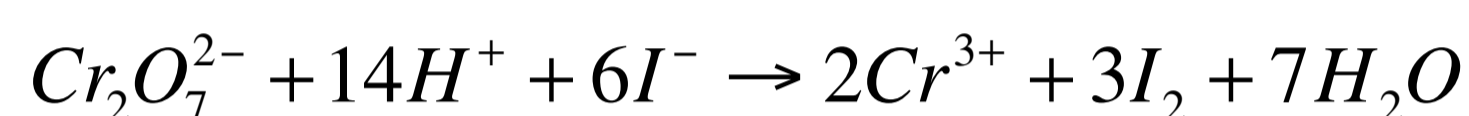
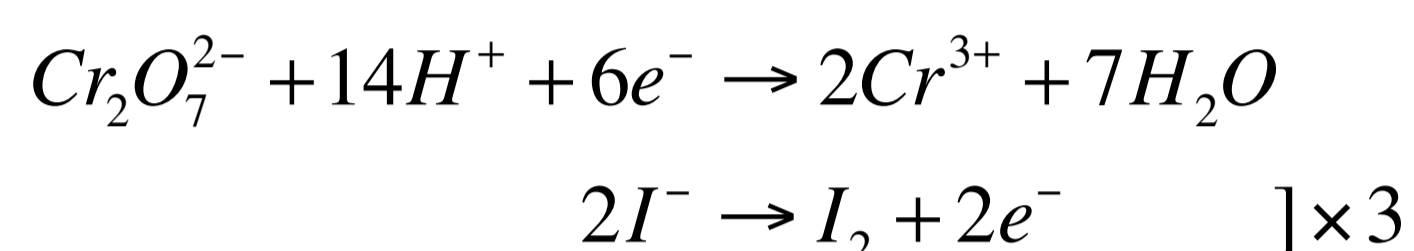
### Answer 8.15

In the acidic medium, potassium dichromate acts as a very strong oxidising agent.

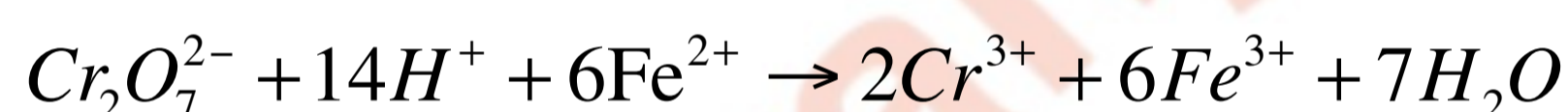
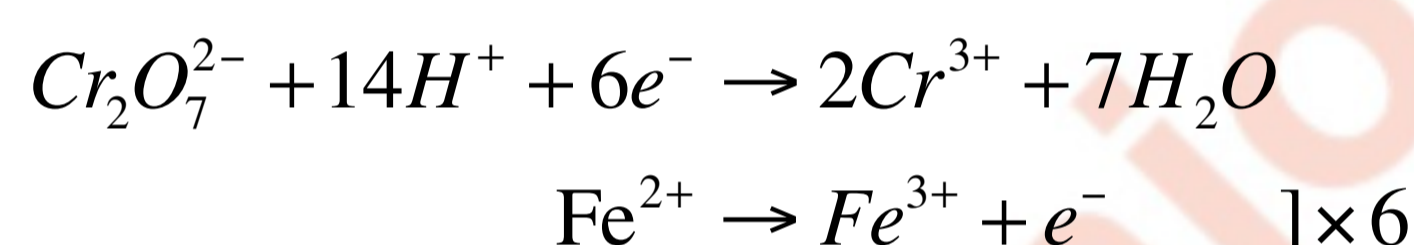


It takes up electrons to get reduced and acts as an oxidising agent.

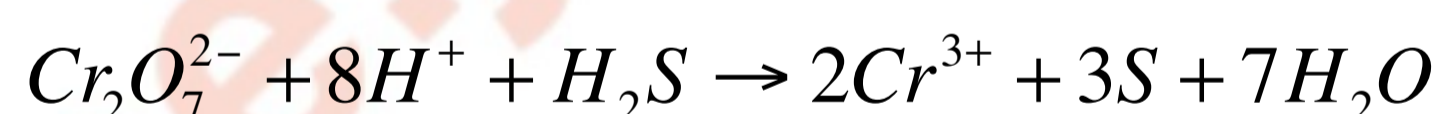
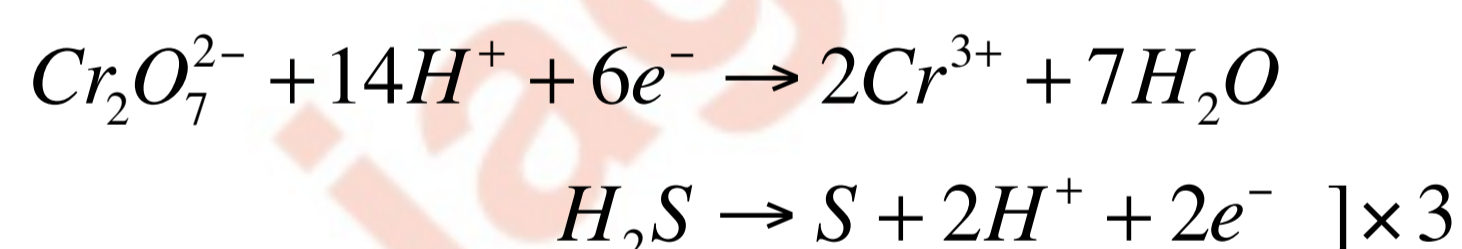
- i. Potassium dichromate oxidizes iodide to iodine.



- ii. Potassium dichromate oxidizes iron (II) solution to iron (III) solution i.e., ferrous ions to ferric ions.



- iii. Potassium dichromate oxidizes H<sub>2</sub>S to sulphur.



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

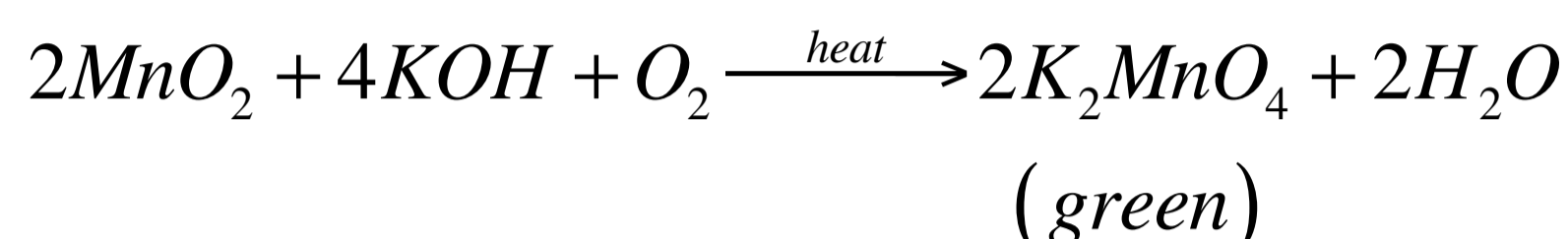
- i. iron(II) ions
- ii. SO<sub>2</sub> and
- iii. oxalic acid

Write the ionic equations for the reactions.

**Answer 8.16**

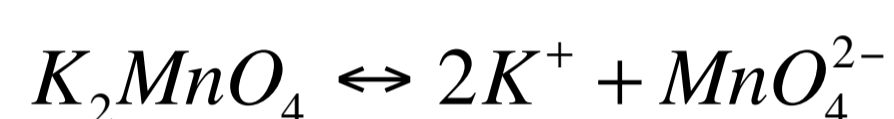
Preparation of Potassium permanganate: -

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

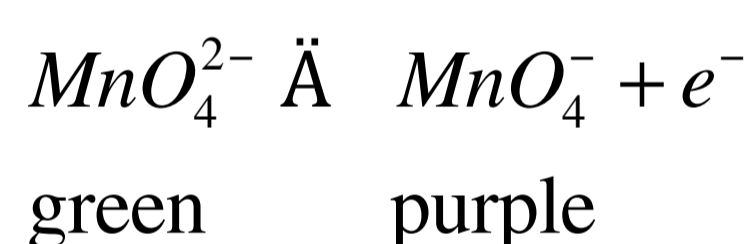


The green mass can be extracted with water and then oxidized either electrolytically or by passing chlorine/ozone into the solution.

**Electrolytic oxidation: -**

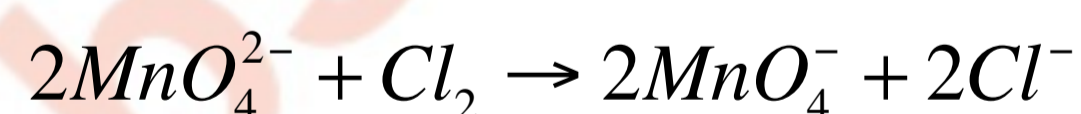


At anode,

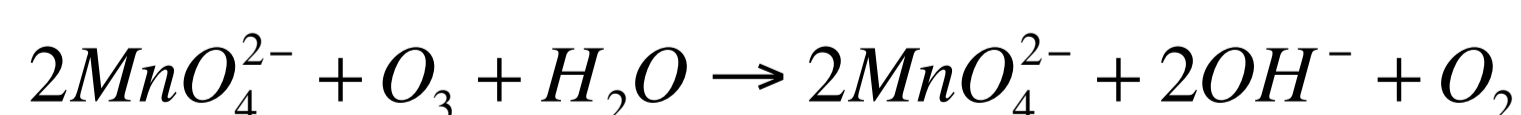
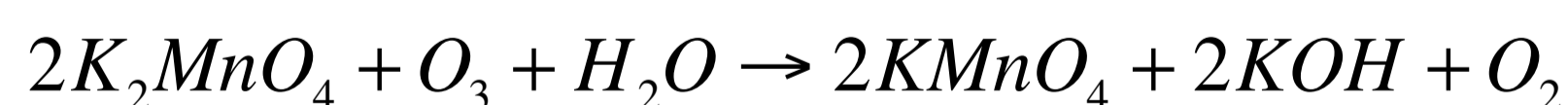


Manganate ions are oxidized to permanganate ions.

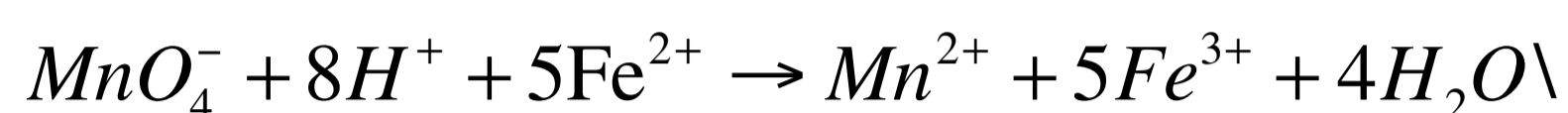
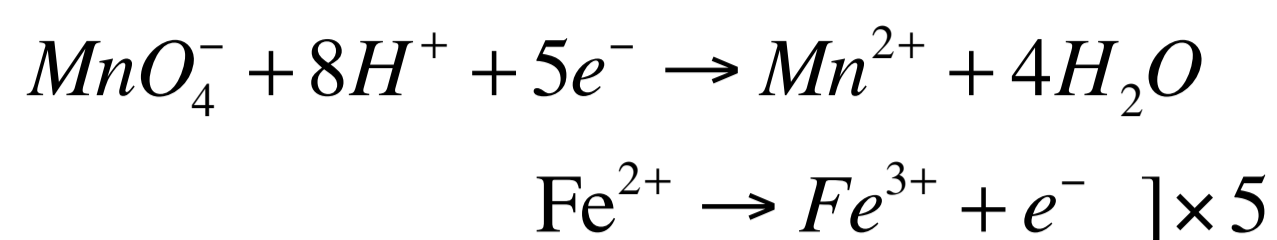
**Oxidation by chlorine: -**



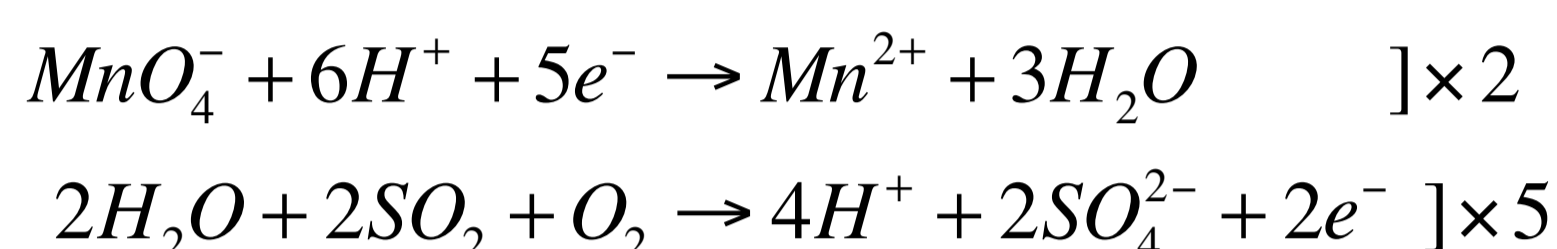
**Oxidation by ozone: -**



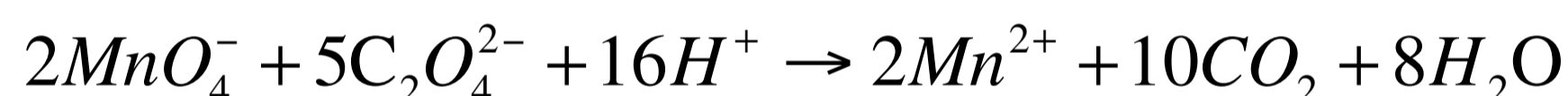
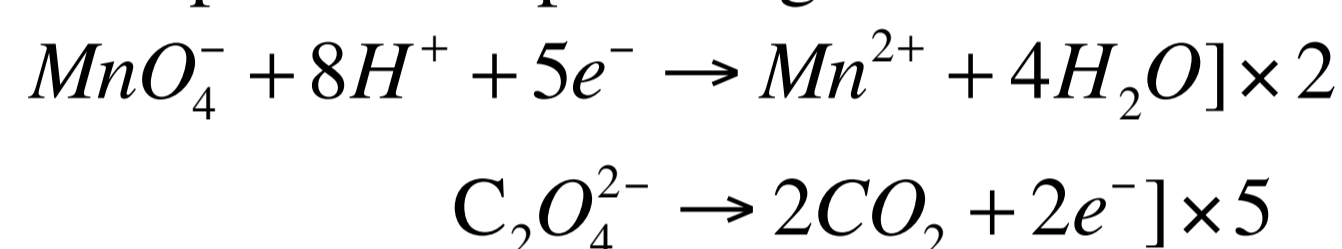
- i. Acidified  $\text{KMnO}_4$  solution oxidizes  $\text{Fe (II)}$  ions to  $\text{Fe (III)}$  ions i.e., ferrous ions to ferric ions.



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



- iii. Acidified potassium permanganate oxidizes oxalic acid to carbon dioxide.



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:

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

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

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

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

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

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

Use this data to comment upon:

- i. The stability of  $\text{Fe}^{3+}$  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.

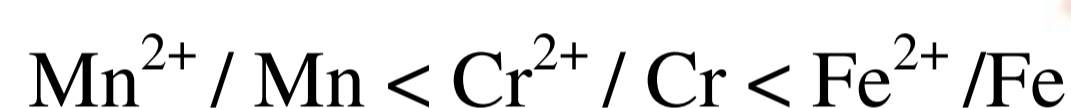
## Answer 8.17

- 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  $\text{Mn}^{3+} / \text{Mn}^{2+}$ .

These metal ions can be arranged in the increasing order of their stability as:  
 $\text{Mn}^{3+} < \text{Fe}^{3+} < \text{Cr}^{3+}$

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

- ii. The reduction potentials order increases in following order:



Thus, 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  $\text{Mn}^{2+}$ .

**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 8.18

Ion which contains 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	$\text{Ti}^{3+}$	$[\text{Ar}] 3d^1$
V	23	$\text{V}^{3+}$	$[\text{Ar}] 3d^2$
Cu	29	$\text{Cu}^+$	$[\text{Ar}] 3d^{10}$
Sc	21	$\text{Sc}^{3+}$	$[\text{Ar}]$

Mn	25	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>

Now, 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.

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

### Answer 8.19

The number of oxidation states increases on moving from Sc to Mn. In first transition series, maximum number of oxidation states is shown by Mn, from +2 to +7. 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 happens because of inert pair effect. On moving from top to bottom, it becomes more and more difficult to remove the third electron from the *d*-orbital.

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

- Electronic configuration
- Atomic and ionic sizes and
- Oxidation state
- Chemical reactivity.

### Answer 8.20

- Electronic configuration: -

The general electronic configuration for lanthanoids:  $[Xe]^{54} 4f^{0-14} 5d^{0-1} 6s^2$

The general electronic configuration for actinoids:  $[Rn]^{86} 5f^{1-14} 6d^{0-1} 7s^2$

Unlike 4f orbital, 5f orbital is not deeply buried.

## ii. Oxidation states

The principal oxidation state of lanthanoids is (+3). However, + 2 and + 4 oxidation states are also observed. This is because of extra stability of fully-filled and half-filled orbitals.

Actinoids exhibit multiple ranges of oxidation states because the 5f, 6d, and 7s levels are of comparable energies. Here, +3 is the principal oxidation state.

## iii. Atomic and ionic sizes

Similar to lanthanoids, actinoids also exhibit actinoid contraction. Here, 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. Their reactivity is comparable to Calcium. With the increase in atomic number, the lanthanides start behaving similar to Al.

On the other hand, Actinoids 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. They don't react with alkalies. In case of acids, they are slightly affected by nitric acid (because of the formation of a protective oxide layer)..

### 8.21 How would you account for the following?

- Of the  $d^4$  species,  $Cr^{2+}$  is strongly reducing while manganese (III) is strongly oxidising.
- Cobalt (II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised.
- The  $d^1$  configuration is very unstable in ions.

### Answer 8.21

- i.  $\text{Cr}^{2+}$  acts as a strongly reducing in nature. When it acts as a reducing agent, it gets oxidized to  $\text{Cr}^{3+}$  and attains  $d^3$  configuration ( $t_{2g}^3$  configuration), which is a more stable configuration.

In the case of  $\text{Mn}^{3+}$ , it acts as an oxidizing agent. While acting as an oxidising agent, it gets reduced to  $\text{Mn}^{2+}$  ( $d^5$ ). By doing this, it attains stable configuration because half-filled  $d$ -orbital is highly stable.

- ii. We know that, 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. This CFSE overcomes the ionization energy. Thus, Co (II) is stable in aqueous solutions but in the presence of strong field complexing reagents, it is oxidized to Co (III).
- iii. As by losing one electron, ion gets stability by attaining noble gas configuration. Also, the hydration is more than sufficient to remove the only electron present in the  $d$ -orbital of these ions. Therefore, they act as reducing agents.

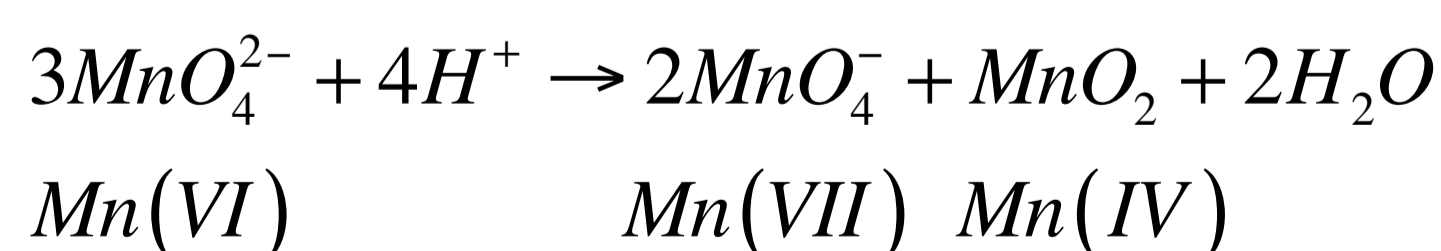
## 8.22 What is meant by ‘disproportionation’? Give two examples of disproportionation reaction in aqueous solution.

### Answer 8.22

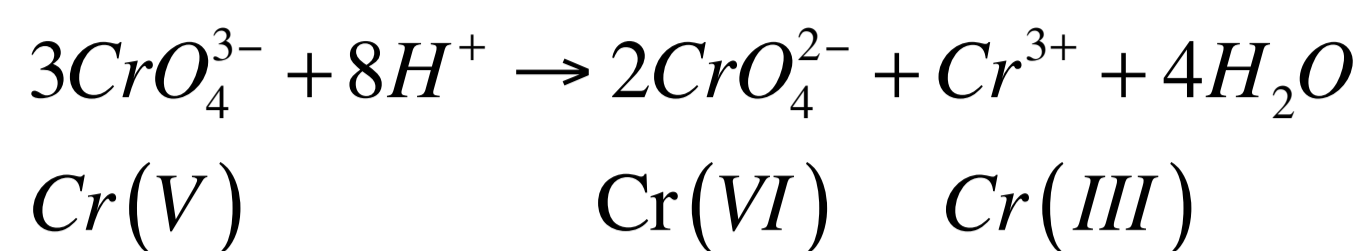
Disproportionation: - when a relatively less stable oxidation state undergoes an oxidation-reduction reaction in which it is simultaneously oxidised and reduced. It is called disproportionation.

For example,

- i. Here, Mn (VI) is oxidized to Mn (VII) and reduced to Mn (IV).



- ii. Here, Cr(V) is oxidized to Cr(VI) and reduced to Cr(III)



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

### Answer 8.23

Cu exhibits +1 oxidation state very frequently. This happens because Cu (+1) has an electronic configuration of  $[\text{Ar}]3d^{10}$  and we know that, completely filled  $d$ -orbital are stable.

**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 8.20

Gaseous ions	Electronic configuration	Number of unpaired electrons
$\text{Mn}^{3+}$	$[\text{Ar}]3d^4$	4
$\text{Cr}^{3+}$	$[\text{Ar}]3d^3$	3
$\text{V}^{3+}$	$[\text{Ar}]3d^2$	2
$\text{Ti}^{3+}$	$[\text{Ar}]3d^1$	1

$\text{Cr}^{3+}$  is the most stable in aqueous solutions.

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

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

## Answer 8.25

- i. Metal atom has a low oxidation state in the case of a lower oxide. In this case, some of the valence electrons of the metal atom are not involved in bonding. Thus, it can donate electrons and behave as a base. For example,  $MnO$  is basic

On the other hand, in higher oxide, the metal atom has a high oxidation state. Thus, the valence electrons are involved in bonding and are unavailable. It can accept electrons because of presence of high effective nuclear charge.

Thus, it can behave as an acid. For example,  $Mn_2O_7$  is acidic.

- ii. Fluorine & Oxygen have high electronegativities and small sizes. Thus, they can act as strong oxidising agents. Because of this reason, they bring out the highest oxidation states from the transition metals.

Thus, transition metal exhibits higher oxidation states in oxides and fluorides. For example, in  $V_2O_5$ , the oxidation state of V is +5.

- iii. Oxygen has high electronegativity and small size. Thus, it acts as a strong oxidising agent. Hence, metal shows highest oxidation state in oxo-anions. For example, in  $MnO_4^-$ , the oxidation state of Mn is +7.

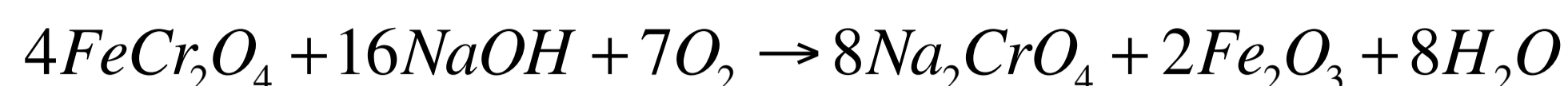
## 8.26 Indicate the steps in the preparation of:

- i.  $K_2Cr_2O_7$  from chromite ore.  
ii.  $KMnO_4$  from pyrolusite ore.

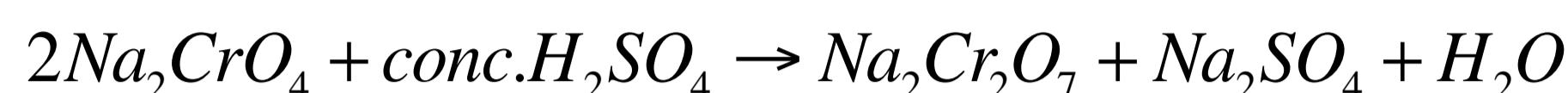
## Answer 8.26

- i. Preparation of Potassium dichromate from chromite ore: -

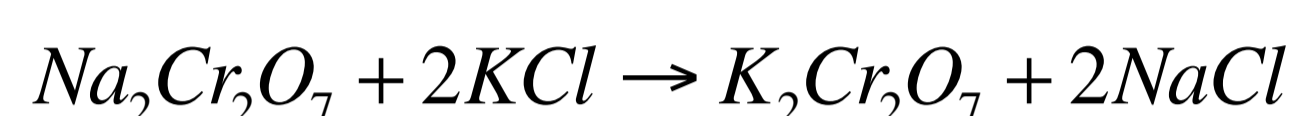
Step 1: Preparation of sodium chromate



Step 2: Conversion of sodium chromate into sodium dichromate

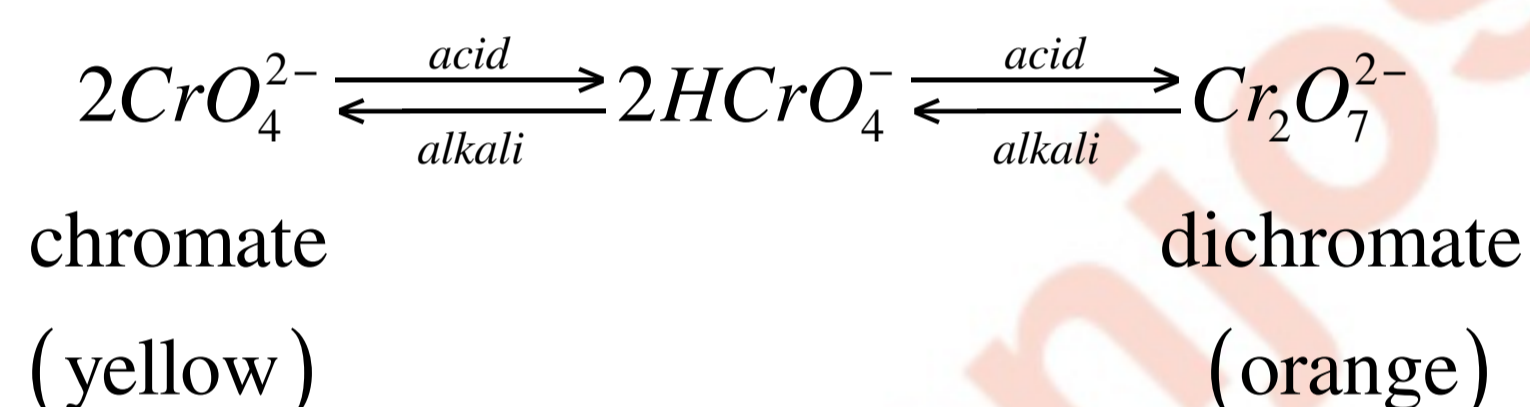


Step 3: Conversion of sodium dichromate to potassium dichromate



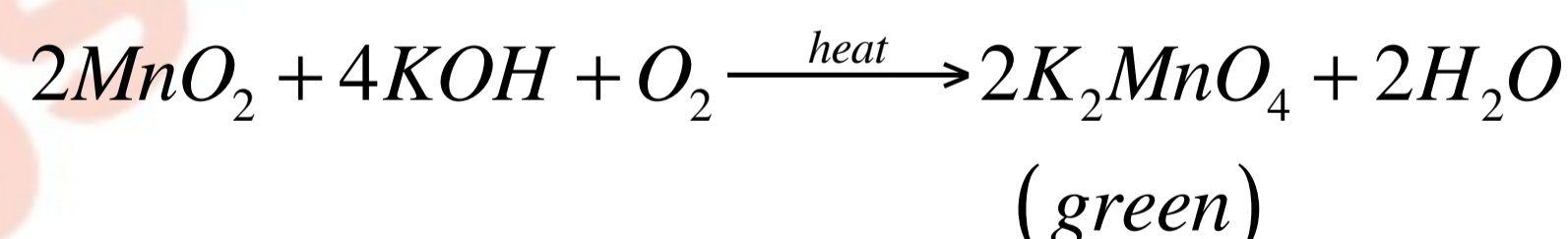
Potassium chloride being less soluble than sodium chloride is obtained in the form of orange coloured crystals and can be removed by filtration.

The dichromate ion exists in equilibrium with chromate ion at pH 4. On changing the pH, they can be inter-converted.



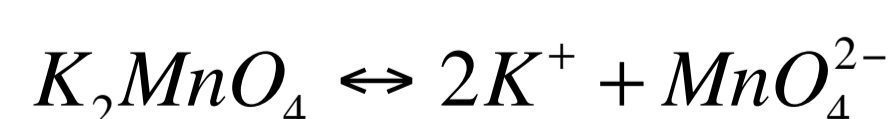
## ii. Preparation of Potassium permanganate: -

It 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  $K_2MnO_4$ .

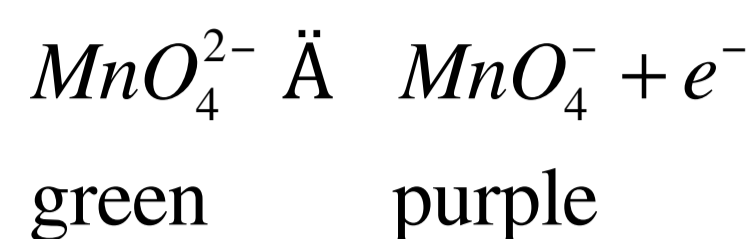


The green mass can be extracted with water and then oxidized either electrolytically or by passing chlorine/ozone into the solution.

### **Electrolytic oxidation: -**

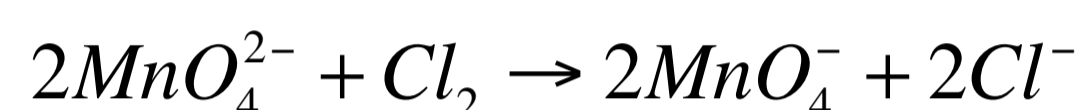
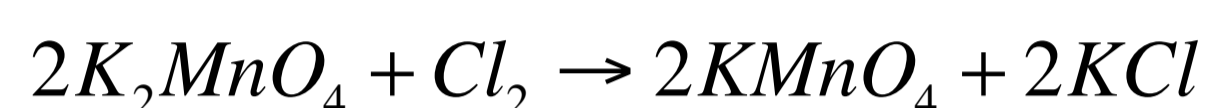


At anode,

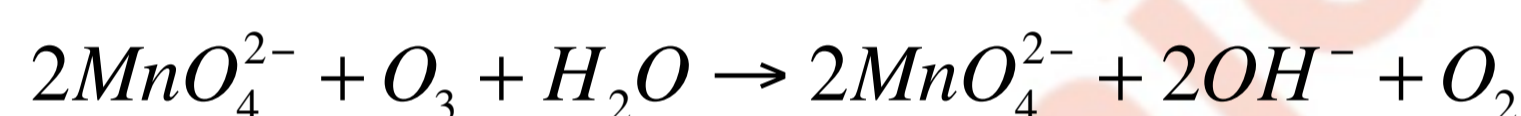
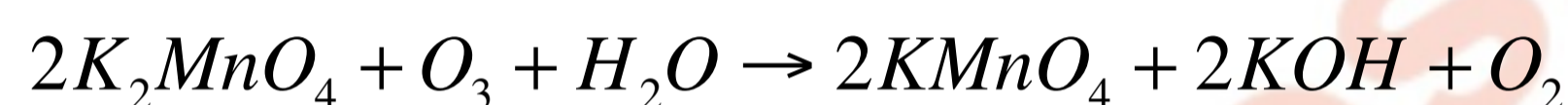


Manganate ions are oxidized to permanganate ions.

**Oxidation by chlorine: -**



**Oxidation by ozone: -**



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

**Answer 8.27**

Alloys: -

It can either be a partial solid solution or a complete solid solution. It is a solid solution of two or more elements in a metallic matrix.

Alloys 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: -**

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

**8.28 What are inner transition elements? Decide which of the following atomic numbers the atomic numbers of the inner transition elements are: 29, 59, 74, 95, 102, and 104.**

### Answer 8.28

**Inner transition elements:** - these 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.

**8.29 The chemistry of the actinoid elements is not as smooth as that of the Lanthanoids. Justify this statement by giving some examples from the oxidation state of these elements.**

Primary oxidation states of Lanthanoids are +2, +3, and +4. Among these oxidation states, +3 is the most common state. As compared to actinoids, Lanthanoids show a limited number of oxidation states because the energy difference between  $4f$ ,  $5d$ , and  $6s$  orbitals is quite large.

In the case of actinoids, the energy difference between  $5f$ ,  $6d$ , and  $7s$  orbitals is very less. Hence, actinoids show multiple oxidation states. For example, uranium shows +3, +4, +5, and +6 oxidation states while neptunium displays +3, +4, +5, and +7.

**9 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.**

The last element in the actinoid series - Lawrencium, Lr

Atomic number - 103

Electronic configuration -  $[Rn]5f^{14}6d^17s^2$

The most common oxidation state displayed by it is +3; because after losing 3 electrons it attains stable  $f^{14}$  configuration.

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

Electronic configuration of Ce:  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^1 5d^1 6s^2$

Magnetic moment can be calculated as:

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

Where,  $n$  = number of unpaired electrons

In Ce,  $n = 2$

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

$$= \sqrt{8}$$

$$= 2\sqrt{2}$$

$$= 2.828 \text{ BM}$$

**11 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 behaviour with the electronic configurations of these elements.**

The lanthanides that exhibit +2 and +4 states are shown as: -

+2	+4
Nd (60)	Ce (58)
Sm	Pr (59)

(62)	
Eu (63)	Nd (60)
Tm (69)	Tb (65)
Yb (70)	Dy (66)

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

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

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

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

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

- Electronic configuration**
- Oxidation states and**
- Chemical reactivity.**

**a. Electronic configuration: -**

The general electronic configuration for lanthanoids:  $[\text{Xe}]^{54} 4f^{0-14} 5d^{0-1} 6s^2$

The general electronic configuration for actinoids:  $[\text{Rn}]^{86} 5f^{1-14} 6d^{0-1} 7s^2$

Unlike  $4f$  orbital,  $5f$  orbital is not deeply buried.

**b. Oxidation states**

The principal oxidation state of lanthanoids is (+3). However, + 2 and + 4 oxidation states are also observed. This is because of extra stability of fully-filled and half-filled orbitals.

Actinoids exhibit multiple ranges of oxidation states because the  $5f$ ,  $6d$ , and  $7s$  levels are of comparable energies. Here, +3 is the principal oxidation state.

## c. Chemical reactivity

In the lanthanide series, the earlier members of the series are more reactive. Their reactivity is

Calcium. With the atomic number, the start behaving

On the other hand, highly reactive especially when divided. When they

boiling water, they give a mixture of oxide and hydride. Actinoids combine with most of the non-metals at moderate temperatures. They don't react with alkalies. In case of acids, they are slightly affected by nitric acid (because of the formation of a protective oxide layer).

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

comparable to increase in lanthanides similar to Al.

Actinoids are metals, they are finely are added to

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

**14 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.**

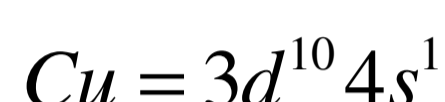
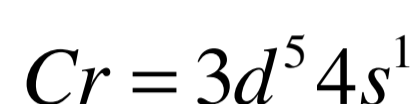
**Give special emphasis on the following points:**

- Electronic configurations
- Oxidation states
- Ionisation enthalpies
- Atomic sizes

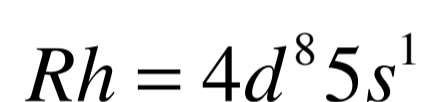
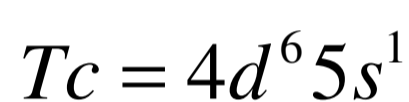
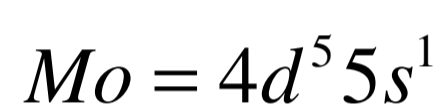
a. General electronic configuration of transition elements is:  $ns^2(n-1)d^{1-10}$

In 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.

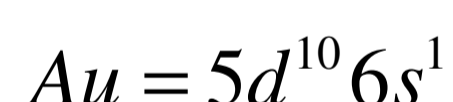
Exceptions of the first transition series are :



Some exceptions of the second transition series are:



Some exceptions of the third transition series are:



Including all these exceptions, the electronic configurations of the elements present in the same group are dissimilar.

b. All of the three transition series show maximum oxidation states in the middle and the minimum at the extreme ends.

+2 and +3 oxidation states are quite stable in the first transition series. The stability of the +2 and +3 oxidation states decreases in the second and the third transition series. There higher oxidation states are common.

c. First ionisation enthalpy increases from left to right in all of the three transition series as nuclear charge increases. But, there are some exceptions.

The first ionisation enthalpies of the third transition series are higher than those of the first and second transition series. It happens because of the poor shielding effect of 4f electrons in the third transition series.

**d.** On moving across the group (left to right), atomic size generally decreases because of increase in effective nuclear charge.

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.

In case of second & third transition series, lanthanoid contraction comes in action. Because of this, 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.

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

$\text{Ti}^{2+}$ ,  $\text{V}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{CO}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$

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

Metal ion	Number of <i>d</i> -electrons	Filling of <i>d</i> -orbitals
$\text{Ti}^{2+}$	2	$t_{2g}^2$
$\text{V}^{2+}$	3	$t_{2g}^3$
$\text{Cr}^{3+}$	3	$t_{2g}^3$
$\text{Mn}^{2+}$	5	$t_{2g}^3 e_g^2$
$\text{Fe}^{2+}$	6	$t_{2g}^4 e_g^2$
$\text{Fe}^{3+}$	5	$t_{2g}^3 e_g^2$
$\text{CO}^{2+}$	7	$t_{2g}^5 e_g^2$
$\text{Ni}^{2+}$	8	$t_{2g}^6 e_g^2$
$\text{Cu}^{2+}$	9	$t_{2g}^6 e_g^3$

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

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

- a. The atomic sizes of the elements of the first transition series are smaller than those of the 2<sup>nd</sup> and 3<sup>rd</sup> transition series. But due to lanthanoid contraction, 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
- b. +2 and +3 oxidation states are more common in the first transition series, while higher oxidation states are more common for the heavier elements.
- c. Because of stronger metallic bonding, the melting and boiling points of the first transition series are lower than those of the heavier transition elements.
- d. First transition series elements form low-spin & high-spin complexes depending upon the strength of the ligand field. But, the heavier transition elements form only low-spin complexes.

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

**Example Magnetic Moment (BM)**

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

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

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

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

For transition metals, the magnetic moment is calculated as:

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

$$\mu = 2.2$$

Thus,  $n : 1$

In this complex, Mn is in the +2 oxidation state. This means that Mn has 5 electrons in the  $d$ -orbital.

Thus, we can say that CN<sup>-</sup> is a strong field ligand that causes the pairing of electrons.



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

$$n : 4$$

In this complex, Fe is in the +2 oxidation state. This means that Fe has 6 electrons in the *d*-orbital.

Thus, we can say that  $\text{H}_2\text{O}$  is a weak field ligand and does not cause the pairing of electrons.



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

$$n : 5$$

In this complex, Mn is in the +2 oxidation state. This means that Mn has 5 electrons in the *d*-orbital.

Thus, that  $\text{Cl}^-$  is a weak field ligand and does not cause the pairing of electrons.