

## d and f Block Elements

### Weightage – 7 marks (2022-23)

#### KEY POINTS-

Elements from 3<sup>rd</sup> group to 12<sup>th</sup> group in the Modern Periodic table are called d-block elements. In these elements their last electron enters in the penultimate d- sub shell. They are placed in between s-block and p-block elements. They show a regular transition from the highly electropositive metals of s-block elements to the less electropositive p-block elements. So, they are called **transition elements**.

Transition elements can be defined as elements which contain partially filled d-orbitals in their atomic state or in any of their oxidation state. This definition does not include Zn, Cd and Hg. So, they are not regarded as transition elements. Or, they are called **pseudo transition elements**.

#### **Electronic Configuration**

General outer electronic configuration of d-block elements is  $(n-1) d^{1-10} ns^{1-2}$ . There is only a small difference in energy between (n-1) d orbital and ns orbital. So, in some cases ns electrons are also transferred to (n-1) d level. The electronic configurations of Cr and Cu in the 3d series show some exceptions.



This is due to the extra stability of half-filled and completely-filled electronic configurations. ( $d^5$  or  $d^{10}$ ) The electronic configurations of Zn, Cd and Hg are represented by the general formula  $(n-1) d^{10} ns^2$ . The orbitals in these elements are completely filled in the ground state as well as in their common oxidation states. So, they are not regarded as transition elements.

#### **General characteristics of transition elements**

##### **1. Atomic and ionic radii**

In a given transition series, the atomic and ionic radii first decrease, then become constant and increases towards the end of the series. This is because in transition elements the new electron enters in a d orbital. Initially since there is a few numbers of d electrons, the shielding effect is very poor. As the atomic number increases,

##### **2. Melting and boiling points**

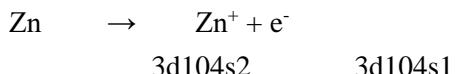
In a given transition series the melting and boiling points 1<sup>st</sup> increases up to the middle and then decreases. This can be explained in terms of metallic bond strength which depends on the number of unpaired electrons. As the number of unpaired electron increases, the metallic bond strength increases. Hence the melting point also increases.

##### **3. Ionisation enthalpy**

The ionisation enthalpy of transition elements generally increases from left to right. This is Another factor which affects the m.p is heat of atomization. Mn and Tc have low melting point even though they have  $d^5$  due to increase in nuclear charge. But the increase is not regular. This can be explained as follows.

After the removal of one electron, the relative energies of 4s and 3d orbitals get changed. Hence the remaining electron in the 4S level is transferred to 3d level. So, the unipositive ions have  $d^n$  configuration with no 4s electrons. During this re-organisation of electrons, some energy is released and it is known as exchange energy. So the net energy required to remove the 1<sup>st</sup> electrons is equal to the sum of ionisation enthalpy and exchange energy.

The first ionisation enthalpies of Cr and Cu are low. This is because the removal of one electron does not change their d configuration. Similarly, first ionisation enthalpy of Zn is high because after the removal of one electron there is no change in the d configuration.



The 2<sup>nd</sup> I.E of Cr and Cu are very high. This is because the removal of one more e<sup>-</sup> from these metals disrupted their stable configuration (d<sup>5</sup> or d<sup>10</sup>)

The 2<sup>nd</sup> I.Es of Mn and Zn are low, this is because after the removal of one more electron, they attain the stable half-filled or completely filled electronic configuration.

**4. Oxidation State** -Transition metals show variable oxidation states. This is because in these elements d and s electrons have comparable energies. So in chemical reaction along with s-electrons, d-electrons also participate. In a given transition series, the

maximum oxidation state increases up to the middle and then decreases. This is due to the half-filled or noble gas configuration. The common oxidation state of 1<sup>st</sup> row transition elements is +2. The maximum oxidation state increases from top to bottom in a group. In lower oxidation state, the transition element mainly forms ionic compounds.

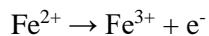
Sc generally shows +3 oxidation state because after the removal of 3 electrons, it gets a stable noble gas configuration. The oxidation state of Zn is +2 because of the completely filled configuration of Zn<sup>2+</sup>.

#### 5. Electrode Potential -

The electrode potential values of first row transition series generally increases from left to right with some exceptions. The E<sup>0</sup>(Cu<sup>2+</sup>/Cu) is positive (+0.34V), while the E<sup>0</sup> values of all the other first row transition elements are –ve. This is because the high energy to transform Cu(s) to Cu<sup>2+</sup>(aq) is not balanced by its hydration enthalpy. So, Cu does not easily react with acid and liberate H<sub>2</sub>. Only oxidizing acids [HNO<sub>3</sub> and hot Conc. H<sub>2</sub>SO<sub>4</sub>] react with Cu and the acid get reduced.

Along the series the E<sup>0</sup> values become less –ve due to the increase in the sum of 1<sup>st</sup> and 2<sup>nd</sup> ionisation enthalpies. The E<sup>0</sup> values of Mn<sup>2+</sup> and Zn<sup>2+</sup> are more –ve, this is because of the half-filled configuration of Mn<sup>2+</sup> (d<sup>5</sup>) and completely filled configuration of Zn<sup>2+</sup> (d<sup>10</sup>). E<sup>0</sup>(M<sup>3+</sup>/M<sup>2+</sup>) value of Sc is very low and that for Zn is very high. This is because of their stable electronic configuration.

E<sup>0</sup>(Mn<sup>3+</sup>/Mn<sup>2+</sup>) is high because of the stable half-filled configuration of Mn<sup>2+</sup>. Similarly E<sup>0</sup>(Fe<sup>2+</sup>/Fe<sup>3+</sup>) is low, this is because after the removal of one electron from Fe<sup>2+</sup>, it gets a stable electronic configuration.



Q. Explain why Cu<sup>+</sup> is not stable in aqueous solution?

This is due to the much more –ve hydration enthalpy of Cu<sup>2+</sup> (aq) than Cu<sup>+</sup>. In the case of Cu<sup>2+</sup>, the hydration enthalpy is more compensated by ionisation enthalpy than in Cu<sup>+</sup>.

#### 6. Magnetic Properties

Transition metals show mainly two types of magnetic properties- paramagnetism and diamagnetism. Some transition metals also show ferromagnetism which is an extreme case of paramagnetism.

Paramagnetism arises from the presence of unpaired electrons. Each unpaired e<sup>-</sup> is associated with a spin magnetic moment and an orbital magnetic moment. For the compounds of 1<sup>st</sup> row transition elements, the contribution of orbital magnetic moment is effectively cancelled and so only spin magnetic moment is considered. It is determined by the no. of unpaired e<sup>-</sup>s and is calculated by the spin only formula:

$\mu_s = \sqrt{n(n+2)}$  where n is the no. of unpaired electrons and  $\mu_s$  is the spin only magnetic moment in the unit of Bohr Magneton (B.M).

The magnetic moment increases with increase in no. of unpaired e<sup>-</sup>s. Thus, the observed magnetic moment gives an idea about the no. of unpaired e<sup>-</sup>s present in the atom or ion.

## 7. Formation of coloured ions or compounds

Most of the Transition metals ions or compounds are coloured. This is because of the presence of partially filled d orbitals. When an electron from a lower energy d orbital is excited to higher d level, it absorbs energy and this is equal to the energy of certain colours in visible region. So, the colour observed is the complementary colour of the light absorbed.

In aqueous solution most of the Transition metal ions are coloured since water molecules act as the ligands.

Among Ti<sup>2+</sup> and Ti<sup>4+</sup>, Ti<sup>2+</sup> is coloured while Ti<sup>4+</sup> is colourless. This is because Ti<sup>4+</sup> has no partially filled d orbitals.



Similarly, among Cu<sup>+</sup> and Cu<sup>2+</sup>, Cu<sup>2+</sup> is coloured while Cu<sup>+</sup> is colourless. This is due to the lack (absence) of partially filled d orbitals in Cu<sup>+</sup>.

## 8. Formation of Complexes

Transition metals form a large no. of complexes. This is due to:

1. Comparatively smaller size
2. High ionic charge
3. Presence of partially filled d orbitals
4. Ability to show variable oxidation state
5. Eg: K<sub>4</sub>[Fe(CN)<sub>6</sub>], K<sub>3</sub>[Fe(CN)<sub>6</sub>], [Ni(CO)<sub>4</sub>] etc.

## 9. Catalytic Property

Transition metals act as catalysts in a large no. of chemical reactions. This is due to –

- a) their large surface area and
- b) their ability to show variable oxidation state.

## 10. Interstitial Compound Formation

These are formed when smaller atoms like H, N, C, B etc. are trapped inside the crystal lattice of the metal. They are usually non-stoichiometric and neither typically ionic nor covalent. E.g.: Fe<sub>3</sub>H, Mn<sub>4</sub>N, TiC, VH<sub>0.56</sub>, TiH<sub>1.7</sub> etc.

Some the properties of these compounds are:

- 1) They have high melting point.
- 2) They are very hard.
- 3) They retain metallic conductivity.
- 4) They are chemically inert.

**11. Alloy Formation-** Alloys are homogeneous solid solutions of elements in which at least one element is a metal. They are formed by atoms with metallic radii within about 15% of each other. Because of similar radii and other characteristics of Transition metals, they readily form alloys. The alloys formed are hard and have high m.p. e.g.: Bronze (Cu, Zn), Stainless steel (Fe, C, Ni, Mn and Cr).

## Some Important Compounds of Transition Elements

### 1. Potassium dichromate ( K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> )

Potassium dichromate is generally prepared from chromite ore (FeCr<sub>2</sub>O<sub>4</sub>). The preparation involves three steps.

1. Conversion of chromite ore to sodium chromate

Chromite ore is first fused with sodium carbonate in presence of air to form sodium chromate.  $4 \text{FeCr}_2\text{O}_4 + 8 \text{Na}_2\text{CO}_3 + 7 \text{O}_2 \rightarrow 8 \text{Na}_2\text{CrO}_4 + 2 \text{Fe}_2\text{O}_3 + 8 \text{CO}_2$

## 2. Acidification of sodium chromate to sodium dichromate

The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to orange sodium dichromate.

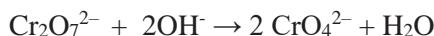
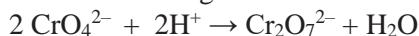


## 3. Conversion of sodium dichromate to potassium dichromate

The solution of sodium dichromate is treated with potassium chloride so that orange crystals of potassium dichromate crystallise out.  $\text{Na}_2\text{Cr}_2\text{O}_7 + 2 \text{KCl} \rightarrow \text{K}_2\text{Cr}_2\text{O}_7 + 2 \text{NaCl}$

### Properties

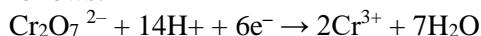
The chromate and dichromate are inter convertible in aqueous solution depending upon pH of the solution. Chromate on acidification gives dichromate and the dichromate on treating with alkali gives chromate.



The oxidation state of chromium in chromate and dichromate is +6.

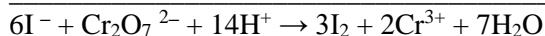
Sodium and potassium dichromates are strong oxidising agents; the sodium salt has a greater solubility in water and is extensively used as an oxidising agent in organic chemistry. Potassium dichromate is used as a primary standard in volumetric analysis.

Oxidising Property  $\text{K}_2\text{Cr}_2\text{O}_7$  is a good oxidising agent in acidic medium. Its oxidising action can be represented as follows:

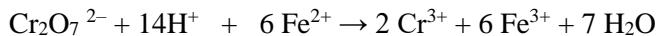
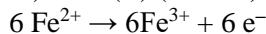


Thus, acidified potassium dichromate will oxidise.

1) Iodides to iodine-



2) Iron(II) (ferrous) to iron(III) (ferric)



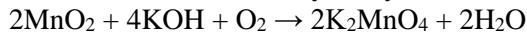
Thus, acidified potassium dichromate will oxidise

The green manganate is paramagnetic with one unpaired electron but the permanganate is diamagnetic.

### 2. Potassium permanganate ( $\text{KMnO}_4$ )

Potassium permanganate is commercially prepared from Pyrolusite ( $\text{MnO}_2$ ). The preparation involves two steps. In the first step  $\text{MnO}_2$  is fused with KOH to form potassium manganate ( $\text{K}_2\text{MnO}_4$ ).

Then  $\text{K}_2\text{MnO}_4$  is electrolytically oxidised to potassium permanganate.



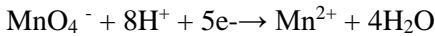
### Properties -

Potassium permanganate forms dark purple crystals which are iso-structural with those of  $\text{KClO}_4$ .

When heated it decomposes and liberate  $\text{O}_2$ .

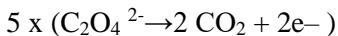


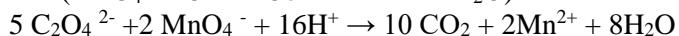
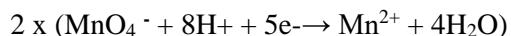
$\text{KMnO}_4$  is a good oxidizing agent in acidic, basic and neutral media. The oxidizing action in acidic medium is due to the reaction:



Acidified permanganate solution oxidises:

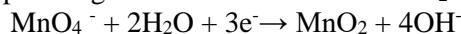
1) Oxalates to carbon dioxide:





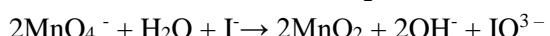
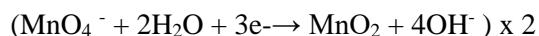
**In alkaline or neutral medium,**

permanganate ion is reduced to  $\text{MnO}_2$



**In alkaline medium it oxidises**

1) Iodide to iodate



**Uses:** It is used as an oxidising agent in acidic, basic and neutral medium. It is used as a primary standard in volumetric analysis. It is used for the bleaching of wool, cotton, silk and other textile fibres and also for the decolourisation of oils.

### THE INNER TRANSITION ELEMENTS ( f-BLOCK)

The elements in which the last electron enters in the anti-penultimate f-subshell are called f-block elements. They include lanthanides of the 6<sup>th</sup> period and actinides of the 7<sup>th</sup> period. They are also called inner transition elements. Since lanthanum (<sup>57</sup>La) closely resembles lanthanides, it is also included along with them. Similarly, actinium (<sup>89</sup>Ac) is included along with actinoids because of its close resemblance with them.

#### The Lanthanoids or lanthanides

The 14 elements after lanthanum of the 6<sup>th</sup> period are called lanthanides or lanthanoids or lanthanons or rare earths. They include elements from <sup>58</sup>Ce to <sup>71</sup>Lu. They are generally represented as Ln.

#### Atomic and ionic radii - Lanthanide Contraction

In lanthanides, the atomic and ionic radii decrease regularly from lanthanum to lutetium. This regular decrease in the atomic and ionic radii along lanthanide series (though very slightly) is called lanthanide contraction.

**Reason:** In lanthanides, as the atomic number increases, the nuclear charge increases one by one and the electrons are added to the anti-penultimate f subshell. Due to its diffused shape, f orbitals have poor shielding effect. So the nucleus can attract the outer most electrons strongly and as a result the radii decreases.

#### Consequences:

- Due to Lanthanide Contraction the 2<sup>nd</sup> and 3<sup>rd</sup> row transition series elements have similar radii. E.g. Zr – 160pm and Hf -159pm
- Lanthanides have similar physical properties and they occur together in nature. So their isolation is difficult.
- The basic character of their hydroxides decreases from lanthanum to lutetium. i.e,  $\text{La(OH)}_3$  is more basic than  $\text{Lu(OH)}_3$ .

#### Oxidation number

In lanthanoids, the most common oxidation state is +3. However, +2 and +4 ions in solution or in solid compounds are also obtained. This irregularity arises mainly from the extra stability of empty, half-filled or filled f subshells. Cerium shows the oxidation state +4 due to its noble gas configuration. Pr, Nd, Tb and Dy also exhibit +4 state but only in oxides,  $\text{MO}_2$ . Eu and Yb shows +2 oxidation state because of the stable  $f^7$  or  $f^{14}$  configuration. Sm shows +2 oxidation state also.

#### General properties of Lanthanoids

All the lanthanoids are silvery white soft metals and tarnish rapidly in air. Their hardness increases with increasing atomic number. They have typical metallic structure and are good conductors of heat and electricity.

Most of the lanthanoid ions are coloured both in the solid state and in aqueous solutions. Colour of these ions is due to the presence of f electrons. But  $\text{La}^{3+}$  or  $\text{Lu}^{3+}$  ion are colourless. The lanthanoid ions other than the  $f^0$  type ( $\text{La}^{3+}$  and  $\text{Ce}^{4+}$ ) and the  $f^{14}$  type ( $\text{Yb}^{2+}$  and  $\text{Lu}^{3+}$ ) are all paramagnetic. The paramagnetism rises to maximum in neodymium.

#### Uses of Lanthanides -

The main use of the lanthanoids is for the production of alloy steels. An important alloy is mischmetall which consists of a lanthanoid metal (~ 95%) and iron (~ 5%) and traces of S, C, Ca and Al. A great deal of mischmetall is used in Magnesium based alloy to produce bullets, shell and lighter flint. Mixed oxides of lanthanoids are employed as catalysts in petroleum cracking. Some Ln oxides are used as phosphors in television screens and similar fluorescing surfaces.

### The Actinoids or Actinones

The 14 elements after actinium in the 7<sup>th</sup> period of modern periodic table are called actinides or actinoids or actinones. They include elements from  $_{90}\text{Th}$  to  $_{103}\text{Lr}$ . Most of them are artificially prepared and are short lived. They are radioactive. The elements after Uranium are artificially prepared and so they are called **trans-uranium elements or trans-uranic elements**.

#### Atomic and ionic radii

In actinoid series the atomic and ionic radii decreases regularly from left to right. This is known as Actinoid contraction. **Oxidation state**

Common oxidation state of actinoids is +3. The elements in the first half of the series show higher oxidation states. The maximum oxidation state increases from +4 in Th to +5, +6 and +7 respectively in Pa, U and Np but decreases in succeeding elements. The actinoids resemble the lanthanoids in having more compounds in +3 state than in the +4 state.

#### Comparison between lanthanoids and actinoids

1. Most of the actinoids are artificially prepared and are radioactive.
2. The first ionisation enthalpy of early actinoids is lower than those of lanthanoids.
3. Actinoid contraction is greater from elements to elements than lanthanoid contraction. This is due to greater shielding effect of 5f electrons.

### Multiple Choice Questions-

**Q.1-** The ability of d- block elements to form complexes is due to -

- (A) small and highly charged ions
- (B) Vacant low energy orbital to accept lone pair of electrons from ligands
- (C) Both A & B are correct
- (D) None is correct

**Q.2-** Mohr's salt is a -

- (A) Normal salt      (B) Acid salt
- (C) Basic salt      (D) Double salt

**Q3-** In alkaline solution  $\text{MnO}_4^-$  changes to-

- (A)  $\text{MnO}_4^{2-}$       (B)  $\text{MnO}_2$
- (C)  $\text{Mn}_2\text{O}_3$       (D)  $\text{MnO}$

**Q.4-** Which of the following is not a characteristic property of transition metal -

- (A) High enthalpy of atomisation
- (B) Formation of interstitial compounds
- (C) Diamagnetism
- (D) Variable oxidation state

**Q.5-** Which of the following is not a transition metal ?

- (A) Sc
- (B) Mn
- (C) Zn
- (D) Co

**Q.6-** catalysts used in contact process of manufacture of sulphuric acid are –

- (A) NO      (B) V<sub>2</sub>O<sub>5</sub>
- (C) Mo      (D) Platinised asbestos

**Q.7-** If a transition-metal compound absorbs violet radiation in the visible region, its colour would be

## **Assertion Reason Questions –**

The following questions given below consist of an "Assertion" (A) and "Reason" (R) Type questions. Use the following Key to choose the appropriate answer.

- (A) If both (A) and (R) are true, and (R) is the correct explanation of (A).
  - (B) If both (A) and (R) are true but (R) is not the correct explanation of (A).
  - (C) If (A) is true but (R) is false.
  - (D) If (A) is false but (R) is true.
  - (E) If Assertion & Reason are false.

**Q.11- Assertion :** Tungsten has a very high melting point.

**Reason :** Tungsten is a covalent compound.

**Q.12- Assertion :**  $\text{TiCl}_4$  is colourless compounds.

**Reason :**  $\text{Ti}_4^+$  has no unpaired electron.

**Q.13- Assertion :** Mn atom loses ns electrons first during ionisation as compared to  $(n - 1)d$  electrons.

**Reason :** The effective nuclear charge experienced by  $(n - 1)$  d electrons is greater than that by ns electrons.

**Q.14- Assertion :** KMnO<sub>4</sub> is oxidising agent in neutral, acidic and basic medium.

**Reason :** Equivalent mass of KMnO<sub>4</sub> in acidic medium is 31.6.

**Q.15- Assertion :** All the members of actinide series are radioactive in nature.

**Reason :** The electrons are gradually accommodated in 5f-energy subshell.

**O.16- Assertion :** Ionisation of transition metals involve loss of ns electrons before (n - 1) d electrons.

**Reason :** Filling of ns orbitals take place before the filling of  $(n - 1)d$  orbitals—

### **Short Answer Type Questions (2)**

Q.17- Why is  $\text{Cr}^{2+}$  reducing and  $\text{Mn}^{3+}$  oxidising when both have  $d^4$  configuration.

O.18- Give two uses of potassium permanganate.

Q.19- Transition metal form coloured compounds. why?

Q 20-Explain why  $\text{Cu}^+$  ion is not stable in aqueous solutions?

**Q21- What are transition elements?**

### **Short Answer Type Questions (3)**

**Q22-** With the help of ionic equations describe what happens when-

- (a) pH of a solution of dichromate ions is raised.  
 (b) Potassium manganate is electrochemically oxidised.

**Q23- Suggest reasons for the following features of the transition metals-**

- (a) A transition metal exhibits higher oxidation states in oxide and fluorides.
- (b) The highest oxidation state is exhibited in oxoanions in metal.
- (c) Write the different oxides of chromium and mention basic and acidic oxides.

**Q.24 How will you obtain the following?**

- (a) Cuprous chloride from copper sulphate.
- (b) Silver from silver nitrate.
- (c) Ferrous sulphate from ferrous ammonium sulphate.

**Q.25- Give reasons for the following:**

- (a) Transition metals have high enthalpy of atomisation.
- (b) Among the lanthanoids, Ce (III) is easily oxidised to Ce (IV).
- (c)  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox couple has less positive electrode potential than  $\text{Mn}^{3+}/\text{Mn}^{2+}$  couple.

**Q.26-(a) Write the steps involved in the preparation of :  $\text{K}_2\text{Cr}_2\text{O}_7$  from  $\text{Na}_2\text{CrO}_4$  .**

**(b) What is meant by lanthanoid contraction ? What effect does it have on the chemistry of the elements which follow lanthanoids ?**

## **Case Study Based Questions**

**Q.27- Read the given passage and answer the questions that follow:**

The d-block of the periodic table contains the elements of the groups 3 to 12 and are known as transition elements. In general, the electronic configuration of these elements is  $(n - 1)\text{d}^{1-10}\text{ns}^{1-2}$ . The d-orbitals of the penultimate energy level in their atoms receive electrons giving rise to the three rows of the transition metals i.e. 3d, 4d and 5d series. However, Zn, Cd and Hg are not regarded as transition elements. Transition elements exhibit certain characteristic properties like variable oxidation stables, complex formation, formation of coloured ions, alloys, catalytic activity etc. Transition metals are hard (except Zn, Cd and Hg) and have a high melting point.

- (a) Why are Zn, Cd and Hg non-transition elements?
- (b) Which transition metal of 3d series does not show variable oxidation state?
- (c) Why do transition metals and their compounds show catalytic activity?
- (d) Why are melting points of transition metals high?
- (e) Why is  $\text{Cu}^{2+}$  ion coloured while  $\text{Zn}^{2+}$  ion is colourless in aqueous solution?

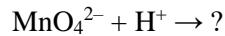
**Q.28- Read the following passage and answer the questions that follow:**

$\text{KMnO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  are most important chemicals which are used as oxidising agents and disinfectants.

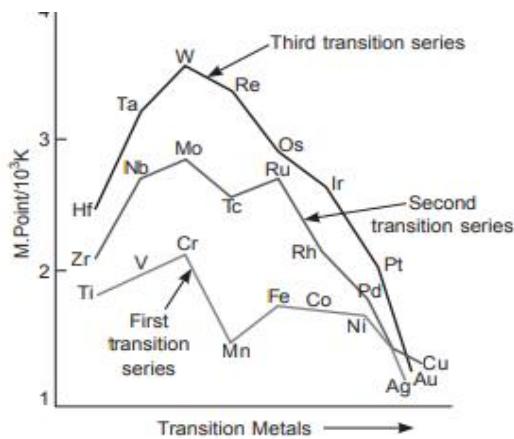
$\text{K}_2\text{MnO}_4$  is prepared by fusing  $\text{MnO}_2$  with KOH in presence of  $\text{O}_2$ .  $\text{K}_2\text{MnO}_4$  is electrolysed to get purple coloured  $\text{KMnO}_4$ .  $\text{Na}_2\text{CrO}_4$  is prepared by heating chromite ore with  $\text{Na}_2\text{CO}_3$  in presence of  $\text{O}_2$ .  $\text{Na}_2\text{CrO}_4$  is converted into  $\text{Na}_2\text{Cr}_2\text{O}_7$  by reacting with concentrated  $\text{H}_2\text{SO}_4$ .  $\text{Na}_2\text{Cr}_2\text{O}_7$  is reacted with KCl to get  $\text{K}_2\text{Cr}_2\text{O}_7$ , orange coloured solid, soluble in water, changes to yellow coloured  $\text{CrO}_4^{2-}$  in basic medium,  $\text{KMnO}_4$  acts as oxidising agent in acidic, neutral as well basic medium. In acidic medium, it converts  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ ,  $\text{Sn}^{2+}$  to  $\text{Sn}^{4+}$ ,  $\text{COO}^-$  to  $\text{CO}_2$ . In basic medium it converts  $\text{I}^-$  to  $\text{IO}_3^-$ .  $\text{K}_2\text{Cr}_2\text{O}_7$  acts as oxidising agent only in acidic medium, converts  $\text{H}_2\text{S}$  to  $\text{S}$ ,  $\text{SO}_2$  to  $\text{SO}_4^{2-}$ ,  $\text{I}^-$  to  $\text{I}_2$ . Lanthanoids and actinoids belong to f-block elements with general electronic configuration  $(n - 2)\text{f}^{1 \text{ to } 14}(n - 1)\text{d}^{0-2}\text{ns}^2$ . All actinoids are radioactive. Both show contraction in atomic and ionic radii but actinoid contraction is more than lanthanoid contraction. Lanthanoid show +3 oxidation state, few elements show +2 and +4 oxidation states also. Actinoids show +3, +4, +5, +6, +7 oxidation states.

- (a) Which lanthanoid shows +4 oxidation state and why?
- (b) Give two similarities between lanthanoids and actinoids.
- (c) Complete the equation and balance:  $\text{Cr}_2\text{O}_7^{2-} + \text{Fe}^{2+} + \text{H}^+ \rightarrow ?$
- (d) Convert sodium chromate to sodium dichromate. Give chemical equation.  
 $2\text{Na}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 \text{ (conc.)} \rightarrow ?$

(e) Complete the following:



**Q.29-**Observe the graph of transition metal and their melting points and answer the questions based on the graph and related concepts.



- (a) Why does W (tungsten) has highest melting point?
- (b) Which element in 3d series has lowest enthalpy of atomisation and why?
- (c) Why is mercury liquid?

(d) Why are transition metals less electropositive than 's'-block elements?

(e) How does density vary from left to right in 3d series and why?

**Q.30 (a)-** Write the steps involved in the preparation of  $\text{K}_2\text{Cr}_2\text{O}_7$  from chromite ore.

(b) Name one alloy of lanthanoid metal. Write any one use.

**Q.31 -** Give reasons for the following features of the transition metals-

(i) Out of the  $\text{Cu}^+$  and  $\text{Cr}^+$  which would not be the coloured ion ?

(ii) The common oxidation state of lanthanoids is +3. Why?.

(iii) Basic character of hydroxides decreases from La to Lu. Why?.

(iv) Cadmium is used to extinguish nuclear fire.

(v) Blue colour of  $\text{CuSO}_4$  solution is discharged slowly when an iron rod is dipped into it.

## ANSWERS

### **Multiple Choice Questions**

Ans.1- C

Ans.2- D

Ans.3- B

Ans.4- C

Ans.5- C

Ans.6- B

Ans.7- A

Ans.8- B

Ans.9- A

Ans.10- B

### **Assertion Reason -**

Ans.11- C

Ans.12- A

Ans 13- A

Ans 14- B

Ans 15- B

Ans 16- B

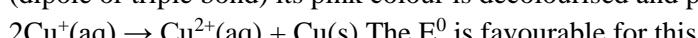
### **Short Answer Type Question (2 Marks) :-**

Ans.17-  $\text{Cr}^{2+}$  changes from  $d^4$  to  $d^3$ (stable half filled  $t_{2g}$ ).On the other hand, the change from  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$  results in the half-filled ( $d^5$ )

Ans. 18- (a) It is used as volumetric reagent for the estimation of ferrous salt, oxalate etc.



(b) When 1% alkaline KMnO<sub>4</sub> solution (Baeyer's reagent) is added to an organic compound having C = C or C ≡ C (dipole or triple bond) its pink colour is decolourised and presence of double bond or triple bond is detected.



Ans 19- Due to incompletely filled d-orbital there is d-d electron transition

Ans 20-  $\text{Cu}^+$  in aqueous solution undergoes disproportionation to form  $\text{Cu}$  &  $\text{Cu}^{2+}$

Ans.21- d-block elements which have incompletely filled d subshell in ground state as well as normal oxidation state are called as transition elements.

### **Short Answer Type Question (3 Marks) -**

**Ans 22- a)** The reactions are described with the help of the following ionic equations :



Orange              high PH              yellow

When pH is increased, i.e. solution is more basic, orange coloured dichromate ion changes to yellow coloured chromate ion.

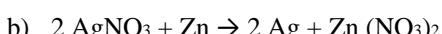


Ans.23- (a) Because oxygen and fluorine are most electronegative elements so the transition metals are oxidised to their higher oxidation states with oxygen and fluorine.

(b) Because the highest oxidation state of metal in oxoanions is stabilised by  $O_2^-$  ion, therefore, the metal shows highest oxidation state in oxoanions. Example:  $Cr_2O_7^{2-}$  (dichromate) and  $MnO_4^-$  (permanganate) have the highest oxidation states of metal i.e., Cr(VI) and Mn(VII) respectively.

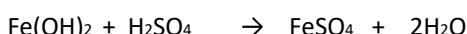
(c) Oxides of Cr :  $\text{CrO}$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{CrO}_2$  and  $\text{CrO}_3$  Oxidation state of Cr : +2 +3 +4 +6 respectively. Nature of the oxide: Basic, Amphoteric & Acidic respectively.

**Ans. 24 (a) Ans. 24 (a)**- $2\text{CuSO}_4 + 2\text{NaCl} + \text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Cu}_2\text{Cl}_2 + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4$   
Cuprous Chloride



$$(c) \text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6 \text{H}_2\text{O} + 4\text{NaOH} \rightarrow \text{Fe(OH)}_3 + 2\text{NH}_3 + 2\text{Na}_2\text{SO}_4 + 8 \text{H}_2\text{O}$$

ppt.



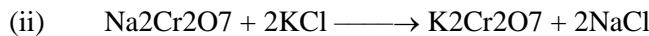
### Ferrous sulphate

Ans.25 (a)- Transition elements have large number of unpaired electrons in their atoms. Because of which they have stronger interatomic interaction. Thus, stronger bonding between the atoms resulting in higher enthalpies of atomisation.

Ans.25 (b)-Ce (III) has 4f<sub>1</sub> 5d<sub>0</sub> 6s<sub>0</sub> configuration. It can have extra stability due to empty f-orbitals by changing into Ce (IV). Due to this reason Ce (III) is easily oxidised to Ce (IV).

Ans.(c)- Mn<sup>2+</sup> is more stable than Mn<sup>3+</sup> due to extra stability of Mn<sup>2+</sup> (d<sup>5</sup> i.e., half-filled d-orbitals) while Fe<sup>3+</sup> (d<sup>5</sup>) has extra stability than Fe<sup>2+</sup>. The less positive value of E° of Fe<sup>3+/Fe<sup>2+</sup> than E° Mn<sup>3+/Mn<sup>2+</sup> indicates that the tendency to change Fe<sup>2+</sup> into Fe<sup>3+</sup> is more than that of Mn<sup>2+</sup> into Mn<sup>3+</sup>.</sup></sup>

Ans.26-(a) Steps involved in the preparation of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> are :



Ans.26-(b) The decrease in atomic and ionic size with the increase in atomic number in lanthanoids is called lanthanoid contraction. It has the following effects :

(i) The ionisation energy in 5d series is more than that in 3d and 4d series.

(ii) Atomic & ionic size of 4d ad 5d elements becomes almost identical.

(iii) There is resemblance between properties of elements 4d and 5d transition series.

## Case Study Based Questions

Ans.27-- a) It is because neither they nor their ions have incompletely filled d-orbitals.

b) Scandium (Sc) and Zinc (Zn).

c) It is because they show variable oxidation state, can form intermediate complexes and have large surface area for adsorption of gases.

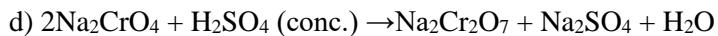
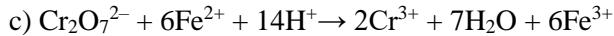
d) It is due to strong interatomic forces of attraction due to presence of unpaired electrons.

e) It is because Cu<sup>2+</sup> has one unpaired electron and undergoes d-d transition by absorbing light from visible region and radiate blue colour, whereas Zn<sup>2+</sup> is colourless due to absence of unpaired electron.

Ans.28- a) 'Ce' shows +4 oxidation state because it has stable noble gas electronic configuration.

b) (i) Both show contraction, lanthanoid and actinoid contraction.

(ii) Both form-coloured ions and undergo f-f transition.



Ans.29 (a). It is due to presence of most number of unpaired electrons and there is more frequent metal-metal bonding in 5d series than 3d and 4d series.

Ans. (b) Zinc has lowest enthalpy of atomisation due to weak metallic bond which is due to absence of unpaired electrons.

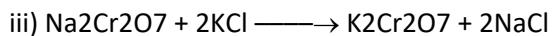
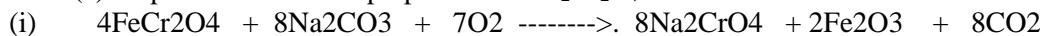
Ans (c). It is due to larger size, absence of unpaired electron and weak interatomic attraction and weaker metallic bond.

Ans (d). It is due to smaller atomic size and higher ionisation enthalpies.

Ans (e). Density goes on increasing from Sc to Cu because atomic mass increase more than atomic volume.

## Long Answer Type Questions (5 Marks) –

Ans. 30- (a) Steps involved in the preparation of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> are :



(b) The name of alloy of lanthanoid is Mischmetall. It is used in bullet shells & lighter flint.

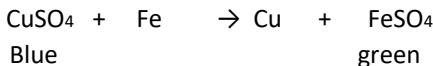
Ans 31-(i) Cu+, because there is no unpaired electron in d-orbitals.

Ans-(ii) It is due to lanthanoid contraction.

Ans-(iii) It is due to lanthanoid contraction.

Ans.(iv) Cadmium absorbs neutrons, stops nuclear fission reaction and extinguishes nuclear fire.

Ans. (v) Because Cu<sup>2+</sup> is reduced to Cu in presence of iron rod



## CONCEPT MAP

The purple solution so obtained is concentrated and dark purple, needle-like crystals of  $\text{KMnO}_4$  having metallic lustre are obtained.

- \* **Potassium dichromate:** Potassium dichromate is obtained from chromite ( $\text{FeCr}_2\text{O}_4$ ). The ore is mixed with soda ash and lime and roasted to obtain sodium chromate.

$$4\text{FeCr}_2\text{O}_4 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2(\text{g}) + 8\text{Na}_2\text{CrO}_4$$

sodium chromate

$$2\text{Na}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$$

sodium chromate

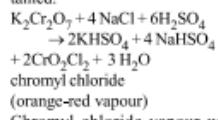
Sodium sulphate crystals are removed first and then the solution is cooled to obtain crystals of sodium dichromate dihydrate.  
Hot concentrated solution of sodium dichromate is mixed with potassium chloride to obtain crystals of potassium dichromate.

$$\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{KCl} \rightarrow \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{NaCl}$$

potassium dichromate

- \* **Chromyl chloride test:** This is a confirmatory test for chlorides. When a solid chloride salt is heated with potassium dichromate and

conc.  $\text{H}_2\text{SO}_4$ , orange coloured vapour of chromyl chloride is obtained.



Chromyl chloride vapour when passed through water give yellow-coloured solution containing chromic acid.

- \* **The f-block elements (inner-transition elements):**

The elements which in their elemental or ionic form have partly filled f-orbitals are called f-block elements. There are two series of inner-transition elements, each having 14 elements. The elements in which 4f orbitals are progressively filled are called lanthanoids. The elements in which 5f orbitals are progressively filled are termed actinoids.

**Lanthanoids:** The fourteen elements after lanthanum (atomic no. 58-71) are called lanthanoids or lanthanons.

The general electronic configuration of lanthanoids is  $4f^{1-14} 5d^{0-1} 6s^2$ .

**Oxidation states:** Lanthanoids in aqueous solution and in the solid

### THE d-AND f-BLOCK ELEMENTS

state exhibit oxidation states of +2, +3 and +4. The trivalent state (+3) being more stable.

**Magnetic properties:** Trivalent ions of lanthanoids (except  $\text{La}^{3+}$  and  $\text{Lu}^{3+}$ ) are paramagnetic.

- \* **Lanthanoid contraction:** The steady cumulative decrease in the atomic and ionic sizes in going from Ce to Lu is called lanthanoid contraction. It arises due to the increased nuclear charge and poor shielding effect of the 4f electrons. Direct consequences of the lanthanoid contraction are (a) Almost equal size of

$\text{Hf}^{4+}$  and  $\text{Zr}^{4+}$ . (b) Decrease in the basic character of lanthanoid hydroxides with increase in the atomic number.  $\text{La}(\text{OH})_3$  is the most basic, while  $\text{Lu}(\text{OH})_3$  is least basic.

- \* **Actinoids:** The fourteen elements (atomic number 90-103) after actinium are called actinoids. These are also called second series of inner-transition elements. The general electronic configuration of actinoids is  $5f^{1-14} 6d^{0-1} 7s^2$ .

**Oxidation states:** Actinoids show variable oxidation states. The oxidation state of 3+ is the most common.

**Coloured ions/salts:** Most  $\text{M}^{3+}$ ,  $\text{M}^{4+}$  ions of actinoids are coloured. Ions having 0, 1 and 7 electrons in f-subshells are colourless. The ions having 2, 3, 4, 5 and 6 electrons f-orbitals are coloured.

- \* **Misch metal:** The alloy containing 94.95% a rare earth element, iron up to 5% and traces of sulphur, carbon,

calcium and aluminium is called misch metal.

- \* **Pyrophoric alloys:** A typical composition of a pyrophoric alloy is cerium 40.5%, lanthanum + neodymium 44%, iron 4.5%, aluminium 0.5% and the remainder calcium, silicon and carbon. The pyrophoric alloys containing rare-earth metals are used in the preparation of ignition devices, e.g., tracer bullets and shells and flints for lighters.