## d & f BLOCK ELEMENTS

Q1. Cu(I) ion is not stable in an aqueous solution. Why?

Ans.  $Cu^+$  (aq)  $\rightarrow Cu(s) + Cu^{2+}(aq)$ 

Thus Cu(I) ion undergoes disproportionation in aqueous medium because  $Cu^{2+}$  is more stable than  $Cu^+$  due to higher hydration .

Q2. Account for the following:-

(i) The enthalpies of atomisation of transition elements are high.

Ans. This is because transition elements/metals have strong metallic bonds as they have a large number of unpaired electrons in them.

(ii) Many of the transition elements and their compounds can act as good catalysts. Ans. The catalytic activity of transition metals is attributed due to the following reasons:

(a) Because of their variable oxidation states

(b) The transition metal provides a suitable large surface

(iii) Among the 3d series of transition elements, the largest number of oxidation states are exhibited by manganese.

Ans. This is because manganese has electronic configuration  $[Ar]3d^54s^2$ , with five unpaired electrons in 3*d* orbitals.

(c) Transition metals and many of their compounds show paramagnetic behaviour. Ans. Because of presence of unpaired electrons in them.

(d) Transition metals generally form coloured compounds.

Ans. Because of d-d transition of unpaired electrons and absorption of certain wavelengths in the visible region of electromagnetic spectrum.

Q. Actinoid metals display a variety of structures. Why? Or, What is the reason of structural variability in actinoids?

Ans. The structural variability in actinoids is due to irregularities in metallic radii.

Q. Actinoid contraction is greater from element to element than lanthanide contraction. Why?

Ans. Due to poorer shielding effect by 5-f electrons then 4-f electrons.

Q. Which is the last element in the series of the actinoids? Write the electronic configuration of this element. Comment on the possible oxidation state of this element.

Ans. The last element in the series of actinoids is Lawrencium (Lr). Its electronic configuration is  $[Rn]_{86}$  5f<sup>14</sup>6d<sup>1</sup>7s<sup>2</sup>. The possible oxidation state for this element is +3, because +3 oxidation state has stable complete d-orbitals.

Q. Name the element of lanthanide series which is well known to exhibit +4 oxidation state.

Ans. Cerium (Ce) (atomic number: 58)

Q. What is meant by 'disproportionation' of an oxidation state? Give an example.

Ans. When a particular oxidation state becomes less stable relative to other oxidation states, one lower, one higher, it is said to undergo disproportionation. For example, manganese (VI) becomes unstable relative to manganese(VII) and manganese (IV) in acidic solution.

 $3 MnO_4^{2-} + 4 H^+ \rightarrow 2 MnO_4^- + MnO_2 + 2 H_2O$ 

It is the chemical reaction in which the same chemical species undergoes oxidation and reduction.

Other examples:  $2 H_2O_2 \rightarrow 2 H_2O + O_2$   $P_4 + NaOH + H_2O \rightarrow NaH_2PO_2 + PH_3$ Q. Calculate the 'spin only' magnetic moment of M<sup>2+</sup> (aq) ion (Z = 27). Ans. The outer electronic configuration of M (= 27): 3d<sup>7</sup> 4s<sup>2</sup>. The outer electronic configuration of M<sup>2+</sup> : 3d<sup>7</sup> or



Therrefore, the number of unpaired electrons, n = 3

So, the magnetic moment,  $\mu = \sqrt{n(n+2)}$  B. M.  $= \sqrt{15}$  B. M. = 3.87 B. M.

- Q Why is the  $E^{\odot}$  value for the  $Mn^{3*}/Mn^{2*}$  couple much more positive than that for  $Cr^{3*}/Cr^{2*}$  or  $Fe^{3*}/Fe^{2*}$ ? Explain.
- Ans. Much larger ionization enthalpy of Mn (where the required change is  $d^5$  to  $d^4$ ) is mainly responsible for this.

Q.Why are Zn,Cd and Hg not regarded as transition elements?

Ans.The d-Orbitals in these elements are completely fillede in ground state as well as in their common oxidation states.

Q.Why do Zr and Hf exhibit similar properties .

Ans.Because their atomic radii are similar due to lanthanoid contraction .

Q.Why are  $Zn^{2+}$  salts white but  $Cu^{2+}$  salts blue?

Ans. This is due to fulfilled d-Orbitals in  $Zn^{2+}$  salts and unpaired electron in  $Cu^{2+}$  salts. It causes d-d transistion in  $Cu^{2+}$  salts .

Q.What is lanthanoid contraction?

Ans. The filling of 4-f Orbitals before 5-d orbitals results in a regular decrease in atomic size of element which is called lanthanoid contraction.

Q.Compare the chemistry actinoids that of lanthanoids with special reference to (a) Electronic configuration

(b)Oxidation states

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Ans. Lanthenoids

- (a) Electronic configuration Filling of 4-f orbitals takes place.
- (b) Oxidation states
  - +2,+3 and +4 Oxidation states are Shown but +3 is common
- © Chemical Reactivity
- Lanthanoids are less reactive

Actinoids

Filling of 5-f orbitals takes place

+2 to +7 oxidation states are shown but +3 is common

Actinoida are more reactive.

## Minimum learning content

Preparation of Potassiumdichromate

4 FeCr<sub>2</sub>O<sub>4</sub> + 8 Na<sub>2</sub>CO<sub>3</sub> + 7 O<sub>2</sub>  $\rightarrow$  8 Na<sub>2</sub>CrO<sub>4</sub> + 2 Fe<sub>2</sub>O<sub>3</sub> + 8 CO<sub>2</sub> Yellow Yellow 2Na<sub>2</sub>CrO<sub>4</sub> + 2 H<sup>+</sup>  $\rightarrow$  Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + 2 Na<sup>+</sup> + H<sub>2</sub>O Orange Sodium dichromate Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + 2 KCl  $\rightarrow$  K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + 2 NaCl Orange Potassium dichromate

Preparation of Potassium permanganate

 $\begin{array}{l} 2MnO_2 \ + \ 4KOH \ + \ O_2 \ \rightarrow \ 2K_2MnO_4 \ + \ 2H_2O \\ 3MnO_4^{\ 2-} \ + \ 4H^+ \ \rightarrow \ 2MnO_4^{\ -} \ + \ MnO_2 \ + \ 2H_2O \end{array}$ 

Reactions of potassium permanganate  $Cr_2O_7^{2^-} + 14H^+ + 6e^- \rightarrow 2Cr^{3^+} + 7H_2O$ 6 I<sup>-</sup> → 3I<sub>2</sub> + 6 e<sup>-</sup>; 3 H<sub>2</sub>S → 6H<sup>+</sup> + 3S + 6e<sup>-</sup> 3 Sn<sup>2+</sup> → 3Sn<sup>4+</sup> + 6 e<sup>-</sup> 6 Fe<sup>2+</sup> → 6Fe<sup>3+</sup> + 6 e<sup>-</sup>

The full ionic equation may be obtained by adding the half-reaction for potassium dichromate to the half-reaction for the reducing agent, for e.g.,

 $\operatorname{Cr}_2\operatorname{O_7}^{2-}$  + 14 H<sup>+</sup> + 6 Fe<sup>2+</sup>  $\rightarrow$  2 Cr<sup>3+</sup> + 6 Fe<sup>3+</sup> + 7 H<sub>2</sub>O

## Reactions of Potassium permanganate

Acidified permanganate solution oxidises oxalates to carbon dioxide, iron(II) to iron(III), nitrites to nitrates and iodides to free iodine. The half-reactions of reductants are:

In alkaline / neutral medium

oxidation of iodide to iodate:

 $2MnO_4^{-} + H_2O + I^{-} \longrightarrow 2MnO_2 + 2OH^{-} + IO_3^{-}$ 

Thiosulphate is oxidised almost quantitatively to sulphate:  $8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$