CHAPTER 08

The *d*-and *f*-Block Elements

1. **Transition elements** having partially or fully filled *d*-orbitals in ground or most common oxidation state are called ***d*-block elements**. These are also called **transition elements** (having incomplete *d*-orbitals in ground or most common oxidation state), because their properties are intermediate of *s*- and *p*-block elements. General electronic configuration of this block is $(n-1)d^{1-10}\,ns^{1-2}$.

   Zn, Cd, Hg of group 12 have full d^{10} configuration in their ground state as well as in their common oxidation states, thus, they are not regarded as transition metals.

2. **General Properties**
   - The transition metals have high enthalpy of atomisation. It first increases, reaches to the maximum in the middle of each series and then decreases. It can be explained on the basis of strong interatomic interaction due to unpaired electrons. Greater is the number of unpaired electrons, stronger is the resultant bonding.
   - Metals of second (4*d*) and third (5*d*) series have high enthalpy of atomisation than the corresponding elements of 3*d*-series because of stronger metal-metal bond.
   - Ionisation enthalpy increases from left to right in a series, but irregularities are observed due to irregular trends in electronic configuration. Members show little difference in values and are fairly close. Zn shows quite high value due to extra stability of completely filled orbital.
   - There is a fall in IE_2 from Cr to Mn and from Cu to Zn because after the removal of first electron, Cr and Cu acquire a stable configuration, i.e. d^5 and d^{10}. The high values of IE_3 for Cu, Ni and Zn explains, why they show a maximum oxidation state of +2.
   - Cu^+ is unstable in aqueous solution and undergoes disproportionation.

     $2Cu^+ \longrightarrow Cu^{2+} + Cu$; Cu^{2+} is more stable than Cu^+ due to much more (–)ve ΔH (hydration) of Cu^{2+} (*aq*) than Cu^+. This is more than that required to compensate high IE_2 of Cu.
   - The values of $E^\ominus$ across the series are less negative because of general increase in the sum of the first and second ionisation enthalpies.
   - $E^\ominus$ value for any metal depends on three factors; hydration enthalpy, ionisation enthalpy, enthalpy of atomisation.

     Copper has high value of enthalpy of atomisation and low value of hydration enthalpy and also then high energy to transform Cu(*s*) to Cu^{2+}(*aq*) is not balanced by its hydration enthalpy, therefore it has positive $E^\ominus$.
   - Transition elements exhibit colour due to *d*-*d* transition, structure defects and charge transfer. Electrons of lower energy level of *d*-orbital absorb energy from visible region for excitation to higher level.
   - Many transition metals and their compounds are used as catalyst because of their ability to adopt multiple oxidation states and to form complexes.
   - Both oxygen and fluorine being highly electronegative can increase the oxidation state of a particular transition metal. In certain oxides, the element oxygen is involved in multiple bonding with the metal and this is responsible for the higher oxidation state of the metal.
   - **Magnetic properties** The magnetic moment is determined by the number of unpaired electrons and is calculated by using the 'spin-only' formula, i.e. $\mu = \sqrt{n(n+2)}$ BM.
   - The compounds in which small atoms like H, C, N etc., occupy interstitial sites in the crystal lattice are called **interstitial compounds**. These compounds are well known for transition metals because small atoms can easily occupy the positions in the interstitial sites present in the crystal lattices of transition metals.
   - **Acidic strength of oxides of transition elements** increases with the increase in oxidation state of the element, e.g. MnO (Mn^{2+}) is basic, whereas Mn_2O_7 (Mn^{7+}) is acidic in nature.

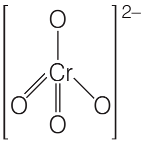
3. Important Compounds of Transition Elements

- **Potassium dichromate** is obtained from chromite ore as:

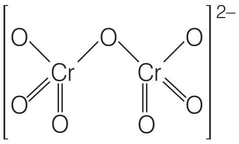
$$\underset{\text{Iron chromate}}{4FeCr_2O_4} + 8Na_2CO_3 + 7O_2 \longrightarrow 2Fe_2O_3 + 8\,\underset{\text{Sodium chromate}}{Na_2CrO_4} + 8CO_2$$

$$\underset{\text{Sodium chromate}}{2Na_2CrO_4} + 2H^+ \longrightarrow \underset{\text{Sodium dichromate}}{Na_2Cr_2O_7} + 2Na^+ + H_2O$$

$$\underset{\text{Sodium dichromate}}{Na_2Cr_2O_7} + 2KCl \longrightarrow \underset{\text{Potassium dichromate}}{K_2Cr_2O_7} + 2NaCl$$



Chromate ion



Dichromate ion

- **Potassium dichromate** is used as a primary standard solution in volumetric analysis. In acidic medium,

$$\underset{\text{Dicromate}}{Cr_2O_7^{2-}} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$
$$(E^\ominus = 1.33\text{ V})$$

Thus, acidified potassium dichromate oxidises, iodides to iodine, sulphides to sulphur, iron (II) salts to iron (III) and tin (II) to tin (IV).

Effect of pH on $Cr_2O_7^{2-}$, $Cr_2O_7^{2-} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} CrO_4^{2-}$

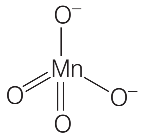
- When pyrolusite ore is fused with alkali in the presence of air or an oxidising agent like KNO_3, **potassium permanganate** is formed.

$$2MnO_2 + 4KOH + O_2 \longrightarrow \underset{\text{Potassium manganate}}{2K_2MnO_4} + 2H_2O$$

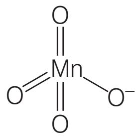
$$3MnO_4^{2-} + 4H^+ \longrightarrow \underset{\text{Permanganate ion}}{2MnO_4^-} + MnO_2 + 2H_2O$$

$$MnO_4^{2-} \xrightarrow[\text{in alkaline solution}]{\text{Electrolytic oxidation}} \underset{\text{Permanganate ion}}{MnO_4^-}$$

$$MnO_2 \xrightarrow[\text{with air or } KNO_3]{\text{Fused with KOH, oxidised}} \underset{\text{Manganate ion}}{MnO_4^{2-}}$$



Manganate ion
(Green)



Permanganate ion
(Purple)

- In acidic medium, $KMnO_4$ oxidises Fe^{2+} to Fe^{3+}, SO_3^{-2} to SO_4^{-2}, I^- to I_2 whereas in neutral medium, it converts I^- to IO_3^- and $S_2O_3^{2-}$ to SO_4^{2-}.

4. Inner-transition Elements

- The *f*-block consists of the two series, lanthanoids and actinoids.
- The electronic configuration of all the tripositive ions (the most stable oxidation state of all the lanthanoids) are of the form $4f^n$.
- Due to the poor shielding effect of $4f$-electrons, effective nuclear charge increases and radius decreases from lanthanum to lutetium. Ionic radii decreases in regular pattern but atomic radii follow irregular pattern because configuration is irregular. The gradual and steady decrease in radii across the period is known as **lanthanoid contraction**.
- Due to lanthanoid contraction, the basic character of oxides and hydroxides decreases from $La(OH)_3$ to $Lu(OH)_3$. Zr/Hf; Nb/Ta and Mo/W are almost identical in size.
- **Misch metal** is an alloy of rare earth elements (94%), iron (5%) and traces of C, S, Ca and Al. It is used in making bullets, shells and lighter flint. Pyrophoric alloys contain Ce (40.5%), La + Nd (44%) Al, Ca and S.
- .**Actinoids ions** are generally coloured due to *f*- *f* transition. It depends upon the number of electrons in 5*f*-orbitals.
- The decrease in atomic (or ionic) radii in actinoid elements (actinoid contraction) is greater than lanthanoid contraction because 5*f*-electrons have poor shielding effect as compared to 4*f*-electrons. Therefore, the effect of increased nuclear charge leading to contraction in size is more in case of actinoid elements.
- Actinoids exhibit more number of oxidation states than lanthanoids. This is due to the fact that 5f, 6d and 7s levels are of comparable energies.
- Actinoids have stronger tendency towards complex formation as compared to lanthanoids.

Practice Questions

1. Which of the following element does not have $(n-1)\,d^{10}ns^2$ electronic configuration?

(a) Zn *(b)* Cd
(c) Hg *(d)* Cu

2. The ground state electronic configuration of neutral titanium atom is

(a) $[\mathrm{Ar}]\,4s^2 4p^2$ *(b)* $[\mathrm{Ar}]\,3d^2 4s^2$
(c) $[\mathrm{Ar}]\,4s^2 p_x^1 p_y^1$ *(d)* $[\mathrm{Ar}]\,3d^5$

3. The third ionisation enthalpy is minimum form

(a) Mn *(b)* Ni
(c) Co *(d)* Fe

4. Which element can have oxidation state from 4 to 6?

(a) Fe *(b)* Mg
(c) Co *(d)* Cr

5. Magnetic moment of a transition metal ion is found to be 3.87 BM. The number of unpaired electrons present in it is

(a) 2 *(b)* 3
(c) 4 *(d)* 5

6. Which of the following aqueous solutions will be coloured?

(a) $Zn(NO_3)_2$ *(b)* $LiNO_3$
(c) $CoNO_3$ *(d)* $HgCl_2$

7. Which of the following alloys contain Cu and Zn?

(a) Brass *(b)* Bronze
(c) Bell metal *(d)* All of these

8. Acidified potassium dichromate oxidises

(a) iodides to iodine *(b)* sulphides to sulphur
(c) tin (IV) to tin (II) *(d)* Both (a) and (b)

9. Which of the following can react with $K_2Cr_2O_7$?

(a) SO_3^{-2} *(b)* CO_3^{-2}
(c) SO_4^{-2} *(d)* NO_3^-

10. Dichromates are generally prepared by the fusion of chromite ore with

(a) sodium carbonate *(b)* potassium carbonate
(c) Both (a) and (b) *(d)* Neither (a) nor (b)

11. Permanganate ion (MnO_4^-) is dark purple coloured though Mn is in + 7 oxidation state with d^0 configuration. This is due to

(a) *d-d* transition
(b) charge transfer from metal to ligand
(c) charge transfer from ligand to metal
(d) All of the above

12. Name the gas that can readily decolourise acidified $KMnO_4$ solution.

(a) CO_2 *(b)* SO_2
(c) NO_2 *(d)* P_2O_5

13. The product of following reaction is

$$K_2CrO_4 + \text{dil. } HNO_3 \text{ (excess)} \longrightarrow$$

(a) Cr^{3+} and $Cr_2O_7^{2-}$
(b) $Cr_2O_7^{2-}$, NO_3^- and H_2O
(c) Only Cr^{3+}
(d) Only Cr^{7+}

14. The green manganate and purple permanganate are respectively

(a) paramagnetic, diamagnetic
(b) diamagnetic, paramagnetic
(c) paramagnetic, paramagnetic
(d) diamagnetic, diamagnetic

15. The most common lanthanoid among the following is

(a) lanthanum *(b)* cerium
(c) promethium *(d)* plutonium

16. Which of the following pairs has the same size?

(a) Zn^{2+}, Hf^{4+} *(b)* Fe^{2+}, Ni^{2+}
(c) Zr^{4+}, Ti^{4+} *(d)* Zr^{4+}, Hf^{4+}

17. The correct order of ionic radii of Ce, Pm, Gd and Dy in +3 oxidation state is

(a) $Ce^{3+} < Gd^{3+} < Pm^{3+} < Dy^{3+}$
(b) $Ce^{3+} < Pm^{3+} < Gd^{3+} < Dy^{3+}$
(c) $Dy^{3+} < Gd^{3+}$`$< Pm^{3+} < Ce^{3+}$
(d) $Pm^{3+} < Ce^{3+} < Dy^{3+} < Gd^{3+}$

18. A man made white silvery metal, radioactive in nature, has strong tendency to form oxocations and complexes. It is used as a nuclear fuel in atomic reactor. This metal is a

(a) actinide
(b) lanthanide
(c) representative element
(d) transition metal

19. All the actinoids are believed to have the electronic configuration of

(a) $6s^2$ *(b)* $7s^2$
(c) $5f^{14}$ *(d)* $6d^{10}$

20. What will be the most common oxidation state shown by the actinoids?

(a) −3 *(b)* +3
(c) −4 *(d)* +4

21. Which of the following elements shows maximum number of different oxidation states in its compounds?

(a) Eu *(b)* La

(c) Gd *(d)* Am

22. The actinoids resemble the lanthanoids in having more compounds in

(a) +3 state *(b)* +4 state

(c) +5 state *(d)* +2 state

23. Compound(s) useful in the battery industries is/are

(a) MnO_2 *(b)* Zn

(c) Ni/Cd *(d)* All of these

24. Catalyst used in the oxidation of SO_2 in the manufacture of H_2SO_4 is

(a) $CuCl_2$

(b) V_2O_5

(c) MnO_2

(d) None of thesee

25. Which of the following compounds form the basis, if Ziegler-Natta catalysts is used to manufacture of polythene?

(a) $TiCl_4$ *(b)* $Al(CH_3)_3$

(c) $TiCl_4$ with $Al(CH_3)_3$ *(d)* None of these

ANSWERS

1. (d)	**2.** (b)	**3.** (d)	**4.** (d)	**5.** (b)	**6.** (c)	**7.** (a)	**8.** (d)	**9.** (a)	**10.** (c)
11. (c)	**12.** (b)	**13.** (b)	**14.** (a)	**15.** (b)	**16.** (d)	**17.** (c)	**18.** (a)	**19.** (b)	**20.** (b)
21. (d)	**22.** (a)	**23.** (d)	**24.** (b)	**25.** (c)					

Hints & Solutions

1. (*d*) 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.

Cu has electronic configuration $3d^{10}4s^1$. Thus, Cu does not have $(n-1)d^{10}ns^2$ electronic configuration.

3. (*d*) Fe has minimum value of third ionisation enthalpy. Ground state electronic configuration of Fe is $[Ar]3d^6 4s^2$.

Fe^{2+} has $[Ar]3d^6$ configuration, whereas Fe^{3+} has $[Ar]3d^5$. The latter is a stable configuration and easier to ionise Fe^{2+} to Fe^{3+} than expected.

Hence possess least value.

Ni has highest value of third ionisation enthalpy due to its greater nuclear charge and smaller size.

Due to the same reason, Co > Fe > Mn should be the order for the remaining elements, but the anomalous order is due to greater stability of Mn^{2+} having $[Ar]3d^5$ configuration than Mn^{3+} with $[Ar]3d^4$.

Whereas for Co^+, the electronic configuration is $[Ar]3d^7$, Thus, ionisation enthalpy needed to remove third electron is less as compared to that of Mn^{2+}.

4. (*d*) Oxidation state of alkaline earth metal (i.e. Mg) is fixed and equal to (+)2.

Oxidation state of *d*-block elements can vary, i.e. for Fe and Co it is as follows :

Oxidation state of Co = (+) 2 to (+) 4 and oxidation state of Fe = (+) 2 to (+) 6, but (+) 6 is less stable.

Oxidation state of Cr = (+) 2 to (+) 6, where (+) 6 state is more stable.

5. (*b*) Magnetic moment of a transition metal ion

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

$$\therefore \quad 3.87 = \sqrt{n(n+2)} \qquad (\text{Given}, \mu = 3.87)$$

On solving, $n = 3$

Thus, number of unpaired electrons are 3.

6. (*c*) Only Co^+, because of the presence of unpaired electrons in *d*-orbitals show *d-d* transition and, hence it is coloured.

8. (*d*) Acidified potassium dichromate oxidises iodides to iodine, sulphides to sulphur, tin(II) to tin(IV), iron(II) salts to iron (III).

9. (*a*) Oxidation state of central atoms are as follows :

Sulphur in $SO_3^{-2} = +4$

Carbon in $CO_3^{-2} = +4$

Sulphur in $SO_4^{-2} = +6$

Nitrogen in $NO_3^- = +5$

Since, $K_2Cr_2O_7$ is a strong oxidising agent it can oxidise the species, which is not in its most possible positiveoxidising state.

Thus, SO_3^{-2} can react with $K_2Cr_2O_7$ as follows :

$$Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) + 8H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + 4H_2O(l)$$

10. (*c*) Dichromates are generally prepared from chromate which in turn are obtained by the fusion of chromite ore ($FeCr_2O_4$) with sodium or potassium carbonate in free access of air.

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

$$2Na_2CrO_4 + 2H^+ \longrightarrow Na_2Cr_2O_7 + 2Na^+ \; H_2O$$

11 (*c*) In MnO_4^- ,

$$x + (-2)4 = -1$$

$$\Rightarrow \qquad x = +7$$

${}_{25}Mn^{+7} = [Ar]$, no unpaired electrons.

Thus, it will not show *d-d* transition. It is dark purple coloured due to charge transfer from ligand to metal.

12. (*b*) SO_2 gas can readily decolourise acidified $KMnO_4$ solution because $KMnO_4$ is an oxidising agent that easily oxidises SO_2,

$$2MnO_4^- + 5SO_2 + 2H_2O \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$$

while other options such as NO_2 (strong oxidising agent), CO_2 (neither oxidising agent nor reducing agent) cannot decolourise acidified $KMnO_4$ solution.

13. (*b*) The product of given reaction is $Cr_2O_7^{2-}$, NO_3^- and H_2O,

$$\underset{\substack{\text{Chromate}\\\text{(yellow)}}}{2CrO_4^{2-}} + \underset{\text{(Dil.)}}{2HNO_3} \longrightarrow \underset{\substack{\text{Dichromate}\\\text{(orange)}}}{Cr_2O_7^{2-}} + 2NO_3^- + H_2O$$

14. (*a*) The manganate and permanganate ions are tetrahedral. Here, the π-bonding takes place by overlap of *p*-orbitals of oxygen with *d*-orbitals of manganese. The green manganate is paramagnetic because of one unpaired electron but the purple permanganate is diamagnetic due to charge transfer.

15. (*b*) Lanthanum is a *d*-block element, whereas plutonium is an actinoid. Both cerium and promethium are lanthanoids. But cerium is a common lanthanoid because it occurs naturally, whereas Pm does not occur naturally and is radioactive.

16. (*d*) Zr^{4+} and HF^{4+} have same size due to lanthanoid contraction.

18. (*a*) Actinide is a man-made white silvery metal, radioactive in nature has a strong tendency to form oxocations and complexes.

19. (*b*) All the actinoids are believed to have the electronic configuration of $7s^2$ and variable occupancy of $5f$ and $6d$-subshell.

25 (*c*) $TiCl_4$ with $Al(CH_3)_3$ forms the basis of *Ziegler-Natta* catalysts that is used to manufacture polythene.