CHAPTER-4

d- AND f-BLOCK ELEMENTS

d-Block : 3d, 4d and 5d Series

Concepts covered: Transition elements, Electronic configuration, Properties of transition metals, Interstitial compounds.

Revision Notes

Topic-1

- > *d*-Block elements: The elements in which last electron enters the *d*-subshell of penultimate shell. The general electronic configuration of these element is $(n-1)d^{1-10}ns^{1-2}$, where n is outermost shell. The *d*-block consisting of groups 3–12 occupies the large middle section of the periodic table.
- Transition elements: The elements of *d*-block are known as transition elements as they possess properties that are transitional between the *s*-block and *p*-block elements. Transition elements are defined as elements which have incompletely filled *d*-orbitals in its ground state or in any of its oxidation state. Transition elements have four series:
 - (i) First transition series: These elements have incomplete 3*d* orbitals and they are from Sc(21) to Zn(30).
 - (ii) Second transition series : These elements have incomplete 4*d* orbitals and they are from Y(39) to Cd(48).
 - (iii) Third transition series: These elements have incomplete 5*d* orbitals and they are from La(57) and Hf(72) to Hg(80).
 - (iv) Fourth transition series: These elements have incomplete 6*d* orbitals. The series are starts with Ac (89) followed by Rf (104) to Cn (112).
- **Cancel and Section 2** General electronic configuration: $(n 1)d^{1-10}$, ns^{1-2} where (n 1) stands for penultimate shell.
- General characteristics:
 - **Metallic character:** Almost all the transition elements exhibit typical metallic properties like metallic lustre, malleability, ductility, high tensile strength, etc.
 - Atomic radii: Atomic radii of transition elements first decreases till the middle, become almost constant and then increases towards the end of the period. This decrease in atomic radii in the beginning is due to increase in effective nuclear charge. However, with an increase in the number of electrons in (n 1) subshell, the screening effect of the *d*-electrons on the outermost *ns* electrons increases.



Fig. 1 : Trends in melting points of transition elements

- **Ionic radii:** The ionic radii of the transition elements follow the same order as their atomic radii. It decreases with an increase in oxidation number.
- **Ionisation enthalpy:** The ionisation energies of transition elements are quite high and lies between those of *s*-block and *p*-block elements. The first ionisation energy increases with an increase in atomic number across a given transition series, although the increase is not very regular.



Fig. 2 : Trends in enthalpies of atomisation of transition elements

• Variable oxidation state: Since, the energies of ns and (n - 1)d electrons are almost equal, therefore the electrons of both these orbitals take part in the reactions, due to which transition elements show variable oxidation states. Oxidation state is the measure of the electronic state of an atom in a particular compound, equal to the number of electrons it has more than or less than the number of electrons in free atom. Transition metal ions show variable oxidation states.

Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn
	+2	+2	+2	+2	+2	+2	+2	+1	
+3	+3	+3	+3	+3	+3	+3	+3	+2	+2
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

- Electrode potential: The electrode potential developed on a metal electrode when it is in equilibrium with a solution of its ions, leaving electrons from the electrode. Transition metals have lower value of reduction potential. Variation in *E*°, value is irregular due to regular variation in ionisation enthalpies (I.E₁ + I.E₂), sublimation and hydration enthalpies.
- Catalytic properties: Many of the transition metals and their compounds, particularly oxides act as catalysts for a number of chemical reactions. Iron, cobalt, nickel, platinum, chromium, manganese and their compounds are commonly used catalysts.

Magnetic properties: On the basis of the behaviour of substances in magnetic field, they are of two types:
 (i) Diamagnetic,
 (ii) Paramagnetic

Diamagnetic substances have paired electrons only. e.g., Zn has only paired electrons.

In paramagnetic substances, it is necessary to have at least one unpaired electron. Paramagnetism increases with the increase in number of unpaired electrons.

Paramagnetism may be measured by magnetic moment.

Magnetic moment (μ) = $\sqrt{n(n+2)}$ B.M.

where, n = number of unpaired electrons in an atom or ion and B.M. = Bohr Magneton (unit of magnetic moment). Diamagnetic and paramagnetic substances are repelled and attracted in the magnetic field respectively (Magnetic properties of transition elements).

Ion	Outer electronic configuration	Unpaired electrons	Magnetic moment calculated (B.M.)	Magnetic moment experimental (B.M.)	
Sc ³⁺	$3d^0$	0	0	0	
Ti ³⁺	$3d^1$	1	1.73	1.75	
Ti ²⁺	$3d^{2}$	2	2.84	2.86	
V^{2+}	$3d^3$	3	3.87	3.86	
Cr ²⁺	$3d^4$	4	4.90	4.80	
Mn ²⁺	$3d^{5}$	5	5.92	5.95	
Fe ²⁺	$3d^{6}$	4	4.90	5.0–5.5	
Co ²⁺	3d ⁷	3	3.87	4.4–5.2	
Ni ²⁺	$3d^{8}$	2	2.84	2.9–3.4	
Cu ²⁺	3d ⁹	1	1.73	1.4-2.2	
Zn ²⁺	$3d^{10}$	0	0	0	

- Formation of coloured compounds: Transition metals form coloured ions due to the presence of unpaired *d*-electrons. As a result, light is absorbed in the visible region to cause excitation of unpaired *d*-electrons (*d*-*d* transition) and colour observed corresponds to the complementary colour of the light absorbed. Cu²⁺, Zn²⁺ and Cd²⁺ are colourless due to the absence of unpaired *d*-electron (*d*¹⁰).
- **Melting and boiling points:** These elements have high melting and boiling points because of strong interatomic bonding.
- **Formation of alloys:** Alloy formation is due to almost similar size of the metal ions, their high ionic charges and the availability of *d*-orbitals for bond formation.
- Coinage metals and currency metals: Copper (Cu), silver (Ag) and gold (Au) present in group 11 are known as coinage or currency metals.
- Interstitial compounds: These are those compounds in which small atoms occupy the interstitial sites in the crystal lattice. Interstitial compounds are well known for transition metals because small sized atoms of H, B, C, N, etc., can easily occupy position in the voids present in the crystal lattice of transition metals.
- Metal-Metal bonding: The heavier transition metals show strong tendency to form strong M-M bonds than their light congeners. This is due to their greater enthalpy of atomisation.
- > The atomic size or the ionic radii of tri-positive ions decrease steadily from La^{3+} to Lu^{3+} due to increasing nuclear charge and electrons entering inner (*n*-2) *f* orbital. This gradual decreases in the size with an increasing atomic number is called Lanthanide Contraction.

Mnemonics

f-Block Elements: 4f and 5f Series

Concept covered: Lanthanoid and their properties, Actinoid and their properties

Revision Notes

Topic-2

- Elements in which last electron enters into *f*-orbital are called *f*-block elements.
- > The elements in which the differentiating electrons enter into (n 2) *f*-subshell are called inner-transition elements.
- It consists of two series called lanthanoid series and actinoid series.
- ▷ **Lanthanoids:** The series involving the filling of 4*f*-orbitals following Lanthanum La (Z = 57) is called the lanthanoid series. There are 14 elements in this series starting with Ce (Z = 58) to Lu (Z = 71).
 - Electronic configuration: $[Xe] 4f^{0-14}5d^{0-1}6s^2$
 - Highly dense metals.
 - High melting points.
 - Form alloy easily with other metals.
 - Soft, malleable and ductile with low tensile strength.
 - **Oxidation state:** The most common oxidation state is +3. It exhibits +2 and +4 oxidation state.
 - **Colour:** Some of the trivalent ions are coloured. This is due to the absorption in visible region of the spectrum, resulting in *f*-*f* transitions as they have partly filled orbitals.
 - **Magnetic properties:** La³⁺ and Lu³⁺ have 4^{f0} or 4^{f14} electronic configurations which are diamagnetic and all the other trivalent lanthanoid ions are paramagnetic due to presence of unpaired electrons.
 - Reactivity: Highly electropositive metals have an almost same chemical reactivity.
 - Combines with hydrogen gas on gentle heating to form hydride.
 - On heating with carbon form carbides of formula Ln₃C, LnC₂, Ln₂C₃.
 - With dilute acids, they liberate hydrogen.

$$2Ln + 6H^+ \longrightarrow 2Ln^{3+} + 3H_2$$

With halogens, burn to form halides.

$$2Ln + 3X_2 \longrightarrow 2LnX_3$$

• Burn in oxygen to form oxides

$$2Ln + 3O_2 \longrightarrow Ln_2O_3$$

- Form oxides and hydroxides of formula M₂O₃ and M(OH)₃.
- Lanthanoid contraction is a steady decrease in the size of lanthanoids with increase in atomic number. On moving from Ce to Lu, the size of atoms and ions decreases regularly. The 4*f* orbitals are too diffused to screen the nucleus as effectively as the more localised inner shell. So, the attraction of the nucleus for the outermost electrons increases steadily with the atomic number.

• Uses:

- For producing alloy steels for plates and pipes. e.g., Mischmetal, which is an alloy of cerium and various other lanthanoid elements.
- Steel mixed with La, Ce, Pr and Nd is used in the manufacture of flame throwing tanks.
- Used as a catalyst for hydrogenation, dehydrogenation and petroleum cracking.
- Pyrophoric alloys are used for making tracer bullets and shells.
- ➤ Actinoids:
 - Elements following actinium, Ac (Z = 89) upto lawrencium (Z = 103) are called as actinoids.
 - General electronic configuration: $[Rn] 5^{t0-14} 6 d^{0-27} s^2$
 - Highly dense metals with a high melting point.
 - Form alloys with other metals, specially iron.
 - Silvery white metals which are highly reactive.
 - Gets tarnished when exposed to alkalies.
 - Actinoid contraction: The atomic and ionic size decrease with an increase in atomic number. Electrons when added to the 5*f*-shell, result in an increase in the nuclear charge causing the shells to shrink inwards.
 - Oxidation state: All actinoids show +3 oxidation state. The elements in the first actinoid series show higher states also.
 - Colour: Actinoid ions are coloured.
 - **Magnetic properties:** All the actinoids and their compounds are paramagnetic.
 - **Reactivity:** Highly electropositive and form salts as well as complexes.
 - Uses:
 - Thorium is used in the treatment of cancer, incandescent gas mantles and in nuclear chemistry.
 - Uranium is used in the glass industry, textile industry, in medicines and as nuclear fuel.
 - Plutonium is used in nuclear reactors.



Difference between Lanthnoids and Actinoids: ≻

Lanthanoids	Actinoids
Lunthunoiub	nemonas
• 4 <i>f</i> orbitals is filled progressively.	 5f orbital is filled progressively.
Only Pm is radioactive.	All are radioactive.
 Less reactive than actinoids. 	More reactive.
• Common oxidation is +3 where other oxidation	• Common oxidation state is +3 where other
states are $+2$, $+4$. It is due to a large energy gap	oxidation states are $+2$, $+4$, $+5$ and $+7$ due to small
between 4 <i>f</i> , 5 <i>d</i> and 6 <i>s</i> subshell.	energy difference between 5 <i>f</i> , 6 <i>d</i> , and 7 <i>s</i> orbitals.
Paramagnetic properties are easily explainable.	 Paramagnetic properties are hard to explain.

Key Terms ©–₩

Topic-3

- Transuranic elements: All the elements beyond uranium are known as transuranic or man-made elements. \geq \geq
 - Platinum black: It is the finely reduced form of platinum in the form of velvety black powder.



Mnemonics:ActionThor is pro, Uranus, Neptune, PlutoPlanets sees in America, Curious Berks in California, Einstein Fermium, Mendeleuim, NobeliumInterpretation :AA : ActiniumTT : Thoriumpp : ProtactiniumU : UraniumN : Neptunium	 P : Plutonium A : Americium C : Curium B : Berkelium C : Californium E : Einsteinium F : Fermium M : Mendelevium N : Nobelium 1 : Lawrencium
--	---

_ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _

Concepts covered: Preparation and Properties of Potassium Permanganate and Potassium Dichromate



Revision Notes

- Preparation of Potassium permanganate:
 - (i) It is prepared from pyrolusite ore with KOH in the presence of oxidising agent like KNO_3 . The dark green potassium manganate undergoes electrolytic oxidation to produce potassium permanganate. $2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$

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

(ii) Commercially, it is prepared by alkaline oxidative fusion of MnO_2 followed by electrolytic oxidation of manganate (VI).

$$\begin{array}{ccc} MnO_{2}+2e^{-} & \xrightarrow{Fused with KOH} & MnO_{4}^{2-} \\ \hline Oxidised with air/KNO_{3} & MnO_{4}^{2-} \\ \hline MnO_{4}^{2-} & \xrightarrow{Electrolytic oxidation} & MnO_{4}^{-} & +1e^{-} \\ \hline & nalkaline solution & Permanganate ion \end{array}$$

(iii) In laboratory, by oxidation of manganese(II) ion salt by peroxodisulphate.

$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$$

Peroxodisulphate

- Properties: \geq
 - Dark purple crystalline solid.
 - Sparingly soluble in water.
 - Decomposes on heating at 513 K.

$$2KMnO_4 \xrightarrow{513K,\Delta} K_2MnO_4 + MnO_2 + O_2$$

• Oxidising properties:

- Acts as a powerful oxidising agent in acidic, alkaline and neutral medium. For example:
 - 1. In acidic medium oxidises:
 - (i) Iodide to iodine :

$$[MnO_{4}^{-} + 8H^{+} + 5e^{-} \longrightarrow Mn^{2+} + 4H_{2}O] \times 2$$
$$[2I^{-} \longrightarrow I_{2} + 2e^{-}] \times 5$$
$$2MnO_{4}^{-} + 10I^{-} + 16H^{+} \longrightarrow 2Mn^{2+} + 5I_{2} + 8H_{2}O$$

(ii) Ferrous to ferric :

$$\begin{array}{c} MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \\ \hline Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 5 \\ \hline MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O \\ \end{array}$$

(iii) Oxalate to carbon dioxide :

$$\begin{split} & [\mathrm{MnO_{4^-}}+8\mathrm{H^+}+5\mathrm{e^-} \longrightarrow \mathrm{Mn^{2+}}+4\mathrm{H_2O}] \times 2 \\ & [\mathrm{C_2O_4^{2-}} \longrightarrow 2\mathrm{CO_2}+2\mathrm{e^-}] \times 5 \\ & 2\mathrm{MnO_{4^-}}+5\mathrm{C_2O_4^{2-}}+16\mathrm{H^+} \longrightarrow 2\mathrm{Mn^{2+}}+10\mathrm{CO_2}+8\mathrm{H_2O} \end{split}$$

(iv) Hydrogen sulphide to sulphur :

 $[\mathrm{MnO_4^-} + 8\mathrm{H^+} + 5\mathrm{e^-} \longrightarrow \mathrm{Mn^{2+}} + 4\mathrm{H_2O}] \times 2$

$$[S^{2-} \longrightarrow S + 2e^{-}] \times 5$$
$$2MnO_4^{-} + 5S^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 5S + 8H_2O$$

(v) Sulphite to sulphate :

$$[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$
$$[SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-] \times 5$$
$$\overline{5SO_3^{2-} + 2MnO_4^- + 6H^+} \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$

(vi) Nitrite to nitrate :

$$[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$
$$[NO_2^- + H_2O \longrightarrow NO_3^- + 2H^+ + 2e^-] \times 5$$
$$2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$$

2. In neutral alkaline medium:

(i) Iodide to iodate :

$$[MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-] \times 2$$

$$I^- + 6OH^- \longrightarrow IO_3^- + 3H_2O + 6e^-$$

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

(ii) Manganous to manganese dioxide :

$$2MnO_4^{-} + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$$

- > Uses of Potassium permanganate:
 - In analytical chemistry (titration).
 - In decolourisation of oils.
 - In sterilising wells of drinking water and washing wounds.
- Structure of Potassium permanganate: Both manganate and permanganate ions are tetrahedral. The green MnO₄²⁻ is paramagnetic with one unpaired electron but the purple MnO₄²⁻ is diamagnetic.



- Preparation of Potassium Dichromate (K₂Cr₂O₇):
 - From chromite ore (FeO. Cr_2O_3 or Fe Cr_2O_4)
 - (i) Chromite ore is roasted in a reverberatory furnace with sodium carbonate in the presence of air to give sodium chromate.

$$2FeCr_2O_4 + 4Na_2CO_3 + 7/2O_2 \xrightarrow{Roasted} 4Na_2CrO_4 + Fe_2O_3 + 4CO_2$$

(ii) Yellow solution of Na₂CrO₄ is filtered and acidified with conc. H₂SO₄ to give Na₂Cr₂O₇.

$$2Na_{2}CrO_{4} + H_{2}SO_{4} \longrightarrow Na_{2}Cr_{2}O_{7} + Na_{2}SO_{4} + H_{2}O$$

(iii) Sodium dichromate solution is treated with the calculated amount of KCl and the mixture obtained is cooled when orange crystals of potassium dichromate are obtained.

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

Properties of Potassium dichromate: ۶

- Orange crystalline solid.
- With alkali dichromate gives chromate:

$$Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$$

Chromate ion
(Yellow)

With acid chromate gives dichromate:

$$2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$$

Dichromate ion
(Orange Red)

Oxidising nature: (i) It oxidises ferrous to ferric:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$
$$[Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 6$$

 $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$ (ii) It oxidises stannous to stannic:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$
$$[Sn^{2+} \longrightarrow Sn^{4+} + 2e^-] \times 3$$

$$Cr_2O_7^{-} + 3Sn^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$$

(iii) It oxidises hydrogen sulphide to sulphur:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$
$$[H_2S \longrightarrow 2H^+ + S + 2e^-] \times 3$$

 $Cr_2O_7^{2-} + 3H_2S + 8H^+ \longrightarrow 2Cr^{3+} + 3S + 7H_2O$ (iv) It oxidises iodides to iodine:

$$\frac{\text{Cr}_{2}\text{O}_{7}^{2^{-}} + 14\text{H}^{+} + 6e^{-} \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_{2}\text{O}}{[2\text{I}^{-} \longrightarrow \text{I}_{2} + 2e^{-}] \times 3}$$

$$\frac{\text{Cr}_{2}\text{O}_{7}^{2^{-}} + 6\text{I}^{-} + 14\text{H}^{+} \longrightarrow 2\text{Cr}^{3+} + 3\text{I}_{2} + 7\text{H}_{2}\text{O}}{\text{Cr}_{2}^{3^{+}} + 3\text{I}_{2} + 7\text{H}_{2}\text{O}}$$

Structure of chromate and dichromate ions: Chromate ion has tetrahedral structure with four oxygen atoms ≻ around central chromium atom. Dichromate ion contains two tetrahedral sharing corner with Cr — O — Cr bond angle of 126°.



- Uses of Potassium dichromate: ≻
 - Estimation of Fe²⁺ and I⁻ ions in volumetric analysis.

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 7H_2O + 3I_2$$

$$K_{2}Cr_{2}O_{7} + 7H_{2}SO_{4} + 6FeSO_{4} \longrightarrow K_{2}SO_{4} + Cr_{2}(SO_{4})_{3} + 3Fe_{2}(SO_{4})_{3} + 7H_{2}O_{4} + Cr_{2}(SO_{4})_{3} + 2Fe_{2}(SO_{4})_{3} + 2Fe_{2}(SO_{4}$$

- For chrome tanning in leather industry.
- Preparation of azo compounds.