Chapter 4

d & f block

Day - 1

D -BLOCK ELEMENTS

d -Block elements: The elements lying in the middle of periodic table belonging to groups 3 to 12 are known as d – block elements. Their general electronic configuration is $(n-1)d^{1-10}\,ns^{1-2}$ where (n – 1) stands for penultimate (last but one) shell.

Transition element: A transition element is defined as the one which has incompletely filled *d* orbitals in its ground state or in any one of its oxidation states.

Zinc, cadmium, mercury are not regarded as transition metals due to completely filled d – orbital.

Four transition series:

3d – transition series. The transition elements with atomic number 21(Sc) to 30(Zn) and having incomplete 3d orbitals is called the first transition series. The configuration of Cr and Cu are different than expected. Cr = $3d^5 4s^1$ instead of $3d^4 4s^2$. Cu= $3d^{10} 4s^1$ instead of $3d^9 4s^2$.

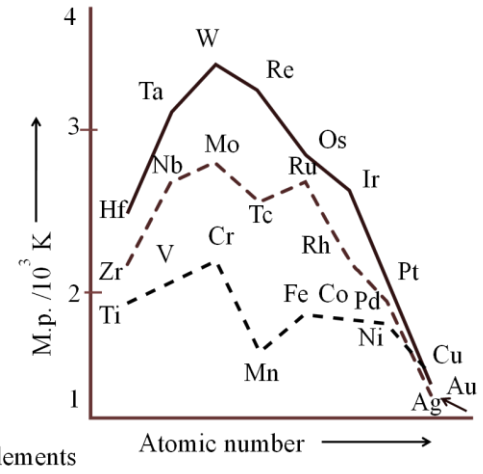
4d – transition series. It consists of elements with atomic number 39(Y) to 48 (Cd) and having incomplete 4d orbital. Here Nb, Mo, Ru, Rh, Pd and Ag have anomalous electronic configuration.

5d – transition series. It consists of elements with atomic number 57(La), 72(Hf) to 80(Hg) having incomplete 5d orbitals. It is called third transition series.

6d – transition series. It consists of elements with atomic number 89(Ac), 104(Rf) to 112(Uub) having incomplete 6d orbitals. It is called fourth transition series

GENERAL CHARACTERISTICS OF TRANSITION ELEMENTS

a. Metallic character: All transition elements are metallic in nature, i.e. they have strong metallic bonds. This is because of presence of unpaired electrons. This gives rise to properties like high density, high enthalpies of atomization, and high melting and boiling points.



Trends in melting points of transition elements

b. Atomic radii: The atomic radii decrease from Sc to Cr because the effective nuclear charge increases. The atomic size of Fe, Co, Ni is almost same because the attraction due to increase in

nuclear charge is cancelled by the repulsion because of increase in shielding effect. Cu and Zn have bigger size because the shielding affects increases and electron repulsions repulsion increases.

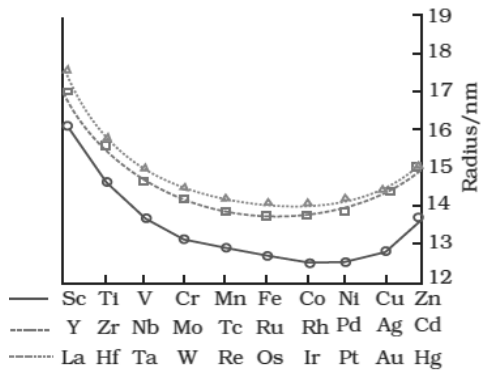


Fig. 8.3: Trends in atomic radii of transition elements

c. Lanthanoid Contraction: The steady decrease in the atomic and ionic radii of the transition metals as the atomic number increases. This is because of filling of 4f orbitals before the 5d orbitals. This contraction is size is quite regular. This is called Lanthanoid contraction. It is because of lanthanoid contraction that the atomic radii of the second row of transition elements are almost similar to those of the third row of transition elements.

d. Ionisation enthalpy: There is slight and irregular variation in ionization energies of transition metals due to irregular variation of atomic size. The I.E. of 5d transition series is higher than 3d and 4d transition series because of Lanthanoid Contraction.

e. Oxidation state: Transition metals show variable oxidation states due to tendency of (n-1)d as well as ns electrons to take part in bond formation.

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

f. Magnetic properties: Most of transition metals are paramagnetic in nature due to presence of unpaired electrons. It increases from Sc to Cr and then decreases because number of unpaired and then decrease because number of unpaired electrons increases from Sc to Cr and then decreases.

Magnetic moment (μ) = $\sqrt{n(n+2)}BM$ here n = number of unpaired electrons. The units are Bohr Magnetron. One BM = 9.27400968×10^{-24} meter^2 amperes (J/T)

g. Catalytic properties: Most of transition metals are used as catalyst because of

(i) Presence of incomplete or empty d – orbitals,

(ii) Large surface area,

(iii) Variable oxidation state,

(iv) Ability to form complexes, e.g., Fe, Ni, V_2O_3, Pt, Mo, Co and used as catalyst.

h. Formation of coloured compounds: They form coloured ions due to presence of incompletely filled d – orbitals and unpaired electrons; they can undergo d – d transition by absorbing colour from visible region and radiating complementary colour.

Configuration	Example	Colour
$3d^{\circ}$	Sc^{3+}	colourless
$3d^{\circ}$	Ti^{4+}	colourless
$3d^1$	Ti^{3+}	purple
$3d^1$	V^{4+}	blue
$3d^2$	V^{3+}	green
$3d^3$	V^{2+}	violet
$3d^3$	Cr^{3+}	violet
$3d^4$		violet
$3d^4$	Cr^{2+}	blue
$3d^5$		pink

g. Formation of complexes: Transition metals form complexes due to

(i) presence of vacant d – orbitals of suitable energy

(ii) smaller size

(iii) Higher charge on cations.

A few examples are: $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, $[Cu(NH_34]^{2+}$ and $[PtCl_4]^{2-}$. (The chemistry of complex compounds is dealt with in detail in chapter 18).

h. Ionic radius: the ionic radii are generally smaller than the transition elements. The ionoc radius decreases with increase in charge for same element.

$Fe^{3+} < Fe^{2+}$

$Mn^{3+} < Mn^{2+}$

$Ni^{3+} < Ni^{2+}$

Interstitial compounds: Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. They are usually non stoichiometric and are neither typically ionic nor covalent, for example, TiC, Mn_4N, Fe_3H, $VH_{0.56}$ and $TiH_{1.7}$, etc.

- The principal physical and chemical characteristics of these compounds are as follows:
- They have high melting points, higher than those of pure metals.
- They are very hard, some borides approach diamond in hardness.
- They retain metallic conductivity.
- They are chemically inert.
- Alloys formation: They form alloys due to similar ionic size. Metals can replace each other in crystal lattice, e.g., brass, bronze, steel etc.

SOME COMMON ALLOYS		
Alloy	Composition	Uses

Brass	Cu 60-80%, Zn 20-40%	Coins, utensils, machine parts,
Bronze	Cu 75-90%, Sn 10-25%	Utensils, statues, coins, machinery parts
Bell metal	Cu 80%, Sn 20%	Making bells
German silver	Cu 25-50%, Zn 25-35%, Ni 10-20%	Utensil, ornaments, resistance coils
Alloy	**Composition**	**Uses**
Gun Metal	Cu 87.5%, Sn 10%, Zn 2%, Pb 0.5%	Making gears. Bearings etc.
Red metal	Cu 92.5%, Sn 7.5%	Copper coins
White metal	Cu 40%, Ag 50%, Zn 5%, Ni 5%	Silver coins
Solder	Sn 67%, Pb 33%	soldering
Type metal	Pb 82%, Sb 15%, Sn 3%	making type of printing
Mischmetall	Lanthanoids 90-95%, Rare earth metals 5-10%	Bullets, shells, lighter flint
Pig iron or cast iron	Pig iron having 2.5-4.5% carbon. It is brittle, low M.P. and cannot (b)	moulding and casting

Alloy	Composition	Uses
Wrought iron	Purest form of iron, obtained from blast furnace. Least % C 0.5%,.	Making chain bolts and framework. Now replaced by mild steel
Mild steel	C 0.1 - 0.5%,	Making chain bolts and framework.
Hard steel	C 0.6 - 1.5%,	Making chain bolts and framework.
Stainless steel	Cr 11-26%, Ni-1-8%, Co, Mo etc in different proportion. C<0.5%	utensils, various specialty uses

Oxidation Number	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+6			CrF_6						
+5		VF_5	CrF_5						
+4	TiX_4	VX_4^{I}	CrX_4	MnF_4					
+3	TiX_3	VX_3	CrX_3	MnF_3	FeX_3^{I}	CoF_3			
+2	TiX_2	VX_2	CrX_2	MnX_2	FeX_2	CoX_2	NiX_2	CuX_2	ZnX_2
+1								CuX^{III}	

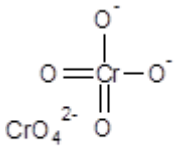
Key: X= F → I: X^{I} = F → Br: X^{II} = F & Cl: X^{III} = Cl → I

SOME IMPORTANT COMPOUNDS

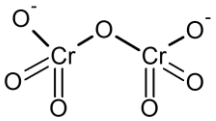
Potassium dichromate ($K_2Cr_2O_7$)

(a) Preparation: It is prepared by fusion of chromate ore ($FeCr_2O_4$) with sodium carbonate in excess of air.

- $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$
- $2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2\,Na^+ + H_2O$
- $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2\,NaCl$



chromate ion



$Cr_2O_7^{2-}$ dichromate ion

Effect of pH on chromate and dichromate ions: The chromates and dichromate's are inter-convertible in aqueous solution depending upon pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.

- $2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$
- $Cr_2O_7^{2-} + 2OH^- \rightarrow 2\,CrO_4^{2-} + H_2O$

Potassium dichromate acts as a strong oxidizing agent in acidic medium.

- $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ (E^O = 1.33V)

POTASSIUM PERMANGANATE ($KMNO_4$)

(a). Laboratory preparation: Mn^{2+} salt can be oxidized by peroxodisulphate ion to permanganate ion.

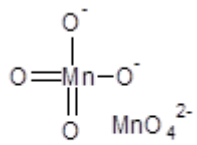
$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$

(b) Commercial preparation: it is prepared by the alkaline oxidative fusion of MnO_2 followed by the electrolytic oxidation of manganate (Vl).

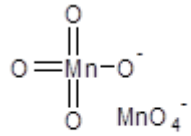
$$2MnO_2 + 4KOH + O_2 \xrightarrow{heat} \underset{\text{Potassium magnate}}{2K_2MnO_4} + 2H_2O \qquad \underset{\text{Potassium magnate}}{2K_2MnO_4} + 4HCl \longrightarrow \underset{\text{Potassium Permagnate}}{2KMnO_4} + MnO_2 + H_2O + 4KCl$$

(c) Other method: Potassium permanganate is prepared by fusion of MnO_4 with alkali metal hydroxide (KOH) in presence of O_2 or oxidising agent like HNO_3. It produces dark green K_2MnO_4 which undergoes oxidation as well as reduction in neutral or acidic solution to give

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



manganate ion



permanganate ion

(d) Chemical Properties

Potassium permanganate acts as a strong oxidizing agent in acidic, neutral or faintly basic medium.

Acidic: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$.

Basic: $2H_2O + MnO_4^- + 3\,e^- \rightarrow MnO_2 + 4\,OH^-$

Neutral: $MnO_4^- + e^- \rightarrow MnO_4^{2-}$

When heated it decomposes at 513 K.

$2KMnO_4 \text{–(513K)}\rightarrow K_2MnO_4 + MnO_2 + O_2$

It is a common oxidising reagent. Some reactions are given below:

$10I^- + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5I_2$

$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$

$5S^{2-} + 2MnO^-_4 + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5S$

$5SO_3^{2-} + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-}$

$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$

$5NO_2^- + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$

$8MnO_4^- + 3S_2O_3^{2-} + H_2O \rightarrow 8MnO2 + 6SO_4^{2-} + 2OH^-$

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

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

f-BLOCK ELEMENTS

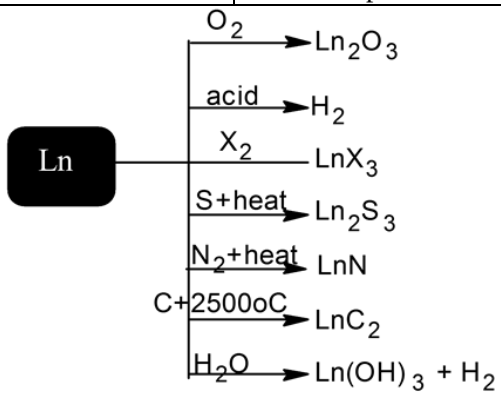
f-Block elements constituting the *f* -block are those in which the 4 *f* and 5 *f* orbitals are progressively filled in the latter two long periods.

Lanthanoids: The 14 elements immediately following lanthanum, i.e., Cerium (58) to Lutetium (71) are called lanthanoids. They belong to first inner transition series. Lanthanum (57) has similar properties. Therefore, it is studied along with lanthanoids.

Actinoids: The 14 elements immediately following actinium (89), with atomic numbers 90 (Thorium) to 103 (Lawrencium) are called actinoids. They belong to second inner transition series. Actinium (89) has similar properties. Therefore, it is studied along with actinoids.

LANTHANOIDS	ACTINOIDS
The general electronic configuration of the Lanthanoid is [Xe] $4f^{1-14}\,5d^{0-1}\,6s^2$	The general electronic configuration of Actinoids is [Rn] $5f^{1-14}\quad 6d^{0-1}\quad 7s^2$
The regular decrease in size amongst Lanthanoids atomic number increases is known as Lanthanoid contraction. This is due to the imperfect shielding of one electron by	Like Lanthanoids, Actinoids also show regular decrease in atomic and ionic size, which is called Actinoid Contraction

another in the same 4f sub shell	
+3 oxidation state is most common along with +2 and +4	Actinoids also show higher oxidation states such as +4, +5, +6 and +7. They are more reactive
Except Promethium, they are non – Radioactive.	They all are radioactive
The magnetic properties of lanthanoids are less complex than actinoids	The magnetic properties of the actinoids are more complex than those of the lanthanoids



Some **Important** Terms : **Compounds** / **Minerals** / **Reagents** or mixtures etc of d- and f- block elements.

- Argentite — Ag_2S
- Argentiferous galena — PbS + Ag_2S
- Azurite — Cu $(OH)_2$. 2 $CuCO_3$
- Benedict's Solution — Alkaline Solution cupric ions complexed with citrate ions.
- Blue Vitriol — CuSO4 . 5 H2O
- (Blue Stone)
- Bayer's Reagent — Cold alkaline $KMnO_4$ Solution.
- Blister Copper — 99% Pure Copper
- Corrosive Sublimate — $HgCl_2$
- Calomel — $Hg_2C\ l_2$
- Calamine — $ZnCO_3$
- Coinage metal — Cu, Ag and Au
- Copper Pyrite — $CuFeS_2$ or Cu_2S . Fe_2S_3
- Copper glance — Cu_2S
- Cinnabar — HgS
- Chromyl Chloride — CrO_2Cl_2
- Chrome Yellow — $PbCrO_4$
- (Lemon Chrome)
- Calaverite — $AuTe_2$
- Chromic acid mixture — K_2CrO_7 + Con. H_2SO_4
- Dolomite — $CaCO_3$. $MgCO_3$
- Delta Metal — Cu (55%), Zn (41%), Fe (4%)
- Fischer's Salt — K_3 [CO $(NO_2)_4$]

- Fehling Solution — $CuSO_4$ + Sod. Pot. Tartrate + NaOH
- Green Vitriol — $FeSO_4 . 7 H_2O$
- (Hara Kasis)
- Ferro Chrome — Fe + 2 Cr + 4 CO
- Guigret's green — $Cr_2O_3 . 2 H_2O$
- Haematite — Fe_2O_3
- (Red Haematite)
- Horn Silver — AgCl
- (Chloragynite)
- Lucas reagent — Conc. HCl + anhydrous $ZnCl_2$
- Lunar Caustic — $AgNO_3$
- Lithopone — ZnS + $BaSO_4$
- Lindlar's Catalyst — Palletised Charcoal deactivated with Sulphur compounds.
- Malachite — $Cu (OH)_2 . 2 CuCO_3$
- Monel Metal — Cu, Ni and Mn
- Nessler's reagent — K_2HgI_4
- Prussian blue — $Fe_4 [Fe (CN)_6]_3$
- Pyrites (Fool's Gold) — FeS_2
- Quick Silver — Hg
- Schweitzer reagent — Tetramine Copper (II) Sulphate
- Sterling Silver — Solution of Cu in Hg
- Scheelite — $CaWO_4$ (Calcium tungstate)
- Tollen's reagent — $AgNO_3$ + NaOH
- Tailing of mercury — Hg_2O
- Vermilion — HgS
- Willemite — Zn_2SiO_4
- Zincite — ZnO
- Zinc butter — $ZnCl_2. 3H_2O$