d & f-Block ELEMENTS

2.0 INTRODUCTION:

(i) d-block elements are often called as transition elements because their position in periodic table is between the s-block and p-block elements.

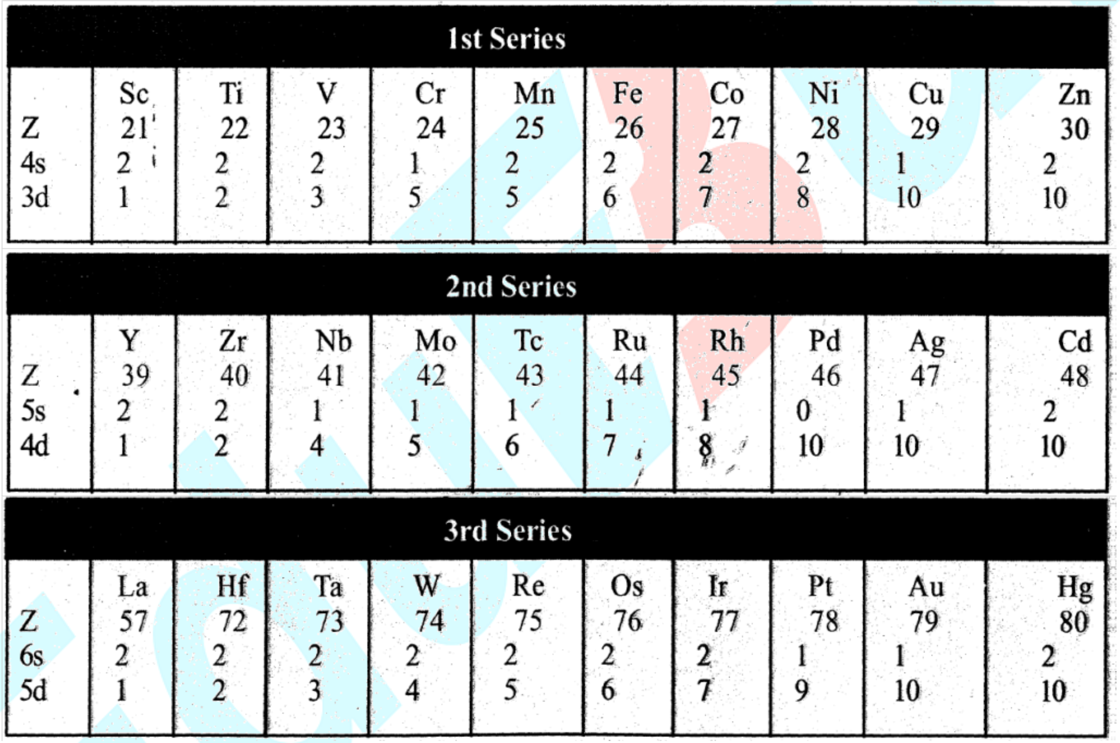
(ii) Their properties are transitional between the highly reactive metallic elements of s-block (which form ionic compounds) and the elements of p-block (which are largely covalent).

(iii) Typically the transition elements have an incompletely filled d-orbital. A transition element may be defined as the element whose atom in ground state or ion in one of common oxidation states, party filled chub shell i.e. having electrons between 1 to 9.

(iv) Group 12 (the zinc group) elements have completely filled d-orbitals in the ground state as well as in their common oxidation states. Therefore, they are not regarded as transition elements.

(v) The general electronic configuration of d-block elements is $(n–1)d^{1–10}$ $ns^{1–2}$, where n is the outer most shell. However, palladium does not follow this general electronic configuration. It has electron configuration $[Kr]^{36} 4d^{10} 5s^0$ in order to have stability.

(vi) Zn, Cd and Hg are involved in transition series but they are called non transition elements due to completely filled d-orbitals.



1st Series

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Z	21	22	23	24	25	26	27	28	29	30
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10

2nd Series

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Z	39	40	41	42	43	44	45	46	47	48
5s	2	2	1	1	1	1	1	0	1	2
4d	1	2	4	5	6	7	8	10	10	10

3rd Series

	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Z	57	72	73	74	75	76	77	78	79	80
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10

2.1 GENERAL TRENDS IN THE CHEMISTRY OF TRANSITION ELEMENTS.

(A) Metallic character :

(i) In d-block elements the last but one (i.e. the penultimate) shell of electrons is expanding. Thus they have many physical and chemical properties in common.

(ii) Nearly all the transition elements display typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lustre.

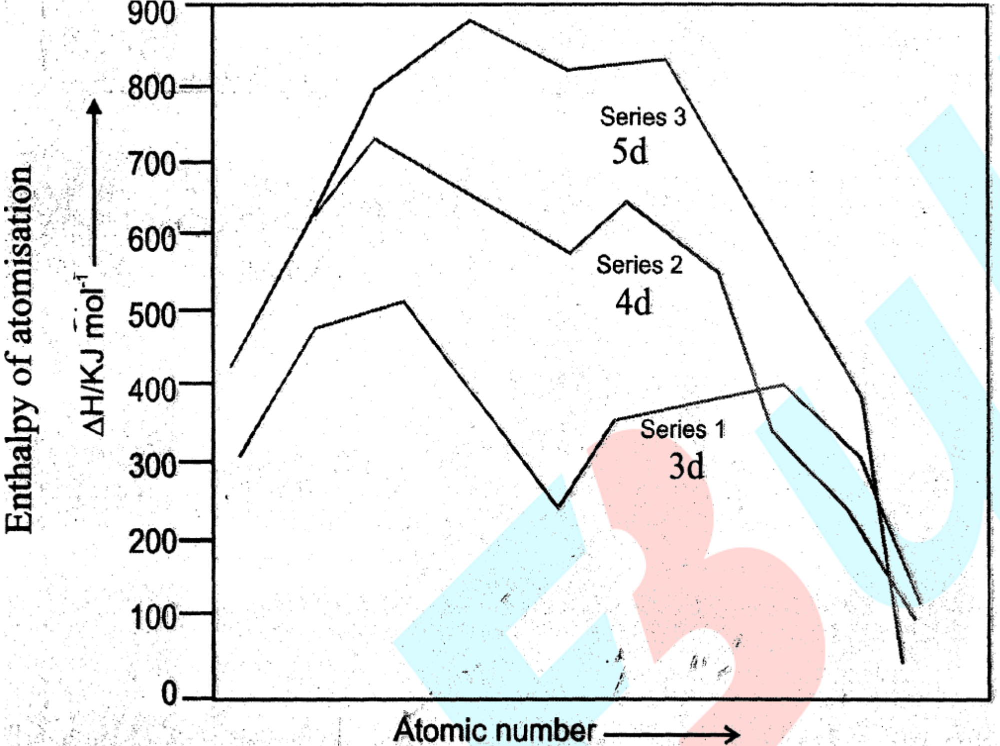
(iii) Most transition elements have ccp/hcp type structures.

(iv) The transition elements are very much hard and have low volatility, they have high enthalpy of atomisation.

(v) Cr, Mo and W have maximum number of unpaired electrons and therefore, these are very hard metals and have maximum enthalpies of atomisation in their respective period.

(vi) The metals with very high enthalpy of atomisation (i.e., very high boiling point) tend to be noble in their reactions.

(vii) The metals of the 4d and 5d series have greater enthalpies of atomisation than the corresponding elements of the 3d and this is an important factor indicating for the occurrence of much more frequent metal-metal bonding in compounds of the heavy transition metals.



Graph showing Trends in enthalpies of atomisation of transition elements

(B) MELTING AND BOILING POINTS

(i) Melting and boiling point of d-block > s-block

Reason : Stronger metallic bond formed present by unpaired d-electrons.

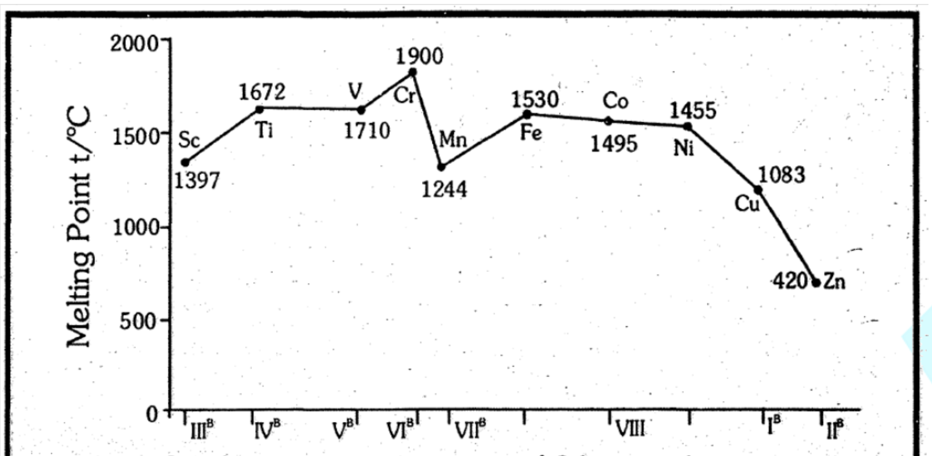
(ii) In Zn, Cd, and Hg there is no unpaired electron present in d-orbital, hence due to absence of covalent bond melting and boiling point are very low in series. (Volatile metals Zn, Cd, Hg)

(iii) In 3d series Sc to Cr melting and boiling point increases then Mn to Zn melting and boilin point decreases.

(iv) As the number of unpaired d-electron increases, the number of covalent bond and bond energy between the atoms is expected to increase up to Cr–Mo–W family where each of the d-orbital has only unpaired electron and the opportunity for covalent sharing is greatest.

(v) Mn and Tc have comparatively low melting point, due; to weak metallic bond because of stable half filled (d^5) configuration and high IP.

(vi) Lowest melting point Hg (–38°C) ; Highest melting point W ($\propto$ 3400°C)



Graphic representation m.p. of 3d-series elements

Illustrations

Illustration 1 :

Why do the transition elements have higher boiling& melting points?

Solution.

Because of having larger number of unpaired electrons in their atoms, they have stronger interatomic interaction and hence stronger bonding between atoms. Hence strong metallic bonds between the atoms of these elements attribute to their high melting and boiling points.

(C) DENSITY

(i) The atomic volumes of the transition elements are low compared with the elements of group 1 and 2. This is because the increased effective nueclear charge. In addition, the extra electrons added occupy inner orbitals. Consequently the densities of the transition metals are high,

(ii) Across a period from left to right atomic volumes decrease and atomic masses increase. Hence the densities also increase across a period.

$$Sc \leq Ti \leq V \leq Cr \leq Mn \leq Fe \leq Co \leq Ni \approx Cu > Zn$$

(zinc is an exception, having large atomic volume and hence has lower density)

(iii) 3d < 4d << 5d Series.

(iv) Maximum density : Ir ≥ Os

(D) Ionisation energies or Ionisation enthalpies :

(i) The first ionisation energy of Zn, Cd, and Hg are very high because of their fully filled $(n-1)d^{10}\,ns^2$ configuration.

(ii) Order of second ionisation energy: Sc < Ti < V < Mn < Cr

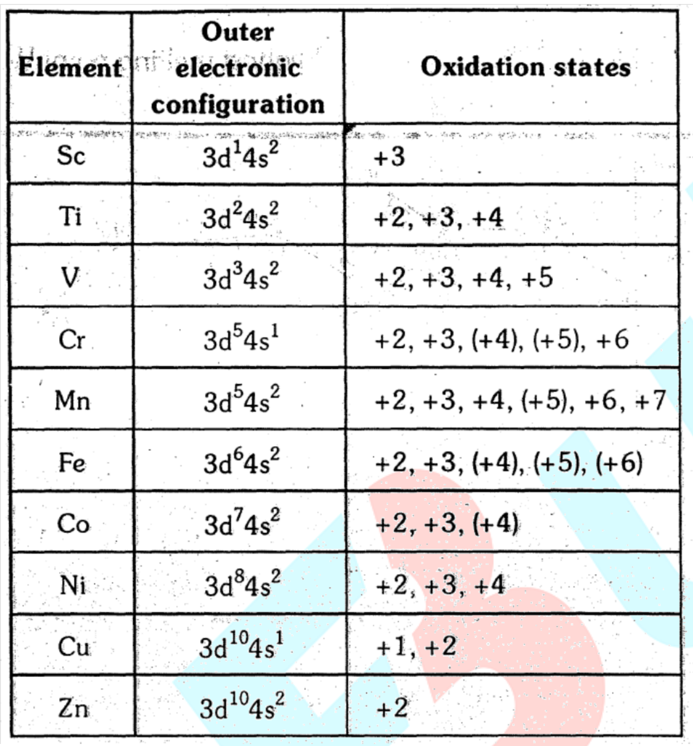
(E) Oxidation states :

(i) The transition metals exhibit a large number of oxidation states. With the exception of a few elements, most of these show variable oxidation states. These different oxidation states are related to the electronic configuration of their atoms,

(ii) The existence of the transition elements in different oxidation states means that their atoms can lose different number of electrons. This is due to the participation of inner (n–1) d-electrons in addition to outer ns-electrons because, the energies of the ns and (n–1) d-sub-shells are nearly same.

(iii) In general oxidation state of d-block element is given as minimum oxidation state = number of 's' electrons maximum oxidation state = number of 's' electrons + unpaired 'd' electron.

Different oxidation states of first transition series.



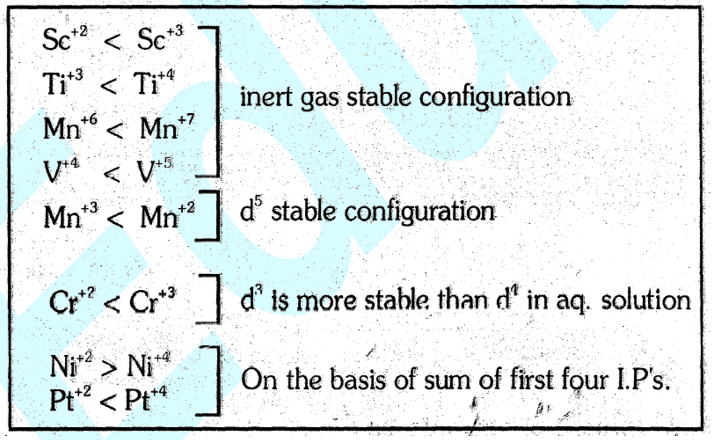
Element	Outer electronic configuration	Oxidation states
Sc	$3d^1 4s^2$	+3
Ti	$3d^2 4s^2$	+2, +3, +4
V	$3d^3 4s^2$	+2, +3, +4, +5
Cr	$3d^5 4s^1$	+2, +3, (+4), (+5), +6
Mn	$3d^5 4s^2$	+2, +3, +4, (+5), +6, +7
Fe	$3d^6 4s^2$	+2, +3, (+4), (+5), (+6)
Co	$3d^7 4s^2$	+2, +3, (+4)
Ni	$3d^8 4s^2$	+2, +3, +4
Cu	$3d^{10} 4s^1$	+1, +2
Zn	$3d^{10} 4s^2$	+2

- **Oxidation states given in parenthesis are unstable.**

Higher oxidation state in d-block - 18 (Os, Ru)

Zero oxidation state for e.g. $[Ni(CO)_4]$, $[Fe(CO)_5]$

(iv) Relative stability of oxidation state :



$Sc^{+2} < Sc^{+3}$ $Ti^{+3} < Ti^{+4}$ $Mn^{+6} < Mn^{+7}$ $V^{+4} < V^{+5}$	inert gas stable configuration
$Mn^{+3} < Mn^{+2}$	d^5 stable configuration
$Cr^{+2} < Cr^{+3}$	d^3 is more stable than d^4 in aq. solution
$Ni^{+2} > Ni^{+4}$ $Pt^{+2} < Pt^{+4}$	On the basis of sum of first four I.P's.

(v) On moving in a period stability of higher oxidation state decreases.

e.g. $VO_3^- > CrO_4^{2-} > MnO_4^-$

(vi) On moving down the group stability of higher oxidation state increases

e.g. - $\overset{+6}{Cr}O_3 < \overset{+6}{Mo}O_3 < \overset{+6}{W}O_3$

$$\underset{+7}{Mn}O_4^- < \underset{+7}{Tc}O_4^- < \underset{+7}{Re}O_4^-$$

(F) ELECTRODE POTENTIALS :

In addition to ionisation enthalpy, the other factors such as enthalpy of sublmation, hydration enthalpy, ionization enthalpy etc. determine the stability of a particular oxidation state in solution. This can be explained in terms of their electrode potential values. The oxidation potential of a metal involves the following process:

$$M(s) \longrightarrow M^+(aq) + e^-$$

This process actually takes place in the following three steps as given in following flowchart :

$$\begin{tikzcd}
M(s) \arrow[r, "\Delta H"] \arrow[d, "\Delta H_{sub.}", "(i)"'] & M^+(aq) \\
M(g) \arrow[r, "I.E.", "(ii)"'] & M^+(g) \arrow[u, "(iii)"', "\Delta H_{hyd.}"]
\end{tikzcd}$$

The oxidation potential which gives the tendency of the overall change to occur, depends upon the net effect of these three steps. The· overall energy change is $\Delta H = \Delta_{sub}H^{\oplus} + \Delta H + \Delta_{hyd}H$

If SOP is +ve → Means Oxidation easy

If SRP is +ve → Means reduction easy

Some important examples :

1. $E^0_{M^{+2}/M} \Rightarrow$ +ve only for Cu among 3d elements because HE of Cu^{+2} is not enough to compensate for sublimation energy, IP_1 and IP_2 for Cu.

2. $E^0_{M^{+3}/M^{+2}} \Rightarrow$

(a) $E^0_{Cr^{+3}/Cr^{+2}} = -ve$

Reason : $t_2g^3eg^0 \leftarrow d_3 > d^4$

(b) $E^0_{M^{+3}/M^{+2}} = +ve$ (high)

Reason : $d^4 < d^5$

(c) $E^0_{Fe^{+3}/Fe^{+2}}$ = less +ve (learn)

Reason : $d^5 > d^6$

Note : The SRP of $E^0_{Fe^{+3}/Fe^{+2}}$ is less then expected because of extra stability of d^5 configuration of Fe^{+3} ion.

(G) TRENDS IN STABILITY OF HIGHER OXIDANTON STATES

Standard electrode potential data provide valuable information about the stabilities of different oxidation states shown by an element, The highest oxidation states are shown generally among halides and oxides.

Halides of first transition series

(i) **In metal halides** - transition elements react with at high temperature to transition metal halides. These reactions have very high heat of reaction. But once the reaction starts, the heat of reaction is sufficient to continue the reaction. The halogens react in the following decreasing order ; $F_2 > Cl_2 > Br_2 > I_2$

(ii) In general, the elements of first transition series tend to in low oxidation states. chromium to zinc form stable different and the other chlorides are also known.

(iii) Since fluorine is the electronegative element, the transition metals show highest oxidation states with fluorine. The highest oxidation states are found in TiX_4 (tetrahalides, X = F, Cl, Br and I), VF_5 and CrF_6.

(iv) The +7 oxidation state for Mn is not shown by simple halides. However, MnO_3F is known in which the oxidation state of Mn is +7.

(v) The tendency of fluorine to stabilise the highest oxidation state is due to either higher lattice enthalpy as in case of CoF_3 or higher bond enthalpy due to higher covalent bonds e.g., VF_5 and CrF_6

(vi) Fluorides are relatively unstable in their low oxidation states. For example, vanadium form only VX_2(X = Cl, Br or I) and copper can form CuX (X = Cl, I). All copper (II) halides are known except the iodide. This is because, Cu^{2+} oxidises I^- to I_2.

$$2Cu^{2+} + 4I^- \longrightarrow Cu_2I_2(s) + I_2$$

It has been observed that many copper (I) compounds are unstable in aqueous solution and they undergo disproportionation to Cu(II) and Cu(O) as :

$$2Cu^{2+} \longrightarrow Cu^{2+} + Cu$$

Copper in +2 oxidation state is more stable than in +1 oxidation state. This can be explained on the basis of much larger negative hydration enthalpy ($\Delta_{hyd}H^{\oplus}$) of Cu^{2+} (aq) than Cu^+, which is much more than compensates for the large energy required to remove the second electron i.e., second ionization enthalpy of copper.

(H) IN METAL OXIDES AND OXOCATIONS.

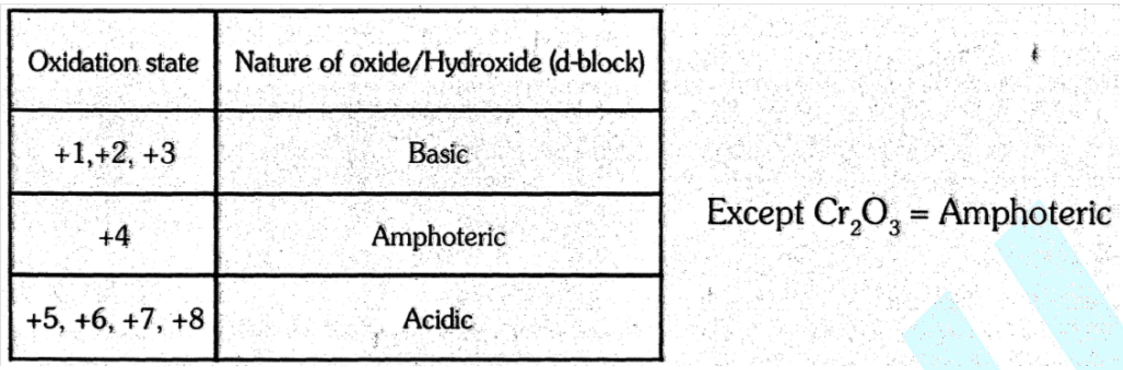
(i) The ability of oxygen to stabilize the highest oxidation state is demonstrated in their oxides. The highest oxidation states in their oxides concides with the group number. For example, the highest oxidation state of scandium of group 3 is +3 in its oxides, Sc_2O_3 whereas the highest oxidation state of manganese of group 7 is + 7, in Mn_2O_7.

(ii) Besides the oxides, oxidation of the metals also stabilise higher oxidation states. For example, V^V as V_2^+, V^{IV} as VO^{2+} and Ti^{IV} as TiO^{2+}.

(iii) It may be noted that the ability of oxygen to stabilise these high oxidation states exceeds that of fluorine. For example, manganese forms highest fluoride as MnF_4 whereas the highest oxide is Mn_2O_7. This is due to the fact that oxygen has great ability to form multiple bonds to metals.

(iv) The transition elements in the +2 and +3 oxidation states mostly form ionic bonds whereas with higher oxidation states, the bonds are essentially covalent e.g., in MnO_4^- all bonds are covalent. As the oxidation number of a metal increases, the ionic character of their oxides decrease. For example, in case of Mn, Mn_2O_7 is a covalent. In these higher oxides the acidic character is predominant. Thus CrO_3 gives H_2CrO_4 and $H_2Cr_2O_7$ and $HMnO_7$ gives MnO_4, V_2O_5 is, however amphoteric though mainly acidic and with alkalies as well as acids gives VO_4^{3-} and VO_2^+ respectively.

In general



Oxidation state	Nature of oxide/Hydroxide (d-block)
+1,+2, +3	Basic
+4	Amphoteric
+5, +6, +7, +8	Acidic

Except Cr_2O_3 = Amphoteric

(I) **FORMATION OF COLOURED IONS :** See coordination compound

(J) **MAGNETIC PROPERTIES**

It is interesting to note that when the various substances are placed in a magnetic field, they do not behave in a similar way i.e., they snow different behaviour which are known as magnetic behaviour.

These are classified as :

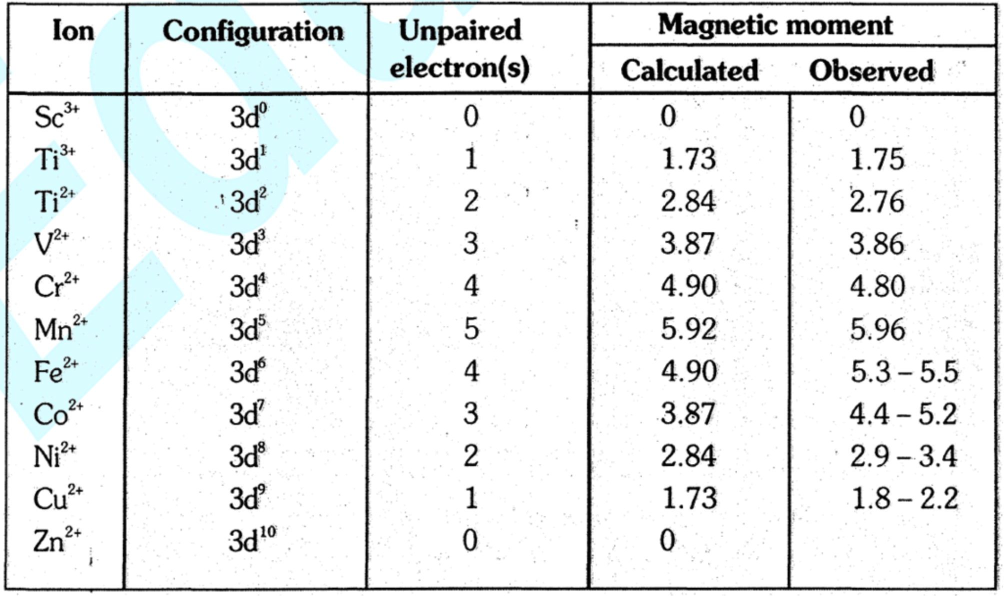
(i) **Paramagnetic substances.** The substances which are attracted by magnetic field are called paramagnetic substances and this character arises due to the presence of unpaired electrons in the atomic orbitals.

(ii) **Diamagnetic substances.** The substances which are repelled by magnetic field are called diamagnetic substances and this character arises due to the presence of paired electrons in the atomic orbitals. Most of the compounds of transition elements are paramagnetic in nature and are attracted by the magnetic field.

The transition elements involve the partial filling of d-sub-shells. Most of the transition metal ions or their compounds have unpaired electrons in d-sub-shell (from configuration d1 to d^9) and therefore, they give rise to paramagnetic character.

(iii) The magnetic moment arise only from the spin of the electrons. This can be calculated from the relation $\mu = \sqrt{n(n+2)}$ B.M. n = Number of unpaired electrons

Table :.Calculated and Observed Magnetic Moments (BM)



Ion	Configuration	Unpaired electron(s)	Magnetic moment	
			Calculated	Observed
Sc^{3+}	$3d^0$	0	0	0
Ti^{3+}	$3d^1$	1	1.73	1.75
Ti^{2+}	$3d^2$	2	2.84	2.76
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	5.96
Fe^{2+}	$3d^6$	4	4.90	5.3 – 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	1.8 – 2.2
Zn^{2+}	$3d^{10}$	0	0	

(K) **FORMATION OF COMPLEXES :** See coordination compound

(L) FORMATION OF INTERSTITIAL COMPOUNDS

Transition metals form interstitial compounds with elements such as hydrogen, boron, carbon and nitrogen. The small atoms of these non-metallic elements (H, B, C, N, etc.) get trapped in vacant spaces of the lattices of the transition metal atoms as shown below.

e.g. WC, Fe_3C, $TiH_{1.30-1.80}$

Properties :

(1) They are generally non-stoichiometric compound.
(2) Neither typical ionic nor covalent
(3) Harder then pure metal
(4) High melting point then pure metal
(5) Male ability and ductility fess then pure metal
(6) Chemically inert

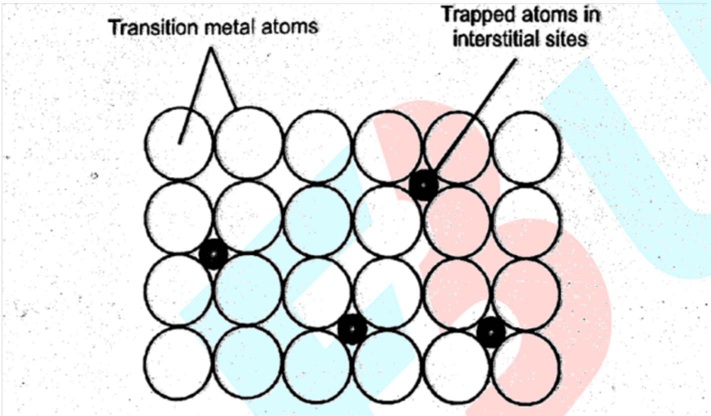


Figure showing formation of interstitial compounds

(M) CATALYTIC PROPERTIES

d-block metals or their compound act as catalyst in many reaction due to :
(i) Possibility of variable oxidation state
(ii) Presence of free valencies over metal surface (adsorption power)
(iii) Presence of vacant d-orbital

e.g.

(1) $SO_2 + \frac{1}{2}O_2 \xrightleftharpoons{V_2O_5} SO_3$

$V_2O_5 + SO_2 \longrightarrow SO_3 + V_2O_4$ (divanadium tetroxide)

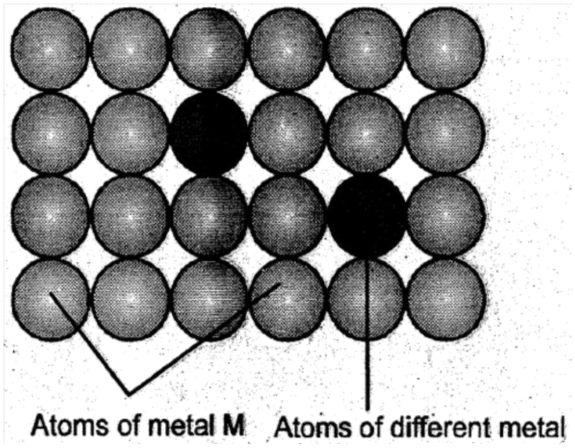
$2V_2O_4 + O_2 \longrightarrow 2V_2O_5$

(2) $2I^- + S_2O_8^{2-} \xrightarrow{Fe(III)} I_2\ 2SO_4^{2-}$

(3) Veg oil + $H_2 \xrightarrow{Ni/Pt}$ Veg ghee

(N) ALLOY FORMATION :

Alloy are homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other metal. The alloys are generally formed by those atoms which have metallic radii within about 15% of each other. Transition metals form a large number of alloys. The transition metals are quite similar in size and therefore the atoms of one metal can substitute the atoms of other metal in its crystal lattice.



Alloy formation

Note : Fe, Co, NI do not form amalgam with Hg (Due to large difference in size)

BEGINNER'S BOX-1

1. The general electronic configuration of d-block element is $(n-1)d^{1-10}$ ns^{1-2}. This generalization has several exveptions mainly due to
(1) strong shielding of (n–1) d-electrons
(2) very little energy difference between (n–1)d and ns orbitals
(3) presence of unpaired electrons
(4) high energy difference between (n–1)d and ns orbitals

2. Select group of transition elements
(1) Pb, Sc, V (2) Pd, Cd, La (3) Pd, La, Fe (4) Zn, Pd, Bi

3. Which element is having lowest melting and boiling point :
(1) Ti (2) Cu (3) Zn (4) Mn

4. Density of which of the following element is highest
(1) Pt (2) Hg (3) Mn (4) Cu

5. Not more than one oxidation state is shown by :
(1) Mn (2) Cr (3) Fe (4) Sc

6. Consider the ions Fe^{2+}, Fe^{3+}, Cr^{2+}, Cr^{3+}, Mn^{2+}, Mn^{3+}
(i) Strongest oxidising ion is
(1) Fe^{2+} (2) Cr^{3+} (3) Mn^{3+} (4) Mn^{2+}
(ii) Strongest reducing ion is
(1) Fe^{2+} (2) Mn^{2+} (3) Cr^{2+} (4) Mn^{3+}

7. Which compound does exist
(1) MnO_3F (2) $K_2[CuI_4]$
(3) MnF_7 (4) CrF_7

8. In the form of dichromate, Cr(VI) is a strong oxidising agent in acidic medium but Mo(VI) in MoO_3 and W(VI) in WO_3 are not because
(1) Cr(VI) is more stable than Mo(VI) & W(VI)

(2) Mo(VI) and W(VI) are less stable than Cr(VI)
(3) H.O.S. of heavier members of group 6 of transition metals are more stable
(4) L.O.S. of heavier members of group 6 of transition metals are more stable

9. By which of the following species, a transitional metal can brought in to its highest oxidation state

(1) F_2 (2) Cl_2 (3) Br_2 (4) I_2

2.2 COMPOUNDS OF d-BLOCK ELEMENTS :

POTASSIUM PERMANGANATE ($KMnO_4$) :

(a) Preparation

This is the most important and well known salt of permangantic acid and is prepared from the pyrolusite ore. It is prepared by fusing pyrolusite ore either with KOH or K_2CO_3 in presence of atmospheric oxygen or any other oxidising agent such as KNO_3. The fused mass turns green with the formation of potassium manganate, K_2MnO_4.

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

$$2MnO_2 + 2K_2CO_3 + O_2 \rightarrow 2K_2MnO_4 + 2CO_2$$

The fused mass is extracted with water and the solution is now treated with a current of chlorine or ozone or carbon dioxide to convert manganate into permanganate.

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$$

$$2K_2MnO_4 + H_2O + O_3 \longrightarrow 2KMnO_4 + 2KOH + O_2$$

$$3K_2MnO_4 + 2CO_2 \longrightarrow 2KMnO_4 + MnO_2 + 2K_2CO_3$$

(disproportionate in acidic medium)

Commercially it is prepared by fusion of MnO_2 with KOH followed by electrolytic oxidation of manganate.

$$MnO_4^{2-} \text{ (green)} \longrightarrow MnO_4^{-} \text{ (purple)} + e^{-}$$

In the laboratory, a manganese (IO ion salt is oxidised by peroxodisulphate to permanganate.

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

(b) Physical property

(b) Physical property : It is purple coloured crystalline compound. It is moderately soluble in water at room temperature.

(c) Chemical property :

- Effect of heating $2KMnO_4 \xrightarrow{750\,K} K_2MnO_4 + MnO_2 + O_2$
- On treatment with concentrated H_2SO_4 ($KMnO_4$ is taken in excess), it forms manganese heptoxide via permanganyl sulphate which decomposes explosively on heating.

$$KMnO_4 \xrightarrow{\text{conc.}\,H_2SO_4} Mn_2O_7 \text{ (an explosive)}$$

- Potassium permanganate is a powerful oxidising agent.
  Potassium permanganate acts as an oxidising agent in alkaline, neutral or acidic solutions.
- In alkaline & neutral medium :
  In strongly alkaline medium KMnO 4 is reduced to manganate.

$$2KMnO_4 + 2KOH \text{ (conc.)} \longrightarrow 2K_2MnO_4 + H_2O + [O]$$

or

$$e^{-} + MnO_4^{-} \longrightarrow MnO_4^{2-}$$

However if solution is dilute then K_2MnO_4 is converted in to MnO_2 which appears as a brownish precipitate.

$$2K_2MnO_4 + 2H_2O \longrightarrow 2MnO_2 + 4KOH + 2[O]$$

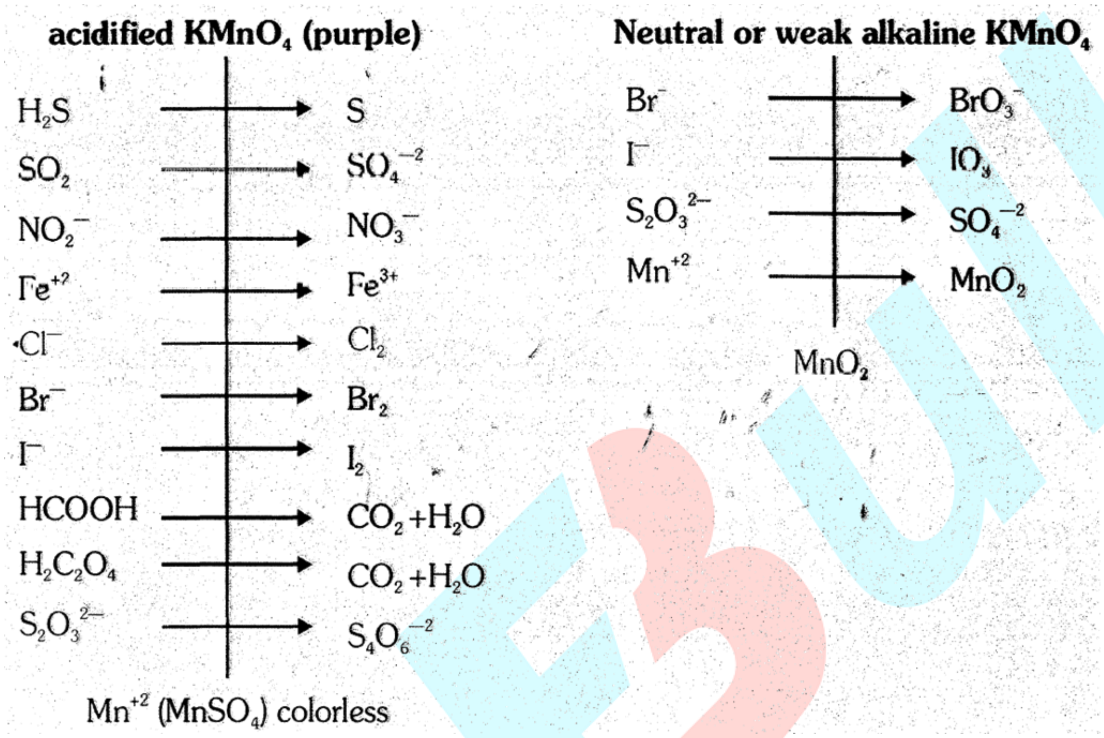
or

$$2e^- + 2H_2O + MnO_4^{2-} \longrightarrow MnO_2 + 4OH^-$$

This type of behaviour is shown by $KMnO_4$ itself in neutral medium.

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

(d) Other reactions



POTASSIUM DICHROMATE ($K_2Cr_2O_7$) :

(a) Preparation : The chromite ore is roasted with sodium carbonate in presence of air in a reverberatory furnace.

$$4FeO.\ Cr_2O_3 \text{ (chromite ore)} + 8Na_2CO_3 + 7O_2 \xrightarrow[\text{in air}]{\text{Roasting}} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

The roasted mass is extracted with water when Na_2CrO_4 goes into the solution leaving behind insoluble Fe_2O_3. The solution is then treated with calculated amount o H_2SO_4.

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

The solution is concentrated when less soluble Na_2SO_4 crystallises out. The solution is further consent when crystals of $Na_2Cr_2O_7$ are obtained. Hot saturated solution of $Na_2Cr_2O_7$ is then treated with KCl when orange red crystals of $K_2Cr_2O_7$ are obtained on crystallisation.

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

- $K_2Cr_2O_7$ is preferred over $Na_2Cr_2O_7$ as a primary standard in volumetric estimation because $Na_2Cr_2O_7$ is hygroscopic in nature but $K_2Cr_2O_7$ is not.
- $CrO_4^{-2} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} Cr_2O_7^{2-}$
- Solubility of $Na_2Cr_2O_7$ is higher than $K_2Cr_2O_7$.

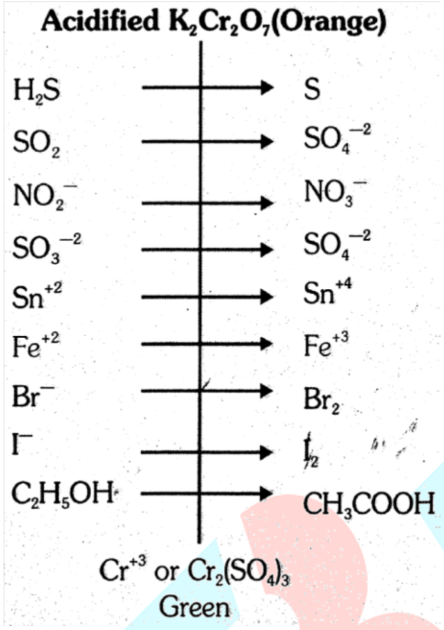
(b) Physical property : It is orange-red coloured crystalline compound. It is moderately soluble in cold water but freely soluble in hot water. It melts at 398°C.

(c) Chemical property :

- **Effect of heating :** On strongly heating, it decomposes with liberating oxygen.

$$2K_2Cr_2O_7 \longrightarrow 2K_2CrO_4 + Cr_2O_3 + \frac{3}{2}O_2$$

(d) Other reactions



1. Chromyl chloride test :

$$NaCl + K_2Cr_2O_7 + H_2SO_4 \rightarrow CrO_2Cl_2 \text{ (Red orange vapour)}$$
$$\downarrow NaOH$$
$$Na_2CrO_4 \text{ (Yellow)}$$

2. Acidified $K_2Cr_2O_7$ solution reacts with H_2O_2 in a etheral solution to give a deep blue solution due to the formation of CrO_5.

$$Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \longrightarrow 2CrO_5 + 5H_2O$$

Note : Reaction with C_2H_5OH is used in drunken driver test.

2.3 INNER TRANSITION ELEMENTS

The elements in which the additional electron eneters in (n–2)f orbitals are called inner transition elements or f-block elements.

Position In The Periodic Table

The lanthanoids resemble with yttrium in most of their properties. So it became necessary to accommodate all the fifteen elements together at one place. This has been done by placing the first element, lanthanum below yttrium and placing the remaining fourteen elements separately in the lower part of the periodic table.

Lanthanoid series	(Z = 58 – 71)	(Ce – Lu)
Actinide- series	(Z = 90 – 103)	(Th – Lr)

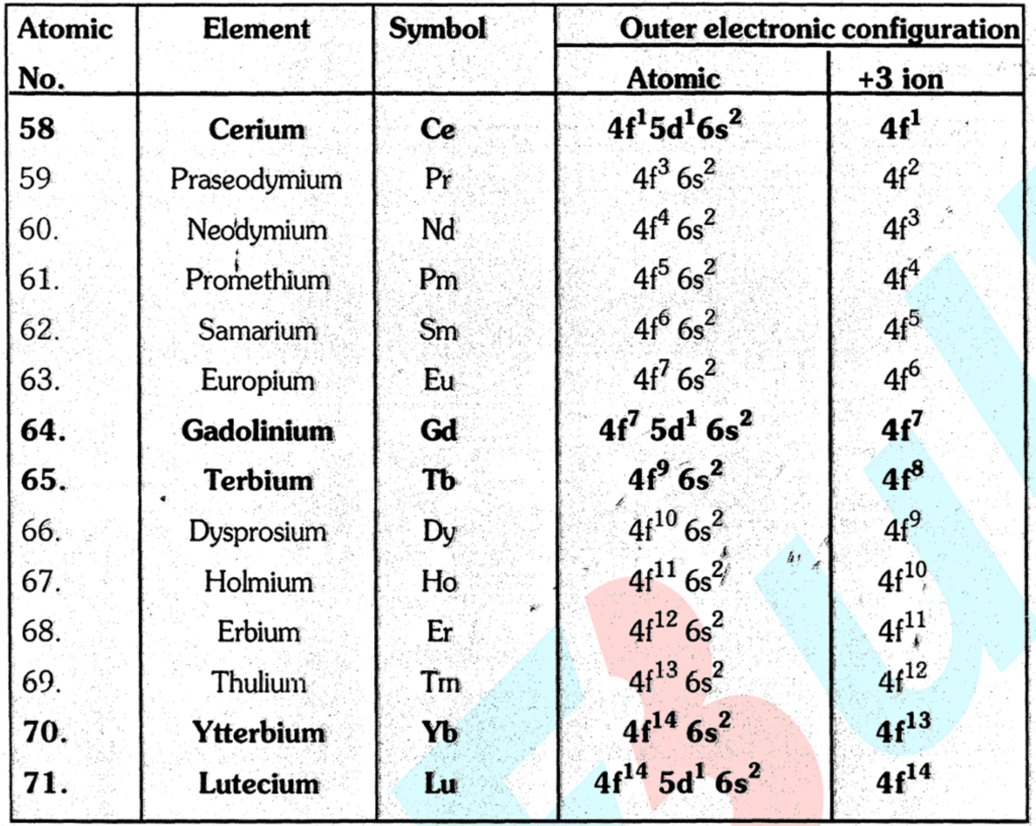
2.4 IANTHANIODS (Rare Earths or Lanthanones)

(i) Lanthanoids are react are reactive elements so do not found in free state in nature.

(ii) Most important minerals for lighter Lanthanoids are - Monazite, cerites and orthite and for heavier lanthanoids - Gadolinite and Xenotime

(a) Electronic configuration

(i) The general configuration of lanthanoids may be given as [Xe]$4f^{1-14}\,5s^2 5p^6 5d^{0-1} 6s^2$.



Atomic No.	Element	Symbol	Outer electronic configuration	
			Atomic	+3 ion
58	**Cerium**	**Ce**	$4f^1 5d^1 6s^2$	$4f^1$
59	Praseodymium	Pr	$4f^3\,6s^2$	$4f^2$
60.	Neodymium	Nd	$4f^4\,6s^2$	$4f^3$
61.	Promethium	Pm	$4f^5\,6s^2$	$4f^4$
62.	Samarium	Sm	$4f^6\,6s^2$	$4f^5$
63.	Europium	Eu	$4f^7\,6s^2$	$4f^6$
64.	**Gadolinium**	**Gd**	$4f^7\,5d^1\,6s^2$	$4f^7$
65.	**Terbium**	**Tb**	$4f^9\,6s^2$	$4f^8$
66.	Dysprosium	Dy	$4f^{10}\,6s^2$	$4f^9$
67.	Holmium	Ho	$4f^{11}\,6s^2$	$4f^{10}$
68.	Erbium	Er	$4f^{12}\,6s^2$	$4f^{11}$
69.	Thulium	Tm	$4f^{13}\,6s^2$	$4f^{12}$
70.	**Ytterbium**	**Yb**	$4f^{14}\,6s^2$	$4f^{13}$
71.	**Lutecium**	**Lu**	$4f^{14}\,5d^1\,6s^2$	$4f^{14}$

(ii) It is to be noted that filling of 4f orbitals in the atoms is not regular. A 5d electron appears in gadolinium (Z = 64) with an outer electronic configuration of $4f^7\,5d^1\,6s^2$ (and not $4f^8\,6s^2$). This is because the 4f and 5d electrons are at about the same potential energy and that the atoms have a tendency to retain stable half filled configuration.

(iii) On the other hand, the filling of f-orbitals is regular in tripositive ions.

(iv) After losing outer electrons, the f-orbitals shrink in size and became more stable.

(v) Pm is the only synthetic radioactive lanthanoid.

(b) Oxidation states

(i) In lanthanoids +3 oxidation state is most common.

(ii) Except Ce, Tb, Nd, Dy, Pr which also exhibit +4.

(iii) Sm, Eu, Tm, and Yb, also exhibit +2 state.

(c) Magnetic Properties

(i) In tripositive lanthanoid ions the number of unpaired electrons regularly increases from lanthanum to Gadolinium (0 to 7) and then continuously decreases upto lutecium (7 to 0).

(ii) Lanthanum and lutecium ions are diamagnetic, while all other tripositive lanthanoid ions are paramagnetic. (Exception - Neodymium is the most paramagnetic lanthanoid).

(iii) Ce^{+4} and Yb^{+2} are also diamagnetic ions.

(d) Colour

(i) The lanthanoid ions have unpaired electrons in their 4f orbitals. Thus these ions absorbs visible region of light and undergo f-f transition and hence exhibit colour.

(ii) The colour exhibited depends on the number of unpaired electrons in the 4f orbitals.

(iii) The ions often with $4f^n$ configuration have similar colour to those ions having $4f^{14-n}$ configuration.

(iv) Lanthanoid ions having $4f^0$, $4f^{14}$ are colourless.

(e) Lanthanoid Contraction

(i) In the lanthanoid series with-increasing atomic number, there is a progressive decrease in the size from lanthanum to lutecium or from La^{+3} to Lu^{+3}. This contraction in size is known as lanthanoid contraction.

(ii) The general electronic configuration of these elements is $4f^{1-14}\,5s^2p^6d^{0-1}6s^2$. In these elements the added electron enters the deep seated f-orbitals and therefore experiences considerable pull by the nucleus.

(iii) Due to very poor shielding effect of (n–2)f electrons, they exert very little screening effect on the outermost $6s^2$ electrons.

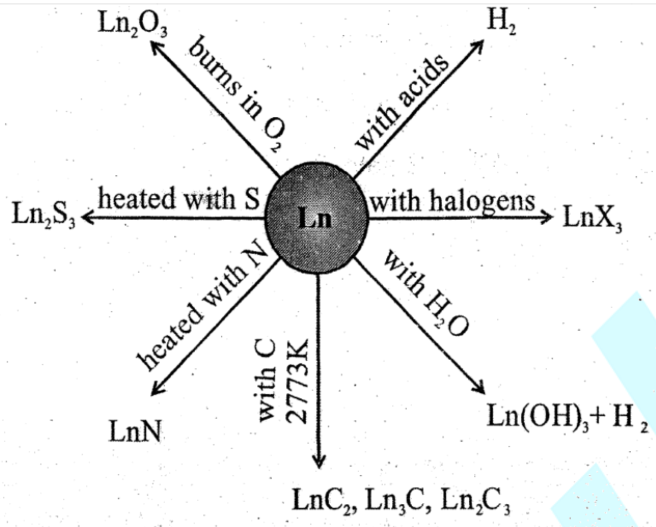
Hence with increasing atomic number, the enhanced nuclear charge leads to contraction in the size of atoms and ions.

APPUCATIONS OF LANTHANOID CONTRACTION

- **Atomic size :** The ionic radii of Zr^{+4} is about 9% more than Te^{+4}. Similar trend is not maintained on passing from the second to third transition series. The ionic radius of Hf^{+4}, Instead of increasing (because of inclusion of one more electronic shell), decreases (or is virtually equal to Zr^{+4+}) as a consequence of the lanthanoid contraction.

  This explains the dose similarities between the members of the second and third transition series than between the elements of the first and second series.
- **Basic nature of hydroxide :** The effect of lanthanoid contraction basic nature of hydroxide regularly decreases.
- **Similarity in properties of lanthanoid :** Due to small difference in· size the chemical properties of lanthanoids are similar and their seperation is difficult.

(e) Important reactions of Lanthanoids



Chemical reactions of the lanthanoids

Mish metal is an alloy of lanthanoids (Mainly cerium) and iron.

2.5 ACTINOIDS OR (5f - SERIES)

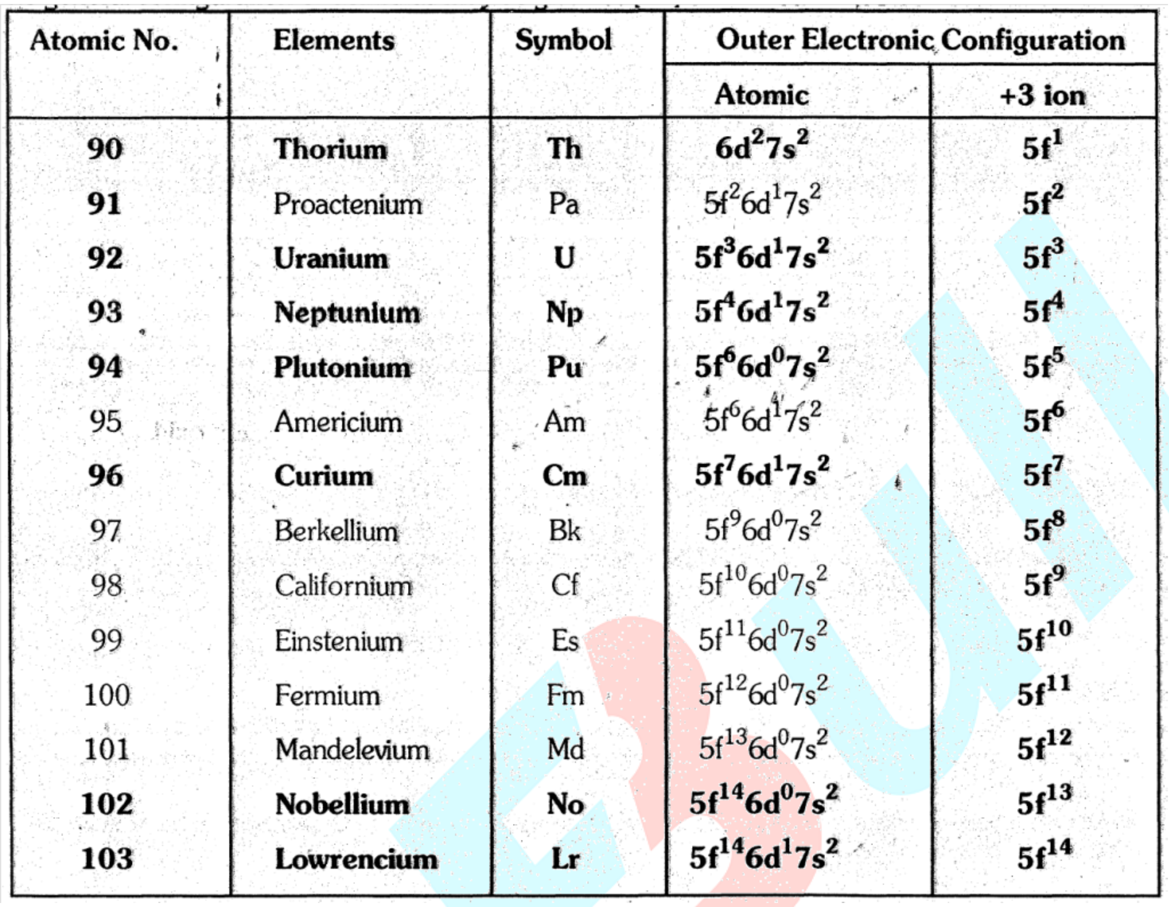
(i) The elements in which the extra electron enters 5f-orbitals of (n–2)th main shell are known as actinoids.

(ii) The man-made eleven elements Np_{93} – Lr_{103} are placed beyond uranium in the periodic table and are collectively called trans-uranium elements.

(iii) Th, Pa and U first three actinoids are natural elements.

(a) Electronic Configuration

The general configuration of actinoids may be given as [Rn] $5f^{1-14}$ $6d^{0,1,2}$, $7s^2$.



Atomic No.	Elements	Symbol	Outer Electronic Configuration	
			Atomic	+3 ion
90	**Thorium**	**Th**	$6d^2 7s^2$	$5f^1$
91	Proactenium	Pa	$5f^2 6d^1 7s^2$	$5f^2$
92	**Uranium**	**U**	$5f^3 6d^1 7s^2$	$5f^3$
93	**Neptunium**	**Np**	$5f^4 6d^1 7s^2$	$5f^4$
94	**Plutonium**	**Pu**	$5f^6 6d^0 7s^2$	$5f^5$
95	Americium	Am	$5f^6 6d^1 7s^2$	$5f^6$
96	**Curium**	**Cm**	$5f^7 6d^1 7s^2$	$5f^7$
97	Berkellium	Bk	$5f^9 6d^0 7s^2$	$5f^8$
98	Californium	Cf	$5f^{10} 6d^0 7s^2$	$5f^9$
99	Einstenium	Es	$5f^{11} 6d^0 7s^2$	$5f^{10}$
100	Fermium	Fm	$5f^{12} 6d^0 7s^2$	$5f^{11}$
101	Mandelevium	Md	$5f^{13} 6d^0 7s^2$	$5f^{12}$
102	**Nobellium**	**No**	$5f^{14} 6d^0 7s^2$	$5f^{13}$
103	**Lowrencium**	**Lr**	$5f^{14} 6d^1 7s^2$	$5f^{14}$

(b) Oxidation states

(i) In lanthanoids and actinoids +3 oxidation is the most common for both of the series of elements.

(ii) This oxidation state becomes increasingly more stable as the a comic number increases in the actinide series.

(iii) Highest oxidation states in the actinoids is +7 exhibited by Np_{93} & Pu_{94}, it is unstable.

(iv) Highest stable oxidation state is +6 shown by U_{92}.

Other Properties

- **Physical appearance :** Acitinides are silvery white metals. They get tarnished when exposed to the attack of alkalies.
- **Density :** All the actinoids except thorium arid americium have high densities.
- **Colour :** Actinide ions are generally coloured. The colour of actinide ions depends upon the number of Sf-electrons. The ions containing no unpaired 5f-electrons. (exactly full filled f-subshell) are colourless, as expected.
- **Ionisation energies :** Ionisation energies values of actinoids are low.
- **Electropositive character :** All the known actinide metals are highly electropositive. They resemble lanthanoid series in this respect.
- **Melting Boiling properties :** They have **high melting and boiling points**. They do not follow regular gradation of melting or boiling points with increase in atomic number.
- **Magnetic properties :** The actinide elements are paramagnetic due to the presence of unpaired electrons.

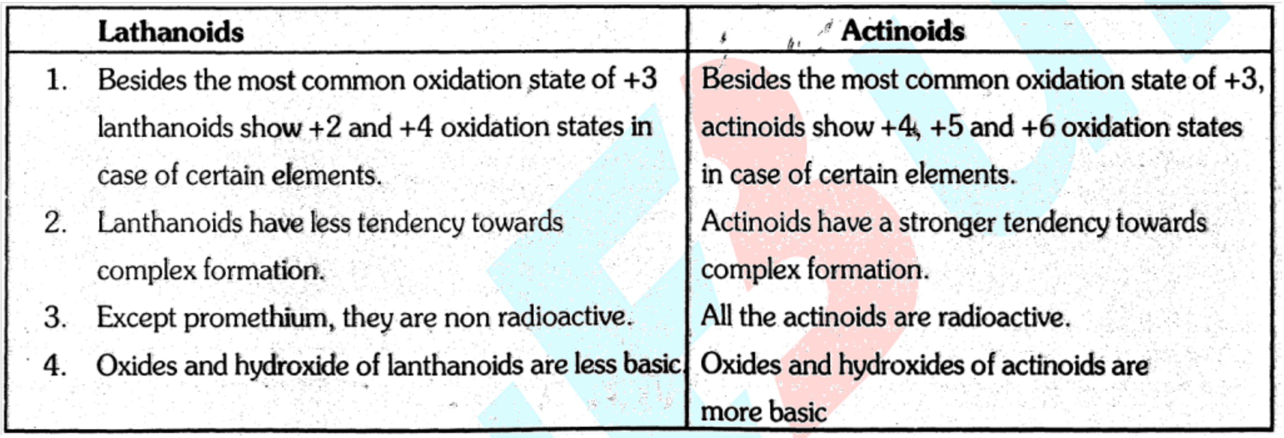
- **Radioactive nature :** All the actinoids are radioactive in nature.
- **Actinide contraction :** The size of atom/cation decrease regularly along the actinoids series. The steady decrease in ionic radii with increase in atomic number is referred to as actinide contraction. This is due to poor shielding of 5f-electrons.

Comparison of Lanthanides and Actinoids

Points of Resemblance :

(i) Both lanthahoids and actinoids show a dominant oxidation state of +3.
(ii) Both are electropositive and act as strong reducing agents.
(iii) Cations with unpaired electrons in both of them are paramagnetic.
(iv) Most of the cations of lanthanoids and actinoids are coloured.
(v) Both of them show a steady decrease in their ionic radii along the series. Thus, lanthanoids show lanthanoid contraction and actinoids show actinide contraction.

POINTS OF DISTINCTION



	Lathanoids	Actinoids
1.	Besides the most common oxidation state of +3 lanthanoids show +2 and +4 oxidation states in case of certain elements.	Besides the most common oxidation state of +3, actinoids show +4, +5 and +6 oxidation states in case of certain elements.
2.	Lanthanoids have less tendency towards complex formation.	Actinoids have a stronger tendency towards complex formation.
3.	Except promethium, they are non radioactive.	All the actinoids are radioactive.
4.	Oxides and hydroxide of lanthanoids are less basic	Oxides and hydroxides of actinoids are more basic

Some important of actinoids are as follows-

Thorium : Thorium is used in atomic reactors as fuel rods and in the treatment of cancer.

Uranium : Uranium is used as nuclear fuel. Its salts are in glass industry (for imparting green colour). textile industry and also in medicines

Plutonium : Plutonium is used as fuel for atomic reactors as well as in atomic bombs.

BEGINNER'S BOX-2

1. $KMNO_4$ can be acidified by

(1) Dil. HCl (2) conc. H_2SO_4 (3) conc. HNO_3 (4) dil. H_2SO_4

2. NaCl conc. $\xrightarrow[X]{\text{conc.}H_2SO_4}$ yellow green gas, X is

(1) $K_2Cr_2O_7$ (2) MnO_2 (3) $KMnO_4$ (4) both (2) & (3)

3. X $\xrightarrow[K_2Cr_2O_7]{\text{conc.}H_2SO_4}$ red brown vapours. X can be

(1) NaI (2) NaBr (3) Both (1) & (2) (4) None of these

4. $\underset{\text{black coloured ore}}{X} \xrightarrow[\text{air}]{KOH} \underset{\text{dark green}}{Y} \xrightarrow{H^+} \underset{\text{an oxidising agent}}{Z} + X$

True statement is

(1) X can't be MnO_2
(2) Y can be $KMnO_4$
(3) Z can be K_2MnO_4
(4) step (1) is oxidation while step (ii) is disproportionation

5. $X \underset{OH}{\overset{H^+}{\rightleftharpoons}} Y$; $Y \xrightarrow{SO_2} Z + SO_4^{-2}$

X and Y are oxy anion of Cr than oxidation state of Cr in X, Y, Z Will be respectively

(1) +3, +6, +6 (2) +6, +3, +6 (3) +6, +6, +6 (4) +6, +6, +3

6. When $KMnO_4$ solution is added to oxalic acid, solution, the decolourisation is slow in beginning but become instantaneous after some time because

(1) CO_2 is a by product
(2) Mn^{2+} acts as a catalyst
(3) Reaction in exothermic
(4) MnO_4^- catalyses the reaction

7. The elements from cerium (At. No. 58) to lutetium (At. No. 71) in which 4f energy levels are filled up are called :

(1) lanthanides (2) rare earths (3) lanthanones (4) all the above

8. Which of with following is a lanthanide :

(1) Ta (2) Rh (3) Th (4) Gd

9. The element with the electronic configuration $[Xe]^{54}\ 4f^{14}\ 5d^1 6s^2$ is a

(1) representative element
(2) transition element
(3) lanthanide
(4) actinide

10. Name the three lanthanides which show +2 oxidation state also :

(1) Sm, Tb, Gd (2) Sm, Eu, Yb (3) La, Gd, Lu (4) Yb, Pm, Sm

ANSWER KEY

BEGINNER'S BOX-1

1.	(2)	**2.**	(3)	**3.**	(3)	**4.**	(1)	**5.**	(4)	**6.**	(3,3)	**7.**	(1)
8.	(3)	**9.**	(1)										

BEGINNER'S BOX-2

1.	(4)	**2.**	(4)	**3.**	(2)	**4.**	(4)	**5.**	(4)	**6.**	(2)	**7.**	(4)
8.	(4)	**9.**	(3)	**10.**	(2)								

NCERT QUESTIONS (REASONING)

Q.1 Why do the transition elements have higher boiling & melting points ?

Ans. Because of having larger number of unpaired electrons in their atoms, they have stronger interatomic interaction and hence stronger bonding between atoms. Hence strong metallic bonds between the atoms of these elements attribute to their high melting and boiling points.

Q.2 Give the main difference in oxidation states of transition elements & p-block elements.

Ans. (i) The variation of oxidation state in transition elements is in such a way that their oxidation state differ from each other by unity e.g. V^{+2}, V^{+3}, V^{+4}, V^{+5}. While in p block elements oxidation states normally differ by two due to inert pair effect.

(ii) Stability of higher oxidation state in transition elements increase down the group
e.g. Pt^{+4} is more stable than Pt^{+2}

While in p block elements lower oxidation state become increasingly stable down the group as result of inert pair effect.

Q.3 For the first series of transition metals the $E^{\oplus}$ values are

E°	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**
(M^{2+}/M)	**–1.18**	**–0.91**	**–1.18**	**–0.44**	**–0.28**	**–0.25**	**+0.34**

Explain the irregularity in the above values.

Ans. This is because of irregular variation of ionization energies ($IE_1 + IE_2$) and also the sublimation energies which are much less for manganese and vanadium.

Q.4 Zinc does not show variable valency because of:

(A) complete 'd' sub-shell
(B) inert pair effect
(C) $4s^2$ sub-shell
(D) none

Ans. Zn = $[Ar]^{18}\ 3d^{10}\ 4s^2$. Zinc has completely filled g-sub-shell so removal of electron from completely filled 4d sub-shell would be quite difficult. Thus it does not show variable valency.

Q.5 Explain the blue colour of $CuSO_4.5H_2O$.

Ans. Cu^{2+} ion ($3d^9$) absorbs red light from the visible region, for the promotion of 3d electrons, the ions reflect blue light and appear blue.

Q.6 How iron (III) catalyses the reaction between iodide & persulphate?

Ans.

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

$$2Fe^{2+} + S_2O_8^{2-} \longrightarrow 2Fe^{3+} + 2SO_4^{2-}$$

$$2I^- + S_2O_8^{2-} \xrightarrow{Fe(III)} I_2 + 2\,SO_4^{2-}$$