D & F BLOCK ELEMENTS

General Characteristics

Position in periodic Table

1. The d-block of the periodic table contains the elements of the groups 3-12 in which the d-orbitals are progressively filled in each of the four long periods.
2. There are four series of the d-block elements.

3d series

21 **Sc** Scandium	22 **Ti** Titanium	23 **V** Vanadium	24 **Cr** Chromium	25 **Mn** Manganese	26 **Fe** Iron	27 **Co** Cobalt	28 **Ni** Nickel	29 **Cu** Copper	30 **Zn** Zinc

4d Series

39 **Y** Yttrium	40 **Zr** Zirconium	41 **Nb** Niobium	42 **Mo** Molybdenum	43 **Tc** Technetium	44 **Ru** Ruthenium	45 **Rh** Rhodium	46 **Pd** Palladium	47 **Ag** Silver	48 **Cd** Cadmium

5d Series

57 **La** Lanthanum	72 **Hf** Hafnium	73 **Ta** Tantalum	74 **W** Tungsten	75 **Re** Rhenium	76 **Os** Osmium	77 **Ir** Iridium	78 **Pt** Platinum	79 **Au** Gold	80 **Hg** Mercury

6d Series

89 **Ac** Actinium	104 **Rf** Rutherfordium	105 **Db** Dubnium	106 **Sg** Seaborgium	107 **Bh** Bohrium	108 **Hs** Hassium	109 **Mt** Meitnerium	110 **Ds** Darmstadtium	111 **Rg** Roentgenium	112 **Cn** Copernicium

Q. Why d-block elements are called transition elements ?

(i) Their ultimate & Penultimate shell is incomplete as well as they show variable oxidation state.

(ii) 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 state.

(iii) Zinc, Cadmium and Mercury of group 12 have full d^{10} configuration in their ground state as well as in their common oxidation states and hence, are not regarded as transition metals.

(iv) All transition elements are 'd' block elements, but all 'd' block elements are not transition-elements.

All d-block elements are metals, they show all metallic properties

(A) General Electronic Configurations

$(n-1)d^{1-10}\ ns^{1-2}$

The (n−1) stands for the inner d orbitals which may have one to ten electrons.

The (n) stands for the outer most s orbital which may have one or two electrons.

(B) Exceptions

(a) Above generalization has several exceptions because

- **(i)** The energy difference between (n – 1)d and ns orbitals is very less.
- **(ii)** Half and completely filled sets of orbitals are relatively more stable.

(b) A consequence of this factor is reflected in the electronic configuration of following elements.

- **(i)** In 3d series — Cr and Cu
- **(ii)** In 4d series — Nb, Mo, Tc, Ru, Rh, Pd, and Ag
- **(iii)** In 5d series — Pt and Au
- **(iv)** In 6d series — Rg

(C) Electronic configuration of all d-block elements.

(a) 3d–series

Sc → $_{18}[Ar]\ 3d^1\ 4s^2$
Ti → $_{18}[Ar]\ 3d^2\ 4s^2$
V → $_{18}[Ar]\ 3d^3\ 4s^2$
Cr → $_{18}[Ar]\ 3d^5\ 4s^1$
Mn → $_{18}[Ar]\ 3d^5\ 4s^2$
Fe → $_{18}[Ar]\ 3d^6\ 4s^2$
Co → $_{18}[Ar]\ 3d^7\ 4s^2$
Ni → $_{18}[Ar]\ 3d^8\ 4s^2$
Cu → $_{18}[Ar]\ 3d^{10}\ 4s^1$
Zn → $_{18}[Ar]\ 3d^{10}\ 4s^2$

(b) 4d–series

Y → $_{36}[Kr]\ 4d^1\ 5s^2$
Zr → $_{36}[Kr]\ 4d^2\ 5s^2$
Nb → $_{36}[Kr]\ 4d^4\ 5s^1$
Mo → $_{36}[Kr]\ 4d^5\ 5s^1$
Tc → $_{36}[Kr]\ 4d^6\ 5s^1$
Ru → $_{36}[Kr]\ 4d^7\ 5s^1$
Rh → $_{36}[Kr]\ 4d^8\ 5s^1$
Pd → $_{36}[Kr]\ 4d^{10}\ 5s^0$
Ag → $_{36}[Kr]\ 4d^{10}\ 5s^1$
Cd → $_{36}[Kr]\ 4d^{10}\ 5s^2$

(c) 5d–series

La → $_{54}[Xe]\ 5d^1\ 6s^2$
Hf → $_{54}[Xe]\ 5d^2\ 6s^2$
Ta → $_{54}[Xe]\ 5d^3\ 6s^2$
W → $_{54}[Xe]\ 5d^4\ 6s^2$
Re → $_{54}[Xe]\ 5d^5\ 6s^2$
Os → $_{54}[Xe]\ 5d^6\ 6s^2$
Ir → $_{54}[Xe]\ 5d^7\ 6s^2$
Pt → $_{54}[Xe]\ 5d^9\ 6s^1$
Au → $_{54}[Xe]\ 5d^{10}\ 6s^1$
Hg → $_{54}[Xe]\ 5d^{10}\ 6s^2$

(d) 6d–Series

Ac → $_{86}[Rn]\ 6d^1\ 7s^2$
Rf → $_{86}[Rn]\ 6d^2\ 7s^2$
Db → $_{86}[Rn]\ 6d^3\ 7s^2$
Sg → $_{86}[Rn]\ 6d^4\ 7s^2$
Bh → $_{86}[Rn]\ 6d^5\ 7s^2$
Hs → $_{86}[Rn]\ 6d^6\ 7s^2$
Mt → $_{86}[Rn]\ 6d^7\ 7s^2$
Ds → $_{86}[Rn]\ 6d^8\ 7s^2$
Rg → $_{86}[Rn]\ 6d^{10}\ 7s^1$
Cn → $_{86}[Rn]\ 6d^{10}\ 7s^2$

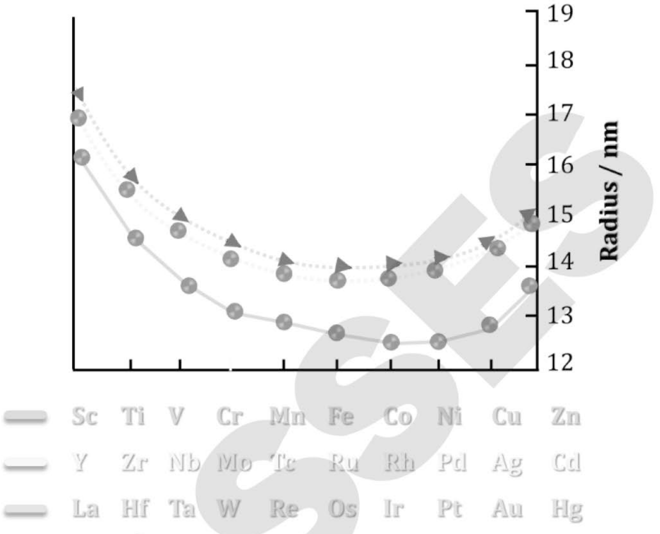
Atomic Radius

In period

In initial five elements attraction between nucleus and valence shell remains more as compared to repulsion between valence shell and penultimate shell that's why atomic radius decreases from Sc to Mn.

In next three elements attraction between nucleus and valence shell becomes equal to repulsion between valence shell and penultimate shell that's why atomic radius of Fe, Co and Ni remains almost equal.

In last two elements attraction between nucleus and valence shell remains less as compared to repulsion between valence shell and penultimate shell that's why atomic radius from Cu to Zn increases.



Trends in atomic radii of transition elements

In group

Atomic radii of 4d series elements are more than 3d series elements.

4d and 5d series elements nearly same atomic radii due to lanthanide contraction.

Magnetic Properties

(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 transition metal ions or their compounds have unpaired electrons in d-sub-shell (from configuration d^1 to d^9) and therefore, they give rise to paramagnetic character.

(iii) Metals, which have unpaired electrons show para-magnetism.

Spin only magnetic moment $\mu = \sqrt{n(n+2)}$

here n = no. of unpaired electron

Unit : Bohr Magneton (B.M.)

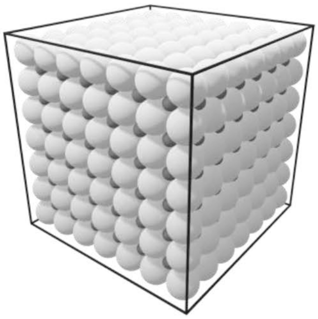
Ferromagnetism

Substances attracted very strongly are said to be ferromagnetic, extreme form of paramagnetic.

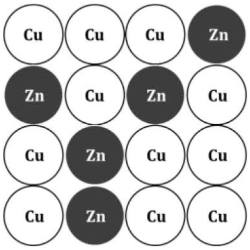
Ferromagnetic materials ⇒ Fe, Co, Ni

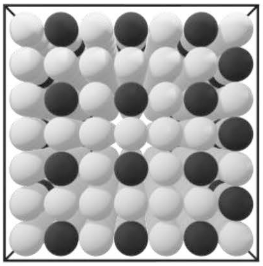
Formation of interstitial compounds

- H, C, N trapped inside Crystal lattice of metals
- Non-stoichiometric
- TiC, Mn_4N, Fe_3H, $VH_{0.56}$, $TiH_{1.7}$
- Retain metallic conductivity
- High melting point than pure metal
- They are very hard
- They are chemically inert



Formation of alloys





(i) Transition elements have maximum tendency to form alloys.

(ii) The reactivity of transition elements is very less and their sizes are almost similar. Due to this a transition metal atom in the lattice can be easily replaced by other transition metal atom and hence they have maximum tendency to form alloys.

(iii) In the alloys, ratio of component metals is fixed.

(iv) These are extremely hard and have high melting point.

Some important alloys

(a)	**Bronze**	Cu + Sn
(b)	**Brass**	Cu + Zn
(c)	**Gun metal**	Cu + Zn + Sn
(d)	**German Silver**	Cu + Zn + Ni
(e)	**Stainless Steel**	Cr + Ni
(f)	**Invar**	Ni 36
(g)	**Alnico**	Al + Ni + Co
(h)	**Duralumin**	Cu + Al + Mn
(i)	**22 Carrot gold**	Au + Ag
(j)	**18 Carrot gold**	Au + Ag + Cu
(k)	**Silver UK coins**	Cu + Ni
(l)	**White Metal**	Li + Pb
(m)	**Solder**	Sn + Pb
(n)	**Nichrome**	Ni + Cr + Fe
(o)	**Bell Metal**	Cu + Sn

Amalgam is a semisolid alloy which is formed by mixing a metal with Hg. Fe, Co, Ni do not form amalgam due to large difference in size.

Formation of complex compounds

- Small size
- High charge density
- Availability of vacant orbital

Example :

$$FeSO_4 + KCN \longrightarrow Fe(CN)_2 + K_2SO_4$$

$$Fe(CN)_2 \xrightarrow{\text{KCN (excess)}} K_4[Fe(CN)_6]$$

Melting Point

(i) Melting and boiling point of d-block elements is more than that of s block elements.
Reason : Stronger metallic bond formed by present 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)

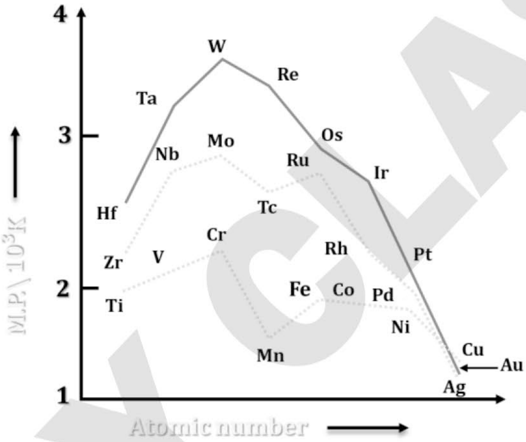
(iii) In 3d series Sc to Cr melting and boiling point increases then Mn to Zn melting and boiling point decreases

(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 (3400°C)

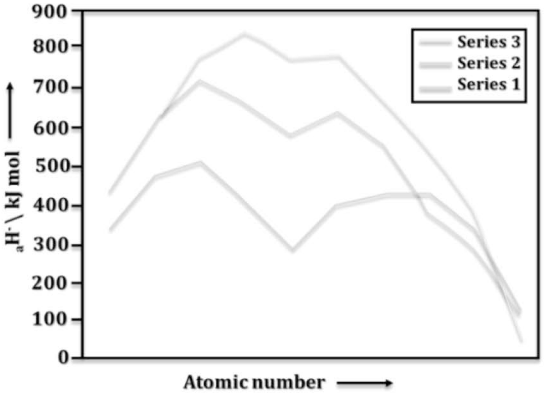
Trends in melting points of transition elements



Heat of atomisation

- Enthalpy of atomization means the energy required to break the metallic bond.
- Stronger is the metallic bond more will be the heat of atomisation.
- More number of unpaired electrons will favour the formation of metallic bond.
- In case of Mn due to stable (n–1)d & ns configuration metallic bond is weak.
- Mn and Zn has low heat of atomisation due to stable configuration electron are not available for metallic bonding.

Heat of Atomisation



Catalytic Properties

- The transition metals and their compounds are known for their catalytic activity.
- This is due to -
  Multiple oxidation states & presence of vacant orbital.

Catalyst	Used
Fe	Haber's process for manufacture of NH_3
V_2O_5	Contact process for H_2SO_4 manufacture
Pt	Ostwald's process of nitric acid
Ni	Hydrogenation of oils.

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 nuclear charge. 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 increases across a period.

Sc < Ti < V < Cr < Mn < Fe < Co < Ni = Cu > Zn (Zn has lower density because of its large atomic volume)

Minimum density in 3d series → **Sc**

Maximum density in 3d series → **Ni** and **Cu**

In Group : **3d < 4d < 5d**

Elements with highest densities are

Osmium (Os) = 22.51 g/cm^3, Iridium (Ir) = 22.61 g/cm^3

Oxidation States

1. d-block element shows variable oxidation state due to partially filled configuration.

2. It has two types of oxidation states -

(a) Minimum oxidation state = ns electron

(b) Maximum oxidation state = ns electron + (n-1)d unpaired electron

3. The variability of oxidation states, a characteristic of transition elements arises out of incomplete filling of d–orbitals in such a way that their oxidation states differ from each other by unity.

Example :-

V^{+2} V^{+3} V^{+4} V^{+5}

4. In d-block elements the higher oxidation states are favoured by the heavier members.

Example :-

In group – 6 Mo (VI) and W(VI) are found to be more stable than Cr (VI).

Thus Cr (VI) in form of dichromate ($Cr_2O_7^{2-}$) in acidic medium is a strong oxidizing agent, whereas MoO_3 and WO_3 are not.

5. Low oxidation states are found when a complex compound has ligand capable of π-acceptor character in addition to the σ-bonding. (synergic ligand like CO)

Example :-

In $Ni(CO)_4$ and $Fe(CO)_5$, the oxidation state of nickel and iron is zero.

They show variable oxidation state.

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

- Underlined states are the most stable ones.

Electrode Potential

In addition to ionisation enthalpy, the other factors such as enthalpy of sublimation, hydration 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:

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

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

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

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

$\Delta H = \Delta_{sub}H^{\Theta} + \Delta_{IE}H + \Delta_{hyd}H$

If SOP is +ve that means oxidation will be easy

If SRP is +ve that means reduction will be easy.

Some important examples :

1. $E^0_{M^{+2}/M} \Rightarrow$ +ve only for Cu among 3d elements because hydration energy of Cu^{+2} is not enough to compensate for sublimation energy, IE_1 and IE_2 for Cu.

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

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

that means Cr^{+2} acts as a reducing agent because Cr^{+3} has t_{2g} half filled stable configuration.

(ii) $E^0_{Mn^{+3}/Mn^{+2}} = +ve$

that means Mn^{+3} acts as an oxidising agent due to stability of half filled (d^5) configuration.

Trends in stability of higher oxidation states

The highest oxidation states are shown generally among halides and oxides of transition elements.

(I) In halides of transition elements

(i) The transition elements react with halogens at high temperatures to form transition metal halides.

(ii) Since fluorine is the most 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.

(iii) 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.

(iv) 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 terms for the higher covalent compounds. eg. VF_5 and CrF_6.

(v) 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, Br, I). On the other hand all copper (II) halides are known except the iodide. This is because, Cu^{2+} oxidises I^- to I_2.

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

(vi) It has been observed that many copper (I) compounds are unstable in aqueous solution and they undergo disproportionation

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

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 ($\Delta_{hyd}H$) of Cu^{2+} (aq) than Cu^+, which is sufficiently high to compensate second ionisation enthalpy of copper.

(II) 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, oxocation of the metals also stabilise higher oxidation states. For example, V^V as VO_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 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. In these higher oxides the acidic character is predominant. Thus CrO_3 gives H_2CrO_4 and $H_2Cr_2O_7$ and Mn_2O_7 gives $HMnO_4$. **V_2O_5 is, however amphoteric though mainly acidic and with alkalies as well as acids gives VO_4^{3-} and VO_2^+ respectively**.

Element (M)	$E^o_{M^{3+}/M^{2+}}$	$E^o_{M^{2+}/M}$	Comments
Ti	−0.37	−1.63	+3 Oxidation state is more stable
V	−0.26	−1.18	+3 Oxidation state is more stable
Cr	−0.41	−0.9	+3 Oxidation state is more stable
Mn	1.57	−1.18	+2 Oxidation state is more stable
Fe	0.77	−0.44	+2 Oxidation state is more stable
Co	1.97	−0.28	+2 Oxidation state is more stable
Ni	-	−0.25	+3 Oxidation state does not exist for Ni
Cu	-	0.34	+3 Oxidation state does not exist for Cu. 0 Oxidation state is more stable
Zn	-	−0.76	+3 Oxidation state does not exist for Zn

Potassium Dichromate $K_2Cr_2O_7$

Preparation :

- 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.
- The reaction with sodium carbonate occurs as follows:

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

The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate, $Na_2Cr_2O_7.\,2H_2O$ can be crystallised.

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

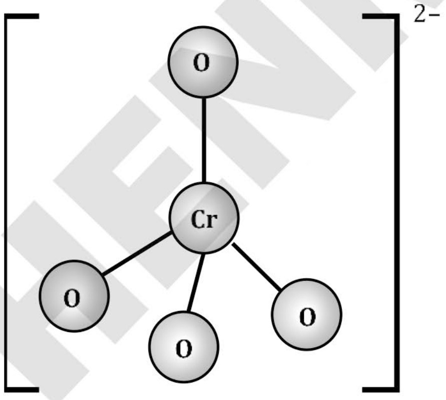
- Sodium dichromate is more soluble than potassium dichromate. The latter is therefore, prepared by treating the solution of sodium dichromate with potassium chloride.

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

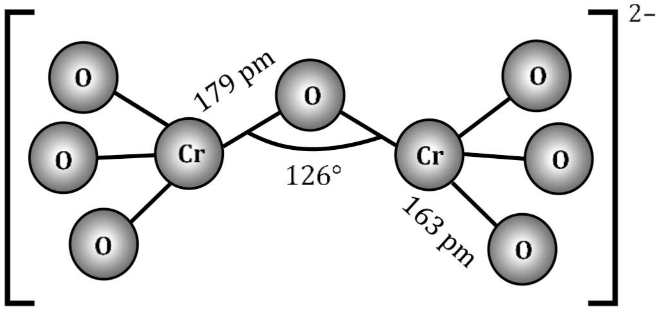
Orange crystals of potassium dichromate crystallise out. The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.

$$2CrO_4^{2-} \xrightarrow[(2H^+)]{\text{Acidic medium}} Cr_2O_7^{2-} + H_2O \qquad Cr_2O_7^{2-} \xrightarrow[(2OH^-)]{\text{Basic medium}} 2CrO_4^{2-} + H_2O$$

- $K_2Cr_2O_7$ is preferred over $Na_2Cr_2O_7$ as a primary standard in volumetric analysis (titration) because $Na_2Cr_2O_7$ is hygroscopic in nature but $K_2Cr_2O_7$ is not.
- The structures of chromate ion, CrO_4^{2-} and the dichromate ion, $Cr_2O_7^{2-}$ are shown below. The chromate ion is tetrahedral whereas the dichromate ion consists of two tetrahedra, sharing one corner with Cr–O–Cr bond angle of 126°.

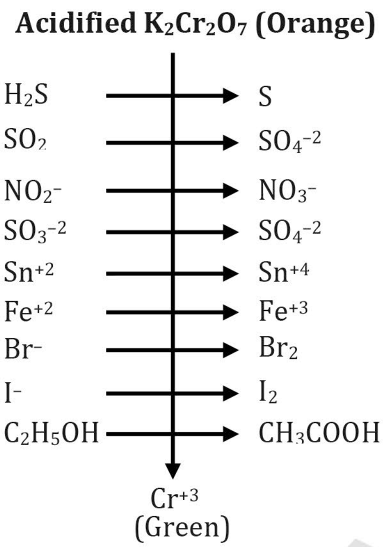


Chromate ion



Dichromate ion

Oxidising Property :-



Chromyl chloride test (used to identify ionic chlorides)

Generally Ionic or water soluble chloride gives chromyl chloride test.

$$4NaCl + K_2Cr_2O_7 + 6H_2SO_4 \longrightarrow 2CrO_2Cl_2 \text{ (Red orange vapour)} + 2KHSO_4 + 4NaHSO_4 + 3H_2O$$

$$\downarrow \text{NaOH solution}$$

$$Na_2CrO_4 \text{ (Yellow)}$$

AgCl, $HgCl_2$ & $PbCl_2$ are covalent or water insoluble chloride so they can't give chromyl chloride test.

Potassium Permanganate ($KMnO_4$)

Preparation :

- Potassium permanganate is prepared by fusion of MnO_2 (Pyrolusite) with an alkali metal hydroxide and an oxidising agent like KNO_3.

  This produces the dark green K_2MnO_4 which disproportionate in a neutral or acidic solution to give permanganate.

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

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

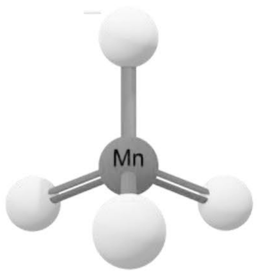
- Commercially it is prepared by the alkaline oxidative fusion of MnO_2 followed by the electrolytic oxidation of manganate (Vl).

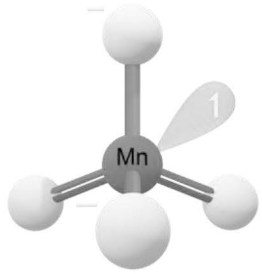
$$\underset{}{MnO_2} \xrightarrow[]{\text{Fused with KOH, oxidised with air or } KNO_3} \underset{\text{manganate ion}}{MnO_4^{2-}} \quad ; \quad \underset{\text{manganate}}{MnO_4^{2-}} \xrightarrow{\text{Electrolytic oxidation in alkaline solution}} \underset{\text{permanganate ion}}{MnO_4^-}$$

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

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

Physical Property :





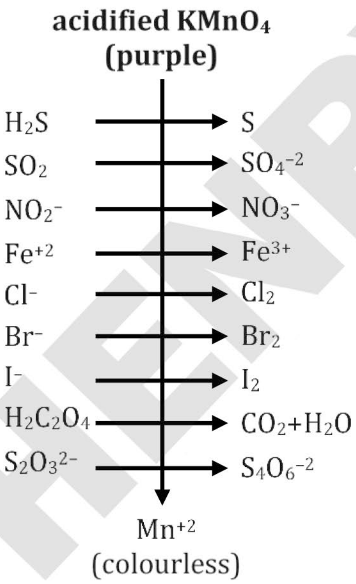
- Potassium permanganate forms **dark purple (almost black)** crystals which are isostructural with those of $KClO_4$. The salt is not very soluble in water (6.4 g/100 g of water at 293 K), but when heated it decomposes at 513 K.

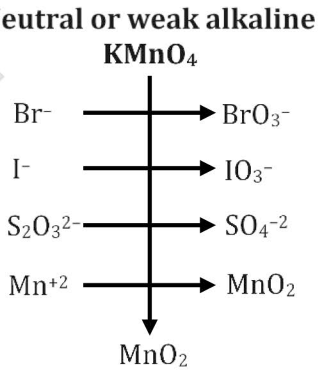
$$\mathbf{2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2}$$

The manganate and permanganate ions are tetrahedral; 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 permanganate is diamagnetic due to the absence of unpaired electron.

Oxidising Property :





f-BLOCK ELEMENTS

Introduction

(a) The elements constituting the f – block are those in which the 4f and 5f orbitals are progressively filled.

(b) These elements are formal members of group 3 from which they have been taken out to form a separate f–block of the periodic table.

(c) The name inner transition metals are often used to refer to the elements of f–block.

(d) The f-block consists of the two series

(i) Lanthanides

The fourteen elements following lanthanum.

Because lanthanum closely resembles the lanthanides, it is usually included in any discussion of the lanthanides.

(ii) Actinides

The fourteen elements following actinium.

Because actinium closely resembles the actinides, it is usually included in any discussion of the actinides.

The lanthanides :

Name **Electronic Configuration**

$_{59}\text{Ce} \longrightarrow {}_{54}[\text{Xe}]\ 4f^3\ 5d^0\ 6s^2$ **(Cerium)**

$_{59}\text{Pr} \longrightarrow {}_{54}[\text{Xe}]\ 4f^3\ 5d^0\ 6s^2$ **(Praseodymium)**

$_{60}\text{Nd} \longrightarrow {}_{54}[\text{Xe}]\ 4f^4\ 5d^0\ 6s^2$ **(Neodymium)**

$_{61}\text{Pm} \longrightarrow {}_{54}[\text{Xe}]\ 4f^5\ 5d^0\ 6s^2$ **(Promethium)**

$_{62}\text{Sm} \longrightarrow {}_{54}[\text{Xe}]\ 4f^6\ 5d^0\ 6s^2$ **(Samarium)**

$_{63}\text{Eu} \longrightarrow {}_{54}[\text{Xe}]\ 4f^7\ 5d^0\ 6s^2$ **(Europium)**

$_{64}\text{Gd} \longrightarrow {}_{54}[\text{Xe}]\ 4f^7\ 5d^1\ 6s^2$ **(Gadolinium)**

$_{65}\text{Tb} \longrightarrow {}_{54}[\text{Xe}]\ 4f^9\ 5d^0\ 6s^2$ **(Terbium)**

$_{66}\text{Dy} \longrightarrow {}_{54}[\text{Xe}]\ 4f^{10}\ 5d^0\ 6s^2$ **(Dysprosium)**

$_{67}\text{Ho} \longrightarrow {}_{54}[\text{Xe}]\ 4f^{11}\ 5d^0\ 6s^2$ **(Holmium)**

$_{68}\text{Er} \longrightarrow {}_{54}[\text{Xe}]\ 4f^{12}\ 5d^0\ 6s^2$ **(Erbium)**

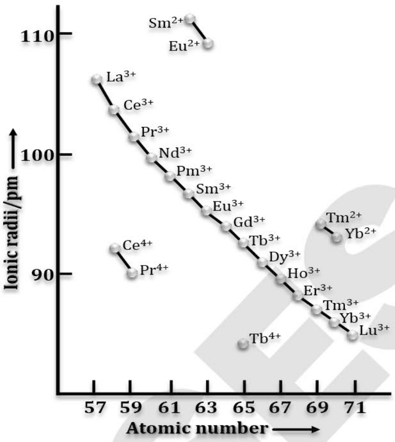
$_{69}\text{Tm} \longrightarrow {}_{54}[\text{Xe}]\ 4f^{13}\ 5d^0\ 6s^2$ **(Thulium)**

$_{70}\text{Yb} \longrightarrow {}_{54}[\text{Xe}]\ 4f^{14}\ 5d^0\ 6s^2$ **(Ytterbium)**

$_{71}\text{Lu} \longrightarrow {}_{54}[\text{Xe}]\ 4f^{14}\ 5d^1\ 6s^2$ **(Lutetium)**

- It may be noted that atoms of these elements have electronic configuration with $6s^2$ common but variable occupancy of 4f level.
- The irregularities in the electronic configuration of lanthanides are related to the stabilities of the f^0, f^7, f^{14} occupancies of the 4f orbitals.

Atomic and Ionic Radius



Trends in ionic radii of lanthanides

1. The overall decrease in ionic radii from lanthanum to lutetium is a unique feature in the chemistry of the lanthanides.
2. This is due to poor shielding of nucleus by inner penultimate 4f orbital.
3. The cumulative effect of the contraction in size of the lanthanide series, known as lanthanide contraction.
4. The decrease in atomic radii is not quite regular.
5. The decrease in ionic radii of M^{3+} comparatively more regular.

Consequences of lanthanide contraction

- Small size difference between size of 4d and 5d series of transition element.
- Effect of basic strength, Basic strength decreases on moving left to right.
- Steady decrease in size.

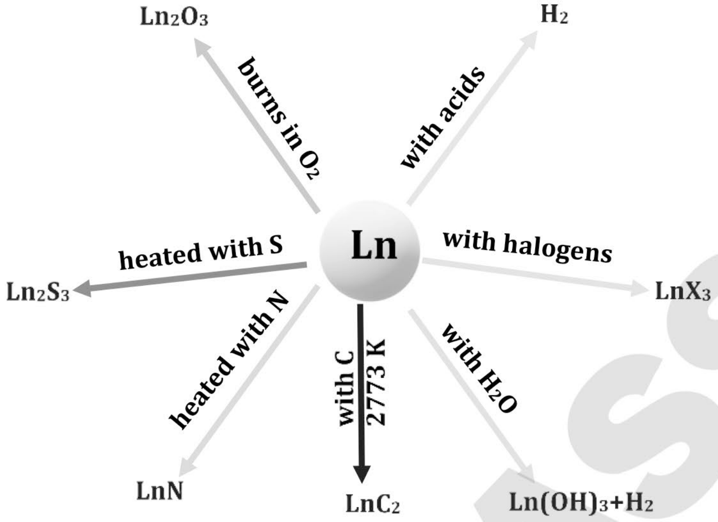
Oxidation States

1. The common oxidation state for lanthanides is +3 but it also shows +2 and +4 state.
2. **(i)** Ce → +4 and +3. Ce^{+4} act as a oxidant & used in volumetric Analysis.
   (ii) Pr, Nd, Tb and Dy also exhibit +4 state but only in oxides, MO_2.
   (iii) Eu^{2+} is a strong reducing agent changing to the common +3 state.
   (iv) Yb^{2+} has f^{14} configuration is a reductant.
   (v) Tb^{+4} has f^7 configuration is a oxidant.
   (vi) The behaviour of samarium is very much like europium, exhibiting both +2 and +3 oxidation states.

General characteristics

1. Silvery white
2. Soft metals
3. Tarnish rapidly in air
4. Typical metallic structure
5. Good conductors of heat
6. Good conductors of electricity
7. **(i)** Many trivalent lanthanide ions are coloured both in the solid state and in aqueous solutions.
   (ii) Colour of these ions may be attributed to the presence of unpaired f electrons However, absorption bands are narrow, probably because of the excitation within f orbitals, called f-f transition.
   (iii) La^{3+} and Lu^{3+} ions does not show any colour but the rest do so.

8. **(i)** The lanthanide ions other than the f^0 type (La^{3+} and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic.
   (ii) The paramagnetism rises to maximum in Nd.



Other Properties

Alloy Formation

Alloy of lanthanide with iron called misch metal (composition) → Ce – 50%, La – 25%, Nd – 15% & 10% other rare – earth metal & iron or Lanthanoid metal (95%) + Iron (5%)

The Actinides :

Name		Electronic configuration
$_{90}$Th	⟶	$_{86}$[Rn] $5f^0\ 6d^2\ 7s^2$ (Thorium)
$_{91}$Pa	⟶	$_{86}$[Rn] $5f^2\ 6d^1\ 7s^2$ (Protactinium)
$_{92}$U	⟶	$_{86}$[Rn] $5f^3\ 6d^1\ 7s^2$ (Uranium)
$_{93}$Np	⟶	$_{86}$[Rn] $5f^4\ 6d^1\ 7s^2$ (Neptunium)
$_{94}$Pu	⟶	$_{86}$[Rn] $5f^6\ 6d^0\ 7s^2$ (Plutonium)
$_{95}$Am	⟶	$_{86}$[Rn] $5f^7\ 6d^0\ 7s^2$ (Americium)
$_{96}$Cm	⟶	$_{86}$[Rn] $5f^7\ 6d^1\ 7s^2$ (Curium)
$_{97}$Bk	⟶	$_{86}$[Rn] $5f^9\ 6d^0\ 7s^2$ (Berkelium)
$_{98}$Cf	⟶	$_{86}$[Rn] $5f^{10}\ 6d^0\ 7s^2$ (Californium)
$_{99}$Es	⟶	$_{86}$[Rn] $5f^{11}\ 6d^0\ 7s^2$ (Einstenium)
$_{100}$Fm	⟶	$_{86}$[Rn] $5f^{12}\ 6d^0\ 7s^2$ (Fermium)
$_{101}$Md	⟶	$_{86}$[Rn] $5f^{13}\ 6d^0\ 7s^2$ (Mendelevium)
$_{102}$No	⟶	$_{86}$[Rn] $5f^{14}\ 6d^0\ 7s^2$ (Nobelium)
$_{103}$Lr	⟶	$_{86}$[Rn] $5f^{14}\ 6d^1\ 7s^2$ (Lawrencium)

- It may be noted that atoms of these elements have electronic configuration with $7s^2$ common but variable occupancy of 5f and 6d sub shell.
- The irregularities in the electronic configuration of actinides are related to the stabilities of the f^0, f^7, f^{14} occupancies of the 5f orbitals.

Ionic Sizes

- The general trend in lanthanides is observable in the actinides as well. There is a gradual decrease in the size of atoms or M^{3+} ions across the series. This may be referred to as the actinide contraction (like lanthanide contraction). The contraction is, however, greater from element to element in this series resulting from poor shielding by 5f electrons.

Actinide Contraction

- Due to poor shielding of 5f orbitals. Actinide contraction is more effective than lanthanide contraction.

Colour

- Actinides are generally coloured.
- The colour of actinides depends upon the number of 5f electrons.
- If there is no unpaired electrons it will be colourless.

Oxidation State

⇒ Most common oxidation state is +3 beside that they show +4, +5, +6 oxidation state in certain elements.

Complex Formation

- Actinides have stronger tendency towards complex formation.

Radioactivity

- All actinides are radioactive while lanthanides are non-radioactive [except promethium (pm)].
- Oxides and hydroxides of actinides are more basic than lanthanide.

BEGINNER'S BOX ANSWERS KEY

BEGINNER'S BOX-1	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	**2**	**4**	**3, 3**	**1**	**3**	**3**	**2**	**4**	**2**	**2**

BEGINNER'S BOX-2	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	**2**	**4**	**4**	**2**	**4**	**4**	**4**	**1**	**1**	**1**