P- BLOCK ELEMENTS

GROUP 13 ELEMENTS

Physical Property

- Boron to indium show +3 oxidation state in their compounds while thallium show +1 oxidation state (due to inert pair effect) in their compounds. Relative stability of M^+ and M^{3+} ions may be given as:

$$B^+ < Al^+ < Ga^+ < In^+ < Tl^+$$
$$B^{3+} > Al^{3+} > Ga^{3+} > In^{3+} > Tl^{3+}$$

Chemical Properties

- **Action of air:**

$$4M + 3O_2 \longrightarrow 2M_2O_3$$

Reaction occurs at high temperature. With Al, a protective oxide layer is formed which makes it passive. Tl also forms Tl_2O. Ga_2O_3, In_2O_3 also form.

- **Action of Water:**

$$2M + 3H_2O \longrightarrow M_2O_3 + 3H_2$$

Boron is not affected by water. It reacts with steam at red hot. Al decomposes cold water if it is not passive by oxide layer formation. Ga and In are not attacked by cold or hot water unless oxygen is present. Tl reacts with moist air to form TlOH.

- **Action of nitrogen :** $2M + N_2 \longrightarrow 2MN$
- **Action of halogen :** $2M + 3X_2 \longrightarrow 2MN_3$

All the group 13 elements form trihalide except Tl. Tl from TlX. TlI reacts with I_2 and form TlI_3 ($Tl^+ I_3^-$)

- **Action of acids :** $2M + 6H^+ \longrightarrow 2M^{3+} + 3H_2$

Boron is not affected by non-oxidizing acids like HCl and dilute H_2SO_4 while other elements dissolve to form trivalent salts.

$$3Mg + 2B \longrightarrow Mg_3B_2$$
$$Mg_3B_2 + 6HCl \longrightarrow 3MgCl_2 + B_2H_6$$

The rest of the elements do not combine with metals. This shows that boron is a non-metal and rest of the elements are metal.

Important Compounds of Group 13 Elements

Boron is known to exist in two form (a) amorphous and (b) crystalline.
Amorphous boron is obtained by reduction of B_2O_3 with Na or K and Mg at high temperature in a covered crucible.
Crystalline form is obtained by the reduction of B_2O_3 with Al-powder.
Crystalline boron is black and chemically inert in nature. It is very hard. Amorphous boron is brown and chemically active. Boron is used as a deoxidiser in the casting of copper and for making boron steel which are used as control rods in nuclear reactors.

- **Hydrides**

Boron forms a number of stable covalent hydrides called diboranes with general formula B_nH_{n+4} (Called nido boranes) and B_nH_{n+6} called arachno boranes, less stable).
Aluminium forms a polymeric hydride called alane /alumane with general formula $(AlH_3)_n$.
Ga forms Ga_2H_6 and In forms $(InH_3)_n$. Tl does not form hydrides.

- **Oxides and hydroxides**

The members of boron family form oxides and hydroxides of the general formula M_2O_3 and $M(OH)_3$ respectively.

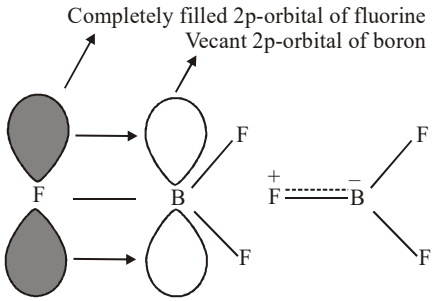
Oxides :	$B_2O_3 > Al_2O_3 > Ga_2O_3 > In_2O_3 > Tl_2O_3$	(stability)
Hydroxides :	$B(OH)_3 > Al(OH)_3 > Ga(OH)_3 > In(OH)_3 > Tl(OH)_3$	(stability)
Nature :	Acidic Amphoteric Amphoteric Basic Strongly Basic	

- **Halides :**

BX_3 is electron deficient so behaves as a Lewis acid.

$BX_3 + :NH_3 \longrightarrow [H_3N \longrightarrow BX_3]$
Lewis acid Lewis base Adduct

Relative Lewis acid strength of boron halides are as follows:
$BI_3 > BBr_3 > BCl_3 > BF_3$ (due to $p\pi - p\pi$ back bonding)
In BF_3, each F has completely filled unutillised 2p orbitals while B has a vacant 2p-orbital. Now since both of these orbitals belong to same energy level (2p) they can overlap effectively as a result of which electrons of B resulting in the formation of an additional $p\pi$–$p\pi$ bond. This type of bond formation of back as dative or back bonding. Formation of back bonding between B and F in BF_3 molecule as given below figure.



As a result of back donation of electrons from F to B, the electron deficiency of B is reduced and Lewis acid character is decreased. the tendency for the back bonding is maximum in BF_3 and decreases from BF_3 to Bl_3. Thus Bl_3, BBr_3 and BCl_3 are stronger Lewis acids then BF_3.

Anomalous Behaviour of Boron :

Boron shows anomalous behaviour due to its small size, high nuclear charge, high electronegativity and non-availability of d-orbitals.

IMPORTANT COMPOUNDS OF BORON

Boric acid (H_3BO_3)

- **Preparation :**

(a) From borax ($Na_2B_4O_7.\ 10H_2O$):

Boric acid can be prepared by adding a hot concentrated solution of borax to a calculated quantity of conc. H_2SO_4. The solution on cooling gives crystals of boric acid, which can be separated by filtration.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3\downarrow$$

(boric acid)

(b) From colemanite ($Ca_2B_6O_{11}.5H_2O$):

$$Ca_2B_6O_{11} + 4SO_2 + 11H_2O \longrightarrow 2Ca(HSO_3)_2 + 6H_3BO_3\downarrow$$

- **Properties :**

(a) Action of heat:

$$\underset{\text{boric acid}}{H_3BO_3} \xrightarrow[-H_2O]{100^\circ C} \underset{\text{meta boric acid}}{HBO_2} \xrightarrow[-H_2O]{160^\circ C} \underset{\text{tetra boric acid}}{H_2B_4O_7} \xrightarrow[-H_2O]{\text{redhot}} \underset{\text{boron trioxide}}{B_2O_3}$$

(b) Reaction with alcohol (test of boric acid):

$$H_3BO_3 + 3(C_2H_5OH) \rightarrow \underset{\text{Triethyl borate (volatile)}}{B(OC_2H_5)_3} + 3H_2O$$

Borax $(Na_2B_4O_7.10H_2O)$ or $Na_2[B_4O_5(OH)_4].8H_2O$

- **Properties :**

(i) Its solution is basic in nature due to hydrolysis.

$$Na_2B_4O_7 + 7H_2O \rightarrow \underset{\text{Strong base}}{2NaOH} + \underset{\text{weak acid}}{4H_3BO_3}$$

(ii) $Na_2B_4O_7.\ 10H_2O \xrightarrow[-10H_2O]{\Delta} \underset{\text{anhydrous (Swell up)}}{Na_2B_4O_7} \xrightarrow{740^oC} \underbrace{2NaBO_2 + B_2O_3}_{\text{(transparent glassy bead)}}$

(iii) Borax bead test : Borax on strong heating forms B_2O_3 which forms coloured glassy bead with coloured compounds of certain metals. It is called borax bead test.

Colour of beads $\underset{\text{Green}}{Cr}$ $\underset{\text{Pink}}{Mn}$ $\underset{\text{Green}}{Fe}$ $\underset{\text{Blue}}{Co}$ $\underset{\text{Brown}}{Ni}$ $\underset{\text{Blue}}{Cu}$

eg. $\underset{\text{Blue bead}}{Cu(BO_2)_2}$

Dibrorane (B_2H_6)

- **Preparation :**

(i) $3Mg + 2B \xrightarrow{\Delta} Mg_3B_2 \xrightarrow{H_3PO_4} \text{Mixture of boranes} \xrightarrow{\Delta} \underset{\text{diborane}}{B_2H_6}$

(ii) $B_2O_3 + 3H_2 + 2Al \xrightarrow[\text{pressure}]{150^oC} B_2H_6 + Al_2O_3$

(iii) $2BF_3 + 6NaH \xrightarrow{180^oC} B_2H_6 + 6NaF$

- **Properties :**

(i) Reaction with ammonia:

$$B_2H_6.2NH_3 \xleftarrow[\text{temperature}]{\text{low}} B_2H_6 + \underset{\text{(excess)}}{NH_3} \xrightarrow[\text{temperature}]{\text{high}} \underset{\text{Inorganic graphite or Borazone}}{(BN)_n}$$

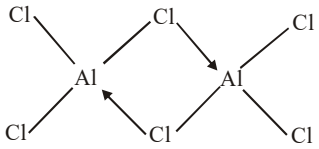
$$[BH_2(NH_3)_2]^+[BH_4]^- \text{or } \underset{\text{Ratio 1:2}}{B_2H_6 + NH_3} \xrightarrow{\text{high Temperarure}} \underset{\text{(borazine)}}{B_3N_3H_6}$$

(ii)Reaction with amine :

$$\underset{\text{(Lewis acid)}}{B_2H_6} + 2\underset{\text{(Lewis base)}}{(Me_3N)} \rightarrow \underset{\text{adduct}}{[N(Me_3)_3} \rightarrow 2BH_3]$$

– Borazine is known as inorganic benzene.

Anhydrous $AlCl_3$ is prepared by passing dry HCl or Cl_2 gas over heated aluminium turnings in absence of air. It is also obtained by passing Cl_2 gas over heated mixture of Al_2O_3 and coke. It is used as a catalyst in Friedel - Craft's reaction. The molecule is an autocomplex and is represented as:



Anhydrous $AlCl_3$ is a Lewis acid. Anhydrous form is covalent while hydrated $AlCl_3.6H_2O$ is ionic.

ALUMS

Alums are the double sulphates of the type $M_2SO_4.\ M_2(SO_4)_3.\ 24H_2O$ where M is a univalent cation like Na^+, K^+ and $NH_4^+$and M' is a trivalent cation like Al^{3+}, Fe^{3+} and Cr^{3+}.

Potash alum	$K_2SO_4.\ Al_2(SO_4)_3.\ 24H_2O$
Sodium	$Na_2SO_4.\ Al_2(SO_4)_3.\ 24H_2O$
Ferric alum	$(Na_4)_2SO_4.\ Fe_2(SO_4)_3.\ 24H_2O$
Ammonium alum	$(NH_4)Al(SO_4)_2.\ 12H_2O$
Chrome alum	$K_2SO_4.\ Cr_2(SO_4)_3.\ 24H_2O$

Ultramarine is an artifical Lapis-Lazuli, a rare mineral ($Na_3Al_3Si_3S_3O_{12}$) which has fine blue colour. It is used in making blue paint.

Precious stones such as sapphire, ruby, topaz etc., are Al_2O_3 containing oxides of transition metals.

(GROUP 14 ELEMENTS)

PHYSICAL PROPERTIES

Stability order

$C^{+4} > Si^{+4} > Ge^{+4} > Sn^{+4} > Pb^{+4}$

$C^{+2} < Si^{2+} < Ge^{+2} < Sn^{2+} < Pb^{2+}$

(due to inert pair effect)

I.P. order

$C > Si > Ge > Sn < Pb$

(due to lanthanoid contraction)

Catenation $C >> Si > Ge = Sn = Pb$

Except lead, all other elements of this group show allotropy. Diamond, fullerene and graphite are allotropes of carbon.

CHEMICAL PROPERTIES

Action of air:

(i) Monoxides : $2M + O_2 \longrightarrow 2MO$

eg. $\xrightarrow[\text{unstable}]{CO, SiO, GeO, SnO, PbO}$

(ii) Dioxides : $M + O_2 \longrightarrow MO_2$

Acidic Nature $\underset{\text{Acidic}}{CO_2 > SiO_2} > \underset{\text{Amphoteric}}{GeO_2 > SnO_2} > \underset{\text{Basic}}{PbO_2}$

- **Action of water :**

Si, Ge and Pb are unaffected by H_2O.

$Sn + 2H_2O$ (steam) $\longrightarrow SnO_2 + 2H_2O$

- **Action of acids :** Non-oxidising acids do not attack C and Si, Ge is not attacked by dilute HCl. When Ge is heated in a steam of HCl gas, germanium chloroform is formed.

Sn dissolves slowely in dilute HCl but readily in concentrated HCl.

Pb dissolves in conc. HCl forming chloroplumbous acid, but the reaction stops after sometime due to deposition of $PbCl_2$.

- **Action of alkali :** C is unaffected by cold alkali, Si reacts slowly with cold aqueous NaOH and readily with hot NaOH forming silicate. Sn and Pb form stannate and plumbate respectively on reaction with hot alkali.

Important compounds of group 14 elements :

- **HYDRIDES :** MH_4 (General formula)

CH_4 Methane On moving top to bottom

SiH_4 Silane $\rightarrow$ Bond length increases

GeH_4 Germane $\rightarrow$ Thermal Stability decreases

SnH_4 stanane $\rightarrow$ Acidic nature increases

Pbh_4 Plambane $\rightarrow$ reducing Nature incresaes

- **Halides :**

All the element forms covalent halides, MX_4 (except $PbBr_4$ and PbI_4) the thermal stability of halide decreases as:

$CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$.

$MF_4 > MCl_4 > MBr_4 > MI_4$

The halides are readily hydrolysed by water (except CX_4, due to absence of d-orbital). the order of ease of hydrolysis is

$SiCl_4 > GeCl_4$ $SnCl_4 > PbCl_4$.

Degree of hydrolysis α covalent character.

- **Carbides :**

The binary compounds of carbon with elements other than hydrogen are called carbides.

Ionic carbides are formed by the most electropositive metals such as alkali and alkaline earth metals and Al. both Be_2C and Al_4C_3 are called methamides because they react with H_2O yielding methane.
Covalent carbides are formed by metalloids like Si and B. SiC (carborundum) has a diamond like structure, hence it is called artificial diamond. B_4C (Norbide) is hardest known artificial substance.Interstitial carbides are formed by transition elements in which C-atoms occupy tetrahedral holes in the close-packed metal atoms. W, Zr, Ti and Mo can form ideal intersitial carbides.

- **Silicones :**

Silicones are polymeric organo-silicon compounds contaning Si-O-Si linkages. The name silicon has been given from similarity of their empirical formula (R_2SiO) with ketones (R_2O) Silicones are formed by the hydrolysis of alkyl or aryl substituted chlorosilanes and their subsequent polymerisation.

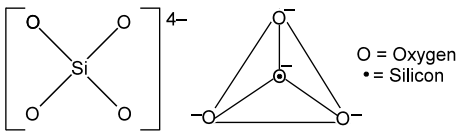
$$2RCl + Si \xrightarrow[570K]{\text{Cu powder}} \underset{\text{dialkyldichloro silane}}{R_2SiCl_2}$$

$$R_2SiCl_2 \xrightarrow[-HCl]{+H_2O} [R_2Si(OH)_2] \xrightarrow{-H_2O} \underset{\text{Silicone}}{\left[-O-\overset{R}{\overset{|}{Si}}-O-\overset{R}{\overset{|}{Si}}-O-\right]_n}$$

Silicones have good thermal, oxidative stability. These are excellent water repellants and chemically inert substances. Liquid silicones are used as excellent lubricants.
Silicates: Silicates are metal derivatives of silicic acid [H_4SiO_4 or $Si(OH)_4$]. Silicates are made up of SiO_4^{4-} tetrahedral units in which Si is sp^3 hybridised and is surrounded by four oxygen atoms.
All these elements combine with halogens forming corresponding halides.
Note: Boron and aluminium combine with nitrogen and carbon on heating to form nitride, carbide respectively.
Types of Silicates :

(A) Orthosilicates :

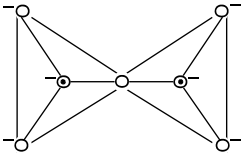
These contain discrete $[SiO_4]^{4-}$ units i.e., there is no sharing of corners with one another as shown is figure.



e.g. Zircon ($ZrSiO_4$), Forsterite of Olivine (Mg_2SiO_4), Willemite (Zn_2SiO_4)

(B) Pyrosilicate :

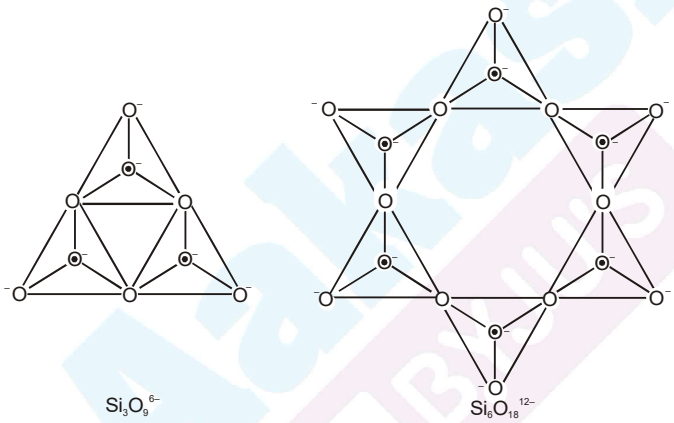
In these silicates two tetrahedral units are joined by sharing oxygen at one corner thereby giving $[Si_2O_7]^{6-}$ units.



e.g. Thorteveitite ($Sc_2Si_2O_7$), Hemimorphite ($Zn_3(Si_2O_7)\ Zn(OH)_2H_2O$)

(C) Cyclic silicates :

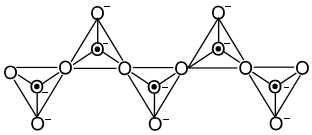
If two oxygen atoms per tetrahedron are shared to form closed rings such that the structure with general formula $(SiO_3^{2-})_n$ or $(SiO_3)_n^{2n-}$ is obtained, the silicates containing these anions are called cyclic silicates.



(D) Chain silicates :

Chain silicates may be further classified into simple chain & double chain compounds.

In case of simple chains two corners of each tetrahedron are shared & they form a long chain of tetrahedron. Their general formula is also same as the cyclic silicates i.e. $(SiO_3)_n^{2n-}$



(E) Two dimensional sheet silicates :

In such silicates, three oxygen atoms of each tetrahedral are shared with adjacent SiO_4^{4-} tetrahedrals. Such sharing forms two dimension sheet structure with general formula $(Si_2O_5)_n^{2n-}$

e.g. Talc $(Mg(Si_2O_5)_2\ Mg(OH)_2$, Kaolin $Al_2(OH)_4\ (Si_2O_5)$

(F) Three dimensional silicates :

These silicates involve all four oxygen atom in sharing with adjacent SiO_4^{4-} tetrahedral units.

e.g. Quartz, Tridymite, Crystobalite, Feldspar, Zeolite and Ultramarines.

d & f-BLOCK ELEMENT

Transition Elements

Definition: They are often called "transition elements" because their position in the periodic table is between s-block and p-block elements.

Typically, the transition elements have an incompletely filled d-level. Since Zn group has d^{10} configuration, are not considered as transition elements but they are d-block elements.

General Characteristics :

(i) Metallic character : They are all metal and good conductor of heat & electricity.

(ii) Electronic configuration : $(n-1)d^{1-10}ns^{1-2}$

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
other are as usual				$4s^1$ $3d^5$					$4s^1$ $3d^{10}$	

(iii) Melting point Cr, Mo, W → Maximum 6 number of unpaired e^- s are involved in metallic bonding

Zn, Cd, Hg → lowest melting point due to no unpaired e^- for metallic bonding

(iv) Variation in atomic radius :

Sc $\xrightarrow{\text{decreases}}$ Mn Fe Co Ni Cu Zn

Mn Fe Co: remains same

Ni Cu Zn: increases again

(v) Variable oxidation states possible

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
			+1					+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					

Colour : (aquated)

Sc^{3+} → colourless
Ti^{3+} → purple
V^{3+} → green
Cr^{2+} → blue
Mn^{3+} → violet
Fe^{2+} → light green
Co^{2+} → pink
Cu^{2+} → blue

Colour : (aquated)

Ti^{4+} → colourless
V^{4+} → blue
V^{2+} → violet
Cr^{3+} → green
Mn^{2+} → light pink
Fe^{3+} → yellow
Ni^{2+} → green
Zn^{2+} → colourless

CHROMATE-DICHROMATE

Preparation : →

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \xrightarrow[\text{red hot in presence of air}]{1000^oC\text{-}1300^oC} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

(chromite ore)

Residue (Fe_2O_3)

Filtrate (Na_2CrO_4) — Dissolve in water and filtered

[Lime (CaO) is added with Na_2CO_3 which keeps the mass porous so that air has access to all parts and prevents fusion]

Then, $2Na_2CrO_4 + H_2SO_4 \xrightarrow{conc.} Na_2SO_4\downarrow + Na_2Cr_2O_7 + H_2O$

It's solubility upto 32°C increases and then decreases } Hence, suitable temperature is to be employed to crystallise out Na_2SO_4 first.

Then $Na_2Cr_2O_7$ is crystallised out as $Na_2Cr_2O_7.2H_2O$ on evaporation.
(red crystal)

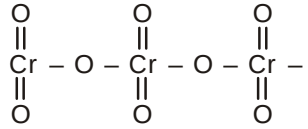
$$K_2Cr_2O_7,\ Na_2Cr_2O_7 + KCl \xrightarrow[\text{decomposition}]{\text{double}} K_2Cr_2O_7 + 2NaCl$$

hot conc.

NaCl crystallizes out first and filtered off. Then $K_2Cr_2O_7$ crystallized out on cooling.

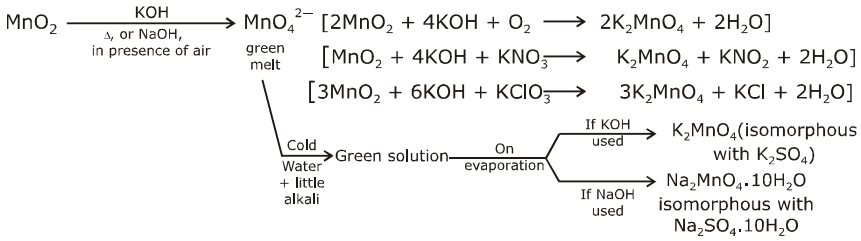
* Other properties & test of CrO_4^{2-} & $Cr_2O_7^{2-}$: Already discussed
* Similarities between hexavalent Cr & S–compounds.

(i) SO_3 & CrO_3 → both acidic.
(ii) S → SO_4^{2-}, $S_2O_7^{2-}$; Cr → CrO_4^{2-}, $Cr_2O_7^{2-}$
(iii) CrO_4^{2-} & SO_4^{2-} are isomorphous.
(iv) SO_2Cl_2 & $CrO_2Cl_2 \xrightarrow{OH^-}$ SO_4^{2-} & CrO_4^{2-} respectively
(v) CrO_3 & β(SO_3) has the same structure.



Manganate & permanganate

Preparation of Manganate (MnO_4^{2-}):–



In presence of $KClO_3$ & KNO_3 the above reaction is faster because these two on decomposition provides O_2 easily.

Manganate is also obtained when $KMnO_4$ is boiled with KOH.

$$4KMnO_4 + 4KOH \xrightarrow{\text{boiled}} 4K_2MnO_4 + 2H_2O + O_2$$

Properties : The above green solution is quite stable in alkali, but in pure water and in presence of acids, depositing MnO_2 and a purple solution of permanganate is obtained.

$$3K_2MnO_4 + 2H_2O \rightleftharpoons 2KMnO_4 + MnO_2\downarrow + 4KOH$$

purple drak brown

Problem : $E^{o}_{MnO_4^{2-}/MnO_2} = 2.26\ V$

$E^{o}_{MnO_4^{2-}/MnO_4^{-}} = -0.56\ V$

Prove that MnO_4^{2-} will disproportionate in acidic medium.

Another Method of Preparation :

$$3K_2MnO_4 + 2H_2SO_4 \rightarrow 2KMnO_4 + MnO_2\downarrow + 2K_2SO_4 + 2H_2O$$

or $$3K_2MnO_4 + 2H_2O + 4CO_2 \rightarrow 2KMnO_4 + MnO_2 + 4KHCO_3$$

But in the above method $\frac{1}{3}$ of Mn is lost as MnO_2 but when oxidised either by Cl_2 or by O_3

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

[Unwanted MnO_2 does not form]

OR

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

Oxidising Property of $KMnO_4$: (in acidic medium)

(i) $MnO_4^- + Fe^{+2} + H^+ \rightarrow Fe^{+3} + Mn^{+2} + H_2O$

(ii) $MnO_4^- + I^- + H^+ \rightarrow Mn^{+2} + I_2 + H_2O$

(iii) $MnO_4^- + H_2O_2 + H^+ \rightarrow Mn^{+2} + O_2 + H_2O$

(iv) $MnO_4^- + SO_2 \xrightarrow{H^+} Mn^{+2} + H_2SO_4$

(v) $MnO_4^- + NO_2^- + H^+ \rightarrow Mn^{+2} + NO_3^- + H_2O$

(vi) $MnO_4^- + H_2C_2O_4 + H^+ \rightarrow Mn^{+2} + CO_2 + H_2O$

(vii) $MnO_4^- + H_2S \rightarrow Mn^{2+} + S\downarrow + H_2O$

*(1) It is not a primary standard since it is difficult to get it in a high degree of purity and free from traces of MnO_2.

*(2) It is slowly reduced to MnO_2 especially in presence of light or acid.

$4MnO_4^- + 4H^+ \rightarrow 4MnO_2 + 2H_2O + 3O_2$

Hence it should be kept in dark bottles and standardise just before use.

(viii) $2KMnO_4 + 16HCl \rightarrow 2KCl + 5Cl_2 + 8H_2O + 2MnCl_2$

Oxidising Property of $KMnO_4$ in alkline medium :

$2MnO_4^- + 2OH^- \rightarrow 2MnO_4^{2-} + H_2O + O$ $2MnO_4^{2-} + 2H_2O \rightarrow 2MnO_2 + 4OH^- + 2O$

(i) $2KMnO_4 + H_2O + KI \rightarrow 2MnO_2 + 2KOH + KIO_3$

(ii) $2KMnO_4 + 3HCO_2K \rightarrow 2MnO_2 + KHCO_3 + 2K_2CO_3 + H_2O$

(iii) $2KMnO_4 + 3H_2O_2 \rightarrow 2MnO_2 + 2KOH + 2H_2O + 3O_2$

Oxidising Property in neutral or weakly basic solution:

(i) $2KMnO_4 + 3MnSO_4 + 2H_2O \xrightarrow{\text{in presence of } Zn^{2+} \text{ or ZnO}} 5MnO_2 + K_2SO_4 + 2H_2SO_4$

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

In absence of Zn^{+2} ions, some of the Mn^{+2} ion may escape, oxidation through the formation of insoluble $Mn^{II}[Mn^{IV}O_3]$ manganous permanganite.

(ii) $8KMnO_4 + 3Na_2S_2O_3 + H_2O \rightarrow 8MnO_2 + 3Na_2SO_4 + 3S + 2KOH$

Conversion of Mn^{+2} to MnO_4^-

(i) PbO_2 (ii) $Pb_3O_4 + HNO_3$

(iii) Pb_2O_3 (iv) $NaBiO_3/H^+$

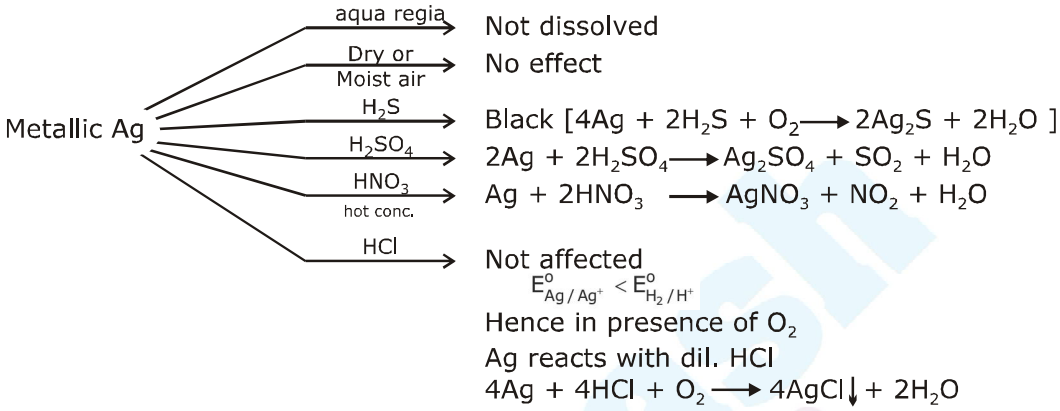
(v) $(NH_4)_2S_2O_8/H^+$ (vi) KIO_4/H^+

Heating effect : $2KMnO_4 \xrightarrow[200°C]{\Delta} \underset{\text{Black}}{K_2MnO_4} + MnO_2 + O_2$
(green)

$2K_2MnO_4 \xrightarrow[\text{hot}]{\text{at red}} 2K_2MnO_3 + O_2$

Silver and its compound

(I)



In the same way in presence of O_2, Ag complexes with NaCN/KCN.

$4Ag + 8KCN + 2H_2O + O_2 \rightarrow 4K[Ag(CN)_2] + 4KOH$

$AgNO_3$

Preparation : Silver nitrate is usually prepared by combaining silver with nitric acid.

$Ag \xrightarrow{HNO_3} AgNO_3$ $Ag \xrightarrow{HNO_3} AgNO_3 + NO_2 + H_2O$

Properties :

(i) It is called as lunar caustic because in contact with skin it produces burning sensation like that of caustic soda with the formation of finely divided silver (black colour).

(ii) Thermal decomposition :

$2AgNO_3 \rightarrow 2Ag + 2NO_2 + O_2$

(iii) Props. of $AgNO_3$: [Already done in basic radical]

$6AgNO_3 + 3I_2 + 3H_2O \rightarrow 5AgI + AgIO_3 + 6HNO_3$

(excess)

(iv) $Ag_2SO_4 \xrightarrow{\Delta} 2Ag + SO_2 + O_2$

(v) $A(AgNO_3) \xrightarrow[\text{added}]{B}$ white ppt(precipitate) appears quickly

$B(Na_2S_2O_3) \xrightarrow[\text{added}]{A}$ It takes time to give white ppt.

Explanation

When we add $Na_2S_2O_3$ solution (dropwise) in $AgNO_3$(excess), we get $Ag_2S_2O_3$ (white ppt) quickly. But when we add $AgNO_3$ solutions (dropwise) in $Na_2S_2O_3$ (excess) solution, here also $Ag_2S_2O_3$ is form but due to excess of thiosulphate it is dissolved. Hence here we not get any ppt quickly, but when concentration of $AgNO_3$ become equal or excess of $Na_2S_2O_3$, we get white ppt of $Ag_2S_2O_3$ and this process take time.

(vi) $Ag_2S_2O_3 + H_2O \xrightarrow{\Delta} Ag_2S + H_2SO_4$

AgCl, AgBr, AgI (but not Ag_2S) are soluble in $Na_2S_2O_3$ forming $[Ag(S_2O_3)_2]^{-3}$ complex

(vii) $AgNO_3 \xrightarrow{KBr}$ AgBr + KNO_3

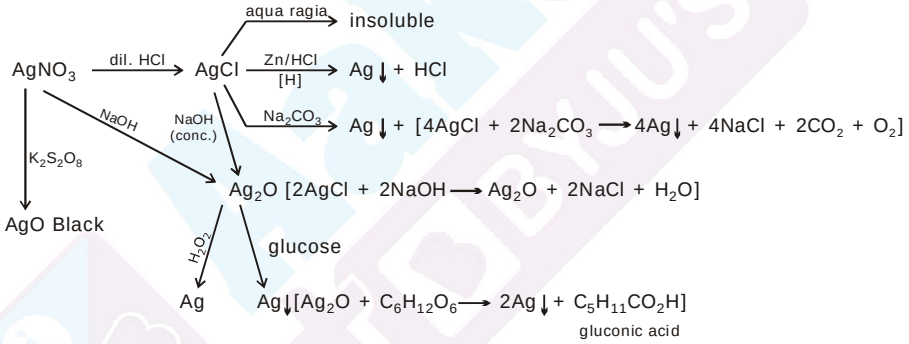
Pale yellow ppt.

Heating effect :

$2AgNO_3 \xrightarrow{212^oC} 2AgNO_2 + O_2$

$2AgNO_3 \xrightarrow{500^oC} 2Ag + 2NO + O_2$

(viii)



$Ag_2O + H_2O_2 \rightarrow 2Ag + H_2O + O_2$

$K_2S_2O_8 + 2AgNO_3 + 2H_2O \rightarrow 2AgO + 2KHSO_4 + 2HNO_3$

* AgO supposed to be paramagnetic due to d^9 configuration. But actually it is diamagnetic and exists as $Ag^I[Ag^{III}O_2]$

* Reaction involved in developer:

$K_2Fe^{II}(C_2O_4)_2 + AgBr \rightarrow KFe^{III}(C_2O_4)_2 + Ag\downarrow + KBr$

Zinc compounds

ZnO : It is called as philospher's wool due to its wooly flock type appearance.

Preparation :

[1] $2Zn + O_2 \rightarrow 2ZnO$

[2] $ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$

[3] $2Zn(NO_3)_2 \xrightarrow{\Delta} 2ZnO + 4NO_2 + O_2$

[4] $Zn(OH)_2 \xrightarrow{\Delta} ZnO + H_2O$

Purest ZnO : $4ZnSO_4 + 4Na_2CO_3 + 3H_2O \rightarrow ZnCO_3.3Zn(OH)_2\downarrow + 4Na_2SO_4 + 3CO_2$

white basic zinc carbonate

$\downarrow \Delta$

$4ZnO + 3H_2O\uparrow + CO\uparrow$

Pure

Properties :

[1] $ZnO(cold) \underset{}{\overset{\Delta}{\rightleftharpoons}} ZnO(hot)$

white yellow

[2] It is insoluble in water.

[3] It sublimes at 400°C.

[4] It is amphoteric oxide.

$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O$

$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$

$ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O$

[5] $ZnO \rightarrow Zn$ by H_2 & C

$ZnO + H_2 \xrightarrow{>400^oC} Zn + H_2O$

$ZnO + C \longrightarrow Zn + CO$

[6] It forms Rinmann's green with $Co(NO_3)_2$

$2Co(NO_3)_2 \rightarrow 2CoO + 4NO_2 + O_2$

$CoO + ZnO \rightarrow CoZnO_2$ or CoO– ZnO

Rinmann's green

Uses : (1) As white pigment. It is superior than white lead because it does not turn into black.

(2) Rinmann's green is used as green pigment.

(3) It is used as zinc ointment in medicine.

$ZnCl_2$

Preparation :

$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O$

$ZnCO_3 + 2HCl \rightarrow ZnCl_2 + H_2O + CO_2$

$Zn(OH)_2 + 2HCl \rightarrow ZnCl_2 + 2H_2O$

} It crystallizes as $ZnCl_2 . 2H_2O$

Anhydrous $ZnCl_2$ cannot be made by heating $ZnCl_2 . 2H_2O$ because

$ZnCl_2.2H_2O \xrightarrow{\Delta} Zn(OH)Cl + HCl + H_2O$

$Zn(OH)Cl \xrightarrow{\Delta} ZnO + HCl$

To get anhydrous $ZnCl_2$: $Zn + Cl_2 \rightarrow ZnCl_2$

$Zn + 2HCl(dry) \rightarrow ZnCl_2 + H_2$

or $Zn + HgCl_2 \rightarrow ZnCl_2 + Hg$

Properties : (i) It is deliquescent white solid (when anhydrous)

(ii) $ZnCl_2 + H_2S \rightarrow ZnS + NaOH \rightarrow Zn(OH)_2 \xrightarrow{\text{excess NaOH}} Na_2[Zn(OH)_4] + NH_4OH$

$Zn(OH)_2 \xrightarrow{\text{excess } NH_4OH} [Zn(NH_3)_4]^{2+}$

Uses :

1] Used for impregnating timber to prevent destruction by insects
2] As dehydrating agent when anhydrous
3] ZnO. $ZnCl_2$ used in dental filling

$ZnSO_4$:

Preparation :

$Zn + \text{dil. } H_2SO_4 \rightarrow ZnSO_4 + H_2$
$ZnO + \text{dil } H_2SO_4 \rightarrow ZnSO_4 + H_2O$
$ZnCO_3 + \text{dil } H_2SO_4 \rightarrow ZnSO_4 + H_2O + CO_2$
$ZnS + 2O_2 \rightarrow ZnSO_4$
$ZnS + \frac{3}{2}O_2 \rightarrow ZnO + SO_2$
$ZnS + 4O_3 \rightarrow ZnSO_4 + 4O_2$
} parallel reaction

Props.:

1] $ZnSO_4 . 7H_2O \xrightarrow{39\text{-}70^oC} ZnSO_4 . 6H_2O \xrightarrow{>70^oC} ZnSO_4.H_2O \xrightarrow{>280^oC} ZnSO_4$

$\xrightarrow{>800^oC} \frac{1}{2}O_2 + SO_2 + ZnO$

Uses :

1] In eye lotion
2] Lithophone making ($ZnS + BaSO_4$) as white pigment.

COPPER COMPOUNDS

CuO :

Preparation :

(i) $CuCO_3 . Cu(OH)_2 \xrightarrow{\Delta} 2CuO + H_2O + CO_2$ (commercial process)
Malachite Green
(native Cu-carbonate)

(ii) $2Cu + O_2 \rightarrow 2CuO$ & $Cu_2O + \frac{1}{2}O_2 \rightarrow 2CuO$

(iii) $Cu(OH)_2 \xrightarrow{\Delta} CuO + H_2O$

(iv) $2Cu(NO_3)_2 \xrightarrow{250^oC} 2CuO + 4NO_2 + O_2$

Properties :

(i) CuO is insoluble in water
(ii) Readily dissolves in dil. acids

$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$
$HCl \rightarrow CuCl_2$
$HNO_3 \rightarrow Cu(NO_3)_2$

(iii) It decomposes when heated above 1100°C Ir
(iii) It decomposes when heated above 1100°C
$4CuO \rightarrow 2Cu_2O + O_2$
(iv) CuO is reduced to Cu by H_2 or C under hot condition
$CuO + C \rightarrow Cu + CO\uparrow$
$CuO + H_2 \rightarrow Cu + H_2O\uparrow$

$CuCl_2$:
Preparation :
$CuO + 2HCl\ (conc.) \rightarrow CuCl_2 + H_2O$
$Cu(OH)_2.CuCO_3 + 4HCl \rightarrow 2CuCl_2 + 3H_2O + CO_2$

Properties :
(i) It is crystallised as $CuCl_2.\ 2H_2O$ of emerald green colour.
(ii) Dilute solution in water is blue in colour due to fromation of $[Cu(H_2O)_4]^{2+}$ complex.
(iii) When conc. HCl or KCl added to dil. solution of $CuCl_2$ then the colour changes into yellow, owing to the formation of $[CuCl_4]^{2-}$.
(iv) The conc. aq. solution is green in colour having the two complex ions in equilibrium
$2[Cu(H_2O)_4]Cl_2 \rightleftharpoons [Cu(H_2O)_4]^{2+} + [CuCl_4]^{2-} + 4H_2O$
(v) $CuCl_2 \rightarrow CuCl$ by no. of reagents
(a) $CuCl_2 + Cu\text{-turnings} \xrightarrow{\Delta} 2CuCl$
(b) $2CuCl_2 + H_2SO_3 + H_2O \rightarrow 2CuCl + 2HCl + 2H_2SO_4$
(c) $2CuCl_2 + Zn/HCl \rightarrow 2CuCl + ZnCl_2$
(d) $CuCl_2 + SnCl_2 \rightarrow CuCl + SnCl_4$

Halides of Copper :

$CuF_2.2H_2O \rightarrow$ light blue
$CuCl_2.2H_2O \rightarrow$ green
$CuBr_2 \rightarrow$ almost black

{ Anhydrous. $CuCl_2$ is dark brown mass obtained by heating $CuCl_2.2H_2O$ at 150°C in presence of HCl vapours.

CuI_2 does not exist

$CuCl_2.2H_2O \xrightarrow[HCl\ gas]{150°C} CuCl_2 + 2H_2O$

$CuSO_4$:
Preparation :
$CuO + H_2SO_4(dil) \rightarrow CuSO_4 + H_2O$
$Cu(OH)_2 + H_2SO_4(dil) \rightarrow CuSO_4 + 2H_2O$
$Cu(OH)_2.CuCO_3 + H_2SO_4(dil) \rightarrow CuSO_4 + 3H_2O + CO_2$

$Cu + H_2SO_4 + \frac{1}{2}O_2 \rightarrow CuSO_4 + H_2O$
(Scrap) [Commercial scale]

Cu + dil. H_2SO_4 → no reaction {Cu is below H in electrochemical series}

Properties :

(i) It is crystallised as $CuSO_4.5H_2O$

(ii) $CuSO_4.\ 5H_2O \underset{\text{efflorescence}}{\overset{\text{On exposure}}{\rightleftharpoons}} CuSO_4.3H_2O \overset{100^oC}{\rightleftharpoons} CuSO_4.H_2O$

Blue — Pale blue — Bluish white

$CuSO_4.H_2O \overset{230^oC}{\rightleftharpoons} CuSO_4$ (anhydrous) white

$CuSO_4 \xrightarrow{800^oC} CuO + SO_2 + \frac{1}{2}O_2$

$CuSO_4 \xrightarrow{750^oC} CuO + SO_3$

(iii) We will do revision of it's properties with other reagents

Iron Compounds

$FeSO_4.7H_2O$

Preparation :

(i) Scrap Fe + H_2SO_4 (dil.) → $FeSO_4 + H_2\uparrow$

(ii) From Kipp's waste

$FeS + H_2SO_4$ (dil.) → $FeSO_4 + H_2S\uparrow$

(iii) $FeS_2 + 2H_2O + \frac{7}{2}O_2 \rightarrow FeSO_4 + H_2SO_4$

Properties :

(i) It undergoes aerial oxidation forming basic ferric sulphate.

$4FeSO_4 + H_2O + O_2 \rightarrow 4Fe(OH)SO_4$

(ii) $FeSO_4.7H_2O \xrightarrow[\text{anh.white}]{300^oC} FeSO_4 \xrightarrow[\text{temp.}]{\text{high}}$

$Fe_2O_3 + SO_2 + SO_3$

(iii) Aqueous solution is acidic due to hydrolysis.

$FeSO_4 + 2H_2O \rightleftharpoons \underset{\text{weak base}}{Fe(OH)_2} + H_2SO_4$

(iv) It is a reducing agent.

(a) $Fe^{2+} + MnO_4^- + H^+ \rightarrow Fe^{3+} + Mn^{2+} + H_2O$

(b) $Fe^{2+} + Cr_2O_7^{2-} + H^+ \rightarrow Fe^{3+} + Cr^{3+} + H_2O$

(c) $Au^{3+} + Fe^{2+} \rightarrow Au + Fe^{3+}$

(d) $Fe^{2+} + HgCl_2 \rightarrow Hg_2Cl_2\downarrow + Fe^{3+}$
white ppt.

(v) It forms double salt.

Example $(NH_4)_2SO_4.FeSO_4.6H_2O$

FeO(Black) :

Preparation : $FeC_2O_4 \xrightarrow[\text{in absence of air}]{\Delta} FeO + CO + CO_2$

Props : It is stable at high temperature and on cooling slowly disproportionates into Fe_3O_4 and iron.

$4FeO \rightarrow Fe_3O_4 + Fe$

$FeCl_2$:

Preparation :

$Fe + 2HCl \xrightarrow[\text{a current of HCl}]{\text{heated in}} FeCl_2 + H_2$

or $2FeCl_3 + H_2 \xrightarrow{\Delta} 2FeCl_2 + 2HCl$

Properties :

(i) It is deliquescent in air like $FeCl_3$

(ii) It is soluble in water, alcohol and ether also because it is sufficiently covalent in nature.

(iii) It volatilises at about 1000°C and vapour density indicates the presence of Fe_2Cl_4. Above 1300°C density becomes normal.

(iv) It oxidises on heating in air.

$12FeCl_2 + 3O_2 \rightarrow 2Fe_2O_3 + 8FeCl_3$

(v) H_2 evolves on heating in steam.

$3FeCl_2 + 4H_2O \rightarrow Fe_3O_4 + 6HCl + H_2$

(vi) It can exist as different hydrated forms.

$FeCl_2.2H_2O \rightarrow$ Colourless

$FeCl_2.4H_2O \rightarrow$ pale green

$FeCl_2.6H_2O \rightarrow$ green

<table>
<tr><th colspan="3">f-block elements</th></tr>
<tr><th>S.No.</th><th>Properties</th><th>Characteristics</th></tr>
<tr><td>1.</td><td>No. of elements</td><td>Total number of f-block elements – (28)</td></tr>
<tr><td>2.</td><td>General characters</td><td>All the f-block elements are heavy metals.
It shows high melting and boiling point.
The most common oxidation state of these elements is +3.</td></tr>
<tr><td>3.</td><td>Groups</td><td>III B/3rd group is called the longest group having 32 elements including 14
Lanthanides and 14 Actinides.
<table><tr><td>III B/ 3rd</td><td></td></tr><tr><td>Sc</td><td></td></tr><tr><td>Y</td><td></td></tr><tr><td>La</td><td>Lanthanides (14) Ce_{58} – Lu_{71}</td></tr><tr><td>Ac</td><td>Actinides (14) Th_{90} – Lr_{103}</td></tr></table></td></tr>
<tr><td>4.</td><td>Electronic configuration</td><td>Lanthanide series $4f^{1-14}\ 5d^{0\ or\ 1}\ 6s^2$
Actinide series $5f^{1-14}\ 6d^{0\ or\ 1}\ 7s^2$</td></tr>
<tr><td>5.</td><td>Period</td><td><table><tr><th>Period</th><th>III B/ 3rd</th><th></th></tr><tr><td></td><td>Sc</td><td></td></tr><tr><td></td><td>Y</td><td></td></tr><tr><td>6th period</td><td>La</td><td>Lanthanides (14) Ce_{58} – Lu_{71}</td></tr><tr><td>7th period</td><td>Ac</td><td>Actinides (14) Th_{90} – Lr_{103}</td></tr></table></td></tr>
<tr><td>6.</td><td>Inner transition elements</td><td>The elements in which all the three shells that is ultimate (n) penultimate (n– 1) and pre or antipenultimate (n – 2) shell are incomplete are called inner transition elements.Ce_{58} = [Xe] $6s^2$, $5d^1$, $4f^1$ Inner transition elements are divided into two series</td></tr>
<tr><td></td><td>(i) Lanthanide series or Rare earth elements or Lanthanides</td><td>Ce_{58} – Lu_{71} 14 elements
Lanthanides are found rarely on earth so these are called rare earth metals.
The first element of this series is Cerium and not Lanthanum.
In these elements, last electron enters into 4f subshell.
They are present in III B group and 6th period of the periodic table.
Promethium (Pm_{61}) is the only lanthanide which is synthetic and radioactive in nature.</td></tr>
<tr><td></td><td>(ii) Actinide series or Man made elements or Actinones</td><td>Th_{90} – Lr_{103} →14 elements.
All the actinides are radioactive elements.
The first element of this series is Thorium and not Actinium.
In these elements, last electron enters into 5f subshell.
They are present in IIIB group and 7th period of the periodic table.
All the actinides are radioactive in nature.
First three elements (Th, Pa, U) are found in nature while others are synthetic in nature.
Transuranic actinides are man-made elements (Np_{93} – Lw_{103})
After U_{92} i.e. from Np_{93} onwards elements are called transuranic elements because
(i) They are heavier than uranium.
(ii) They are derived from uranium by nuclear reactions.</td></tr>
</table>

f-Block elements

Differentiating electrons enters in (n – 2)f subshell.
f-block elements lies on the bottom portion of periodic table.

GENERAL CHARACTERISTICS OF LANTHANIDES

The general characteristics are similar to transition metals, i.e., d-block elements

1. Electronic configuration

The energies of 5d- and 4f- orbitals are nearly similar and thus their fillings show certain irregularities. The electronic configurations of the atoms of the lanthanides in their ground state are given in the following table.

Name of the element	Symbol	Atomic number	Electronic configuration	Oxidation states
Lanthanum	La	57	$[Xe]5d^16s^2$	+3
Cerium	Ce	58	$[Xe]4f^15d^16s^2$	+3, +4
Praseodymium	Pr	59	$[Xe]4f^36s^2$	+3, (+4)
Neodymium	Nd	60	$[Xe]4f^4s^2$	(+2), +3
Promethium	Pm	61	$[Xe]4f^56s^2$	(+2), +3
Samarium	Sm	62	$[Xe]4f^66s^2$	(+2), +3
Europium	Eu	63	$[Xe]4f^76s^2$	+2,+3
Gadolinium	Gd	64	$[Xe]4f^75d^16s^2$	+3
Terbium	Tb	65	$[Xe]4f^96s^2$	+3, +4
Dysprosium	Dy	66	$[Xe]4f^{10}6s^2$	+3, (+4)
Holmium	Ho	67	$[Xe]4f^{11}6s^2$	+3
Erbium	Er	68	$[Xe]4f^{12}6s^2$	+3
Thulium	Tm	69	$[Xe]4f^{13}6s^2$	(+2), +3
Ytterbium	Yb	70	$[Xe]4f^{14}6s^2$	+2,+3
Lutetium	Lu	71	$[Xe]4f^{14}5d^16s^2$	+3

(i) The electronic configuration of europium

(Z = 63) is $4f^76s^2$ and that of gadolinium (Z = 64) is $4f^75d^16s^2$and this is explained on the basis of extra stability of the half-filled orbitals in their cores.

(ii) The electronic configuration of ytterbium

(Z = 70) is $4f^{14}6s^2$ and that of lutetium (Z = 71) is $4f^{14}5d^16s^2$. This is also explained on the basis of extra stability of the completely filled orbitals in their cores.

Oxidation states : The common stable oxidation state of all the lanthanides is +3. The oxidation states of +2 and +4 are also exhibited by some of the elements. These are shown by those elements which by losing 2 or more electrons acquire a stable configuration of f^0, f^7 or f^{14}e.g. Eu^{2+} is $[Xe]\ 4f^7$, Yb^{2+} is $[Xe]\ 4f^{14}$, Ce^{4+} is $[Xe]\ 4f^0$ and Tb^{4+} is $[Xe]\ 4f^7$. Each case tends to revert to the more stable oxidation state of +3 by loss or gain of an electron. That is why Sm^{2+}, Eu^{2+} and Yb^{2+} ions in solutions are good reducing agents and aqueous solution of Ce^{4+} and Tb^{4+} are good oxidising agents. The compounds of lanthanides are mainly ionic in nature.

Exceptions : Some elements show an oxidation state of +2 or +4, even though their ions do not have f^0, f^6 or f^{14} configuration,. e.g., Pr^{4+} $(4f^1)$, Nd^{2+} $(4f^4)$, Nd^{4+} $(4f^2)$, Sm^{2+} $(4f^6)$, Dy^{4+} $(4f^8)$ etc.

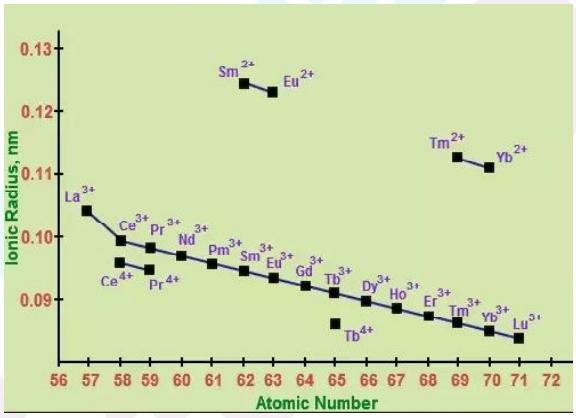
Note :

(i) Lanthanoids show limited number of oxidation states because the energy gap between 4f and 5d subshell is large.

(ii) Comparing with transition metals, which show many different oxidation states, the obvious reason is that in case of transition elements, the d-electrons are present in the (n – 1) d-subshell which can easily participate in bond formation but in case of lanthanoids, the f-electrons are present in the deeper (n – 2) f-subshell which cannot participate in bond formation.

Atomic and ionic radii (Lanthanide contraction) :

In lanthanides series, there is a regular decrease in the atomic as well as ionic radii of trivalent ions (M^{3+}) as the atomic number increases from cerium to lutetium. This decrease in size of atoms and ions is known as **Lanthanide contraction.** Although the atomic radii show some irregularities but ionic radii decrease continuously from La to Lu.The decrease in atomic radii or ionic radii are very small in comparison to the elements of other groups and periods.



Cause of lanthanide contraction: As we proceed from one element to the next element in the lanthanide series, the nuclear charge, i.e. atomic number increases by one unit and the addition of one electron occurs at the same time in 4f-energy shell. On account of the very diffused shapes of f-orbitals, the 4f-electrons shield each other quite poorly from the nuclear charge. Thus, the effect of nuclear charge increase is somewhat more than the change in shielding effect.This brings the valence shell nearer to the nucleus and hence the size of atom or ion goes on decreasing as we move in the series. The decrease is very small. In lanthanoids, the decrease in the atomic radius for 14 elements [Ce (58) to Lu (71)] is only 11 pm (from 183 to 172 pm). Similarly, the decrease in ionic radii from Ce^{3+} to Lu^{3+}, is only 17 pm (103 to 86 pm).

Consequences of lanthanide contraction:

(i) Similar chemical properties : Since the change in the ionic radii in the lanthanide series is very small, their chemical properties are similar. Thus, it is very difficult to separate these elements in the pure state. However, lanthanide contraction brings some differences in properties like solubility, complex ion formation, hydration, etc. These differences help in the separation of lanthanide elements by fractional crystallisation or ion exchange methods.

(ii) Basic strength of hydroxides : As the size of the lanthanide ions decreases from Ce^{3+} to Lu^{3+} the covalent character of M-OH bond increases and hence the basic strength decreases. Thus, $Ce(OH)_3$ is most basic while $Lu(OH)_3$ is least basic.

(iii) Similarity of second and third transition series: In vertical columns of transition elements, there is an increase in size from first member to second member as expected but from second member to third member, there is very small change in size and sometimes size is same. This is due to lanthanide contraction. The pairs of elements such as Zr-Hf, Mo-W, Nb-Ta etc, possess almost the same properties.

Physical properties:

(1) All the lanthanides are metals.
(2) They are soft, malleable and ductile in nature.
(3) They are not good conductors of heat and electricity.
(4) They are highly dense metals and their densities are in the range of 6.77 to 9.74 g cm^{-3}. The densities and atomic volumes, in general, increase with increase in atomic number, but a regular trend is not observed.
(5) They have high melting points in the range 1000 to 1200 K except samarium which has a very high melting point of 1623 K.

Coloured ions: Many of the lanthanide ions are coloured in solid state as well as in solutions.The colour is due to partially filled f-orbitals which allow f-f-transitions. M^{3+} ion having $4f^o$, $4f^7$ or $4f^{14}$ configurations are colourless.

La^{3+} ($4f^o$), Gd^{3+} ($4f^7$) and Lu^{3+} ($4f^{14}$)

Pairs of M^{3+} ions having the same number of unpaired electrons in 4f-orbitals have the same colour.

{Pr^{3+}($4f^2$) , Tm^{3+}($4f^{14}$)} Green
{Sm^{3+} ($4f^5$) , Dy^{3+} ($4f^9$)} Yellow
{Nd^{3+} ($4f^3$), Er^{3+} ($4f^{11}$)} Pink
{Eu^{3+} ($4f^6$) , Tb^{3+} ($4f^8$)} Pale pink

Exceptions : Ce^{+3}, Yb^{+3} are colourless. These exceptions are difficult to explain.

Magnetic properties: Ions having unpaired electrons are paramagnetic while those having all the orbitals paired are diamagnetic.

Ionization enthalpies : The first and second ionization enthalpies of lanthanoids are around 600 kJ/mol and 1200 kJ/mol which are comparable with those of calcium. The variation of the third ionization enthalpies shows that just as in case of 3d transition series. Due to low values of ionisation energies, lanthanides are highly electropositive in nature. These elements react with cold and hot water to liberate hydrogen. The reactions are, however, slow with cold water but fast with hot water.

Standard electrode potentials

The values of standard reduction potential (E° values) increase from La to Lu. E° values becomes less negative in the series. The values are given in volts .

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
−2.48	−2.46	−2.43	−2.42	−2.41	−2.4	−2.39	−2.39	−2.35	−2.32	−2.3	−2.28	−2.27	−2.25

All the lanthanides are thus strong **reducing agents.** The reducing power decreases from La to Lu

Electropositive character: They are highly electropositive because of their low ionization enthalpies.

Complex formation : The lanthanides do not have much tendency to form complexes due to low charge density because of their large size. However, the tendency to form complexes and their stability increases with the increase of atomic number and then decreases.

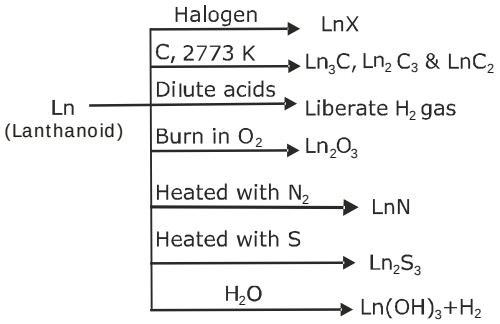
Chemical behaviour: The first few members of the series are quite reactive, almost like calcium. However, with increasing atomic number, their behaviour becomes similar to that of aluminium. A few properties are given below:

(i) They combine with H_2 on gentle heating. When heated with carbon, they form carbides. On burning in the presence of halogens, they form halides.

(ii) They react with dilute acids to liberate H_2 gas.

(iii) They form oxides and hydroxides of the type M_2O_3 and $M(OH)_3$ which are basic like alkaline earth metal oxides and hydroxides.

Representing the lanthanoids by the general symbol Ln the general reactions may be represented as follows.



Uses of Lanthanoids

(1) Lanthanoids do not find any use in the pure state. The most important use of lanthanoids is in the production of alloy steels to improve the strength and workability of steel. The following are two important alloys of rare earth elements:

NAME OF THE ALLOYS	COMPOSITION
Misch metal	Rare earth elements.....94-95% Iron ..... 5 % Sulphur, carbon, calcium and aluminium .....traces
Pyrophoric alloys (**Uses**: These alloys find their use in the preparation of ignition devices such as tracer bullets and shells and flints for lighters)	Cerium .....40.5% Lanthanum + Neodymium .....44% Iron ..... 4.5% Aluminium .....0.5% Calcium, silicon and carbon .....Remaining

(2) Cerium salts are used in dyeing cotton, in lead accumulators and as catalyst.

(3) Lanthanum oxide is used for polishing glass. Neodymium and praseodymium oxides are used for making coloured glasses for goggles. CeO_2 is used in gas mantles.

(4) Ceric sulphate is a well known oxidising agent in volumetric analysis.

(5) Many lanthanide oxides are used as phosphor in colour TV tubes.

(6) Various compounds of lanthanides are used as catalysts for hydrogenation, dehydrogenation, oxidation and petroleum cracking.

(7) Neodymium oxide dissolved in selenium oxy-chloride is used these days as a powerful liquid laser.

(8) Lanthanum oxides (e.g., L_2O_3) are used in glass industry, for polishing glass and for making coloured glasses for goggles as they give protection against UV light and as phosphor for television screens and similar fluorescence surfaces.

(9) Because of their paramagnetic and ferromagnetic properties, their compounds are used in making magnetic and electronic devices.

(10) Magnesium mixed with about 3% misch metal (to increase the strength) is used in making jet engine parts.

General Characteristics of Actinides

Except Ac, Th, Pa and U which occur in nature in uranium minerals, all the remaining actinides are unstable and synthetic elements. These have been made by artificial nuclear transmutations. All the actinides are radioactive.

General characteristics of actinides:

(i) Electronic configuration

The irregularities in the electronic configurations of actinoids like those in the lanthanoids, are related to the stabilities of f^0, f^7 and f^{14} configurations.

Name of the element	Symbol	Atomic number	Electronic configuration	Oxidation states
Actinium	Ac	89	$[Rn]5f^0 6d^1,7s^2$	+3
Thorium	Th	90	$[Rn]5f^0 6d^2,7s^2$	+3,+4
Protactinium	Pa	91	$[Rn]5f^2,6d^1,7s^2$	+3,+4,+5
Uranium	U	92	$[Rn]5f^3,6d^1,7s^2$	+3,+4,+5,+6
Neptunium	Np	93	$[Rn]5f^4,6d^1,7s^2$	+3,+4,+5,+6,+7
Plutonium	Pu	94	$[Rn]5f^6,7s^2$	+3,+4,+5,+6,+7
Americium	Am	95	$[Rn]5f^7,7s^2$	+2,+3,+4,+5,+6
Curium	Cm	96	$[Rn]5f^7,6d^1,7s^2$	+3,+4
Berkelium	Bk	97	$[Rn]5f^9,7s^2$	+3,+4
Californium	Cf	98	$[Rn]5f^{10},7s^2$	+2,+3
Einsteinium	Es	99	$[Rn]5f^{11},7s^2$	+2,+3
Fermium	Fm	100	$[Rn]5f^{12},7s^2$	+2,+3
Mendelevium	Md	101	$[Rn]5f^{13},7s^2$	+2,+3
Nobelium	Nm	102	$[Rn]5f^{14},7s^2$	+2,+3
Lawrencium	Lr	103	$[Rn]5f^{14}6d^1,7s^2$	+3

Oxidation States of Actinoids :

Unlike lanthanoids, actinoids show a large number of oxidation states. This is because of very small energy gap between 5f, 6d and 7s sub-shells. Hence, all their electrons can take part in bond formation. The dominant oxidation state of these elements is +3 (similar to lanthanoids). Besides +3 state, actinoids also exhibit an oxidation state of +4. Some actinoids shows still higher oxidation states. The maximum oxidation state increases upto the middle of the series and then decreases, e.g., it increase from +4 for Th to + 5,+6, and +7 for Pa, U and Np but decreases in the succeeding elements.

The actinoids resemble lanthanoids in having more compound in +3 state than in the +4 state. However, the compound in the +3 and +4 state tend to undergo hydrolysis.

(ii) Ionic radii and actinide contraction: The actinides show actinide contraction (very much like lanthanide contraction) due to poor shielding effect of the 5f- electrons. As a result, the radii of the atoms or ions of these metals decreases regularly across the series.

(iii) Colour : These metals are silvery white. However actinide cations are generally coloured. The colour of the cation depends upon the number of 5f-electrons. The cations containing no 5f-electron or having seven 5f-electrons (exactly half-filled f-subshell) are colourless. The cations containing 2 to 6 electrons in the 5f-subshell are coloured both in the crystalline state as well as in aqueous solution. The colour arises due to f-f transition e.g. Ac^{+3} ($5f^0$) = colourless, U^{3+} ($5f^3$) = Red, Np^{+3} ($5f^4$) = Blue, Pu^{+3} ($5f^5$) = Violet,

Am^{+3} ($5f^6$) = Pink, Cm^{+3} ($5f^7$) = Colourless, Th^{+4} ($5f^0$) = Colourless and so on.

(iv) Melting and Boiling points: The actinides like lanthanides have high melting and boiling points. However they do not show any regular trend with rise in atomic number.

(v) Density: All the actinides except Thorium and Americium have high densities.

(vi) Ionization energies: The actinides have low ionization energies.

(vii) Electropositive character: All the known actinide metals are highly electropositive. They resemble the elements of lanthanide series in this respect.

(viii) Magnetic behaviour: Like lanthanides, the actinide elements are strongly paramagnetic.

(ix) Reducing agents: All the actinides are strong reducing agents.

(x) Radioactivity: All the actinide elements are radioactive. First few members have relatively long half lives. However the remaining members have half lives ranging from few days to few minutes (**e,g.** 3 minute for Lr)

(xi) Chemical behaviour: They are highly reactive metals especially in the finely divided state. A few properties are given below:
(a) They react with boiling water to give a mixture of oxide and hydride.
(b) They combine with most of the non-metals at moderate temperature.
(c) All these metals are attacked by hydrochloric acid but the effect of nitric acid is very small due to the formation of a protective oxide layer on their surface.
(d) Alkalies have no action on them.

Uses of Actinides :

The three most important actinides which find uses as such or in the form of their compounds are thorium, uranium and plutonium. A few uses of these elements are as follows.

(a) Uses of thorium. It is used in atomic reactors and in the treatment of cancer. Its salts are used in making incandescent gas mantles.

(b) Uses of uranium: It is used as a nuclear fuel. Its salts are used in glass industry (for imparting green colour), textile industry, ceramic industry and in medicines.

(c) Uses of plutonium: It is used as a fuel for atomic reactors as well as for making atomic bombs.

Comparison of Lanthanides and Actinides:

Similarities

As both lanthanides and actinides involve filling of f-orbitals, they show similarities in many respects as follows.

(i) Both show mainly an oxidation state of +3.
(ii) Both are electropositive and very reactive.
(iii) Both exhibit magnetic and spectral properties.
(iv) Actinides exhibit actinide contraction like lanthanide contraction shown by lanthanides.

Differences: They show differences in some of their characteristics as follows:

	LANTHANIDES	ACTINIDES
(i)	Besides +3 oxidation state, they show +2 and +4 show higher +2	(a) Besides +3 oxidation state, they and +4 oxidation states only in few cases oxidation states of +4, +5, +6, +7 also.
(ii)	Most of their ions are colourless.	(b) Most of their ions are coloured.
(iii)	They have less tendency towards complex	(c) They have greater tendency towards formation complex formation.
(iv)	Lanthanide compounds are less basic. basic.	(d) Actinide compounds are more
(v)	Do not form oxocation.	(e) Form oxocations e.g UO^{+}, PuO^{+} and UO_2^{2+}
(vi)	Except promethiun, they are nonradioactive	(f) They are radioactive.
(vii)	Their magnetic properties can be explained	(g) Their magnetic properties cannot be explained easily.