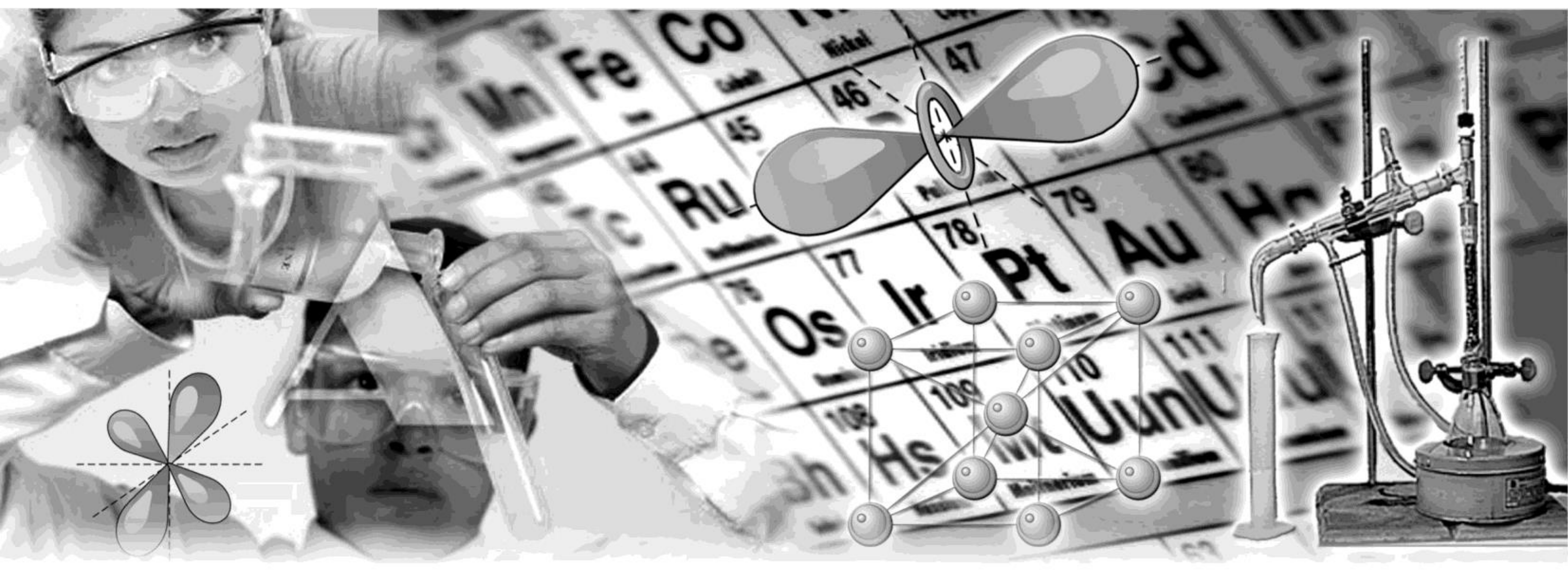


Chapter 18

s and p-Block Elements

Alkali Metals and Their Compounds

The group 1 of the periodic table contains six elements, namely lithium (*Li*), sodium (*Na*), potassium (*K*), rubidium (*Rb*), caesium (*Cs*) and francium (*Fr*). All these elements are ***typical metals***. Francium is radioactive with longest lived isotope ^{223}Fr with half life period of only 21 minute. These are usually referred to as alkali metals since their hydroxides form strong bases or alkalies.

(1) **Electronic configuration**

Elements	Discovery	Electronic configuration (ns^1)
$_3Li$	Arfwedson (1817)	$[He]^2\,2s^1$
$_{11}Na$	Davy (1807)	$[Ne]^{10}\,3s^1$
$_{19}K$	Davy (1807)	$[Ar]^{18}\,4s^1$
$_{37}Rb$	Bunsen (1861)	$[Kr]^{36}\,5s^1$
$_{55}Cs$	Bunsen (1860)	$[Xe]^{54}\,6s^1$
$_{87}Fr$	Percy (1939)	$[Rn]^{86}\,7s^1$

(2) **Occurrence :** Alkali metals are very reactive and thus found in combined state some important ores of alkali metals are given ahead.

(i) ***Lithium*** : Triphylite, Petalite, lepidolite, Spodumene [$LiAl(SiO_3)_3$], Amblygonite [$Li(Al\,F)PO_4$]

(ii) ***Sodium*** : Chile salt petre ($NaNO_3$), Sodium chloride ($NaCl$), Sodium sulphate (Na_2SO_4), Borax ($Na_2B_4O_710H_2O$), Glauber salt ($Na_2\,SO_4.10H_2O$)

(iii) ***Potassium*** : Sylime (KCl), carnallite ($KCl.MgCl_2.6H_2O$) and Felspar ($K_2O.Al_2O_3.6SiO_2$)

(iv) ***Rubidium*** : Lithium ores Lepidolite, triphylite contains 0.7 to 3% Rb_2O

(v) ***Caesium*** : Lepidolite, Pollucite contains 0.2 to 7% Cs_2O

(3) **Extraction of alkali metals :** Alkali metals cannot be extracted by the usual methods for the extraction of metals due to following reasons.

(i) Alkali metals are strong reducing agents, hence cannot be extracted by reduction of their oxides or other compounds.

(ii) Being highly electropositive in nature, it is not possible to apply the method of displacing them from their salt solutions by any other element.

(iii) The aqueous solutions of their salts cannot be used for extraction by electrolytic method because hydrogen ion is discharged at cathode instead of an alkali metal ions as the discharge potentials of alkali metals are high. However, by using *Hg* as cathode, alkali metal can be deposited. The alkali metal readily combines with *Hg* to form an amalgam from which its recovery difficult. The only successful method, therefore, is the electrolysis of their fused salts, usually chlorides. Generally, another metal chloride is added to lower their fusion temperature.

Fused $NaCl$: $NaCl \xrightarrow{fusion} Na^+ + Cl^-$

$$\text{Electrolysis : Anode } : 2Cl^- \to Cl_2 + 2e^-$$
$$\text{of fused salt : Cathode } : 2Na^+ + 2e^- \to 2Na$$

(4) **Alloys Formation**

(i) The alkali metals form alloys among themselves as well as with other metals.

(ii) Alkali metals also get dissolved in mercury to form amalgam with evolution of heat and the amalgamation is highly exothermic .

Physical properties

(1) **Physical state**

(i) All are silvery white, soft and light solids. These can be cut with the help of knife. When freshly cut, they have bright lustre which quickly tarnishes due to surface oxidation.

(ii) These form diamagnetic colourless ions since these ions do not have unpaired electrons, (*i.e.* M^+ has ns^0configuration). That is why alkali metal salts are colourless and diamagnetic.

(2) **Atomic and ionic radii**

(i) The alkali metals have largest atomic and ionic radii than their successive elements of other groups belonging to same period.

(ii) The atomic and ionic radii of alkali metals, however, increases down the group due to progressive addition of new energy shells.

No doubt the nuclear charge also increases on moving down the group but the influence of addition of energy shell predominates

	Li	*Na*	*K*	*Rb*	*Cs*	*Fr*
Atomic radius (pm)	152	186	227	248	265	375
Ionic radius of M^+ ions (pm)	60	95	133	148	169	–

(3) **Density**

(i) All are light metals, *Li*, *Na* and *K* have density less than water. Low values of density are because these metals have high atomic volume due to larger atomic size. On moving down the group the atomic size as well as atomic mass both increase but increase in atomic mass predominates over increase in atomic size or atomic volume and therefore the ratio mass/volume *i.e.* density gradually increases down the groups

(ii) The density increases gradually from *Li* to *Cs*, *Li* is lightest known metal among all.

Li = 0.534, *Na* = 0.972, *K* = 0.86, *Rb* = 1.53 and *Cs* = 1.87 g/ml at 20°*C*.

(iii) *K* is lighter than *Na* because of its unusually large atomic size.

(iv) In solid state, they have body centred cubic lattice.

(4) **Melting point and Boiling point**

(i) All these elements possess low melting point and boiling point in comparison to other group members.

	Li	*Na*	*K*	*Rb*	*Cs*	*Fr*
melting point (K)	453.5	370.8	336.2	312.0	301.5	–
boiling point (K)	1620	1154.4	1038.5	961.0	978.0	–

(ii) The lattice energy of these atoms in metallic crystal lattice relatively low due to larger atomic size and thus possess low melting point and boiling point on moving down the group, the atomic size increases and binding energy of their atoms in crystal lattice decreases which results lowering of melting point.

(iii) Lattice energy decreases from *Li* to *Cs* and thus melting point and boiling also decreases from *Li* to Cs.

(5) **Ionisation energy and electropositive or metallic character**

(i) Due to unpaired lone electron in ns sub-shell as well as due to their larger size, the outermost electron is far from the nucleus, the removal of electron is easier and these low values of ionisation energy. (*I.E.*)

(ii) Ionisation energy of these metal decreases from *Li* to *Cs*.

Ionisation energy	*Li*	*Na*	*K*	*Rb*	*Cs*	*Fr*
IE_1	520	495	418	403	376	–
IE_2	7296	4563	3069	2650	2420	–

A jump in 2nd ionisation energy (huge difference) can be explained as,

$$Li{:}1s^2\,2s^1 \xrightarrow[2s\,electron]{\text{Removal of}} Li^+{:}1s^2 \xrightarrow[1s\,electron]{\text{Removal of}} Li^{2+}{:}1s^1$$

Removal of 1s electrons from Li^+ and that too from completely filled configuration requires much more energy and a jump in 2nd ionisation is noticed.

(iii) Lower are ionisation energy values, greater is the tendency to lose ns^1 electron to change in M^+ ion (*i.e.* $M \rightarrow M^+ + e^-$) and therefore stronger is electropositive character.

(iv) Electropositive character increases from *Li* to *Cs*.

Due to their strong electropositive character, they emit electrons even when exposed to light showing ***photoelectric effect***. This property is responsible for the use of *Cs* and *K* in photoelectric cell.

(6) **Oxidation number and valency**

(i) Alkali metals are univalent in nature due to low ionisation energy values and form ionic compounds. Lithium salts are, however, covalent.

(ii) Further, the M^+ ion acquires the stable noble gas configuration. It requires very high values of energy to pull out another electron from next to outer shell of M^+ ion and that is why their second ionisation energy is very high. Consequently, under ordinary conditions, it is not possible for these metals to form M^{2+} ion and thus they show +1 oxidation state.

(iii) Since the electronic configuration of M^+ ions do not have unpaired electron and thus alkali metal salts are diamagnetic and colourless. Only those alkali metal salts are coloured which have coloured anions e.g. $K_2Cr_2O_7$ is orange because of orange coloured $Cr_2O_7^{2-}$ ion, $KMnO_4$ is violet because of violet coloured MnO_4^{1-} ion.

(7) **Hydration of Ions**

(i) Hydration represents for the dissolution of a substance in water to get adsorb water molecule by weak valency force. Hydration of ions is the exothermic process (*i.e* energy is released during hydration) when ions on dissolution water get hydration.

(ii) The energy released when 1 mole of an ion in the gaseous state is dissolved in water to get it hydrated is called hydration energy $M_{(g)}{}^{+} + Aq \rightarrow M^{+}{}_{(aq)}; \Delta H = -ve.$

(iii) Smaller the cation, greater is the degree of hydration. Hydration energy is in the order of, $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

(iv) Li^+ being smallest in size has maximum degree of hydration and that is why lithium salts are mostly hydrated, $LiCl.\ 2H_2O$ also lithium ion being heavily hydrated, moves very slowly under the influence of electric field and, therefore, is the poorest conductor current among alkali metals ions It may, therefore, be concluded that it is the degree of hydration as well as the size of ion is responsible for the current carried by an ion.

Relative ionic radii	$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$
Relative hydrated ionic radii	$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$
Relative conducting power	$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$

(8) **Electronegativity, Electro positivity and metallic character.**

(i) These metals are highly electropositive and thereby possess low values of electronegativities. Metallic character and electro positivity increase from Li to Cs ($Li < Na < K < Rb < Cs$)

(ii) Electronegativity of alkali metals decreases down the group as the trend of numerical values of electronegativity given below on Pauling scale suggests.

	Li	Na	K	Rb	Cs	Fr
Electronegativity	0.98	0.93	0.82	0.82	0.79	–

Fr being radioactive elements and thus studies on physical properties of this element are limited.

(9) **Specific heat :** It decreases from *Li* to *Cs*.

	Li	Na	K	Rb	Cs	Fr
Specific heat (Cal/g)	0.941	0.293	0.17	0.08	0.049	–

(10) **Conduction power :** All are good conductors of heat and electricity, because of loosely held valence electrons.

(11) **Standard oxidation potential and reduction properties**

(i) Since alkali metals easily lose ns^1 electron and thus they have high values of oxidation potential *i.e.*,

$$M + aq \rightarrow M^{+}{}_{(aq)} + e$$

(ii) The standard oxidation potentials of a alkali metals (in volts) are listed below,

Li	Na	K	Rb	Cs
+3.05	+2.71	+2.93	+2.99	+2.99

(iii) More is oxidation potential, more is the tendency to get oxidized and thus more powerful is reducing nature in aqueous medium that is why alkali metals liberate H_2 from H_2O and HCl.

$$2H_2O + 2M \rightarrow 2MOH + H_2 \ ; \ 2HCl + 2M \rightarrow 2MCl + H_2$$

(iv) However, an examination of ionisation energy for alkali metals reveals that *Li* should have the minimum tendency to lose electron and thus its reducing nature should be minimum. The greatest reducing nature of *Li* in aq. medium is accounted due to the maximum hydration energy of Li^+ ion. For Lithium

$Li_{(s)} \rightarrow Li_{(g)};$ ΔH_1 = Heat of sublimation, ΔH_s

$Li_{(g)} \rightarrow Li^{+}{}_{(g)} + e;$ $\Delta H_2 = IE_1$

$Li^{+}{}_{(g)} \rightarrow Li^{+}{}_{(aq);}$ ΔH_3 = – Heat of hydration, ΔH_h

$$Li_{(s)} + H_2O \rightarrow Li^{+}{}_{(aq)} + e; \Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 = \Delta H_s + IE_1 - \Delta H_h$$

Similarly, for sodium,

$$Na_{(s)} + H_2O \rightarrow Na^{+}{}_{(aq)} + e; \Delta H = \Delta H_{(s)} + IE_1 - \Delta H_h$$

ΔH_h for Li > ΔH_h for Na. Therefore, large negative ΔH values are observed in case of *Li* and this explains for more possibility of *Li* to get itself oxidized or have reducing nature.

(12) **Characteristic flame colours :** The alkali metals and their salts give characteristic colour to Bunsen flame. The flame energy causes and excitation of the outermost electron which on reverting back to its initial position gives out the absorbed energy as visible light. These colour differ from each other *Li* –crimson, *Na*–Golden yellow, *K* – Pale violet , *Rb*-Red violet and *Cs* –Blue violet. These different colours are due to different ionisation energy of alkali metals. The energy released is minimum in the case of Li^+ and increases in the order.

Energy released	: $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$
λ released	: $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$
Frequency released	: $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$

Chemical properties

(1) **Formation of oxides and hydroxides**

(i) These are most reactive metals and have strong affinity for O_2 quickly tranish in air due to the formation of a film of their oxides on the surface. These are, therefore, kept under kerosene or paraffin oil to protect them from air,

$$M + O_2 \rightarrow \underset{\text{Oxide}}{M_2O} \longrightarrow \underset{\text{Peroxide}}{M_2O_2}$$

(ii) When burnt air (O_2), lithium forms lithium oxide (Li_2O) sodium forms sodium peroxide (Na_2O_2) and other alkali metals form super oxide (Mo_2 *i.e.* KO_2,RbO_2 or CsO_2)

$$2Li + \frac{1}{2}O_2 \rightarrow \underset{\text{Lithuim oxide}}{Li_2O} \ ; \ 2Na + O_2 \rightarrow Na_2O_2$$

$$K + O_2 \rightarrow \underset{\text{Potassium super oxide}}{KO_2}$$

The reactivity of alkali metals towards oxygen to form different oxides is due to strong positive field around each alkali metal cation. Li^+ being smallest, possesses strong positive field and thus combines with small anion O^{2-} to form stable Li_2O compound. The Na^+ and K^+ being relatively larger thus exert less strong positive field around them and thus reacts with larger oxygen anion i.e, O_2^{2-} and O_2^{1-} to form stable oxides.

The monoxide, peroxides and superoxides have O_2 and O_2^{2-}, O_2^{1-} ions respectively. The structures of each are,

Monoxide (O_2) Peroxide (O_2^{2-}) Superoxide

The O_2^{-1} ion has a three electron covalent bond and has one electron unpaired. It is therefore superoxides are paramagnetic and coloured KO_2 is light yellow and paramagnetic substance.

(iii) The oxides of alkali metals and metal itself give strongly alkaline solution in water with evolution of heat

$$M + H_2O \rightarrow MOH + \frac{1}{2}H_2; \qquad \Delta H = -ve$$

$$Li_2O + H_2O \rightarrow 2LiOH; \qquad \Delta H = -ve$$

$$Na_2O_2 + 2H_2O \rightarrow 2NaOH + H_2O_{2(l)}\ ; \qquad \Delta H = -ve$$

$$2KO_2 + 2H_2O \rightarrow 2KOH + H_2O_{2(l)} + O_{2(g)}\ ; \qquad \Delta H = -ve$$

The peroxides and superoxides act as strong oxidising agents due to formation of H_2O_2

(iv) The reactivity of alkali metals towards air and water increases from Li to Cs that is why lithium decomposes H_2O very slowly at 25^oC whereas Na does so vigorously, K reacts producing a flame and Rb, Cs do so explosively.

$$M + H_2O \rightarrow MOH + \frac{1}{2}H_2$$

(v) The basic character of oxides and hydroxides of alkali metals increases from Li to Cs. This is due to the increase in ionic character of alkali metal hydroxides down the group which leads to complete dissociation and leads to increase in concentration of OH^- ions.

(2) **Hydrides**

(i) These metals combine with H to give white crystalline ionic hydrides of the general of the formula MH.

(ii) The tendency to form their hydrides, basic character and stability decreases from Li to Cs since the electropositive character decreases from Cs to Li.

$2M + H_2 \rightarrow 2MH$; Reactivity towards H_2 is $Cs < Rb < K < Na < Li$.

(iii) The metal hydrides react with water to give MOH and H_2 ; $MH + H_2O \rightarrow MOH + H_2$

(iv) The ionic nature of hydrides increases from Li to Cs because of the fact that hydrogen is present in the these hydrides as H^- and the smaller cation will produce more polarisation of anion (according to Fajans rule) and will develop more covalent character.

(v) The electrolysis of fused hydrides give H_2 at anode. NaH_{fused} Contains Na^+ and H^- *i.e.*,

At cathode: $Na^+ + e^- \rightarrow Na$; At anode: $H^- \rightarrow \frac{1}{2}H_2 + e^-$

(vi) Alkali metals also form hydrides like $NaBH_4$, $LiAlH_4$ which are good reducing agent.

(3) **Carbonates and Bicarbonates**

(i) The carbonates (M_2CO_3) & bicarbonates ($MHCO_3$) are highly stable to heat, where M stands for alkali metals.

(ii) The stability of these salts increases with the increasing electropositive character from Li to Cs. It is therefore Li_2CO_3 decompose on heating, $Li_2CO_3 \rightarrow Li_2O + CO_2$

(iii) Bicarbonates are decomposed at relatively low temperature, $2MHCO_3 \xrightarrow{300^0C} M_2CO_3 + H_2O + CO_2$

(iv) Both carbonates and bicarbonates are soluble in water to give alkaline solution due to hydrolysis of carbonate ions or bicarbonate ions.

(4) **Halides**

(i) Alkali metals combine directly with halogens to form ionic halide M^+X^-.

(ii) The ease with which the alkali metals form halides increases from Li to Cs due to increasing electropositive character from Li to Cs.

(iii) Lithium halides however have more covalent nature. Smaller is the cation, more is deformation of anion and thus more is covalent nature in compound. Also among lithium halides, lithium iodide has maximum covalent nature because of larger anion which is easily deformed by a cation. Thus covalent character in lithium halides is, $LiI > LiBr > LiCl > LiF$

(iv) These are readily soluble in water. However, lithium fluoride is sparingly soluble. The low solubility of LiF is due to higher forces of attractions among smaller Li^+ and smaller F^- ions (high lattice energy).

(v) Halides having ionic nature have high m.pt. and good conductor of current. The melting points of halides shows the order, $NaF > NaCl > NaBr > NaI$

(vi) Halides of potassium, rubidium and caesium have a property of combining with extra halogen atoms forming polyhalides.

$KI + I_2 \rightarrow KI_3$; In $KI_{3(aq)}$ the ions K^+ and I^-_3 are present

(5) **Solubility in liquid NH_3**

(i) These metals dissolve in liquid NH_3 to produce blue coloured solution, which conducts electricity to an appreciable degree.

(ii) With increasing concentration of ammonia, blue colour starts changing to that of metallic copper after which dissolution of alkali metals in NH_3 ceases.

(iii) The metal atom is converted into ammoniated metal in i.e. M^+ (NH_3) and the electron set free combines with NH_3 molecule to produce ammonia solvated electron.

$$Na + (x+y)NH_3 \rightarrow \underset{\text{Ammoniated cation}}{[Na(NH_3)_x]^+} + \underset{\text{Ammoniated electron}}{[e(NH_3)_y]^-}$$

(iv) It is the ammoniated electron which is responsible for blue colour, paramagnetic nature and reducing power of alkali metals in ammonia solution. However, the increased conductance nature of these metals in ammonia is due to presence of ammoniated cation and ammonia solvated electron.

(v) The stability of metal-ammonia solution decreases from Li to Cs.

(vi) The blue solution on standing or on heating slowly liberates hydrogen, $2M + 2NH_3 \rightarrow 2MNH_2 + H_2$. Sodamide ($NaNH_2$) is a waxy solid, used in preparation of number of sodium compounds.

(6) **Nitrates :** Nitrates of alkali metals (MNO_3) are soluble in water and decompose on heating. $LiNO_3$ decomposes to give NO_2 and O_2 and rest all give nitrites and oxygen.

$2MNO_3 \rightarrow 2MNO_2 + O_2$ (except Li)

$4\,LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$

(7) **Sulphates**

(i) Alkali metals' sulphate have the formula M_2SO_4 .

(ii) Except Li_2SO_4, rest all are soluble in water.

(iii) These sulphates on fusing with carbon form sulphides, $M_2SO_4 + 4C \rightarrow M_2S + 4CO$

(iv) The sulphates of alkali metals (except Li) form double salts with the sulphate of the trivalent metals like Fe, Al, Cr etc. The double sulphates crystallize with large number of water molecules as alum. e.g. $K_2SO_4 . Al_2(SO_4)_3 . 24\,H_2O$.

(8) **Reaction with non-metals**

(i) These have high affinity for non-metals. Except carbon and nitrogen, they directly react with hydrogen, halogens, sulphur, phosphorus etc. to form corresponding compounds on heating.

$2Na + H_2 \xrightarrow{300^0 C} 2NaH$; $2K + H_2 \rightarrow 2KH$

$2Na + Cl_2 \rightarrow 2NaCl$; $2K + Cl_2 \rightarrow 2KCl$

$2Na + S \rightarrow Na_2S$; $2K + S \rightarrow K_2S$

$3Na + P \rightarrow Na_3P$; $3K + P \rightarrow K_3P$

(ii) Li reacts, however directly with carbon and nitrogen to form carbides and nitrides.

$2Li + 2C \rightarrow LiC_2$; $6Li + 2N_2 \rightarrow 2\,Li_3N$

(iii) The nitrides of these metals on reaction with water give NH_3.

$M_3N + 3H_2O \rightarrow 3MOH + NH_3$

(9) **Reaction with acidic hydrogen :** Alkali metals react with acids and other compounds containing acidic hydrogen (*i.e,* H atom attached on F, O, N and triply bonded carbon atom, for example, HF, H_2O, ROH, RNH_2, $CH \equiv CH$) to liberate H_2 .

$$M + H_2O \rightarrow MOH + \frac{1}{2}H_2 \;\; ; \;\; M + HX \rightarrow MX + \frac{1}{2}H_2$$

$$M + ROH \rightarrow ROH + \frac{1}{2}H_2 \; ; \; M + RNH_2 \rightarrow RNHNa + \frac{1}{2}H_2$$

(10) **Complex ion formation :** A metal shows complex formation only when it possesses the following characteristics, (i) Small size (ii) High nuclear charge (iii) Presence of empty orbitals in order to accept electron pair ligand. Only Lithium in alkali metals due to small size forms a few complex ions Rest all alkali metals do not possess the tendency to form complex ion.

Anomalous behaviour of Lithium

Anomalous behaviour of lithium is due to extremely small size of lithium its cation on account of small size and high nuclear charge, lithium exerts the greatest polarizing effect out of all alkali metals on negative ion. Consequently lithium ion possesses remarkable tendency towards solvation and develops covalent character in its compounds. Li differs from other alkali metals in the following respects,

(1) It is comparatively harder than other alkali metals. Li can'nt be stored in kerosene as it floats to the surface, due to its very low density. Li is generally kept wrapped in parrafin wax.

(2) It can be melted in dry air without losing its brilliance.

(3) Unlike other alkali metals, lithium is least reactive among all. It can be noticed by the following properties,

(i) It is not affected by air. (ii) It decomposes water very slowly to liberate H_2. (iii) It hardly reacts with bromine while other alkali metals react violently.

(4) Lithium is the only alkali metal which directly reacts with N_2 to form Lithium nitride (Li_3N)

(5) Lithium when heated in NH_3 forms amide, Li_2NH while other metals form amides, MNH_2.

(6) When burnt in air, lithium form Li_2O sodium form Na_2O and Na_2O_2 other alkali metals form monoxide, peroxide and superoxide.

(7) Li_2O is less basic and less soluble in water than other alkali metals.

(8) $LiOH$ is weaker base than $NaOH$ or KOH and decomposes on heating.

$$2LiOH \xrightarrow{\Delta} Li_2O + H_2O$$

(9) $LiHCO_3$ is liquid while other metal bicarbonates are solid.

(10) Only Li_2CO_3 decomposes on heating

$$Li_2CO_3 \xrightarrow{heat} Li_2O + CO_2 .$$

Na_2CO_3, K_2CO_3 etc. do not decompose on heating.

(11) $LiNO_3$ and other alkali metal nitrates give different products on heating

$4LiNO_3 = 2Li_2O + 4NO_2 + O_2$; $2NaNO_3 = 2NaNO_2 + O_2$

(12) $LiCl$ and $LiNO_3$ are soluble in alcohol and other organic solvents. These salts of other alkali metals are, however, insoluble in organic solvents.

(13) $LiCl$ is deliquescent while $NaCl$, KBr etc. are not. Lithium chloride crystals contain two molecules of water of crystallisation ($LiCl.\ 2H_2O$). Crystals of $NaCl$ KBr, KI etc do not conation water of crystallisation.

(14) Li_2SO_4 does not form alums like other alkali metals.

(15) Li reacts with water slowly at room temperature Na reacts vigorously Reaction with K. Rb and Cs is violent.

(16) Li reacts with Br_2 slowly. Reaction of other alkali metals with Br_2 is fast.

(17) $Li_2\ CO_3$ $Li_2C_2O_4$, LiF , Li_3PO_4 are the only alkali metal salts which are insoluble or sparingly soluble in water.

Diagonal Relationship of *Li* with *Mg*

Due to its small size lithium differs from other alkali metals but resembles with Mg as its size is closer to Mg Its resemblance with Mg is known as diagonal relationship. Generally the periodic properties show either increasing or decreasing trend along the group and vice versa along the period which brought the diagonally situated elements to closer values. Following are the characteristic to be noted.

Period	Group I	Group II
2	Li	Be
3	Na	Mg

(1) Both Li and Mg are harder and higher m.pt than the other metals of their groups.

(2) Due to covalent nature, chlorides of both Li and Mg are deliquescent and soluble in alcohol and pyridine while chlorides of other alkali metals are not so.

(3) Fluorides, phosphates of Li and Mg are sparingly soluble in water whereas those of other alkali metals are soluble in water.

(4) Carbonates of Li and Mg decompose on heating and liberate CO_2 Carbonates of other alkali metals are stable towards heat and decomposed only on fusion.

$$Li_2CO_3 \rightarrow Li_2O + CO_2 \ ; \ Mg\,CO_3 \rightarrow MgO + CO_2$$

(5) Hydroxides and nitrates of both Li and Mg decompose on heating to give oxide. Hydroxides of both Li and Mg are weak alkali.

$$4\,LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$$

$$2Mg(NO_3)_2 \rightarrow 2MgO + 4NO_2 + O_2$$

$$2LiOH \rightarrow Li_2O + H_2O \ ; \ Mg(OH)_2 \rightarrow MgO + H_2O$$

Hydroxides of other alkali metals are stable towards heat while their nitrates give O_2 and nitrite.

$$2KNO_3 \rightarrow 2KNO_2 + O_2$$

(6) Both Li and Mg combine directly with N_2 to give nitrides Li_3N and Mg_3N_2. Other alkali metals combine at high temperature, $6Li + N_2 \rightarrow 2Li_3N$; $3Mg + N_2 \rightarrow Mg_3N_2$. Both the nitrides are decomposed by water to give NH_3

$$Li_3N + 3H_2O \rightarrow 3LiOH + NH_3 \ ;$$

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$$

(7) Bicarbonates of Li and Mg are more soluble in water than carbonates whereas carbonates of alkali metals are more soluble.

(8) Both Li and Mg combine with carbon on heating.

$$2Li + 2C \rightarrow Li_2C_2 \ ; \ Mg + 2C \rightarrow Mg\,C_2$$

(9) The periodic properties of Li and Mg are quite comparable

	Li	Mg
Electronegativity	1.0	1.2

Atomic radii 1.23 1.36

Ionic radii 0.60(Li^+) 0.65(Mg^{+2})

Atomic volume 12.97 c.c 13.97 c.c

(10) Both have high polarizing power.

Polarizing Power = Ionic charge / (ionic radius)^2.

(11) *Li* and *Mg* Form only monooxide on heating in oxygen.

$$4Li + O_2 \rightarrow 2\,Li_2O\ ;\ 2Mg + O_2 \rightarrow 2\,MgO$$

(12) Li_2SO_4 like $MgSO_4$ does not form alums.

(13) The bicarbonates of *Li* and *Mg* do not exist in solid state, they exist in solution only.

(14) Alkyls of *Li* and *Mg* (R. *Li* and R.*MgX*) are soluble in organic solvent.

(15) Lithium chloride and $MgCl_2$ both are deliquescent and separate out from their aqueous solutions as hydrated crystals, $LiCl.\ 2H_2O$ and $MgCl_2\ .\ 2H_2O$.

Uses of Lithium

(1) It is used as a deoxidiser in metallurgy of *Cu* and *Ni*.

(2) It is used as an alloying metal with

(i) *Pb* to give toughened bearings.

(ii) *Al* to give high strength *Al*-alloy for aircraft industry.

(iii) *Mg* (14% *Li*) to give extremely tough and corrosion resistant alloy which is used for armour plate in aerospace components.

Sodium and its compounds

(1) **Ores of sodium :** $NaCl$ (common salt), $NaNO_3$ (chile salt petre), $Na_2SO_4.10H_2O$ (Glauber's salt), borax (sodium tetraborate or sodium borate, $(Na_2B_4O_7.10H_2O)$.

(2) **Extraction of sodium :** It is manufactured by the electrolysis of fused sodium chloride in the presence of $CaCl_2$ and KF using graphite anode and iron cathode. This process is called ***Down process***.

$NaCl \rightleftharpoons Na^+ + Cl^-$.

At cathode : $Na^+ + e^- \rightarrow Na$;

At anode : $Cl^- \rightarrow Cl + e^-$; $Cl + Cl \rightarrow Cl_2 \uparrow$

Sodium cannot be extracted from aqueous $NaCl$ because $E^0_{H_2O/H_2}$ (–0.83*V*) is more than $E^0 Na^+/Na$ (–2.71*V*).

Anode and cathode are separated by means of a wire gauze to prevent the reaction between *Na* and Cl_2.

(3) **Compound of sodium**

(i) ***Sodium chloride*** : It is generally obtained by evaporation of sea water by sun light. However *NaCl* so obtained contains impurities like $CaSO_4, CaCl_2$ and $MgCl_2$ which makes the salt deliquescent. It is then purified by allowing HCl gas to pass through the impure saturated solution of $NaCl$. The concentration of Cl^- ions increases and as a result pure $NaCl$ gets precipitated due to common ion effect.

(ii) ***Sodium hydroxide NaOH*** *(Caustic soda)*

Preparation

(a) *Gossage process* :

$$\underset{\text{(10\% solution)}}{Na_2CO_3} + Ca(OH)_2 \rightarrow 2NaOH \downarrow + CaCO_3$$

(b) *Electrolytic method* : Caustic soda is manufactured by the electrolysis of a concentrated solution of $NaCl$.

At anode: Cl^- discharged; At cathode: Na^+ discharged

(c) *Castner - Kellener cell* (Mercury cathode process) : $NaOH$ obtained by electrolysis of *aq.* solution of brine. The cell comprises of rectangular iron tank divided into three compartments.

Outer compartment – Brine solution is electrolysed ; Central compartment – 2% $NaOH$ solution and H_2

Properties : White crystalline solid, highly soluble in water, It is only sparingly soluble in alcohol.

(a) *Reaction with salt* :

$$FeCl_3 + 3NaOH \rightarrow \underset{\text{(Insoluble hydroxide)}}{Fe(OH)_3} \downarrow + 3NaCl$$

$$HgCl_2 + 2NaOH \rightarrow 2NaCl + \underset{\text{unstable}}{Hg(OH)_2} \rightarrow H_2O + \underset{\text{yellow}}{HgO} \downarrow$$

$$AgNO_3 + 2NaOH \rightarrow 2NaNO_3 + 2AgOH \rightarrow \underset{\text{Brown}}{Ag_2O} \downarrow + H_2O$$

Zn, Al, Sb, Pb, Sn and As forms insoluble hydroxide which dissolve in excess of $NaOH$ (amphoteric hydroxide).

$$NH_4Cl + NaOH \xrightarrow{\text{heat}} NaCl + NH_3 \uparrow + H_2O$$

(b) *Reaction with halogens* :

$$X_2 + 2NaOH\ \text{(cold)} \rightarrow NaX + \underset{\text{sod. hypohalite}}{NaXO} + H_2O$$

$$3X_2 + 6NaOH\ \text{(hot)} \rightarrow 5NaX + \underset{\text{(Sod. halate)}}{NaXO_3} + 3H_2O\ ;$$

$$(X = Cl, Br, I)$$

(c) *Reaction with metals* : Weakly electropositive metals like Zn, Al and Sn etc.

$$Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2 \uparrow$$

(d) *Reaction with sand, SiO₂* :

$$2NaOH + SiO_2 \rightarrow \underset{\text{Sod. silicate (glass)}}{Na_2SiO_3} + H_2O$$

(e) *Reaction with CO*:

$$NaOH + CO \xrightarrow[5-10\ atm]{150-200^o C} \underset{\text{Sod. formate}}{HCOONa}$$

$NaOH$ breaks down the proteins of the skin flesh to a pasty mass, therefore it is commonly known as caustic soda.

Caustic property : sodium hydroxide breaks down the proteins of the skin flesh to a pasty mass, therefore, it is commonly known as caustic soda.

Uses : Sodium hydroxide is used :

(a) in the manufacture of soidum metal, soap (from oils and fats), rayon, paper, dyes and drugs,

(b) for mercurinzing cotton to make cloth unshrinkable and

(c) as a reagent in the laboratory.

(iii) ***Sodium carbonate or washing soda,*** $\mathbf{Na_2CO_3}$

It exists in various forms, namely anhydrous sodium carbonate Na_2CO_2 (soda-ash); monohydrate $Na_2CO_3.H_2O$ (crystal carbonate); hyptahydrate $Na_2CO_3.7H_2O$ and decahydrate $Na_2CO_3.10H_2O$ (washing soda or sal soda).

Preparation **:** (a) *Solvay process* : In this process, brine $(NaCl)$, NH_3 and CO_2 are the raw materials.

$$NH_3 + CO_2 + H_2O \rightarrow NH_4HCO_3$$

$$NH_4HCO_3 + NaCl \xrightarrow{30^o C} NaHCO_3 \downarrow + NH_4Cl$$

$$2NaHCO_3 \xrightarrow{250^o C} Na_2CO_3 + H_2O + CO_2$$

$$2NH_4Cl + \underset{\substack{\text{slaked}\\\text{lime}}}{Ca(OH)_2} \rightarrow CaCl_2 + 2H_2O + 2NH_3$$

$CaCl_2$ so formed in the above reaction is a by product of solvay process.

Properties

(a) $$\underset{\text{(decahydra te)}}{Na_2CO_3.10H_2O} \xrightarrow{\text{dry air}} \underset{\text{(Monohydrate)}}{Na_2CO_3.H_2O} + 9H_2O$$

$$Na_2CO_3.H_2O \xrightarrow{\Delta} Na_2CO_3$$

It does not decompose on funrther heating even to redness (m.pt. 853°C)

(b) It is soluble in water with considerable evolution of heat.

$$Na_2CO_3 + H_2O \rightarrow \underset{\text{Weakacid}}{H_2CO_3} + 2Na^+ + 2OH^-$$

(c) It is readily decomposed by acids with the evolution of CO_2 gas.

(d) $Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3$

Uses **:** In textile and petroleum refining, Manufacturing of glass, $NaOH$ soap powders etc.

(iv) ***Sodium peroxide (Na₂O₂)***

Preparation **:** It is manufactured by heating sodium metal on aluminium trays in air (free from CO_2)

$$2Na + O_2\text{ (air)} \xrightarrow{\Delta} Na_2O_2$$

Properties **:** (a) When pure it is colourless. The faint yellow colour of commercial product is due to presence of small amount of superoxide (NaO_2).

(b) On coming with moist air it become white due to formation of $NaOH$ and Na_2CO_3.

$$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2\ ;$$

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

(c) It is powerful oxidising agent. It oxidises Cr (III) hydroxide to sodium chromate, Mn (II) to sodium manganate and sulphides to sulphates.

Uses : As a bleaching agent and it is used for the purification of air in confined spaces such as submarines because it can combine with CO_2 to give Na_2CO_3 and oxygen, $2CO_2 + 2Na_2O_2 \rightarrow 2Na_2CO_3 + O_2$.

(v) ***Micro cosmic salt*** **[Na (*NH₄*) *HPO₄*. 4*H₂O*]**

Prepared by dissolving equimolar amounts of Na_2HPO_4 and NH_4Cl in water in 1 : 1 ratio followed by crystallization

$$NH_4Cl + Na_2HPO_4 \longrightarrow Na(NH_4)HPO_4 + NaCl$$
$$\downarrow Crystallization$$

$$\underset{\text{(Colourless crystal)}}{Na(NH_4)HPO_4.4H_2O}$$

Chemical properties :

On heating M.C.S, $NaPO_3$ is formed. $NaPO_3$ forms coloured beads with oxides of transition metal cloudy SiO_2

$$Na(NH_4)HPO_4 \xrightarrow{\Delta} \underset{\text{(Sodium meta phosphate)}}{NaPO_3} + H_2O + NH_3$$

$$\underset{\text{(Transparent glassy bead)}}{NaPO_3} + CuO \xrightarrow{\Delta} \underset{\text{(blue bead)}}{CuNaPO_4}$$

$NaPO_3 + CoO \longrightarrow CoNaPO_4$ (blue bend)

$NaPO_3 + MnO \longrightarrow NaMnO_4$ (blue bead)

Uses : (a) For the formation of sodium meta phosphate and copper sodium phosphate

(b) It is used for the detection of colured ion

(c) It is espacially used for testing silica with which a cloudy bead containing floating properties of silica is obtained.

(vi) ***Sodium bi Carbonate (NaHCO₃, Baking soda)***

Preparation : It is an inter mediate compound in manufacture of sodium carbonate by the solvay's process

$$NaCl + NH_3 + CO_2 + H_2 \longrightarrow NaHCO_3 + NH_4Cl$$

Properties:

$$2NaHCO_3 \xrightarrow{50-100^o C} Na_2CO_3 + H_2O + CO_2$$

It is amphiprotic $HCO_3^- + H^+ \rightleftharpoons H_2CO_3$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

Uses : (a) Baking powder contains $NaHCO_3$, $Ca(H_2PO_4)_2$ and starch.

Improved Baking powder contains 40% starch 30% $NaHCO_3$, 20% $NaAl(SO_4)_2$ and 10% $CaH_2(PO_4)$

(b) In pharmacentical industry (Antacids etc.)

(c) Fire extingerishers.

(vii) ***Sodium Sulphate Na₂SO₄* or *salt cake***

Preparation : It is the by-product of HCl industry

$$2NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + HCl$$

Properties : When aqueous solution of Na_2SO_4 is cooled below $32^o C$ Glauber's salt $(Na_2SO_4.10H_2O)$ gets crystallised and if cooled to $12^o C$, $Na_2SO_4 7H_2O$ crystals are formed.

$$Na_2SO_4.10H_2O \xrightarrow{\text{(indry air)}} Na_2SO_4 + 10H_2O$$

Uses : Na_2SO_4 finds use in paper industry detergent and glass manufacturing.

Alkaline Earth Metals and Their Compounds

The group 2 of the periodic table consists of six metallic elements. These are beryllium (*Be*), magnesium (*Mg*), calcium (*Ca*), strontium (*Sr*), barium (*Ba*) and radium (*Ra*). These (except *Be*) are known as alkaline earth metals as their oxides are alkaline and occur in earth crust.

(1) **Electronic configuration**

Element	**Electronic configurations (ns^2)**
$_4Be$	$[He]2s^2$
$_{12}Mg$	$[Ne]3s^2$
$_{20}Ca$	$[Ar]4s^2$
$_{38}Sr$	$[Kr]5s^2$
$_{56}Ba$	$[Xe]6s^2$
$_{88}Ra$	$[Rn]7s^2$

Radium was discovered in the ore pitch blende by madam Curie. It is radioactive in nature.

(2) **Occurrence :** These are found mainly in combined state such as oxides, carbonates and sulphates *Mg* and *Ca* are found in abundance in nature. *Be* is not very abundant, *Sr* and *Ba* are less abundant. *Ra* is rare element. Some important ores of alkaline earth metals are given below,

(i) ***Baryllium*** : Beryl ($3BeO.Al_2O_3.6SiO_2$); Phenacite (Be_2SiO_4)

(ii) ***Magnesium*** : Magnesite ($MgCO_3$); Dolomite ($CaCO_3$. $MgCO_3$); Epsomite($MgSO_4$. $7H_2O$); Carnallite ($MgCl_2.KCl$. $6H_2O$); Asbestos [$CaMg_3(SiO_3)_4$]

(iii) ***Calcium*** : Limestone ($CaCO_3$); Gypsum : ($CaSO_4.2H_2O$), Anhydrite ($CaSO_4$); Fluorapatite [($3Ca_3(PO_4)_2.CaF_2$)] Phosphorite rock [$Ca_3(PO_4)_2$]

(iv) ***Barium*** : Barytes ($BaSO_4$) ; witherite ($BaCO_3$)

(v) ***Radium*** : Pitch blende (U_3O_8); (*Ra* in traces); other radium rich minerals are carnotite [K_2UO_2)] $(VO_4)_2$ $8H_2O$ and antamite [$Ca(UO_2)_2$]

(3) **Extraction of alkaline earth metals**

(i) *Be* and *Mg* are obtained by reducing their oxides carbon,

$$BeO + C \rightarrow Be + CO \ ; \ MgO + C \rightarrow Mg + CO$$

(ii) The extraction of alkaline earth metals can also be made by the reduction of their oxides by alkali metals or by electrolysing their fused salts.

(4) **Alloy formation** : These dissolve in mercury and form amalgams.

Physical properties

(1) **Physical state :** All are greyish-white, light, malleable and ductile metals with metallic lustre. Their hardness progressively decrease with increase in atomic number. Although these are fairly soft but relatively harder than alkali metals.

(2) **Atomic and ionic radii**

(i) The atomic and ionic radii of alkaline earth metals also increase down the group due to progressive addition of new energy shells like alkali metals.

	Be	*Mg*	*Ca*	*Sr*	*Ba*	*Ra*
Atomic radius (pm)	112	160	197	215	222	–
Ionic radius of M²⁺ ion (pm)	31	65	99	113	135	140

(ii) The atomic radii of alkaline earth metals are however smaller than their corresponding alkali metal of the same period. This is due to the fact that alkaline earth metals possess a higher nuclear charge than alkali metals which more effectively pulls the orbit electrons towards the nucleus causing a decrease in size.

(3) **Density**

(i) Density decreases slightly upto *Ca* after which it increases. The decrease in density from *Be* to *Ca* might be due to less packing of atoms in solid lattice of *Mg* and *Ca*.

Be	*Mg*	*Ca*	*Sr*	*Ba*	*Ra*
1.84	1.74	1.55	2.54	3.75	6.00

(ii) The alkaline earth metals are more denser, heavier and harder than alkali metal. The higher density of alkaline earth metals is due to their smaller atomic size and strong intermetallic bonds which provide a more close packing in crystal lattice as compared to alkali metals.

(4) **Melting point and Boiling point**

(i) Melting points and boiling points of alkaline earth metals do not show any regular trend.

	Be	*Mg*	*Ca*	*Sr*	*Ba*	*Ra*
melting points (K)	1560	920	1112	1041	1000	973
boiling point (K)	2770	1378	1767	1654	1413	–

(ii) The values are, however, more than alkali metals. This might due to close packing of atoms in crystal lattice in alkaline earth metals.

(5) **Ionisation energy and electropositive or metallic character**

(i) Since the atomic size decreases along the period and the nuclear charge increases and thus the electrons are more tightly held towards nucleus. It is therefore alkaline earth metals have higher ionisation energy in comparison to alkali metals but lower ionisation energies in comparison to p-block elements.

(ii) The ionisation energy of alkaline earth metals decreases from *Be* to *Ba*.

	Be	*Mg*	*Ca*	*Sr*	*Ba*	*Ra*
First ionisation energy ($kJ\ mol^{-1}$)	899	737	590	549	503	509
Second ionisation energy ($kJ\ mol^{-1}$)	1757	1450	1146	1064	965	979

(iii) The higher values of second ionisation energy is due to the fact that removal of one electron from the valence shell, the remaining electrons are more tightly held in which nucleus of cation and thus more energy is required to pull one more electron from monovalent cation.

(iv) No doubt first ionisation energy of alkaline earth metals are higher than alkali metals but a closer look on 2nd ionisation energy of alkali metals and alkaline earth metals reveals that 2nd ionisation energy of alkali metals are more

	Li	*Be*
1st ionisation energy ($kJ\ mol^{-1}$)	520	899
2nd ionisation energy ($kJ\ mol^{-1}$)	7296	1757

This may be explained as,

$$Li : 1s^2, 2s^1 \xrightarrow[\text{electron}]{\text{removal of 2s}} Li^+ : 1s^2 \xrightarrow[\text{electron}]{\text{removal of 1s}} Li^{2+} : 1s^1$$

$$Be : 1s^2, 2s^2 \xrightarrow[\text{electron}]{\text{removal of 2s}} Be^+ : 1s^2, 2s^1 \xrightarrow[\text{electron}]{\text{removal of 2s}} Be^{2+} : 1s^2$$

The removal of 2nd electron from alkali metals takes place from 1s sub shell which are more closer to nucleus and exert more nuclear charge to hold up 1s electron core, whereas removal of 2nd electron from alkaline earth metals takes from 2s sub shell. More closer are shells to the nucleus, more tightly are held electrons with nucleus and thus more energy is required to remove the electron.

(v) All these possess strong electropositive character which increases from *Be* to *Ba*.

(vi) These have less electropositive character than alkali metals as the later have low values of ionisation energy.

(6) **Oxidation number and valency**

(i) The IE_1 of the these metals are much lower than IE_1 and thus it appears that these metals should form univalent ion rather than divalent ions but in actual practice, all these give bivalent ions. This is due to the fact that M^{2+} ion possesses a higher degree of hydration or M^{2+} ions are extensively hydrated to form $[M(H_2O)_x]^{2+}$, a hydrated ion. This involves a large amount of energy evolution which counter balances the higher value of second ionisation energy.

$$M \rightarrow M^{2+}, \qquad \Delta H = IE_1 + E_2$$

$$M^{2+} + {}_xH_2O \rightarrow [M(H_2O)_x]^{2+};\ \Delta H = -\text{ hydration energy.}$$

(ii) The tendency of these metals to exist as divalent cation can thus be accounted as,

(a) Divalent cation of these metals possess noble gas or stable configuration.

(b) The formation of divalent cation lattice leads to evolution of energy due to strong lattice structure of divalent cation which easily compensates for the higher values of second ionisation energy of these metals.

(c) The higher heats of hydration of divalent cation which accounts for the existence of the divalent ions of these metals in solution state.

(7) **Hydration of ions**

(i) The hydration energies of alkaline earth metals divalent cation are much more than the hydration energy of monovalent cation.

	Mg^+	Mg^{2+}
Hydration energy or Heat of hydration ($kJ\ mol^{-1}$)	353	1906

The abnormally higher values of heat of hydration for divalent cations of alkaline earth metals are responsible for their divalent nature. $MgCl_2$ formation occurs with more amount of heat evolution and thus $MgCl_2$ is more stable.

(ii) The hydration energies of M^{2+} ion decreases with increase in ionic radii.

	Be^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
Heat of hydration $kJ\ mol^{-1}$	2382	1906	1651	1484	1275

(iii) Heat of hydration are larger than alkali metals ions and thus alkaline earth metals compounds are more extensively hydrated than those of alkali metals e.g $MgCl_2$ and $CaCl_2$ exists as $Mg\ Cl_2\ .6H_2O$ and $CaCl_2.\ 6H_2O$ which $NaCl$ and KCl do not form such hydrates.

(iv) The ionic mobility, therefore, increases from Be^{2+} to Ba^{2+}, as the size of hydrated ion decreases.

(8) **Electronegativities**

(i) The electronegativities of alkaline earth metals are also small but are higher than alkali metals.

(ii) Electronegativity decreases from *Be* to *Ba* as shown below,

	Be	*Mg*	*Ca*	*Sr*	*Ba*
Electronegativity	1.57	1.31	1.00	0.95	0.89

(9) **Conduction power :** Good conductor of heat and electricity.

(10) **Standard oxidation potential and reducing properties**

(i) The standard oxidation potential (in volts) are,

Be	*Mg*	*Ca*	*Sr*	*Ba*
1.69	2.35	2.87	2.89	2.90

(ii) All these metals possess tendency to lose two electrons to give M^{2+} ion and are used as reducing agent.

(iii) The reducing character increases from *Be* to *Ba*, however, these are less powerful reducing agent than alkali metals.

(iv) Beryllium having relatively lower oxidation potential and thus does not liberate H_2 from acids.

(11) **Characteristic flame colours**

The characteristic flame colour shown are : *Ca* - brick red; *Sr* –crimson ; *Ba*-apple green and *Ra*-crimson.

Chemical Properties

(1) **Formation of oxides and hydroxides**

(i) The elements (except *Ba* and *Ra*) when burnt in air give oxides of ionic nature $M^{2+}O^{2-}$ which are crystalline in nature. *Ba* and *Ra* however give peroxide. The tendency to form higher oxides increases from *Be* to *Ra*.

$$2M + O_2 \rightarrow 2MO \qquad (M \text{ is } Be, Mg \text{ or } Ca)$$

$$2M + O_2 \rightarrow MO_2 \qquad (M \text{ is } Ba \text{ or } Sr)$$

(ii) Their less reactivity than the alkali metals is evident by the fact that they are slowly oxidized on exposure to air, However the reactivity of these metals towards oxygen increases on moving down the group.

(iii) The oxides of these metals are very stable due to high lattice energy.

(iv) The oxides of the metal (except *BeO* and *MgO*) dissolve in water to form basic hydroxides and evolve a large amount of heat. *BeO* and *MgO* possess high lattice energy and thus insoluble in water.

(v) *BeO* dissolves both in acid and alkalies to give salts *i.e. BeO* possesses amphoteric nature.

$$BeO+2NaOH \rightarrow \underset{\text{Sod. beryllate}}{Na_2BeO_2}+H_2O\ ; \quad BeO+2HCl \rightarrow \underset{\text{Beryllium chloride}}{BeCl_2}+H_2O$$

(vi)The basic nature of oxides of alkaline earth metals increases from *Be* to *Ra* as the electropositive Character increases from *Be* to *Ra*.

(vii)The tendency of these metal to react with water increases with increase in electropositive character *i.e. Be* to *Ra*.

(viii) Reaction of *Be* with water is not certain, magnesium reacts only with hot water, while other metals react with cold water but slowly and less energetically than alkali metals.

(ix) The inertness of *Be* and *Mg* towards water is due to the formation of protective, thin layer of hydroxide on the surface of the metals.

(x) The basic nature of hydroxides increase from *Be* to *Ra*. It is because of increase in ionic radius down the group which results in a decrease in strength of $M-O$ bond in $M-(OH)_2$ to show more dissociation of hydroxides and greater basic character.

(xi) The solubility of hydroxides of alkaline earth metals is relatively less than their corresponding alkali metal hydroxides Furthermore, the solubility of hydroxides of alkaline earth metals increases from *Be* to *Ba*. $Be\ (OH)_2$ and $Mg\ (OH)_2$ are almost insoluble, $Ca\ (OH)_2$ (often called lime water) is sparingly soluble whereas $Sr(OH)_2$ and $Ba\ (OH)_2$ (often called baryta water) are more soluble.

The trend of the solubility of these hydroxides depends on the values of lattice energy and hydration energy of these hydroxides. The magnitude of hydration energy remains almost same whereas lattice energy decreases appreciably down the group leading to more –Ve values for $\Delta H_{\text{solution}}$ down the group.

$$\Delta H_{\text{solution}} = \Delta H_{\text{lattice energy}} + \Delta H_{\text{hydration energy}}$$

More negative is $\Delta H_{\text{solution}}$ more is solubility of compounds.

(xii) The basic character of oxides and hydroxides of alkaline earth metals is lesser than their corresponding alkali metal oxides and hydroxides.

(xiii) Aqueous solution of lime water $[Ca(OH)_2]$ or baryta water $[Ba(OH)]_2$ are used to qualitative identification and quantative estimation of carbon dioxide, as both of them gives white precipitate with CO_2 due to formation of insoluble $CaCO_3$ or $BaCO_3$

$$Ca(OH)_2 + CO_2 \rightarrow \underset{\text{(white ppt)}}{CaCO_3} + H_2O \ ; \ Ba(OH)_2 + CO_2 \rightarrow \underset{\text{(white ppt)}}{BaCO_3} + H_2O$$

SO_2 also give white ppt of $CaSO_3$ and $BaSO_3$ on passing through lime water or baryta water. However on passing CO_2 in excess, the white turbidity of insoluble carbonates dissolve to give a clear solution again due to the formation of soluble bicarbonates,

$$CaCO_3 \rightarrow H_2O + CO_2 \rightarrow Ca(HCO_3)_2$$

(2) **Hydrides**

(i) Except Be, all alkaline earth metals form hydrides (MH_2) on heating directly with H_2 . $M + H_2 \rightarrow MH_2$.

(ii) BeH_2 is prepared by the action of $LiAlH_4$ On $BeCl_2$

$$2BeCl_2 + LiAlH_4 \rightarrow 2BeH_2 + LiCl + AlCl_3.$$

(iii) BeH_2 and MgH_2 are covalent while other hydrides are ionic.

(iv) The ionic hydrides of Ca, Sr, Ba liberate H_2 at anode and metal at cathode.

$$CaH_2 \xrightleftharpoons{\text{fusion}} Ca^{2+} + 2H^-$$

Anode : $2H^- \rightarrow H_2 + 2e^-$ Cathode : $Ca^{2+} + 2e^- \rightarrow Ca$

(v) The stability of hydrides decreases from Be to Ba.

(vi) The hydrides having higher reactivity for water, dissolves readily and produce hydrogen gas.

$$CaH_{2(s)} + 2H_2O \rightarrow Ca(OH)_2 + 2H_2\uparrow$$

(3) **Carbonates and Bicarbonates**

(i) All these metal carbonates (MCO_3) are insoluble in neutral medium but soluble in acid medium. These are precipitated by the addition of alkali metal or ammonium carbonate solution to the solution of these metals.

$$(NH_4)_2CO_3 + CaCl_2 \rightarrow 2NH_4Cl + CaCO_3$$

$$Na_2CO_3 + BaCl_2 \rightarrow 2NaCl + BaCO_3$$

(ii) Alkaline earth metal carbonates are obtained as white precipitates when calculated amount of carbon dioxide is passed through the solution of the alkaline metal hydroxides.

$$M(OH)_{2\,(aq)} + CO_{2\,(g)} \rightarrow MCO_{3(s)} + H_2O_{(l)}$$

and sodium or ammonium carbonate is added to the solution of the alkaline earth metal salt such as $CaCl_2$.

$$CaCl_{2\,(aq)} + Na_2CO_{3\,(aq)} \rightarrow CaCO_{3(s)} + 2\,NaCl_{(aq)}$$

(iii) Solubility of carbonates of these metals also decreases downward in the group due to the decrease of hydration energy as the lattice energy remains almost unchanged as in case of sulphates.

(vi) The carbonates of these metals decompose on heating to give the oxides, the temperature of decomposition increasing from Be to Ba. Beryllium carbonate is unstable.

$$MCO_3 \xrightarrow{Heat} MO + CO_2$$

(4) **Halides**

(i) The alkaline earth metals combine directly with halogens at appropriate temperatures forming halides, MX_2. These halides can also be prepared by the action of halogen acids (HX) on metals, metal oxides, hydroxides and carbonates.

$$M + 2HX \rightarrow MX_2 + H_2 \ ; \ MO + 2HX \rightarrow MX_2 + H_2O$$

$$M(OH)_2 + 2HX \rightarrow MX_2 + 2H_2O$$

$$MCO_3 + 2HX \rightarrow MX_2 + CO_2 + H_2O$$

Beryllium chloride is however, conveniently obtained from oxide

$$BeO + C + Cl_2 \xrightarrow{870-1070\,K} BeCl_2 + CO$$

(ii) $BeCl_2$ is essentially covalent, the chlorides $MgCl_2$, $CaCl_2$, $SrCl_2$ and $BaCl_2$ are ionic; the ionic character increases as the size of the metal ion increases. The evidence is provided by the following facts,

(a) Beryllium chloride is relatively low melting and volatile whereas $BaCl_2$ has high melting and stable.

(b) Beryllium chloride is soluble in organic solvents.

(iii) The halides of the members of this group are soluble in water and produce neutral solutions from which the hydrates such : $MgCl_2\ 6H_2O$, $CaCl_2.6H_2O$. $BaCl_2\ 2H_2O$ can be crystallised. The tendency to form hydrated halides decreases with increasing size of the metal ions.

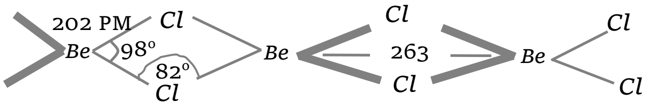
(iv) $BeCl_2$ is readily hydrolysed with water to form acid solution, $BeCl_2 + 2H_2O \rightarrow Be\ (OH)_2 + 2HCl$.

(v) The fluorides are relatively less soluble than the chlorides due to high lattice energies. Except $BeCl_2$

and $MgCl_2$ the chlorides of alkaline earth metals impart characteristic colours to flame.

$CaCl_2$	$SrCl_2$	$BaCl_2$
Brick red colour	Crimson colour	Grassy green colour

Structure of $BeCl_2$: In the solid phase polymeric chain structure with three centre two electron bonding with *Be*-Cl-*Be* bridged structure is shown below,



In the vapour phase it tends to form a chloro-bridged dimer which dissociates into the linear triatomic monomer at high temperature at nearly 1200 *K*.

(5) **Solubility in liquid ammonia :** Like alkali metals, alkaline earth metals also dissolve in liquid ammonia to form coloured solutions When such a solution is evaporated, hexammoniate, $M(NH_3)_6$ is formed.

(6) **Nitrides**

(i) All the alkaline earth metals direct combine with N_2 give nitrides, M_3N_2.

(ii) The ease of formation of nitrides however decreases from *Be* to *Ba*.

(iii) These nitrides are hydrolysed water to liberate

NH_3, $M_3N_2 + 6H_2O \rightarrow 3M(OH)_2 + 2NH_3$

(7) **Sulphates**

(i) All these form sulphate of the type $M\ SO_4$ by the action of $H_2\ SO_4$ on metals, their oxides, carbonates or hydroxides.

$M + H_2SO_4 \rightarrow MSO_4 + H_2$; $MO+H_2SO_4 \rightarrow MSO_4+H_2O$

$MCO_3+ H_2SO_4 \rightarrow MSO_4 + H_2O+CO_2$

$M(OH)_2 + H_2SO_4 \rightarrow MSO_4 + 2H_2O$

(ii) The solubility of sulphates in water decreases on moving down the group $BeSO_4$ and $MgSO_4$ are fairly soluble in water while $BaSO_4$ is completely insoluble. This is due to increases in lattice energy of sulphates down the group which predominates over hydration energy.

(iii) Sulphate are quite stable to heat however reduced to sulphide on heating with carbon.

$MSO_4 + 2C \rightarrow MS+2CO_2$

(8) **Action with carbon** : Alkaline metals (except *Be*, *Mg*) when heated with carbon form carbides of the type MC_2 These carbides are also called acetylides as on hydrolysis they evolve acetylene.

$MC_2 + 2H_2O \rightarrow M(OH)_2 + C_2H_2$

(9) **Action with sulphur and phosphorus :** Alkaline earth metals directly combine with sulphur and phosphorus when heated to form sulphides of the type *MS* and phosphides of the type M_3P_2 respectively.

$M + S \rightarrow MS$; $3M + 2P \rightarrow M_3P_2$

Sulphides on hydrolysis liberate H_2S while phosphides on hydrolysis evolve phosphine.

MS + dil. acid $\rightarrow H_2S$; M_3P_2 + dil. acid $\rightarrow PH_3$

Sulphides are phosphorescent and are decomposed by water

$2MS + 2H_2O \rightarrow M(OH)_2 + M(HS)_2$

(10) **Nitrates :** Nitrates of these metals are soluble in water On heating they decompose into their corresponding oxides with evolution of a mixture of nitrogen dioxide and oxygen.

$$M(NO_3)_2 \rightarrow MO + 2NO_2 + \left(\frac{1}{2}\right)O_2$$

(11) **Formation of complexes**

(i) Tendency to show complex ion formation depends upon smaller size, high nuclear charge and vacant orbitals to accept electron. Since alkaline metals too do not possess these characteristics and thus are unable to form complex ion.

(ii) However, Be^{2+} on account of smaller size forms many complex such as $(BeF_3)^{1-}$, $(BeF_4)^{2-}$.

Anomalous behaviour of Beryllium

Beryllium differs from rest of the alkaline earth metals on account of its small atomic size, high electronegativity Be^{2+} exerts high polarizing effect on anions and thus produces covalent nature in its compounds. Following are some noteworthy difference of *Be* from other alkaline earth metals,

(1) *Be* is lightest alkaline earth metal.

(2) *Be* possesses higher m.pt. and b.pt than other group members.

(3) *BeO* is amphoteric in nature whereas oxides of other group members are strong base.

(4) It is not easily effected by dry air and does not decompose water at ordinary temperature.

(5) $BeSO_4$ is soluble in water.

(6) *Be* and *Mg* carbonates are not precipitated by $(NH_4)_2CO_3$ in presence of NH_4Cl.

(7) *Be* and *Mg* salts do not impart colour to flame.

(8) *Be* does not form peroxide like other alkaline earth metals.

(9) It does not evolve hydrogen so readily from acids as other alkaline earth metals do so.

(10) It has strong tendency to form complex compounds.

(11) Be_3N_2 is volatile whereas nitrides of other alkaline earth metals are non-volatile.

(12) It's salts can never have more than four molecules of water of crystallization as it has only four available orbitals in its valence shell.

(13) Berylium carbide reacts water to give methane whereas magnesium carbide and calcium carbide give propyne and acetylene respectively.

$Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + CH_4$

$Mg_2C_3 + 4H_2O \rightarrow 2Mg(OH)_2 + C_3H_6$

$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_4$

Diagonal relationship of *Be* with *Al*

Due to its small size *Be* differs from other earth alkaline earth metals but resembles in many of its properties with *Al* on account of diagonal relationship.

(1) Be^{2+} and Al^{3+} have almost same and smaller size and thus favour for covalent bonding.

(2) Both these form covalent compounds having low m. pt and soluble in organic solvent.

(3) Both have same value of electronegativity (*i.e.* 1.5).

(4) The standard O.P of these elements are quite close to each other ; Be^{2+}=1.69 volts and Al^{3+}= 1.70 volts.

(5) Both become passive on treating with conc. HNO_3 in cold.

(6) Both form many stable complexes e.g. $(BeF_3)^-$, $(AlH_4)^-$.

(7) Like *BeO*, Al_2O_3 is amphoteric in nature. Also both are high melting point solids.

$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$

$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$

(8) Be and Al both react with *NaOH* to liberate H_2 forming beryllates and alluminates.

$Be + 2NaOH \rightarrow Na_2BeO_2 + H_2$

$2Al + 6NaOH \rightarrow 2Na_3AlO_3 + 3H_2$

(9) $Be_2\ C$ and Al_4C_3 both give CH_4 on treating with water.

$Be_2C + 2H_2O \rightarrow CH_4 + 2BeO$

$Al_4C_3 + 6H_2O \rightarrow 3CH_4 + 2Al_2O_3$

(10) Both occur together in nature in beryl ore, $3BeO.\ Al_2O_3.\ 6SiO_2$.

(11) Unlike other alkaline earths but like aluminium, beryllium is not easily attacked by air (Also *Mg* is not attacked by air)

(12) Both *Be* and *Al* react very slowly with dil. *HCl* to liberate H_2.

(13) Both *Be* and *Al* form polymeric covalent hydrides while hydrides of other alkaline earth are ionic.

(14) Both $BeCl_2$ and $AlCl_3$ are prepared is similar way.

$BeO + C + Cl_2 \rightarrow BeCl_2 + CO$

$Al_2O_3 + 3C + 3Cl_2 \rightarrow 2AlCl_3 + 3CO$

(15) Both $BeCl_2$ and $AlCl_3$ are soluble in organic solvents and act as catalyst in Friedel –Crafts reaction.

(16) Both *Be* $(OH)_2$ and *Al* $(OH)_3$ are amphoteric whereas hydroxides of other alkaline earths are strong alkali.

(17) The salts of *Be* and *Al* are extensively hydrated.

(18) $BeCl_2$ and $AlCl_3$ both have a bridged polymeric structure.

(19) *Be* and *Al* both form fluoro complex ions $[BeF_4]^{2-}$ and $[AlF_6]^{3-}$ in solution state whereas other members of 2nd group do not form such complexes.

Magnesium and its compounds

(1) **Ores of magnesium :** Magnesite $(MgCO_3)$, Dolomite $(MgCO_3.CaCO_3)$, Epsomite (epsom salt) $(MgSO_4.7H_2O)$ Carnallite $(MgCl_2.KCl.6H_2O)$ Asbestos $(CaMg_3(SiO_3)_4)$, Talc $(Mg_2\ (Si_2O_5)_2.Mg(OH)_2)$.

(2) **Extraction of magnesium :** It is prepared by the electrolysis of fused magnesium chloride which in turn is obtained from carnallite and magnesite.

Carnallite $(MgCl_2.KCl.6H_2O)$ can't be directly converted into anhydrous $MgCl_2$ by heating because all the water of crystallisation cannot be removed by heating. Moreover, strong heating may change it to MgO.

$$MgCl_2 + 2H_2O \xrightarrow{\Delta} MgO + 2HCl + H_2O$$

In Dow's process, magnesium chloride is obtained from sea water as $MgCl_2.6H_2O$. It is rendered anhydrous by heating it in a current of dry HCl gas. The anhydrous magnesium chloride is fused with $NaCl$ (to provide conductivity to the electrolyte and to lower the fusing temperature of anhydrous $MgCl_2$) and then electrolysed at 700^oC.

(3) **Compounds of magnesium**

(i) ***Magnesia (MgO)* :** It is used as magnesia cement. It is a mixture of MgO and $MgCl_2$. It is also called Sorel's cement.

(ii) ***Magnesium hydroxide* :** It aqueous suspension is used in Medicine as an antacid. Its medicinal name is milk of magnesia.

(iii) ***Magnesium sulphate or Epsom salt*** $(MgSO_4.7H_2O)$: It is isomorphous with $ZnSO_4.7H_2O.$ It is used as a purgative in medicine, as a mordant in dyeing and as a stimulant to increase the secretion of bile.

(iv) ***Magnesium chloride*** $(MgCl_2.6H_2O)$: It is a deliquescent solid. Hydrated salt on heating in air undergoes partial hydrolysis.

$$MgCl_2.6H_2O \xrightarrow{\text{Heat}} Mg(OH)Cl + HCl + 5H_2O\ .$$

Calcium and its compounds

(1) **Ores of calcium :** Lime stone or marble or chalk $(CaCO_3)$, Gypsum $(CaSO_4.2H_2O)$, Dolomite $(CaCO_3.MgCO_3)$, Fluorspar (CaF_2), phosphorite $Ca_3(PO_4)_2$. Calcium phosphate is a constituent of bones and teeth.

(2) **Manufacture :** It is manufactured by the electrolysis of a molten mixture of calcium chloride containing some calcium fluoride. Calcium chloride is obtained as a by product of the solvay process.

(3) **Compounds of calcium**

(i) ***Calcium oxide or Quick lime or Burnt lime (CaO)*** : It's aqueous suspension is known as slaked lime.

$$CaO + H_2O \xrightarrow{\text{hissing sound}} \underset{\substack{\text{slaked} \\ \text{lime}}}{Ca(OH)_2} + \text{Heat},$$

When exposed to oxy-hydrogen flame, it starts emitting light called lime light.

CaO is used as basic flux, for removing hardness of water, as a drying agent (for NH_3 gas) for preparing mortar (CaO+ sand +water).

Mortar : Mortar used in making buildings is a mixture of lime (CaO) and sand in the ratio 1 : 3 with enough water to make a thick paste. When the mortar is placed between bricks, it slowly absorbs CO_2 from the air and the slaked lime revers to $CaCO_3$.

$$Ca(OH)_2(s) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$$

Although the sand in the mortar is chemically inert, the grains are bound together by the particles of calcium carbonate and a hard material results.

(ii) ***Calcium chloride*** $(CaCl_2.6H_2O)$: Fused $CaCl_2$ is a good dessicant (drying agent). It can't be used to dry alcohol or ammonia as it forms additional products with them.

(iii) ***Calcium carbonate (CaCO₃)* :**

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O.$$

It is insoluble in water but dissolves in the presence of CO_2 due to the formation of calcium bicarbonate.

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$$

It is a constituent of protective shells of marine animals.

(iv) ***Gypsum*** $(CaSO_4.2H_2O)$: On partially dehydrates to produce plaster of paris.

$$\underset{\text{Gypsum}}{CaSO_4.2H_2O} \xrightarrow{120\,^oC} \underset{\text{Plaster of paris}}{CaSO_4}.\frac{1}{2}H_2O + 1\frac{1}{2}H_2O$$

Plaster of paris :

$$\underset{\text{Plaster of paris}}{CaSO_4.\frac{1}{2}H_2O} \xrightarrow[\text{Setting}]{H_2O} \underset{\text{orthorhomb ic}}{CaSO_4.2H_2O} \xrightarrow{\text{Hardening}} \underset{\text{Monoclinic (gypsum)}}{CaSO_4.2H_2O}$$

$$\underset{\text{Gypsum}}{CaSO_4.2H_2O} \xrightarrow{200^oC} \underset{\text{dead burnt plaster}}{CaSO_4(\text{anhydrous})}$$

Gypsum when heated to about 200^oC is converted into anhydrous calcium sulphate. The anhydrous form (anhydrite) is known as dead burnt plaster because it does not set like plaster of paris when moistened with water.

(v) ***Calcium Hydroxide*** $Ca(OH)_2$ (slaked lime)

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + Ca(HCO_3)_2$$

Suspension of $Ca(OH)_2$ in water is called milk of lime.

$$Ca(OH)_2 + Cl_2 \rightarrow CaOCl_2 + H_2O$$

(vi) **Cement :** (a) It is essentially a mixture of lime stone and clay. It is also called Portland cement because in presence of water it sets to a hard stone-like mass resembling with the famous Portland rock, a famous building stone of England. The approximate composition of cement is

Calcium oxide (CaO)	50 – 60 %
Silica (SiO_2)	20 – 25%
Alumina (Al_2O_3)	5 – 10%
Magnesia (MgO)	1 – 3%
Ferric oxide (Fe_2O_3)	1 – 3%

The above compounds are provided by the two raw materials, namely lime stone (which provides CaO) and clay which provides SiO_2, Al_2O_3 and Fe_2O_3. In cement, almost entire amount of lime is present in the combined state as calcium silicates ($2CaO.SiO_2$ and $3CaO.SiO_2$) and calcium aluminates ($3CaO.Al_2O_3$ and $4CaO.Al_2O_3$).

(b) Cement containing excess amount of lime cracks during setting; while cement containing less amount of lime is weak in strength.

(c) Cement with excess of silica is slow-setting and that having an excess of alumina is quick-setting.

(d) Cement containing no iron oxide is white but hard to burn.

Cement is manufactured by two processes, viz, wet and dry. A small amount (2–3%) of gypsum is added to slow down the setting of the cement so that it gets sufficiently hardened. Setting of cement is an exothermic process and involves hydration of calcium aluminates and calcium silicates.

Boron Family

Group 13 of long form of periodic table (previously reported as group III A according to

Mendeleefs periodic table) includes boron (B) ; aluminium (Al) , gallium (Ga), indium (In) and thallium (Tl) Boron is the first member of group 13 of the periodic table and is the only non-metal of this group. The all other members are metals. The non-metallic nature of boron is due its small size and high ionisation energy. The members of this family are collectively known as boron family and sometimes as aluminium family.

(1) **Electronic configuration**

Element	**Electronic configuration** ($ns^2\ np^1$)
$_5B$	$[He]2s^2 2p^1$
$_{13}Al$	$[Ne]3s^2 3p^1$
$_{31}Ga$	$[Ar]3d^{10} 4s^2 4p^1$
$_{49}In$	$[Kr]4d^{10} 5s^2 5p^1$
$_{81}Tl$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^1$

(2) **Occurrence :** The important of this group elements are given below,

Boron : Borax (Tincal) ($Na_2B_4O_7.10H_2O$), Colemanite ($Ca_2B_6O_{11}5H_2O$)

Boracite ($2Mg_3B_8O_{15}.MgCl_2$), Boronatro calcite ($CaB_4O_7.NaBO_2.8H_2\ O$),

Kernite ($Na_2B_4O_7.4H_2O$), Boric acid (H_3BO_3)

Aluminium : Corundum (Al_2O_3), Diaspore ($Al_2O_3.H_2O$), Bauxite ($Al_2O_3.\ 2H_2O$), and Cryolite (Na_3AlF_6).

Physical properties

(1) A regular increasing trend in density down the group is due to increase in size.

(2) Melting points do not vary regularly and decrease from B to Ga and then increase.

(3) Boron has very high melting point because it exist as giant covalent polymer in both solid and liquid state.

(4) Low melting point of Ga (29.8°C) is due to the fact that consists of only Ga_2 molecule; it exist as liquid upto 2000°C and hence used in high temperature thermometry.

(5) Boiling point of these elements however show a regular decrease down the group.

(6) The abrupt increase in the atomic radius of Al is due to greater screening effect in Al (it has 8 electrons in its penultimate shell) than in B (it has 2 electrons in its penultimate shell)

(7) The atomic radii of group 13 elements are smaller than the corresponding s-block elements. This is due to the fact that when we move along the period, the new incoming electron occupy the same shell whereas the nuclear charge increases regularly showing more effective pull of nucleus towards shell electrons. This ultimately reduces the atomic size.

(8) The atomic radius of Ga is slightly lesser than of Al because in going from Al to Ga, the electrons have already occupied $3d$ sub shell in Ga. The screening effect of these intervening electrons being poor and has less influence to decrease the effective nuclear charge, therefore the electrons in Ga experience more forces of attractions towards nucleus to result in lower size of Ga than Al

(9) **Oxidation state**

(i) All exhibit +3 oxidation state and thus complete their octet either by covalent or ionic union.

(ii) Boron being smaller in size cannot lose its valence electrons to form B^{3+} ion and it usually show +3 covalence. The tendency to show +3 covalence however decreases down the group even Al shows +3 covalence in most of its compounds.

(iii) Lower elements also show +1 ionic state e.g Tl^+, Ga^+. This is due to inert pair effect. The phenomenon in which outer shell 's' electrons (ns^2) penetrate to (n-1) d-electrons and thus become closer to nucleus and are more effectively pulled the nucleus. This results in less availability of ns^2 electrons pair for bonding or ns^2 electron pair becomes inert. The inert pair effect begins after $n \geq 4$ and increases with increasing value of n.

(iv) The tendency to form M^+ ion increases down the gp. $Ga^{+1} < Tl^{+1}$

(10) **Hydrated ions :** All metal ions exist in hydrated state.

(11) **Ionisation energy**

(i) Inspite of the more charge in nucleus and small size, the first ionisation energies of this group elements are lesser than the corresponding elements of s block. This is due to the fact that removal of electron from a p-orbitals (being far away from nucleus and thus less effectively held than s-orbitals) is relatively easier than s-orbitals.

(ii) The ionisation energy of this group element decrease down the group due to increases in size like other group elements.

(iii) However, ionisation energy of Ga are higher than that of Al because of smaller atomic size of Ga due to less effective shielding of $3d$ electrons in Ga. Thus valence shell exert more effective nuclear charge in *Ga* to show higher ionisation energies.

(12) **Electropositive character**

(i) Electropositive character increases from *B* to *Tl*.

(ii) Boron is semi metal, more closer to non-metallic nature whereas rest all members are pure metals.

(iii) Furthermore, these elements are less electropositive than *s*-block elements because of smaller size and higher ionisation energies.

(13) **Oxidation potential**

(i) The standard oxidation potentials of these element are quite high and are given below,

	B	*Al*	*Ga*	*In*	*Tl*
E^oop for $M \rightarrow M^{3+} + 3e$	–	+1.66	+0.56	+0.34	+1.26
E^oop for $M \rightarrow M^{+} + e$	–	+0.55	–	+0.18	+0.34

(ii) However Boron does not form positive ions in aqueous solution and has very low oxidation potential.

(iii) The higher values of standard oxidation potentials are due to higher heats of hydration on account of smaller size of trivalent cations.

(iv) Aluminium is a strong reducing agent and can reduce oxides which are not reduced even by carbon. This is due to lower ionisation energy of aluminium than carbon. The reducing character of these elements is A*l* > *Ga* > *In* > *Tl.*

(14) **Complex formation :** On account of their smaller size and more effective nuclear charge as well as vacant orbitals to accept elements, these elements have more tendency to form complexes than-*s* block elements.

Chemical properties

(1) **Hydrides**

(i) Elements of group 13 do not react directly with hydrogen but a number of polymeric hydrides are known to exist.

(ii) Boron forms a large no. of volatile covalent hydrides, known as boranes *e.g.* B_2H_6,B_4H_{10},B_5H_{11},B_6H_{10} Two series of borones with general formula B_nH_{n+4} and B_nH_{n+6} are more important.

(iii) Boranes are electron deficient compounds. It is important to note that although BX_3 are well known, BH_3 is not known. This is due of the fact that hydrogen atoms in BH_3 have no free electrons to form $p\pi$–$p\pi$ back bonding and thus boron has incomplete octet and hence BH_3 molecules dimerise to form B_6H_6 having covalent and three centre bonds.

(iv) Al forms only one polymeric hydride $(AlH_3)_n$ commonly known as alane It contains *Al*.....*H*......*Al* bridges.

(v) *Al* and *Ga* forms anionic hydrides e.g. $LiAlH_4$ and $LiGa\ H_4$,

$$4LiH + AlCl_3 \xrightarrow{ether} Li[AlH_4] + 3LiCl$$

(2) **Reactivity towards air**

(i) Pure boron is almost unreactive at ordinary temperature. It reacts with air to form B_2O_3 when heated It does react with water. Al burns in air with evolution of heat give Al_2O_3.

(ii) *Ga* and *In* are not effected by air even when heated whereas *Tl* is little more reactive and also form an oxide film at surface. In moist air, a layer of *Tl* (*OH*) is formed.

(iii) *Al* decomposes H_2O and reacts readily in air at ordinary temperature to form a protective film of its oxides which protects it from further action.

(3) **Oxides and hydroxides**

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

(ii) The acidic nature of oxides and hydroxides changes from acidic to basic through amphoteric from *B* to *Tl*.

B_2O_3 and $B(OH)_3$> Al_2O_3 and $Al(OH)_3$ >
(acidic) (amphoteric)

Ga_2O_3 and $Ga(OH)_3$> In_2O_3 $In\ (OH)_3$> Tl_2O_3 $Tl(OH)_3$
(amphoteric) (basic) (strong basic)

$B(OH)_3$ or H_3BO_3 is weak monobasic Lewis acid.

(iii) Boric acid, $B(OH)_3$ is soluble in water as it accepts lone pair of electron to act as Lewis acid. Rest all hydroxides of group 13 are insoluble in water and form a gelatinous precipitate.

$$B(OH)_3 + H_2O \rightarrow B(OH)_4^{1-} + H^+$$

(iv) Al_2O_3 being amphoteric dissolves in acid and alkalies both.

$$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2\ (SO_4)_3 + 3H_2O$$

$$Al_2O_3 + 2NaOH \xrightarrow{fuse} \underset{\text{Sodium meta aluminate}}{2NaAlO_3} + H_2O$$

(v) One of the crystalline form of alumina (Al_2O_3) is called corrundum. It is very hard and used as abrasive. It is prepared by heating amorphous form of Al_2O_3 to 2000 *K*.

(4) **Action of Acids**

(i) Boron does not react with non oxidizing acids, however, it dissolves in nitric acid to form boric acids.

(ii) Al, *Ga* and In dissolve in acids forming their trivalent cations; however, *Al* and *Ga* become passive due to the formation of protective film of oxides.

(iii) Thallium dissolves in acids forming univalent cation and becomes passive in *HCl* due to the formation of water insoluble *TICl*.

(5) **Action of Alkalies**

(i) Boron dissolves only in fused alkalies,

$2B + 6NaOH$ (fused)$\rightarrow 2Na_3BO_3 + 3H_2$

(ii) Al and Ga dissolves in fused as well as in aqueous alkalies, $2Al + 2\ NaOH + 2H_2O \rightarrow 2NaAl\ O_2 + 3H_2$

(iii) Indium remains unaffected in alkalies even on heating.

(6) **Halides**

(i) All the group 13 elements from the trihalides, MX_3 on directly combining with halogens.

$M + X_2 \rightarrow MX_3$

(ii) All the trihalides of group 13 elements are known except Tl (III) iodide.

(iii) Due to small size and high electronegativity of boron, all boron halides are covalent and Lewis acids. These exist as monomeric molecules having plane triangular geometry (${sp}^2$ hybridization).

(iv) All Boron trihalides except BF_3 are hydrolysed to boric acid.

$BX_3 + 3H_2O \rightarrow B(OH)_3 + 3HX;$ $[X=Cl, Br, I]$

However, BF_3 forms as addition product with water,

$BF_3 + H_2O \rightarrow \mathrm{H}^+ [BF_3OH]^- \xrightleftharpoons{\mathrm{H_2O}} H_3O^+ [BF_3OH]^-$

.

BF_3 having less tendency for hydrolysis as well as Lewis acid nature, is extensively used as a catalyst in organic reactions e.g. Friedel- Crafts reaction.

(v) Boron atom, in BX_3, has six electrons in the outermost orbit and thus it can accept a pair of electrons form a donor molecule like NH_3 to complete its octet. Hence boron halides act as very efficient Lewis acids. The relative Lewis acid character of boron trihalides is found to obey the order ; $BI_3 > BBr_3 > BCl_3 > BF_3$.

However, the above order is just the reverse of normally expected order on the basis relative electronegativities of the halogens. Fluorine, being the most electronegative, should create the greatest electron deficiency on boron and thus B in BF_3 should accept electron pair from a donor very rapidly than in other boron trihalides. But this is not true.

This anomalous behaviour has been explained on the basis of the relative tendency of the halogen atom to back-donate its unutilised electrons to the vacant p orbitals of boron atom. In boron trifluoride, each fluorine has completely filled unutilised $2p$ orbitals while boron 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 fluorine electrons are transferred into the vacant $2p$ orbital of boron resulting in the formation of an additional $p\pi - p\pi$ bond. This type of bond formation is known as ***back bonding*** or ***back donation***. Thus the B- F bond has some double bond character. Back bonding may take place between boron and of the three fluorine atoms and thus boron trifluoride is regarded as a resonance hybrid of some structures.

Resonance in boron trifluoride is also evidenced by the fact that the three boron-fluorine bonds are *indentical* and are shorter than the usual single boron-fluorine bond As a result of back bonding, the electron deficiency of boron is reduced and hence Lewis acid nature is decreased. The tendency for the formation of back bonding ($p\pi$- $p\pi$ bond) is maximum in BF_3 and decreases very rapidly from BF_3 to BI_3 This is probably due to the fact that overlapping of the vacant $2p$ orbitals of boron cannot take place easily with the p-orbitals of high energy levels ($3p$ in Cl, $4p$ in Br and $5p$ in iodine). Thus BI_3Br_3 and BCl_3 are stronger Lewis acids than the BF_3.

(vi) Lewis acid character of halides of the group 13 elements decreases in the order, $B > Al > Ga > In$.

(vii) Boron halides form complex halides of the type, $[BF_4^-]$, in which boron atom extends its coordination number to four by utilising empty p-orbital. It cannot extend its coordination number beyond four due to non availability of d-orbitals. However, the other trihalides of this group form complex halides of the type $(AlF_6)^{3-}$, $(GaCl_6)^{3-}$ and $(InCl_6)^{3-}$, etc where the central atom extends its coordination number to 6 by the use of d-orbitals.

(viii) The fluorides of Al, Ga In and Tl are ionic and have high melting points. The high melting points of metal fluorides can be explained on the basis that their cations are sufficiently large and have vacant d-orbitals for attaining a coordination number of six towards the relatively small fluorine atom.

(ix) Other halides of Al, Ga, In and Tl are largely covalent in anhydrous state and possess low melting point. These halides do not show backbonding because of increases in the size of the element. However, the make use of vacant p-orbitals by co-ordinate bond *i.e.* metal atoms complete their octet by forming dimers. Thus aluminium chloride, aluminium bromide and indium iodide exist as dimers, both in the vapour state and in non-polar solvents.

The dimer structure for Al_2Cl_6 is evidenced by the following facts,

(a) Vapour density of aluminium chloride measured at 400^oC corresponds to the formula Al_2Cl_6.

(b) Bond distance between aluminium chlorine bond forming bridge is greater (2.21Å) than the distance between aluminum-chlorine bond present in the end (2.06 Å). The dimeric structure disappears when the halides are dissolved in water This is due to high heat of hydration which split the dimeric structure into $[M(H_2O)_6]^{3+}$ and $3X^-$ ions and the solution becomes good conductor of electricity.

$Al_2Cl_6 + 2H_2O \rightarrow 2[Al(H_2O)_6]^{3+} + 6Cl^-$; Therefore Al_2Cl_6 is ionic in water.

The dimeric structure may also split by reaction with donor molecules e.g. R_3N. This is due to the formation of complexes of the type R_3NAlCl_3 The dimeric structure of Al_2Cl_6 exist in vapour state below $473K$ and at higher temperature it dissociates to trigonal planar $AlCl_3$ molecule.

Boron halides do not exist as dimer due to small size of boron atom which makes it unable to co-ordinate four large-sized halide ions.

(x) BF_3 and $AlCl_3$ acts as catalyst and Lewis acid in many of the industrial process.

Anomalous Behaviour of Boron

Like *Li* and *Be*, Boron – the first member of group 13 also shows anomalous behaviour due to extremely low size and high nuclear charge/size ratio, high electronegativity and non-availability of d electrons. The main point of differences are,

(1) Boron is a typical non- metal whereas other members are metals.

(2) Boron is a bad conductor of electricity whereas other metals are good conductors.

(3) Boron shows allotropy and exists in two forms – crystalline and amorphous. Aluminium is a soft metal and does not exist in different forms.

(4) Like other non-metals, the melting point and boiling point of boron are much higher than those of other elements of group 13.

(5) Boron forms only covalent compounds whereas aluminium and other elements of group 13 form even some ionic compounds.

(6) The hydroxides and oxides of boron are acidic in nature whereas those of others are amphoteric and basic.

(7) The trihalides of boron (BX_3) exist as monomers On the other hand, aluminium halides exist as dimers (Al_2X_6).

(8) The hydrides of boron *i.e.* boranes are quite stable while those of aluminium are unstable.

(9) Dilute acids have no action on boron Others liberate H_2 from them.

(10) Borates are more stable than aluminates.

(11) Boron exhibit maximum covalency of four e.g., BH^-_4 ion while other members exhibit a maximum covalency of six e.g., $[Al(OH)_6]^{3-}$.

(12) Boron does not decompose steam while other members do so.

(13) Boron combines with metals to give borides e.g. Mg_3B_2. Other members form simply alloys.

(14) Concentrated nitric acid oxidises boron to boric acid but no such action is noticed other group members.

$B + 3HNO_3 \rightarrow H_3BO_3 + 3NO_2$

Diagonal relationship between Boron and Silicon

Due to its small size and similar charge/mass ratio, boron differs from other group 13 members, but it resembles closely with silicon, the second element of group 14 to exhibit diagonal relationship. Some important similarities between boron and silicon are given below,

(1) Both boron and silicon are typical non-metals, having high m.pt. b.pt nearly same densities ($B=2.35 gml^{-1}$ $S=2.34$ $g//ml$). low atomic volumes and bad conductor of current. However both are used as semiconductors.

(2) Both of them do not form cation and form only covalent compounds.

(3) Both exists in amorphous and crystalline state and exhibit allotropy.

(4) Both possess closer electronegativity values ($B=2.0$; $Si=1.8$).

(5) Both form numerous volatile hydrides which spontaneously catch fire on exposure to air and are easily hydrolysed.

(6) The chlorides of both are liquid, fume in most air and readily hydrolysed by water.

$BCl_3 + 3H_2O \rightarrow B(OH)_3 + 3HCl$

$SiCl_4 + H_2O \rightarrow Si(OH)_4 + 4HCl$

(7) Both form weak acids like H_3BO_3 and H_2SiO_3.

(8) Both form binary compounds with several metals to give borides and silicide. These borides and silicide react with H_3PO_4 to give mixture of boranes and silanes.

$3Mg+2B \rightarrow Mg_3B_2$; $Mg_3B_2+H_3PO_4 \rightarrow$ Mixture of boranes

(Magnesium boride)

$2Mg$ + Si $\rightarrow Mg_2Si$; $Mg_2Si + H_3PO_4 \rightarrow$Mixture of silanes

(magnesium silicide)

(9) The carbides of both Boron and silicon (B_4C and SiC) are very hard and used as abrasive.

(10) Oxides of both are acidic and can be reduced by limited amount of *Mg* In excess of *Mg* boride and silicide are formed.

$B_2O_3+3Mg \rightarrow 3MgO+2B$; $SiO_2+2Mg \rightarrow 2MgO+Si$

(11) Both the metals and their oxides are readily soluble in alkalies.

$$2B + 6NaOH \rightarrow \underset{\text{(borate)}}{2Na_3BO_3} + 3H_2\uparrow$$

$$Si + 2NaOH + H_2O \rightarrow \underset{\text{(silicate)}}{Na_2SiO_3} + 2H_2\uparrow$$

$$B_2O_3 + 6NaOH \rightarrow 2Na_3BO_3 + 3H_2O$$

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$

Both borates and silicates have tetrahedral structural units BO_4^{n-} and SiO_4^{n-} respectively. Boro silicates are known in which boron replaces silicon in the three dimensional lattice. Boron can however form planar BO_3 units.

(12) Acids of both these elements form volatile esters on heating with alcohol in presence of conc. H_2SO_4.

$$B(OH)_3 + 3ROH \rightarrow B(OR)_3 + 3H_2O$$

$$Si(OH)_4 + 4ROH \rightarrow Si(OR)_4 + 4H_2O$$

Boron and its compounds

Boron is the first member of group –13 (IIIA) of the periodic table. Boron is a non- metal . It has a small size and high ionization energy due to which it can not lose its valence electrons to form B^{+3} ion. Its compounds especially the hydrides and halides are electron deficient and behave as Lewis acid.

(1) **Ores of boron**

(i) *Borax or tincal* : $Na_2B_4O_7 . 10H_2O$

(ii) *Kernite or Rasorite* : $Na_2B_4O_7 . 4H_2O$

(iii) *Colemanite* : $Ca_2B_6O_{11} . 5H_2O$

(iv) *Orthoboric acid* : H_3BO_3 (It occurs in the jets of steam called soffioni escaping from ground in the volcanic region of the *Tuscany*). Boron is present to a very small extent (0.001%) in earth's crust.

(2) **Isolation :** Elemental boron in the form of dark brown powder is obtained either by reduction of boric oxide with highly electropositive metals like *K*, *Mg*, *Al*, *Na*, etc. in the absence of air and boron halides with hydrogen at high temperature eg.

$$B_2O_3 + 6K \xrightarrow{Heat} 2B + 3K_2O$$

$$2BCl_3 + 3H_2 \xrightarrow{1270\,K} 2B + 6HCl.$$

By thermal decomposition of boron triiodide over red hot tungsten filament and boron hydrides for example,

$$2BI_3 \xrightarrow{W,heat} 2B + 3I_2 \ ; \ B_2H_6 \xrightarrow{Heat} 2B + 3H_2$$

(3) **Properties :** It exists in mainly two allotropic forms *i.e.* amorphous dark brown powder and crystalline black very hard solid. It occurs in two isotopic forms, *i.e.*, ${}_5B^{10}$ (20% abundance) and ${}_5B^{11}$ (80% abundance). With air, boron forms B_2O_3 and BN at 973*K*, with halogens, trihalides (BX_3) are formed, with metals borides are formed. eg.

$$4B + 3O_2 \xrightarrow{Heat} \underset{\text{Boron trioxide}}{2B_2O_3}$$

$$2B + N_2 \xrightarrow{Heat} \underset{\text{Boron nitride}}{2BN}$$

$$2B + 3X_2 \longrightarrow \underset{\text{Boron trihalide}}{2BX_3}$$

$$3Mg + 2B \xrightarrow{Heat} \underset{\text{Magnesium boride}}{Mg_3B_2}$$

Water, steam and *HCl* have no action on *B*. oxidising acids (HNO_3, H_2SO_4) convert boron to H_3BO_3.

$$B + 3HNO_3 \longrightarrow H_3BO_3 + 3NO_2$$

$$2B + 3H_2SO_4 \longrightarrow 2H_3BO_3 + 3SO_2$$

Fused alkalies (*NaOH*, *KOH*) dissolve boron forming borates, liberating hydrogen.

$$2B + 6KOH \xrightarrow{Fused} 2K_3BO_3 + 3H_2$$

(4) **Uses of Boron :** Boron is used in atomic reactors as protective shields and control rods, as a semiconductors for making electronic devices in steel industry for increasing the hardness of steel and in making light composite materials for air crafts.

(5) **Compounds of Boron**

(i) ***Boron Hydrides***

Boron forms hydrides of the types B_nH_{n+4} and B_nH_{n+6} called boranes. Diborane is the simplest boron hydride which is a dimer of BH_3.

Preparation

(a) $8BF_3 + 6LiH \xrightarrow{450\,K} B_2H_6 + 6LiBF_4$

(b) $4BCl_3 + LiAlH_4 \longrightarrow 2B_2H_6 + 3AlCl_3 + 3LiCl$

(c) In the laboratory, it is prepared by the oxidation of sod. Borohydride with I_2.

$$2NaBH_4 + I_2 \xrightarrow{\text{Polyether}} B_2H_6 + 2NaI + H_2$$

Properties : (a) Since Boron in boranes never complete its octet of electrons hence all boranes are called as electron-deficient compounds or Lewis acids.

(b) All boranes catch fire in the presence of oxygen to liberated a lot of heat energy. Thus, they can also be used as high energy fuels.

$$B_2H_6 + 3O_2 \longrightarrow 2B_2O_3 + 3H_2O; \Delta H = -1976\,KJ/mole$$

(c) Boranes are readily hydrolysed by water.

$$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$$

(d) With carbon monoxide

$$B_2H_6 + 2CO \longrightarrow (BH_3 \leftarrow CO)_2$$

(e) Boranes are used for formation of hydroborates or borohydrides such as $LiBH_4$ or $NaBH_4$, which are extensively used as reducing agents in organic synthesis.

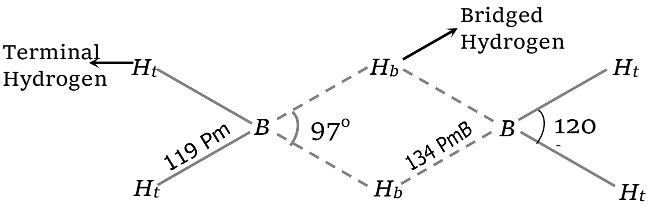
$$2LiH + B_2H_6 \xrightarrow{\text{Diethyl ether}} 2Li^+[BH_4]^-$$

$$2NaH + B_2H_6 \xrightarrow{\text{Diethyl ether}} 2Na^+[BH_4]^-$$

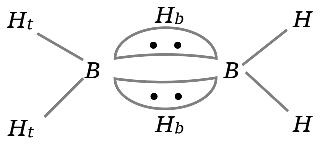
Structure of diborane : B_2H_6 has a three centre electon pair bond also called a banana shape bond.

(a) $B-H_t$: It is a normal covalent bond (two centre electron pair bond *i.e.*, $2c-2e$).

(b) $B-H_b$: This is a bond between three atoms, $B-H_b-B$, (three centre electron pair bond *i.e.,* $3c-2e$).



or



Structure of diborane (B_2H_6)

The other boron hydrides are $B_5H_9, B_4H_{10}, B_5H_{11}$ etc.

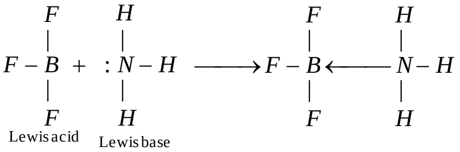
(ii) ***Boron Halides***

Boron reacts with halogens on strong heating to form boron halides .

$$2B + 3X_2 \xrightarrow{Heat} 2BX_3 (X = F, Cl, Br, I)$$

BF_3 and BCl_3 are gases, BBr_3 is a volatile liquid while BI_3 is a solid.

In these halides, the central boron atom has three shared pairs of electrons with the halogen atoms. Therefore, these have two electrons less than the octet and are electron deficient compounds. They acts as Lewis acids.



$$\underset{\text{Lewis acid}}{F-\overset{\overset{F}{|}}{\underset{\underset{F}{|}}{B}}} + \underset{\text{Lewis base}}{:\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}-H} \longrightarrow F-\overset{\overset{F}{|}}{\underset{\underset{F}{|}}{B}} \longleftarrow \overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}-H$$

The relative acidic strength of boron trihalides decreases as : $BI_3 > BBr_3 > BCl_3 > BF_3$.

(iii) ***Borax*** ($Na_2B_4O_7 . 10H_2O$)

It occurs naturally as **tincal** (Suhaga) which contains about 50% borax in certain land, lakes. It is also obtained from the mineral colemanite by boiling it with a solution of Na_2CO_3.

$$\underset{\text{Colemanite}}{Ca_2B_6O_{11}} + 2Na_2CO_3 \longrightarrow \underset{\text{Borax}}{Na_2B_4O_7} + 2CaCO_3 + 2NaBO_2$$

Properties : (a) Its aqueous solution is alkaline due to hydrolysis,

$$Na_2B_4O_7 + 7H_2O \longrightarrow 2NaOH + 4H_3BO_3 .$$

(b) On heating borax loses its water of crystallization and swells up to form a fluffy mass. On further heating, it melts to give a clear liquid which solidifies to a transparent glassy bead consisting of sodium metaborate ($NaBO_2$) and boric anhydride (B_2O_3),

$$Na_2B_4O_7.10H_2O \xrightarrow[-10H_2O]{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} \underset{\text{Borax bead}}{2NaBO_2 + B_2O_3}$$

Borax bead is used for the detection of coloured basic radicals under the name borax bead test.

Borax bead test **:** Borax bead is a mixture of $NaBO_2$ and B_2O_3. B_2O_3 on heating combines readily with a number of coloured transition metal oxides such as *Co*, *Ni*, *Cr*, *Cu*, *Mn*, etc. to form the corresponding metaborates which possess characteristic colours,

$$CoSO_4 \xrightarrow{\Delta} CoO + SO_3 \; ; \; CoO + B_2O_3 \longrightarrow \underset{\substack{\text{Cobalt meta borate} \\ \text{(Blue)}}}{Co(BO_2)_2}$$

Colours of some important metaborates are : Cupric metaborate, $Cu(BO_2)_2$ is dark blue, chromium metaborate, $Cr(BO_2)_2$ is green, nickel metaborate, $Ni(BO_2)_2$ is brown and manganese metaborate, $Mn(BO_2)_2$ is pink violet.

(c) When heated with C_2H_5OH and conc. H_2SO_4 it gives volatile vapours of triethyl borate which burns with a green edged flame.

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

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

This reaction is used as a test for borate radical in qualitative analysis.

Uses : (a) In making optical and hard glasses. (b) In the laboratory for borax bead test. (c) In softening of water. (d) In the preparation of medicinal soaps due to its antiseptic character.

(iv) **Boric acid or orthoboric acid (** H_3BO_3)

It is obtained from borax by treating with dil. *HCl* or dil. H_2SO_4,

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4H_3BO_3$$

It can also be obtained from the mineral colemanite by passing SO_2 through a mixture of powdered mineral in boiling water,

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

Properties : (a) It is a very weak monobasic acid, does not act as a proton doner but behaves as a Lewis acid *i.e.* it accepts a pair of electrons from OH^- ion of H_2O ,

$$H_3BO_3 + H_2O \longrightarrow [B(OH)_4]^- + H^+$$

It acts as a strong acid in presence of polyhydroxy compounds such as glycerol, mannitol etc. and can be titrated against strong alkali .

(b) With *NaOH* it forms, sodium metaborate,

$$H_3BO_3 + NaOH \longrightarrow NaBO_2 + 2H_2O$$

(c) With C_2H_5OH and conc. H_2SO_4, it gives triethyl borate

$$H_3BO_3 + 3C_2H_5OH \xrightarrow{Conc.H_2SO_4} B(OC_2H_5)_3 + 3H_2O$$

(d) ***Action of heat*** **:** The complete action of heat on boric acid may be written as,

$$\underset{\text{Boric acid}}{H_3BO_3} \xrightarrow{373\,K} \underset{\text{Metaboric acid}}{HBO_2} \xrightarrow{433\,K} \underset{\text{Tetra boric acid}}{H_2B_4O_7} \xrightarrow{\text{Red hot}} \underset{\text{Boron oxide}}{B_2O_3}$$

Structure : In boric acid, planar BO_3^{-3} units are joined by hydrogen bonds to give a layer structure.

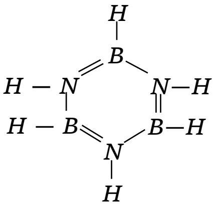
Uses : (a) As a food preservative. (b) As a mild antiseptic for eye wash under the name boric lotion. (c) For the preparation of glazes and enamels in pottery.

(v) **Borazine or Borasole or Triborine triamine (** $B_3N_3H_6$)

It is a compound of B, N and H. It is a colourless liquid and is also called inorganic benzene.

$$2\,B_2H_6 + 6NH_3 \xrightarrow{180^oC} 2B_3N_3H_6 + 12H_2 .$$

It has a six membered ring of alternating B and N atoms, each is further linked to a H- atom.



Borazine

(vi) **Boron nitride (*BN*)**

It is prepared by treating BCl_3 with an excess of NH_3 and pyrolysing the resulting mixture in an atmosphere of NH_3 at 750°C,

$$BCl_3 + NH_3 \longrightarrow [H_3N \longrightarrow BCl_3] \xrightarrow[\text{Excess}\,NH_3]{750^oC} BN + 3HCl .$$

It is a colourless, good insulator, diamagnetic and almost unreactive solid

Aluminium and its compounds

(1) **Ores of Aluminium :** Bauxite ($Al_2O_3.2H_2O$), Cryolite (Na_3AlF_6, Felspar ($KAlSi_3O_8$), Kaolinite ($Al_2O_3.2SiO_2.2H_2O$), Mica ($K_2O.3Al_2O_3.6SiO_2.2H_2O$), Corundum ($Al_2O_3$), Diaspore ($Al_2O_3.H_2O$), Alunite or alum stone [$K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$].

(2) **Extraction :** Aluminium is obtained by the electrolysis of the oxide (alumina) dissolved in fused cryolite. This involves following steps,

Purification of ore

(i) ***Baeyer's process***

$$\underset{\substack{\text{Finely powdered}\\ \text{(red)}}}{\text{Bauxite}} \xrightarrow[FeO \to Fe_2O_3]{\text{Roasted}} \text{Roasted ore} \xrightarrow[\substack{\text{High pressure (150}^o\text{C, 80 atm)}\\ \text{filtered, }Fe_2O_3\text{ as residue}}]{+\text{Caustic soda solution}}$$

$$\underset{\text{(Sod. Aluminate)}}{Filtrate} \xrightarrow[CO_2]{Filtered} Pure\ Al_2O_3 \xrightarrow{Heat} Al(OH)_3$$

(ii) ***Hall's process***

$$\underset{\substack{\text{(Finely powdered)}\\ \text{(red)}}}{\text{Bauxite}} \xrightarrow[\substack{\text{Fused, extracted with}\\ \text{water. Residue }Fe_2O_3}]{+Na_2CO_3} \text{Solution} \xrightarrow[\substack{\text{50-60}^o\text{C and filtered.}\\ \text{Filtrate }(Na_2CO_3)}]{CO_2}$$

$$\text{Precipitate } Al(OH)_3 \xrightarrow{Heat} Pure\ Al_2O_3$$

(iii) ***Serpek's process***

$$\underset{\substack{\text{(Finely powdered)}\\ \text{(white)}}}{\text{Bauxite}} \xrightarrow[\substack{\text{Heated to}\\ 1800^o\text{C}}]{+Coke+N_2} \underset{\text{Si which volatalises}}{\text{Silica reduced to}} + \underset{\text{aluminium nitride}}{\text{Alumina form}}\ AIN$$

$$\xrightarrow{Hydrolysis} Pure\ Al_2O_3 \xrightarrow{Heated} Al(OH)_3$$

(iv) ***Hall and Heroult process*** : It is used for extraction of aluminium. In this process a fused mixture of alumina (20%), cryolite (60%) and fluorspar (20%) is electrolysed using carbon electrodes. Whereas cryolite makes Al_2O_3 conducting fluorspar decreases the melting point of alumina.

Aluminium is refined by Hoope's electrolytic process.

(3) **Compounds of Aluminium**

(i) ***Aluminium oxide or Alumina*** (Al_2O_3) **:** It occurs in nature as colourless corundum and several coloured minerals like ruby (red), topaz (yellow), Sapphire (blue), amethyst (violet) and emerald (green). These minerals are used as ***precious stones*** (gems).

(ii) ***Aluminium chloride*** (Al_2Cl_6) **:** It is prepared by passing dry chlorine over aluminium powder.

$$Al_2O_3 + 3C + 3Cl_2 \to \underset{\text{(anhydrous)}}{2AlCl_3} + 3CO(g)$$

It exists as dimer Al_2Cl_6, in inert organic solvents and in vapour state. It sublimes at $100\,^oC$ under vacuum. Dimeric structure disappears when $AlCl_3$ is dissolved in water. It is hygroscopic in nature and absorbs moisture when exposed to air.

(iii) ***Thermite*** **:** A mixture of aluminium powder and Fe_2O_3 in the ratio 1:3. It is used for welding of iron. The reaction between Al and Fe_2O_3 is highly exothermic,

$$Al + Fe_2O_3 \to Al_2O_3 + Fe + \text{Heat}$$

(iv) ***Aluminium sulphate*** **[*Al₂(SO₄)₃*] :** It is used for the preparation of alums e.g., potash alum $Al_2(SO_4)_3.K_2SO_4\ .24H_2O$. It is also used for making fire proof clothes.

(iv) **Alums :** In general, the term alum is given to 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^+, M' is a trivalent cation like Al^{3+}, Fe^{3+} and Cr^{3+}.

Some important points to be noted about the alums are

(a) General formula is $M_2SO_4.M_2'(SO_4)_3.24H_2O$

$M =$ Monovalent metal; $M' =$ Trivalent metal

In alum crystals, 6 water molecules are held by monovalent ion, 6 water molecules are held by trivalent ion, 12 water molecules are held in the crystal structure.

(b) All alums are isomorphous. Aqueous solutions of alums are acidic due to cationic hydrolysis of trivalent cation.

(c) Double sulphates of divalent ions and trivalent ions with 24 water molecules in their crystals are known as Pseudoalums. General formula is $MSO_4.M'_2(SO_4)_3.24H_2O$

$M =$ Bivalent metal; $M' =$ Trivalent metal

(d) Pseudoalums are not isomorphous with alums.

(e) Feather alum or ‘Hair-salt’ $Al_2SO_4.18H_2O$ is a native form of aluminium sulphate.

(f) Potash alum is used for tanning of leather, as mordant in dyeing and calico printing, for sizing paper, as a syptic to stop bleeding and purification of water.

Some important alums are

Potash alum	$K_2SO_4.Al_2(SO_4)_3.24H_2O$
Sodium alum	$Na_2SO_4.Al_2(SO_4)_3.24H_2O$
Ammonium alum	$(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$
Chrome alum	$K_2SO_4.Cr_2(SO_4)_3.24H_2O$

Carbon Family

Carbon is the first member of group 14 or IVA of the periodic table. It consists of five elements carbon (*C*), silicon (*Si*), germanium (*Ge*), tin (*Sn*) and lead (*Pb*). Carbon and silicon are nonmetals, germanium is metalloid and tin and lead are metals.

(1) **Electronic configuration**

Elements	**Electronic configuration ($ns^2\ np^2$)**
$_6C$	$[He]2s^2 2p^2$
$_{14}Si$	$[Ne]3s^2 3p^2$
$_{32}Ge$	$[Ar]3d^{10} 4s^2 4p^2$
$_{50}Sn$	$[Kr]4d^{10} 5s^2 5p^2$
$_{82}Pb$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^2$

Physical properties

(1) **Non-metallic nature :** The non-metallic nature decreases along the group.

C Si	Ge	Sn	Pb
Non-metals	metalloid	metal	metal

(2) **Abundance :** Carbon and silicon are most abundant elements in earth's crust whereas germanium occurs only as traces. Tin and lead also occur in small amounts. Only carbon occurs in free state as coal, diamond and graphite and in combined state as carbonates, CO_2 petroleum and natural gas Silicon is the second most abundant element after oxygen in earth's crust in form of silicates and silica. Germanium found in traces in coal and in certain deposits. It important constituent for making conductors and transistors The important ore of tin is tin stone (SnO_2) or cassiterite. Lead is found is form of galena (PbS) anglesite ($PbSO_4$) and cerussite ($PbCO_3$) The abundance ratio in earth's crust is given below,

(3) **Density :** The density of these elements increases down the group as reported below

Element	C	Si	Ge	Sn	Pb
Density (g/ml)	3.51 (for diamond) 2.22 (for graphite)	2.34	5.32	7.26	11.34

(4) **Melting point and boiling points**

(i) The melting point and boiling point of this group members decrease down the group.

Element	C	Si	Ge	Sn	Pb
m.pt.(K)	4373	1693	1218	505	600
b.pt.(K)	–	3550	3123	2896	2024

(ii) The melting point and boiling point of group 14 elements are however, higher than their corresponding group 13 elements. This is due to the formation of four covalent bonds on account of four electrons in their valence shells which results in strong binding forces in between their atoms in solid as well as in liquid state.

(5) **Atomic radii and atomic volume**

(i) Both atomic radii and atomic volume increases gradually on moving down the group due to the effect of extra shell being added from member to member.

	C	Si	Ge	Sn	Pb
Atomic radius (pm)	0.77	111	122	141	144
Atomic volume (ml)	3.4	11.4	13.6	16.3	18.27

(ii) The atomic radii of group 14 elements are than their corresponding group 13 elements due to increase in nuclear charge in the same period.

(iii) Some of the ionic radii involving six co-ordination of these group elements are given below,

	C	Si	Ge	Sn	Pb
Ionic radius (M^{2+}) in pm	–	–	73	118	119
Ionic radius (M^{++}) in pm	–	40	53	69	78

(6) **Electronegativity :** The electronegativity decreases from C to Si and then becomes constant.

	C	Si	Ge	Sn	Pb
Electronegativity on pauling scale	2.5	1.8	1.8	1.7	1.6

The electronegativity from silicon onwards is almost is almost constant or shows a comparatively smaller decreases due to screening effects of d^{10} electrons in elements from Ge onwards.

(7) **Ionisation energy**

(i) The ionisation energy decreases regularly down the group; Pb however shows a higher value than Sn due to poor shielding of inner f-orbitals as a result of which effective nuclear charge experienced by outer shell electrons becomes more in Pb.

Ionisation energy ($kJ\ mol^{-1}$)	C	Si	Ge	Sn	Pb
IE_1	1086	786	761	708	715
IE_2	2352	1577	1537	1411	1450

(ii) The first ionisation energies of group 14 elements are higher than their corresponding group 13 elements because of smaller size.

(iii) The electropositive character of these elements increases down the group because of decreases in ionisation energy.

(8) **Oxidation state**

(i) Presence of four electrons in outermost shell of these elements reveals that the members of this family can gain four electrons forming M^{4+} or M^{4-} ions to show ionic nature or exhibit tetravalent covalent nature by sharing of four electron pairs in order to attain stable configuration.

(ii) The formation of M^{4+} or M^{4-} ions require huge amount of energy which is normally not available during normal course of reactions, therefore, these elements usually do not form M^{4+} or M^{4-} ions, but they usually form compounds with covalence of four.

(iii) *Ge, Sn* and *Pb* also exhibit +2 oxidation state due to inert pair effect.

(iv) Sn^{2+} and Pb^{2+} show ionic nature.

(v) The tendency to form +2 ionic state increases on moving down the group due to inert pair effect.

(9) **Catenation**

(i) The tendency of formation of long open or closed atom chains by the combination of same atoms in themselves is known as catenation.

(ii) The catenation is maximum in carbon and decreases down the group.

(iii) This is due to high bond energy of catenation.

(iv) Only carbon atoms also form double or triple bonds involving pπ-pπ multiple bond within itself.

$>C=C<;\ -C\equiv C-$

(v) Carbon also possesses the tendency to form closed chain compounds with *O, S* and *N* atoms as well as forming *pπ-pπ* multiple bonds with other elements particularly nitrogen and oxygen e.g. $C=O$; $C=N$; $C\equiv N$; $C=S$ are the functional groups present in numerous molecules due to this reason.

(vi) Carbon can form chain containing any number of carbon atoms *Si* and *Ge* cannot extend the chain beyond 6 atoms, while *Sn* and *Pb* do not form chains containing more than one or two atoms.

(vii) The reason for greater tendency of carbon for catenation than other elements in the group may further be explained by the fact that the $C-C$ bond energy is approximately of the same magnitude as the energies of the bond between *C* and other elements. On the other hand, the $Si-Si$ bond is weaker than the bond between silicon and other elements.

Bond	**Bond energy** (*k J/mol*)	**Bond**	**Bond energy** (*kJ/mol*)
$C-C$	348	$Si-Si$	180
$C-O$	315	$Si-O$	372
$C-H$	414	$Si-H$	339
$C-Cl$	326	$Si-Cl$	360
$C-F$	439	$Si-F$	536

(10) **Allotropy**

The phenomenon of existence of a chemical element in two or more forms differing in physical properties but having almost same chemical nature is known as allotropy. If an element or compound exists in two or more forms, it is also known as polymorphism e.g. zinc blende and wurtzite are polymorphs of *ZnS*.

Kinds of allotropy. Allotropy is of three types :

(i) ***Enantiotropy*** : When two forms of a solid substance exist together in equilibrium with each other at a particular temperature under normal pressure it is called enantiotropy.

For example, at normal pressure and temperature between $368.6\,K$ and $285\,K$, sulphur (solid) exist in two forms (rhombic sulphur), S_R and (monoclinic sulphur), S_M in equilibrium with each other. $S_R \rightleftharpoons S_M$

(ii) ***Monotropy*** : It is the type of allotropy in which only one allotrope is stable, under normal conditions the other being unstable e.g., diamond and graphite, oxygen and ozone etc.

(iii) ***Dynamictropy*** : It is the type of allotropy in which there is a true equilibrium between the two allotropes, one changing into the other at exactly the same rate as the reverse occurs. Both allotropes are stable over a wide range of temperature.

For example, liquid sulphur exist in two forms, the pale yellow mobile form called S_λ and dark viscous form called S_μ in equilibrium with each other. $S_\lambda \rightleftharpoons S_\mu$

With increase in temperature, the later form is formed at the expense of the former but when the liquid is cooled, the reverse change occur. Thus sulphur shows both enantiotropy and dynamictropy.

Cause of allotropy : (i) In general the allotropy among solid substances is due to the difference in crystalline structure. (ii) It may also be due to the presence of different number of atoms e.g., O_2 and O_3, S_8, S_2 etc. (iii) It may be due to the difference in nuclear spins e.g., ortho and para hydrogen.

Different allotropic forms Except lead, all elements show allotropy.

(i) Carbon has two crystalline allotropic forms i.e., diamond and graphite. In diamond C atom is sp^3 hybridised and it has a three dimensional network structure. Since no valence electron is available, hence diamond is a bad conductor of electricity. However in graphite C atom is sp^2 hybridised and has a delocalised π-electron cloud responsible for its high electrical conductivity. It may be noted that diamond is thermodynamically less stable than graphite at ordinary temperatures.

(ii) Silicon has both crystalline and amorphous forms.

(iii) Tin has three crystalline modifications with the following equilibrium temperature

$$\underset{\text{(Grey)}}{\alpha - tin} \overset{15.2^oC}{\rightleftharpoons} \underset{\text{(White)}}{\beta - Sn} \overset{161^oC}{\rightleftharpoons} \underset{\text{(Rhombic)}}{\gamma - Sn} \overset{232^oC}{\rightleftharpoons} Liquid\ tin$$

The conversion of white tin to grey tin is accompanied by an increase in volume and the latter, being very brittle, easily crumbles down to powder. This phenomenon is called tin disease tin pest or tin plague.

Chemical properties

(1) **Hydrides :** All the elements of group 14 combine with hydrogen directly or indirectly to form the covalent hydrides, MH_4 (*M* = *C, Si, Ge, Sn* or *Pb*). The number of hydrides and the ease of preparation decrease on going from carbon to lead.

The hydrides of silicon are called *silanes* having the general formula Si_nH_{2n+2}. The hydrides of germanium are called *germanes* while those of tin are called the *stannanes*. Only lead forms an unstable hydride of the formula, PbH_4 called the *plumbane*.

Three hydrides of germanium, *i.e.*, GeH_4, Ge_2H_6 and Ge_3H_8 and only two hydrides of tin *i.e.,* SnH_4 and Sn_2H_6 are well known.

(2) **Oxides :** *Carbon forms five oxides* CO, CO_2, C_3O_2 (carbon suboxide), C_5O_2 and $C_{12}O_9, C_3O_2$ is the anhydride of malonic acid and CO_2 is the anhydride of H_2CO_3 (carbonic acid) CO_2 *is a non-polar linear molecule due to maximum tendency of C to form* $p\pi$–$p\pi$ *multiple bond with oxygen. Si* forms SiO_2. *Pb* forms a number of oxides. *PbO* can be obtained by heating $Pb(NO_3)_2$, $2Pb(NO_3)_2 \xrightarrow{\text{Heat}} 2PbO + 4NO_2 + O_2$.

The red form of *PbO* is called ***litharge*** and the yellow form is ***massicot***. Pb_3O_4 (Red lead, or Sindur) is prepared by heating litharge in air at 470°*C*, $6PbO + O_2 \xrightarrow{470^oC} 2Pb_3O_4$, Pb_3O_4 is a mixed oxide of $PbO_2.2PbO.Pb_2O_3$ is called lead sesquioxide. GeO_2, SnO_2 etc. are also network solids.

CO_2 and SiO_2 is acidic, GeO_2 is weakly acidic while SnO_2 and PbO_2 are amphoteric in nature.

All the elements of group 14 except silicon from monoxides *e.g.,* CO, GeO, SnO and *PbO*. Out of these monoxides only *CO* is neutral, while all other monoxides are basic.

(3) **Halides :** Elements of group 14 react with halogens directly to form tetrahedral and covalent halides except *C* where its halide is produced by the action of halogens on hydrocarbons. $PbBr_4$ and PbI_4 do not exist because Pb^{4+} is a strong oxidant and Br^- and I^- are strong reductants. Hence Pb^{4+} ion is difficult to survive in presence of strong reductants Br^- and I^- and is immediately reduced to Pb^{2+}.

(4) **Carbides :** Carbides are binary compounds of carbon with elements of lower or about equal electronegativity.

Preparation : Carbides are generally prepared by heating the elements orits oxide with carbon or hydrocarbon at very high temperatures.

$$Ca + 2C \longrightarrow BaC_2\ ;\quad 2Li + 2C \longrightarrow Li_2C_2$$

$$CaO + 3C \longrightarrow CaC_2 + CO$$

$$4Li + C_2H_2 \longrightarrow Li_2C_2 + LiH$$

Carbides are classified into three types on the basis of chemical bonding.

(1) **Salt like carbides :** These carbides are formed by the metals of groups IA, IIA, IIIA (except boron), coinage metals, Zinc, cadmium & some lanthanides.

(i) ***Acetylides*** *:* These are ionic carbides which yield acetylene on hydrolysis. The alkali metals and copper, silver and gold form M_2C_2 type compounds. These contain C_2^{2-} ions.

(ii) ***Methanides*** : These carbides evolve methane on hydrolysis. Al_4C_3, Be_2C, Mn_3C etc are some are of methanides. These contains C^{4-} groups.

(iii) ***Allylides*** : These carbides evolve allylene (methyl acetylene) on hydrolysis. This type of the carbides is only Mg_2C_3 it contains C_3^{4-} discrete groups.

(2) **Mixed carbides :** These carbides yield a mixture of hydrocarbons on hydrolysis, carbides of iron group, UC_2 and ThC_2 belong to this group.

(3) **Covalent carbides :** The only true covalent carbides are those of SiC (carborundum) and $B_4C, B_{13}C_2$ etc. These are chemicallyinert so become hard.

On account of hardness, these are used as abrasives.

(4) **Metallic or interstitial carbides :** If these carbides possess metallic lustre high electrical conductivity and chemically inert. These are extremely hard like diamond and possess very high melting points.

Ability to form complexes : The ability of group 14 elements to form complexes is highly favoured by a high charge, small size and availability of empty orbitals of the right energy. The compounds in which carbon shows a covalency of four possess a closed shell electronic configuration of a noble gas and therefore carbon does not form complexes. Silicon and other heavier elements, however, can form complexes due to the availability of energetically suitable empty d-orbitals and a coordination number of six is found in these complexes. For example, in the formation of $[SiF_6]^{2-}$, four covalent and two co-ordinate bonds are formed as a result of sp^3d^2 hybridisation. As such the resulting ion has an octahedral geometry. Thus elements like Si, Ge, Sn and Pb have an ability to increase their co-ordination number from four to six. Other examples of hexa co-ordianted species are : $[GeF_6]^{2-}, [SnCl_6]^{2-}, [PbCl_6]^{2-}$ etc.

Anomalous behaviour of Carbon

Carbon is found differ in many properties from the rest of the members of group 14. This is because of the following : (i) Its smallest size (ii) Its high electronegativity (iii) Its property to catenate (iv) Absence of d-orbitals in it.

Some of the properties in which it differs from other members are,

(1) The melting and boiling points of carbon are very high as compared to the rest to the members of the family.

(2) Carbon in its diamond form is one of the hardest substance known.

(3) It has maximum tendency to show catenation.

(4) Carbon has high tendency to form $P\pi - P\pi$ multiple bonds with other elements like nitrogen, oxygen, sulphur etc. Other members of the family form $P\pi - d\pi$ bonds and that also to a lesser extent.

(5) CO_2 is a gas while the dioxides of all other members are solids.

(6) Carbon is not affected by alkalies whereas other members react on fusion. For example, silicon form silicates, $Si + 2NaOH + 1/2\,O_2 \rightarrow \underset{\text{Sodium silicate}}{Na_2SiO_3} + H_2$.

Silicon and its compounds

Silicon, being a second member of group – 14, has a much larger size and lower electronegativity than that of carbon. As a result silicon does not form double bond with itself or with oxygen. Thus SiO bonds are much stronger than $Si - Si$ and $Si - H$ bonds. Silicon has vacant 3d-orbitals in its valence shell due to which it can extend its covalency from four to five and six.

(1) **Occurrence :** Silicon is the second most abundant element (27.7%) in earth's crust next to oxygen .It does not occur in free state. It occurs mainly in the form of Silica and silicates. Silicates are formed in rocks and clay as silicates of Mg, Al, K or Fe. e.g. Feldspar ; $K_2Al_2O_3.6SiO_2$, Kaolinite; $Al_2O_3.2SiO_2.2H_2O$.

(2) **Preparation :** Elemental silicon is obtained by reduction of silica with high purity coke in an electric furnace using excess of silica e.g. $SiO_2 + 2C \longrightarrow Si + 2CO$

Very high purity silicon required for making semiconductors is obtained by reduction of highly purified $SiCl_4$ form ($SiHCl_3$) with hydrogen followed by purification by zone refining eg.

$$SiCl_4 + 2H_2 \longrightarrow Si + 4HCl \; ; \; SiHCl_3 + H_2 \longrightarrow Si + 3HCl$$

(3) **Properties :** (i) Silicon exists in three isotopes ${}_{14}Si^{29}$ (most common), ${}_{14}Si^{30}$ with air at high temperature SiO_2 form,

$$Si + O_2 \longrightarrow SiO_2.$$

(ii) With steam, Si reacts when heated to redness to liberate hydrogen, $Si + 2\,H_2O \xrightarrow{\text{Redness}} Si\,O_2 + 2\,H_2$.

(iii) With halogens, Si reacts at elevated temperature forming SiX_4 except fluorine which reacts at room temperature.

(iv) Silicon combines with C at 2500K forming Silicon Carbide (SiC) known as carborundum (an extremely hard substance),

$$Si + C \xrightarrow{2500\,K} SiC.$$

(v) It reacts with metals like Ca, Mg etc in an electric arc furnace to form Silicides (Ca_2Si, Mg_2Si etc.)

(vi) Silicon dissolves in hot aqueous alkalies liberating hydrogen, $Si + 4NaOH \xrightarrow{Heat} Na_4SiO_4 + 2H_2 \uparrow$

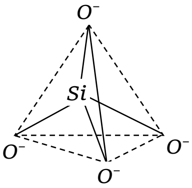
(vii) It also dissolves in fused Na_2CO_3 displacing carbon $Na_2SiO_3 + C$.

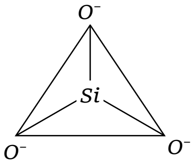
(4) **Uses of silicon :** (i) It is added to steel as ferrosilicon (an alloy of *Fe* and *Si*) to make it acid resistant.

(ii) It is used in the pure form as a starting material for production of silicon polymers (Silicones).

(5) **Compounds of silicon**

(i) ***Silicates*** : Silicates are the metal derivatives of silicic acid (H_4SiO_4). The basic of all silicates is the SiO_4^{4-} anion. In SiO_4^{4-} anion, *Si* is sp^3 hybridised, and it forms four covalent bonds with four negatively charged oxygen atoms. SiO_4^{4-} anion has a tetrahedral shape.

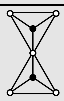
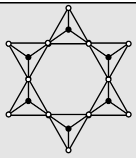
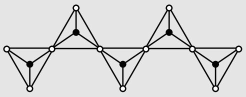
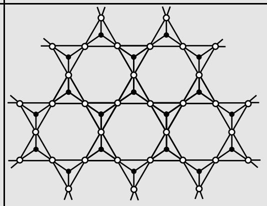




Alkali metal silicates are commonly prepared by fusing metal oxides or metal carbonates with sand (SiO_2) at high temperatures. For examples, sodium silicate can be prepared by fusing sand with sodium carbonate.

$$\underset{\text{sand}}{Na_2CO_3 + SiO_2} \xrightarrow{\text{Fusion}} \underset{\text{sodium silicate}}{Na_2SiO_3} + CO_2(g)$$

Table 18.1 Classification of silicates

No. of carners of SiO_4 tetrahedra shared	No. of common oxygen atoms	Structure ● **Silicon** ○ **Oxygen** Diagram and Description	Net charge and Anion in the silicate structure	Example
Zero	Zero	 Discrete SiO_4^{4-}anion	$Si = +4$ $O = -8$ Net = –4 SiO_4^{4-}	ortho-silicates Mg_2SiO_4
1	1	 Island structure	$Si = +8$ $O = -14$ Net = –6 $(Si_2O_7)^{6-}$	Pyro-silicates
2	2	Ring anion	$Si = +12$ $O = -18$ Net = –6 $(Si_3O_9)^{6-}$	Wollas-tonite $Ca_3Si_3O_9$
2	2	 Ring anion	$Si = +24$ $O = -36$ Net=–12 $(Si_6O_{18})^{12-}$	Beryl, $Be_3Al_2Si_6O_{18}$
2	2	 Chain anion	$Si = +4$ $O = -6$ Net = –2 $(SiO_3^{2-})_n$	Pyroxenes, e.g., $MgCaSi_2O_6$ Asbestos
3	3	 Two dimensional sheet structure	$Si = +8$ $O = -10$ Net = –2 $(Si_2O_5^{2-})_n$	Clays, talc kaolinite
4	4	– Three dimensional network	$Si = +4$ $O = -4$ $(SiO_3)_n$	Quartz, Tridymite and Cristo-balite

(ii) ***Silica or silicon dioxide* (SiO_2)**

It occurs in nature in various forms such as sand, quartz and flint .It is also a constituent of various rocks. It is solid at room temperature. It is insoluble in water.

Silica has a three dimensional network structure in which each *Si* is bonded to four oxygen atoms which are tetrahedrally disposed around silicon atom. Each *O* atom is shared by two *Si* atoms. It may be noted that CO_2 is a gas, while SiO_2 is hard solid with very high melting point.

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

$$SiF_4 + 2HF \longrightarrow \underset{\text{(Hydroflouro silicic acid)}}{H_2SiF_6}$$

HF readily dissolves Silica, therefore *HF* can not be store in glass bottles which contain Silica.

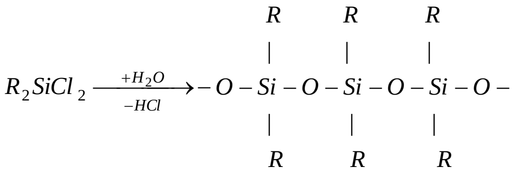
It is used in large amount to form mortar which is a building material. It is also used in the manufacture of glass and lenses.

(iii) ***Silicones***

Polymeric organo-silicon compounds containing $Si-O-Si$ bonds are called silicones. These have the general formula $(R_2SiO)_n$. Where R is CH_3-group (majority cases) or C_6H_5-group.

Preparation : The preparation of silicones is generally carried out by the hydrolysis of dialkyldichlorosilanes (R_2SiCl_2) or diaryldichlorosilanes (Ar_2SiCl_2), which are prepared by passing vapours of RCl or $ArCl$ over silicon at $570\,K$ with copper as a catalyst.

$$2RCl + Si \xrightarrow{Cu,\,570\,K} R_2SiCl_2$$



$$R_2SiCl_2 \xrightarrow[-HCl]{+H_2O} -O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-$$

Silicones may be obtained in the form of oils, rubber on resins depending upon the extent of polymerisation which depends upon reaction conditions and nature of alkyl groups.

Properties and Uses : Silicones are water repellent and quite inert chemically. These resist oxidation, thermal decomposition and attack by organic reagents. These are also good electrical insulators and antifoaming agents. These have found the following uses :

(a) Silicones have been used for making waterproof papers, wools, textiles, wood etc., after coating these articles with silicones.

(b) The viscosities of silicones do not change with changes in temperature, therefore, these are used as all weather lubricants.

(c) As antifoaming agent in industrial processes.

(d) As a mould releasing agent in rubber industry and foundry. It avoids the sticking of the castings to the mould.

(e) For making body implants in cosmetic surgery due to its inert nature.

(f) Silicones are now incorporated in paints for resisting dampness and for water proofing.

(g) Due to their water repellent nature and high dielectric constant, silicones are used in electrical condensers.

(iv) ***Silica gel* :** When a mineral acid (Such as HCl) is added to a concentrated solution of a silicate, gelatinous white ppt. of hydrated silica (silicic acid) separate out.

$$Na_2SiO_3 + 2HCl \longrightarrow 2NaCl + SiO_2.xH_2O$$

The white ppt. thus obtained is heated to lose water. When the water content is very low, the solid product is called silica gel. It possesses excellent absorptive properties due to its porous nature and is used for absorbing moisture and an adsorbent in chromatography.

(v) ***Silanes* :** The hydrides of silicon are called silanes. For example; SiH_4 Silane, Si_2H_6 disilane, Si_3H_8 Trisilane Si_4H_{10} Tetrasilane.

Silanes are poisonous. These are much less stable than the corresponding alkanes and are decomposed into elements on heating above $450\,^oC$. Their thermal stability decreases with increase in molecular mass. Unlike alkanes, silanes are reducing agents.

(vi) ***Glass***

Glass is an amorphous and transparent solid which is obtained by solidification of various silicates and borates of potassium and calcium.

Preparation : Ordinary glass is a mixture of sodium and calcium silicates and is produced by fusing together a mixture of sodium carbonate, calcium oxide and silicon dioxide (Silica) in a furnace at about 1700K

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2 \uparrow$$

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

On continuously heating the entire amount of CO_2 is driven out and clear viscous fused mass is obtained. It is poured into moulds to get different types of articles, which are allowed to cool gradually.

This typed of glass is called soda glass or soft glass which has the approximate composition, $Na_2SiO_3, CaSiO_3, 4SiO_2$.

Various varieties of glass : The different varieties of glasses and their special constituents are given below,

Table 18.2

Type of glass	Constituents	Special use
Soft glass	$Na_2CO_3, CaCO_3, SiO_2$	Ordinary glass for window panes, test tubes, bottles, etc.
Hard glass	$K_2CO_3, CaCO_3, SiO_2$	For combustion tubes and chemical glassware
High refractive index glass (Flint glass)	Lead oxide, K_2CO_3	For making lenses cut glasses
Pyrex glass	Na_2CO_3, Al_2O_3, B_2O_3 or borax, sand	For high quality glass apparatus cooking utensils
Crook's glass	$K_2CO_2, PbCO_3$, CeO_2, sand	Absorbs ultra violet rays, for making lenses
Jena glass	Zinc and Barium Boro silicates	It is resistant to heat shock and common reagent. It is used for making good quality of glass wares.

Coloured glass : Addition of transition metal compounds to glass give coloured glasses . Small amounts of Cr(III), Mn(IV), Co(II) and Fe(III) compounds impart green, violet blue or brown colour respectively

Table 18.3

Compound added – Colour imparted	Compound added – Colour imparted
Cobalt axide (CoO) – Blue	Chromium oxide (Cr_2O_3) – Green
Cuprous oxide (Cu_2O) – Red	Auric chloride ($AuCl_3$) – Ruby
Cadmium sulphide (CdS) – Lemon yellow	Manganese dioxide (MnO_2) – Purple

Etching of glass : Glass is attacked by hydrofluoric acid. This property is used in the etching of glass. The glass to be etched is coated with a thin layer of wax and the design to be produced is scratched with a needle. An aqueous solution of HF is applied to the exposed part. After some time it is placed in hot water and wax is removed from the surface. The marks are engraved on the exposed parts.

Tin and its Compounds

(1) **Important ore :** Cassiterite (tin stone) SnO_2

(2) **Extraction of tin from tin stone.**

(i) ***Concentration*** : The powdered tin stone is concentrated by gravity separation and the magnetic impurities like wolframite etc., are separated from tin stone by magnetic separators.

(ii) ***Roasting*** : The concentrated ore is heated in a current of air when impurities like S and As are oxidised to volatile SO_2 and As_2O_3. Iron pyrites change to their oxides and sulphates.

(iii) ***Leaching and washing*** : The roasted ore is treated with water when $CuSO_4$ and $FeSO_4$ are washed away from the main ore. Further lighter ferric oxide is washed away leaving behind heavier ore particles known as black tin containing 60 to 70% SnO_2.

$$SnO_2 + 2C \longrightarrow Sn + 2CO$$

$$\underset{\text{Flux}}{CaCO_3} \longrightarrow CaO + CO_2 \,;\; CaO + SiO_2 \longrightarrow \underset{\text{Slag}}{CaSiO_3}$$

Molten tin is drawn into blocks. It contains 99.5 percent of tin metal and is called block tin.

Refining of tin : It is purified by liquation, poling and electrolytic refining.

For very high purity, it is purified by electrolytic method. The electrolyte consists of tin sulphate containing a small amount of hydrofluorosilicic acid (H_2SiF_6) and sulphuric acid. Impure tin makes anode while pure tin sheet serves as cathode.

(3) **Comounds of Tin**

(i) ***Stannic oxide, SnO₂*** **:** It is prepared by heating tin strongly in air. $Sn + O_2 \longrightarrow SnO_2$

It can also be prepared by heating metastannic acid obtained by the action of conc. HNO_3 on tin.

$$Sn + 4HNO_3(conc.) \longrightarrow H_2SnO_3 + 4NO_2 + H_2O$$

$$H_2SnO_3 \xrightarrow{\Delta} SnO_2 + H_2O$$

It occurs in nature as tin stone. It is a white solid insoluble in water and is amphoteric in nature. With $NaOH$ it forms Na_2SnO_3. It is used for making enamels and glazes for tiles, pottery etc. it is also used as a polishing powder.

(ii) ***Stannous oxide, SnO*** **:** It is prepared by heating stannous oxalate $SnC_2O_4 \xrightarrow{\Delta} SnO + CO + CO_2$

Oxidation of SnO to SnO_2 is checked by CO. It is a grey solid which oxidises readily to SnO_2 when heated in air.

$$2SnO + O_2 \longrightarrow 2SnO_2$$

It is amphoteric in nature and reacts both with acids and alkalies. With $NaOH$ it forms Na_2SnO_2.

(iii) ***Stannous sulphide, SnS*** **:** It is insoluble in water but soluble in hot conc. HCl. In yellow ammonium polysulphide it gets converted to ammonium thiostannate $(NH_4)_2SnS_3$.

(iv) ***Stannous chloride, SnCl₂*** **:** When Sn is heated with HCl (conc.) $SnCl_2$ is formed.

$$Sn(s) + HCl(Conc.) \longrightarrow SnCl_2(aq) + H_2(g)$$

On concentrating the resulting solution, crystals of $SnCl_2.2H_2O$ are obtained. When it is heated, basic tin chloride is obtained.

$$SnCl_2.2H_2O(s) \xrightarrow{\Delta} Sn(OH)Cl + HCl + H_2O$$

To obtain anhydrous $SnCl_2$, heat Sn in dry HCl gas.

$$Sn + 2HCl \xrightarrow{\Delta} SnCl_2 + H_2$$

(a) It exists as a anhydrous (white powder, m.p. = $520K$, rhombic solid) as well as dihydrate $SnCl_2.2H_2O$ (white, m.p. $= 480K$, monoclinic) and is used as a strong reducing agent in conc. HCl in laboratory.

$SnCl_2$ also reduces $HgCl_2$

$$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$$

$$Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg + SnCl_4$$

(b) It is precipitated as hydroxide by an alkali.

(c) If forms addition compounds with NH_3 such as $SnCl_2.NH_3$ and $SnCl_2.2NH_3$.

(v) ***Stannic chloride, SnCl₄*** **:** It is obtained by the action of Cl_2 on molten Sn

$$Sn + 2Cl_2 \longrightarrow SnCl_4$$

It can also be obained by distilling tin with mercuric chloride.

$$Sn + 2HgCl_2 \longrightarrow SnCl_4 + 2Hg$$

(a) It is a colourless fuming liquid (b.p $388K$) soluble in water.

It is used as a strong reducing agent in laboratory. It is also used as a mordant in dyeing.

(b) It can exist as $SnCl_4.5H_2O$ and with excess water it is hydrolysed to form basic chloride and ultimately stannic acid (H_2SnO_4).

$$SnCl_4 + H_2O \longrightarrow Sn(OH)Cl + HCl$$

$$Sn(OH)Cl + 3H_2O \longrightarrow Sn(OH)_4 \text{ or } H_2SnO_4 + 3HCl$$

Its hydrolysis is prevented by HCl which forms complex anion $[SnCl_6]^{2-}$

(c) It forms double salts with NH_3, N_2O, PCl_5 e.g., $SnCl_4.4NH_3$.

It is used as a mordant and tinning agent.

(vi) ***Stannous fluoride, SnF₂*** **:** It is obtained by dissolving SnO in HF

$$SnO + 2HF \longrightarrow SnF_2 + H_2O$$

It is a white crystalline solid insoluble in water. It is used in tooth pastes to help in controlling dental decay.

Tinning : During cooking, organic acids present in food stuff attack the household utensils made of copper, brass etc. in the presence of air. since tin is not attacked by organic acids, the utensils are protected by tinning.

Lead

(1) **Some important ores**

Galena; $-PbS$ (Main); Cerussite $-PbCO_3$

Anglesite $-PbSO_4$, lararkite $PbO.PbSO_4$

(2) **Extraction from galena**

(i) ***Concentration*** **:** The finely powdered ore is concentrated by froth floatation process.

(ii) ***Reduction process***

(a) *Self reduction process*

• **Roasting** : The concentrated ore is heated in air. lead sulphide is partially converted into lead oxide and lead sulphate.

$$2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2$$

$$PbS + 2O_2 \xrightarrow{\Delta} PbSO_4$$

• **Self reduction :** The supply of air is cut off and the temperature is raised to melt the charge. The galena reduces both PbO and $PbSO_4$ to metallic lead.

$$PbS + 2PbO \xrightarrow{\Delta} 3Pb + SO_2$$

$$PbS + PbSO_4 \xrightarrow{\Delta} 2Pb + 2SO_2$$

(b) *Carbon reduction process*

• **Roasting :** The powdered ore is mixed with lime and roasted in excess of air. the impurities like S and As are oxidised to their volatile oxides while PbS is converted to PbO.

$$S + O_2 \xrightarrow{\Delta} SO_2\ ;\ 4As + 3O_2 \xrightarrow{\Delta} 2As_2O_3$$

$$2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2$$

• **Smelting :** Roasted ore is mixed with coke and lime (flux) and smelted in a blast furnance. PbO is reduced to Pb.

$$PbO + C \xrightarrow{\Delta} Pb + CO\ ;\ PbO + CO \xrightarrow{\Delta} Pb + CO_2$$

$$\underset{\text{Lime}}{CaCO_3} \xrightarrow{\Delta} CaO + CO_2\ ;\ CaO + SiO_2 \xrightarrow{\Delta} \underset{\text{Slag}}{CaSiO_3}$$

(iii) ***Purification*** **:** It is purified electrolytically. The electrolyte consists of lead silicofluoride $(PbSiF_6)$ and hydrofluosilicic acid. Impure lead is made anode and sheet of pure lead serves as cathode.

Properties of Lead

With oxygen lead form oxides, with chlorine it forms chloride $PbCl_2$, with sulphur it gives sulphide PbS and with H_2SO_4 the corresponding sulphate $PbSO_4$. With $NaOH$ it forms plumbate.

$$Pb + 2NaOH \longrightarrow Na_2PbO_2 + H_2$$

(3) **Compounds of Lead**

(i) ***Lead oxide (Litharge), PbO*** **:** It is prepared by heating the nitrate.

$$2Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + 4NO_2 + O_2$$

It exist in two varieties yellow form (messicol) and red form (litherage). Yellow form is prepared by gently heating lead in air while fusion yield red form. It is insoluble in water and amphoteric in nature.

It dissolves in $NaOH$ to form sod. Plumbite.

$$PbO + 2NaOH \longrightarrow Na_2PbO_2 + H_2O$$

It can be reduced with various reducing agents (C, H_2, CO etc.) to lead.

It is used in paints and varnishes, for making flint glass, for making lead (II) salts and for glazing pottery.

(ii) ***Lead dioxide, PbO₂*** **:** It is prepared by heating $Pb_3O_4(2PbO + PbO_2)$ with dilute HNO_3

$$Pb_3O_4 + 4HNO_3 \xrightarrow{\Delta} 2Pb(NO_3)_2 + 2H_2O + PbO_2$$

It is amphoteric in nature and dissolve in $NaOH$ to form sodium plumbate.

$$2NaOH + PbO_2 \longrightarrow Na_2PbO_3 + H_2O$$

It is a powerful oxidising agent. It reacts with conc. HCl on warming to give $PbCl_4$

$$PbO_2 + 4HCl \xrightarrow{Warm} PbCl_4 + H_2O$$

It is a chocolate brown solid insoluble in water and nitric acid. It is a powerful oxidizing agent. It is amphoteric in nature and is used in lead storage batteries and in safety matches.

(iii) ***Minium or sindhur or Red lead, Pb₃O₄*** **:** It is prepared by heating PbO in air to above $673K$.

$$6PbO + O_2 \xrightarrow{673K} 2Pb_3O_4$$

It is a red crystalline solid insoluble in water.

It is a mixed oxide $PbO_2 + 2PbO$ and reacts with HNO_3 to form $Pb(NO_3)_2$ and PbO_2

$$2PbO.PbO_2 + 4HNO_3 \to Pb(NO_3)_2 + 2H_2O + PbO_2$$

It is a strong oxidising agent. It liberates chlorine with conc. HCl and O_2 with conc. H_2SO_4

$$Pb_3O_4 + 8HCl \longrightarrow 3PbCl_2 + 4H_2O + Cl_2$$

$$2Pb_3O_4 + 6H_2SO_4 \longrightarrow 6PbSO_4 + 6H_2O + O_2$$

It is used as a protective paint in iron, steel and silver mirrors and in glass industry.

(iv) ***Lead chloride, PbCl₂*** **:** It can be prepared by treating a salt of lead with dil. HCl

$$Pb(NO_3)_2 + 2HCl \longrightarrow PbCl_2 + 2HNO_3$$

It can also be obtained by dissolving lead (II) oxide to lead (II) carbonate in HCl. It is soluble in hot water but precipitate out in cold water. it is soluble in conc. HCl due to the formation of a complex, tetrachloroplumbate (II) ion.

$$PbCl_2 + 2HCl \longrightarrow H_2[PbCl_4]$$

It also reacts with hot lime water to give $Pb(OH)Cl$ which is used as white pigment.

$$PbCl_2 + Ca(OH)_2 \longrightarrow Pb(OH)Cl + CaO + HCl$$

(v) ***Lead tetrachloride, PbCl₄*** **:** It is obtained by heating of PbO_2 with conc. HCl.

It is a yellow oily fuming liquid which decomposes into $PbCl_2$ at $373K$.

$$PbCl_4 \xrightarrow{373K} PbCl_2 + Cl_2$$

It also combines with HCl to form complex hexachloroplumbate (IV) ion.

$$PbCl_4 + 2HCl \longrightarrow H_2[PbCl_6]$$

Nitrogen Family

Nitrogen is the first member of group 15 or VA of the periodic table. It consists of five elements nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi). The elements of this group are collectively called ***pnicogens*** and their compounds as pniconides. The name is derived from Greek word "Pniomigs" meaning suffocation. Pniconide contain M^{3-} species.

(1) **Electronic configuration**

Elements	Electronic configuration ($ns^2\ np^3$)
$_7N$	$[He]2s^2 2p^3$
$_{15}P$	$[Ne]3s^2 3p^3$
$_{33}As$	$[Ar]3d^{10} 4s^2 4p^3$
$_{51}Sb$	$[Kr]4d^{10} 5s^2 5p^3$
$_{83}Bi$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^3$

Physical properties

(1) **Physical state :** Nitrogen– (gas), phosphorus – (solid) (vaporises easily), *As*, *Sb*, *Bi*–solids.

Nitrogen is the most abundant gas in the atmosphere. It constitutes about 78% by volume of the atmosphere. Phosphorus is the most reactive element in this group and its yellow form is always kept under water.

(2) **Atomic radii :** Atomic radii increases with atomic number down the group i.e., from *N* to *Bi* due to addition of extra principal shell in each succeding elements.

(3) **Ionisation energy :** The ionisation values of the elements of this group decreases down the group due to gradual increases in atomic size.

(4) **Electronegativity :** Generally the elements of nitrogen family have high value of electronegativity. This value shows a decreasing trend in moving down the group from nitrogen to bismuth.

(5) **Non-metallic and metallic character :** Nitrogen and phosphorus are non-metals, arsenic and antimony are metalloids (semi-metal) and bismuth a typical metal.

(6) **Molecular state :** Nitrogen readily forms triple bond (two $p\pi - p\pi$ bonds) and exists as discrete diatomic gaseous molecule $(N \equiv N)$ at room temperature. Phosphorus, arsenic and antimony exist in the form of discrete tetra atomic molecules such as P_4, As_4, Sb_4 in which the atoms are linked to each other by single bonds.

(7) **Melting and boiling points :** The melting points and boiling points of group 15 elements do not show a regular trend. M.pt. first increases from *N* to As and then decreases from *As* to *Bi*. Boiling point increases from *N* to *Sb*. Boiling point of *Bi* is less than *Sb*.

(8) **Allotropy :** All the members of group 15 except *Bi* exhibit the phenomenon of allotropy.

(i) Nitrogen exists in two solid and one gaseous allotropic forms.

(ii) Phosphorus exists in several allotropic forms such as white, red, scarlet, violet and black form.

(a) *White or yellow phosphorus* : White phosphorus is prepared from rock phosphate $Ca_3(PO_4)_2, SiO_2$ and coke which are electrically heated in a furnace.

$$2Ca_3(PO_4)_2 + 6SiO_2 \xrightarrow{\Delta} 6CaSiO_3 + P_4O_{10};$$

$$P_4O_{10} + 10C \xrightarrow{\Delta} P_4 + 10CO$$

When exposed to light, it acquires a yellow colour.

(b) *Red phosphorus* : It is obtained by heating yellow phosphorus, between 240 –250°*C* in the presence of an inert gas. Yellow phosphorus can be separated from red phosphorus by reaction with *NaOH* (*aq*) or *KOH* (*aq*) when the former reacts and the latter remains unreacted.

(iii) Arsenic exists in three allotropic forms namely grey, yellow and black. Antimony also exists in three forms, viz., metallic, yellow and explosive.

(9) **Oxidation state :** The members of the group 15 exhibit a number of positive and negative oxidation states.

(i) ***Positive oxidation states*** **:** The electronic configuration $(ns^2np^3)$for the valence shell of these elements shows that these elements can have +3 and +5 oxidation states. In moving down this group, the stability of +3 oxidation state increases. It may be pointed out here that nitrogen does not exhibit an oxidation state of +5, because it fails to expand its octet due to nonavailability of vacant *d*-orbitals.

(ii) ***Negative oxidation states*** **:** For example oxidation state of nitrogen is –3. The tendency of the elements to show –3 oxidation state decreases on moving down the group from *N* to *Bi*.

(10) **Catenation** (self linkage) **:** Elements of group 15 also show some tendency to exhibit catenation. This tendency goes on decreasing in moving down the group due to gradual decrease in their bond (*M*–*M*) energies.

Chemical properties

(1) **Hydrides :** All the members form volatile hydrides of the type AH_3. All hydrides are pyramidal in shape. The bond angle decreases on moving down the

group due to decrease in bond pair–bond pair repulsion.

$$\underset{107^o}{NH_3}\quad \underset{94^o}{PH_3}\quad \underset{92^o}{AsH_3}\quad \underset{91^o}{SbH_3}\quad \underset{90^o}{BiH_3}$$

The decreasing order of basic strength of hydrides is as follows : $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$.

The increasing order of boiling points is as follows :

$$PH_3 < AsH_3 < NH_3 < SbH_3.$$

NH_3 is thermally most stable and BiH_3 is least stable. This is because in NH_3, $N - H$ covalent bond is the strongest due to small size of N atom. Hence, the *decomposition temperature of* NH_3 *will be the highest*. The increasing order of reducing character is as follows, $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$.

(2) **Halides :** The members of the family form trihalides (MX_3) and pentahalides (MX_5). The trihalides are sp^3-hybridized with distorted tetrahedral geometry and pyramidal shape while pentahalides are sp^3d-hybridized and are trigonal *bi*pyramidal in shape. The trihalides are hydrolysed by water and ease of hydrolysis decreases when we move down the group. Hence, NCl_3 is easily hydrolysed but $SbCl_3$ and $BiCl_3$ are partly and reversibly hydrolysed. NF_3 is not hydrolysed due to lack of vacant *d*-orbital with nitrogen. PF_3 and PF_5 are also not hydrolysed because the $P - F$ bond is stronger than $P - O$ covalent bond. The hydrolysis products of the halides are as follows :

$$NCl_3 + 3H_2O \rightarrow NH_3 + 3HOCl$$

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

$$2AsCl_3 + 3H_2O \rightarrow As_2O_3 + 6HCl$$

$$SbCl_3 + H_2O \rightarrow SbOCl + 2HCl$$

$$BiCl_3 + H_2O \rightarrow BiOCl + 2HCl$$

Their basic character follows this decreasing order as $NI_3 > NBr_3 > NCl_3 > NF_3$. Except NF_3, the trihalides of nitrogen are unstable and decompose with explosive violence. NF_3 is stable and inert. NCl_3 is highly explosive. Trifluorides and trichlorides of phosphorus and antimony act as Lewis acid. The acid strength decreases down the group. For example, acid strength of tri-chlorides is in the order ; $PCl_3 > AsCl_3 > SbCl_3$.

Nitrogen does not form pentahalides due to non-availability of vacant *d*-orbitals. The pentachloride of phosphorus is not very stable because axial bonds are longer (and hence weaker) than equitorial bond. Hence, PCl_5 decomposes to give PCl_3 and Cl_2 ;

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2.$$

The unstability of PCl_5 makes it a very good chlorinating agent. All pentahalides act as lewis acids since they can accept a lone pair of electron from halide ion.

Solid PCl_5 *is an ionic compound consisting of* $[PCl_4]^+$ $[PCl_6]^-$, $[PCl_4]^+$ has a tetrahedral structure, while $[PCl_6]^-$ has an octahedral structure.

Since, PCl_5 reacts readily with moisture it is kept in well stoppered bottles.

PI_5 does not exist due to large size of I atoms and lesser electronegativity difference between phosphorus and iodine.

Down the group, the tendency to form pentahalides decreases due to inert pair effect. *e.g.,* BiF_5 *does not exist.*

(3) **Oxides :** These elements form oxides of the type X_2O_3, X_2O_4 and X_2O_5.

The acidic strength of oxides :

$$N_2O < NO < N_2O_3 < N_2O_4 < N_2O_5.$$

The decreasing order of stability of oxides of group 15 follows as,

$$P_2O_5 > As_2O_5 > Sb_2O_5 > Bi_2O_5$$

The nature of oxides of group 15 elements is as follows,

N_2O_3 and P_2O_3 (acidic) ; As_2O_3 and Sb_2O_3 (amphoteric); Bi_2O_3 (basic)

(4) **Oxyacids :** N_2 and P_4 of this group forms oxyacids which are discussed further. In this chapter.

Anamalous behaviour of Nitrogen

Nitrogen is known to differ form other members of the family because of the following facts,

(1) Its small size (2) Its high electronegativity (3) Its high ionisation energy (4) non-availability of *d*-orbital in the valence shell. (5) Its capacity to form $p\pi$-$p\pi$ multiple bonds.

The main points of difference are,

(i) Nitrogen is a gas while other members are solids.

(ii) Nitrogen is diatomic while other elements like phosphorus and arsenic form tetra-atomic molecules (P_4, As_4).

(iii) Nitrogen form five oxides $(N_2O, NO, N_2O_3, N_2O_4$ and $N_2O_5)$ while other members of the family form two oxides (tri and pentaoxides).

(iv) Hydrides of nitrogen show H-bonding while those of other elements do not.

(v) Nitrogen does not show pentacovalency because of absence of *d*-orbitals while all other elements show pentacovalency.

(vi) Nitrogen dos not form complexes because of absence of d-orbitals while other elements show complex formation e.g., $[PCl_6]^-, [AsCl_6]^-$ etc.

(vii) The hydride of nitrogen (NH_3) is highly basic in nature while the hydrides of other elements are slightly basic.

(viii) Except for NF_3, other halides of nitrogen e.g., NCl_3, NBr_3 and NI_3 are unstable.

Nitrogen and its compounds

N_2 was discovered by ***Daniel Rutherford***. It is the first member of group 15 in the periodic table.

Occurrence : N_2, occurs both in the free state as well as in the combined state. N_2 occurs in atmosphere to the extent of 78% by volume in free state. N_2 is present in many compounds such as potassium nitrate (nitre). Sodium nitrate (Chile salt peter) and many ammonium compounds. N_2 is an important constituent of proteins in plants and animals in combined state.

Preparation : It is prepared by the following methods,

(1) **Laboratory method** : In the laboratory N_2 is prepared by heating an aqueous solution containing an equivalent amounts of NH_4Cl and $NaNO_2$.

$$NH_4Cl\,(aq.) + NaNO_2(aq.) \xrightarrow{\text{Heat}} N_2(g) + 2H_2O(l) + NaCl$$

(2) **Commercial preparation :** Commercially N_2 is prepared by the fractional distillation of liquid air.

Physical properties : N_2 is a colourless, odourless and tasteless gas. It is a non-toxic gas. It's vapour denstiy is 14. It has very low solubility in water.

Chemical properties

(1) N_2 is neutral towards litmus. It is chemically unreactive at ordinary temp. It is neither combustible nor it supports combustion.

(2) The *N* – *N* bond in N_2 molecule is a triple bond $(N \equiv N)$ with a bond distance of 109.8 *pm* and bond dissociation energy of 946 $kJ\ mol^{-1}$

(3) **Combination with compounds :** N_2 combines with certain compounds on strong heating . eg

$$\underset{\text{Calsium carbide}}{CaC_2} + N_2 \xrightarrow{1300\,K} \underset{\text{Calsium cyanamide}}{CaCN_2 + C}$$

$$\underset{\text{Aluminium oxide}}{Al_2O_3} + N_2 + 3C \xrightarrow{2100\,K} \underset{\text{Al.nitride}}{2AlN} + 3CO$$

Both these compounds are hydrolysed on boiling with water to give ammonia.

$$CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3$$

$$AlN + 3H_2O \longrightarrow Al\,(OH)_3 + NH_3$$

Therefore, calcium cyanamide is used as a fertilizer under the name nitrolim $(CaCN_2 + C)$

Uses of nitrogen : N_2 is mainly used in the manufacture of compounds like $NH_3, HNO_3, CaCN_2$ etc.

Compounds of nitrogen

(1) **Hydrides of nitrogen – Ammonia**

Preparation of ammonia : Ammonia is prepared in the laboratory by heating a mixture of NH_4Cl and slaked lime, $Ca(OH)_2$

$$2NH_4Cl + Ca(OH)_2 \xrightarrow{\Delta} CaCl_2 + 2NH_3 + 2H_2O$$

Moist NH_3 gas is dried over quick lime, CaO. However, it cannot be dried over conc. H_2SO_4, P_2O_5 because being basic it forms salts with them. Anhydrous $CaCl_2$ also cannot be used because it forms a complex $CaCl_2.8NH_3$ with it.

Manufacture : (i) Ammonia is manufacture by Haber's process. A mixture of pure N_2 and H_2 (in the ratio 1 : 3 by volume) is compressed to 200 – 1000 atmospheres and passed over finely divided Fe (as catalyst) and Mo (as promoter) at $750\,K$

$$N_2 + 3H_2 \overset{Fe + Mo,\ 750\text{K},\ 200\text{–}1000}{\rightleftharpoons} 2NH_3 + 93.6\,KJ\,mol^{-1}$$

Favourable conditions for maximum yield of NH_3 are :

(a) excess of reactants (N_2 and H_2) (b) high pressure (c) low temperature and (d) use of catalyst and a promoter.

(ii) By the hydrolysis of calcium cyanamide $(CaCN_2)$ with super-heated steam at $450\,K$. $CaCN_2$ itself is obtained by heating CaC_2 and N_2 at $1270\,K$.

$$CaC_2 + N_2 \xrightarrow{\Delta} CaCN_2 + C$$

$$CaCN_2 + 3H_2O \xrightarrow{450\,K} CaCO_3 + 2NH_3$$

Properties of NH_3 : It is a colourless gas with pungent smell, highly soluble in H_2O and basic in nature. It liquefies on cooling under pressure to give liquid ammonia (bp. 240*K*). On heating, it causes intense cooling and hence is used as a refrigerant in ice, factories and cold storages.

It burns in excess of air to give N_2 and H_2O and is oxidised to NO when passed over heate Pt at $1075\,K$.

$$4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O$$

$$4NH_3 + 5O_2 \xrightarrow{Pt.1075\,K} 4NO + 6H_2O$$ (ostwald process)

It reduces heated CuO to Cu and Cl_2 to HCl (which combines with NH_3 to give NH_4Cl).

$$2NH_3 + 3CuO \xrightarrow{Heat} 3Cu + 3H_2O + N_2$$

$$\underset{\text{Excess}}{8NH_3} + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$$

With excess of Cl_2, it gives NCl_3. With Br_2 it gives NH_4Br and N_2 is set free.

$$NH_3 + \underset{\text{Excess}}{3Cl_2} \longrightarrow NCl_3 + 3HCl$$

$$8NH_3 + 3Br_2 \longrightarrow 6NH_4Br + N_2$$

With I_2, it gives nitrogen triiodide ammonia (brown ppt) which is explosive in dry state and decomposes when struck

$$2NH_3 + 3I_2 \longrightarrow NH_3.NI_3 + 3HI$$

$$8NH_3.NI_3 \longrightarrow 5N_2 + 9I_2 + 6NH_4I$$

It forms amides with active metals like Na, K etc.

$$2Na + 2NH_3 \xrightarrow{575\,K} 2NaNH_2 + H_2$$

It forms complexes with many substances, *e.g.,*

$[Ca(NH_3)_6]\ Cl_2$, $[Co(NH_3)_6]Cl_2, [Cu(NH_3)_4]SO_4$,

$[Ag(NH_3)_2]Cl$, $[Cd(NH_3)_4Cl_2$ etc.

Its aqueous solution is weakly basic due to the formation of OH^- ions, $NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$

With sodium hypochlorite in presence of glue or gelatine, excess of ammonia gives hydrazine

$$2NH_3 + NaOCl \longrightarrow NH_2.NH_2 + NaCl + H_2O$$

It undergoes self ionization in liquid state and acts as a solvent. $2NH_3 \longrightarrow NH_4^+ + NH_2^-$

Many polar compounds are soluble in liquid ammonia.

With Nessler's reagent (an alkaline solution of K_2HgI_4), ammonia and ammonium salts give a brown precipitate due to the formation of Millon's base.

$$K_2HgI_4 \rightleftharpoons 2KI + HgI_2$$

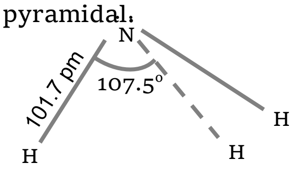
$$HgI_2 + 2NH_3 \longrightarrow I - Hg - NH_2 + NH_4I$$

$$2NH_2 - Hg - I + H_2O \longrightarrow NH_2 - Hg - O - Hg - I + NH_4I$$

or $2K_2HgI_4 + NH_3 + 3KOH \longrightarrow H_2N - Hg - O - Hg - I + 7KI + 2H_2O$

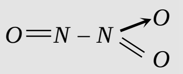
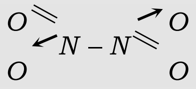
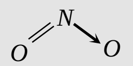
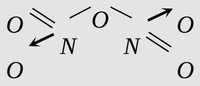
It is used as a refrigerant and in the manufacture of fertilizers.

Strcture of NH_3 : The N atom in NH_3 is sp^3-hybridized containing a lone pair of electrons due to which the $H-N-H$ bond angle is 107.5^o. As a result NH_3 molecule is pyramidal.



(2) **Oxides of nitrogen :** Nitrogen combines with O_2 under different conditions to form a number of binary oxides which differ with respect to the oxidation state of the nitrogen atom. The important oxides are $N_2O, NO, N_2O_3, NO_2, N_2O_4$ and N_2O_5. N_2O and NO both are neutral. Nitrous oxide (N_2O) has a sweet taste and its main use is as anaesthetic. When inhaled in mild quantities it causes hysterical laughter so it is also called Laughing gas. Nitric oxide (NO) can be obtained by treating a mixture of sodium nitrite and ferrous sulphate with dil. H_2SO_4. N_2O_5 is the strongest oxidising agent.

Table : 18.4 *Oxides of Nitrogen*

Oxide	Structure	Physical appearance	Preparation
Nitrous oxide (N_2O) +1	$N \equiv N \rightarrow O$	Colourless gas	By heating ammonium nitrate upto 240°C $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$, It is Collected over hot water
Nitric oxide (NO) +2	$N = O$	Colourless	(a) By the action of cold dil. HNO_3 on copper turnings (Laboratory method) $3Cu + 8$ dil. $HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$ (b) By the action of H_2SO_4 on a mixture of $FeSO_4$ and KNO_3 (4:1) $2KNO_3 + 5H_2SO_4 + 6FeSO_4 \rightarrow 2KHSO_4 + 3Fe_2(SO_4)_3 + 4H_2O + 2NO$ (c) By catalytic oxidation of ammonia. $4NH_3 + 5O_2 \xrightarrow[850^0C]{Pt} 4NO + 6H_2O$
Dinitrogen trioxide (N_2O_3) +3		Blue solid	(a) By the action of 50% HNO_3 on arsenious oxide. $2HNO_3 + As_2O_3 + 2H_2O \rightarrow NO + NO_2 + 2H_3AsO_4$ $\downarrow$ 250 K N_2O_3
Dinitrogen tetraoxide (N_2O_4) +4		Colourless liquid	(a) By heating nitrates of heavy metals, e.g., lead nitrate. $2Pb(NO_3)_2 \xrightarrow{673\,K} 4NO_2 + 2PbO + 2O$ (b) By heating copper turnings with conc. HNO_3. $Cu + 4\ HNO_3$ (conc.) $\rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$
Nitrogen dioxide (NO_2) +4		Brown gas	
Dinitrogen pentoxide (N_2O_5) +5		Colourless gas	(a) By dehydrating HNO$_3$ with phosphorus pentoxide $4HNO_3 + P_4O_{10} \rightarrow 2N_2O_5 + 4HPO_3$

(3) **Oxyacids of nitrogen *:*** Oxyacids of nitrogen are HNO_2, HNO_3, $\underset{\text{(Nitroxylic acid)}}{H_4N_2O_4}$ and $\underset{\text{(Pernitric acid)}}{HNO_4}$, which are explosive.

(i) ***Nitrous acid (HNO₂)* :** It is prepared by adding ice cold dil, HCl or dil, H_2SO_4 to a well cooled solution of any nitrite $(NaNO_2, Ba(NO_2)_2$ etc.).

$$NaNO_2 + HCl \longrightarrow NaCl + HNO_2$$

$$2KNO_2 + H_2SO_4 \longrightarrow K_2SO_4 + 2HNO_2$$

It oxidises H_2S to S, KI to I_2 and acts as a reducing agent in presence of strong oxidising agent, i.e., it reduces acidified $KMnO_4, K_2Cr_2O_7, H_2O_2$ etc. to Mn^{2+}, Cr^{3+} and H_2O respectively.

(ii) ***Nitric acid (HNO₃)*** : HNO_3 is called aqua fortis. It is prepared in the laboratory by distillation of nitre with conc. H_2SO_4.

$$2NaNO_3 + H_2SO_4 \longrightarrow 2HNO_3 + Na_2SO_4\,.$$

Commercially, it is obtained by Ostwald's process. In this process, NH_3 is first catalytically oxidised to NO which is cooled to about $300\,K$ and then oxidised by air to NO_2. Absorption of NO_2 in water in presence of oxygen gives HNO_3

$$4NH_3 + 5O_2 \xrightarrow{Pt.1975\ K} 4NO + 6H_2O$$

$$2NO + O_2 \rightleftharpoons 2NO_2\ ;\ 4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$

From air (Birkeland Eyde electric arc process)

$$N_2 + O_2 \rightleftharpoons 2NO\ ;\ \Delta H_f^o = +135\ kJ\ mol^{-1}$$

$$2NO + O_2 \xrightarrow{50^o C} 2NO_2$$

$$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$

$$3HNO_2 \longrightarrow HNO_3 + H_2O + 2NO$$

Properties : It is a very strong acid and decomposes on boiling or in presence of sunlight. It acts as a strong oxidising agent. It oxidises nonmetals and metalloids to their respective oxy-acids, *i.e.*, C to H_2CO_3, S to H_2SO_4, P to H_3PO_4, I_2 to HIO_3, As to H_3AsO_4 (arsenic acid) and Sb to H_3SbO_4 (antimonic acid), while nitric acid itself is reduced to NO_2.

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

Nitric acid reacts with metals to form nitrates and is itself reduced to NO, N_2O, NO_2 or NH_3 (which further reacts with HNO_3 to give NH_4NO_3) depending upon the concentration of the acid, activity of the metal and the temperature of the reaction.

(i) Very active metals such as Mn, Mg, Ca, etc. give H_2 on treatment with very dilute HNO_3 (2%).

(ii) Less active metals like Cu, Hg, Ag, Pb etc. give NO with dil. HNO_3. Zinc, however, gives N_2O with dil HNO_3 and NH_4NO_3 with very dilute HNO_3.

$$Zn + 10HNO_3(\text{dilute}) \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$

$$Zn + 10HNO_3(\text{very dilute}) \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

Similarly, Fe and Sn react with dilute nitric acid to give NH_4NO_3.

(iii) Conc. HNO_3 gives NO_2 both with active metals (Zn, Pb etc.) and less active metals (Cu, Hg, Ag etc.)

$$Cu + 4HNO_3(\text{Conc.}) \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

Tin is, however, oxidized by conc. HNO_3 to metastannic acid (H_2SnO_3).

$$Sn + 4HNO_3 \longrightarrow H_2SnO_3 + 4NO_2 + H_2O$$

Passivity : Fe, Cr, Ni and Al become passive in conc. HNO_3 (i.e., lose their normal reactivity) due to the formation of a thin protective layer of the oxide on the surface of the metal which prevents further action. Nitric acid has no action on noble metals (Au, Pt) but these metals dissolve in aqua regia (3 vol. HCl + 1 vol. HNO_3) forming their respective chlorides.

$$HNO_3 + 3HCl \longrightarrow 2H_2O + NOCl + 2[Cl]$$

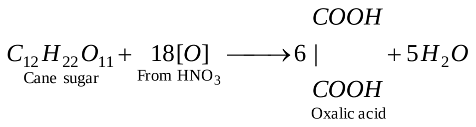
$$Au + 3[Cl] \longrightarrow AuCl_3;\ Pt + 4[Cl] \longrightarrow PtCl_4$$

These chlorides subsequently dissolve in excess of HCl forming their corresponding soluble complexes. Thus,

$$\underset{\text{Auric chloride}}{AuCl_3} + HCl \longrightarrow \underset{\text{Aurochloric acid}}{HAuCl_4}$$

$$\underset{\text{Platinic chloride}}{PtCl_4} + 2HCl \longrightarrow \underset{\text{Chloro platinic acid}}{H_2PtCl_6}$$

Sugar on oxidation with nitric acid gives oxalic acid. Nitric acid reacts with glycerine to give glycerol trinitrate or nitro glycerine, with toluene it gives 2, 4, 6-trinitrotoluene (T.N.T.) and with cellulose (cotton) it gives cellulose trinitrate (gun cotton). All these are used as explosives.



$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + \underset{\text{From HNO}_3}{18[O]} \longrightarrow 6\underset{\text{Oxalic acid}}{\begin{array}{c} COOH \\ | \\ COOH \end{array}} + 5H_2O$$

Table : 18.5 ***Oxyacids of nitrogen***

Name of oxoacid	la M.	Structure	Oxidation State of N	Basicity	pKa	Nature

Hyponitrous acid	$H_2N_2O_2$	$\begin{array}{c} \ddot{N}-OH \\ \parallel \\ HO-\underset{\cdot\cdot}{N} \end{array}$	+1	2(dibasic)	Very weak	Highly explosive
Nitrous acid	HNO_2	$H-\underset{\underset{O}{\downarrow}}{N}=O$	+3	1 (monobasic)	3.3	Unstable, Weak acid
Nitric acid	HNO_3	$H-O-\underset{\underset{O}{\downarrow}}{N}=O$	+5	1 (monobasic)	-3.0	Stable, Strong acid
Pernitric acid	HNO_4	$O=\underset{\underset{O}{\downarrow}}{N}-O-O-H$	+5	1 (monobasic)		Unstable and explosive

Phosphorus and its compounds

It is the second member of group 15 (VA) of the Periodic table. Due to larger size of *P*, it can not form stable $P\pi$ - $P\pi$ bonds with other phosphorous atoms where as nitrogen can form $P\pi - P\pi$ bonds .

(1) **Occurrence :** Phosphorous occurs mainly in the form of phosphate minerals in the crust of earth. Some of these are :

(i) Phosphorite $Ca_3(PO_4)_2$, (ii) Fluorapatite $Ca_5(PO_4)_3F$, (iii) Chlorapatite $3Ca_3(PO_4)_2.CaCl_2$, (iv) Hydroxyapatite; $Ca_5(PO_4)_3OH$. Phosphates are essential constituents of plants and animals. It is mainly present in bones, which contains about 58% calcium phosphate.

(2) **Isolation :** Elemental phosphorus is isolated by heating the phosphorite rock with coke and sand in an electric furnace at about 1770*K*,

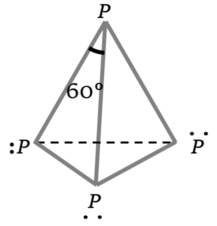
$$2Ca_3(PO_4)_2+6SiO_2 \longrightarrow \underset{\text{Calicum silicate}}{6CaSiO_3}+P_4O_{10} \text{ ;}$$

$$P_4O_{10}+10C \longrightarrow P_4+10CO$$

(3) **Allotropic forms of phosphorus :** Phosphorus exists in three main allotropic forms,

(i) White phosphorus, (ii) Red phosphorus, (iii) Black phosphorus

(i) ***White or yellow phosphorus*** **:** It is obtained from phosphate rock or phosphorite as explained above. It exists as P_4 units where four P atoms lie at the corners of a regular tetrahedron with $\angle PPP = 60^o$. Each P atom is linked to three other P atoms by covalent bonds. there are total six bonds and four lone pairs of electrons present in a P_4 molecule of white phosphorus.



Properties : White phosphorus is extremely reactive due to strain in the P_4 molecule, poisonous, soft, low melting $(317\,K)$ solid, soluble in CS_2, alcohols and ether. It has a garlic odour. Persons working with white P develop a disease known as Phossy jaw in which jaw bones decay. It turns yellow on exposure to light. Hence, it is also called yellow phosphorus.

It spontaneously catches fire in air with a greenish glow which is visible in the dark $(P_4+3O_2 \rightarrow P_4O_6)$. This phenomenon is called phosphorescence. Because of its very low ignition temperature $(303\,K)$, it is always kept under water.

With sulphur it gives tetraphoshorus trisulphide with explosive violence which is used in “strike anywhere matches”.

$$8P_4+3S_8 \longrightarrow 8P_4S_3$$

With metals phosphorus forms phosphides. For example,

$$P_4+6Mg \longrightarrow 2Mg_3P_2$$

With aqueous alkalies, on heating, white phosphorus gives phosphine

$$\overset{0}{P_4}+3NaOH+3H_2O \longrightarrow \underset{\text{(Phosphine)}}{\overset{-3}{PH_3}} + \underset{\text{Sod. hypophosph ite}}{3NaH_2\overset{+1}{PO_2}}$$

It is an example of a disproportionation reaction where the oxidation state of P decreases from 0 to –3 (in PH_3) and increases to +1 (in NaH_2PO_2)

White phosphorus acts as a strong reducing agent. It reduces HNO_3 to NO_2 and H_2SO_4 to SO_2. It also reduces solutions of Cu, Ag and Au salts to their corresponding metals. For examples,

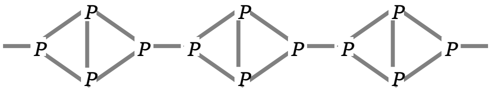
$$P_4+8CuSO_4+14H_2O \longrightarrow 8Cu+8H_2SO_4+4H_3PO_4$$

$$P_4+20AgNO_3+16H_2O \longrightarrow 20Ag+4H_3PO_4+20HNO_3$$

(ii) ***Red phosphorus*** : It is obtained by heating white phosphorus at $540-570K$ out of contact with air in an inert atmosphere (CO_2 or coal gas) for several hours.

White phosphorus $\xrightarrow[CO_2 \text{ or coal gas}]{540-570K}$ Red phosphorus

Red phosphorus exists as chains of P_4 tetrahedra linked together through covalent bonds to give a polymeric structure as shown.



Due to its polymeric structure, red phosphorus is much less reactive and has m.p. much higher than that of white phosphorus.

Properties : Red phosphorus is a hard, odourless, non poisonous solid, insoluble in organic solvents such as CS_2, alcohol and ether. Its ignition temperature is much higher than that of white phosphorus and thus does not catch fire easily. It does not show phosphorescence.

It sublimes on heating giving vapours which condense to give white phosphorus. It is denser than white phosphorus and is a bad conductor of electricity.

It burns in oxygen at $565K$ to give phosphorus pentoxide, reacts with halogens, sulphur and alkali metals only when heated forming their corresponding salts.

It does not react with caustic alkalies and this property is made use in separating red phosphorus from white phosphorus.

(iii) ***Black phosphorus*** : It is obtained by heating white phosphorus at $470K$ under high pressure (4000–12000atm) in an inert atmosphere.

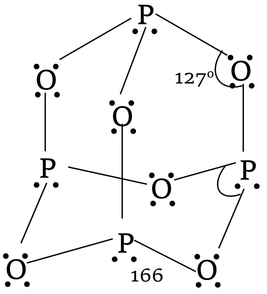
White phosphorus $\xrightarrow[4000-12000 \text{ atm. pressure}]{470K}$ Black phosphorus

It has a double layered structure. Each layer is made up of zig-zag chains with $P-P-P$ bond angle of 99^o. Since it is highly polymeric, it has high density. It is the most stable (inactive) form of phosphorus and has a black metallic luster. It is a good conductor of heat and electricity.

(4) **Compounds of phosphorus**

(i) ***Oxides and oxyacids of phosphorus*** : Phosphorus is quite reactive and forms number of compounds in oxidation states of –3 , +3 and +5. Phosphorus forms two common oxides namely, (a) phosphorus trioxide (P_4O_6) and (b) phosphorus penta oxide (P_4O_{10}).

(a) *Phosphorus (III) oxide* (P_4O_6) **:**



Phosphorus trioxide

It is formed when P is burnt in a limited supply of air, $P_4 + \underset{\text{(limited)}}{3O_2} \rightarrow P_4O_6$.

It is a crystalline solid with garlic odour. It dissolves in cold water to give phosphorous acid,

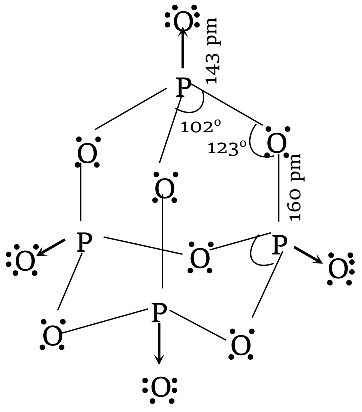
$P_4O_6 + \underset{\text{cold}}{6H_2O} \rightarrow \underset{\text{Phosphorous acid}}{4H_3PO_3}$, It is therefore, considered as anhydride of phosphorus acid.

With hot water, it gives phosphoric acid and inflammable phosphine, $P_4O_6 + 6H_2O$ (hot)$\rightarrow \underset{\text{Phosphoric acid}}{3H_3PO_4} + PH_3$

It reacts vigorously with Cl_2 to form a mixture of phosphoryl chloride and meta phosphoryl chloride.

$$P_4O_6 + 4Cl_2 \rightarrow \underset{\text{Phosphoryl chloride}}{2POCl_3} + \underset{\text{Metaphosphoryl chloride}}{2PO_2Cl}$$

(b) *Phosphorus (V) oxide* (P_4O_{10}):



Phosphorus

It is prepared by heating white phosphorus in excess of air, $P_4 + 5O_2(excess) \rightarrow P_4O_{10}$. It is snowy white solid. It readily dissolves in cold water forming metaphosphoric acid.

$P_4O_{10} + \underset{(\text{Cold})}{2H_2O} \rightarrow \underset{\text{Metaphosphoric acid}}{4HPO_3}$. With hot water, it gives phosphoric acid, $P_4O_{10} + \underset{\text{Hot}}{6H_2O} \rightarrow \underset{\text{Phosphoric acid}}{4H_3PO_4}$.

P_4O_{10} is a very strong dehydrating agent. It extracts water from many compounds including H_2SO_4 and HNO_3,

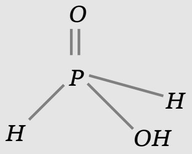
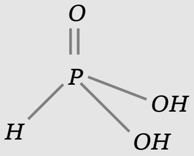
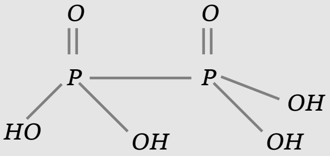
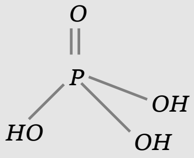
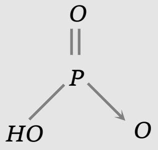
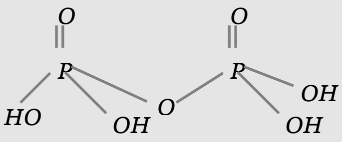
$$H_2SO_4 \xrightarrow[-H_2O]{P_4O_{10}} SO_3\ ;\ 2HNO_3 \xrightarrow[-H_2O]{P_4O_{10}} N_2O_5$$

$$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[-H_2O]{P_4O_{10}} \underset{\text{Methylcyanide}}{CH_3CN}$$

(ii) ***Oxyacids of phosphorus*** **:** Phosphorus forms a number of oxyacids which differs in their structure and oxidation state of phosphorus. These are $H_3PO_2, H_3PO_3, H_4P_2O_6, H_3PO_4$, $(HPO_3)_n, H_4P_2O_5, H_4P_2O_7$. From these H_3PO_2, H_3PO_3 are reducing agents. $H_4P_2O_5$ (pyrophosphoric acid) is dibasic acid.

$(HPO_3)_n$ is formed by dehydration of H_3PO_4 at 316^oC.

Table : 18.6 *Oxyacids of phosphorus*

Name	Oxidation state of P and Basicity	Structure
Hypophosphorous acid H_3PO_2	+1 Monobasic	
Phosphorous acid H_3PO_3	+3 Dibasic	
Hypophosphoric acid $H_4P_2O_6$	+4 Tetrabasic	
Orthophosphoric acid H_3PO_4	+5 Tribasic	
Metaphosphoric acid $(HPO_3)_n$	+5 Monobasic	
Pyrophospric acid (Diphosphoric acid). $H_4P_2O_7$	+5 Tetrabasic	

(5) **Chemical Fertilizers :** The chemical substances which are added to the soil to keep up the fertility of soil are called fertilizers.

Types of fertilizers : Chemical fertilizers are mainly of four types,

(i) ***Nitrogenous fertilizers*** : e.g. Ammonium sulphate $(NH_4)_2SO_4$, Calcium cyanamide $CaCN_2$, Urea NH_2CONH_2 etc.

(ii) ***Phosphatic fertilizers*** : e.g. $Ca(H_2PO_4)_2.H_2O$ (Triple super phosphate), Phosphatic slag etc.

(iii) ***Potash fertilizers*** **:** e.g. Potassium nitrate (KNO_3), Potassium sulphate (K_2SO_4) etc.

(iv) ***Mixed fertilizers*** **:** These are made by mixing two or more fertilizers in suitable proportion. e.g. *NPK* (contains nitrogen, phosphorus and potassium).

NPK is formed by mixing ammonium phosphate, super phosphate and some potassium salts.

Oxygen Family

Oxygen is the first member of group 16 or VIA of the periodic table. It consists of five elements Oxygen (O), sulphur (S), selenium (Se), tellurium (Te) and polonium (Po). These (except polonium) are the ore forming elements and thus called ***chalcogens***.

(1) **Electronic configuration**

Elements	Electronic configuration ($ns^2\ np^4$)
$_8O$	$[He]2s^2 2p^4$
$_{16}S$	$[Ne]3s^2 3p^4$
$_{34}Se$	$[Ar]3d^{10} 4s^2 4p^4$
$_{52}Te$	$[Kr]4d^{10} 5s^2 5p^4$
$_{84}Po$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^4$

Physical properties

(1) **Physical state :** Oxygen is gas while all other are solids.

(2) **Atomic radii :** Down the group atomic radii increases because the increases in the number of inner shells overweighs the increase in nuclear charge.

(3) **Ionisaion energy :** Down the group the ionisation energy decrease due to increase in their atomic radii and shielding effect.

(4) **Electronegativity :** Down the group electronegativity decreases due to increase in atomic size.

(5) **Electron affinity :** Element of this group have high electron affinity, electron affinity decreases down the group.

(6) **Non – metallic and metallic character :** These have very little metallic character because of their higher ionisation energies.

(7) **Nature of bonding :** Compound of oxygen with non metals are predominantly covalent. *S, Se*, and *Te* because of low electronegativities show more covalent character.

(8) **Melting and boiling points :** The melting point and boiling points increases on moving down the group.

(9) **Catenation :** Oxygen has some but sulphur has greater tendency for catenation.

$$\underset{(H_2O_2)}{H-O-O-H}, \quad \underset{(H_2S_2)}{H-S-S-H},$$

$$\underset{(H_2S_3)}{H-S-S-S-H}, \quad \underset{(H_2S_4)}{H-S-S-S-S-H}$$

(10) **Allotropy**

Oxygen – O_2 and O_3

Sulphur – Rhombic , monoclinic, plastic sulphur

Selenium – Red (non-metallic) grey (metallic)

Tellurium – Non-metallic and metallic (more stable)

Polonium – α and β (both metallic)

(11) **Oxidation states :** Oxygen shows – 2, + 2 and –1 oxidation states. Other elements show +2 ,+4 and +6 oxidation states.

Chemical properties

(1) **Hydrides :** The elements of this group form hydrides such as H_2O, H_2S, H_2Se, H_2Te an H_2Po. Following are their characteristics.

(i) ***Physical states*** **:** Water is colourless and odourless while hydrides of the rest of the elements of this group are colourless, unpleasant smelling poisonous gases.

(ii) ***Volatile nature*** **:** Volatility increases from H_2O to H_2S and then decreases. The low volatility and abnormally high boiling point of water is due to the association of water molecules on account of hydrogen bonding because of strongly electronegative oxygen atom linked to hydrogen atom. thus, water is liquid while H_2S and other hydrides are gases under normal condition of temperature and pressure.

(iii) ***Acidic character*** **:** The hydrides of this group behave as weak diprotic acids in aqueous solution, the acidic character increasing from H_2S to H_2Te when H_2O is neutral.

(iv) ***Thermal stability*** **:** The thermal stability decreases from H_2O to H_2Po because the size of the central atom (from O to Po) increases resulting in longer and weaker $M-H$ bond consequently the bond strength decreases. This results in the decrease of the thermal stability.

(v) ***Reducing character*** **:** The reducing power of the hydrides increases from H_2O to H_2Po due to the decreasing bond strength from H_2O to H_2Po.

(vi) ***Bond angle*** **:** All these hydrides are angular molecules and the bond angle $H-X-H$ (X is O, S, Se, Te) decreases from H_2O to H_2Te.

Increasing order of reducing power of hydrides :

$$H_2O < H_2S < H_2Se < H_2Te$$

Increasing order of bond angles in hydrides :

$$H_2Te < H_2Se < H_2S < H_2O$$

The order of stability of hydrides :

$$H_2O > H_2S > H_2Se > H_2Te$$

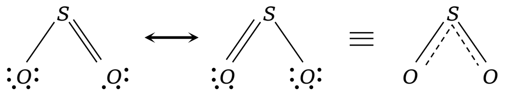
The order of increasing acidic nature of hydrides :

$$H_2O < H_2S < H_2Se < H_2Te$$

(2) **Oxides :** These elements form monoxides (MO), dioxides (MO_2) and trioxides (MO_3).

(i) ***Dioxides*** : Sulphur, selenium and tellurium burn in air to form SO_2, SeO_2 and TeO_2. The dioxide molecules contain $p\pi - p\pi$ bonds which become weaker with increase in atomic number because of the increase in the bond length.

(a) Sulphur dioxide, SO_2 is a gas at room temperature and exists as individual molecules even in the solid state. Its molecule has bent structure and is a resonance hybrid of the following canonical structures.



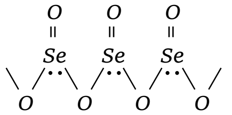
SO_2 is acidic in nature and also called the anhydride of sulphurous acid. It can act as reducing and oxidising agent. SO_2 also acts as a beleaching agent in the presence of moisture, but in contrast to Cl_2, its bleaching action is temporary.

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2[H]$$

Colouring matter $+2[H] \rightleftharpoons$ Colourless compound

Hence, SO_2 bleaches due to reduction and the bleaching action is temporary.

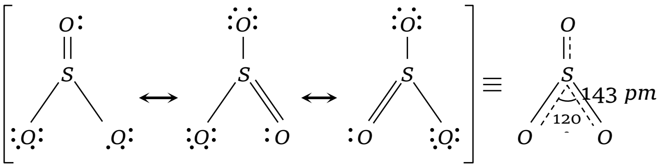
(b) Selenium dioxide, SeO_2 is a solid with polymeric zig-zag structure at room temperature however it exist as discrete molecules in the gaseous phase.



(c) Tellurium dioxide, TeO_2 is also a solid with polymeric zig-zag structure at room temperature very similar to that of selenium dioxide.

(ii) ***Trioxides*** : Sulphur, selenium and tellurium can form trioxides also.

(a) *Sulphur trioxide,* SO_3 : In the gaseous state monomeric SO_3 has a planar structure with $S-O$ bond distance of 143 pm and $O-S-O$ bond angle of $120^{o}.SO_3$ molecule is a resonance hybrid of following structures.



Canonical structures Resonance

In the solid phase sulphur trioxide polymerises to cyclic trimer or to a stable linear chain structure. SO_3 is the anhydride of H_2SO_4. It is acidic in nature and acts as oxidising agent.

(b) *Selenium trioxide,* SeO_3 : it is a solid substance which exists as a cyclic tetramer, however in the vapour phase it exists as a monomer

(c) *Tellurium trioxide,* TeO_3 : It is a solid at room temperature existing as a polymer.

The increasing order of acidic nature of oxides is $TeO_3 < SeO_3 < SO_3$.

(3) **Oxyacids :**

$$H_2SO_3, H_2SO_4, H_2S_2O_3, H_2SO_5, H_2S_2O_8, H_2S_2O_7, H_2S_2O_6$$

(4) **Halides :** Oxygen : OF_2, Cl_2O, Br_2O

Sulphur : $S_2F_2, S_2Cl_2, SF_2, SCl_2, SBr_2, SF_4, SCl_4$ and SF_6

Selenium and tellurium : SeF_6 and TeF_6

Anamolous Behaviour of Oxygen

Oxygen is the first member of the group 16 family and differs from the other members of the family because of

(1) Its small size

(2) Its high electronegativity

(3) Its high ionisation energy

(4) Absence of d-orbitals in the valence shell

It differs from the other members of the family as follows

(1) **Elemental state :** Oxygen is a diatomic gas while others are octa-atomic solids with eight membered puckered ring structure.

(2) **Oxidation states :** Oxygen shows O.S. of –2 in most of its compounds. It also shows an O. S. of +2 in F_2O and –1 in H_2O_2 or other peroxides. It cannot show O.S. beyond 2. Other elements show oxidation states of +2, +4 and +6 because these elements have vacant d-orbitals so that their valence shell can expand.

(3) **Hydrogen-bonding :** Oxygen atom is very small and has quite high nuclear charge. therefore, it has high value of electronegativity and is able to form H-bonds. the other elements, because of their large size, cannot form H-bonds. As a result, H_2O is liquid while H_2S is a gas and H_2Se etc., are solids.

(4) **Maximum covalency :** Oxygen has a maxium covalency of two while other elements can show a maximum covalency of six. This is because these elements have vacant d-orbitals while oxygen has not.

(5) **Types of compounds :** The compounds of oxygen are mainly ionic and polar covalent due to high electronegativity of oxygen while those of others are not.

(6) **Magnetic character :** Oxygen is paramagnetic while others are not.

Oxygen and its compounds

Oxygen is the most abundant element in the earth crust (46.5%). It was discovered by ***Karl Scheele*** and ***Joseph Priestley***. It occurs in three isotopic forms :

$$\underset{(Abundance:99.76\%)}{{}_8O^{16}} \qquad \underset{(Abundance:0.037\%)}{{}_8O^{17}} \qquad \underset{(Abundance:0.204\%)}{{}_8O^{18}}$$

Out of the three isotopes, ${}_8O^{18}$ is radioactive.

Occurrence : In free state, it occurs in air and constitutes 21% by volume of air.

Preparation of Dioxygen : Oxygen is prepared by the following methods.

(1) **By the decomposition of oxygen rich compounds** : e.g.

$$\underset{Pot.\,Nitrate}{2KNO_3} \xrightarrow{Heat} 2KNO_2 + O_2\,;\; \underset{Pot.\,Chlorate}{2KClO_3} \xrightarrow[MnO_2]{Heat} 2KCl + 3O_2$$

(2) **By heating dioxides, Peroxides and higher oxides** : e.g.

$$\underset{\text{Silver oxide}}{2Ag_2O} \xrightarrow{Heat} 4Ag + O_2 \; ; \quad \underset{\text{Manganese dioxide}}{3MnO_2} \xrightarrow{Heat} Mn_3O_4 + O_2$$

$$\underset{\text{Barium peroxide}}{2BaO_2} \xrightarrow{Heat} \underset{\text{Barium oxide}}{2BaO} + O_2$$

(3) **Laboratory Method** : In the laboratory, O_2 is prepared by thermal decomposition of potassium chlorate.

$$2KClO_3 \xrightarrow[MnO_2]{420\ K} 2KCl + 3O_2$$

In the absence of MnO_2 catalyst, the decomposition takes place at 670-720 *K*. Therefore, MnO_2 acts as a catalyst and also lowers the temperature for the decomposition of $KClO_3$.

(4) O_2 can also be prepared by the action of water on sodium peroxide as, $2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$.

(5) **Industrial preparation :** The main sources for the industrial preparation of dioxygen are air and water.

(i) ***From air*** *:* O_2 is prepared by fractional distillation of air. During this process, N_2 with less boiling point (78 *K*) distills as vapour while O_2 with higher boiling point (90 *K*) remains in the liquid state and can be separated.

(ii) ***From water*** *:* O_2 can also be obtained by the electrolysis of water containing a small amount of acid or alkali, $2H_2O \xrightarrow{Electrolysis} 2H_2(g) + O_2(g)$.

Physical properties of O₂ : It is a colourless, tasteless and odourless gas. It is slightly soluble in water and its solubility is about $30\,cm^3$ per litre of water at 298 *K*.

Table : 18.7 ***Physical properties of atomic and molecular oxygen***

Atomic properties	Molecular properties
Atomic radius (pm) – 73	Bond length (pm) – 120.7
Ionic radius O^{2-} (pm) – 140	Bond energy ($kJ\ mol^{-1}$) – 493
Electronegativity – 3.5	Density at S.T.P. (gcm^{-3})– 1.429
Ionisation energy ($kJ\ mol^{-1}$) – 1310	Melting point (*K*) – 54.4
Electron affinity ($kJ\ mol^{-1}$) – 140	Boiling point (*K*) – 90.2

Chemical properties of O₂ : It does not burn itself but helps in burning. It is quite stable in nature and its bond dissociation energy is very high. Therefore, it is not very reactive as such, $O_2 \rightarrow O + O$.

Therefore, dioxygen reacts at higher temperatures. However, once the reaction starts, it proceeds of its own. This is because the chemical reactions of dioxygen are exothermic and the heat produced during the reaction is sufficient to sustain the reactions.

(1) **Action with litmus** : Like dihydrogen, it is also neutral and has no action on blue or red litmus.

(2) **Reaction with metals** : Active metals like *Na, Ca* react at room temp. to form their respective oxides.

$$4Na + O_2 \rightarrow 2Na_2O \; ; \quad 2Ca + O_2 \rightarrow 2CaO$$

It reacts with *Fe, Al, Cu* etc. metals at high temperature

$$4Al + 3O_2 \rightarrow 2Al_2O_3 \; ; \quad 4Fe + 3O_2 \rightarrow 2Fe_2O_3$$

(3) **Action with Non-metals** : It form oxides.

$$2H_2 + O_2 \xrightarrow[\text{Electric discharge}]{1073\ K} 2H_2O \; ;$$

$$N_2 + O_2 \xrightarrow{3273\ K} \underset{\text{Nitric oxide}}{2NO}$$

$$S + O_2 \xrightarrow{Heat} SO_2 \; ; \quad C + O_2 \xrightarrow{Heat} CO_2$$

(4) **Reaction with compounds** : Dioxygen is an oxidising agent and it oxidises many compounds under specific conditions. e.g. $4HCl + O_2 \xrightarrow[CuCl_2]{700\ K} 2H_2O + 2Cl_2$;

$$4NH_3 + 5O_2 \xrightarrow[Pt]{1073\ K} 4NO + 6H_2O$$

$$CS_2 + 3O_2 \xrightarrow{Heat} CO_2 + 2SO_2 \; ;$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Uses of dioxygen

(1) It is used in the oxy-hydrogen or oxy-acetylene torches which are used for welding and cutting of metals.

(2) It is used as an oxidising and bleaching agent,

(3) Liquid O_2 is used as rocket fuel.

(4) It is used in metallurgical processes to remove the impurities of metals by oxidation.

Compounds of Oxygen

(1) **Oxides :** A binary compound of oxygen with another element is called oxide. On the basis of acid-base characteristics, the oxides may be classified into the following four types,

(i) ***Basic oxides*** : Alkali, alkaline earth and transition metals form basic oxides - Na_2O, MgO, Fe_2O_3 etc. their relative basic character decreases in the order : alkali metal oxides>alkaline earth metal oxides>transition metal oxides.

(ii) ***Acidic oxides*** : Non-metal oxides are generally acidic - $CO_2, SO_2, SO_3, NO_2, N_2O_5, P_4O_{10}, Cl_2O_7$ etc.

(iii) ***Amphoteric oxides*** : Al_2O_3, SnO_2 etc.

(iv) ***Neutral oxides*** : H_2O, CO, N_2O, NO etc.

Trends of oxides in the periodic Table : On moving from left to the right in periodic table, the nature of the oxides change from basic to amphoteric and then to acidic. For example, the oxides of third period has the following behaviour,

Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_2	Cl_2O_7
strongly basic	basic	amphoteric	weakly acidic	acidic	strongly acidic	very strongly acidic

Basic to acidic character increases

However, on moving down a group, acidic character of the oxides decreases. For example in the third group, the acidic character of oxides decreases as:

B_2O_3	Al_2O_3	Ga_2O_3	In_2O_3, Tl_2O_3
acidic	amphoteric	(weakly basic)	basic

Acidic to basic character increases

On the basis of oxygen content the oxides may be classified into the following types,

Normal oxides : These contain oxygen atoms according to the normal oxidation number *i.e.* – 2. For example, $MgO,\ H_2O,\ CaO, Li_2O, Al_2O_3$ etc.

Polyoxides : These contain oxygens atoms more than permitted by the normal valency. Therefore, these contain oxygen atoms in oxidation state different than –2.

Peroxides : These contains O_2^{2-} ion having oxidation number of oxygen as –1. For example, $H_2O_2, Na_2O_2, BaO_2, PbO_2$ etc.

Superoxides : These contains O_2^- ion having oxidation number of oxygen as –1/2. For example, KO_2, PbO_2, etc.

Suboxides : These oxides contain less oxygen than expected from the normal valency. For example, N_2O.

Mixed oxides : These oxides are made up of two simple oxides. For example, red lead $Pb_3O_4(2PbO_2 + PbO_2)$, magnetic oxide of iron, $Fe_3O_4(FeO + Fe_2O_3)$ and mixed oxide of manganese, $Mn_3O_4(MnO_2 + 2MnO)$.

Ozone or trioxygen

Ozone is an allotrope of oxygen. It is present in the upper atmosphere, where it is formed by the action of U. V. radiations on O_2, $3O_2 \xrightarrow{U.V.\text{ radiation}} \underset{Ozone}{2O_3}$.

O_3 protects us from the harmful U. V. radiations which causes skin cancer. Now a days, ozone layer in the atmosphere is depleting due to *NO* released by supersonic aircrafts and chlorofluoro carbons (CFC'S) *i.e.* freon which is increasingly being used in aerosols and as a refrigerant.

Preparation : Ozone is prepared by passing silent electric discharge through pure, cold and dry oxygen in a specially designed apparatus called ozoniser. The formation of ozone from oxygen is an endothermic reaction.

$$3O_2 \underset{\text{discharge}}{\overset{Silent\ electric}{\rightleftharpoons}} 2O_3 \quad \Delta H = +285.4\,kJ$$

Ozone is prepared in the laboratory by the following two types of ozonisers,

(a) Siemen's ozoniser, (b) Brodie's ozoniser

For the better yield of ozone : (a) Only pure and dry oxygen should be used. (b) The ozoniser must be perfectly dry. (c) A fairly low temperature $(\approx 273\ K)$ must be maintained. (d) The electric discharge must be sparkless.

Physical properties : Ozone is a light blue coloured gas, having pungent odour. It is heavier than air. Its vapour density is 24. It is slightly soluble in water.

Chemical properties : The important chemical properties of ozone are discussed below,

(1) **Decomposition** : Pure ozone decomposes on heating above 475 *K* to form O_2 gas.

$$2O_3 \xrightarrow{475\ K} 3O_2 \quad \Delta H = -285.4\,kJ$$

(2) **Oxidising agent** : Ozone is one of the most powerful oxidising agent with the liberation of dioxygen. In fact, ozone is a stronger oxidising agent than molecular oxygen because ozone has higher energy content and decomposes to give atomic oxygen as:

$$O_3 \rightarrow O_2 + \underset{\text{Atomic oxygen}}{O}$$

Therefore, ozone oxidises a number of non-metals and other reducing agents. e.g.

$$\underset{Metal}{2Ag} + O_3 \rightarrow \underset{Silver\ oxide}{Ag_2O} + O_2\ ; \quad \underset{Non-metal}{S} + 3O_3 \rightarrow SO_3 + 3O_2$$

$$\underset{Compound}{PbS} + 4O_3 \rightarrow PbSO_4 + 4O_2$$

Mercury is oxidised to mercurous oxide,

$$2Hg + O_3 \rightarrow \underset{Mercurous\ oxide}{Hg_2O} + O_2$$

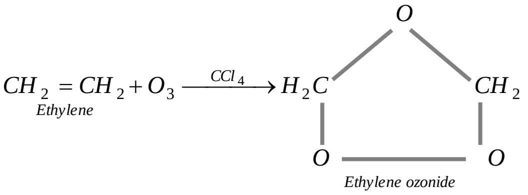
During this reaction mercury loses its meniscus and starts sticking to the sides of the glass. This is known as tailing of mercury. Mercurous oxide formed in this reaction dissolves in mercury and starts sticking to the glass surface.

(3) **Bleaching agent :** Due to the oxidising action of ozone, it acts as a mild bleaching agent as well as a sterilizing agent. It acts as a bleaching agent for vegetable colouring matter.

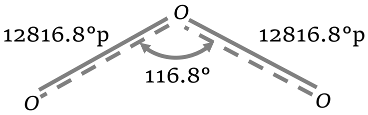
$$Vegetable\ \ colouring\ \ matter + O_3 \rightarrow \underset{(Colourless)}{Oxidised\ coloured\ \ matter} + O_2$$

For example, ozone bleaches indigo, ivory, litmus, delicate fabrics etc.

(4) **Formation of ozonides :** Ozone reacts with alkenes in the presence of CCl_4 to form an ozonide. e.g.



Structure of O_3 : The structure of O_3 molecule is angular as shown in fig. The $O-O-O$ bond angle is 116.8° and $O-O$ bond length is 128 pm.



Uses of ozone

(1) O_3 is used for disinfecting water for drinking purposes because ozone has germicidal properties.

(2) It is used for purifying air of crowded places such as cinemas, under ground railway, auditoriums, tunnels, mines etc.

(3) It is used in industry for the manufacture of $KMnO_4$, artificial silk, synthetic camphor etc.

Sulphur and its compounds

Sulphur is the second member of oxygen family and belongs to group-16 (VI A) of the periodic table.

Occurrence : Sulphur occurs in the earth's crust to the extent of 0.05%. It occurs in the free state as well as in combined state. Sulphur occurs mainly as sulphides and sulphates. eg.

Table 18.8

Sulphide Ores	Sulphate Ores
Iron pyrites (fool's gold) – FeS_2	Gypsum – $CaSO_4.2H_2O$
Galena – PbS	Epsom salt – $MgSO_4.7H_2O$
Copper pyrites – $CuFeS_2$	Barytes – $BaSO_4$
Cinnabar – HgS	Zinc blende – ZnS

Extraction of sulphur (Frasch process) **:** Sulphur is generally extracted from underground deposits by drilling three concentric pipes upto the beds of sulphur (700 – 1200 feet deep).

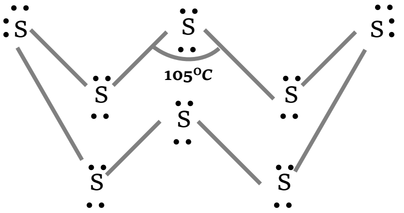
Allotropy in sulphur : Sulphur exists in four allotropic forms,

(1) **Rhombic or octahedral or α-sulphur** : It is a bright yellow solid, soluble in CS_2 and stable at room temp. All other varieties of sulphur gradually change into this form on standing.

(2) **Monoclinic sulphur or prismatic or β-sulphur**: It is prepared by melting the sulphur and then cooling it till a crust is formed. On removing the crust, needle shaped crystals of monoclinic sulphur separate out. It is dull yellow in colour, soluble in CS_2 and stable only above $369K$. Below this temperature it changes into rhombic form.

Thus, at $369K$ both these varities co-exist. This temperature is called transition temperature and the two sulphurs are called enantiotropic substances. It also exist as molecules similar to that of rhombic sulphur but the symmetry of the crystals is different.

(3) **Plastic or amorphous or γ -sulphur** : It is a super cooled liquid insoluble in CS_2, soft and amorphous. It consists of long zig-zag chains of S-atoms.



(4) **Colloidal or δ -sulphur** : It is prepared by passing H_2S through a solution of an oxidizing agent or water or by treating sodium thiosulphate with dil. HCl.

Properties of sulphur : It burns in air with, a blue flame forming SO_2, gives sulphur hexafluoride with F_2 and sulphur mono chloride with Cl_2, sulphides with metals like Na, Ca, Zn, Hg, Fe, Cu etc., reduces HNO_3 to NO_2 and H_2SO_4 to SO_2. With $NaOH$ solution on heating,

$$S_8 + 12NaOH \longrightarrow 4Na_2S + 2Na_2S_2O_3 + 6H_2O.$$

It gives sodium sulphide and sodium thiosulphate, with excess of sulphur, $2Na_2S + S_8 \longrightarrow 2Na_2S_5$.

Uses of sulphur : It is used in the manufacture of matches, gun powder (mixture of charcoal, sulphur and potassium nitrate), explosives and fire works SO_2, H_2SO_4, CS_2 and dyes, sulpha drugs and ointment for curing skin diseases and in the vulcanization of rubber.

Compounds of Sulphur

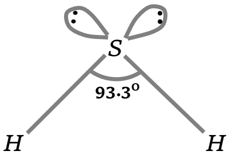
(1) **Hydrogen Sulphide :** It is prepared in the laboratory by the action of dil. H_2SO_4 on ferrous sulphide in kipp's apparatus, $FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S$. It is colourless gas having foul smell resembling that of rotten eggs. It reacts

with many cations (of group II and IV) to give coloured sulphides,

$$Cu^{+2}+S^{-2}\rightarrow \underset{\text{Black}}{CuS}\ ;\ Cd^{+2}+S^{-2}\rightarrow \underset{\text{(Yellow)}}{CdS}\ ;$$

$$Ni^{+2}+S^{-2}\rightarrow \underset{\text{(Black)}}{NiS}\ ;\ Co^{+2}+S^{-2}\rightarrow \underset{\text{(Black)}}{CoS}$$

The solubility of sulphides can be controlled by the H^+ ions concentration and therefore, H_2S finds extensive use in qualitative analysis of cation radicals.



(2) **Halides of sulphur :** Two important halides of sulphur are SF_4 and SF_6.

(i) ***Sulphur tetrafluoride*** : SF_4 is formed by the reaction of sulphur with CoF_3.

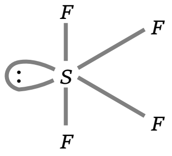
$$S+4CoF_3 \longrightarrow SF_4+4CoF_2$$

It is a colour gas which is quite reactive. It is hydrolysed with water.

$$SF_4+2H_2O \longrightarrow SO_2+4HF$$

It is used for fluorinating inorganic and organic compounds.

Structure : It has see-saw structure with sp^3d -hybrdization and is derived from triogonal bipyramid geometry in which an equatorial position is occupied by a lone pair of electrons.

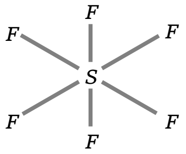


(ii) ***Sulphur hexafluoride*** : SF_6 is prepared by burning sulphur in a stream of fluorine. OF_6 is not known though sulphur forms SF_6. This is because oxygen has no d -orbitals in its valence shell.

SF_6 is a colourless gas. It is extremely inert substance even at red heat. It does not react with water. on account of its chemical inertness and dielectric strength, it is used as an insulator in high voltage generators and switch-gears.

Structure : It has an octahedral structure with sp^3d^2 -hybridisation around the central sulphur atom.

Therefore, all $S-F$ bond distances are equal in its structure.



(3) **Oxides of sulphur :** Sulphur forms several oxides of which sulphur dioxide (SO_2) and sulphur trioxide (SO_3) are most important.

(i) ***Sulphur dioxide*** **(SO_2)** : It is prepared by burning sulphur or iron pyrites in air.

$$S_8+8O_2\rightarrow 8SO_2\ ;$$

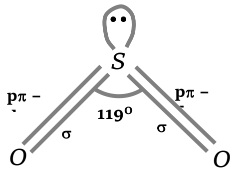
$$4FeS_2+11O_2\rightarrow 2Fe_2O_3+8SO_2$$

In laboratory, it is prepared by heating copper turnings with conc. H_2SO_4

$$Cu+2H_2SO_4\rightarrow CuSO_4+SO_2+2H_2O$$

It is a colourless gas with irritating and suffocating smell.

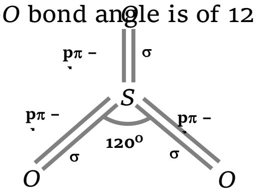
SO_2 molecule has a bent structure with a $O-S-O$ bond angle of 119°. Sulphur is sp^2 hybridized.



(ii) ***Sulphur trioxide*** **(SO_3)**: It is formed by the oxidation of SO_2.

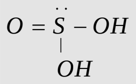
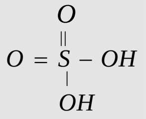
$$2SO_2+O_2\xrightarrow[V_2O_5]{700\,K,\,2atm.}2SO_3$$

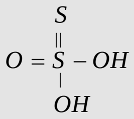
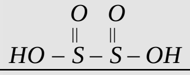
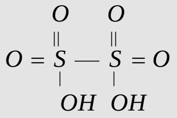
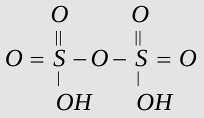
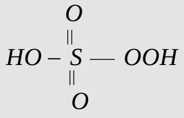
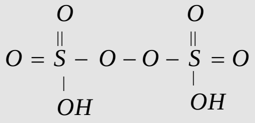
In the gaseous phase, it exists as planar triangular molecular species involving hybridization of the S-atom. It has three S–O σ bonds and three S–O π bonds. The O–S–O bond angle is of 120°.



(4) **Oxyacids of sulphur :** Sulphur forms many oxyacids. Some of these are,

Table : 18.9 Oxyacids of sulphur

Formula	*Name*	Important properties	Structural formula
$H_2SO_3(+4)$	Sulphurous acid	Free acid does not exist diprotic, strong reducing agent	 $O=\overset{\cdot\cdot}{S}-OH$ $\underset{OH}{\vert}$
$H_2SO_4\,(+6)$ (Oil of vitrioI)	Sulphuric acid	Stable diprotic, dehydrating agent	 $O=\overset{\overset{O}{\Vert}}{S}-OH$ $\underset{OH}{\vert}$

$H_2S_2O_3$ (–2 and +6)	Thiosulphuric acid	Free acid does not exist but its salts e.g. $Na_2S_2O_3$ All quite stable reducing agent	 $O=\underset{\underset{OH}{\mid}}{\overset{\overset{S}{\|}}{S}}-OH$
$H_2S_2O_4$ (+3)	Dithionous acid		 $HO-\overset{\overset{O}{\|}}{S}-\overset{\overset{O}{\|}}{S}-OH$
$H_2S_2O_6$ (+5)	Dithionic acid	Free acid is moderately stable but its salts are quite stable.	 $O=\underset{\underset{OH}{\mid}}{\overset{\overset{O}{\|}}{S}}-\underset{\underset{OH}{\mid}}{\overset{\overset{O}{\|}}{S}}=O$
$H_2S_2O_7$ (+6) (Oleum)	Disulphuric acid (Pyrosulphuric acid)	Strong oxidising agent	 $O=\underset{\underset{OH}{\mid}}{\overset{\overset{O}{\|}}{S}}-O-\underset{\underset{OH}{\mid}}{\overset{\overset{O}{\|}}{S}}=O$
H_2SO_5 (+6) (Caro's acid)	Peroxomonosulphuric acid (Its salts known as persulphates)	Stable crystalline solid, powerfull oxidising agent	 $HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OOH$
$H_2S_2O_8$ (+6) (Marshals acid)	Peroxodisulphuric acid (its salts are known as disulphates)	Strong oxidising agent.	 $O=\underset{\underset{OH}{\mid}}{\overset{\overset{O}{\|}}{S}}-O-O-\underset{\underset{OH}{\mid}}{\overset{\overset{O}{\|}}{S}}=O$

Sulphuric acid (H_2SO_4) **:** H_2SO_4 is a very stable oxyacid of sulphur. It is often called king of chemicals, since it is one of the most useful chemicals in industry.

Manufacture of sulphuric acid : H_2SO_4 can be manufactured by following process,

Lead chamber process : In this process, SO_2 is oxidized to SO_3 by the oxides of nitrogen and the SO_3 thus formed is dissolved in steam to form H_2SO_4.

$$SO_2 + NO_2 \rightarrow SO_3 + NO \;;\; 2NO + O_2 \rightarrow 2NO_2$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Contact process : In the contact process, SO_2 obtained by burning of S or iron pyrities is catalytically oxidized to SO_3 in presence of finely divided Pt or V_2O_5 as catalyst.

$$S + O_2 \rightarrow SO_2 \text{ or } 4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

$$2SO_2 + O_2 \xrightleftharpoons{V_2O_5 \text{ or Pt, 673-732 K}} 2SO_3 .$$

V_2O_5 is, however, preferred since is much cheaper than Pt and is also not poisoned by arsenic impurities.

The favorable conditions for maximum yield of SO_3 are,

(a) High concentration of SO_2 and O_2. (b) Low temperature of 673 to 723 K, (c) High pressure about 2 atmospheres.

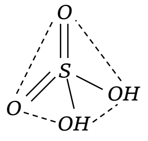
SO_3 thus obtained is absorbed in 98% H_2SO_4 to form oleum which on dilution with water gives H_2SO_4 of desired concentration.

$$SO_3 + H_2SO_4 \rightarrow \underset{\text{oleum}}{H_2S_2O_7} \;;\; H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$$

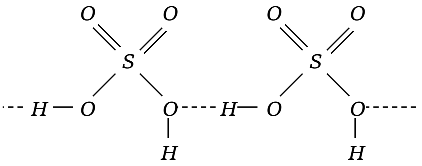
Contact process is preferred over lead chamber process (gives 98% pure H_2SO_4) since it gives H_2SO_4 of greater purity (100%).

Structure : H_2SO_4 is a covalent molecule with sulphur in a +6 oxidation state. The two oxygen atoms are linked to sulphur by double bonds while the other two oxygen atoms.

Are linked by single covalent bonds. Thus it has tetrahedral structure. Infact, sulphuric acid has an associated structure due to the presence of hydrogen bonds. As a result, it is a dense and viscous liquid and has a high boiling point of $590\,K$



Structure of



H-bonding in conc. H_2SO_4

Properties : H_2SO_4 has high b.p. (611K) and is also highly viscous due to H-bonding. It has strong affinity for H_2O and a large amount of heat is evolved when it is mixed with water.

(i) H_2SO_4 is a strong dibasic acid. It neutralizes alkalies, liberates CO_2 from carbonates and bicarbonates.

(ii) It reacts with more electropositive (than hydrogen) metals to evolve H_2 and produces SO_2 on heating with less electropositive metals than hydrogen .eg.,

$$H_2SO_4 + 2KOH \rightarrow K_2SO_4 + 2H_2O \;;$$

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$$

(iii) It is a strong oxidizing agent and oxidises as follows,

$$H_2SO_4 \rightarrow H_2O + SO_2 + O$$

$$C + 2H_2SO_4 \rightarrow 2SO + CO + 2H_2O$$

$$S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$$

$$P_4 + 10H_2SO_4 \rightarrow 4H_2PO_4 + 10SO_2 + 4H_2O$$

$$2HBr + H_2SO_4 \rightarrow Br_2 + 2H_2O + SO_2$$

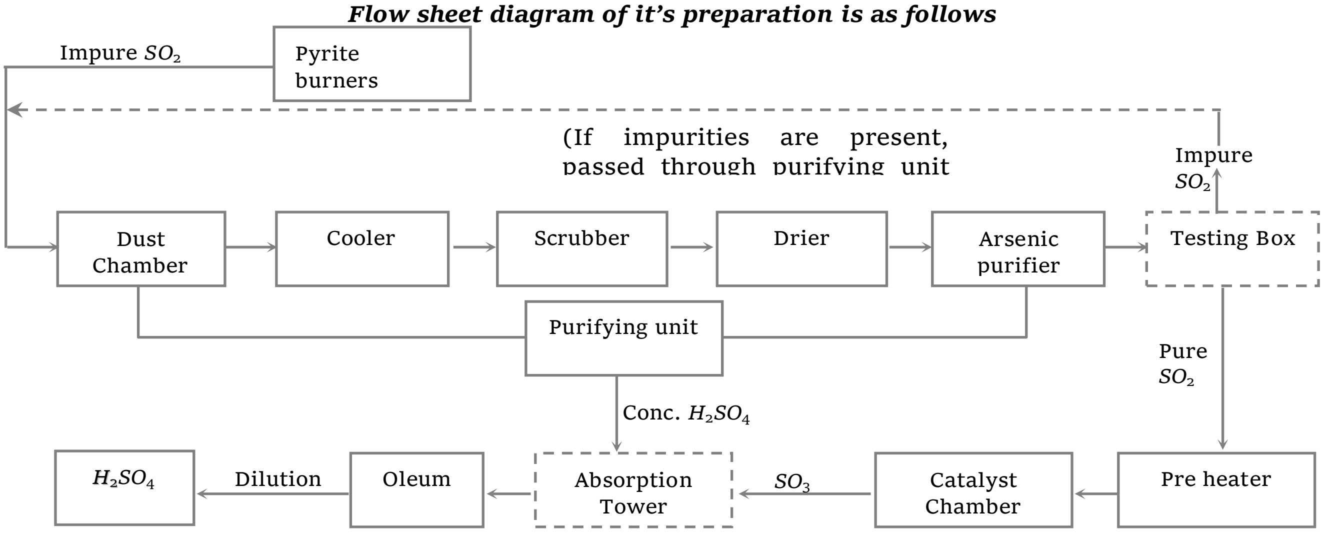
$$2HI + H_2SO_4 \rightarrow 2H_2O + I_2 + 2SO_2$$

(iv) It reacts with number of salts. It liberates HCl from chlorides, H_2S from sulphides, HNO_3 from nitrates.

(v) It acts as a strong dehydrating agent, as it dehydrates, sugar to sugar charcoal (carbon), formic acid to CO, oxalic acid to $CO + CO_2$ and ethyl alcohol to ethylene.

(vi) It is also a good sulphonating agent and used for sulphonation of aromatic compounds. eg.,

Flow sheet diagram of it's preparation is as follows



$$BaCl_2 + H_2SO_4 \rightarrow \underset{\text{(white ppt)}}{BaSO_4} + 2HCl$$

$$Pb(NO_3)_2 + H_2SO_4 \rightarrow \underset{\text{(white ppt.)}}{PbSO_4} + 2HNO_3$$

$$\underset{\text{Sugar}}{C_{12}H_{22}O_{11}} \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{Carbon}}{12C} + 11H_2O$$

$$HCOOH \xrightarrow{Conc.H_2SO_4} CO + H_2O$$

Uses : H_2SO_4 is used (i) in the preparation of fertilizers like $(NH_4)_2SO_4$ and super phosphate of lime, (ii) in lead storage batteries (iii) in preparation of dyes, paints and explosives (iv) in textile and paper industry (v) for training of tanning (vi) as a dehydrating agent.

(5) **Sodium thiosulphate** $Na_2S_2O_3.5H_2O$ **:** It is manufactured by saturating a solution of sodium carbonate with SO_2 which gives a solution of sodium sulphite,

$$Na_2CO_3 + SO_2 + H_2O \rightarrow Na_2SO_3 + CO_2 + H_2O$$

The resulting solution is boiled with powdered sulphur as, $Na_2SO_3 + S \xrightarrow{373K} Na_2S_2O_3$

The solution is then cooled to get crystals of sodium thiosulphate.

Physical properties : (i) Sodium thiosulphate is a colourless crystalline solid. In the hydrated form, it is called hypo. (ii) It melts at 320 K and loses its water molecules of crystallization on heating to 490K.

Chemical properties

(i) ***Action with halogens*** : It reacts with halogens as,

(a) Chlorine water oxidizes sodium thiosulphate to sodium sulphate and sulphur is precipitated,

$$Na_2S_2O_3 + Cl_2 + H_2O \rightarrow 2HCl + Na_2SO_4 + S$$

This property enables it to act as an antichlor in bleaching *i.e.* it destroys the unreacted chlorine in the process of bleaching.

(b) Bromine water also oxidizes sodium thiosulphate to sodium sulphate and sulphur,

$$Na_2S_2O_3 + Br_2 + H_2O \rightarrow Na_2SO_4 + 2HBr + S$$

(c) With iodine it forms a soluble compound called sodium tetrathionate,

$$2Na_2S_2O_3 + I_2 \rightarrow \underset{\text{Sod. tetrathionate}}{Na_2S_4O_6} + 2NaI$$

Therefore, hypo is commonly used to remove iodine stains from the clothes.

(ii) ***Action of heat*** : Upon heating, sodium thiosulphate decomposes to form sodium sulphate and sodium pentasulphide,

$$4Na_2S_2O_3 \xrightarrow{\text{Heat}} 3Na_2SO_4 + \underset{\text{Sodium pentasulphide}}{Na_2S_5}$$

(iii) ***Action with acids*** : Sodium thiosulphate reacts with dilute hydrochloric acid or Sulphuric acid forming sulphur dioxide and sulphur. The solution turns milky yellow due to sulphur.

$$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + SO_2 + H_2O + S$$

(iv) ***Action with silver halides*** **:** Sodium thiosulphate forms soluble complex when treated with silver chloride or silver bromide,

$$2Na_2S_2O_3 + 2AgBr \rightarrow \underset{\substack{\text{Sodium dithiosulphate} \\ \text{argentate (I)compex}}}{Na_3Ag(S_2O_3)_2} + NaBr \ .$$

This property of hypo is made use in photography.

Uses of sodium thiosulphate

(i) It is largely used in photography as a fixing agent.

(ii) It is used as a preservative for fruit products such as jams and squashes.

(iii) It is used as an antichlor in bleaching.

(iv) It is used as a volumetric agent for the estimation of iodine.

(v) It is used in medicine.

Halogen Family

Fluorine is the first member of group 17 or VIIA of the periodic table. It consists of five elements Fluorine (F), Chlorine (Cl), bromine (Br), iodine (I) and astatine (At). These are known as halogen because their salts are found in sea water. Halogen is a greek word meaning a sea salt.

(1) **Electronic configuration**

Elements	Electronic configuration ($ns^2\ np^5$)
$_{9}F$	$[He]2s^2 2p^5$
$_{17}Cl$	$[Ne]3s^2 3p^5$
$_{35}Br$	$[Ar]3d^{10} 4s^2 4p^5$
$_{53}I$	$[Kr]4d^{10} 5s^2 5p^5$
$_{85}At$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^5$

Physical properties

(1) **Atomic and ionic radii :** A halogen atom has the smallest radius as compared to any other element in its period. This is due to the increased effective nuclear charge which results in greater attraction of the electrons by the nucleus. The atomic radii. Increase from fluorine to iodine down the group due to increase in number of shells.

Element	F	Cl	Br	I
Covalent radius (pm)	72	99	114	133
Ionic radius (pm)	133	184	196	220

(2) **Ionization energy :** Ionization energy of these elements are higher than those of the corresponding elements of group 16 due to increased nuclear charge. these values decrease systematically as we move down the group from F to 1

Element	F	Cl	Br	I
I.E$_1$ ($kJ\ mol^{-1}$)	1680	1256	1142	1008

Thus iodine which has a comparatively low value of I.E., has a tendency to lose an electon to form positive iodinium ion, I^+ and thus shown electropositive or metallic character.

(3) **Electronegativity :** Fluorine is the most electronegative element in the periodic table. With increase in atomic number down the group, the electronegativity decreases.

Element	F	Cl	Br	I	At
Electronegativity	4.0	3.2	3.0	2.7	2.2

The decreasing order of electronegativity is $F > Cl > Br > I$

(4) **Electron affinity :** Electron affinity of chlorine, bromine and iodine decrease as the size of the atom increases. The electron affinity of fluorine is, however, lower than that of Cl and Br, because of its small size as a result of which inter-electronic repulsions present in its $2p$ subshell are comparatively large. Thus chlorine has the highest electron affinity.

Element	F	Cl	Br	I
Electron affinity ($kJ\ mol^{-1}$)	333	348	325	296

The decreasing order of electron affinity is $Cl > F > Br > I$

(5) **Oxidation states :** All the halogens show an oxidation state of –1. Fluorine being the most electronegative element always shows an oxidation state of –1 while other halogens also show positive oxidation states up to a maximum of +7 (*i.e.* +1, +3, +5 and +7) due to the availability of vacant d-orbitals in the valence shell of these atoms. Some halogens also show +4 and +6 oxidation states in oxides and oxy acids.

(6) **Nature of bonds :** All the halogens have seven electrons in the valence shell and hence require one more electron to acquire the nearest inert gas configuration either by gaining an electron from the metallic atom to form halide, X^- ion, or by sharing an electron with an electronegative element. Thus, halogens form both ionic and covalent compounds. The halides of highly electropositive metals are ionic while those of weakly electropositive metals and non-metals are covalent. The tendency to form ionic compounds decreases from F to I. Thus, F because of its high electronegativity forms ionic compounds even with less electropositive metals like Hg, Bi, Sn etc. while other halogens form only covalent compounds.

(7) **Non-metallic character :** All the halogens are non-metallic in nature due to their high ionization energies. The non-metallic character gradually decreases down the group. However, iodine is, solid and has metallic lustre.

(8) **Atomicity and physical state :** All the halogens exist as diatomic covalent molecules (F_2, Cl_2, Br_2 and I_2). F_2 and Cl_2 are gases at room temperature, Br_2 is corrosive liquid and I_2 is volatile solid.

(9) **Colour :** All the halogens have characteristic colours. F_2 is light yellow, Cl_2 is greenish yellow, Br_2 is reddish brown and I_2 is deep violet. The colour of halogens is due to the reason that their molecules absorb light in the visible region as a result of which electron are excited to higher energy levels. The amount of energy needed for excitation decreases

progressively from F_2 to I_2 and consequently there is a progressive deepening of colour of the halogens from F_2 to I_2. Since, fluorine atom requires large amount of energy for excitation of electrons and therefore absorbs violet light and apears yellow. On the other hand, iodine requires low energy for excitation of electrons (absorbs yellow light) and appears deep violet.

(10) **Bond dissociation energy :** Bond dissociation energies of chlorine, bromine and iodine decrease down the group as the size of the atom increases. The bond dissociation energy of fluorine, is however, lower than those of chlorine and bromine because of inter electronic repulsions present in the small atom of fluorine

X_2	F_2	Cl_2	Br_2	I_2
Bond dissociation energy ($kJ\ mol^{-1}$)	158	243	192	151

Hence bond energy decreases in the order $Cl_2 > Br_2 > F_2 > I_2$

(11) **Bond length in X_2 molecule :** As the size of the halogen atom increase, the bond length of $X-X$ bond in X_2 molecule increases from F_2 to I_2

$X–X$ bond	$F–F$	$Cl–Cl$	$Br–Br$	$I–I$
Bond length (pm)	143	199	228	266

Thus, the bond length increases in the order $F_2 < Cl_2 < Br_2 < I_2$.

(12) **Melting points and boiling points :** Melting points and boiling points of these elements increase as we move down the group from F to I due to an increase in the vander Waals forces of attraction which increase down the group as the size of the atom increases.

Element	F	Cl	Br	I
Melting point (K)	54	172	266	386
Boiling point (K)	85	239	332	458

Hence, the melting points and boiling points show the order as $F < Cl < Br < I$.

(13) **Solubility :** Halogens, being non polar in nature do not readily dissolve in a polar solvent like water. however, fluorine reacts with water vigorously even at low temperature (exothermally) forming a mixture of ozone and oxygen

$$2F_2 + 2H_2O \longrightarrow 4HF + O_2$$

$$3F_2 + 3H_2O \longrightarrow 6HF + O_3$$

Chlorine and bromine are fairly soluble but iodine is very little soluble in water. chlorine, bromine and iodine are more soluble in organic solvents like CCl_4, CS_2 or $CHCl_3$ and produce coloured solutions. Thus Cl_2, Br_2 and I_2 give yellow, brown and violet colour respectively. It is believed that in non-polar solvents, halogens exist as free molecules just as in the gas phase.

In nucleophilic (electron donating) polar solvents like alcohols, ketones or liquid SO_2, halogens produce brown solution. This colour is due to the complex formation (solvent → halogen) which are charge transfer compounds.

The solubility of iodine (I_2) in water increases with addition of KI or NaI due to the formation of polyhalide (triiodide, I_3^-) ion, $KI + I_2 \rightleftharpoons KI_3$

However, this solution behaves as a simple mixture of KI and free I_2 and contains K^+ and I^- ions and free I_2 molecules. It has a brown colour. The solution of iodine in water (due to its very little solubility) is also brown.

(14) **Oxidising power :** All the halogens acts as strong oxidising agents since they have a strong tendency to attract electrons and have positive values of electrode potentials (E^o). The oxidising power, however, decreases as we move down the group from F to I. *i.e.*, $F_2 > Cl_2 > Br_2 > I_2$

Since F_2 is the strongest oxidising agent, it will oxidise all other halide ions to halogens.

$$F_2 + 2X^- \longrightarrow 2F^- + X_2 (X = Cl, Br, I)$$

Similarly, Cl_2 will displace Br^- and I^- ions from their solutions while Br_2 will displace I^- ions only.

$$Cl_2 + 2X^- \longrightarrow 2Cl^- + X_2 (X = Br, I)$$

$$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$$

Hence F_2 is the strongest and I_2 is the weakest oxidising agent. This is also indicated by the decrease in the electrode potential (E^o) for the reaction $X_2(aq) + 2e^- \longrightarrow 2X^-(aq)$ on moving down the group.

X_2	F_2	Cl_2	Br_2	I_2	At_2
E^o (volts)	2.87	1.36	1.09	0.53	0.3

The electron affinity of fluorine is less than that of chlorine but still it is the strongest oxidising agent. This is because of its low bond dissociation energy $(158\, kJ\, mol^{-1})$ and high heat hydration $(510\, kJ\, mol^{-1})$ as compared to chlorine (for which the values are 243 and $372\, kJ\, mol^{-1}$, respectively).

(15) **Heat of hydration :** The heat of hydration of the halide ion (X^-) decreases as the size of the halogen decreases down the group from F to I.

X^- ion	F^-	Cl^-	Br^-	I^-
Heat of hydration (kJ mol^{-1})	510	372	339	301

Thus, the decreasing order of heat of hydration of halides is as follows :

$$F^- > Cl^- > Br^- > I^-$$

Chemical properties

(1) **Reactivity :** The halogen are most reactive elements due to their low bond dissociation energy, high electron affinity and high enthalpy of hydration of halide ion. $F > Cl > Br > I$

(2) **Reaction with H_2O :** Halogens readily decomposes water. This tendency decreases on moving down the group. Fluorine decomposes water very energetically to give oxygen and ozone,

$$2H_2O + 2F_2 \rightarrow 4HF + \underset{\text{Oxygen}}{O_2}\ ;\quad 3H_2O + 3F_2 \rightarrow 6HF + \underset{\text{Ozone}}{O_3}$$

Fluorine gives fumes in moist air. This is due to the formation of *HF*, which is a liquid and can absorb moisture to form liquid droplets and therefore, gives fumes with moist air. Chlorine and bromine react less vigorously,

$$Cl_2 + H_2O \rightarrow HCl + \underset{\text{Hypochlorous acid}}{HClO}$$

$$Br_2 + H_2O \rightarrow HBr + \underset{\text{Hypobromous acid}}{HBrO}$$

In the presence of sunlight, *HClO* (hypochlorous acid) *HBrO* (hypobromous acid) liberate oxygen.

$$2HClO \rightarrow 2HCl + O_2\ ;\quad 2HBrO \rightarrow 2HBr + O_2$$

Iodine is only slightly soluble in water. However, it dissolves in 10% aqueous solution of *Kl* due to the formation of I_3^- ions. $I_2 + KI \rightleftharpoons$

$$KI_2 + I^- \rightleftharpoons \underset{\text{Complex ion}}{I_3^-}$$

(3) **Reaction with hydrogen** : Form covalent halides.

$$H_2 + F_2 \xrightarrow{-200^o C} 2HF \text{ (very violent)}$$

$$H_2 + Cl_2 \xrightarrow{\text{Sunlight}} 2HCl$$

$$H_2 + Br_2 \xrightarrow[\text{pt. catalyst}]{\text{Heat}} 2HBr$$

$$H_2 + I_2 \xrightleftharpoons{\text{Heat}} 2HI \text{ (poor yield)}$$

- Acidic strength in aqueous solution is in the order,

  HI > *HBr* > *HCl* < *HF*.

- Reducing character of hydrides follow the order,

  HI > *HBr* > *HCl* > *HF*.

- Boiling point *HF* > *HI* > *HBr* > *HCl*. Thermal stability,

  H – *F* > *H* – *Cl* > *H* – *Br* > *H* – *I*.

HCl is also called Muriatic acid.

(4) **Hydrides :** All the halogens combine directly with hydrogen to form halogen acids but their reactivity progressively decreases from fluorine to iodine, $H_2 + X_2 \rightarrow 2HX$ ($X = F, Cl, Br$ or I).

(i) ***Boiling points or volatility*** **:** In other words volatility decreases in the order : *HCl* > *HBr* > *HI* > *HF* as the boiling points increase in the order : *HCl (189K)* < *HBr (206K)* < *HI (238K)* < *HF (292.5K).*

(ii) ***Thermal stability*** **:** Thermal stability of the hydrides decrease from *HF to HI i.e., HF* > *HCl* > *HBr* > *HI.*

(iii) ***Acidic strength*** **:** The acidic strength of halogen acids decreases from *HI* to *HF i.e, HI* > *HBr* > *HCl* > *HF.*

(iv) ***Reducing properties*** **:** Since the stability of hydrides decreases from *HF* to *Hl*, their reducing properties increase in the order *HF* < *HCl* < *HBr* < *HI.*

(v) ***Dipole moments*** **:** The dipole moments of hydrogen halides decrease in the order : *HF* > *HCI* > *HBr* > *HI* as the electro negativity of the halogen atom decreases form *F* to *I*.

HX	*HF*	*HCl*	*HBr*	*Hl*

Dipole moment (D) 1.74 1.07 0.78 0.38

(5) **Oxides :** Halogens (except F_2) do not combine readily with oxygen. However, a number of compounds of halogens with oxygen have been prepared by indirect methods. Only two compounds of fluorine with oxygen, *i.e.* oxygen difluorine (OF_2) and oxygen fluoride (O_2F_2) are known. Chlorine forms largest number of oxides *i.e.* Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7 while iodine forms the least, *i.e.* I_2O_5. Bromine, however, forms three oxides $(Br_2O$, BrO_2C $BrO_3)$. In all these compounds, bonds are largely covalent. All the oxides of halogens are powerful oxidizing agents. These compounds are very reactive and are unstable towards heat. The stability of oxides is greatest for iodine while bromine oxides are the least stable. For a particular halogen, higher oxides are more stable than the lower ones.

Iodine-oxygen bond is stable due to greater polarity of the bond (due to larger electro negativity difference between I and O) while in chlorine-oxygen bond, the stability is gained through multiple bond formation involving the d-orbital of chlorine atom. Bromine lacks both these characteristics and hence forms least stable oxides.

Oxides of chlorine, bromine and iodine are acidic and the acidic character increases as the percentage of oxygen increases in them.

Iodine also forms I_2O_4 and I_4O_9 compounds which are believed not to be true oxides but are basic iodyliodate, $IO(IO_3)$ and normal iodine triodate, $I(IO_3)_3$ having tripositive iodine as the cation.

OF_2 is V-shaped having bond angle 103^o, Cl_2O is also V-shaped with bond angle 111^o while ClO_2 is angular with-bond angle 118^o. It is paramagnetic due to odd number of electrons having three-electron bond. It is regarded as a mixed anhydride of chloric and chlorous acids. $2ClO_2 + H_2O \rightarrow HClO_2 + HClO_3$

(6) **Oxoacids of halogens :** Fluorine does not form any oxoacid since it is the strongest oxidizing agent. Chlorine, bromine and iodine mainly form four series of oxoacids namely hypohalous acid (HXO), halous acid (HXO_2) halic acid (HXO_3) and perhalic acid (HXO_4) as given below :

Table 18.10

Oxidation state	**Chlorine**	**Bromine**	**Iodine**	**Thermal stability and acid strength**	**Oxidising power**
+1	$HClO$	$HBrO$	HIO	Increases ↓	Decreases ↓
+3	$HClO_2$	–	–		
+5	$HClO_3$	$HBrO_3$	HIO_3		
+7	$HClO_4$	$HBrO_4$	HIO_4		
	Acidity decreases →				

(i) ***Hybridized ion*** **:** In all these oxoacids, the halogen atom is sp^3 -hybridized.

(ii) ***Acidic character*** **:** All these acids are monobasic containing an$-OH$ group. The acidic character of the oxoacids increases with increase in oxidation number, *i.e.*, $HClO < HClO_2 < HClO_3 < HClO_4$ and the strength of the conjugate bases of these acids follows the order,

$$ClO^- > ClO_2^- > ClO_3^- > ClO_4^-$$

(iii) ***Oxidising power and thermal stability*** **:** The oxidizing power of these acids decreases as the oxidation number increases, *i.e.*, $HClO < HClO_2 < HClO_3 < HClO_4$. Stability of oxoacids of chlorine in the increasing order is, $HClO < HClO_2 < HClO_3 < HClO_4$ and the increasing stability order of anions of oxoacids of chlorine is, $ClO^- < ClO_2^- < ClO_3^- < ClO_4^-$.

As the number of oxygen atoms in an ion increases there will be a greater dispersal of negative charge and thus greater will be the stability of ion formed. For different halogen having the name oxidation number, the thermal stability decreases with increase in atomic number *i.e.*, it is in the order $HClO > HBrO > HIO$ and $ClO^- > BrO^- > IO^-$ However, in HXO_3 is most stable. The stability order being $HClO_3 < HBrO_3 < HIO_3$.

(iv) Perhalates are strong oxidizing agents, the oxidizing power is in the order, $BrO_4^- > IO_4^- > ClO_4^-$.

Thus BrO_4 is the strongest oxidizing agent (though its reaction is quite slow) and ClO_4^- is the weakest.

(v) The acidity of oxoacids of different halogens having the same oxidation number decreases with increase in the atomic size of the halogen i.e. $HClO_4 > HBrO_4 > HIO_4$.

(7) **Reaction with alkalies :**

$$2F_2 + 2\underset{\text{(cold dilute)}}{NaOH} \rightarrow 2NaF + OF_2 + H_2O$$

$$2F + 4\underset{\text{(hot conc.)}}{NaOH} \rightarrow 4NaF + O_2 + 2H_2O$$

Halogen other than fluorine (Cl_2, Br_2, I_2) react with $NaOH$ as follows,

$$\underset{\text{(cold dilute)}}{X_2(g) + 2OH^-} \xrightarrow{15^o C} X^- + \underset{\text{(hypohalite ion)}}{OX^-} + H_2O$$

$$X_2(g) + \underset{\text{(hot conc)}}{6OH^-} \xrightarrow{70^o C} 5X^- + \underset{\text{(halate ion)}}{XO_3^-} + 3H_2O$$

(8) **Bleaching action of halogen :** Cl_2 acts as bleaching agent, its bleaching action is permanent. Cl_2 water can also act as ink remover.

(9) **Reaction with other halides**

$$2KBr(aq.) + Cl_2(g) \rightarrow 2KCl(aq.) + Br_2(aq.)$$

$$2KI(aq.) + Cl_2(g) \rightarrow 2KCl(aq.) + I_2(aq.)$$

(10) **Inter halogen compounds :** The compounds of one halogen with the other are called inter halogens or inter halogen compounds. The main reason for their formation is the large electronegativity and the size differences between the different halogens. Taking *A* as the less electronegative and *B* as the more electronegative halogen, they are divided into the following four types the less electronegative halogen (A) is always written first.

AB	**AB_3**	**AB_5**	**AB_7**
ClF $BrF, BrCl, ICl$ IBr, IF	ClF_3, BrF_3 IF_3, ICl_3	$BrF_5\, IF_5$	IF_7

These interhalogen compounds are unstable and more reactive

(i) ***General properties***

(a) Largest halogen always serves the central atom.

(b) The highest interhalogen compound i.e. IF_7 is obtained with iodine, the largest halogen attached to the smallest one

(c) The bonds in interhalogen compounds are essentially covalent.

(d) Thermal stability decreases as the size difference decreases and increases as the polarity of the bond increases. Thus *ClF* is thermally more stable as compared to *IBr*.

(e) They ionize in solution or in the liquid state,

$$2ICl \rightleftharpoons I^+ + ICl_2^- ; \quad 2ICl_3 \rightleftharpoons ICl_2^+ + ICl_4^-$$

(f) Hydrolysis of interhalogen compounds always produces a halide ion derived from smaller halogen and oxyhalide derived from larger halogen, $ICl + H_2O \rightarrow Cl^- + OI^- + 2H^+$;

$$BrF_5 3H_2O \rightarrow 5F^- + BrO_3^- + 6H^+$$

(g) They are strong oxidizing agents.

(h) Largest number of interhalogens are formed by fluorine due to its smaller size and higher electronegativity or oxidizing power.

(ii) ***Structure*** : Interhalogen compounds are,

(a) *AB* type *i.e. ICl, IBr, IF* etc, are linear

(b) AB_3 type *i.e.* IF_3, ClF_3, BrF_3 have distorted trigonal bipyramidal (dsp^3-hybridization) structures of T-shape due to two lone pairs in equatorial positions ICl_3 is dimeric, I_2Cl_6 and has a planar structure.

(c) AB_5 types *i.e.* BrF_5, IF_5 have distorted octahedral (d^2sp^3-hybridization) shapes or square pyramidal due to a lone pair one of the axial positions.

(d) AB_7 type *i.e.* IF_7, have pentagonal bipyramidal (d^3sp^3-hybridization) structures.

(11) **Polyhalide ions :** Halogens or interhalogens combine with halide ions to form polyhalide ions. The most common example of polyhalide ion formation is furnished by the increase in solubility of iodine in water in the presence of *KI* which is due to the formation of tri iodide ion, I_3^-

$$I^- + I_2 \longrightarrow I_3^-$$

Many other examples of polyhalides ions are

(i) $Cl_3^-, Br_3^-, ICl_2^-, IBr_2^-$ including I_3^-. In these ions, one of the halogen atoms (in case of similar atoms) or halogen atom larger in size undergoes sp^3d-hybridization giving a linear shape with three lone pairs at equatorial positions.

(ii) $Cl_3^+, Br_3^+, I_3^+, ICl_2^+, IBr_2^+$. Here we find central atom sp^3 hybridized giving a bent shape with two lone pairs of electrons on the central atom.

(iii) ICl_4^-, BrF_4^-, I_5^-. Here central atom involves sp^3d^2 hybridization giving square planar shape with two lone pairs of electrons on axial positions.

(iv) ICl_4^+, BrF_4^+, I_5^+. In these ions central atom involves sp^3d hybridization giving a distorted tetrahedral structure with one lone pair of electrons on equatorial position.

(v) I_7^-, IF_6^-. The central atom I undergoes sp^3d^3 hybridization giving a distorted octahedral structure with one lone pair of electrons.

(vi) I_7^+. Here central I atom involves sp^3d^2 hybridization giving an octahedral structure.

Fluorine due to its highest electronegativity (and only –1 oxidation state) does not form polyhalide ions where it acts as a central atom.

(12) **Pseudohalogen and pseudohalides**

Pseudohalogen	**Pseudohalide**

Cyanogen – $(CN)_2$	Cyanide – CN^-
Oxocyanogen – $(OCN)_2$	Cyanate – OCN^-
Thiocyanogen – $(SCN)_2$	Thiocyanate – SCN^-
Selenocyanogen – $(SeCN)_2$	Selenocyanate – $SeCN^-$

(13) **Anomalous behaviour of fluorine :** Fluorine differs from rest of the elements of its family due to (i) its small size (ii) highest electronegativity, (iii) low bond dissociation energy and (iv) absence of *d*-orbitals in the valence shell. The main points of difference are :

(1) Fluorine is most reactive of all the halogens due to lower value of $F-F$ bond dissociation energy ($F_2 = 158, Cl_2 = 243$, bromine = 192 and iodine = 151 *kJ mol*$^{-1}$) .

(2) Being the most electronegative element, it shows only an oxidation state of –1 and does not show positive oxidation states due to absence of d-orbitals in its valence shell. Other halogens show positive oxidation states of +1, +3, +5 and +7.

(3) Due to small atomic size and high electronegativity of F, HF undergoes strong H-bonding while other halogen acids do not. As a result,

(i) HF is a liquid (boiling point 292.5*K*), while other halogen acids are gases at room temperature (boiling point of $HCl = 189K$, $HBr = 206K$, $HI = 238K$).

(ii) HF is weakest of all the halogen acids due to high strength of $H-F$ bond.

(iii) Due to H-bonding, HF can form acid salts of the type KHF_2, *i.e.,* $K^+[H-F.......F^-]$ while HCl, HBr and HI do not form such salts (*i.e.*, no $KHCl_2, KHBr_2$ and KHI_2 are known).

(4) Fluorides have the maximum ionic character. For example AlF_3 is ionic while other halides of Al are covalent.

(5) Of all the halogens, fluorine has the highest positive electrode potential ($F_2 = 2.87, Cl_2 = 1.36, Br_2 = 1.09$ and $I_2 = 0.53$ volt) *i.e.*, it is most easily reduced and hence acts as the strongest oxidising agent. It brings about the highest oxidation of other elements with which it combines. For example with S , it gives SF_6 , with I_2 it gives IF_7 . Other halogens do not always bring about the highest oxidation state. For example, with sulphur Cl_2 gives SCl_4, Br_2 gives SBr_2 while I_2 does not react at all. F_2 is so powerful oxidising agent that it can even oxidise inert-gases.

(6) HF cannot be stored in glass bottles sicne it reacts with silicates to form fluorosilicates.

$$Na_2SiO_3 + 6HF \longrightarrow Na_2SiF_6 + 3H_2O$$

While other halogen acids (HCl, HBr and HI) do not react with silicates and hence can be stored in glass bottles.

(7) AgF is soluble in H_2O while all other silver halides *i.e.*, $AgCl, AgBr$ and AgI are insoluble in water. In constant, CaF_2 is insoluble while other calcium halides *i.e.*, $CaCl_2, CaBr_2, CaI_2$ are soluble in H_2O .

(8) Due to absence of d-orbitals, fluorine, does not form polyhalide ions while other halogens form polyhalides of the type I_3^-, Br_3^-, I_5^- etc.

Preparation of halogens and its uses

(1) **Fluorine**

(i) ***Occurrence of fluorine*** : Fluorine does not occur free in nature but occurs mostly as fluorspar CaF_2 , cryolite, Na_3AlF_6 and fluorapatite, $CaF_2.3Ca_3(PO_4)_2$. Traces of fluoride occur in sea water, bones, teeth, blood, milk etc.

(ii) ***Difficulties encountered during its isolation*** : (a) F_2 attacks all the materials of the apparatus such as glass, platinum, carbon and other metals, (b) F_2 is the strongest oxidising agent and hence no oxidising agent can oxidise F^- ions to F_2. (c) F_2 cannot be prepared even by electrolysis of an aqueous solution of HF because F_2 formed reacts violently with water. If also cannot be prepared by electrolysis of anhydrous HF because it is not only poisonous, corrosive and volatile but also is a bad conductor of electricity.

(iii) ***Preparation*** : F_2 is now prepared by electrolysis of a solution of KHF_2 (1 part) in anyhydrous HF (5 parts) in a vessel (modern method) made of $Ni-Cu$ alloy or $Ni-Cu-Fe$ alloy called the monel metal using carbon electrodes. During the electrolysis following reactions occur.

$$KHF_2 \longrightarrow KF + HF \text{ ; } KF \longrightarrow K^+ + F^-$$

At cathode : $K^+ + e^- \longrightarrow K$; $2K + 2HF \longrightarrow 2KF + H_2 \uparrow$

At anode : $F^- \longrightarrow F + e^-$; $F + F \longrightarrow F_2$

(iv) ***Properties*** : It is the most reactive of all the halogens. It Combines with metals as well as non-metals to form fluorides. It decomposes water forming O_2 and O_3 and reacts vigorously with hydrogen of hydrocarbons leaving behind fluorinated hydrocarbons.

$$2H_2O + 2F_2 \xrightarrow[\text{Oxidation}]{\text{Cold}} 4HF + O_2$$

$$3H_2O + 3F_2 \xrightarrow[\text{Oxidation}]{\text{Hot}} 6HF + O_3$$

(HF being a volatile liquid fumes in air)

$$CH_4 \xrightarrow{F_2} CH_3F \xrightarrow{F_2} CH_2F_2 \xrightarrow{F_2} CHF_3 \xrightarrow{F_2} CF_4$$

It is a strong oxidising agent and oxidises $KClO_3$ to $KClO_4, KIO_3$ to KIO_4 and bisulphates to peroxy sulphates.

$$KClO_3 + F_2 + H_2O \longrightarrow KClO_4 + H_2F_2$$

$$2NaHSO_4 + F_2 \longrightarrow Na_2S_2O_8 + 2HF$$

It reacts with NH_3 to form nitrogen and with H_2S forming SF_6.

$2NH_3 + 3F_2 \longrightarrow N_2 + 6HF$ (oxidation reaction)

$$H_2S + 4F_2 \longrightarrow SF_6 + 2HF$$

Fluorine reacts with cold and dilute sodium hydroxide solution to give oxygen difluoride (OF_2)

$$2F_2 + 2NaOH \text{ (cold, dil)} \longrightarrow 2NaF + H_2O + OF_2$$

However, with hot and concentrated sodium hydroxide solution it gives oxygen

$$2F_2 + 4NaOH \text{(Hot, conc.)} \longrightarrow 4NaF + 2H_2O + O_2$$

Since F_2 is the strongest oxidising agent, it is always reduced and hence does not show disproportionation reactions while others halogens do.

F_2 oxidises all other halide ions to the corresponding halogens $(F_2 + 2X^- \longrightarrow 2F^- + X_2)$; $(X = Cl, Br$ or $I)$

(v) ***Uses of fluorine*** : Fluorine is used in the manufacture of UF_6 (which is used for nuclear power generation), SF_6 (which is used as an electrical insulator), chlorofluorocarbons, teflon, cryolite and HF.

(vi) *Fluorocarbons* are the derivatives of hydrocarbons in which H-atoms are replaced by F-atoms. these are obtained by fluorination of hydrocarbons with F_2 diluted with an inert gas such as N_2 in presence of CuF_2 as catalyst. Fluorocarbons are widely used in industry because of their extreme inertness (non-in-flammability and extreme stability). Freon (CF_2Cl_2) is used as a refrigerant, tetrafluoroethylene $(F_2C = CF_2)$ is used for the manufacture of teflon which is highly non-inflammable, has high thermal stability and is chemically inert *i.e.*, is not attacked by acids and corrosive chemicals. It is used for making pipes, surgical tubes, non-stick utensils and as an electrical insulator.

(2) **Chlorine**

(i) ***Occurrence*** : Chlorine mainly occurs as rock salt $(NaCl)$ Carnallite, $(KCl, MgCl_2.6H_2O)$ and Calcium chloride. $(CaCl_2)$.

(ii) ***Preparation*** : On a commercial scale chlorine is prepared by electrolysis of an aqueous solution of sodium chloride (brine solution) (Nelson cell, Castner and Kellner's cell for the manufacture of $NaOH$) when Cl_2 is evolved at the anode and H_2 is evolved at the cathode.

$$2NaCl + 2H_2O \xrightarrow{\text{Electrolysis}} 2NaOH + Cl_2 \uparrow + H_2 \uparrow$$

It can also be prepared by electrolysis of molten $NaCl$ (Down's cell for the manufacture of metallic sodium). When Cl_2 is evolved at the anode and sodium metal at the cathode.

$$2NaCl \xrightarrow{\text{Electrolysis}} 2Na + Cl_2 \uparrow$$

In the laboratory, Cl_2 is prepared by the action of MnO_2 or $KMnO_4$ or $K_2Cr_2O_7$ on conc. HCl or a mixture of $NaCl$ and Conc. H_2SO_4

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

$$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 5Cl_2 + 8H_2O$$

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$$

$$MnO_2 + 2NaCl + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2$$

$$2KMnO_4 + 10NaCl + 13H_2SO_4 \longrightarrow$$
$$10NaHSO_4 + K_2SO_4 + 2MnSO_4 + 8H_2O + 5Cl_2$$

Other oxidising agents such as $PbO_2, Pb_3O_4, CaOCl_2, O_3$ etc. also react with HCl to liberate Cl_2.

(iii) ***Properties*** : It combines with metals and non metals to form chlorides. it decomposes water forming HCl and $HClO$ (hypochlorous acid) which is unstable and decomposes giving nascent oxygen which is responsible for oxidising and bleaching action of chlorine.

$$Cl_2 + H_2O \longrightarrow HCl + HClO \; ; \; HClO \xrightarrow{hv} HCl + [O]$$

Coloured matter $+ O \longrightarrow$ Colourless matter.

The bleaching action is permanent and colour is not restored on standing. However, it cannot be used for bleaching delicate articles such as straw, silk, wool etc. which are damaged by it.

Cl_2 oxidises Br^- and I^- ions to Br_2 and I_2 respectively.

$$Cl_2 + 2X^- \longrightarrow 2Cl^- + X_2 (X = Br \text{ or } I).$$

It combines with alkalies forming hypochlorite and chlorate salts in cold and hot conditions respectively.

$$2NaOH \text{(dil.)} + Cl_2 \xrightarrow{\text{Cold}} NaCl + NaClO + H_2O$$

$$6NaOH \text{(Conc.)} + 3Cl_2 \xrightarrow{\text{Heat}} 5NaCl + NaClO_3 + 3H_2O$$

During these reactions, halogen is simultaneously reduced to X^- ion and is oxidised to either hypohalite (XO^-) or halate (XO_3^-) ion. Such reactions are called disproportionation reactions.

With slaked lime, Cl_2 gives bleaching powder $(CaOCl_2)$

$$Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 + H_2O$$

With ammonia, Cl_2 reacts as follows :

$$8NH_3(excess) + 3Cl_2 \longrightarrow 6NH_4Cl + N_2 \uparrow$$

$$NH_3 + 3Cl_2(excess) \longrightarrow NCl_3 + 3HCl$$

With SO_2 and CO, addition compounds are formed

$SO_2(dry) + Cl_2 \longrightarrow SO_2Cl_2$ (Sulphuryl chloride)

$CO + Cl_2 \longrightarrow COCl_2$ (Carbonyl chloride or phosgene)

Cl_2 is strong oxidising agent. It oxidises $FeCl_2$ to $FeCl_3$, moist SO_2 to H_2SO_4, SO_3^{2-} to SO_4^{2-}, thiosulphate to sulphate and sulphur.

(iv) ***Uses of chlorine*** : It is used in the manufacture of $HCl, NaOCl$, bleaching powder, chlorates, vinyl chloride, insecticides such as DDT, chlorinated organic solvents like $CHCl_3, CCl_4$. It is also used in sterilisation of drinking water, in the extraction of Au and Pt and as a bleaching agent for paper, pulp and textiles.

(3) **Bromine**

(i) ***Occurrence*** : It mainly occurs in sea water and salt lakes as $NaBr, KBr$ and $MgBr_2$.

(ii) ***Preparation*** : On a commercial scale, bromine is prepared either from sea water (containing $NaBr, KBr$ and $MgBr_2$) or the mother liquor (containing $MgBr_2$) left after crystallisation of chlorides from carnallite. On passing Cl_2 gas through these solutions, bromides get oxidised to bromine which is cooled and condensed to Br_2 liquid.

$$2Br^- + Cl_2 \longrightarrow 2Cl^- + Br_2$$

In the laboratory, bromine can be prepared by heating $NaBr$ with MnO_2 and conc. H_2SO_4.

$$2NaBr + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Br_2$$

It is also obtained by adding HCl to a mixture containing potassium bromide and potassium bromate.

$$5KBr + KBrO_3 + 6HCl \longrightarrow 6KCl + 3Br_2 + 3H_2O$$

(iii) ***Properties*** : Bromine is a reddish brown heavy liquid.

Its reaction with water, oxidising and bleaching action, reaction with alkalies, NH_3, metals and non metals are similar to that of chlorine. Br_2 oxidises only iodide ions to I_2. Bromine water reacts with mercuric oxide to form mercury oxy bromide

$$2HgO + \underset{\text{Bromine water}}{2Br_2 + H_2O} \longrightarrow \underset{\text{Mercuryoxy bromide}}{HgBr_2.HgO} + 2HBrO$$

(iv) ***Uses of bromine*** : The main use of bromine is in the manufacture of ethylene bromide which is used as an additive to leaded petrol. It is also used to prepare $AgBr$, bromine water, dyes, drugs and benzyl bromide (an effective tear gas).

(4) **Iodine**

(i) ***Occurrence*** : It mainly occurs in sea weeds or alkali metal iodides. Caliche (crude chile salt petre) which is mainly sodium nitrate contains iodine as sodium iodate $(NaIO_3)$.

(ii) ***Preparation of iodine*** : On a commercial scale iodine is prepared from sea weeds and caliche.

(a) *From sea weeds* : Sea weeds (Laminaria variety) are dried, burnt and ash (called kelp constains about 1% I_2 as iodides of alkali metals besides chlorides and sulphates) is extracted with hot water. sulphates and chlorides are separated by fractional crystallisation, the mother liquor is treated with Cl_2 gas or heated with MnO_2 and conc. H_2SO_4 to liberate I_2 which is cooled and condensed to give violet crystals.

$$2NaI + Cl_2 \longrightarrow 2NaCl + I_2$$

$$2NaI + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + I_2$$

(b) *From Caliche* : The mother liquor left after crystallisation of $NaNO_3$ is treated with $NaHSO_3$ to liberate I_2 from $NaIO_3$.

$$2NaIO_3 + 5NaHSO_3 \longrightarrow 3NaHSO_4 + 2Na_2SO_4 + H_2O + I_2$$

In the laboratory, I_2 is prepared by heating a mixture of potassium iodide and MnO_2 with conc. H_2SO_4.

$$2KI + MnO_2 + 3H_2SO_4 \longrightarrow 2KHSO_4 + MnSO_4 + H_2O + I_2$$

(iii) ***Properties*** : It is a dark violet shining solid which sublimes on heating. It is least soluble in water. However, its solubility can be increased by adding $10\% KI$ solution due to the formation of I_3^- complex ion in which I^- ion acts as a lewis base (ligand) and I_2 molecule behaves as a lewise acid (central atom) which accommodates lone pair of electrons donated by I^- ion in the antibonding sigma p_z molecular orbital.

$I_2 + I^- \longrightarrow I_3^-$ (complex ion)

The aqueous solution containing I_3^- complex ion has a brown colour. It is soluble in many organic solvents. Its solution in $CS_2, CHCl_3$ and CCl_4 is violet while in strong donor solvents like alcohols, ethers and amines is brown.

With cold, dilute $NaOH$, iodine gives hypoiodous acid

$$NaOH + I_2 \xrightarrow{\text{Cold}} NaI + HIO$$

However, with hot, conc. solution of $NaOH$, the reaction is similar to that of Cl_2 or Br_2.

Iodine does not displace chlorine and bromine from chlorides and bromides respectively, but it displaces them from their oxy salts

$$2KClO_3 + I_2 \longrightarrow 2KIO_3 + Cl_2$$

$$2KBrO_3 + I_2 \longrightarrow 2KIO_3 + Br_2$$

With $Na_2S_2O_3$, iodine solution is decolourised due to the formation of colourless iodide and tetrathionate ions.

$$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$$

With ammonia it reacts as follows

$$2NH_3 + 3I_2 \longrightarrow \underset{\text{(explosive)}}{NI_3.NH_3} + 3HI$$

$$8NI_3.NH_3 \longrightarrow 5N_2 + 9I_2 + 6NH_4I$$

With strong oxidising agents such as HNO_3, O_3 and Cl_2, iodine gives iodic acid (HIO_3)

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

$$I_2 + H_2O + O_3 \longrightarrow 2HIO_3 + 5O_2$$

$$I_2 + 5Cl_2 + 6H_2O \longrightarrow 2HIO_3 + 10HCl$$

(iv) ***Uses of iodine*** : It is used to prepare tincture of iodine (2% solution of I_2 in alcohol), iodex, iodoform, KI, iodised salt (which contains KI or NaI, 0.5 *g* per kg of $NaCl$) and as a laboratory reagent.

(5) **Hydrogen halides :** All the halogens combine with hydrogen to form hydrogen halides (HX).

(i) ***Preparation of HF and HCl*** : These are prepared by heating fluorides and chlorides respectively with conc. H_2SO_4.

$$CaF_2 + H_2SO_4 \xrightarrow{\text{Heat}} CaSO_4 + 2HF$$

$$2NaCl + H_2SO_4 \xrightarrow{\text{Heat}} Na_2SO_4 + 2HCl$$

(ii) ***Preparation of HBr and HI*** :These are prepared by heating bromides and iodides respectively with phosphoric acid

$$3NaBr + H_3PO_4 \xrightarrow{\text{Heat}} Na_3PO_4 + 3HBr$$

$$3NaI + H_3PO_4 \xrightarrow{\text{Heat}} Na_3PO_4 + 3HI$$

Conc. H_2SO_4 cannot be used for the preparation of HBr and HI because these being strong reducing agents reduced H_2SO_4 to SO_2 and are themselves oxidised to Br_2 and I_2 respectively.

$$2HBr + H_2SO_4 \longrightarrow SO_2 + Br_2 + 2H_2O$$

(6) **Bleaching powder** is obtained by the action of chlorine on dry slaked lime (Hasenclever method).

$$Ca(OH)_2 + Cl_2 \xrightarrow{313\,K} CaOCl_2 + H_2O$$

An aqueous solution of bleaching powder gives tests for Cl^- and ClO^- ions. On long standing, it undergoes auto-oxidation to form calcium chlorate. However, when heated, in presence of $CoCl_2$, it gives O_2

$$6CaOCl_2 \longrightarrow 5CaCl_2 + Ca(ClO_3)_2$$

$$2CaOCl_2 \xrightarrow{CoCl_2} 2CaCl_2 + O_2$$

It is used for bleaching cotton, wood pulp etc., as a disinfectant, as a germicide for sterilization of drinking water, in the manufacture of chloroform and for making wood unshrinkable.

Noble Gases

Helium is the first member of group 18 or zero of the periodic table. It consists of six elements helium (*He*), Neon (*Ne*), argon (*Ar*), krypton (*Kr*), xenon (*Xe*) and radon (*Rn*). Zero group occupies the intermediate position between the elements of VIIA (17th) and IA (1st) groups. These are collectively called as inactive gases or inert gases. However, these are now called noble gases as some compounds of these gases have been obtained under certain specific conditions.

(1) **Electronic configuration**

Elements	Discovery	Electronic configuration ($ns^2\ np^6$)
$_2He$	Lockyer and Janssen (1868)	$1s^2$
$_{10}Ne$	Ramsay	$1s^2, 2s^2 2p^6$
$_{18}Ar$	Rayleigh and Ramsay (1894)	$1s^2, 2s^2 2p^6, 3s^2 3p^6$
$_{36}Kr$	Ramsay and Travers (1898)	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}$, $4s^2 4p^6$

$_{54}Xe$	Ramsay and Travers (1898)	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}$, $4s^2 4p^6 4d^{10} 4f^{14}$, $5s^2 5p^6$
$_{86}Rn$	Dorn (1900)	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}$, $4s^2 4p^6 4d^{10} 4f^{14}$, $5s^2 5p^6 5d^{10}, 6s^2 6p^6$

(2) **Occurrence :** Due to the inert nature of noble gases, they always occur in the free state. Except radon, all these gases are present in atmosphere in the atomic state.

Element	*He*	*Ne*	*Ar*	*Kr*	*Xe*
Abundance (Volume %)	5.2×10^{-4}	1.8×10^{-3}	9.3×10^{-1}	1.4×10^{-3}	8.7×10^{-6}

He is also present in natural gas to the extent of 2 to 7%.

(3) **Isolation**

(i) ***Helium*** : It is commercially obtained from natural gas. The natural gas contains hydrocarbons (methane etc.), CO_2, H_2S and *He* as the main constituents.

The natural gas is compressed to about 100 *atm* and cooled to 73*K*. *He* remains unliquefied while other gases get liquefied. About 99% pure *He* is prepared by this method.

(ii) ***Argon, Neon, Krypton and Xenon*** : These gases are prepared by the fractionation distillation of liquid air. Fractional distillation of air gives O_2, N_2 and mixture of noble gases. The individual gases may be obtained by adsorption of air on coconut charcoal. The charcoal adsorbs different gases at different temperatures and can be collected.

(iii) ***Radon*** : It can be obtained by radio active disintegration of radium (226), $_{88}Ra^{226} \rightarrow {}_{86}Rn^{222} + {}_2\alpha^4$.

Properties :

(1) **Atomic radii :** The atomic radii of noble gases increases on moving down the group and their atomic radii correspond to the vander Waal's radii.

(2) **Boiling points :** The m.pt. and b.pt. increases from *He* to *Rn*, because of increase in magnitude of vander Waal's forces.

(3) **Polarizabiltiy :** The polarizability increases down the group, $He < Ne < Ar < Kr < Xe$

(4) **Ionisation energy and electron affinity :** Noble gases have stable ns^2np^6 fully filled electronic configuration, so these have no tendency to add or lose electron. Therefore, ionisation energy of noble gases is very high. On the other hand their electron affinity is zero.

(5) **Heat of vaporisation :** They posses very low values of heat of vapourisation, because of presence of very weak vander Waal's forces of attraction between their monoatomic molecules. However the value of heat of vaporisation increases with atomic number down the group and this shows that there is an increasing polarizability of the larger electronic clouds of the elements with higher atomic number.

(6) **Solubility in water :** They are slightly soluble in water. Their solubility generally increases with the increase in atomic number down the group.

(7) **Adsorption by charcoal :** All of them except helium are adsorbed by cocount charcoal at low temperature. The extent of adsorption increases down the group.

(8) **Characteristic spectra :** All of them give characteristic spectra, by which they can be identified.

(9) **Liquification of gases :** It is difficult to liquify noble gases as their atoms are held by weak vander Waal's forces. Ease of liquification increases down the group from *He* to *Rn*. Helium has the lowest boiling point (4.18 *K*) of any known substance. The ease of liquification increases down the group due to increase in intermolecular forces.

The elements helium (*He*), neon (*Ne*), argon (*Ar*), krypton (*Kr*), xenon (*Xe*) and radon (*Rn*), constitute zero group of the periodic table. These are gases at ordinary temperature and do not have chemical reactivity and therefore, these are called inert gases.

Compounds of Xenon

In 1962, *N*. Bartlett noticed that PtF_6 is a powerful oxidizing agent which combines with molecular oxygen to form ionic compound, dioxygenyl hexafluoro platinate (v) $O_2^+[PtF_6]^-$, $O_{2(g)} + PtF_{6(g)} \rightarrow O_2^+[PtF_6]^-$, This indicates that PtF_6 has oxidized O_2 to O_2^+. Now, oxygen and xenon have some similarities,

(i) The first ionization energy of *Xe* gas $(1170\, kJ\, \text{mol}^{-1})$ is fairly close to that of oxygen $(1166\, kJ\, mol^{-1})$.

(ii) The molecular diameter of oxygen and atomic radius of *Xe* are similar (4Å)

On this assumption, Bartlett reacted Xenon and PtF_6 in gas phase and a orange yellow solid of the composition $XePtF_6$ was obtained, $Xe_{(g)} + PtF_{6(g)} \rightarrow \underset{\text{Orange yellow}}{Xe^+[PtF_6]^-_{(s)}}$.

Some important stable compounds of Xe are,

+2	+4	+6
XeF_2	XeF_4, $XeOF_2$	XeF_6, $XeOF_4$, XeO_3

Fluorides : Xenon forms three compounds with fluorine. These are : Xenon difluoride (XeF_2), Xenon tetrafluoride (XeF_4) and Xenon hexafluoride (XeF_6).

(1) **Xenon difluoride** (XeF_2) is formed when a mixture of Xenon and fluorine in the ratio 1 : 3 by volume is passed through a nickel tube at 673 K, $Xe + Fe \xrightarrow{\text{Ni, 673K}} XeF_2$

Structure : XeF_2 has trigonal bipyramid geometry due to sp^3d-hybridization of Xe. Three equatorial positions are occupied by lone pairs of electrons giving a linear shape to the molecule.

Properties : XeF_2 is a colourless crystalline solid, reacts with H_2 to give Xe and HF. It is hydrolysed completely by water,

$$2XeF_2 + 2H_2O \rightarrow 2Xe + O_2 + 4HF.$$

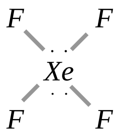
It also forms addition compounds with reactive pentafluorides like SbF_5, TaF_5 etc.

$$XeF_2 + 2SbF_5 \rightarrow XeF_2.2SbF_5$$

It is a mild fluorinating agent and hence reacts with benzene to give fluorobenzene.

(2) **Xenon tetrafluoride** (XeF_4) is prepared by heating a mixture of xenon and fluorine in the ratio 1 : 5 in a nickel vessel at 673 K and then suddenly cooling it in acetone. XeF_4 is also formed when an electric discharge is passed through a mixture of xenon and excess of fluorine, $Xe + 2F_2 \xrightarrow{\text{Ni, 673K}} XeF_4$

Structure : XeF_4 has square planar shape due to sp^3d^2 hybridization of Xe giving octahedral geometry with two trans positions occupied by lone pairs of electrons.



Properties : XeF_4 is a colourless, crystalline solid, soluble in anhydrous HF, reacts with H_2 to form Xe and HF and reacts with water to give highly explosive solid, XeO_3. (complete hydrolysis),

$$6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$$

Partial hydrolysis yields $XeOF_2$,

$$XeF_4 + H_2O \xrightarrow{193K} XeOF_2 + 2HF$$

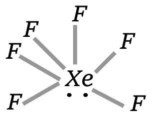
It also forms addition compounds with SbF_5, $XeF_4 + SbF_5 \rightarrow [XeF_3]^+[SbF_6]^-$.

It also acts as a strong fluorinating agent.

(3) **Xenon hexafluoride** (XeF_6) is prepared by heating a mixture of xenon and fluorine in the ratio 1 : 20 at 473—523K under a pressure of 50 atmospheres.

$$Xe + 3F_2 \xrightarrow{473-523\,K,\,50\,atm.} XeF_6$$

Structure : XeF_6 has pentagonal bipyramid geometry due to sp^3d^3 hybridization. One trans position is occupied by a lone pair giving a distorted octahedral shape.



Properties : It is colourless, crystalline solid, highly soluble in anhydrous HF giving solution which is a good conductor of electricity, $HF + XeF_6 \rightarrow XeF_5^+ + HF_2^-$.

It is the most powerful fluorinating agent and reacts with H_2 to give Xe and HF. Partial hydrolysis of XeF_6 yields $XeOF_4$ an complete hydrolysis yields xenon trioxide, XeO_3.

$$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$$

$$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$$

It forms addition compounds with alkali metal fluorides (except LiF) of the formula $XeF_6.MF$ where M represents the alkali metal.

Oxides : Xenon forms two oxides such as xenon trioxide (XeO_3) and xenon tetraoxide (XeO_4).

(1) **Xenon trioxide (XeO_3)** is prepared by complete hydrolysis of XeF_4 and XeF_6

$$6XeF_4 + 12H_2 \rightarrow 2XeO_3 + 4Xe + 3O_2 + 24HF$$

$$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$$

Structure : XeO_3 has tetrahedral geometry due to sp^3 hybridization of Xe. One of the hybrid orbitals contains a lone pair of electrons giving a trigonal pyramidal shape. The molecule has three Xe = O double bonds containing $p\pi - d\pi$ overlapping.

Properties : It is a colourless solid, highly explosive and powerful oxidizing agent.

(2) **Xenon tetraoxide *(XeO_4)*** is prepared by the action of conc. H_2SO_4 on sodium or barium xenate (Na_4XeO_6; Ba_2XeO_6) at room temperature,

$$Na_4XeO_6 + 2H_2SO_4 \rightarrow XeO_4 + 2Na_2SO_4 2H_2O$$

$$Ba_2XeO_6 + 2H_2SO_4 \rightarrow XeO_4 + 2BaSO_4 + 2H_2O$$

XeO_4 is purified by vacuum sublimation at 195 K.

Structure : XeO_4 has tetrahedral structure due to sp^3 hybridization of *Xe*. There are four *Xe–O* double bonds containing $p\pi - d\pi$ overlapping.

Properties : It is quite unstable gas and decomposes to xenon and oxygen, $XeO_4 \rightarrow Xe + 2O_2$.

Oxyfluorides : Xenon forms three types of oxy fluorides such as xenon oxydifluoride ($XeOF_2$), xenon oxytetrafluoride $XeOF_4$ and xenon dioxydifluoride (XeO_2F_2).

(1) **Xenon oxydifluoride ($XeOF_2$)** is formed by partial hydrolysis of XeF_4 at 193 *K*,

$$XeF_4 + H_2O \xrightarrow{193\,K} XeOF_2 + 2HF.$$

Structure : $XeOF_2$ has trigonal bipyramid geometry due to sp^3d-hybridization of *Xe*. Two equatorial positions are occupied by lone pairs of electrons giving a T-shape to the molecule. There is one *Xe–O* double bond containing $p\pi - d\pi$ overlapping.

(2) **Xenon oxytetrafluoride ($XeOF_4$)** is prepared by partial hydrolysis of XeF_6; $XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$. It can also be prepared by the reaction of SiO_2 with XeF_6,

$$2XeF_6 + SiO_2 \rightarrow 2XeOF_4 + SiF_4.$$

Structure : $XeOF_4$ has octahedral geometry due to sp^3d^2-hybridization of Xe. One trans position is occupied by a lone pair giving pyramid shape to the molecule. There is one *Xe–O* double bond containing $p\pi - d\pi$ overlapping.

Properties : It is a colourless volatile liquid which melts at 227 *K*. It reacts with water to give XeO_2F_2 and XeO_3,

$$XeOF_4 + H_2O \rightarrow XeO_2 + 2HF,$$

$$XeO_2F_2 + H_2O \rightarrow XeO_3 + 2HF.$$

It is reduced by H_2 to *Xe,*

$$XeOF_4 + 3H_2 \rightarrow Xe + H_2O + 4HF$$

(3) **Xenon dioxydifluoride (XeO_2F_2)** is formed by partial hydrolysis of $XeOF_4$ or XeF_6

$$XeOF_4 + H_2O \rightarrow XeO_2F_2 + 2HF$$

$$XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$$

It can also be prepared by mixing XeO_3 and $XeOF_4$ at low temperature (195*K*). The product is purified by fractional distillation, $XeO_3 + XeOF_4 \xrightarrow{195\,K} 2XeO_2F_2$

Structure : XeO_2F_2 has trigonal bipyramid geometry due to sp^3d-hybridization of *Xe*. One equatorial position is occupied by a lone pair of electrons giving a see-saw structure (shape) to the molecule. There are two *Xe–O* double bonds containing $p\pi - d\pi$ overlapping.

Properties : It is a colourless solid which melts at 303*K*. It is easily hydrolysed to give XeO_3

$$XeO_2F_2 + H_2O \rightarrow XeO_3 + 2HF$$

Uses of noble gases

(1) He is used for filling of balloons and air ships because of its non-inflammability and high power (which is 92.6% to that of hydrogen).

(2) Oxygen-helium (1 : 4) mixture is used for treatment of asthma and for artificial respiration in deep sea diving because unlike nitrogen, helium is not soluble in blood even under high pressure.

(3) Helium is also used for creating inert atmosphere in chemical reactions.

(4) Liquid helium is used as a cryogenic fluid to produce and maintain extremely low temperatures for carrying out researches and as a coolant in atomic reactors and super conducting magnets.

(5) It is also used in low temperature gas thermometry and as a shield gas for arc welding.

(6) Argon is used for creating inert atmosphere in chemical reactions, welding and metallurgical operations and for filling in incandescent and fluorescent lamps. It is also used in filling Geiger-Counter tubes and thermionic tubes.

(7) Krypton and Xenon are also used in gas filled lamps. A mixture of Krypton and Xenon is also used in some flash tubes for high speed photography.

(8) Radon is used in radioactive research and therapeutics and in the non-surgical treatment of cancer and other malignant growths.

Tips & Tricks

- ✍ Among all the alkalimetals *Li* is the strongest and *Na* is the weakest reducing agent.
- ✍ Lindlar's catalyst is *Pd* poisoned with $BaSO_4$ in quinoline.
- ✍ *Keen's cement* : The setting of plaster of paris may be catalysed by sodium chloride while it is retard by borax or alum. Addition of alum to plaster of paris makes the setting very hard. The mixture is known as keen's cement.
- ✍ B_4C_3 (boron carbide) is one of the hardest known artificial substance and is called norbia.

- Bitter almonds contain *HCN* in free state. It is produced by the action of water on amygadatin (present in bitter almonds) in the presence of enzyme emulsion (also present in bitter almonds).
- Industrial lubricant oildag is a suspension of graphite in oil and colloidal solution of graphite is called aquadag.
- Broken glass pieces added during glass making is known as cullet.