Testprep Kart

Knowledge... Everywhere

Chemistry

S & P Block Element

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1. Hydrogen and Its Compounds.

(1) **Position of hydrogen in the periodic table**

Hydrogen is the first element in the periodic table. Hydrogen is placed in no specific group due to its property of giving electron (When H^- is formed) and also losing electron (When H^+ is formed).

(i) Hydrogen is placed in group I (Alkali metals) as,

(a) It has one electron in its (Outer) Shell- $1s^1$ like other alkali metals which have (inert gas) ns^1 configuration.

(b) It forms monovalent H^+ ion like $Li^+, Na^+ \ldots$

(c) It valency is also 1.

(d) Its oxide (H_2O) is stable as Li_2O, Na_2O.

(e) It is a good reducing agent (In atomic as well as molecular state) like $\mathrm{Na, Li} \ldots$

(ii) Hydrogen also resembles halogens (Group VIII A) as,

(a) It is also diatomic (H_2) like $F_2, Cl_2 \ldots$

(b) It also forms anion H^- like $F^-, Cl^- \ldots$ by gain of one electron.

(c) H^- has stable inert gas (He) configuration as CH_4, C_2H_6 like halogens CCl_4, SF_2Cl_2 etc.

(d) H is one electron short of duplet (Stable configuration) like $F, Cl, \ldots$ which are also one electron deficient than octet, $F - 2s^2 2p^5$; $Cl - 3s^2 3p^5$.

(e) (IE) of $H (1312\ kJ\ mol^{-1})$ is of the same order as that of halogens.

(iii) (IE) of H is very high in comparison with alkali metals. Also size of H^+ is very small compared to that of alkali metal ion. H forms stable hydride only with strongly electropositive metals due to smaller value of its electron affinity $(72.8\, kJ\ mol^{-1})$.

(iv) In view of the anomalous behavior of hydrogen, it is difficult to assign any definite position to it in the periodic table. Hence it is customary to place it in group I (Along with alkali metals) as well as in group VII (Along with halogens).

(2) **Discovery and occurrence:** It was discovered by **Henry Cavendish** in 1766. Its name hydrogen was proposed by **Lavoisier**. Hydrogen is the 9th most abundant element in the earth's crust.

(3) **Preparation of Dihydrogen:** Dihydrogen can be prepared by the following methods,

(i) **Laboratory method:** In the laboratory, dihydrogen can be prepared by the action of dil. H_2SO_4 on granulated Zinc, $Zn + H_2SO_4(\text{dil.}) \rightarrow ZnSO_4 + H_2$

(ii) **Industrial method**

(a) By the electrolysis of water**:** The hydrogen prepared by this method is highly pure. Dihydrogen is collected at cathode. $2H_2O(\text{l}) \xrightarrow{\text{Electrolysis}} 2H_{2(\text{g})} + O_{2(\text{g})}$

(b) Hydrocarbon steam process**:** H_2 is prepared by the action of steam on hydrocarbon. e.g.

$$CH_4 + \underset{\text{(Steam)}}{H_2O} \xrightarrow{1170K} CO + 3H_2$$

(c) Bosch process**:** $\underset{\text{water gas}}{H_2 + CO} + \underset{\text{steam}}{H_2O} \xrightarrow[Fe_2O_3,\, Cr_2O_3]{773K} CO_2 + 2H_2$

(d) Lane's process**:** H_2 is prepared by passing alternate currents of steam and water gas over red hot iron. The method consists of two stages,

Oxidation stage**:** $\underset{Iron\ filings}{3Fe} + \underset{(Steam)}{4H_2O} \xrightarrow{1025\text{–}1075K} \underset{\text{Magnetic oxide of iron}}{Fe_3O_4} + 4H_2 + 161KJ$

Reduction stage: $2Fe_3O_4 + \underset{\text{water gas}}{4CO + 4H_2} \rightarrow 6Fe + 4CO_2 + 4H_2O$

(4) **Physical properties of dihydrogen:** It is a colourless, tasteless and odourless gas. It is slightly soluble in water. It is highly combustible. The Physical constants of atomic hydrogen are, Atomic radius (pm) – 37; Ionic radius of H^- ion (pm) – 210; Ionisation energy $(kJ\,mol^{-1})$ – 1312; Electron affinity $(kJ\,mol^{-1})$ –72.8; Electronegativity – 2.1.

(5) **Chemical properties of dihydrogen:** Dihydrogen is quite stable and dissociates into hydrogen atoms only when heated above 2000 K, $H_2 \xrightarrow{2000K} H + H$. Its bond dissociation energy is very high, $H_2 \rightarrow H + H;\quad \Delta H = 435.9\,kJ\,mol^{-1}$. Due to its high bond dissociation energy, it is not very reactive.

However, it combines with many elements or compounds.

(i) **Action with metals:** To forms corresponding hydrides. $2Na + H_2 \xrightarrow{Heat} 2NaH$; $Ca + H_2 \xrightarrow{Heat} CaH_2$

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With transition metals (elements of d – block) such as Pd, Ni, Pt etc. dihydrogen forms interstitial hydrides in which the small molecules of dihydrogen occupy the interstitial sites in the crystal lattices of these hydrides. As a result of formation of interstitial hydrides, these metals adsorb large volume of hydrogen on their surface. This property of adsorption of a gas by a metal is called **occlusion.** The occluded hydrogen can be liberated from the metals by strong heating.

(ii) **Reaction with Non-metals:** $2H_2 + O_2 \xrightarrow{970K} 2H_2O$; $N_2 + 3H_2 \xrightarrow[750K,\text{ Pressure}]{Fe,\,Mo} 2NH_3$

$H_2 + F_2 \xrightarrow{Dark} 2HF$; $H_2 + Cl_2 \xrightarrow[673K,\text{ Pressure}]{Sunlight} 2HCl$

$H_2 + Br_2 \rightarrow 2HBr$; $H_2 + I_2 \xrightarrow[Pt]{673K} 2HI$

The reactivity of halogen towards dihydrogen decreases as, $F_2 > Cl_2 > Br_2 > I_2$

As a result, F_2 reacts in dark, Cl_2 in the presence of sunlight, Br_2 reacts only upon heating while the reaction with I_2 occurs in the presence of a catalyst.

(iii) **Reaction with unsaturated hydrocarbons:** H_2 reacts with unsaturated hydrocarbons such as ethylene and acetylene to give saturated hydrocarbons.

$$\underset{Ethylene}{H_2C=CH_2}+H_2 \xrightarrow[473K]{Ni\,or\,Pt\,or\,Pd} \underset{Ethane}{CH_3-CH_3}\ ;\quad \underset{Acetylene}{HC\equiv CH}+2H_2 \xrightarrow[473K]{Ni\,or\,Pt\,or\,Pd} \underset{Ethane}{CH_3-CH_3}$$

This reaction is used in the **hydrogenation or hardening of oils**. The vegetable oils such as groundnut oil or cotton-seed oil are unsaturated in nature because they contain at least one double bond in their molecules. Dihydrogen is passed through the oils at about 473 K in the presence of catalyst to form solid fats. The vegetable ghee such as Dalda, Rath, etc. are usually prepared by this process.

$$\underset{(liquid)}{\text{Vegetable oil}}+H_2 \xrightarrow[473K]{Ni} \underset{(solid)}{Fat}$$

(6) **Uses of Dihydrogen**

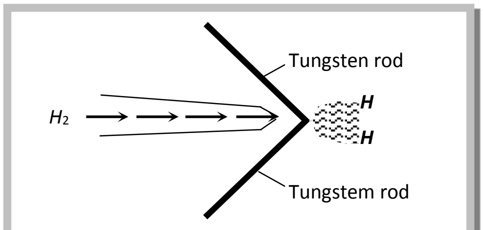
(i) As a reducing agent, (ii) In the hydrogenation of vegetable oils, (iii) As a rocket fuel in the form of liquid H_2 (iv) In the manufacture of synthetic petrol, (v) In the preparation of many compounds such as $NH_3, CH_3OH,$ Urea etc, (vi) It is used in the oxy-hydrogen torch for welding if temperature around 2500°C is required. It is also used in atomic hydrogen torch for welding purposes in which temperature of the order of 4000°C is required.

Different forms of hydrogen

(1) **Atomic hydrogen:** It is obtained by the dissociation of hydrogen molecules. The atomic hydrogen is stable only for a fraction of a second and is extremely reactive. It is obtained by passing dihydrogen gas at atmospheric pressure through an electric arc struck between two tungsten rods.

The electric arc maintains a temperature around 4000 – 4500°C. As the molecules of dihydrogen gas pass through the electric arc, these absorb energy and get dissociated into atoms as

$$H_2(g) \xrightarrow[arc]{Electric} 2H(g) : \Delta H = 435.90 KJ\ mol^{-1}$$



Atomic hydrogen torch

This arrangement is also called atomic hydrogen torch.

(2) **Nascent hydrogen:** The hydrogen gas prepared in the reaction mixture in contact with the substance with which it has to react, is called nascent hydrogen. It is also called newly born hydrogen. It is more reactive than ordinary hydrogen. For example, if ordinary hydrogen is passed through acidified $KMnO_4$ (pink in colour), its colour is not discharged. On the other hand, if zinc pieces are added to the same solution, bubbles of hydrogen rise through the solution and the colour is discharged due to the reduction on $KMnO_4$ by nascent hydrogen.

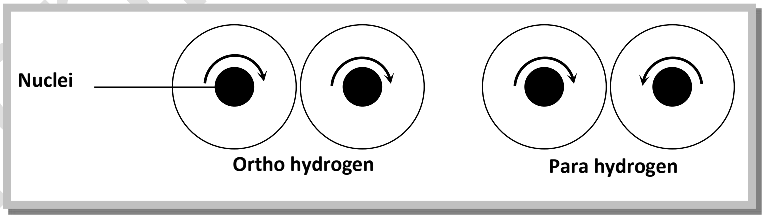
$$KMnO_4 + \underset{Molecular}{H_2} + H_2SO_4 \rightarrow No\ Reaction\ ;\ \ Zn + H_2SO_4 \rightarrow ZnSO_4 + \underset{Nascent\,hydrogen}{2[H]} \times 5$$

$$2KMnO_4 + 3H_2SO_4 + 10H \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O$$

(3) **Ortho and para hydrogen:** A molecule of dihydrogen contains two atoms. The nuclei of both the atoms in each molecule of dihydrogen are spinning. Depending upon the direction of the spin of the nuclei, the hydrogen is of two types,

(i) Molecules of hydrogen in which the spins of both the nuclei are in the same directions, called ortho hydrogen.

(ii) Molecules of hydrogen in which the spins of both the nuclei are in the opposite directions, called para hydrogen.



Ordinary dihydrogen is an equilibrium mixture of ortho and para hydrogen. Ortho hydrogen ⇌ Para hydrogen. The amount of ortho and para hydrogen varies with temperature as,

(a) At 0°K, hydrogen contains mainly para hydrogen which is more stable.

(b) At the temperature of liquefaction of air, the ratio of ortho and para hydrogen is 1:1.

(c) At the room temperature, the ratio of ortho to para hydrogen is 3:1.

(d) Even at very high temperatures, the ratio of ortho to para hydrogen can never be more than 3:1.

Thus, it has been possible to get pure para hydrogen by cooling ordinary hydrogen gas to a very low temperature (close to 20 K) but it is never possible to get a sample of hydrogen containing more than 75% of ortho hydrogen. i.e., Pure ortho hydrogen can not be obtained.

Isotopes of Hydrogen

Isotopes are the different forms of the same element which have the same atomic number but different mass numbers.

Isotopes of hydrogen

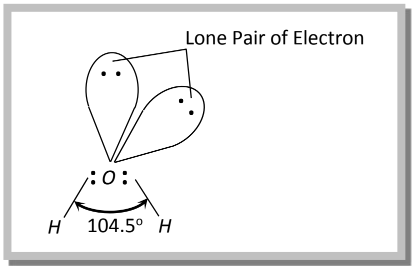
Name	**Symbol**	**Atomic number**	**Mass number**	**Relative abundance**	**Nature radioactive or non-radioactive**
Protium or Hydrogen	$^{1}_{1}H$ or H	1	1	99.985%	Non-radioactive
Deuterium	$^{2}_{1}H$ or D	1	2	0.015%	Non-radioactive
Tritium	$^{3}_{1}H$ or T	1	3	10^{-15} %	Radioactive

Physical constants of H_2 , D_2 and T_2

Property	**H_2**	**D_2**	**T_2**
Molecular mass	2.016	4.028	6.03
Melting point (K)	13.8	18.7	20.63
Boiling point (K)	20.4	23.9	25.0
Heat of fusion $(kJ\,mol^{-1})$	0.117	0.197	0.250
Heat of vaporisation $(kJ\,mol^{-1})$	0.994	1.126	1.393
Bond energy $(kJ\,mol^{-1})$	435.9	443.4	446.9

Water

Water is the oxide of hydrogen. It is an important component of animal and vegetable matter. Water constitutes about 65% of our body. It is the principal constituent of earth's surface.



(1) **Structure:** Due to the presence of lone pairs, the geometry of water is distorted and the $H-O-H$ bond angle is 104.5°, which is less than the normal tetrahedral angle (109.5°) . The geometry of the molecule is regarded as angular or bent. In water, each $O-H$ bond is polar because of the high electronegativity of oxygen (3.5) in comparison to that of hydrogen (2.1). The resultant dipole moment of water molecule is 1.84D.

In ice, each oxygen atom is tetrahedrally surrounded by four hydrogen atoms; **two by covalent bonds and two by hydrogen bonds**. The resulting structure of ice is open structure having a number of vacant spaces. Therefore, the density of ice is less than that of water and ice floats over water. It may be noted that water has maximum density $(1 g\, cm^{-3})$ at 4°C.

(2) **Heavy water:** Chemically heavy water is deuterium oxide (D_2O). It was discovered by **Urey**. It has been finding use in nuclear reactors as a moderator because it slows down the fast moving neutrons and therefore, helps in controlling the nuclear fission process.

(3) **Physical properties:** Water is colorless, odorless and tasteless liquid at ordinary temperature.

Some physical constants of H_2O and D_2O at 298 K

Constant	**Ordinary water H_2O**	**Heavy water D_2O**
Molecular mass	18.015	20.028
Maximum density $(g\, cm^{-3})$	1.000	1.106
Melting point (K)	273.2	276.8
Boiling point (K)	373.2	374.4
Heat of fusion $(kJ\, mol^{-1})$ at 273K	6.01	6.28
Heat of vaporisation $(kJ\, mol^{-1})$ at 373K	40.66	41.61
Heat of formation $(kJ\, mol^{-1})$	– 285.9	– 294.6
Ionisation constant	1.008×10^{-14}	1.95×10^{-15}

(4) **Chemical properties:** Water shows a versatile chemical behaviour. It behaves as an acid, a base, an oxidant, a reductant and as ligand to metals.

(i) **Dissociation of water:** Water is quite stable and does not dissociate into its elements even at high temperatures. Pure water has a small but measurable electrical conductivity and it dissociates as,

$H_2O + H_2O \rightleftharpoons \underset{\text{Hydronium ion}}{H_3O^+} + OH^-$; $K_W = 1.0 \times 10^{-14}\ mol^2 L^2$ at 298K

(ii) **Amphoteric nature:** Water can act both as an acid and a base and is said to be amphoteric. However, water is neutral towards litmus and its pH is 7.

(iii) **Oxidising and reducing nature:** Water can act both as an oxidising and a reducing agent in its chemical reactions. e.g. $2Na + \underset{\text{Oxidising agent}}{2H_2O} \rightarrow 2NaOH + H_2$; $2F_2 + \underset{\text{Reducing agent}}{2H_2O} \rightarrow 4HF + O_2$

(5) **Hard and Soft water**

Water which produces lather with soap solution readily is called **soft water**. e.g. distilled water, rain water and demineralised water.

Water which does not produce lather with soap solution readily is called **hard water**. e.g. sea water, river water, well water and tap water.

(i) **Cause of hardness of water:** The hardness of water is due to the presence of bicarbonates, chlorides and sulphates of calcium and magnesium.

Hard water does not produce lather because the cations $(Ca^{+2}$ and $Mg^{+2})$ present in hard water react with soap to form insoluble precipitates, $\underset{\text{From hard water}}{M^{+2}} + \underset{\text{Sodium stearate (soap)}}{2C_{17}H_{35}COONa} \rightarrow \underset{\text{Metal stearate (PPt.)}}{(C_{17}H_{35}COO)_2M} + 2Na^+$,Where

$M = Ca$ or Mg

Therefore, no lather is produced until all the calcium and magnesium ions are precipitated. This also results into wastage of lot of soap.

(ii) **Type of hardness of water:** The hardness of water is of two types,

(a) Temporary hardness: This is due to the presence of bicarbonates of calcium and magnesium. It is also called carbonate hardness.

(b) Permanent hardness: This is due to the presence of chlorides and sulphates of calcium and magnesium. It is also called non-carbonate hardness.

(iii) **Softening of water:** The process of the removal of hardness from water is called softening of water.

(a) Removal of temporary hardness**:** It can be removed by the following methods,

By boiling**:** During boiling, the bicarbonates of Ca and Mg decompose into insoluble carbonates and give CO_2. The insoluble carbonates can be removed by filtration.

$$\underset{Cal.bicarbonate}{Ca(HCO_3)_2} \xrightarrow{Heat} \underset{PPt.}{CaCO_3} + CO_2 + H_2O;\ \underset{Mag.bicarbonate}{Mg(HCO_3)_2} \xrightarrow{Heat} \underset{PPt.}{MgCO_3} + CO_2 + H_2O$$

Clark's method**:** This process is used on a commercial scale. In this process, calculated amount of lime $[Ca(OH)_2]$ is added to temporary hard water.

$$\underset{\text{Soluble}}{Ca(HCO_3)_2} + \underset{\text{Lime}}{Ca(OH)_2} \longrightarrow \underset{\text{Insoluble}}{2CaCO_3} \downarrow + 2H_2O$$

$$\underset{\text{Soluble}}{Mg(HCO_3)_2} + \underset{\text{Lime}}{Ca(OH_2)} \longrightarrow \underset{\text{(Insoluble)}}{MgCO_3 \downarrow + CaCO_3} \downarrow + 2H_2O$$

(b) Removal of permanent hardness: Permanent hardness can be removed by the following methods,

By washing soda method : In this method, water is treated with a calculated amount of washing soda (Na_2CO_3) which converts the chlorides and sulphates of Ca and Mg into their respective carbonates which get precipitated.

$$CaCl_2 + Na_2CO_3 \longrightarrow \underset{ppt.}{CaCO_3} + 2NaCl\ ;\ MgSO_4 + Na_2CO_3 \longrightarrow \underset{ppt.}{MgCO_3} + Na_2SO_4$$

Permutit method: This is a modern method employed for the softening of hard water. Hydrated sodium aluminium silicate $(Na_2Al_2Si_2O_8.xH_2O)$ is called permutit. These complex salts are also known as zeolites.

The permutit as loosely packed in a big tank over a layer of coarse sand. Hard water is introduced into the tank from the top. Water reaches the bottom of the tank and then slowly rises through the permutit layer in the tank. The cations present in hard water are exchanged for sodium ions. Therefore this method is also called ion exchange method.

$\underset{\text{Sodium zeolite}}{Na_2Z} + \underset{\text{(From hard water)}}{Ca^{+2}} \longrightarrow \underset{\text{Cal zeolite}}{CaZ} + 2Na^+$; $Na_2Z + \underset{\text{(From hard water)}}{Mg^{+2}} \longrightarrow \underset{\text{Magnesium zeolite}}{MgZ} + 2Na^+$, where $Z = Al_2Si_2O_8 .\ xH_2O$

Hydrogen peroxide

Hydrogen peroxide (H_2O_2) was discovered by French chemist **Thenard**.

(1) **Preparation:** It is prepared by

(i) **Laboratory method**: In laboratory, H_2O_2 is prepared by Merck's process. It is prepared by adding calculated amounts of sodium peroxide to ice cold dilute (20%) solution of H_2SO_4.

$$Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$$

(ii) **Industrial method**: On a commercial scale, H_2O_2 can be prepared by the electrolysis of 50% H_2SO_4 solution. In a cell, peroxy disulphuric acid is formed at the anode.

$$2H_2SO_4 \xrightarrow[\text{Elecrolysis}]{} \underset{\text{Peroxy disulphuric acid}}{H_2S_2O_8(aq.)} + H_2(g)$$

This is drawn off from the cell and hydrolyzed with water to give H_2O_2.

$H_2S_2O_8 + 2H_2O \longrightarrow 2H_2SO_4 + H_2O_2$ The resulting solution is distilled under reduced pressure when H_2O_2 gets distilled while H_2SO_4 with high boiling point, remains undistilled.

(2) **Physical properties:** Pure H_2O_2 is a thick syrupy liquid with pale blue color. It is more viscous and dense than water. It is completely miscible with water, alcohol and ether in all proportions.

(3) **Chemical properties**

(i) **Decomposition:** Pure H_2O_2 is an unstable liquid and decomposes into water and O_2 either upon standing or upon heating, $2H_2O_2 \longrightarrow 2H_2O + O_2;\ \Delta H = -196.0\,kJ$

(ii) **Oxidising nature:** It is a powerful oxidizing agent. It acts as an oxidizing agent in neutral, acidic or in alkaline medium. e.g. $2KI + H_2O_2 \longrightarrow 2KOH + I_2$ [In neutral medium]

$2FeSO_4 + H_2SO_4 + H_2O_2 \longrightarrow Fe_2(SO_4)_3 + 2H_2O$ [In acidic medium]

$MnSO_4 + H_2O_2 + 2NaOH \longrightarrow MnO_2 + Na_2SO_4 + 2H_2O$ [In alkaline medium]

(iii) **Reducing nature:** H_2O_2 has tendency to take up oxygen from strong oxidizing agents and thus, acts as a reducing agent, $H_2O_2 + \underset{\text{From oxidising agent}}{O} \longrightarrow H_2O + O_2$. It can act as a reducing agent in acidic, basic or even neutral medium.

In acidic medium, $H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$

In alkaline medium, $H_2O_2 + 2OH^- \longrightarrow 2H_2O + O_2 + 2e^-$

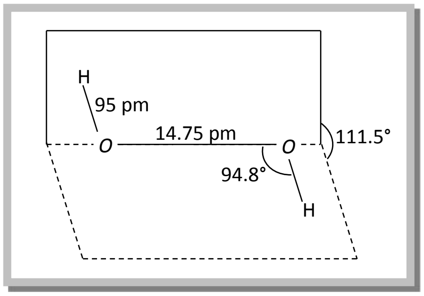
(iv) **Bleaching action:** H_2O_2 acts as a bleaching agent due to the release of nascent oxygen.

$H_2O_2 \longrightarrow H_2O + O$

Thus, the bleaching action of H_2O_2 is due to oxidation. It oxidizes the coloring matter to a colorless product, Coloring matter +O → Color less matter

H_2O_2 is used to bleach delicate materials like ivory, silk, wool, leather etc.

(4) **Structure of H₂O₂:** H_2O_2 has non-planar structure in which two H-atoms are arranged in two directions almost perpendicular to each other and to the axis joining the two oxygen atoms. The O – O linkage is called peroxide linkage.



(5)**Strength of H₂O₂:** The strength of H_2O_2 is expressed in terms of weight or volume,

(i) **As weight percentage:** The weight percentage of H_2O_2 gives the weight of H_2O_2 in 100 g of solution. For example, a 40% solution by wt. means 40 g of H_2O_2 are present in 100 g of solution.

(ii) **As volume:** The strength of H_2O_2 is commonly expressed as volume. This refers to the volume of oxygen which a solution of H_2O_2 will give. For example, a "20 volume" of H_2O_2 means that 1 litre of this solution will give 20 liters of oxygen at NTP.

(6) **Uses of H_2O_2**

(i) It is used as an antichlor in bleaching because it can reduce chlorine. $Cl_2 + H_2O_2 \longrightarrow 2HCl + O_2$

(ii) It is used for restoring the color of lead paintings.

(iii) It is used as an antiseptic for washing wounds, teeth and ears under the name perhydrol.

2. 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**. These are usually referred to as alkali metals since their hydroxides forms strong bases or alkalies.

Electronic configuration

Elements	**Discovery**	**Electronic configuration** (ns^1)
$_3\text{Li}$	Arfwedson (1817)	$1s^2 2s^1$ or $[\text{He}]^2 2s^1$
$_{11}\text{Na}$	Davy (1807)	$1s^2 2s^2 2p^6 3s^1$ or $[\text{Ne}]^{10} 3s^1$
$_{19}\text{K}$	Davy (1807)	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ or $[\text{Ar}]^{18} 4s^1$
$_{37}\text{Rb}$	Bunsen (1861)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$ or $[\text{Kr}]^{36} 5s^1$
$_{55}\text{Cs}$	Bunsen (1860)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^1$ or $[\text{Xe}]^{54} 6s^1$
$_{87}\text{Fr}$	Percy (1939)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6 7s^1$ or $[\text{Rn}]^{86} 7s^1$

Note: Francium is radioactive with longest lived isotope ^{223}Fr with half-life period of only 21 minute.

(1) Because of similarity in electronic configuration, they exhibit similar properties. A regular gradation in their properties with increase in at. no. is observed due to increasing size of atoms/ions and the low binding energy of valency electrons.

(2) Of all the alkali metals, only sodium and potassium are found in abundance in nature. Francium occurs only in minute quantities as a radioactive decay product.

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 luster which quickly tarnishes due to surface oxidation.

(ii) These form diamagnetic colorless ions since these ions do not have unpaired electrons, (i.e. M^+ has ns^0configuration). That is why alkali metal salts are colorless 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 20^0C.

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

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

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

(i) All these elements possess low m.pt and b.pt in comparison to other group members.

Li	Na	K	Rb	Cs	Fr	
m.pt (K)	453.5	370.8	336.2	312.0	301.5	–
b.pt (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 m.pt and b.pt On moving down the group, the atomic size increases and binding energy of their atoms in crystal lattice decreases which results lowering of m.pts.

(iii) Lattice energy decreases from Li to Cs and thus m.pt and b.pt also decrease from Li to Cs.

(5) **Ionization energy & 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 ionization energy.(I.E.)

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

Ionization 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 ionization energy (huge difference) can be explained as,

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

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

(iii) Lower are ionization 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) These elements easily form **univalent** + ve ion by losing solitary ns^1 electron due to low ionization energy values.

(ii) Alkali metals are univalent in nature and form ionic compounds. Lithium salts are, however, covalent.

(iii) 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 ionization 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.

(iv) Since the electronic configuration of M^+ ions do not have unpaired electron and thus alkali metal salts are diamagnetic and colouress. Only those alkali metal salts are colored which have colored anions e.g. $K_2Cr_2O_7$ is orange because of orange colored $Cr_2O_7^{2-}$ ion, $KMnO_4$ is violet because of violet colored 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 when ions on dissolution water get hydration.

(ii) The hydration is an exothermic process i.e energy is released during hydration.
(iii) 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 $M_{(g)}{}^{+} + Aq \rightarrow M^{+}{}_{(aq)}\,;\Delta H = -energy.$

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

(v) 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) **Electronegativities**

(i) These metals are highly electropositive and thereby possess low values of electronegativities.

(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	–

Note: 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 & electricity, because of loosely held valence electrons.

(11) **Standard oxidation potential and reducting 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.

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

(iv) However, an examination of ionization 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, $Na_{(s)} + H_2O \rightarrow Na^+_{(sq)} + e; \Delta H = \Delta H_5 + IE_1 - \Delta H_h$

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 colors:** The alkali metals and their salts give characteristic color 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 color differ from each other Li – crimson, Na–Golden yellow, K – Pale violet, Rb and Cs –violet. These different colors are due to different ionization 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) **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 ($Na_2B_4O_7 10H_2O$), 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% $Rb_2\ O$

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

(2) **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 fussion temperature.

Fused NaCl : $NaCl \xrightarrow{fusion} Na^{+} + Cl^{-}$ $\begin{matrix} Electrolysis : Anode : 2Cl^{-} \rightarrow Cl_2 + 2e \\ of\ fused\ salt : Cathode : 2Na^{+} + 2e \rightarrow 2Na \end{matrix}$

(3) **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.

(4) **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,

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

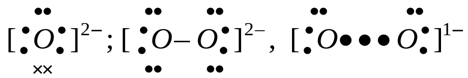
(ii) When burnt air (O_2), lithium forms lithium oxide (Li_2O) sodium forms sodium peroxide (Na_2O_2) and other alkali metals form super oxide (Mo_2 i.e. KO_2,RbO_2 or CsO_2)

$$2Li + \frac{1}{2}O_2 \rightarrow \underset{\text{Lithuim oxide}}{Li_2O} \ ;\ 2Na + O_2 \rightarrow Na_2O_2 \ ;\ K + O_2 \rightarrow \underset{\text{Potassium super oxide}}{KO_2}$$

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,



$$[\underset{\times\times}{\overset{\bullet\bullet}{:O:}}]^{2-};\ [\underset{\bullet\bullet}{\overset{\bullet\bullet}{:O}}-\underset{\bullet\bullet}{\overset{\bullet\bullet}{O:}}]^{2-},\ [\overset{\bullet\bullet}{:O}\bullet\bullet\bullet\overset{\bullet\bullet}{O:}]^{1-}$$

The O_2^{-1} ion has a three electron covalent bond and has one electron unpaired. It is therefore superoxides are paramagnetic and colored 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 oxidizing 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°C 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.

(5) **Hydrides**

(i) These metal combines 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 & 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 hydrides as H^- and the smaller cation will produce more polarization of anion (according to Fajan 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.

(6) **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,

$$2MHCO_3 \xrightarrow{300^0 C} M_2CO_3 + H_2O + CO_2$$

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

(7) **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 (The Fajan's rule) 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

(8) **Solubility in liquid NH_3**

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

(ii) With increasing concentration of ammonia, blue color 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.

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

(iv) It is the ammoniated electron which is responsible for blue color, 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.

(9) **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); $4\ LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$

(10) **Sulphates**

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

(ii) Except Li_2SO_4, rest all are soluble 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. $K_2SO_4 . Al_2(SO_4)_3 . 24\ H_2O$.

(11) **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. $M_3N + 3H_2O \rightarrow 3MOH + NH_3$

(12) **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 .

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

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

(13) **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 behavior of Lithium

Anomalous behavior of lithium is due to extremely low 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.

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

(3) Unlike other alkali metals, lithium is 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.

(5) Lithium when heated in NH_3 forms imide, 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 crystallization ($LiCl.\ 2H_2O$). Crystals of NaCl KBr, KI etc do not conation water of crystallization.

(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_3PO4 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 $Li_3\ N$ and $Mg_3\ N_2$. Other alkali metals combine at high temperature, $6Li + N_2 \rightarrow 2Li_3N$; $3Mg + N_2 \rightarrow Mg_3\ N_2$. 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 whereas carbonates of alkali metals are more soluble.

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

$2Li + 2C \rightarrow Li_2C_2$; $Mg + 2C \rightarrow MgC_2$

(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) Lithium and Mg Form only monoxide 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 $MgCl_2.\,2H_2O$.

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

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

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

(3) **Compound of sodium**

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

(i) **Preparation**

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

(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 electrolyzed ; Central compartment – 2% $NaOH$ solution and H_2

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

(a) Reaction with salt : $FeCl_3 + 3NaOH \rightarrow \underset{(\text{Insolublehydroxide})}{Fe(OH)_3} \downarrow + 3NaCl$

$$HgCl_2 + 2NaOH \rightarrow 2NaCl + \underset{\text{unstable}}{Hg(OH)_2} \rightarrow \text{H}_2O + \underset{\text{yellow}}{HgO \downarrow}$$

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

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

$3X_2 + 6NaOH$ (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: $NaOH + CO \xrightarrow[5-10\ atm]{150-200^o C} \underset{\text{Sod. formate}}{HCOONa}$

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

(iii) **Uses:** In the manufacturing of sodium metal, soap, rayon, paper, dyes and drugs. For mercuring cotton to make cloth unshrinkable and reagent in lab.

Sodium carbonate or washing soda, Na_2CO_3

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

$NH_3 + CO_2 + H_2O \rightarrow NH_4HCO_3$

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

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

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

Note: $CaCl_2$ so formed in the above reaction is a byproduct of solvay process.

(ii) **Properties:** (a) $\underset{\text{(decahydrate)}}{Na_2CO_3.10H_2O} \xrightarrow{\text{dry air}} \underset{\text{(Monohydrate)}}{Na_2CO_3.H_2O + 9H_2O}$

$Na_2CO_3.H_2O \xrightarrow{\Delta} Na_2CO_3 \rightarrow$ It does not decompose on further heating even to redness (m.pt. 853^{o} C)

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

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

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

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

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

Sodium peroxide (Na_2O_2)

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

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

(ii) **Properties:** (a) When pure it is colorless. The faint yellow color 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 oxidizing agent. It oxidizes Cr (III) hydroxide to sodium chromate, Mn (II) to sodium manganite and sulphides to sulphates.

(iii) **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, $2CO_2 + 2Na_2O_2 \rightarrow 2Na_2CO_3 + O_2$.

3. 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.

Electronic configuration

Element	**Electronic configurations (ns^2)**
${}_{4}Be$	$1s^2 2s^2$ or $[He]2s^2$
${}_{12}Mg$	$1s^2 2s^2 2p^6 3s^2$ or $[Ne]3s^2$
${}_{20}Ca$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ or $[Ar]4s^2$
${}_{38}Sr$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$ or $[Kr]5s^2$
${}_{56}Ba$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$ or $[Xe]6s^2$
${}_{88}Ra$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6 7s^2$ or $[Rn]7s^2$

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

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. Althought 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 M^{2+} 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 up to 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
m.pt. (K)	1560	920	1112	1041	1000	973
b.pt (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) **Ionization 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 ionization energy in comparison to alkali metals but lower ionization energies in comparison to p-block elements.

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

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

(iii) The higher values of second ionization 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 : $1s^2, 2s^1 \xrightarrow[electron]{removal\ of\ 2s} Li^+ : 1s^2 \xrightarrow[electron]{removal\ of\ 1s} Li^{2+} : 1s^1$

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

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 1 s 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 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 ionization energy.

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

$M^{2+} + {}_xH_2O \rightarrow [M(H_2O)_x]^{2+}$; $\Delta H = -$ 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 ionization 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 Ba^{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 colors**

(i) The characteristic flame color shown are : Ca-brick red; Sr –crimson ; Ba-apple green and Ra- crimson.

(ii) Alkaline earth metals except Be and Mg produce characteristic color to flame due to easy excitation of electrons to higher energy levels.

(iii) Be and Mg atoms due to their small size, bind their electrons more strongly (because of higher effective nuclear charge) Hence these requires high excitation energy and are not excited by the energy of flame with the result that no flame color is shown by them.

Chemical properties

(1) **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) **Beryllium**: 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 [$Ca(UO_2)_2$]

(2) **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 electrolyzing their fused salts.

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

(4) **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.

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

$2M + O_2 \rightarrow MO_2$ (M is Ba 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.

$BeO + 2NaOH \rightarrow Na_2BeO_2 + H_2O$; $BeO + 2HCl \rightarrow BeCl_2 + H_2O$

Sod. beryllate Beryllium chloride

(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 $\Delta H_{solution}$ down the group.

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

More negative is $\Delta H_{solution}$ 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 $BaCO_3$

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$; $Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O$

(white ppt) (white ppt)

Note: 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,

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

(5) **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 Li Al H_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.

$$\xrightleftharpoons{fusion}$$

$CaH_2 \qquad Ca^{2+} + 2H^-$

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.

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

(6) **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.

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

(7) **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

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

(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.

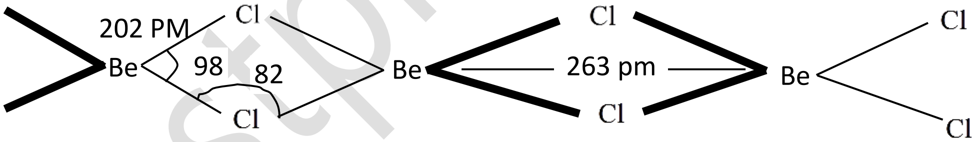
(iii) The halides of the members of this group are soluble in water and produce neutral solutions from which the hydrates such : $MgCl_2\ 6H_2O$, $CaCl_2.6H_2O.BaCl_2\ 2H_2O$ can be crystallised. The tendency to form hydrated halides decreases with increasing size of the metal ions.

(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 2 electron bonding with Be-Cl-Be bridged structure is shown below,



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

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

(9) **Nitrides**

(i) All the alkaline earth metals directs 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 hydrolyzed water to liberate NH_3, $M_3N_2 + 6H_2O \rightarrow 3M(OH)_2 + 2NH_3$

(10) **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.

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

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

(11) **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.

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

(12) **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.

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

Sulphides are phosphorescent and are decomposed by water

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

(13) **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.

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

(14) **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 $(NH_4)_2\ CO_3$ in presence of $NH_4\ Cl$.
(7) Be and Mg salts do not impart color 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) Its 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 favor 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 m. pt. 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 aluminates.

$Be + 2NaOH \rightarrow Na_2BeO_2 + H_2$; $2Al + 6NaOH \rightarrow 2Na_3AlO_3 + 3H_2$

(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 aluminum, 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.

Difference between alkali metals and alkaline earth metals

Properties	**Alkaline earth metals**	**Alkali metals**
Electronic configuration	Two electrons are present in the valency shell. The configuration is ns^2	One electron is present in the valency shell. The configuration is ns^1
Valency	Bivalent	Monovalent
Electropositive nature	Less electropositive	More electropositive
Carbonates	Insoluble in water. Decompose On heating	Soluble in water. Do not decompose on heating (Li_2CO_3 is an exception).
Hydroxides	Weak bases, less soluble and decompose on heating	Strong bases, highly soluble and stable towards heat.
Bicarbonates	These are not known in free state.	These are known is solid state.
Action of carbon	Exist only in solution Directly combine with carbon and form carbides	Do not directly combine with carbon.
Action of nitrogen	Directly combine with nitrogen and form nitrides	Do not directly combine with nitrogen.
Nitrates	Decompose on heating evolving a mixture of NO_2 and oxygen	Decompose on heating evolving Only oxygen
Hydration of compounds	The compounds are extensively hydrated. $MgCl_2$. $6H_2O$,$CaCl_2$, $6H_2O$, $BaCl_2$, $2H_2O$ are hydrated chlorides	The compounds are less hydrated NaCl, KCl, RbCl form non-hydrated chlorides.
Solubility of salts	Sulphates, phosphates, fluorides, chromates, oxalates etc. are insoluble in water	Sulphates, phosphates, fluorides, chromates, oxalates, etc. are soluble in water

Physical properties	Comparatively harder. High melting points. Diamagnetic	Soft. Low melting points, Paramagnetic

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 is obtained from carnallite and magnesite.

(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 in turn 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.

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

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

Note: 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).

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

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

Gypsum $\xrightarrow{200^o C} \underset{\text{(dead burnt plaster)}}{CaSO_4\,(\text{anhydrous})}$

Gypsum when heated to about $200^o C$ 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)

$$CaO + H_2O \rightarrow Ca(OH)_2; \quad Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + Ca(HCO_3)_2$$

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

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

4. 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.

Electronic configuration

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

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 m.pt because it exist as giant covalent polymer in both solid and liquid state.

(4) Low m.pt of Ga (29.8^{0}C) is due to the fact that consists of only Ga_2 molecule; it exist as liquid upto 2000^{0}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 (table) 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^0op for M $\rightarrow M^{3+} + 3e$	–	+1.66	+0.56	+0.34	+1.26
E^0op 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 Al > 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) **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 ($CaB_4O_7.NaBO_2.8H_2O$),
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).

(2) **Hydrides**

(i) Elements of gp 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 pπ-

pπ 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 A1.....H......Al bridges.

(v) Al and Ga forms anionic hydrides e.g. $LiAlH_4$ and $Li\,Ga\,H_4$, $4LiH + AlCl_3 \xrightarrow{ether} Li[AlH_4] + 3LiCl$

(3) **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.

(4) **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 $Al(OH)_3$ > Ga_2O_3 and $Ga(OH)_3$ > In_2O_3 In $(OH)_3$ > Tl_2O_3 $Tl(OH)_3$
(acidic) (amphoteric) (amphoteric) (basic) (strong basic)

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

(iii) Boric acid, $B(OH)_3$ is soluble in water as it accepts 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.

(5) **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.

(6) **Action of Alkalies**

(i) Boron dissolves only in fused alkalis, $2B + 6NaOH\ (\text{fused}) \rightarrow 2Na_3BO_3 + 3H_2$

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

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

(7) **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, $BF_3 + H_2O \rightarrow H^+ [BF_3OH]^- \xrightleftharpoons{H_2O} H_3O^+ [BF_3OH]^-$.

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_3 Br_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 m.pt. 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 400^0C corresponds to the formula Al_2 Cl_6.

(b) Bond distance between aluminium chlorine bonds forming bridge is greater (2.21A^0) than the distance between aluminum-chlorine bond present in the end (2.06 A^0). 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 $R_3NAl\ Cl_3$ The dimeric structure of Al_2 Cl_6 exist in vapour state below 473 K and at higher temperature it dissociates to trigonal planar $AlCl_3$ molecule.

Note: 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. $Mg_3 B_2$. 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 ($B=2.35g\ ml^{-1}$ $S=2.34$ 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_4 C 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 cannot 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) **Kernit or Rasorite:** $Na_2B_4O_7 . 10H_2O$

(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. $B_2O_3 + 6K \xrightarrow{Heat} 2B + 3K_2O$; $2BCl_3 + 3H_2 \xrightarrow{1270K} 2B + 6HCl$.

By thermal decomposition of boron tri-iodide over red hot tungsten filament and boron hydrides for example, 2 $BI_3 \xrightarrow{W,heat}$ 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 973K, with halogens, trihalides (BX_3) are fromed 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 + 3 $HNO_3 \longrightarrow H_3BO_3 + 3NO_2$; 2B + 3 $H_2SO_4 \longrightarrow 2H_3BO_3 + 3SO_2$

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**

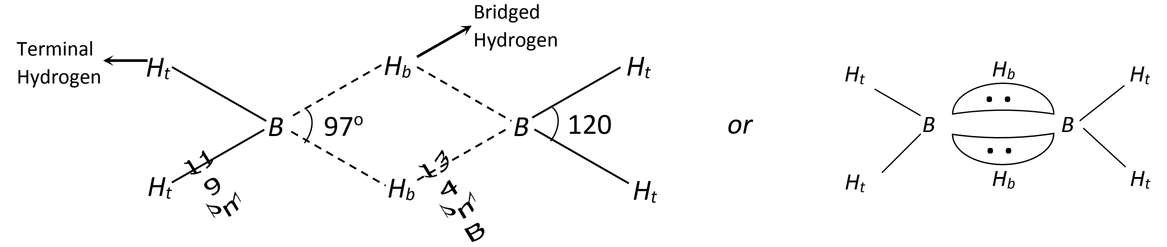
Boron Hydrides

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.

Structure of diborane: B_2H_6 has a three center electron pair bond also called a banana shape bond.

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

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



Structure of diborane (B_2H_6)

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

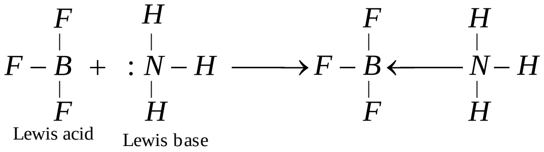
Boron Halides

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.



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

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

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

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

(ii) 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 colored basic radicals under the name borax bead test.

(iii) 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: (1) In making optical and hard glasses. (2) In the laboratory for borax bead test. (3) In softening of water. (4) In the preparation of medicinal soaps due to its antiseptic character.

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 colored transition metal oxides such as Co, Ni, Cr, Cu, Mn, etc. to form the corresponding metaborates which possess characteristic colors, $CoSO_4 \xrightarrow{\Delta} CoO + SO_3$;

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

Colors 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.

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: (i) 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.

(ii) With NaOH it forms, sodium metaborate, $H_3BO_3 + NaOH \longrightarrow NaBO_2 + 2H_2O$

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

$$H_3BO_3 + 3\,C_2H_5OH \xrightarrow{Conc.\,H_2SO_4} \mathrm{B(O}C_2H_5)_3 + 3\,H_2O$$

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

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

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

Uses:

(i) As a food preservative.

(ii) As a mild antiseptic for eye wash under the name boric lotion.

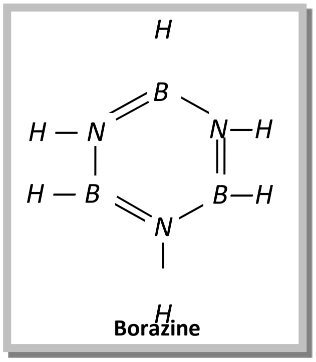
(iii) For the preparation of glazes and enamels in pottery.

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.

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

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



Borazine

Boron nitride (BN)

It is prepared by treating BCl_3 with an excess of NH_3 and paralyzing the resulting mixture in an atmosphere of NH_3 at $750^o C$,

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

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

Aluminum and its compounds

(1) **Ores of Aluminum:** 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:** Aluminum is obtained by the electrolysis of the oxide (alumina) dissolved in fused cryolite. This involves following steps,

Purification of ore

(i) **Baeyer's process**

$$\underset{\substack{\text{Finely powdered}\\ \text{(red)}}}{\text{Bauxite}} \xrightarrow[FeO \to Fe_2O_3]{\text{Roasted}} \text{Roasted ore} \xrightarrow[\substack{\text{High pressure } (150^o\,\text{C}, 80\text{ atm})\\ \text{filtered, Fe}_2O_3 \text{ as residue}}]{+\text{ Caustic soda solution}} \underset{\text{(Sod. Aluminate)}}{Filtrate} \xrightarrow[CO_2]{Filtered} Pure\ Al_2O_3 \xrightarrow{Heat} Al(OH)_3$$

(ii) **Hall's process**

$$\underset{\substack{\text{(Finely powdered)}\\\text{(red)}}}{\text{Bauxite}} \xrightarrow[\substack{\text{Fused, extracted with}\\\text{water. Residue } Fe_2O_3}]{+Na_2CO_3} \text{Solution} \xrightarrow[\substack{50\text{-}60^{o}\,C \text{ and filtered.}\\\text{Filtrate } (Na_2CO_3)}]{CO_2} \text{Precipitate Al(OH)}_3 \xrightarrow{Heat} Pure\ Al_2O_3$$

(iii) **Serpek's process**

$$\underset{\substack{\text{(Finely powdered)}\\\text{(white)}}}{\text{Bauxite}} \xrightarrow[\substack{\text{Heated to}\\1800^{o}\,C}]{+Coke+N_2} \substack{\text{Silica reduced to}\\\text{Si which volatalises}} + \substack{\text{Alumina form}\\\text{aluminium nitride}} \quad AlN \xrightarrow{Hydrolysis} Pure\ Al_2O_3 \xrightarrow{Heated} Al(OH)_3$$

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

Note: Aluminum is refined by Hoope's electrolytic process.

(3) **Compounds of Aluminum**

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

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

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

It exists as dimer Al_2Cl_6, in inert organic solvents and in vapor state. It sublimes at $100\ ^{o}C$ 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 aluminum 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, $Al + Fe_2O_3 \rightarrow Al_2O_3 + Fe + \text{Heat}$

(iv) **Aluminium sulphate [$Al_2(SO_4)_3$] :** 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.

5. 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.

Electronic configuration

Elements	**Electronic configuration (** $ns^2\ np^2$ **)**
${}_{6}C$	$1s^2, 2s^2 2p^2$ or $[He]2s^2 2p^2$
${}_{14}Si$	$1s^2, 2s^2 2p^6, 3s^2 3p^2$ or $[Ne]3s^2 3p^2$
${}_{32}Ge$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^2$ or $[Ar]3d^{10} 4s^2 4p^2$
${}_{50}Sn$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10}, 5s^2 5p^2$ or $[Kr]4d^{10} 5s^2 5p^2$
${}_{82}Pb$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10} 4f^{14}, 5s^2 5p^6 5d^{10}, 6s^2 6p^2$ or $[Xe]4f^{14} 5d^{10} 6s^2 6p^2$

Physical properties

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

C	Si	Ge	Sn	Pb
Non-metal	metalloid	metal	metal	or semi 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,

Element	C	Si	Gs	Sn	Pb
Abundance in earth's crust (ppm)	320	277200	7	40	16

(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)	2.34	5.32	7.26	11.34	2.22 (for graphite)

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

(i) The m.pt and b.pt. 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 m.pt and b.pt 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) **Ionization energy**

(i) The ionization 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.

Ionization energy (kJ mol^{-1})

	C	Si	Ge	Sn	Pb
IE_1	1086	786	761	708	715
IE_2	2352	1577	1537	1411	1450
IE_3	4620	3284	3300	2942	3081
IE_4	6220	4354	4409	3929	4082

(ii) The first ionization 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 ionization 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.

Bond	**Bond energy in kJ mol^{-1}**
C-C	348
Si-Si	180
Ge-Ge	167
Sn-Sn	155
Pb-Pb	No 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≡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.

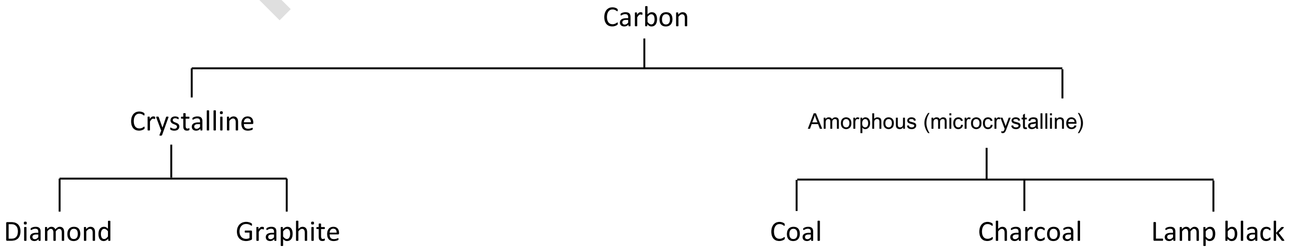
Bond	Bond energy (k J/mol)	Bond	Bond energy (kJ/mol)
C-C	348	Si-Si	180
C-O	315	Si-O	372
C-H	414	Si-H	339
C-Cl	326	Si-Cl	360
C-F	439	Si-F	536

(10) **Allotropy**

(i) 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. This phenomenon is due to the difference either in the number of atoms in the molecules [as in the case of oxygen (O_2) and ozone (O_3)] or arrangement of atoms in the molecules in crystal structure (as in the case of various forms of carbon).

(ii) All the elements of group 14 except lead exhibit allotropy.

(iii) Crystalline carbon occurs mainly into two allotropic forms (i) graphite and (ii) diamond (a third allotropic form called fullerenes e.g. C_{60} and C_{70} were recently discovered by Prof. Richard E. Smalley and his coworkes), amorphous carbon exists in different forms viz coal, coke, carbon black, lamp black, bone charcoal. Amorphous carbon is usually considered to contain microcrystals of graphite.



(iv) **Diamond and Graphite:** The two allotropic forms of crystalline carbon. Diamond is the purest and hardest form of carbon. Its structure involves a giant molecular form where each carbon atom is surrounded by four other carbon atoms (sp^3 hybridization) In doing so, each carbon atom is located in the center of a regular tetrahedron with its four valencies directed towards the four corners which are linked with four other carbon atoms ($C-C-C$ angle = 109^0 28'C-C=154 pm = 1.54 Å). The hardness of diamond result due to the uniformity of the C-C covalent bonds. Since the C-C bond length is very small, it has very high density (3.51 g cm^{-3}) and has more compact structure than graphite (density, 2.25 g cm^{-3}) It does not melt (vaporizes at 3773K) has very high refractive index (2.45) and is insoluble in all ordinary solvents. It does not conduct electricity as all the four valence electrons are used up in forming covalent bonds with other carbon atoms Diamond, because of its hardness is used in cutting, grinding instruments such as glass and drilling equipment's Its ability to reflect and refract light makes diamond an important jewellery material.

Difference between diamond and graphite

Diamond	**Graphite**
Crystalline, transparent with extra brilliance.	Crystalline, opaque and shiny substance
Hardest form	Soft having soapy touch
Bad conductor of electricity	Good conductor of electricity
High Density (3.51 g /cm^3) heavy	Low Density (2.25 g/cm^3), lighter than diamond
Colorless	Greyish white
Tetrahedral shaped	Two dhnensional layer structure having regular hexagonal sheets.
sp^3 hybridization	sp^2 hybridization
Less stable, more energy	More stable, less energy
$C_D \rightarrow C_G$; $\Delta H = -0.5$ k.cal	$C_G \rightarrow C_D$ at high temperature and high P
Used in cutting glass and jewellery; an abrasive	Used as lubricating agent, electrodes, in pencils, crucibles (due to high m.pt)

Carbon also exists in three common microcrystalline or amorphous forms (charcoal, carbon black and cocke) Carbon black is formed when hydrocarbons, petroleum, turpentine oil or substances rich in carbon contents are heated in limited supply of oxygen, $CH_{4(g)} + O_{2\,(g)} \rightarrow C_{(s)} + 2H_2O_{(g)}$

These substances yield a large amount of smoke which is passed into chambers having wet blankets. The soot collected on these blankets is lamp black or carbon black or soot. It is almost pure carbon having as high as 98%to 99% carbon content with small amount of impurities it is a soft black power and is used as a pigment in black inks; large amounts are also used in making automobile tyres.

Charcoal is formed when wood cellulose or other substances containing carbonaceous matter are heated strongly in the absence of air Charcoal has highly open structure, giving it an enormous surface area per unit mass. Charcoal is of various forms such as wood charcoal, sugar charcoal, coconut charcoal, animal charcoal etc. These forms contain varying amount of carbon content. A very pure form of carbon is obtained from sugar. Activated charcoal, a pulverized form whose surface is cleaned. by heating with steam. is widely used to adsorb molecules. It is used in filters to remove offensive odors from air and colored, foul smelling, bad tasting and toxic chemical as impurities from water.

Coke is an impure form of carbon and is produced when coal is heated strongly in the absence of air (as residue in the destructive distillation of coal) It is widely used as a reducing agent in metallurgical operations.
(v) Silicon also exists in crystalline and amorphous allotropic forms Germanium exists in two crystalline allotropic forms Tin has three allotropic forms as grey tin , white tin and rhombic tin.

Graphite occurs in Nature and can also obtained from coke, In graphite, out of four valence electrons, only three form covalent bonds (sp^2 hybridization) with three other carbon atoms. This forms hexagonal rings as sheets of on atom thickness. These sheets are held together by weak attractive forces one electron of each carbon atom is free and this enables these thin sheets slide over one another. For this reason graphite is a soft material with lubricating properties.
Graphite is a dark, opaque and soft material (density = 2250 kg/m^3) although graphite is non-metallic still it possesses a metallic lustre. It is insoluble in ordinary solvents. Graphite is a good conductor of heat and electricity because of the present of one free electron on each carbon atom. Graphite is used as a dry lubricant in making electrodes in electric furnaces. It is chiefly used in lead pencils.

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 pπ–pπ 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,

$6PbO + O_2 \xrightarrow{470^\circ C} 2Pb_3O_4$, 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.

Note: SiO_2, GeO_2, SnO_2 and PbO_2 are all 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+}.

Anomalous behaviour of Carbon

Carbon is found to 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 Pπ – Pπ multiple bonds with other elements like nitrogen, oxygen, sulphur etc. Other members of the family form Pπ – dπ 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 shows a maximum covalency of four while other members of the family may expand their covalency to six e.g., $[SiCl_6]^{2-}, [PbCl_6]^{2-}$ etc.

(7) Carbon is not affected by alkalies whereas other members react on fusion. For example, silicon form silicates, $Si + 2NaOH + 1/2O_2 \rightarrow \underset{\text{Sodium silicate}}{Na_2SiO_3} + H_2$.

Silicon and its compounds

Silicon, being a second member of group – 14, has a much larger size and lower electronegativity than hat 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:** 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.

With steam, Si reacts when heated to redness to liberate hydrogen, Si + 2H_2O $\xrightarrow{\text{Redness}}$ SiO_2 + 2H_2.

With halogens, Si reacts at elevated temperature forming SiX_4 except fluorine which reacts at room temperature.

Silicon combines with C at 2500K forming Silicon Carbide (SiC) known as carborundum (an extremely hard substance), Si + C $\xrightarrow{2500K}$ SiC.

It reacts with metals like Ca, Mg etc in an electric arc furnace to form Silicides (Ca_2Si, Mg_2Si etc.)

Silicon dissolves in hot aqueous alkalies liberating hydrogen, Si + 4NaOH $\xrightarrow{Heat}$ $Na_4SiO_4 + 2H_2 \uparrow$

It also dissolves in fused Na_2CO_3 displacing carbon $Na_2SiO_3 + C$.

(4) **Uses of silicon :** It is added to steel as ferrosilicon (an alloy of Fe and Si) to make it acid resistant. It is used in the pure form as a starting material for production of silicon polymers (Silicones).

(5) **Compounds of silicon**

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.

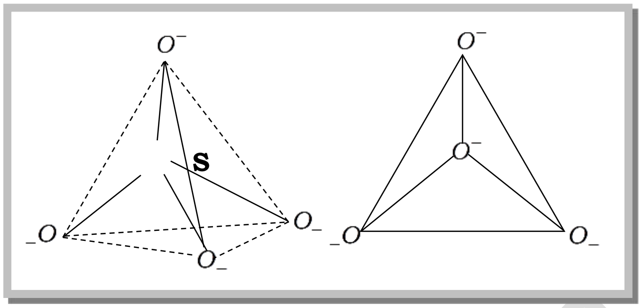
SiO_2 + 4HF $\longrightarrow$ SiF_4 + $2H_2O$; SiF_4 + 2HF $\longrightarrow$ $\underset{\text{(Hydro flouro silicicacid)}}{H_2SiF_6}$

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.

Silicates

Almost all rocks and their products (Soil, clay and sand) are made up of silicate minerals and Silica. The basic unit of all silicates is tetrahedral SiO_4^{-4} ion. Some of the important silicates are quartz, mica, asbestos, felspar and zeolites.



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.

Glass

Glass is an amorphous and transparent solid which is obtained by solidification of various silicates and borates of potassium and calcium.

(1) **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

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2\uparrow; \quad CaO + SiO_2 \longrightarrow CaSiO_3$$

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, $Na_2SiO_3, CaSiO_3, 4SiO_2$.

(2) **Various varieties of glass**: The different varieties of glasses and their special constituents are given below,

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	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

(3) **Colored glass**: Addition of transition metal compounds to glass give colored glasses. Small amounts of Cr(III), Mn(IV), Co(II) and Fe(III) compounds impart green, violet blue or brown colour respectively

Compound added – Color imparted	**Compound added – Color 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

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.

Electronic configuration

Elements	**Electronic configuration ($ns^2\ np^3$)**
$_7N$	$1s^2, 2s^2 2p^3$ or $[He]2s^2 2p^3$
$_{15}P$	$1s^2, 2s^2 2p^6, 3s^2 3p^3$ or $[Ne]3s^2 3p^3$
$_{33}As$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^3$ or $[Ar]3d^{10} 4s^2 4p^3$
$_{51}Sb$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10}, 5s^2 5p^3$ or $[Kr]4d^{10} 5s^2 5p^3$
$_{83}Bi$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10} 4f^{14}, 5s^2 5p^6 5d^{10}, 6s^2 6p^3$ or $[Xe]4f^{14} 5d^{10} 6s^2 6p^3$

Physical properties

(1) **Physical state:** Nitrogen– (gas), phosphorus – (solid) (vaporizes easily), As, Sb, Bi–solids.
Note: 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 pπ –pπ 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.

Note: M.pt. first increases from N to As and then decreases from As to Bi. Boiling point first 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.

Note: Out of the various allotropic forms of phosphorus, black phosphorus is a good conductor of electricity (similarity with graphite).

☐ Proteins, the building blocks of our body contain 16% of nitrogen in them.

☐ Radioactive phosphorus (P^{32}) is used in the treatment of leukemia (blood cancer).

☐ The disease caused by the constant touch with white phosphorus is called Phossy Jaw.

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.

NH_3	PH_3	AsH_3	SbH_3	BiH_3
107^o	94^o	92^o	91^o	90^o

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, $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$.

Note: Diphosphine (P_2H_4) and hydrazine (N_2H_4) are other two important hydrides. Hydrazine a strong reducing agent, is used in organic synthesis and rocket fuels and is prepared as follows,

$$2NH_3 + NaOCl \rightarrow N_2H_4 + NaCl + H_2O$$

☐ Phosphine is poisonous and does not form any complexes.

☐ Phosphine forms vortex rings of P_2O_5 in the form of white smoke when it comes in contact with air due to combustion. This is due to impurities of diphosphine (P_2H_4).

☐ Phosphine is used to prepare smoke screens in warfare. Calcium phosphide reacts with water to form phosphine which burns to give clouds of P_2O_5 which acts as smoke screens.

- ☐ Liquor ammonia is a concentrated solution of NH_3 in water.
- ☐ Ammonia will not burn in air, but burns in pure O_2 with a yellowish flame to produce N_2 and H_2O.

(2) **Halides:** The members of the family form trihalides (MX_3) and pentahalids (MX_5). The trihalides are sp^3-hybridized with distorted tetrahedral geometry and pyramidal shape while pentahalides are sp^3d-hybridized and are trigonal bipyramidal in shape. The trihalides are hydrolyzed by water and ease of hydrolysis decreases when we move down the group. Hence, NCl_3 is easily hydrolyzed but $SbCl_3$ and $BiCl_3$ are partly and reversibly hydrolyzed. NF_3 is not hydrolyzed due to lack of vacant d-orbital with nitrogen. PF_3 and PF_5 are also not hydrolyzed because the P – F bond is stronger than P – O covalent bond. The hydrolysis products of the other 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.

Note: 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.

(i) **Oxides of Nitrogen:** Nitrogen forms two more oxides i.e., N_2O and NO and 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. Other oxides of nitrogen are: NO_2, N_2O_3, N_2O_5.

The acidic strength of oxides: $N_2O < NO < N_2O_3 < N_2O_4 < N_2O_5$.

(ii) **Oxides of phosphorus:** P_4O_6 (Phosphorus trioxide), P_4O_{10} (Phosphorus pentaoxide).

(iii) **Oxides of other elements:** The decreasing order of stability of oxides of group 15 follows as,

$P_2O_5 > As_2O_5 > Sb_2O_5 > Bi_2O_5$

Except P_2O_5, all pentaoxides show oxidising properties. Also P_2O_5 is acidic in nature. N_2O_5 is the strongest oxidising agent. 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:** 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.

Note: HNO_3 is called aqua fortis and prepared from air (Birkel and Eyde process) and NH_3 (Ostwald process). It acts as a strong oxidising agent.

Oxyacids of phosphorus are,

(i) H_3PO_2 (Hypophosphorus acid): Reducing agent and monobasic.

(ii) H_3PO_3 (Orthophosphorus acid): Reducing agent and dibasic.

(iii) H_3PO_4 (Orthophosphoric acid): Weak tribasic acid.

(iv) $H_4P_2P_7$ (Pyrophosphoric acid): It is obtained by heating H_3PO_4 to 220°C. It is tetrabasic.

(v) HPO_3 (Metaphosphoric acid): It is formed by the dehydration of H_3PO_4 at 316°C. Also exists as a trimer and is monobasic.

(vi) $H_4P_2O_6$ (Hypophosphoric acid): Tetrabasic

(vii) $H_4P_2O_5$ (Pyrophosphoric acid): Dibasic acid

Anamalous behaviour of Nitrogen

Nitrogen is known to differ from other members of the family because of the following facts,

(i) Its small size

(ii) Its high electronegativity

(iii) Its high ionization energy

(iv) Non-availability of d-orbital in the valence shell.

(v) Its capacity to form pπ-pπ multiple bonds.

The main points of difference are,

(1) Nitrogen is a gas (N_2) while other members are solids.

(2) Nitrogen is diatomic while other elements like phosphorus and arsenic form tetra-atomic molecules (P_4, As_4).

(3) 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).

(4) Hydrides of nitrogen show H-bonding while those of other elements do not.

(5) Nitrogen does not show pentacovalency because of absence of d-orbitals while all other elements show pentacovalency.

(6) Nitrogen dos not form complexes because of absence of d-orbitals while other elements show complex formation e.g., $[PCl_6]^-, [AsCl_6]^-$ etc.

(7) The hydride of nitrogen (NH_3) is highly basic in nature while the hydrides of other elements are slightly basic.

(8) Except for NF_3, other halides of nitrogen e.g., NCl_3, NBr_3 and NI_3 are unstable while the halides of other elements are fairly stable.

Nitrogen and its compounds

N_2 was discovered by **Daniel Rutherford**. It is the first member of group 15 in the periodic table.

(1) **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.

(2) **Preparation:** It is prepared by the following methods,

(i) **Laboratory method**: In the laboratory N_2 is prepared by heating an aqueous solution containing an equivalent amounts of NH_4Cl and $NaNO_2$.

$$NH_4Cl\,(aq.) + NaNO_2\,(aq.) \xrightarrow{\text{Heat}} N_2(g) + 2H_2O(l) + NaCl$$

(ii) **Commercial preparation:** Commercially N_2 is prepared by the fractional distillation of liquid air.

(3) **Physical properties:** N_2 is a colorless, odorless and tasteless gas. It is a non-toxic gas. Its vapor density is 14. It has very low solubility in water.

(4) **Chemical properties**

(i) N_2 is neutral towards litmus. It is chemically unreactive at ordinary temp. It is neither combustible nor it supports combustion.

(ii) 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}

(iii) **Combination with compounds:** N_2 combines with certain compounds on strong heating . eg

$$\underset{\text{Calsium carbide}}{CaC_2} + N_2 \xrightarrow{1300K} \underset{\text{Calsium cyanamide}}{CaCN_2} + C\ ; \quad \underset{\text{Aluminium oxide}}{Al_2O_3} + N_2 + 3C \xrightarrow{2100K} \underset{\text{Al.nitride}}{2AlN} + 3CO$$

Both these compounds are hydrolyzed on boiling with water to give ammonia.

$CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3; \quad AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$

Therefore, calcium cyanamide is used as a fetilizer under the name nitrolim $(CaCN_2 + C)$

(5) **Uses of nitrogen:** N_2 is mainly used in the manufacture of compounds like $NH_3, HNO_3, CaCN_2$ etc.

(6) **Compounds of nitrogen**

(i) **Hydrides of nitrogen**

Ammonia

Ammonia is the most important compound of nitrogen. It can be manufactured by Haber's process. In this process, a mixture of N_2 and H_2 in the ratio of 1 : 3 is passed over heated Fe at 650 –800K as catalyst and Mo as promotor, $N_2 + 3H_2 \rightleftharpoons 2NH_3, \Delta H = -93.6\,kJ\,mol^{-1}$ This is a reversible exothermic reaction.

Ammonia is prepared in the laboratory by heating ammonium salt (NH_4Cl) with a strong alkali like NaOH

$NH_4Cl + NaOH \longrightarrow NH_3 + H_2O + NaCl$ Ammonia can be dried by passing over quick lime (CaO). However, it cannot be dried with dehydrating agents such as conc. H_2SO_4, P_2O_5 and anhydrous $CaCl_2$ because ammonia reacts with these compounds.

NH_3 is a colorless gas with a characteristic pungent smell called ammonical smell. It is highly soluble in water and its solution is basic in nature, $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

NH_3 is expected to have a tetrahedral geometry, but the lone pair distorts its geometry and the molecule has pyramidal geometry with N – H bond length of 101.7 pm and a bond angle of 107.5°. Liquid ammonia is widely used as a refrigerant due to its high heat of vaporization.

Hydrazine, (NH_2 – NH_2)

Hydrazine is prepared commercially by boiling aqueous ammonia or urea with sodium hypochloride in the presence of glue or gelatin.

$2NH_3 + NaOCl \rightarrow N_2H_4 + NaCl + H_2O$

The resulting solution is concentrated and anhydrous hydrazine may be obtained by further distillation over barium oxide. Alternatively, the hydrazine present in the resulting solution is precipitated as sparingly soluble crystalline hydrazine sulphate on treatment with sulphuric acid, $NH_2NH_2 + H_2SO_4 \rightarrow N_2H_4.H_2SO_4$.

The precipitate is removed and treated with an alkali when hydrazine hydroxide $H_2N.NH_3OH$ is obtained. This is distilled under reduced pressure, over barium oxide to liberate free hydrazine.

$H_2N.NH_3OH + BaO \xrightarrow{distil} NH_2NH_2 + Ba(OH)_2$

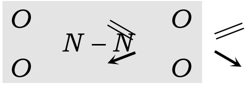
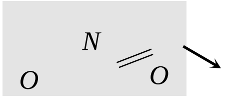
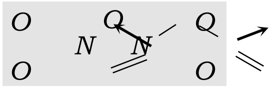
Physical properties: Anhydrous hydrazine is a colorless fuming liquid (m.p. 2^0C and b.p. 114^0C) soluble in water in all proportions. It is also soluble in alcohol. It is strongly hygroscopic.

Chemical properties: It behaves as a diacid base, Thus with hydrochlorides it forms hydrazine monochloride $H_2N.NH_3Cl$ and hydrazine dichloride $ClH_3N.NH_3Cl$.
(i) Hydrazine burns in air with the evolution of heat. $N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$ $\Delta H = -622$ kJ
The alkyl derivative of hydrazine are used as rocket fuels.
(ii) It reduces Fehling's solution to red cuprous oxide and iodates to iodides.
$4Cu^{2+} + NH_2NH_4 \rightarrow 4Cu^+ + 4H^+ + N_2$; $2IO_3^- + 3NH_2NH_2 \rightarrow 2I^- + 6H_2O + 3N_2$

Uses: Hydrazine is used as a rocket fuel. It is also used as a reagent in organic chemistry.

(ii) **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.

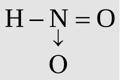
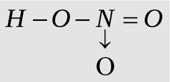
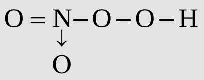
Oxides of Nitrogen

Oxide	**Oxidation State of N**	**Physical appearance**	**Structure**
Nitrous oxide (N_2O)	+1	Colourless gas	$N \equiv N \rightarrow O$
Nitric oxide (NO)	+2	Colourless	N = O
Dinitrogen trioxide (N_2O_3)	+3	Blue solid	
Dinitrogen tetraoxide (N_2O_4)	+4	Colourless liquid	
Nitrogen dioxide (NO_2)	+4	Brown gas	
Dinitrogen pentoxide (N_2O_5)	+5	Colourless gas	

Oxide of Nitrogen	**Preparation**
Nitrous Oxide (N_2O)	By heating ammonium nitrate upto 240^{0}C
	$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$
	Collected over hot water.
Nitrous oxide (NO)	(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.
	$4NH_3 + 5O_2 \xrightarrow[850^0 C]{Pt} 4NO + 6H_2O$
Dinitrogen trioxide(N_2O_3)	(a) By the action of 50% HNO_3 on arsenious oxide. $2HNO_3 + As_2O_3 + 2H_2O \rightarrow NO + NO_2 + 2H_3AsO_4$
	↓ 250 K
Nitrogen dioxide (NO_2)	N_2O_3 (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.
	$Cu + 4$ conc. $HNO_3 \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$
Dinitrogen pentoxide(N_2O5)	(a) By dehydrating HNO_3 with phosphorus pentoxide
	$4HNO_3 + P_4O_{10} \rightarrow 2N_2O_5 + 4\ HPO_3$

(iii) **Oxyacids of nitrogen**

Oxyacids of nitrogen

Name of oxoaci	**M. F.**	**Structure**	**Oxidation State of N**	**Basicity**	**pK$_a$**	**Nature**
Hyponitrous acid	$H_2N_2O_2$		+1	2(dibasic)	Very weak	Highly explosive
Nitrous acid	HNO_2	 $\mathrm{H-\underset{\substack{\downarrow\\ O}}{N}=O}$	+3	1 (monobasic)	3.3	Unstable Weak acid
Nitric acid	HNO_3	 $H-O-\underset{\substack{\downarrow\\ O}}{N}=O$	+5	1 (monobasic)	-3.0	Stable, Strong acid
Pernitric acid	HNO_4	 $\mathrm{O=\underset{\substack{\downarrow\\ O}}{N}-O-O-H}$	+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 cannot form stable Pπ - Pπ bonds with other phosphorous atoms whereas nitrogen can form Pπ - Pπ 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 3$Ca_3(PO_4)_2.CaCl_2$,

(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 1770K, $2Ca_3(PO_4)_2 + 6SiO_2 \longrightarrow \underset{\text{Calicum silicate}}{6CaSiO_3} + P_4O_{10}$;

$$P_4O_{10} + 10C \longrightarrow P_4 + 10CO$$

(3) **Allotropic forms of phosphorus:** Phosphorus exists in three main allotropic forms,
(i) White phosphorus
(ii) Red phosphorus
(iii) Black phosphorus

Some physical properties of three forms of phosphorus

Properties	**White phosphorus**	**Red phosphorus**	**Black phosphorus**
Colour	White but turns yellow on exposure	Dark red	Black
State	Waxy solid	Brittle powder	Crystalline
Density	1.84g cm^{-3}	2.1 g cm^{-3}	2.69 g cm^{-3}
Ignition temperature	307 K	533 K	673 K
Stability	Less stable at ordinary temperature	More stable at ordinary temperature	Most stable
Chemical reactivity	Very reactive	Less reactive	Least reactive

Compounds of phosphorus

(1) **Oxides and oxyacid's of phosphorus:** Phosphorus is quite reactive and forms number of compounds in oxidation states of –3 , +3 and +5.

(i) **Oxides:** 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) : 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, $P_4O_6 + 6H_2O\,\text{(hot)} \rightarrow \underset{\text{Phosphoric acid}}{3H_3PO_4} + PH_3$

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}): 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.

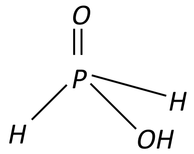
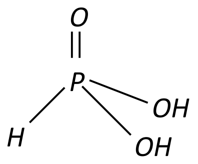
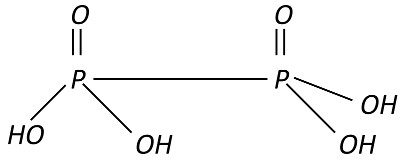
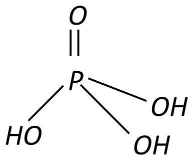
$\underset{}{P_4O_{10}} + \underset{\text{(Cold)}}{2H_2O} \rightarrow \underset{\text{Metaphosphoric acid}}{4HPO_3}$. With hot water, it gives phosphoric acid, $P_4O_{10} + \underset{\text{Het}}{6H_2O} \rightarrow \underset{\text{Phosphoric acid}}{4H_3PO_4}$.

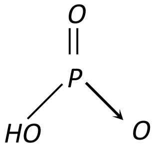
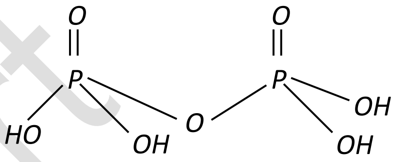
P_4O_{10} is a very strong dehydrating agent. It extracts water from many compounds including H_2SO_4 and HNO_3,

$H_2SO_4 \xrightarrow[-H_2O]{P_4O_{10}} SO_3$; $2HNO_3 \xrightarrow[-H_2O]{P_4O_{10}} N_2O_5$; $\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[-H_2O]{P_4O_{10}} \underset{\text{Methyl cyanide}}{CH_3CN}$

(ii) **Oxyacids of phosphorus:** Phosphorus forms a number of oxyacid's which differs in their structure and oxidation state of phosphorus.

Oxyacid's of phosphorus

Name	**Formula**	**Oxidation state of P**	**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	

(2) **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.

7. 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**.

Electronic configuration

Elements	**Electronic configuration** $(ns^2\ np^4)$
$_8O$	$1s^2, 2s^2 2p^4$ or $[He]2s^2 2p^4$
$_{16}S$	$1s^2, 2s^2 2p^6, 3s^2 3p^4$ or $[Ne]3s^2 3p^4$
$_{34}Se$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^4$ or $[Ar]3d^{10} 4s^2 4p^4$
$_{52}Te$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10}, 5s^2 5p^4$ or $[Kr]4d^{10} 5s^2 5p^4$
$_{84}Po$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10} 4f^{14}, 5s^2 5p^6 5d^{10}, 6s^2 6p^4$ or $[Xe]4f^{14} 5d^{10} 6s^2 6p^4$

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) **Ionization energy**: Down the group the ionization 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 ionization energies.

(7) **Nature of bonding**: Compound of oxygen with nonmetals are predominantly covalent. S, Se, and Te because of low electronegativities show more covalent character.

(8) **Melting and boiling points**: The m. pt. and b. pt increases on moving down the group.

(9) **Catenation:** Oxygen has some but sulphur has greater tendency for catenation.

$$\underset{(H_2O_2)}{H-O-O-H}, \quad \underset{(H_2S_2)}{H-S-S-H}, \quad \underset{(H_2S_3)}{H-S-S-S-H}, \quad \underset{(H_2S_4)}{H-S-S-S-S-H}$$

(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 → – 2 and –1 oxidation state. These element shows +2 ,+4 and +6 oxidation state.

Chemical properties

(1) **Hydrides:** H_2O, H_2S, H_2Se, H_2Te and H_2Po, H_2O - colorless and odorless. H_2S, H_2Se, H_2Te and H_2Po - colorless, unpleasant smell.

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) 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

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.

(1) **Occurrence:** In free state, it occurs in air and constitutes 21% by volume of air.

(2) **Preparation of Dioxygen:** Oxygen is prepared by the following methods.

(i) **By the decomposition of oxygen rich compounds**: e.g.

$$\underset{Pot.\,Nitrate}{2KNO_3} \xrightarrow{Heat} 2KNO_2 + O_2\,; \quad \underset{Pot.\,Chlorate}{2KClO_3} \xrightarrow[MnO_2]{Heat} 2KCl + 3O_2$$

(ii) **By heating dioxides, Peroxides and higher oxides**: e.g.

$$\underset{Silver\ oxide}{2Ag_2O} \xrightarrow{Heat} 4Ag + O_2\,; \quad \underset{Manganese dioxide}{3MnO_2} \xrightarrow{Heat} Mn_3O_4 + O_2\,; \quad \underset{Barium peroxide}{2BaO_2} \xrightarrow{Heat} \underset{Barium oxide}{2BaO} + O_2$$

(iii) **Laboratory Method:** In the laboratory, O_2 is prepared by thermal decomposition of potassium chlorate.

$$2KClO_3 \xrightarrow[MnO_2]{420\,K} 2KCl + 3O_2$$

Note: 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 $KClO_3$.

(iv) O_2 can also be prepared by the action of water on sodium peroxide as, $2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$
.

(v) **Industrial preparation:** The main sources for the industrial preparation of dioxygen are air and water.

(a) 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.

(b) From water: O_2 can also be obtained by the electrolysis of water containing a small amount of acid or alkali, $2H_2O \xrightarrow{Electrolysis} 2H_2(g) + O_2(g)$.

(3) **Physical properties of O₂:** It is a colorless, tasteless and odorless gas. It is slightly soluble in water and its solubility is about $30\ cm^3$ per litre of water at 298 K.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. $(g\ cm^{-3})$ – 1.429
Ionization energy $(kJ\ mol^{-1})$ – 1310	Melting point (K) – 54.4
Electron affinity $(kJ\ mol^{-1})$ – 140	Boiling point (K) – 90.2

(4) **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.

(i) **Action with litmus:** Like dihydrogen, it is also neutral and has no action on blue or red litmus.

(ii) **Reaction with metals:** Active metals like Na, Ca react at room temp. to form their respective oxides.

$4Na + O_2 \rightarrow 2Na_2O$; $2Ca + O_2 \rightarrow 2CaO$

It reacts with Fe, Al, Cu etc. metals at high temperature

$4Al + 3O_2 \rightarrow 2Al_2O_3$; $4Fe + 3O_2 \rightarrow 2Fe_2O_3$

(iii) **Action with Non-metals:** It form oxides.

$2H_2 + O_2 \xrightarrow[\text{Electric discharge}]{1073K} 2H_2O$; $N_2 + O_2 \xrightarrow{3273K} \underset{Nitricoxide}{2NO}$

$S + O_2 \xrightarrow{Heat} SO_2$; $C + O_2 \xrightarrow{Heat} CO_2$

(iv) **Reaction with compounds**: Dioxygen is an oxidizing agent and it oxidizes many compounds under specific conditions. e.g. $4HCl + O_2 \xrightarrow[CuCl_2]{700K} 2H_2O + 2Cl_2$; $4NH_3 + 5O_2 \xrightarrow[Pt]{1073K} 4NO + 6H_2O$

$CS_2 + 3O_2 \xrightarrow{Heat} CO_2 + 2SO_2$; $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

(5) **Uses of dioxygen**

(i) It is used in the oxy-hydrogen or oxy-acetylene torches which are used for welding and cutting of metals.

(ii) It is used as an oxidizing and bleaching agent,

(iii) Liquid O_2 is used as rocket fuel.

(iv) It is used in metallurgical processes to remove the impurities of metals by oxidation.

(6) **Compounds of Oxygen**

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,

(a) 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.

(b) 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.

(c) Amphoteric oxides: Al_2O_3, SnO_2 etc.

(d) 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 behavior,

Na_2O strongly basic	MgO basic	Al_2O_3 amphoteric	SiO_2 weakly acidic	P_4O_{10} acidic	SO_2 strongly acidic	Cl_2O_7 very strongly acidic

Basic to acidic character increase

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 acidic	Al_2O_3 amphoteric	Ga_2O_3 (weakly basic)	In_2O_3, Tl_2O_3 basic

Acidic character decrease

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 oxygen's 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 stratosphere is depleting due to NO released by supersonic aircrafts and Chloro fluoro 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 ozonize. 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 ozonizes,

(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 colored 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 from 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 oxidizing 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.

$$\underset{Metal}{2Ag} + O_3 \rightarrow \underset{Silver\ oxide}{Ag_2O} + O_2;\ \underset{Non-metal}{S} + 3O_3 \rightarrow SO_3 + 3O_2;\ \underset{Compound}{PbS} + 4O_3 \rightarrow PbSO_4 + 4O_2$$

Mercury is oxidised to mercurous oxide, $2Hg + O_3 \rightarrow \underset{Mercurous oxide}{Hg_2O} + O_2$

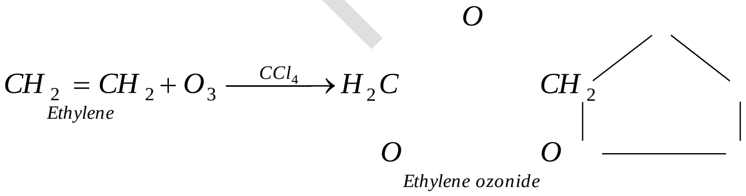
During this reaction mercury loses its meniscus and starts sticking to the sides of the glass. This is known as tailing of mercury. Mercurous oxide formed in this reaction dissolves in mercury and starts sticking to the glass surface.

(3) **Bleaching agent:** Due to the oxidizing action of ozone, it acts as a mild bleaching agent as well as a sterilizing agent. It acts as a bleaching agent for vegetable coloring matter.

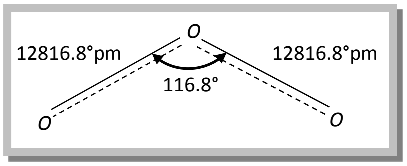
$$Vegetable\ \ colouring\ \ matter + O_3 \rightarrow \underset{(Colourless)}{Oxidised\ coloured\ matter} + O_2$$

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 O₃: 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, underground 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.

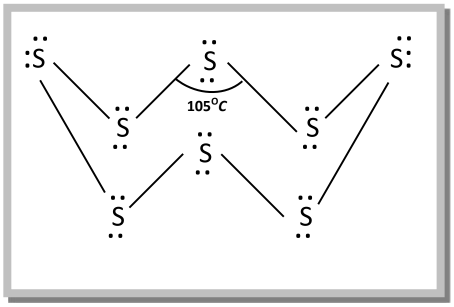
(1) **Occurrence:** Sulphur occurs in the earth's crust to the extent of 0.05%. It occurs in the Free State as well as in combined state. Sulphure occurs mainly as sulphides and sulphates. eg.

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

(2) **Extraction of sulphur** (Frasch process)**:** Sulphur is generally extracted from underground deposits by drilling three concentric pipes up to the beds of sulphur (700 – 1200 feet deep).

(3) **Allotropy in sulphur:** Sulphur exists in four allotropic forms,

(i) **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.



(ii) **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.

(iii) **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.

(iv) **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.

(4) **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, $2Na_2S + S_8 \longrightarrow 2Na_2S_5$.

(5) **Uses of sulphur:** It is used in the manufacture of matches, gun powder (mixture of charcoal, sulphur and potassium nitrate), explosives and fireworks 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

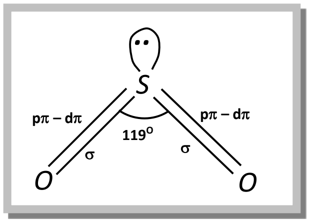
(1) **Hydrogen Sulphide:** It is prepared in the laboratory by the action of dil. H_2SO_4 on ferrous sulphide in kipp's apparatus, $FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S$. It is colorless gas having foul smell resembling that of rotten eggs. It reacts with many cations (of group II and IV) to give colored 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) **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.



$$S_8 + 8O_2 \rightarrow 8SO_2;\quad 4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

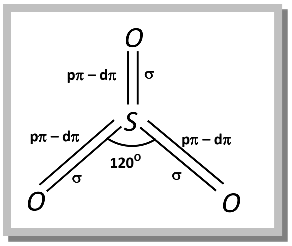
In laboratory, it is prepared by heating copper turnings with conc. H_2SO_4

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$$

It is a colorless 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.

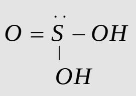
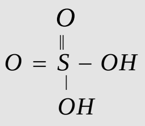
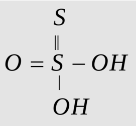
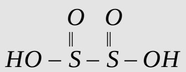
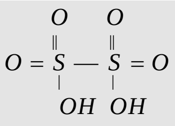
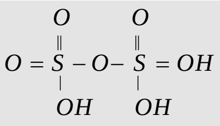
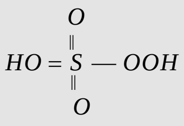
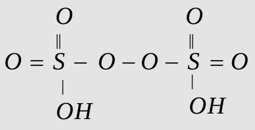
(ii) **Sulphur trioxide** (SO_3)**:** It is formed by the oxidation of SO_2.



$$2SO_2 + O_2 \xrightarrow[V_2O_5]{700K,\ 2atm.} 2SO_3$$

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°.

(3) **Oxyacids of sulphur:** Sulphur forms many oxyacids. Some of these are

Formula	**Name**	**Important properties**	**Structural formula**
H_2SO_3 (+4)	Sulphurous acid	Free acid does not exist diprotic, strong reducing agent	 $O=\underset{\substack{\vert\\OH}}{\ddot{S}}-OH$
H_2SO_4 (+6) (Oil of vitriol)	Sulphuric acid	Stable diprotic, dehydrating agent	 $O=\underset{\substack{\vert\\OH}}{\overset{\substack{O\\ \Vert}}{S}}-OH$
$H_2S_2O_3$ (–2 and +6)	Thiosulphuric acid	Free acid does not exist but its salts e.g. $Na_2S_2O_3$ All quite stable reducing agent	 $O=\underset{\substack{\vert\\OH}}{\overset{\substack{S\\ \Vert}}{S}}-OH$
$H_2S_2O_4$ (+3)	Dithionous acid		 $HO-\overset{\substack{O\\ \Vert}}{S}-\overset{\substack{O\\ \Vert}}{S}-OH$
$H_2S_2O_6$ (+5)	Dithionic acid	Free acid is moderately stable but its salts are quite stable.	 $O=\underset{\substack{\vert\\OH}}{\overset{\substack{O\\ \Vert}}{S}}-\underset{\substack{\vert\\OH}}{\overset{\substack{O\\ \Vert}}{S}}=O$
$H_2S_2O_7$ (+6) (Oleum)	Disulphuric acid (Pyrosulphuric acid)	Strong oxidising agent	 $O=\underset{\substack{\vert\\OH}}{\overset{\substack{O\\ \Vert}}{S}}-O-\underset{\substack{\vert\\OH}}{\overset{\substack{O\\ \Vert}}{S}}=OH$
H_2SO_5 (+6) (Caro's acid)	Peroxomonosulphuric acid (Its salts known as persulphates)	Stable crystalline solid, powerfull oxidising agent	 $HO=\underset{\substack{\Vert\\O}}{\overset{\substack{O\\ \Vert}}{S}}-OOH$
$H_2S_2O_8$ (+6) (Marshals acid)	Peroxodisulphuric acid (its salts are known as disulphates)	Strong oxidising agent.	 $O=\underset{\substack{\vert\\OH}}{\overset{\substack{O\\ \Vert}}{S}}-O-O-\underset{\substack{\vert\\OH}}{\overset{\substack{O\\ \Vert}}{S}}=O$

(4) **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,

(1) **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.

$SO_2 + NO_2 \longrightarrow SO_3 + NO$; $2NO + O_2 \longrightarrow 2NO_2$; $SO_3 + H_2O \longrightarrow H_2SO_4$

(2) **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.

$S + O_2 \longrightarrow SO_2$ or $4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$; $2SO_2 + O_2 \xrightleftharpoons{V_2O_5 \text{ or Pt, 673-732 K}} 2SO_3$.

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,

(i) High concentration of SO_2 and O_2.

(ii) Low temperature of 673 to 723 K,

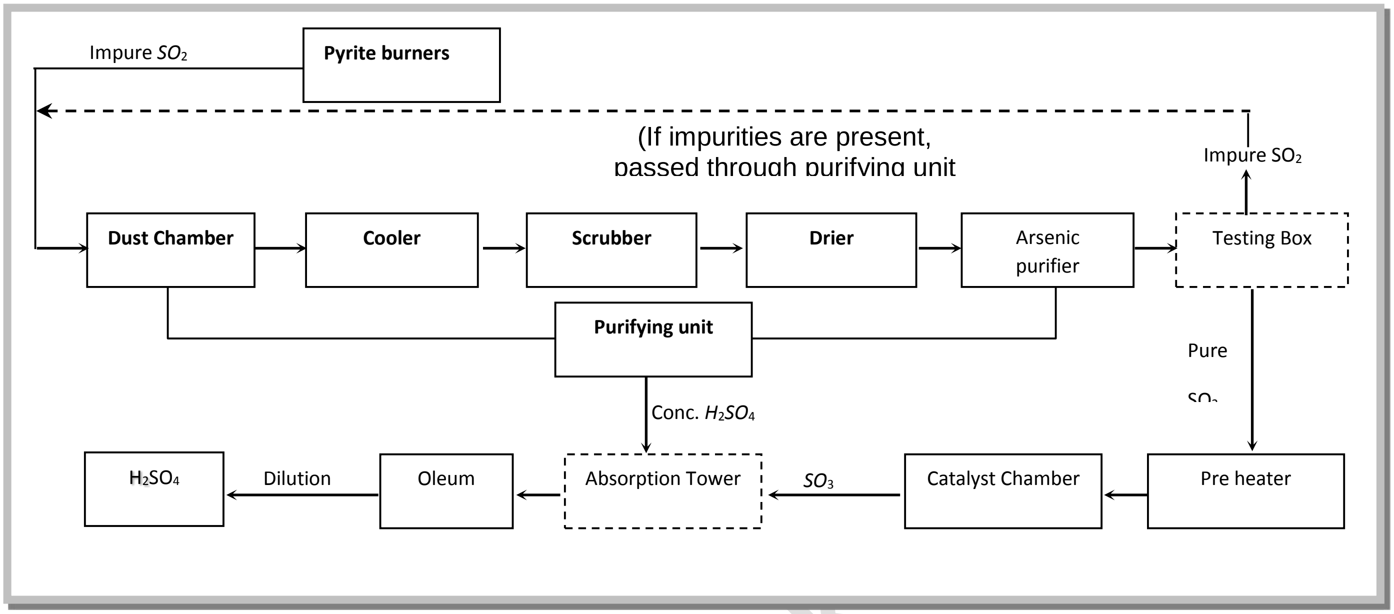
(iii) High pressure about 2 atmospheres.

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%).

Flow sheet diagram of its preparation is as follows



Structure: H_2SO_4 is a covalent compound and has tetrahedral (S is sp^3- hybridized) structure.

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.

(1) H_2SO_4 is a strong dibasic acid. It neutralizes alkalies, liberates CO_2 from carbonates and bicarbonates.

(2) 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.,

$$H_2SO_4 + 2KOH \rightarrow K_2SO_4 + 2H_2O \;;\; Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$$

(3) It is a strong oxidizing agent and oxidizes as follows,

$$H_2SO_4 \rightarrow H_2O + SO_2 + O; \quad C + 2H_2SO_4 \rightarrow 2SO + CO + 2H_2O$$

$$S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O; \quad P_4 + 10H_2SO_4 \rightarrow 4H_2PO_4 + 10SO_2 + 4H_2O$$

$$2HBr + H_2SO_4 \rightarrow Br_2 + 2H_2O + SO_2; \quad 2HI + H_2SO_4 \rightarrow 2H_2O + I_2 + 2SO_2$$

(4) It reacts with number of salts. It liberates HCl from chlorides, H_2S from sulphides, HNO_3 from nitrates.

(5) It acts as a strong dehydrating agent, as it dehydrates, sugar to sugar charcoal (carbon), and formic acid to CO, oxalic acid to CO+ CO_2 and ethyl alcohol to ethylene.

(6) It is also a good sulphonating agent and used for sulphonation of aromatic compounds. eg.,

$$BaCl_2 + H_2SO_4 \rightarrow \underset{\text{(white ppt)}}{BaSO_4} + 2HCl\,; \quad Pb(NO_3)_2 + H_2SO_4 \rightarrow \underset{\text{(white ppt.)}}{PbSO_4} + 2HNO_3$$

$$\underset{\text{Sugar}}{C_{12}H_{22}O_{11}} \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{Carbon}}{12C} + 11H_2O\,; \quad HCOOH \xrightarrow{Conc. H_2SO_4} CO + H_2O$$

Uses : H_2SO_4 is used (i) in the preparation of fertilizers like $(NH_4)_2\ SO_4$ 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:

(1) Sodium thiosulphate is a colourless crystalline solid. In the hydrated form, it is called hypo.

(2) It melts at 320 K and loses its water molecules of crystallization on heating to 490K.

Chemical properties

(1) **Action with halogens:** It reacts with halogens as,

(i) 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.

(ii) Bromine water also oxidizes sodium thiosulphate to sodium sulphate and sulphur,

$Na_2S_2O_3 + Br_2 + H_2O \rightarrow Na_2SO_4 + 2HBr + S$

(iii) With iodine it forms a soluble compound called sodium tetrathionate,

$$2Na_2S_2O_3 + I_2 \rightarrow \underset{\text{Sod. tetrathio nate}}{Na_2S_4O_6} + 2NaI$$

Therefore, hypo is commonly used to remove iodine stains from the clothes.

(2) **Action of heat:** Upon heating, sodium thiosulphate decomposes to form sodium sulphate and sodium pentasulphide, $4Na_2S_2O_3 \xrightarrow{\text{Heat}} 3Na_2SO_4 + \underset{\text{Sodium pentasulphide}}{Na_2S_5}$

(3) **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.

$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + SO_2 + H_2O + S$

(4) **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

(1) It is largely used in photography as a fixing agent.

(2) It is used as a preservative for fruit products such as jams and squashes.

(3) It is used as an antichlor in bleaching.

(4) It is used as a volumetric agent for the estimation of iodine.

(5) It is used in medicine.

8. 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.

Electronic configuration

Elements	**Electronic configuration** ($ns^2\ np^5$)
${}_{9}F$	$1s^2, 2s^2 2p^5$ or $[He]2s^2 2p^5$
${}_{17}Cl$	$1s^2, 2s^2 2p^6, 3s^2 3p^5$ or $[Ne]3s^2 3p^5$
${}_{35}Br$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^5$ or $[Ar]3d^{10} 4s^2 4p^5$
${}_{53}I$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10}, 5s^2 5p^5$ or $[Kr]4d^{10} 5s^2 5p^5$
${}_{85}At$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10} 4f^{14}, 5s^2 5p^6 5d^{10}, 6s^2 6p^5$ or $[Xe]4f^{14} 5d^{10} 6s^2 6p^5$

Physical properties

(1) **Physical state**: Halogens exist as diatomic covalent molecules.
F_2 – gas, Cl_2 – gas, Br_2 – corrosive liquid, I_2 – volatile solid.

(2) **Melting and boiling points:** They increase with increase in atomic number.

(3) **Ionization energy**: The I.E. decreases on moving down the gorup.

(4) **Electron affinity:** F < Cl > Br > I or Cl > F > Br > I.

(5) **Electronegativity:** F > Cl > Br > I.

(6) **Bond energy**

Element	F – F	Cl – Cl	Br – Br	I – I
Bond length (Å)	1.42	1.99	2.28	2.67
Bond dissociation energy (kcal / mole)	38	57	45.5	35.6

(7) **Colour:** F – Light yellow, Cl – Greenish yellow, Br – Reddish brown, I – Deep violet.

(8) **Oxidation state:** All exhibit –1 Oxidation state Except fluorine other element also show +3 ,+5, +7 oxidation state.

(9) **Oxidising power:** $F_2 > Cl_2 > Br_2 > I_2$.

(10) **Solubility:** Halogen being non-polar in nature do not dissolve in water $2F_2 + 2H_2O \rightarrow 4HF + O_2$, $3F_2 + 3H_2O \rightarrow 6HF + O_3$ (fluorine highly soluble) Cl_2 and Br_2 are fairly soluble. I_2 is a least soluble in water.

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 H₂O**: 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 KI due to the formation of I_3^- ions. $I_2 + KI \rightleftharpoons KI_2$ or $I_2 + I^- \rightleftharpoons \underset{\text{Complex ion}}{I_3^-}$

(3) **Reaction with hydrogen**: Form covalent halides.

$H_2 + F_2 \xrightarrow{-200^o C} 2HF$ (very violent); $H_2 + Cl_2 \xrightarrow{\text{Sunlight}} 2HCl$

$H_2 + Br_2 \xrightarrow[\text{pt. catalyst}]{\text{Heat}} 2HBr$; $H_2 + I_2 \overset{\text{Heat}}{\rightleftharpoons} 2HI$ (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 HI, their reducing properties increase in the order HF < HCl < HBr < H.

(v) **Dipole moments:** The dipole moments of hydrogen halides decrease in the order : HF > HCI > HBr > HX as the electro negativity of the halogen atom decreases form F to I.

HX	HF	HCl	HBr	HI
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°, Cl_2O is also V-shaped with bond angle 111° while ClO_2 is angular with-bond angle 118°. 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:

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, $ClO^- > ClO_2^- \rightarrow ClO_3^- > ClO_4^-$.

(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:** $2F_2 + \underset{\text{(cold dilute)}}{2NaOH} \rightarrow 2NaF + OF_2 + H_2O$; $2F + \underset{\text{(hot conc.)}}{4NaOH} \rightarrow 4NaF + O_2 + 2H_2O$

Halogen other than fluorine (Cl_2, Br_2, I_2) react with NaOH as follows,

$$X_2(g) + \underset{\text{(cold dilute)}}{2OH^-} \xrightarrow{15^\circ C} X^- + \underset{\text{(hypohalite ion)}}{OX^-} + H_2O \;;\; X_2(g) + \underset{\text{(hot conc)}}{6OH^-} \xrightarrow{70^\circ C} 5X^- + \underset{\text{(halate ion)}}{XO_3^-} + 3H_2O$$

(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**

$$2KBr(aq.) + Cl_2(g) \rightarrow 2KCl(aq.) + Br(aq.);\quad 2KI(aq.) + Cl_2(g) \rightarrow 2KCl(aq.) + I_2(aq.)$$

(10) **Inter halogen compounds:** The compounds of one halogen with the other are called interhalogens or interhalogen 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, $2ICl \rightleftharpoons I^+ + ICl_2^-$; $2ICl_3 \rightleftharpoons ICl_2^+ + ICl_4^-$

(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) **Polyhalides:** $KI + I_2 \rightarrow KI \rightleftharpoons K^+ + I_3^-$; $Cl_3^-, Br_3^-, I_3^-, ICl_2^-, IBr_2^-, ICl_4^-, BrF_4^-, I_5^-, IF_6^-$ and I_7^-

(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) **Freons:** Freon –11 is CCl_3F; Freon –12 is CCl_2F_2 and it is marketed under the popular brand names such as '**Freon**' and '**Genetron**' ; Freon –113 is $CCl_2F. CClF_2$; Freon –114 is $CClF_2. CClF_2$; Freon –115 is $CClF_2. CF_3$. These cause ozone depletion.

Preparation of halogens

(1) **Preparation of fluorine :** F_2 is prepared by electrolysis of a solution of KHF_2 (1 Part) in HF (5 part) 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, $KHF_2 \rightleftharpoons KF + HF$; $KF \rightleftharpoons K^+ + F^-$.

At cathode : $K^+ + e^- \longrightarrow K$; $2K + 2HF \rightarrow 2KF + H_2 \uparrow$; At anode : $F^- \rightarrow F + e-$; $F + F \rightarrow F_2$

(2) **Preparation of chlorine**: On the industrial scale, Cl_2 is prepared by the electrolysis of concentrated aqueous solution of NaCl. In this process, NaOH and H_2 are by products.

$2\ NaCl\ (aq) + 2H_2O \xrightarrow{Electricity} 2NaOH(aq) + Cl_2 + H_2$

In the laboratory, Cl_2 can be prepared by adding conc HCl on $KMnO_4$ or MnO_2.

$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$; $MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$

(3) **Preparation of Bromine:** In laboratory it is prepared by heating NaBr with MnO_2 and Conc H_2SO_4.

$2NaBr + MnO_2 + 3H_2SO_4 \rightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Br_2$

(4) **Preparation of Iodine** (Lab method): By heating a mixture of MnO_2, H_2SO_4 and an iodide

$2KI + H_2SO_4 \xrightarrow{MnO_2} K_2SO_4 + SO_2 + I_2 + 2H_2O$. $2I^- + Cl_2 \rightarrow I_2 + 2Cl$.

I_2 is commercially prepared from sea weeds.

Uses of Halogens

(1) Uses of Fluorine:

(i) It is used as an oxidizing agent and fluorinating agent. (ii) Fluorine and its compounds such as NF_3, OF_2 are used as rocket fuels. (iii) It is used in the manufacture of a plastic known as Teflon $(CF_2\text{-}CF_2)n$ which is resistant to the action of all acids, alkalies and even boiling aqua regia. (iv) It is used in the manufacture of fluorocarbons like freon which is used as an excellent refrigerant and in air conditioning. (v) It is used for the preparation of uranium hexafluoride, which is used for the separation of isotopes of U(235) and U(238).

(2) **Uses of Chlorine:** (i) Chlorine is used in sterilization of drinking water. (ii) Large quantities of chlorine are used industrially for the bleaching of cotton, paper, wood, textiles, etc. (iii) It is used in making insecticides like D.D.T., germicides, dyes, drugs, etc. (iv) It is used for preparing vinyl chloride which is a starting material for making th plastic PVC. (v) It is used in the manufacture of chlorinated organic solvents like $CHCl_3$, CCl_4, which are used for dry cleaning and degreasing machinery. (vi) It is used in the preparation of HCl, bleaching powder, chlorates, perchlorates, sodium hypochlorite which are important industrial compounds.

(3) **Uses of Bromine:**

(i) Bromine is used in the preparation of ethylene bromide, which is mixed with tetraethyl lead (TEL) and added to the petrol as an anti-knocking agent.

(ii) In the manufacture of AgBr used in photography.

(iii) In the manufacture of dyes, drugs, etc.

(iv) It is used in the manufacture of benzyl bromide which is an effective teargas.

(v) It is used as a laboratory regent.

(4) **Uses of Iodine:**

(i) Iodine is used as a laboratory reagent.

(ii) It is used in making medicines and dyes. Tincture of iodine is an antiseptic.

(iii) AgI is used in photographic emulsions.

(iv) It is used in the preparation of iodized salt. Iodized salt is used to prevent the occurrence of common goiter.

9. 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.

Electronic configuration

Elements	**Electronic configuration** $(ns^2\ np^6)$
$_{2}He$	$1s^2$
$_{10}Ne$	$1s^2, 2s^2 2p^6$
$_{18}Ar$	$1s^2, 2s^2 2p^6, 3s^2 3p^6$
$_{36}Kr$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6$
$_{54}Xe$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10} 4f^{14}, 5s^2 5p^6$
$_{86}Rn$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10} 4f^{14}, 5s^2 5p^6 5d^{10}, 6s^2 6p^6$

(1) **Atomic radii:** The atomic radii of noble gases increases on moving down the group and their atomic radii correspond to the van der 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) **Polarisability:** The polarisability increases down the group, He < Ne < Ar < Kr < Xe

(4) **Ionization 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 possess very low values of heat of vaporization, because of presence of very weak Vander Waal's forces of attraction between their monoatomic molecules. However the value of heat of vaporization increases with atomic number down the group and this shows that there is an increasing polarisability 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 coconut 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) **Liquefication of gases:** It is difficult to liquify noble gases as their atoms are held by weak Vander Waal's forces. Ease of liquefication increases down the group from He to Rn. Helium has the lowest boiling point (4.18 K) of any known substance. The ease of liquefication 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.

(10) **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%.

(11) **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 73K. 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 radioactive disintegration of radium (226), ${}_{88}Ra^{226} \rightarrow {}_{86}Rn^{222} + {}_{2}\alpha^{4}$.

(12) **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 $(1170kJ\ \text{mol}^{-1})$ is fairly close to that of oxygen $(1166kJ\ mol^{-1})$.

(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 Xe PtF₆ 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 (XeF2), Xenon tetrafluoride (XeF₄) and Xenon hexafluoride (XeF₆).

(i) **Xenon difluoride** (XeF₂) 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: XeF₂ has trigonal bipyramid geometry due to sp^3 d-hybridization of Xe. Three equatorial positions are occupied by lone pairs of electrons giving a linear shape to the molecule.

Properties: XeF₂ is a colourless crystalline solid, reacts with H_2 to give Xe and HF. It is hydrolysed completely by water, $2XeF_2 + 2H_2O \rightarrow 2Xe + O_2 + 4HF$.

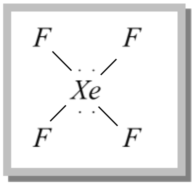
It also forms addition compounds with reactive pentafluorides like SbF₅, TaF₅ etc.

$XeF_2 + 2SbF_5 \rightarrow XeF_2 . 2SbF_5$

It is a mild fluorinating agent and hence reacts with benzene to give fluorobenzene.

(ii) **Xenon tetrafluoride** (XeF₄) 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 colorless, 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$_2$, $XeF_4 + H_2O \xrightarrow{193K} XeOF_2 + 2HF$

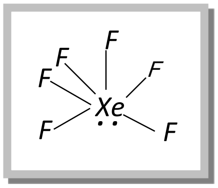
It also forms addition compounds with SbF$_5$, $XeF_4 + SbF_5 \rightarrow [XeF_3]^+[SbF_6]^-$.

It also acts as a strong fluorinating agent.

(iii) **Xenon hexafluoride** (XeF$_6$) is prepared by heating a mixture of xenon and fluorine in the ratio 1 : 20 at 473—523 K under a pressure of 50 atmospheres.

$$Xe + 3F_2 \xrightarrow{473-523K,\,50atm.} XeF_6$$

Structure: XeF$_6$ has pentagonal bipyramid geometry due to sp^{3}d^3 hybridization. One trans position is occupied by a lone pair giving a distorted octahedral shape.



Properties: It is colorless, 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$_3$.

$$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF; \quad XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$$

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$_4$).

(i) **Xenon trioxide** (XeO$_3$) is prepared by complete hydrolysis of XeF$_4$ and XeF$_6$

$$6XeF_4 + 12H_2 \rightarrow 2XeO_3 + 4Xe + 3O_2 + 24HF; \quad XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$$

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 colorless solid, highly explosive and powerful oxidizing agent.

(ii) **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 oxytetrafluride $XeOF_4$ and xenon dioxydifluoride (XeO_2F_2).

(i) **Xenon oxydifluoride** ($XeOF_2$) is formed by partial hydrolysis of XeF_4 at 193 K,

$XeF_4 + H_2O \xrightarrow{193K} XeOF_2 + 2HF$.

Structure: $XeOF_2$ has trigonal bipyramid geometry due to sp^3 d-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.

(ii) **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 $sp^3\ d^2$ 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 colorless 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, $XeOF_4 + 3H_2 \rightarrow Xe + H_2O + 4HF$

(iii) **Xenon dioxydifluoride** (XeO_2F_2) is formed by partial hydrolysis of $XeOF_4$ or XeF_6

$$XeOF_4 + H_2O \rightarrow XeO_2F_2 + 2HF\ ;\quad XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$$

It can also be prepared by mixing XeO_3 and $XeOF_4$ at low temperature (195K). The product is purified by fractional distillation, $XeO_3 + XeOF_4 \xrightarrow{195K} 2XeO_2F_2$

Structure: XeO_2F_2 has trigonal bipyramid geometry due to sp^3 d-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 colorless solid which melts at 303 K. It is easily hydrolyzed to give XeO_3

$$XeO_2F_2 + H_2O \rightarrow XeO_3 + 2HF$$

(13) **Uses of noble gases**

(i) 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).

(ii) 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.

(iii) Helium is also used for creating inert atmosphere in chemical reactions.

(iv) 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.

(v) It is also used in low temperature gas thermometry and as a shield gas for arc welding.

(vi) 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.

(vii) 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.

(viii) Radon is used in radioactive research and therapeutics and in the non-surgical treatment of cancer and other malignant growths.