

Chemistry of Non-Metals-II

(Boron, Silicon, Phosphorus, Sulphur, Halogens, Noble gases and their Compounds)

Boron

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

Occurrence : Boron does not occur in free state. The main ores of boron are :

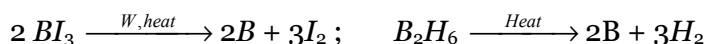
(1) Borax or tincal : $Na_2 B_4 O_7 \cdot 10 H_2 O$; (2) Kernit or Rasorite ; $Na_2 B_4 O_7 \cdot 10 H_2 O$

(3) Colemanite; $Ca_2 B_6 O_{11} \cdot 5 H_2 O$

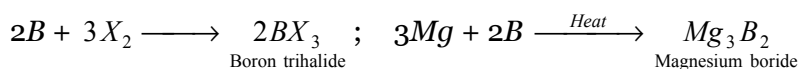
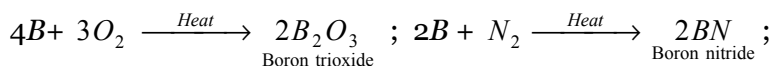
(4) Orthoboric acid ; $H_3 B O_3$ (It occurs in the jets of steam called soffioni escaping from ground in the volcanic region of the **Tuscany**). Boron is present to a very small extent (0.001%) in earth's crust.

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. $B_2 O_3 + 6K \xrightarrow{Heat} 2B + 3K_2 O$; $2BCl_3 + 3H_2 \xrightarrow{1270 K} 2B + 6HCl$

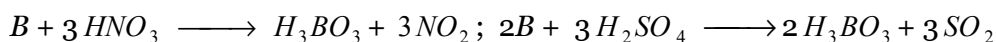
by thermal decomposition of boron tri-iodide over red hot tungsten filament and boron hydrides for example,



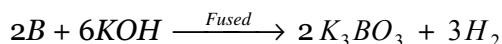
Properties : It exists in mainly two allotropic forms i.e. amorphous dark brown powder and crystalline black very hard solid. It occurs in two isotopic forms, i.e., ${}_5 B^{10}$ (20% abundance) and ${}_5 B^{11}$ (80% abundance). With air, boron forms $B_2 O_3$ and BN at 973K, with halogens, trihalides (BX_3) are formed with metals, borides are formed. eg.



Water, steam and *HCl* have no action on *B*. oxidising acids (HNO_3 , $H_2 SO_4$) convert boron to $H_3 BO_3$.



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



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.

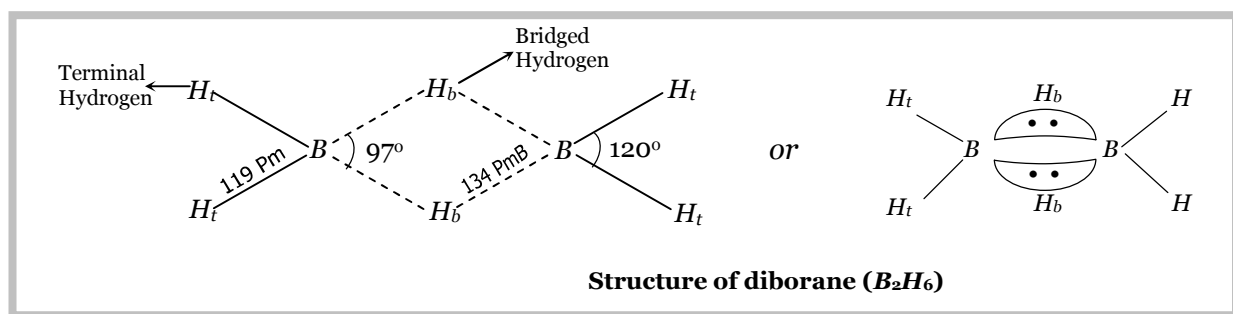
Compounds of Boron

(1) **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 centre electron pair bond also called a banana shape bond.

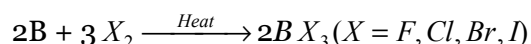
(i) $B-H_t$: It is a normal covalent bond (two centre electron pair bond i.e., $2c-2e$).

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



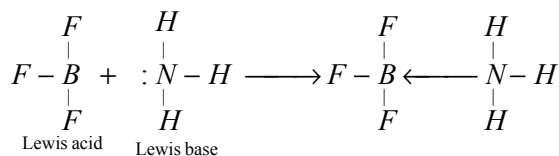
The other boron hydrides are B_5H_9 , B_4H_{10} , B_5H_{11} etc

(2) **Boron halides** : Boron reacts with halogens on strong heating to form boron halides .



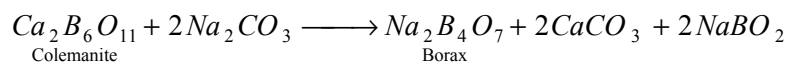
BF_3 and BCl_3 are gases, BBr_3 is a volatile liquid while BI_3 is a solid.

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 act as Lewis acids.

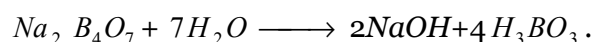


The relative acidic strength of boron trihalides decreases as : $BI_3 > BBr_3 > BCl_3 > BF_3$

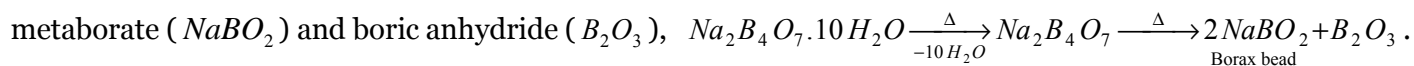
(3) **Borax ($Na_2B_4O_7 \cdot 10H_2O$)** : It occurs naturally as **tincal** (Suhaga) which contains about 50% borax in certain land, lakes. It is also obtained from the mineral colemanite by boiling it with a solution of Na_2CO_3 .



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

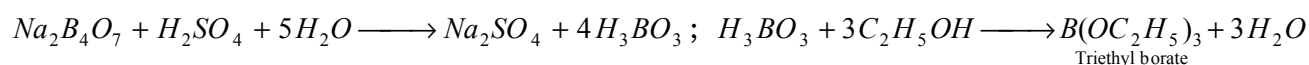


(ii) On heating borax loses its water of crystallization and swells up to form a fluffy mass. On further heating, it melts to give a clear liquid which solidifies to a transparent glassy bead consisting of sodium metaborate ($NaBO_2$) and boric anhydride (B_2O_3),



Borax bead is used for the detection of coloured 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.



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 coloured transition metal oxides such as Co , Ni , Cr , Cu , Mn , etc. to form the corresponding metaborates which possess characteristic colours, $CoSO_4 \xrightarrow{\Delta} CoO + SO_3$; $CoO + B_2O_3 \longrightarrow Co(BO_2)_2$

Cobalt meta borate
(Blue)

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

(4) **Boric acid or orthoboric acid (H_3BO_3)**: It is obtained from borax by treating with dil. HCl or dil. H_2SO_4 , $Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4H_3BO_3$

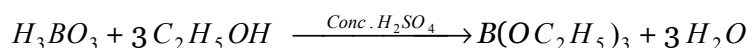
It can also be obtained from the mineral colemanite by passing SO_2 through a mixture of powdered mineral in boiling water, $Ca_2B_6O_{11} + 4SO_2 + 11H_2O \longrightarrow 2Ca(HSO_3)_2 + 6H_3BO_3$

Properties : (i) It is a very weak monobasic acid, does not act as a proton donor but behaves as a Lewis acid i.e. it accepts a pair of electrons from OH^- ion of H_2O , $H_3BO_3 + H_2O \longrightarrow [B(OH)_4]^- + H^+$

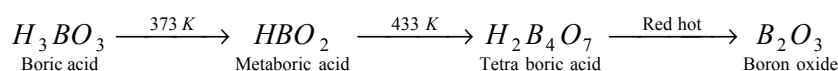
It acts as a strong acid in presence of polyhydroxy compounds such as glycerol, mannitol etc. and can be titrated against strong alkali.

(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



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



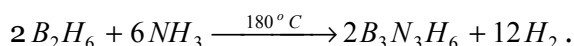
Structure : In boric acid, planar BO_3^{-3} units are joined by hydrogen bonds to give a layer structure.

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.

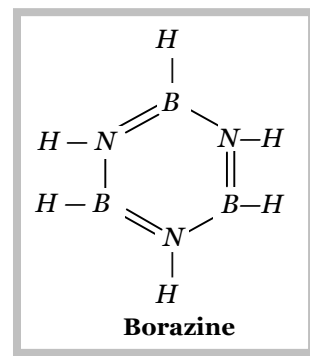
(5) **Carboranes or carbaboranes** : Carboranes or carbaboranes are compounds of *C*, *B* and *H* in which *C* and *B* atoms occupy the vertices of a triangulated polyhedron. These compounds have been derived from boranes by the replacement of BH^- units by CH units .

(6) **Borazine or Borazole 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.



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



(7) **Boron nitride (BN)** : It is prepared by treating BCl_3 with an excess of NH_3 and pyrolysing the resulting mixture in an atmosphere of NH_3 at $750^\circ C$, $BCl_3 + NH_3 \longrightarrow [H_3N \longrightarrow BCl_3] \xrightarrow[\text{Excess } NH_3]{750^\circ C} BN + 3HCl$.

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

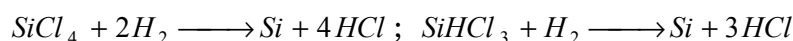
Silicon

Silicon, being a second member of group – 14, has a much larger size and lower electronegativity than that of carbon. As a result silicon does not form double bond with itself or with oxygen. Thus SiO bonds are much stronger than $Si - Si$ and $Si - H$ bonds. Silicon has vacant $3d$ -orbitals in its valence shell due to which it can extend its covalency from four to five and six .

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 ; $K_2Al_2O_3 \cdot 6SiO_2$, Kaolinite; $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$

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.



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, $Si + 2 H_2O \xrightarrow{\text{Redness}} SiO_2 + 2 H_2$.

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), $Si + C \xrightarrow{2500 K} SiC$.

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 alkalis liberating hydrogen, $Si + 4NaOH \xrightarrow{Heat} Na_4SiO_4 + 2H_2 \uparrow$

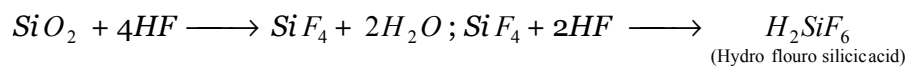
It also dissolves in fused Na_2CO_3 displacing carbon $Na_2SiO_3 + C$.

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).

Compounds of silicon

(1) **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.

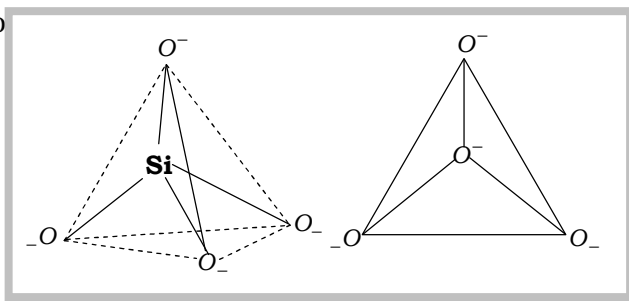
Silica has a three dimensional network structure in which each Si is bonded to four oxygen atoms which are tetrahedrally disposed around silicon atom. Each O atom is shared by two Si atoms. It may be noted that CO_2 is a gas, while SiO_2 is hard solid with very high melting point.



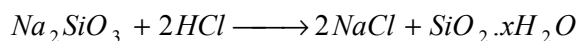
HF readily dissolves Silica, therefore HF can not be store in glass bottles which contain Silica

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 .

(2) **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, feldspar and zeo



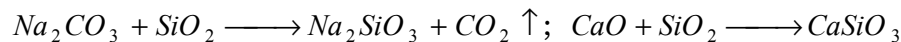
(3) **Silica gel** : When a mineral acid (Such as HCl) is added to a concentrated solution of a silicate, gelatinous white ppt. of hydrated silica (silicic acid) separate out.



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.

(4) **Glass** : Glass is an amorphous and transparent solid which is obtained by solidification of various silicates and borates of potassium and calcium.

Preparation : Ordinary glass is a mixture of sodium and calcium silicates and is produced by fusing together a mixture of sodium carbonate, calcium oxide and silicon dioxide (Silica) in a furnace at about 1700K



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 type of glass is called soda glass or soft glass which has the approximate composition, $Na_2SiO_3, CaSiO_3, 4SiO_2$.

Various varieties of glass : The different varieties of glasses and their special constituents are given below :

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

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

Compound added – Colour imparted	Compound added – Colour imparted
Cobalt oxide (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

Phosphorous

It is the second member of group 15 (VA) of the Periodic table. Due to larger size of P, it can not form stable $P\pi - P\pi$ bonds with other phosphorous atoms where as nitrogen can form $P\pi - P\pi$ bonds.

Occurrence : Phosphorous occurs mainly in the form of phosphate minerals in the crust of earth. Some of these are : (1) Phosphorite $Ca_3(PO_4)_2$, (2) Fluorapatite $Ca_5(PO_4)_3F$, (3) Chlorapatite $3Ca_3(PO_4)_2 \cdot CaCl_2$, (4) 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.

Isolation : Elemental phosphorus is isolated by heating the phosphorite rock with coke and sand in an electric furnace at about $1770K$, $2Ca_3(PO_4)_2 + 6SiO_2 \longrightarrow 6CaSiO_3 + P_4O_{10}$; $P_4O_{10} + 10C \longrightarrow P_4 + 10CO$
Calcium silicate

Allotropic forms of phosphorus : Phosphorus exists in three main allotropic forms :

(1) White phosphorus, (2) Red phosphorus, (3) 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

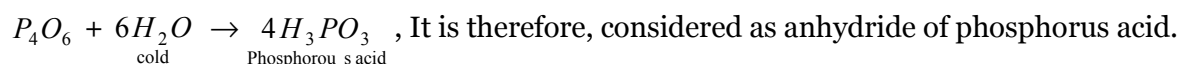
Compounds of phosphorus

(1) **Oxides and oxyacids 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, $P_4 + 3O_2 \rightarrow P_4O_6$ (limited)

It is a crystalline solid with garlic odour. It dissolves in cold water to give phosphorous acid,

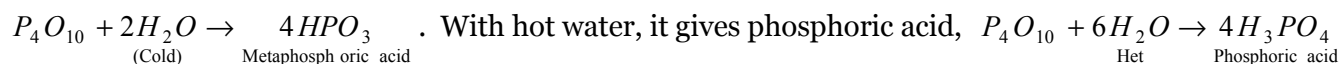


With hot water, it gives phosphoric acid and inflammable phosphine, $P_4O_6 + 6H_2O \text{ (hot)} \rightarrow 3H_3PO_4 + PH_3$
Phosphoric acid

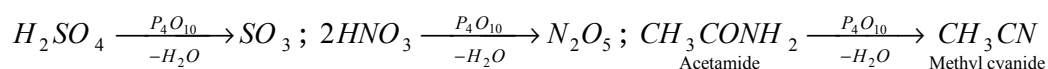
It reacts vigorously with Cl_2 to form a mixture of phosphoryl chloride and meta phosphoryl chloride.



(b) *Phosphorus (V) oxide* (P_4O_{10}) : It is prepared by heating white phosphorus in excess of air, $P_4 + 5O_2 \text{ (excess)} \rightarrow P_4O_{10}$. It is snowy white solid. It readily dissolves in cold water forming metaphosphoric acid.



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



(2) **Oxyacids of phosphorus** : Phosphorus forms a number of oxyacids which differs in their structure and oxidation state of phosphorus.

Oxacids 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	
Pyrophosphoric acid (Diphosphoric acid).	$H_4P_2O_7$	+5	Tetrabasic	

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 :

(1) **Nitrogenous fertilizers :** e.g. Ammonium sulphate $(NH_4)_2SO_4$, Calcium cyanamide $CaCN_2$, Urea NH_2CONH_2 etc.

(2) **Phosphatic fertilizers :** e.g. $Ca(H_2PO_4)_2 \cdot H_2O$ (Triple super phosphate), Phosphatic slag etc.

(3) **Potash fertilizers :** e.g. Potassium nitrate (KNO_3) , Potassium sulphate (K_2SO_4) etc.

(4) **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.

Sulphur

Sulphur is the second member of oxygen family and belongs to group-16 (VI A) of the periodic table.

Occurrence : Sulphur occurs in the earth's crust to the extent of 0.05%. It occurs in the free state as well as in combined state. Sulphure occurs mainly as sulphides and sulphates. eg.

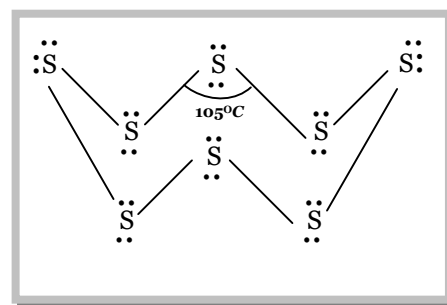
Sulphide Ores		Sulphate Ores	
Iron pyrites (fool's gold)	– FeS_2	Gypsum	– $CaSO_4 \cdot 2H_2O$
Galena	– PbS	Epsom salt	– $MgSO_4 \cdot 7H_2O$
Copper pyrites	– $CuFeS_2$	Barytes	– $BaSO_4$
Cinnabar	– HgS	Zinc blende	– ZnS

(2) **Extraction of sulphur (Frasch process):** Sulphur is generally extracted from underground deposits by drilling three concentric pipes upto 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 varieties 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.

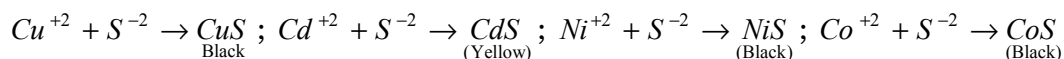
(iv) **Colloidal or δ – sulphur :** It is prepared by passing H_2S through a solution of an oxidizing agent or water or by treating sodium thiosulphate with dil. HCl .

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, $S_8 + 12 NaOH \longrightarrow 4 Na_2S + 2 Na_2S_2O_3 + 6 H_2O$. It gives sodium sulphide and sodium thiosulphate, with excess of sulphur, $2 Na_2S + S_8 \longrightarrow 2 Na_2S_5$.

(5) **Uses of sulphur :** It is used in the manufacture of matches, gun powder (mixture of charcoal, sulphur and potassium nitrate), explosives and fire works SO_2 , H_2SO_4 , CS_2 and dyes, sulpha drugs and ointment for curing skin diseases and in the vulcanization of rubber.

Compounds of Sulphur

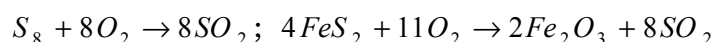
(1) **Hydrogen Sulphide** : It is prepared in the laboratory by the action of dil. H_2SO_4 on ferrous sulphide in kipp's apparatus, $FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S$. It is colourless gas having foul smell resembling that of rotten eggs. It reacts with many cations (of group II and IV) to give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



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.

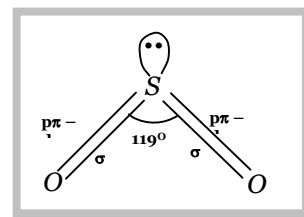


In laboratory, it is prepared by heating copper turnings with conc. H_2SO_4

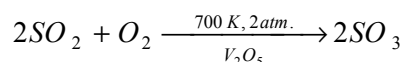


It is a colourless gas with irritating and suffocating smell.

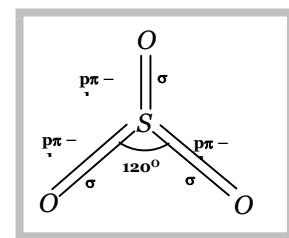
SO_2 molecule has a bent structure with a $O-S-O$ bond angle of 119° . Sulphur is sp^2 hybridized.



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



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 (oxidation number of sulphur)	Name	Important properties	Structural formula
H_2SO_3 (+4)	Sulphurous acid	Free acid does not exist diprotic, strong reducing agent	$O = \overset{\cdot\cdot}{S} - OH$ $ $ OH
H_2SO_4 (+6) (Oil of vitriol)	Sulphuric acid	Stable diprotic, dehydrating agent	O $ $ $O = \overset{\cdot\cdot}{S} - OH$ $ $ 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	S $ $ $O = \overset{\cdot\cdot}{S} - OH$ $ $ OH

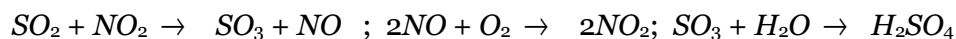
Chemistry of Non-Metals-II

$H_2S_2O_4$ (+3)	Dithionous acid		$\begin{array}{c} O \quad O \\ \quad \\ HO - S - S - OH \end{array}$
$H_2S_2O_6$ (+5)	Dithionic acid	Free acid is moderately stable but its salts are quite stable.	$\begin{array}{c} O \quad O \\ \quad \\ O = S - S = O \\ \quad \\ OH \quad OH \end{array}$
$H_2S_2O_7$ (+6) (Oleum)	Disulphuric acid (Pyrosulphuric acid)	Strong oxidising agent	$\begin{array}{c} O \quad O \\ \quad \\ O = S - O - S = OH \\ \quad \\ OH \quad OH \end{array}$
H_2SO_5 (+6) (Caro's acid)	Peroxomonosulphuric acid (Its salts known as persulphates)	Stable crystalline solid, powerful oxidising agent	$\begin{array}{c} O \\ \\ HO = S - OOH \\ \\ O \end{array}$
$H_2S_2O_8$ (+6) (Marshals acid)	Peroxodisulphuric acid (its salts are known as disulphates)	Strong oxidising agent.	$\begin{array}{c} O \quad O \\ \quad \\ O = S - O - O - S = O \\ \quad \\ OH \quad OH \end{array}$

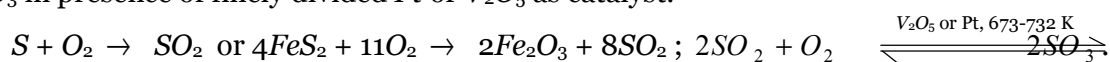
(4) **Sulphuric acid (H_2SO_4)** : H_2SO_4 is a very stable oxyacid of sulphur. It is often called king of chemicals, since it is one of the most useful chemicals in industry.

Manufacture of sulphuric acid : H_2SO_4 can be manufactured by following process.

(i) **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 .



(ii) **Contact process** : In the contact process, SO_2 obtained by burning of S or iron pyrites is catalytically oxidized to SO_3 in presence of finely divided Pt or V_2O_5 as catalyst.

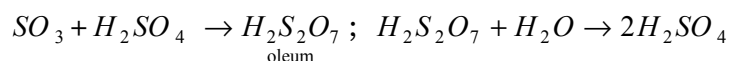


V_2O_5 is, however, preferred since is much cheaper than Pt and is also not poisoned by arsenic impurities.

The favorable conditions for maximum yield of SO_3 are:

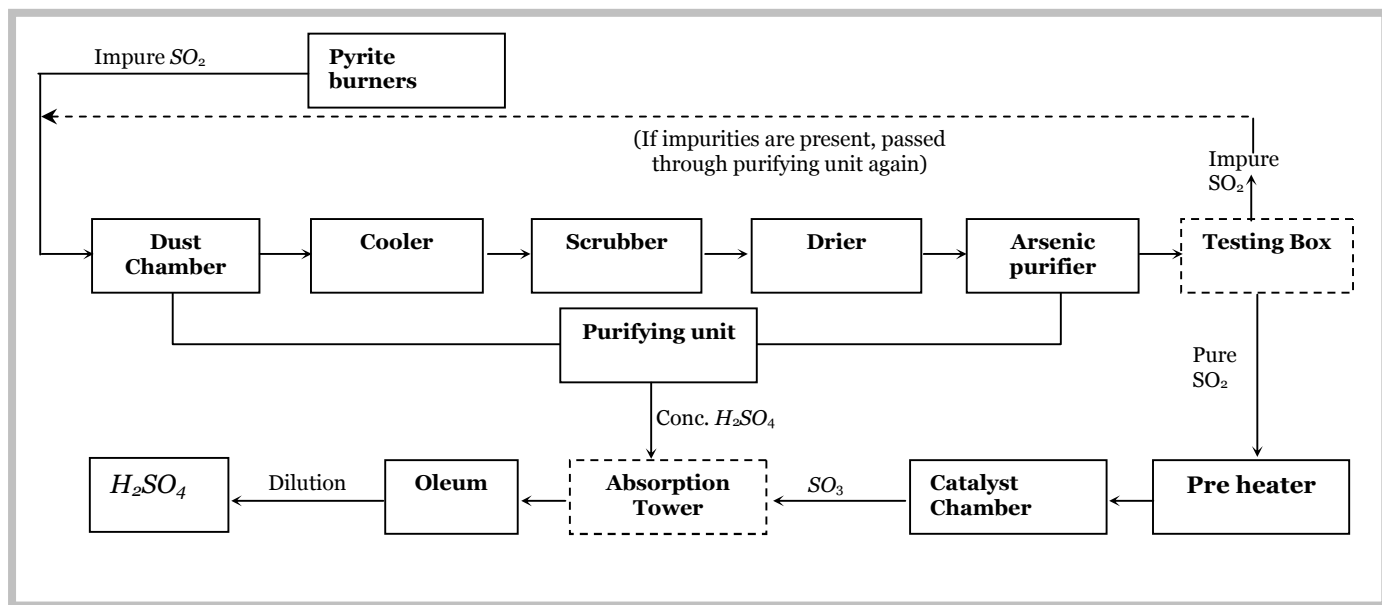
(a) High concentration of SO_2 and O_2 . (b) Low temperature of 673 to 723 K, (c) High pressure about 2 atmospheres.

SO_3 thus obtained is absorbed in 98% H_2SO_4 to form oleum which on dilution with water gives H_2SO_4 of desired concentration.



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.

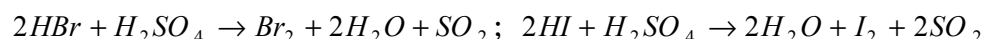
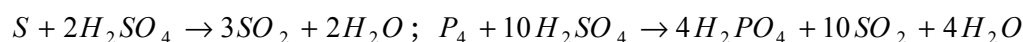
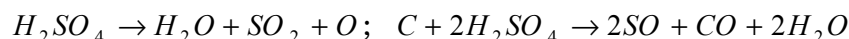
Properties : H_2SO_4 has high b.p. (611K) and is also highly viscous due to H-bonding. It has strong affinity for H_2O and a large amount of heat is evolved when it is mixed with water.

(1) H_2SO_4 is a strong dibasic acid. It neutralizes alkalis, 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



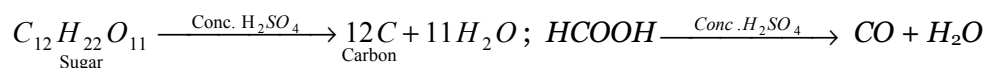
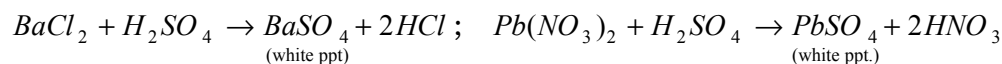
(3) It is a strong oxidizing agent and oxidises as follows,



(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), 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.



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 tanning (vi) as a dehydrating agent.

(5) **Sodium thiosulphate** $Na_2S_2O_3 \cdot 5H_2O$: 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, $Na_2SO_3 + S \xrightarrow{373K} Na_2S_2O_3$

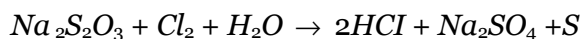
The solution is then cooled to get crystals of sodium thiosulphate.

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 490 K .

Chemical properties :

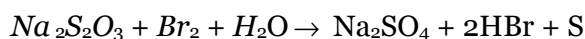
(1) **Action with halogens** : It reacts with halogens as,

(i) Chlorine water oxidizes sodium thiosulphate to sodium sulphate and sulphur is precipitated,

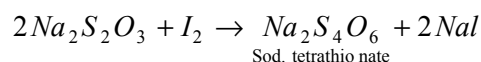


This property enables it to act as an antichlor in bleaching i.e. it destroys the unreacted chlorine in the process of bleaching.

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



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

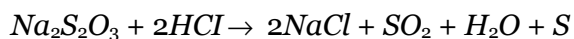


Therefore, hypo is commonly used to remove iodine stains from the clothes.

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

Sodium pentasulphide

(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.



(4) **Action with silver halides** : Sodium thiosulphate forms soluble complex when treated with silver chloride or silver bromide, $2Na_2S_2O_3 + 2AgBr \rightarrow Na_3Ag(S_2O_3)_2 + NaBr$.

Sodium dithiosulphate
argentate (I) complex

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.

Halogens

The name halogen (Greek, halos = sea salts, genes= born) meaning sea salt formers was given to F, Cl, Br, I and at by Schweigger in 1811.

Occurrence : Halogens are very reactive and therefore, do not occur free in nature. They occur in the combined state quite abundantly at many places. For example:

(1) *Fluorine* occurs in the combined state the main ores are



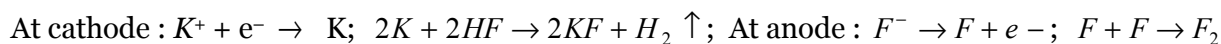
(2) *Chlorine* occurs in the combined state only main source is sea other chloride minerals are carnallite ($\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$) etc. Sodium chloride NaCl (Rock salt). Sea water contains about 2.8% chlorine by weight.

(3) *Bromine* is also present in water as bromides of alkali and alkaline earth metals.

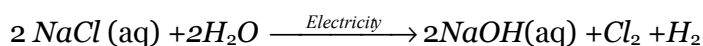
(4) *Iodine* is mainly present in sea weeds as iodides and in chile salt peter as sodium iodate (NaIO_3).

Preparation

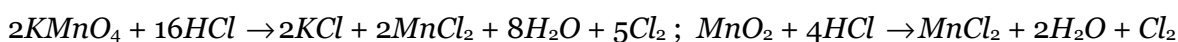
(1) **Preparation of fluorine** : F_2 is prepared by electrolysis of a solution of KHF_2 (1 Part) in HF (5 part) in a vessel (**Modern method**) made of $\text{Ni} - \text{Cu}$ alloy or $\text{Ni} - \text{Cu} - \text{Fe}$ alloy called the monel metal using carbon electrodes. During the electrolysis following reactions occur, $\text{KHF}_2 \rightleftharpoons \text{KF} + \text{HF}$; $\text{KF} \rightleftharpoons \text{K}^+ + \text{F}^-$



(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.



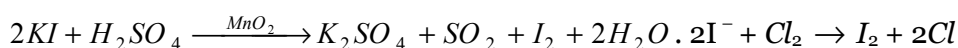
In the laboratory, Cl_2 can be prepared by adding conc HCl on KMnO_4 or MnO_2 .



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



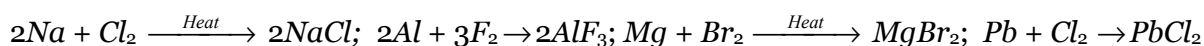
(4) **Preparation of Iodine** : Lab method : By heating a mixture of $\text{MnO}_2, \text{H}_2\text{SO}_4$ and an iodide



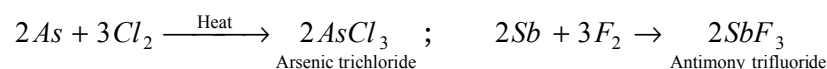
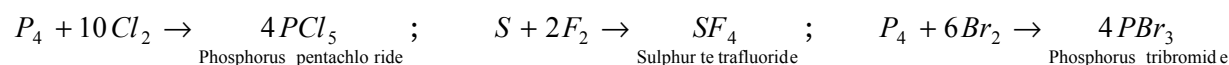
I_2 is commercially prepared from sea weeds.

Properties

(1) **Combination with metals** : Halogens combine with metals as well as with many non metals to form halides.



(2) **Reaction with non-metals** : Halogens combine with non-metals such as P, As, Sb, etc to form halides.

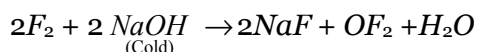


Chemistry of Non-Metals-II

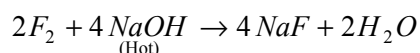
(3) **Action with hydrogen** : All halogens react with hydrogen to form halogen acids. The reactivity towards hydrogen gradually decreases from fluorine to iodine.



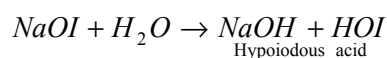
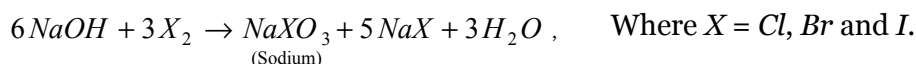
(4) **Action with alkalis** : Fluorine reacts with cold and dilute sodium hydroxide to form oxygen difluoride (OF_2)



However, with hot and concentrated sodium hydroxide it reacts to give oxygen.

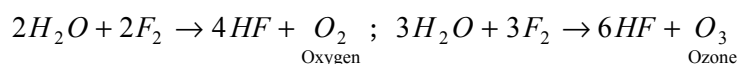


Other halogens react with cold and dilute alkalis to form hypohalites (XO^-) and with hot and concentrated alkalis to form halate (XO_3^-). e.g. $2NaOH + X_2 \xrightarrow{\text{(Dilute, Cold)}} NaXO + NaX + H_2O$ Sod. hypohalite

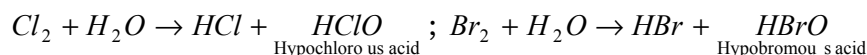


Thus, the reaction of iodine with cold and dilute $NaOH$ is, $NaOH + I_2 \xrightarrow{\text{cold}} NaI + HOI$

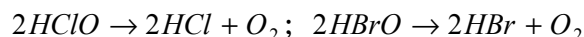
(5) **Action with water** : Halogens readily decomposes water. This tendency decreases on moving down the group. Fluorine decomposes water very energetically to give oxygen and ozone:



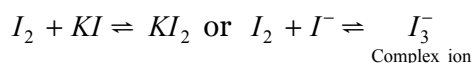
Fluorine gives fumes in moist air. This is due to the formation of HF , which is a liquid and can absorb moisture to form liquid droplets and therefore, gives fumes with moist air. Chlorine and bromine react less vigorously,



In the presence of sunlight, $HClO$ (hypochlorous acid) $HBrO$ (hypobromous acid) liberate oxygen.



Iodine is only slightly soluble in water. However, it dissolves in 10% aqueous solution of KI due to the formation of I_3^- ions.



Uses of Halogens

(1) **Uses of Fluorine** : (i) It is used as an oxidising 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-CF_2) $_n$ which is resistant to the action of all acids, alkalis 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 the 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 tear gas. (v) It is used as a laboratory reagent.

(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.

Compounds of Halogens

(1) 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 $HF < HCl < HBr < HI$

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

HX	HF	HCl	HBr	HI
Dipole moment (D)	1.74	1.07	0.78	0.38

(2) 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_2 and 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. $2ClO_2 + H_2O \rightarrow HClO_2 + HClO_3$

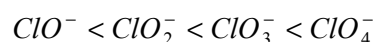
(3) **Oxoacids of halogens** : Fluorine does not form any oxoacid since it is the strongest oxidizing agent. Chlorine, bromine and iodine mainly form four series of oxoacids namely hypohalous acid (HXO), halous acid (HXO_2) halic acid (HXO_3) and perhalic acid (HXO_4) as given below :

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



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 same 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. $HClO_4 > HBrO_4 > HIO_4$.

(4) **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	ClF ₃ , BrF ₃	BrF ₅ , IF ₅	IF ₇
BrF, BrCl, ICl	IF ₃ , ICl ₃		
IBr, IF			

These interhalogen compounds are unstable and more reactive

General properties

(1) Largest halogen always serves the central atom.

(2) The highest interhalogen compound i.e. IF₇ is obtained with iodine, the largest halogen attached to the smallest one

(3) The bonds in interhalogen compounds are essentially covalent.

(4) 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.

(5) They ionize in solution or in the liquid state, $2ICl = I^+ + ICl_2^-$; $2ICl_3 = ICl_2^+ + ICl_4^-$

(6) Hydrolysis of interhalogen compounds always produces a halide ion derived from smaller halogen and oxyhalide derived from larger halogen, $ICl + H_2O \rightarrow Cl^- + OI^- + 2H^+$; $BrF_5 + 3H_2O \rightarrow 5F^- + BrO_3^- + 6H^+$

(7) They are strong oxidizing agents.

(8) Largest number of interhalogens are formed by fluorine due to its smaller size and higher electronegativity or oxidizing power.

Structure : Interhalogen compounds are

(1) AB type i.e. ICl, IBr, IF etc, are linear

(2) AB₃ type i.e. IF₃, ClF₃, BrF₃ have distorted trigonal bipyramidal (dsp^3 -hybridization) structures of T-shape due to two lone pairs in equatorial positions ICl₃ is dimeric, I₂Cl₆ and has a planar structure.

(3) AB₅ types i.e. BrF₅, IF₅ have distorted octahedral (d^2sp^3 -hybridization) shapes or square pyramidal due to a lone pair one of the axial positions.

(4) AB_7 type i.e. IF_7 , have pentagonal bipyramidal (d^3sp^3 -hybridization) structures.

Noble Gases

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.

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	<i>He</i>	<i>Ne</i>	<i>Ar</i>	<i>Kr</i>	<i>Xe</i>
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%.

Isolation :

(1) **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.

(2) **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.

(3) **Radon** : It can be obtained by radio active disintegration of radium (226), ${}_{88}Ra^{226} \rightarrow {}_{86}Rn^{222} + {}_2\alpha^4$.

Compounds of Xenon : In 1962, N. Bartlett noticed that PtF_6 is a powerful oxidizing agent which combines with molecular oxygen to form ionic compound, dioxygenyl hexafluoro platinate (v) $O_2^+[PtF_6]^-$,

$O_{2(g)} + PtF_{6(g)} \rightarrow O_2^+[PtF_6]^-$, This indicates that PtF_6 has oxidized O_2 to O_2^+ . Now, oxygen and xenon have some similarities :

(i) The first ionization energy of *Xe* gas (1170 kJ mol^{-1}) is fairly close to that of oxygen (1166 kJ mol^{-1}).

(ii) The molecular diameter of oxygen and atomic radius of *Xe* are similar (4\AA)

On this assumption, Bartlett reacted Xenon and PtF_6 in gas phase and a orange yellow solid of the composition *Xe PtF₆* was obtained, $Xe_{(g)} + PtF_{6(g)} \rightarrow Xe^+ [PtF_6]_{(s)}^-$.
Orange yellow

Some important stable compounds of *Xe* are :

+2	+4	+6
XeF_2	XeF_4 , $XeOF_2$	XeF_6 , $XeOF_4$, XeO_3

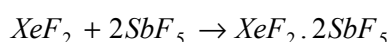
(1) **Fluorides** : Xenon forms three compounds with fluorine. These are : Xenon difluoride (XeF_2), Xenon tetrafluoride (XeF_4) and Xenon hexafluoride (XeF_6).

(i) *Xenon difluoride* (XeF_2) is formed when a mixture of Xenon and fluorine in the ratio 1 : 3 by volume is passed through a nickel tube at 673 K, $Xe + Fe \xrightarrow{Ni, 673K} XeF_2$

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

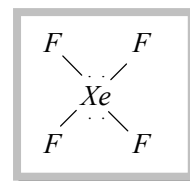
It also forms addition compounds with reactive pentafluorides like SbF_5 , TaF_5 etc.



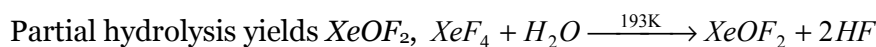
It is a mild fluorinating agent and hence reacts with benzene to give fluorobenzene.

(ii) *Xenon tetrafluoride* (XeF_4) is prepared by heating a mixture of xenon and fluorine in the ratio 1 : 5 in a nickel vessel at 673 K and then suddenly cooling it in acetone. XeF_4 is also formed when an electric discharge is passed through a mixture of xenon and excess of fluorine, $Xe + 2F_2 \xrightarrow{Ni, 673K} XeF_4$

Structure : XeF_4 has square planar shape due to $sp^3 d^2$ hybridization of Xe giving octahedral geometry with two trans positions occupied by lone pairs of electrons.

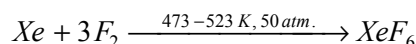


Properties : XeF_4 is a colourless, crystalline solid, soluble in anhydrous HF, reacts with H_2 to form Xe and HF and reacts with water to give highly explosive solid, XeO_3 . (complete hydrolysis), $6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$



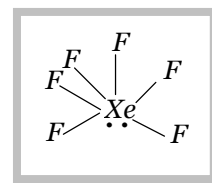
It also acts as a strong fluorinating agent.

(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.

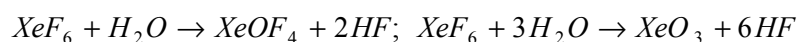


Structure : XeF_6 has pentagonal bipyramid geometry due to $sp^3 d^3$ hybridization. One trans position is occupied by a lone pair giving a distorted octahedral shape.

Properties : It is colourless, crystalline solid, highly soluble in anhydrous HF giving solution which is a good conductor of electricity, $HF + XeF_6 \rightarrow XeF_5^+ + HF_2^-$.



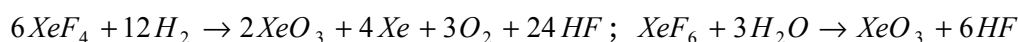
It is the most powerful fluorinating agent and reacts with H_2 to give Xe and HF. Partial hydrolysis of XeF_6 yields $XeOF_4$ an complete hydrolysis yields xenon trioxide, XeO_3 .



It forms addition compounds with alkali metal fluorides (except LiF) of the formula $XeF_6 \cdot MF$ where M represents the alkali metal.

(2) **Oxides** : Xenon forms two oxides such as xenon trioxide (XeO_3) and xenon tetraoxide (XeO_4).

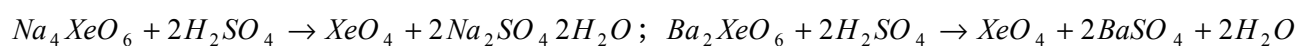
(i) *Xenon trioxide* (XeO_3) is prepared by complete hydrolysis of XeF_4 and XeF_6



Structure : XeO_3 has tetrahedral geometry due to sp^3 hybridization of Xe . One of the hybrid orbitals contains a lone pair of electrons giving a trigonal pyramidal shape. The molecule has three $Xe=O$ double bonds containing $p\pi-d\pi$ overlapping.

Properties : It is a colourless solid, highly explosive and powerful oxidizing agent.

(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,



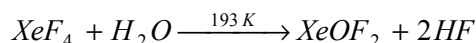
XeO_4 is purified by vacuum sublimation at 195 K.

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, $XeO_4 \rightarrow Xe + 2O_2$.

(iii) **Oxyfluorides :** Xenon forms three types of oxy fluorides such as xenon oxydifluoride ($XeOF_2$), xenon oxytetrafluoride $XeOF_4$ and xenon dioxydifluoride (XeO_2F_2).

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



Structure : $XeOF_2$ has trigonal bipyramid geometry due to sp^3d -hybridization of Xe . Two equatorial positions are occupied by lone pairs of electrons giving a T-shape to the molecule. There is one $Xe-O$ double bond containing $p\pi-d\pi$ overlapping.

(b) *Xenon oxytetrafluoride* ($XeOF_4$) is prepared by partial hydrolysis of XeF_6 ;
 $XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$.

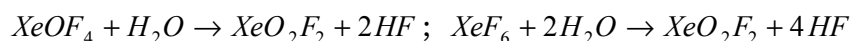
It can also be prepared by the reaction of SiO_2 with XeF_6 , $2XeF_6 + SiO_2 \rightarrow 2XeOF_4 + SiF_4$.

Structure : $XeOF_4$ has octahedral geometry due to sp^3d^2 hybridization of Xe . One trans position is occupied by a lone pair giving pyramid shape to the molecule. There is one $Xe-O$ double bond containing $p\pi-d\pi$ overlapping.

Properties : It is a colourless volatile liquid which melts at 227 K. It reacts with water to give XeO_2F_2 and XeO_3 , $XeOF_4 + H_2O \rightarrow XeO_2 + 2HF$, $XeO_2F_2 + H_2O \rightarrow XeO_3 + 2HF$

It is reduced by H_2 to Xe , $XeOF_4 + 3H_2 \rightarrow Xe + H_2O + 4HF$

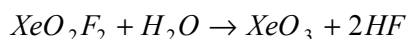
(c) *Xenon dioxydifluoride* (XeO_2F_2) is formed by partial hydrolysis of $XeOF_4$ or XeF_6



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^3d -hybridization of Xe . One equatorial position is occupied by a lone pair of electrons giving a see-saw structure (shape) to the molecule. There are two $Xe-O$ double bonds containing $p\pi - d\pi$ overlapping.

Properties : It is a colourless solid which melts at 303 K. It is easily hydrolysed to give XeO_3



Uses of noble gases

(1) He is used for filling of balloons and air ships because of its non-inflammability and high power (which is 92.6% to that of hydrogen).

(2) Oxygen-helium (1 : 4) mixture is used for treatment of asthma and for artificial respiration in deep sea diving because unlike nitrogen, helium is not soluble in blood even under high pressure.

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

(4) Liquid helium is used as a cryogenic fluid to produce and maintain extremely low temperatures for carrying out researches and as a coolant in atomic reactors and super conducting magnets.

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

(6) Argon is used for creating inert atmosphere in chemical reactions, welding and metallurgical operations and for filling in incandescent and fluorescent lamps. It is also used in filling Geiger-Counter tubes and thermionic tubes.

(7) Krypton and xenon are also used in gas filled lamps. A mixture of krypton and xenon is also used in some flash tubes for high speed photography.

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