p-BLOCK ELEMENTS

1 INNERT PAIR EFFECT

In the s–block, group I elements are univalent and group II elements are divalent. In group III we would expect the elements to be trivalent. In most of their compounds this is the case, but some of the elements show lower valency states as well. There is an increasing tendency to form univalent compounds on descending the group. Compounds with Ga(I), In(I) and Tl(I) are known. With Ga and In the (I) oxidation state is less stable than the (III) state. However, the stability of the lower oxidation state increases on descending the group. Tl(I) thallous compounds are more stable than Tl(III) thallic compounds.

How and why does monovalency occur in group III? The atoms in this group have an outer electronic configuration of s^2p^1. Monovalency is explained by the s–electrons in the outer shell remaining paired and not participating in bonding. This is called the 'inert pair effect'. If the energy required to unpair them exceeds the energy evolved when they form bonds, then the s–electrons will remain paired. The strength of the bonds in MX_3 compounds decreases down the group.

The mean bond energy for chlorides are $GaCl_3$ = 242, $InCl_3$ = 206 and $TlCl_3$ = 153 kJ mol^{-1}. Thus the s–electrons are most likely to be inert in thallium.

The inert pair effect is not the explanation of why monovalency occurs in group III. It merely describes what happens, i.e. two electrons do not participate in bonding. The reason that they do not take part in bonding is energy. The univalent ions are much larger than the trivalent ions and (I) compounds are ionic and are similar in many ways to group I elements.

The inert pair effect is not restricted to group III, but also occurs among the heavier elements in other groups in the p–block. Examples from group IV are Sn^{2+} and Pb^{2+} and examples from group V are Sb^{3+} and Bi^{3+}. The lower oxidation state becomes more stable on descending the group. Thus, Sn^{2+} is a reducing agent but Pb^{2+} is stable and Sb^{3+} is a reducing agent but Bi^{3+} is stable. When the s–electrons remain paired, the oxidation state is always two lower than the usual oxidation state for the group.

Thus, in the s–block, groups I and II show only the group valency. Groups in the p–block show variable valency, differing in steps of two. Variable valency also occurs with elements in the d–block. This arises from using different number of d–electrons for bonding, so in this case the valency can change in steps of one (e.g. Cu^+ and Cu^{2+}, Fe^{2+} and Fe^{3+}).

2 THE GROUP – 13 ELEMENTS (BORON GROUP)

2.1 ISOLATION OF BORON

(i) Reduction of boric oxide with highly electropositive metals like Na, K and Mg in the absence of air.

$B_2O_3\,(s) + 6K(s) \xrightarrow{\Delta} 2B(s) + 3K_2O(s)$

$B_2O_3\,(s) + 3Mg(s) \xrightarrow{\Delta} 2B(s) + 3MgO(s)$

The product thus obtained is boiled with HCl and filtered when K_2O and MgO dissolves, leaving behind elemental B. The powdered B thus obtained is thoroughly washed with water to free it from HCl and is finally dried.

(ii) **Modern Method**

B is obtained these days by the electrolysis of a fused mixture containing boric anhydride, MgO and MgF_2 at 1100°C. The electrolysis is done in a carbon crucible, which acts as anode and Fe rod is used as cathode. The Mg discharged at cathode reduces B_2O_3 to B.

$2MgO \longrightarrow 2Mg + O_2$

$B_2O_3 + 3Mg \longrightarrow 2B + 3MgO$

B thus obtained is heated electrically in vacuum at 1100°C, when the impurities are volatilised off and pure boron is obtained.

(iii) By thermal decomposition of BI_3 over red hot tungsten filament (Van Arkel method)

$$2BI_3 \xrightarrow[1173\,K]{W} 2B(s) + 3I_2(g)$$

2.2 GENERAL PROPERTIES

2.2.1 Melting Points, Boiling Points and structures

The melting points of group III elements donot show a regular trend as did the metals of group I and II. The Group III values are not strictly comparable because B and Ga have unusual crystal structures. Boron has an unusual crystal structure which results in the melting point being very high. Other elements form metallic bonding, but small size and high ionisation energy make this impossible for boron. Boron exists in four different allotropic forms, all of which contains icosahedral units with boron atoms at all 12 corners. (Icosahedral contains 12 corners and 20 faces). Only 37% of the space is occupied by the atoms, compared with 74% for a close–packed arrangement. This shows that icosahedra fill up space ineffectively.

The elements Al, In and Tl all have close-packed metal structures Ga has an unusual structure. Each metal atom has one close neighbour at a distance of 2.43 Å and six more distant neighbours at distance between 2.7 Å and 2.79 Å. This remarkable structure tends towards discrete diatomic molecules rather than a metallic structure. This accounts for the incredibly low melting point of gallium at 30ºC

	Melting Point (ºC)	**Boiling Point (ºC)**
B	2180	3650
Al	660	2467
Ga	30	2403
In	157	2080
Tl	303	1457

As is obvious from the above table, the melting point decreases in the group but irregularities occur. B has very high melting point because of its unique covalent structure. Ga has extremely low melting point again because of its unique structure.

The boiling point for B is unusually high, but the values for Ga, In and Tl decrease on descending the group as expected. Note that the boiling point for Ga is in line with the others, whereas its melting point is not. The very low melting point is due to the unusual crystal structure, but the structure no longer exits in the liquid.

2.2.2 Size of atoms and ions

The metallic radii of the atoms do not increase regularly on descending the group. However, the values are not strictly comparable because of their unique structures.

	Metallic radius (Å)	Ionic radius M^{+3}(Å) M^{+}(Å)	Paulings electronegativity

B	(0.885)	(0.27)	–	2
Al	1.43	0.535	–	1.5
Ga	(1.225)	0.620	1.2	1.6
In	1.67	0.800	1.4	1.7
Tl	1.70	0.885	1.5	1.8

The ionic radii for M^{+3} increase down the group, though not in the regular way as observed in Group I and II. There are two reasons for this.

(i) There is no evidence for the existence of B^{+3} under normal condition and the value of ionic radius is an estimate.

(ii) The electronic structures of the elements are different. Ga and In have a d^{10} inner shell which is poorly screening and so have higher ionisation energies than would otherwise be expected. This contraction in size is sometimes called the d-block contraction.

In a similar way T*l* follows immediately after 14 f–block elements. The size and ionisation energy of T*l* are affected even more by the presence of 14 f electrons, which shield the nuclear charge even less effectively. The contraction in size from these f –block elements is called the lanthanide contraction.

2.2.3 Electropositive Character

The electropositive or metallic nature of the elements increase from B to Al, but then decreases from Al to T*l* as is shown by the standard electrode potentials for the reaction:

$M^{+3} + 3e^- \longrightarrow M$

	M^{+3}|M(Volts)	M^{+1}|M(Volts)
B	(–0.87)*	
Al	–1.66	0.55
Ga	–0.56	-0.79^f
In	–0.34	–0.18
Tl	+1.26	–0.34

* For $H_3BO_3 + 3H^+ + 3e^- \longrightarrow B + 3H_2O$

^{f} Value in acidic solution.

Ga, In and Tl have lesser tendency to lose electrons (and are thus electropositive), because of the poor shielding by d–electrons.

The E° values show that the stability of +3 oxidation state decreases down the group whereas that of +1 increases down the group.

2.2.4 Ionisation Energy

The ionisation energies increase as expected (first ionisation energy < second ionisation energy < third ionisation energy). The sum of the first three ionisation energies for each of the elements is very high. Thus, boron has no tendency to form ions, and always forms covalent bonds. The other elements normally form covalent compounds except in solution where the high hydration energy compensates the high ionisation energy.

The ionisation energy values do not decrease smoothly down the group.

The decrease from B to Al is the usual trend on descending a group associated with increased size. The poor shielding by d–electrons and the resulting d-block contraction affect the values for the later elements.

	Ionisation energy ($kJmol^{-1}$)			
	1st	2nd	3rd	Sum of three

B	801	2427	3659	6887
Al	577	1816	2744	5137
Ga	579	1979	2962	5520
In	558	1820	2704	5082
Tl	589	1971	2877	5437

2.3 SOME DISSIMILARITIES OF BORON WITH OTHER ELEMENTS OF THIS GROUP

(i) Boron is a non–metal, while all other elements of this group are metals.

(ii) Boron forms only covalent compounds, while other elements of this group form both covalent and ionic compounds.

(iii) Boron shows a maximum covalency of four, while other elements of this group show a maximum valency of six, absorbs neutron and is steel grey in colour. Its density is 2.34 gm/cc.

2.4 CHEMICAL PROPERTIES OF BORON

Crystalline B is not active while amorphous B reacts. The reactions are as follows.

(a) Reaction with air

$$4B + 3O_2 \xrightarrow{700°C} 2B_2O_3$$

$$2B + N_2 \xrightarrow{700°C} 2BN$$

The above reaction accompanies red flame.

$$BN + 3H_2O \xrightarrow{\text{High temp. \& press.}} H_3BO_3 + NH_3$$

(b) Action of alkali and acid are given as follows,

$$2B + 2NaOH + 2H_2O \longrightarrow 2NaBO_2 + 3H_2$$

$$2B + 3H_2O \xrightarrow{\text{High temp.}} B_2O_3 + 3H_2$$

$$2B + 3H_2SO_4 \xrightarrow{\text{oxidation}} 2H_3BO_3 + 3SO_2$$

$$2B + 6HNO_3 \xrightarrow{\text{oxidation}} 2H_3BO_3 + 6NO_2$$

(c) Boron reacts with Mg and consequent hydrolysis gives diborane.

$$3Mg + 2B \longrightarrow Mg_3B_2$$

$$3Ca + 2B \longrightarrow Ca_3B_2$$

$$Mg_3B_2 + 6HCl \longrightarrow 3MgCl_2 + B_2H_6$$

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

(d) Boron reduces SiO_2, CO_2

$$3SiO_2 + 4B \longrightarrow 2B_2O_3 + 3Si$$

$$3CO_2 + 4B \longrightarrow 2B_2O_3 + 3C$$

2.5 COMPOUNDS OF BORON

2.5.1 BORON HALIDES

(a) BORON TRIFLUORIDE (BF_3)

Preparation:

$B_2O_3 + 3CaF_2 + 3H_2SO_4$ (conc.) $\longrightarrow 3CaSO_4 + 2BF_3 + 3H_2O$ (colourless liquid).

$$B_2O_3 + 6KBF_4 + 3H_2SO_4 \longrightarrow 3K_2SO_4 + 8BF_3 + 3H_2O$$

Properties: BF_3 undergoes hydrolysis as

$$4BF_3 + 3H_2O \longrightarrow B(OH)_3 + 3HBF_4$$

$$B(OH)_3 + 4HF \longrightarrow HBF_4 + 3H_2O$$

Two stage hydrolysis of BF_3 is

$$H_2O + BF_3 \longrightarrow H^+ (BF_3\,OH)^- \xrightarrow{H_2O} H[BF_2(OH)_2] + HF$$

(b) BORON TRICHLORIDE (BCl_3)

Preparation:

$$B_2O_3 + 3C + 3Cl_2 \longrightarrow 2BCl_3 + 3CO$$

(volatile liquid)

When B_2O_3 is heated with PCl_5 at 150°C, it forms BCl_3

$$B_2O_3 + 3PCl_5 \longrightarrow 2BCl_3 + 3\,POCl_3$$

Properties

BCl_3 hydrolyses as follows

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

$H[BCl_4]$ does not exist but $H[BF_4]$exists

$$BCl_3 + 3NH_3 \xrightarrow{-50°C} B(NH_2)_3 + 3HCl$$

$$BCl_3 + C_2H_5OH \longrightarrow BCl_2\,(OC_2H_5) + HCl$$

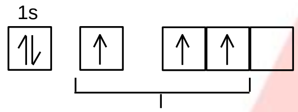
$$BCl_3 + NOCl \longrightarrow [NO]^+\,[BCl_4]^-$$

$$4BCl_3 + 3LiAlH_4 \xrightarrow{Ether} 2B_2H_6 + 3LiCl + 3AlCl_3$$

Let us now discuss the acidic character of boron trihalides.

The shape of the BF_3 molecule is a planar triangle with bond angles of 120°. This is predicted by VSEPR theory as the most stable shape for three outer electron pairs around B. The valence bond theory also predicts a planar triangle with hybridisation of one s and two p orbitals used for bonding. However, the B atom only has six electrons in its outer shell and this is termed electron deficient.

Electronic structure of boron atom –excited state

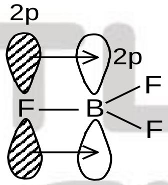


three singly occupied orbitals form bonds with unpaired electrons from three halogen atoms– shape: triangular planar (sp^2 hybridization)

The bond lengths in BF_3 are 1.30 Å each and are significantly shorter than the sum of the covalent radii (B = 0.80 Å, F = 0.72 Å). The bond energy is very high: 646 kJ mol^{-1}, which is higher than for any single bond. The shortness and strength of the bonds is interpreted in terms of a

pπ–pπ interaction, that is the bonds possess some double bond character. The empty $2p_z$ atomic orbital on B which is not involved in hybridisation is perpendicular to the triangle containing the sp^2 hybrid orbitals. This p_z orbital may accept an electron pair from a full p_z orbital on any one of

the three fluorine atoms. Thus, a dative π bond is formed and the B atom attains an octet of electrons. If one localized double bond existed, then there would be one short bond and two longer ones. However, all measurements show that the three bond lengths are identical. The old valence bond explanation of this was resonance between three structures with the double bond in different positions. The modern explanation is that the double bond is delocalised. The p_z atomic orbitals from B and the three F atoms form a four–centre π molecular orbital covering all four atoms which contains two bonding electrons.



The acidic strength of the trihalides is in order

$$BBr_3 > BCl_3 > BF_3$$

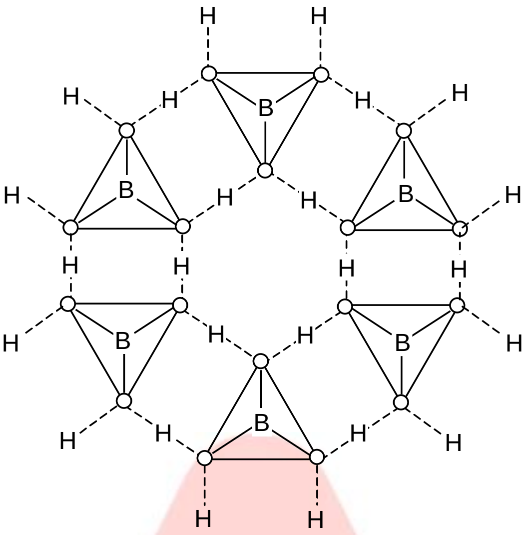
The order is the reverse of what would be normally expected on the basis of electronegativity of halogen and also on the basis of steric grounds.

This is explained on the basis of B–X π–bonding. The tendency to form the pπ–pπ double bond is maximum in BF_3 and decreases very rapidly as we move to BCl_3 and BBr_3.

2.5.2 ORTHOBORIC ACID (H_3BO_3)

Structure of orthoboric acid

Orthoboric acid contains triangular BO_3^{3-} units. In the solid, the $B(OH)_3$ units are hydrogen bonded together into two–dimensional sheets with almost hexagonal symmetry. The layers are quite a large distance apart and thus the crystal breaks quite easily into very fine particles.



Hydrogen bonded structure of orthoboric acid

Preparation

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

$2CaO + 3B_2O_3 + 2SO_2 + 9\,H_2O \longrightarrow 2CaSO_3 + 6H_3BO_3$

$2CaSO_3 + 2H_2O + 2SO_2 \longrightarrow 2Ca\,(HSO_3)_2$

Properties

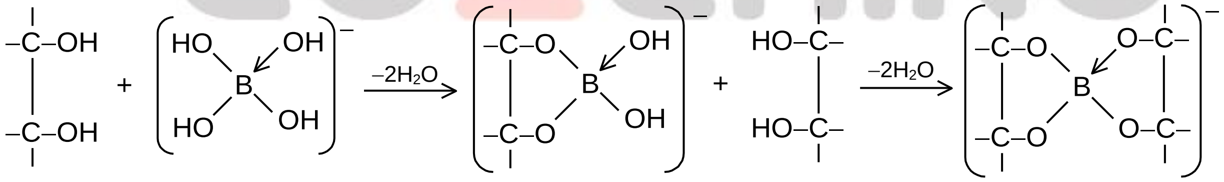
$H_3BO_3 + H_2O \longrightarrow [B(OH_4)]^- + H^+\,(aq)$

Acidic properties of H_3BO_3 or $B(OH)_3$

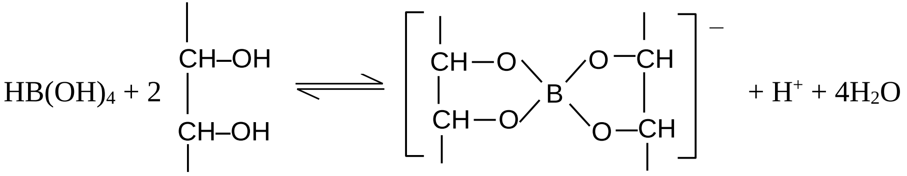
Since $B(OH)_3$ only partially reacts with water to form H_3O^+ and $[B(OH)_4]^-$, it behaves as a weak acid. Thus H_3BO_3 or $[B(OH)_3]$ cannot be titrated satisfactorily with NaOH, as a sharp end point is not obtained. If certain organic polyhydroxy compounds such as glycerol, mannitol or sugars are added to the titration mixture, then $B(OH)_3$ behaves as a strong monobasic acid. It can now be titrated with NaOH and the end point is detected using phenolphthalein as indicator (indicator changes at pH 8.3 – 10.0).

$$B(OH)_3 + NaOH \rightleftharpoons Na[B(OH)_4] \equiv \underset{\text{Sodium metaborate}}{NaBO_2} + 2H_2O$$

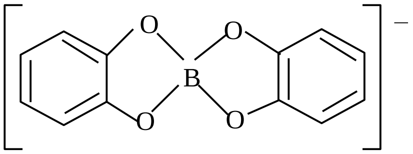
The added compound must be cis–diol, to enhance the acidic properties in this way. (This means that it has OH groups on adjacent carbon atoms in the cis configuration). The cis–diol forms very stable complexes with the $[B(OH)_4]^-$ formed by the forward reaction above, thus effectively removing it from solution. The reaction is reversible. Thus removal of one of the products at the right hand side of the equation upsets the balance and the reaction proceeds completely to the right. Thus all the $B(OH)_3$ reacts with NaOH, in effect it acts as a strong acid in the presence of the cis–diol.

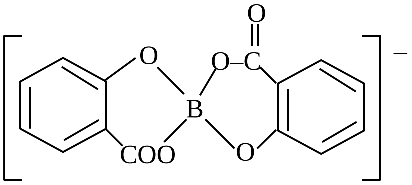


H_3BO_3 forms chelate complex with glycol and thereby shows strong acidity with K_a value. The acidity is due to the high stability of the conjugate bone chelate complex.



Catechol, salicylic acid also form similar complexes but ethanol is failure





$$H_3BO_3 \xrightarrow[-H_2O]{100°C} \underset{\text{meta boric acid}}{HBO_2} \xrightarrow[-H_2O]{140°C} H_2B_4O_7 \xrightarrow[-H_2O]{\text{strong heating}} \underset{\text{Boron sesquioxide}}{2B_2O_3}$$

Again $B_2O_3 + H_2O \longrightarrow H_3BO_3$ (Silky, pearly white crystal)

BF_3 is a strong Lewis acid and forms adduct with NH_3

Uses of Boric acid

(i) Boric acid is used in the manufacture of enamels and pottery glazes.
(ii) Boric acid is used in medicines as an eye wash.
(iii) Boric acid is used for making borosilicate glass.

2.5.3 BORON SESQUIOXIDE (B_2O_3)

Preparation:

$$\underset{\text{Boric acid}}{H_3BO_3} \xrightarrow[\text{heat, } -H_2O]{100°C} HBO_2 \xrightarrow[\text{(2) 400°C, (3) reduced pressure, } -\frac{1}{2}H_2O]{\text{(1) red heat}} B_2O_3$$

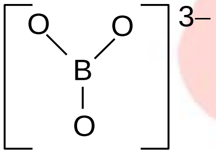
Properties: The crystalline variety melts at 450°C. It reacts with CuO, CoO, P_2O_5 etc.

$B_2O_3 + CuO \longrightarrow Cu(BO_2)_2$ [Borax Bead]

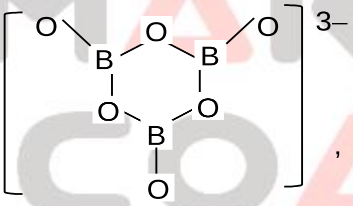
$B_2O_3 + CoO \longrightarrow Co(BO_2)_2$

$B_2O_3 + P_2O_5 \rightleftharpoons 2BPO_4$

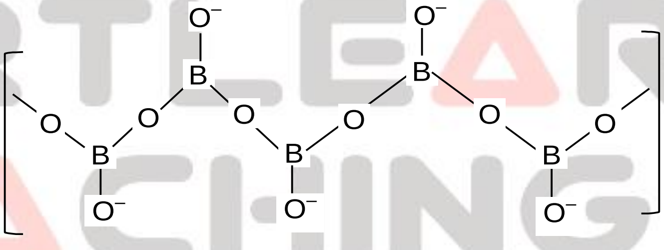
Structures of some orthoborates and metaborates are given as follows,



orthoborates (Planar triangular)



$B_3O_6^{-3}$ ion

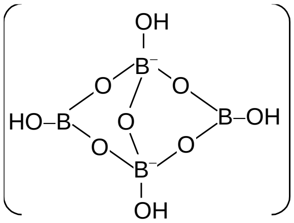


$B_2O_4^{-2}$ ion

2.5.4 BORAX ($Na_2B_4O_7.10H_2O$)

Structure of Borax

In borax, two boron atoms are in triangular geometry and two boron atoms are in tetrahedral geometry. The ion is $[B_4O_5(OH)_4]^{2-}$ and the remaining eight water molecules are associated with the two sodium ions. Hence, the borax contains tetranuclear units $[B_4O_5(OH)_4]^{2-}$ and therefore is formulated as $Na_2[B_4O_5(OH)_4].8H_2O$.



Structure of borax anion

Borax occurs naturally as tincal (contains about 55% borax) in certain inland lakes of India, Tibet and California (U.S.A.).

Borax can also be prepared from certain other minerals such as boracite, colemanite and boranatrocalcite. The minerals are powdered and boiled with sodium carbonate solution.

$$Ca_2B_6O_{11} + 2Na_2CO_3 \longrightarrow 2CaCO_3 + Na_2B_4O_7 + 2NaBO_2$$

Borax is crystallised from the filtrate. Sodium metaborate, present in the mother liquor, is converted into borax by passing carbon dioxide through it

$$\underset{\text{sod. metaborate}}{4NaBO_2} + CO_2 \longrightarrow Na_2B_4O_7 + Na_2CO_3$$

Two important hydrates of borax are known. These are,

(i) Pentahydrate, $Na_2B_4O_7.5H_2O$.

(ii) Decahydrate or monoclinic borax, $Na_2B_4O_7.10H_2O$.

The pentahydrate is obtained when the solution is crystallised at above 60°C, while the monoclinic variety is obtained when crystallisation is carried out below 60°C. Both the varieties on heating form anhydrous borax.

Properties of Borax

(i) Borax is a colourless, crystalline solid sparingly soluble in cold water but dissolves readily in hot water. It forms two important hydrates: octahedral borax $Na_2B_4O_7.5H_2O$ and monoclinic borax $Na_2B_4O_7.10H_2O$.

(ii) Basic nature

Borax is slightly hydrolysed in solution. As boric acid is a weak acid, the solution is alkaline in nature.

$$B_4O_7^{2-} + 7H_2O \rightleftharpoons 2OH^- + 4H_3BO_3$$

(iii) Action of acids

Borax reacts with HCl or H_2SO_4 to form boric acid. On cooling, the white flakes of boric acid are obtained

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + \underset{\text{boric acid}}{4H_3BO_3}$$

(iv) Action of heat

When powdered borax is heated strongly in a bunsen–flame, it loses water of crystallization and forms colourless, transparent glass–like bead which is made up of sodium metaborate and boric anhydride.

$$\underset{\text{borax}}{Na_2B_4O_7.10H_2O} \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} \underbrace{\underset{\text{sod. metaborate}}{2NaBO_2} + \underset{\text{boron oxide}}{B_2O_3}}_{\text{transparent bead}}$$

Uses of Borax

Borax is used,

(i) for manufacturing enamels, glazes and optical glass.

(ii) as a flux for soldering and welding.

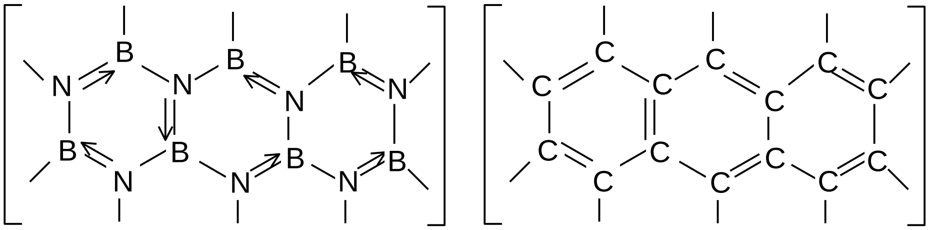
(iii) as an analytical reagent, e.g. in borax bead test.

2.5.5 BORON NITRIDE (INORGANIC GRAPHITE)

$$Na_2B_4O_7 + 2NH_4Cl \xrightarrow{1200°C} 2\,NaCl + H_2O + 2B_2O_3 + 2NH_3$$

$$B_2O_3 + 2NH_3 \longrightarrow 2BN + 3H_2O$$

Structure of boron nitride Structure of Graphite



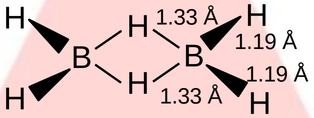
They are soft and used as lubricating material.

2.5.6 BORANES

Structures of the boranes

The bonding and structure of the boranes are of great interest. They are different from all other hydrides. There are not enough valency electrons to form conventional two–electron bonds between all of the adjacent pairs of atoms and so these compounds are termed electron deficient.

In diborane there are 12 valency electrons, three from each B atom and six from the H atoms. Electron diffraction results indicate the structure shown in given figure.

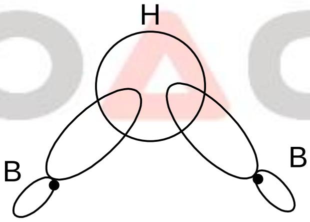


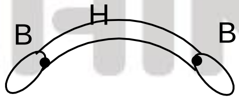
The two bridging H atoms are in a plane perpendicular to the rest of the molecule and prevent rotation between the two B atoms. Specific heat measurements confirm that rotation is hindered. Four of the H atoms are in a different environment from the other two. This is confirmed that diborane cannot be methylated beyond $Me_4B_2H_2$ without breaking the molecule into BMe_3.

The terminal B–H distances are the same as the bond lengths measured in non–electron–deficient compounds. These are assumed to be normal covalent bonds, with two electrons shared between two atoms. We can describe these bonds as two–centre–two–electron bonds (2c–2e), with two electrons shared between two atoms.

Thus, the electron deficiency must be associated with the bridge groups. The nature of the bonds in the hydrogen bridges is now well established. Obviously, they are abnormal bonds as the two bridges involve only one electron from each boron atom and one from each hydrogen atom, making a total of four electrons. An sp^3 hybrid orbital from each boron atom overlaps with the 1s orbital of the hydrogen. This gives a delocalised molecular orbital covering all three nuclei, containing one pair of electrons and making up one of the bridges. This is a three–centre–two–electron bond (3c–2e). A second three–centre bond is also formed.

It contains two 3–centre 2–electron banana bonds (B … H … B). Two electrons from two H atom and two from two Boron atoms consist of four electrons. An overlap of sp^3 hybrid orbital of B and 1s hydrogen orbital gives the delocalised molecular orbitals of a B … H … B bridge.





B – H –B bridge

None of the group III elements react directly with hydrogen, but several interesting hydrides are known. The boron hydrides are sometimes called boranes by analogy with the alkanes (hydrocarbons). Almost 20 boranes have been reported and 11 are well characterized. They fall into two series:

1. $B_nH_{(n+4)}$ (called nido–boranes).
2. A less stable series $B_nH_{(n+6)}$ (called arachno–boranes).

Boron hydrides differ from carbon hydrides (i.e. hydrocarbons) that they don't occur in nature because of their great affinity for H_2O and O_2. The compound BH_3 which would be analogous to BF_3 doesnot exist because H–atom lacks the electrons that would be needed to participate in B–H π–bonding and compensate for the incomplete octet of B. BH_3 can exist only in complex formation with donors such as

$BH_3.CO$, $BH_3.N(CH_3)_3$. Molecules of BH_3 apparently dimerize spontaneously when they come in contact with each other to form diborane, B_2H_6.

Method of preparation

$Mg_3B_2 + 6HCl \xrightarrow{heat} 3MgCl_2 + B_2H_6$

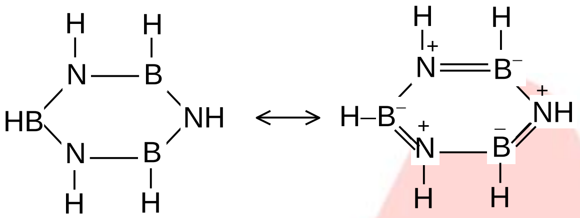
$3LiAlH_4 + 4BF_3 \longrightarrow 3LiF + 3AlF_3 + 2B_2H_6$

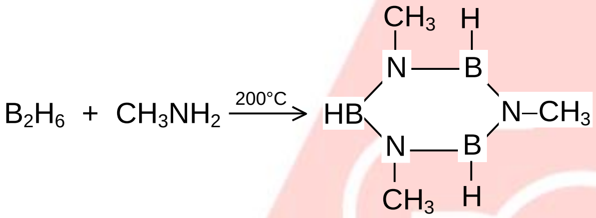
$3LiBH_4 + 4BF_3 \longrightarrow 3LiBF_4 + 2B_2H_6$

2.5.7 BORAZOLE ($B_3N_3H_6$) (INORGANIC BENZENE)

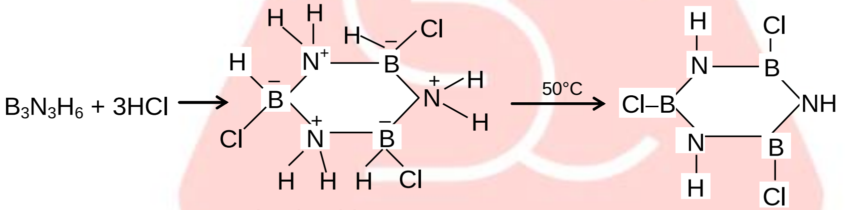
$$3B_2H_6.2NH_3 \xrightarrow[200°C]{heat\ at} 2B_3N_3H_6 + 12H_2$$

Structure of $B_3N_3H_6$ is





(i)



Hydrochloride of Borazole

B-trichloro borazole

(ii) $B_3N_3H_6 + 9H_2O \longrightarrow 3H_3BO_3 + 3NH_3 + 3H_2$

2.6 COMPOUNDS OF ALUMINIUM

2.6.1 ALUMINUM OXIDE OR ALUMINA (Al_2O_3)

Methods of preparation

$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$

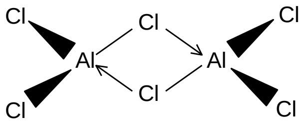
$Al_2(SO_4)_3 \xrightarrow{\Delta} Al_2O_3 + 3SO_3$

$(NH_4)_2SO_4.Al_2(SO_4)_3.24\,H_2O \xrightarrow{\Delta} Al_2O_3 + 2NH_3 + 4SO_3 + 25H_2O$

$2AlF_3 + B_2O_3 \xrightarrow{strong\ \Delta} Al_2O_3 + 2BF_3$

2.6.2 ALUMINIUM HALIDES

The fluorides of Al, Ga, In and Tl are ionic and have high melting points. The other halides are largely covalent when anhydrous. $AlCl_3$, $AlBr_3$ and $GaCl_3$ exist as dimers, thus attaining an octet of electrons. The dimeric formula is retained when the halides dissolve in non-polar solvents such as benzene.



When the halides are dissolved in water, the high enthalpy of hydration is sufficient to break the covalent dimer into $[M.6\ H_2O]^{+3}$ and $3X^-$ ions. At low temperatures, $AlCl_3$ exists as a close packed lattice of Cl^- with Al^{+3} occupying octahedral holes. On heating, Al_2Cl_6 species are formed and the volume of the solid greatly increases. This illustrates how close the bonding in this compound is to the ionic/covalent border.

2.6.3 ALUMS

Alums are the compounds with general formula $M_2SO_4.\ M'_2(SO_4)_3.24H_2O$

M = Monovalent basic radical like Na^+, K^+, Rb^+, Cs^+, Tl^+, NH_4^+

M' = Trivalent basic radical like Al^{+3}, Cr^{+3}, Mn^{+3}, Fe^{+3}, Co^{+3}

Alums are obtained when hot solution of equimolar quantities of their constituent sulphates are mixed and subjected to crystallization. These are acidic and swell on heating.

2.7 OXIDES AND HYDROXIDES OF GROUP III

On moving down the group, there is a gradual change from acidic through amphoteric to basic character of oxides and hydroxides.

$Al(OH)_3$ is amphoteric. It reacts principally as a base, i.e. it reacts with acids to form salts that contain the $[Al(H_2O)_6]^{+3}$ ion. However, $Al(OH)_3$ show some acidic properties when it dissolves in NaOH, forming sodium aluminate. (However, $Al(OH)_3$ is reprecipitated by the addition of CO_2, showing that the acidic properties are very weak).

$$Al(OH)_3 \xrightarrow{\text{excess NaOH}} NaAl(OH)_4$$

$NaAlO_2.2H_2O$

Sodium meta–aluminate

The structure changes with both pH and concentration.

(i) Between pH 8 and 12, the ions polymerise using OH bridges and each aluminium is octahedrally coordinated.

(ii) In dilute solutions, above pH value of 13, a tetrahedral $[Al(OH)_4]^-$ ion exists.

(iii) In concentrated solutions above 1.5 M and pH > 13, the ion exists as a dimer $[(HO)_3\ Al-O-Al(OH)_3]^{2-}$

Ga_2O_3 and $Ga(OH)_3$ are both amphoteric like the corresponding Al compounds. $Ga(OH)_3$ is white and gelatinous and dissolves in alkali, forming gallates. Tl_2O_3 and In_2O_3 are completely basic, and form neither hydrates nor hydroxides.

TlOH is a strong base, and is soluble in water. Thus TlOH differ from the trivalent hydroxides and resembles the Group I hydroxides. Where an element can exist in more than one valency state, there is general tendency for the lowest valency state to be the most basic.

3 THE GROUP – 14 ELEMENTS (CARBON GROUP)

3.1 PHYSICAL PROPERTIES

1. **Covalent radii**

The covalent radii increase down the group. The difference in size between Si and Ge is less than might be otherwise expected because Ge has a full 3d shell, which shields the nuclear charge rather ineffectively. In a similar way the small difference in size between Sn and Pb is because of the filling of the 4f shell.

	Covalent Radius (Å)	Ionisation Energy (KJmol^{-1})				Melting Point (ºC)	Boiling Point (ºC)
		1st	2nd	3rd	4th		
C	0.77	1086	2354	4622	6223	4100	–
Si	1.17	786	1573	3232	4351	1420	3280
Ge	1.22	760	1534	3300	4409	945	2850
Sn	1.4	707	1409	2943	3821	232	2623
Pb	1.46	715	1447	3087	4081	327	1751

2. **Ionisation energy**

The ionisation energy decrease from C to Si, but then change in an irregular way because of the effects of filling of the d and f shells. The amount of energy required to form M^{+4} ions is extremely large and hence simple ionic compounds are rare.

3. **Melting points**

Melting involves breaking the strong covalent bonds in the lattice of C and thus has extremely high melting point. The melting points decrease on descending the group because the M-M bonds become weaker as the atoms increase in size. Sn and Pb are metallic and have much lower melting points. They do not use all four outer electrons for metallic bonding.

4. **Metallic and non-metallic character**

The change from non-metal to metal with increasing atomic number is well illustrated in group IV, where C and Si are non-metals, Ge has some metallic properties, and Sn and Pb are metals. The increase in metallic character shows itself in the structures and appearance of the elements, in physical properties such as malleability and electrical conductivity, and in chemical properties such as the increased tendency to form M^{+2} ions and the acidic or basic properties of the oxides and hydroxides.

3.2 ALLOTROPES OF CARBON

The phenomenon of the existence of an element in different forms, which have different physical properties but similar chemical properties, is known as allotropy. Such different forms of an element are called its allotropes or allotropic forms. Carbon shows allotropy. The various allotropic forms of carbon can be broadly classified into two classes.

(a) Crystalline form

Diamond and graphite are the two crystalline forms of carbon. Graphite is thermodynamically more stable than diamond. Its free energy of formation is 1.9 kJ mol^{-1} lower than that of the diamond under standard conditions. Thus thermodynamically, diamonds should get transformed into graphite on their own. But it does not happen at least on our lifetime scale. This is because, this conversion is not favoured by kinetic factors, for example the activation energy for this reaction is very high.

Structure of diamond

In diamond, the carbon atoms are arranged tetrahedrally (sp^3 hybridisation of C): each C atom is linked to its neighbours by four single covalent bonds. This leads to a three–dimensional network of covalent bonds. It is because of this, that diamond is very hard and has high melting and boiling points. Since, all the valence electrons of carbon are used up in forming the covalent bonds, hence diamond does not conduct electricity.

Structure of graphite

In graphite, the carbon atoms are arranged in regular hexagons in flat parallel layers.

Each carbon in these layers is bonded to three other by sp^2 covalent bonds. This gives some double bond character to graphite. Each layer is bonded to the adjacent layers by weak Vander Waal's forces. As a result, each layer can slide over the other easily. It is because of this structure that graphite is soft and slippery and can act as a lubricant. The presence of double bond character (the presence of delocalised π–electrons) makes graphite a good conductor of electricity.

(b) Amorphous form:

Coal, coke, charcoal (or wood charcoal), animal charcoal (or bone black), lamp black, carbon black, gas carbon and petroleum coke are the amorphous form of carbon.

3.3 COMPOUNDS OF CARBON

3.3.1 CARBON MONOXIDE

Structure of CO

Electronic structure of carbon monoxide may be represented as follows

$$:\overset{-}{C}:::\overset{+}{O}: \quad \text{or} \quad C\overset{\leftarrow}{\equiv}O$$

Preparation:

(i) By the reduction of carbon dioxide with carbon.

$$CO_2 + C \xrightleftharpoons{heat} 2CO$$

(ii) By the reduction of carbon dioxide with zinc or iron.

$$CO_2 + Zn \xrightarrow{heat} ZnO + CO$$

(iii) By the reduction of oxides of heavy metal with carbon. For example,

$$ZnO + C \xrightarrow{heat} Zn + CO$$

(iv) By heating oxalic acid with sulphuric acid.

$$\begin{matrix}\text{COOH}\\ |\\ \text{COOH}\end{matrix} \xrightarrow[-H_2O]{H_2SO_4} CO \quad + \quad CO_2$$

(v) By heating formic acid with sulphuric acid. In this reaction, sulphuric acid acts as a dehydrating agent.

$$HCOOH \xrightarrow[-H_2O]{H_2SO_4,\ 400K} CO$$

Reactions

(i) With hydrogen

Carbon monoxide reacts with hydrogen when heated to 420–670 K under 300 atm pressure and in the presence of a catalyst (ZnO + Cu) to form methyl alcohol.

$$CO + H_2 \xrightarrow[420-670\,K,\ 300\,atm]{ZnO + Cu} \underset{\text{methyl alcohol}}{CH_3OH}$$

(ii) With chlorine

Carbon monoxide reacts with chlorine to give phosgene.

$$CO + Cl_2 \xrightarrow{\text{sunlight}} \underset{\text{phosgene (or carbonyl chloride)}}{COCl_2}$$

3.3.2 CARBON DIOXIDE (CO_2)

Preparation

(i) Carbon dioxide may be prepared by the complete combustion of carbon, hydrocarbons, carbon monoxide etc.

$$2CO + O_2(g) \longrightarrow 2CO_2(g) + \text{Heat}$$

$$CH_4 + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O$$

$$CaCO_3 \xrightarrow{\text{heat}} CaO + H_2O + CO_2(g)$$

(ii) By the action of acids on carbonates

In laboratory, carbon dioxide gas is prepared by the action of dil. HCl on marble chips ($CaCO_3$)

$$CaCO_3(s) + 2HCl(\text{dil.}) \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O$$

(a) With Mg: $CO_2 + 2Mg \longrightarrow 2MgO + C$

(b) With Na: $CO_2 + 4Na \longrightarrow 2Na_2O + C$

Chemical Properties:

(i) Acidic nature

CO_2 dissolves in water to give carbonic acid. Therefore, carbon dioxide is called carbonic anhydride.

$$\underset{\text{carbon dioxide}}{CO_2} + H_2O \rightleftharpoons \underset{\text{carbonic acid}}{H_2CO_3}$$

Carbonic acid is a very weak dibasic acid. It ionises in aqueous solutions as,

$$H_2CO_3(aq) \rightleftharpoons H^+ + HCO_3^-(aq) \qquad K_1 = 4.2 \times 10^{-7}$$

$$HCO_3^-(aq) \rightleftharpoons H^+ + CO_3^{2-}(aq) \qquad K_2 = 4.8 \times 10^{-11}$$

Carbonic acid being a dibasic acid forms two sets of salts, the hydrogen carbonates, HCO_3^- and carbonates, CO_3^{2-}.

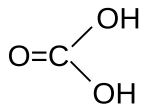
(ii) With lime water

When CO_2 is bubbled through limewater, it turns milky due to the formation of $CaCO_3$. When more CO_2 is bubbled, solution becomes clear due to the formation of $Ca(HCO_3)_2$. On boiling the clear solution, milkiness reappears due to the formation of $CaCO_3$ once again.

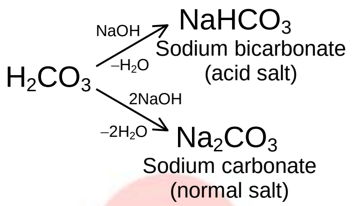
$$\underset{\substack{\text{lime water}\\ \text{(clear soln.)}}}{Ca(OH)_2} \xrightarrow[-H_2O]{+CO_2} \underset{\substack{\text{insoluble}\\ \text{(turns milky)}}}{CaCO_3} \xrightarrow[-H_2O]{+CO_2} \underset{\substack{\text{soluble}\\ \text{(clear soln.)}}}{Ca(HCO_3)_2} \xrightarrow[\substack{-CO_2\\ -H_2O}]{\text{heat}} \underset{\text{milkiness reappears}}{CaCO_3}$$

The reaction forms the basis of lime water test for the detection of CO_3^{2-} and HCO_3^- ions in any salt/salt mixture.

3.3.3 CARBONIC ACID



Carbonic acid (H_2CO_3) has never been isolated, but it gives rise to two series of salts, hydrogen carbonates and carbonates.



3.3.4 CARBONATES $\left(CO_3^{2-}\right)$ AND BICARBONATES $\left(HCO_3^{-}\right)$

Carbonic acid is dibasic acid and gives rise to two series of salts, carbonates (normal salts) and bicarbonates (acid salts) due to successive removal of the replaceable hydrogens from H_2CO_3.

$$H_2CO_3 + NaOH \longrightarrow NaHCO_3 + H_2O$$

These can also be prepared using the following methods

With NaOH

$$2NaOH + CO_2 \longrightarrow \underset{\text{Sodium carbonate}}{Na_2CO_3}$$

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow \underset{\text{Sodium bicarbonate}}{2NaHCO_3}$$

By precipitation:

Heavy metal carbonates are precipitated from their salt solutions with washing soda.

$$BaCl_2 + Na_2CO_3 \longrightarrow BaCO_3\downarrow + 2NaCl$$

While carbonates of many metals are known, bicarbonates of only alkali metals exist in the solid state.

3.3.5 HALIDES OF CARBON

Carbon combines with all the halogens to form tetrahalides, viz, CF_4, CCl_4, CBr_4 and Cl_4, mixed tetrahalides like $CFCl_3$, CF_2Cl_2 and CCl_3Br and trihalides of the formula CHX_3, viz, $CHCl_3$ (chloroform) and CHI_3 (iodoform).

General characteristics

(i) The thermal stability of tetrahalides of carbon follows the order,

$$CF_4 > CCl_4 > CBr_4 > CI_4$$

(ii) The tetrahalides especially those containing both fluorine and chlorine are chemically inert, non–inflammable gases or liquids.

(iii) Freon (CF_2Cl_2) is used as a refrigerant.

3.3.6 CARBIDES AND SULPHIDES

Carbides

Carbides are the binary compounds containing carbon and another less electronegative element or of similar electronegativity. Compounds of carbon and a less electronegative element are called carbides. This excludes compounds with N, P, O, S and the halogens from this section.

Preparation of carbides

(a) Aluminium carbide is obtained by heating aluminium with carbon in an electric furnance.

$$4Al + 3C \xrightarrow{\text{electric furnace}} Al_4C_3$$

(b) Silicon carbide is obtained by heating (sand) with carbon in an electric furnance.

$$SiO_2 + 2C \xrightarrow{2300\,K} SiC + 2CO(g)$$

(c) Calcium carbide is obtained by heating lime (CaO) with coke in a electric furnance.

$$CaO + 3C \xrightarrow[2300\,K]{\text{electric furnace}} CaC_2 + CO$$

Kinds of Carbides

These are of three kinds

(1) Salt like carbides

Based on the product obtained on hydrolysis, they are further subdivided into three types.
(a) Methanide (b) Allylide (c) Acetylide

Both Be_2C and Al_4C_3 are called methanides because they react with H_2O, yielding methane.
Carbides with a C_2 unit are well known. They are formed mainly by the elements in group I $(M^{I}_{2}C_2)$; group II $(M^{II}C_2)$; the coinage metals (Cu, Ag, Au); Zn and Cd and some of the lanthanides (LnC_2 and $Ln_4(C_2)_3$). These are all colourless ionic compounds and contain the carbide ion $(-C\equiv C-)^{2-}$. By far the most important compound is CaC_2. This is made commercially by strongly heating lime and coke:

$$CaO + 3C \longrightarrow CaC_2 + CO \quad ; \quad \Delta H = +466 \text{ kJ mol}^{-1}$$

The reaction is endothermic and a temperature of 2200°C is required. These carbides react exothermically with water, liberating ethyne (formerly called acetylene). So, they are called acetylides.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + HC\equiv CH$$

The acetylides have a NaCl type of lattice, with Ca^{2+} replacing Na^+ and C_2^{2-} replacing Cl^-. In CaC_2, SrC_2 and BaC_2 the elongated shape of the $(C\equiv C)^{2-}$ ion causes tetragonal distortion of the unit cell, that is it elongates the unit cell in one direction. One of the two carbides of magnesium Mg_2C_3 contains a C_3 unit and on hydrolysis with water it yields propyne $CH_3-C\equiv CH$. So, Mg_2C_3 is called allylide.

(2) Covalent carbides

These are extremely hard and chemically inert. SiC and B_4C are the most important covalent carbides. Silicon carbide is hard, infusible and chemically inert. It is widely used as an abrasive called carborundum and about 300000 tonnes are produced annually by heating quartz or sand with an excess of coke in an electric furnace at 2000–2500°C.

$$SiO_2 + 2C \longrightarrow Si + 2CO$$
$$Si + C \longrightarrow SiC$$

SiC is very unreactive. It is unaffected by acids (except H_3PO_4), but it does react with NaOH and air and with Cl_2 at 100°C.

$$SiC + 2NaOH + 2O_2 \longrightarrow Na_2SiO_3 + CO_2 + H_2O$$
$$SiC + 2Cl_2 \longrightarrow SiCl_4$$

SiC is often dark purple, black or dark green due to traces of Fe and other impurities,
but pure samples are pale yellow to colourless. SiC has a three dimensional structure of Si and C atoms, each atom tetrahedrally surrounded by four of the other kind.

(3) Metallic / interstitial carbides

These are formed by bigger transition elements eg.Ti and V. These are formed mostly by transition elements and some of the lanthanides and actinides. The Cr, Mn, Fe, Co and Ni groups form a large number of carbides with a wide range of stoichiometries. They are typically infusible or are very high melting and are very hard. For example, TaC has a melting point of 3900°C, and is very hard and WC is also very hard. Both are used to make cutting tools. Interstitial carbides retain many of the properties of metals. They conduct electricity by metallic conduction and have a lustre like a metal

Uses of Carbides

Aluminium carbide (Al_4C_3) is used for the manufacture of methane. Magnesium carbide (Mg_2C_3) is used for preparing alkyne.

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$
$$Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + CH_3-C\equiv CH$$

Sulphides

CS_2 is prepared from natural gas by the following reaction.

$$CH_4(g) + 4S \xrightarrow[Al_2O_3\,/\,SiO_2]{600^\circ C} CS_2 + 2H_2S$$

3.4 PREPARATION OF SILICON AND ITS REACTIONS

Silicon is the second most abundant element occurring in the earth's crust (about 28% by weight).

Unlike carbon, it is never found in free state but always in combined state. It is an important constituent of igneous rocks, which consists of silicates of magnesium, aluminium, potassium or iron.

Silicon is widely present as silica (SiO_2) in various forms such as sand, quartz, flint etc.

Silicon is obtained by the reduction of silica. It exists in two allotropic forms: (a) amorphous and (b) crystalline. The amorphous variety is obtained by heating dry powered silica with magnesium.

$SiO_2 + 2Mg \longrightarrow Si + 2MgO$

The crystalline variety is obtained by heating a finely powered sand or quartz with carbon in an electric furnace, a small amount of iron is added to prevent the formation of carborundum (SiC).

$SiO_2 + 2C \longrightarrow Si + 2CO$

Amorphous silicon is chemically more reactive than crystalline silicon. Amorphous silicon is brownish powder. It burns brilliantly in oxygen and ignites spontaneously in fluorine.

$Si + O_2 \longrightarrow SiO_2$

$Si + 2F_2 \longrightarrow SiF_4$

$Si + 2KOH + H_2O \longrightarrow K_2SiO_3 + 2H_2$

$Na_2CO_3 + Si \longrightarrow Na_2SiO_3 + C$

It combines with certain metals forming silicides.

$2Mg + Si \longrightarrow Mg_2Si$

When amorphous silicon is strongly heated, it fuses and on cooling solidifies to the crystalline form. It is very hard crystalline silicon, does not burn in oxygen but it readily combines with fluorine. It dissolves in mixture of HNO_3 and HF. When fused with alkali, it gives a silicate.

$Na_2CO_3 + Si \longrightarrow Na_2SiO_3 + C$

Silicon is used in the manufacture of certain alloys such as ferrosilicon, silicon bronze, manganese silicon bronze, etc. These alloys possess high strength and hardness and are resistant to the attack of acids.

3.5 COMPOUNDS OF SILICON

3.5.1 CARBORUNDUM (SILICON CARBIDE), SiC

It is obtained when a mixture of sand, carbon, common salt and saw dust is strongly heated in an electric furnace.

$SiO_2 + 3C \longrightarrow SiC + 2CO$

Salt is added to act as flux and saw dust makes the mass porous. Two carbon rods connected by a thin carbon core act as electrodes in the furnace. Carborundum is
formed round the central core of carbon. It is crushed, washed with H_2SO_4, NaOH, H_2O and then dried.

Properties

(i) Pure carborundum is colourless, but commercial samples posses yellow, green or blue colour.
(ii) It is very hard mass. However, its hardness is less than diamond.
(iii) It is chemically inert and resists the attack of almost all the reagents except fused caustic soda. The fused alkali dissolves it in presence of air.

$4NaOH + SiC + 2O_2 \longrightarrow Na_2SiO_3 + Na_2CO_3 + 2H_2O$

Its structure is similar to diamond.

Uses

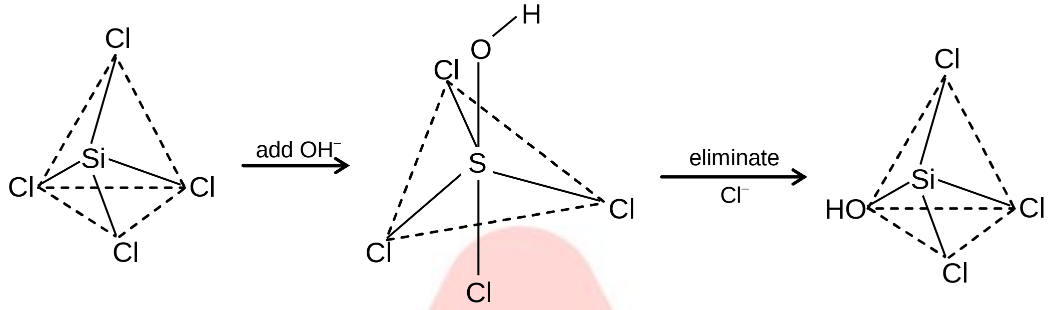
It is used as an abrasive instead of emery. It is used to make grinder, knife sharpeners, etc. Two oxides of silicon SiO and SiO_2 have been reported. SiO is thought to be formed by high temperature reduction of SiO_2 with Si, but its existence at room temperature is in doubt.

$SiO_2 + Si \rightarrow 2SiO$

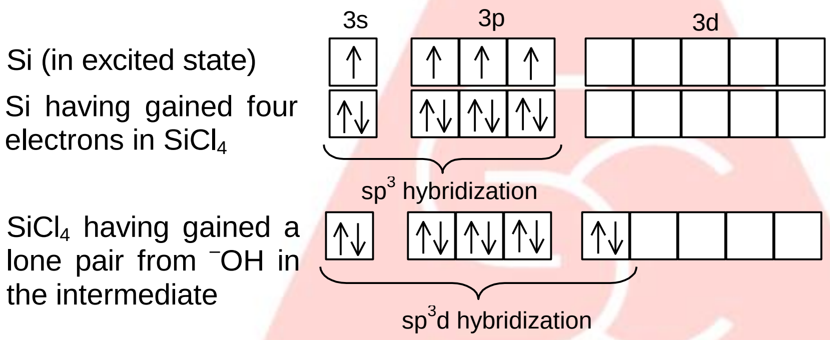
SiO_2 is commonly called silica, and it is widely found as sand and quartz. Group IV elements typically form four bonds. Carbon can form $p\pi$- $p\pi$ double bonds and hence CO_2 is a discrete molecule and is a gas. Silicon cannot form double bonds in this way using $p\pi-p\pi$ orbitals. Thus, SiO_2 forms an infinite three-dimensional structure and hence SiO_2 is a high melting solid.

3.5.2 HYDROLYSIS OF $SiCl_4$

The hydrolysis of $SiCl_4$ is rapid because Si can use a d-orbital to form a five-coordinate intermediate, and the reaction occurs by an S_N2 mechanism.



A lone pair of electrons from the oxygen is donated to an empty d orbital on Si, forming a five-coordinate intermediate, which has a trigonal bipyramidal structure.



If the hydrolysis is performed on an asymmetrically substituted and consequently optically active, silicon compound such as MeEtPhSi*Cl, then Walden inversion will occur, resulting in inversion of the structure from d to *l* or vice-versa. In a similar way, the reduction of $R_1R_2R_3Si^*Cl$ with $LiAlH_4$ to give $R_1R_2R_3Si^*H$ also involves inversion of structure.

3.5.3 SODIUM SILICATE, Na_2SiO_3 (WATER GLASS)

It is commercially called water glass. Chemically it is sodium metasilicate containing an excess of silica. Its composition may vary from $Na_2SiO_3 . SiO_2$ to $Na_2SiO_3.3SiO_2$.

It is obtained by fusing soda ash (Na_2CO_3) with pure sand at a high temperature.

$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2\uparrow$

The resulting mass is extracted with water and the solution is evaporated to get a syrupy mass known as water glass.

Properties

It is soluble in water. The solution is alkaline due to hydrolysis.

$$Na_2SiO_3 + 2H_2O \rightleftharpoons 2NaOH + H_2SiO_3$$

If in a solution of sodium silicate of density 1.1, some coloured salts like cobalt nitrate, nickel chloride, ferrous sulphate, copper sulphate, etc., are placed and whole solution is left as such for a night, beautiful hollow tubes of metallic silicate gels possessing different colours shoot up from these crystals and look like plants. This is called silica garden or chemical garden.

Uses: It is used

(a) in fire proofing of wood and textiles.
(b) as a preservative for eggs.
(c) as an adhesive cement for joining pieces of china clay.
(d) in the soap industry as a filler for a cheaper variety of soap.
(e) in paint industry and calico printing.
(f) for making silica gel $SiO_2 \cdot xH_2O$. When a solution of Na_2SiO_3 is acidified with HCl, a gelatinous

precipitate of silicic acid (H_2SiO_3) is slowly formed.

$Na_2SiO_3 + 2HCl \longrightarrow 2NaCl + H_2SiO_3$

If most of the water is carefully removed, the jelly like precipitate of H_2SiO_3 is converted into a solid product, which is called silica gel. It possesses excellent absorption property of gases and vapours.

3.5.4 SILICONES

These are organosilicon polymers containing Si—O—Si linkages. These are formed by the hydrolysis of alkyl or aryl substituted chlorosilanes and their subsequent polymerisation. The alkyl or aryl substituted chlorosilanes are prepared by the reaction of Grignard reagent and silicon tetrachloride.

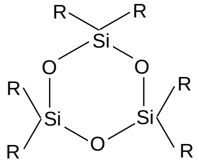
$$\underset{\text{Grignard reagent}}{RMgCl} + SiCl_4 \longrightarrow R—SiCl_3 + MgCl_2$$

$$2RMgCl + SiCl_4 \longrightarrow R_2SiCl_2 + 2MgCl_2$$

$$3RMgCl + SiCl_4 \longrightarrow R_3SiCl + 3MgCl_2$$

R stands for $–CH_3$, $–C_2H_5$ or $–C_6H_5$ groups.

Hydrolysis of substituted chlorosilanes yield corresponding silanols, which undergo polymerisation.



Cyclic silicone

R_3SiCl on hydrolysis forms only a dimmer

$R_3Si\,OH + HOSiR_3 \longrightarrow R_3Si–O–SiR_3 + H_2O$

Properties

(i) The lower silicones are oily liquids but higher members containing long chains or ring structures are waxy and rubber like solids.

(ii) Silicones are stable towards heat.

(iii) Chemical reagents have no action on silicones.

(iv) These are non–toxic.

(v) Viscosity of silicone oils remains the same at different temperatures.

(vi) Silicones are good electrical insulators.

(vii) These are water repellents.

Uses

(i) Silicone oils are used for high temperature oil baths, high vacuum pumps and low temperature lubrication.

(ii) These are used in making water-proof cloth and paper by exposing cloth or paper to the silicone vapour.

(iii) These are used as insulating materials for electric motors and other electrical appliances.

(iv) These are mixed with paints and enamels to make them resistant to the effects of high temperature, sunlight, chemicals and damp.

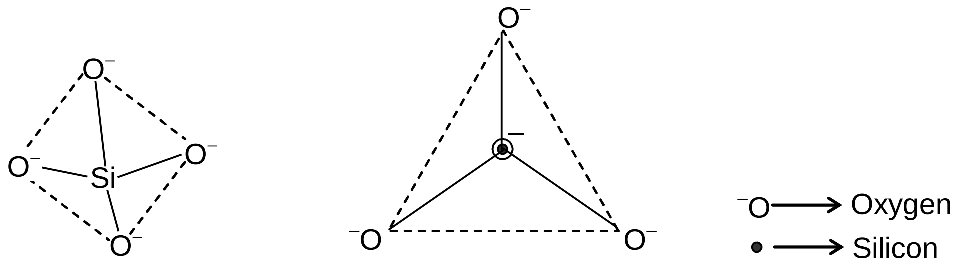
(v) These are used in making Vaseline like greases, which are used as lubricants in aeroplanes.

(vi) Silicone–rubbers are useful as they retain their elasticity over a range of temperatures.

3.5.5 SILICATES

Silicates are metal derivatives of silicic acid, H_4SiO_4 or $Si(OH)_4$. Silicates are formed by heating metal oxide or metal carbonates with sand, e.g.

$$Na_2CO_3 \xrightarrow[SiO_2]{\text{Fused with sand}} Na_4SiO_4,\ Na_2(SiO_3)_n,\ \text{etc.}$$



Plane projection of silicate ion

Silicates have basic unit of SiO_4^{4-}, each silicon atom is bonded with four oxide ions tetrahedrally. There are following types of silicates.

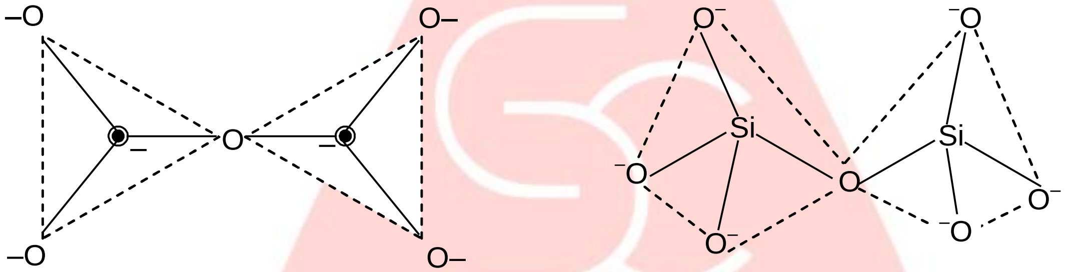
(i) Orthosilicates:

These silicates contain single discrete tetrahedral unit of SiO_4^{4-}

e.g., Zircon	$ZrSiO_4$;	Forsterite or Olivine	Mg_2SiO_4
Phenacite	Be_2SiO_4;	Willemite	Zn_2SiO_4

(ii) Pyrosilicates:

These silicates contain two units of SiO_4^{4-} joined along a corner containing oxygen atom. These are also called as island silicate.

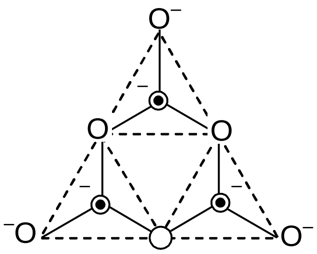


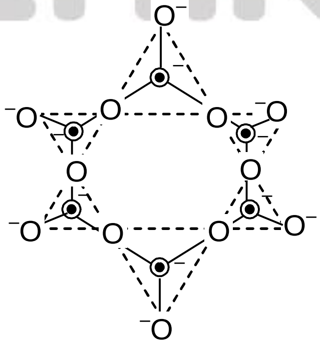
e.g., Thorteveitite $Sc_2Si_2O_7$;
Hemimorphite $Zn_3(Si_2O_7)\ Zn(OH)_2H_2O)$

(iii) Cyclic structure:

Cyclic or ring silicates have general formula $\left(SiO_3^{2-}\right)_n$ or $\left(SiO_3\right)_n^{2n-}$.

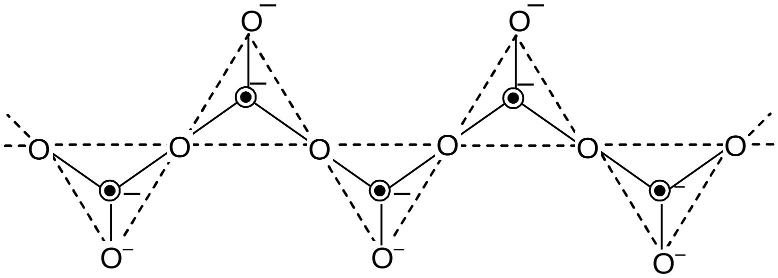
Structure and example of cyclic silicates containing $Si_3O_9^{6-}$ and $Si_6O_{18}^{12-}$ ions are given below.



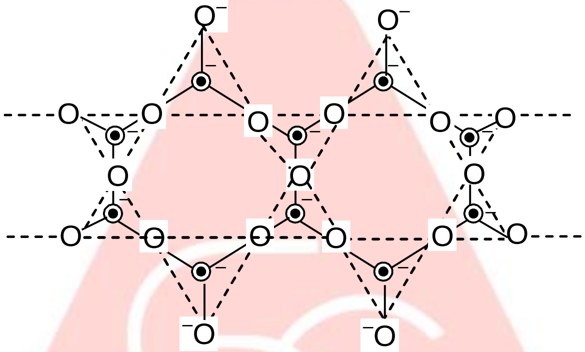


(iv) Chain silicates

(a) Simple chain silicates or pyroxenes are formed by sharing two oxygen atoms by each tetrahedral. Anions of such chain silicates have general formula $(SiO_3)_n^{2n-}$



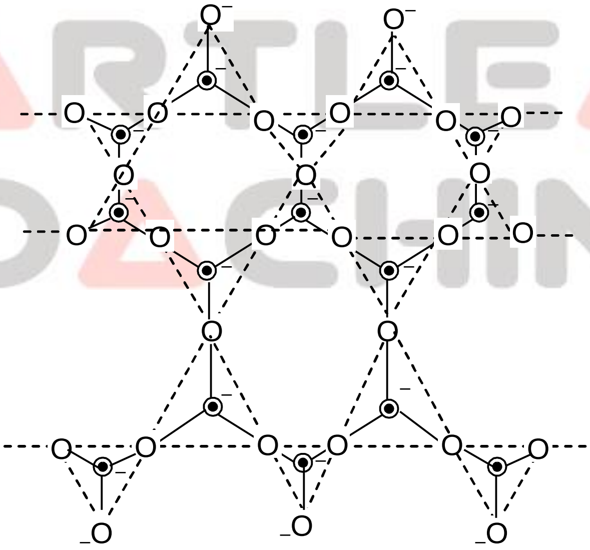
(b) Double chain silicates can be formed when two simple chains are joined together by shared oxygen atoms. These minerals are called amphiboles. The anions of such silicates have general formula $(Si_4O_{11})_n^{6n-}$



e.g.,	
Synthetic silicates	Li_2SiO_3, Na_2SiO_3
Spodumene	$LiAl(SiO_3)_2$
Enstatite	$MgSiO_3$;
Diopsite	$CaMg(SiO_3)_2$
Tremolite	$Ca_2Mg_5(Si_4O_{11})_2 (OH)_2$

(v) Two dimensional sheet silicates

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



e.g.,	Talc	$Mg_2(Si_2O_5)_2 Mg(OH)_2$
	Kaolin	$Al_2(OH)_4 (Si_2O_5)$

(vi) Three dimensional sheet silicates:

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

Quartz, tridymite, crystobalite, feldspar, zeolite and ultramarines.

3.6 OXIDES AND CHLORIDES OF LEAD

3.6.1 LEAD MONOXIDE (PbO)

It is known in two forms:

(i) a yellow powder commonly known as massicot and
(ii) a buff coloured crystalline form known as litharge.

Preparation

It is obtained by heating lead or lead sulphide in air at 300°C (massicot form). When the temperature of oxidation is kept at 900°C, litharge is formed.

$$2Pb + O_2 \longrightarrow 2PbO$$

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$

It is also formed by heating lead nitrate or lead carbonate.

$$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$$

$$PbCO_3 \longrightarrow PbO + CO_2$$

Properties

It is insoluble in water. It is an amphoteric oxide. It dissolves both in acids and alkalies.

$$PbO + 2HNO_3 \longrightarrow Pb(NO_3)_2 + H_2O$$

$$PbO + 2NaOH \longrightarrow Na_2PbO_2 + H_2O$$

On heating in air at 470°C, it forms red lead.

$$6PbO + O_2 \longrightarrow 2Pb_3O_4 \text{ (red lead)}$$

3.6.2 RED LEAD (Pb_3O_4)

Preparation

It is obtained by heating litharge at 470°C in air.

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

Properties

It is a red powder, insoluble in water. When heated, it becomes almost black, but it again becomes red on cooling. On heating above 470°C, it decomposes into PbO and O_2.

$$2Pb_3O_4 \longrightarrow 6PbO + O_2$$

When treated with concentrated HNO_3, lead nitrate and brownish black insoluble oxide, PbO_2, are formed. This indicates that Pb_3O_4 is a compound oxide containing both PbO_2 and PbO in the ratio of 1 : 2.

$$Pb_3O_4 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$$

With H_2SO_4, it evolves oxygen,

$$2Pb_3O_4 + 6H_2SO_4 \longrightarrow 6PbSO_4 + 6H_2O + O_2$$

It acts as an oxidising agent.

$$Pb_3O_4 + 8HCl \longrightarrow 3PbCl_2 + 4H_2O + Cl_2$$

$$Pb_3O_4 + 4C \longrightarrow 3Pb + 4CO$$

$$Pb_3O_4 + 4CO \longrightarrow 3Pb + 4CO_2$$

3.6.3 LEAD CHLORIDE ($PbCl_2$)

It is made by adding hydrochloric acid to a cold solution of lead salt.

$$Pb(NO_3)_2 + 2HCl \longrightarrow PbCl_2 + 2HNO_3$$

It is only slightly soluble in cold water, but appreciably soluble in hot water. It dissolves in concentrated HCl forming a complex ion.

$$PbCl_2 + 2HCl \rightleftharpoons \underset{\text{(Chloroplumbous acid)}}{H_2PbCl_4}$$

Note

Most of the plumbic compound are unimportant because they decompose readily on heating and are hydrolysed to PbO_2 by even cold water. An exception is tetraethyl lead, $Pb(C_2H_5)_4$, a colourless liquid which is used as an anti–knock agent in petrol.

3.7 OXIDES AND CHLORIDES OF TIN

3.7.1 STANNOUS OXIDE (SnO)

Preparation

$$SnCl_2 + 2NaOH \longrightarrow Sn(OH)_2 + 2NaCl$$

Stannous
chloride

$$Sn(OH)_2 \xrightarrow{\text{Heat in } CO_2 \text{ Atmosphere}} SnO + H_2O$$

$$SnCl_2 + Na_2CO_3 \xrightarrow{\text{Heat in atm of } CO_2} SnO + CO_2 + 2NaCl$$

Stannous
chloride

Properties:

(i) It is a dark grey or black powder. It is insoluble in water.

(ii) It is burns in air with incandescence forming stannic oxide, SnO_2.

$$2SnO + O_2 \longrightarrow 2SnO_2$$

(iii) It is an amphoteric oxide. It dissolves both in acids and alkalies.

$$SnO + 2HCl \longrightarrow SnCl_2 + H_2O$$

Stannous
chloride

$$SnO + 2NaOH \longrightarrow Na_2SnO_2 + H_2O$$

Sodium stannite

Stannites are known only in aqueous solutions. Stannites absorb oxygen from air and are oxidised to stannates which are stable in nature.

$$2Na_2SnO_2 + O_2 \longrightarrow 2Na_2SnO_3$$

Sodium stannate

3.7.2 STANNIC OXIDE (SnO_2)

It is found in nature as Cassiterite or tin stone.

Preparation:

$$Sn + O_2 \xrightarrow{\Delta} SnO_2$$

$$Sn + 4HNO_3 \longrightarrow H_2SnO_3 + 4NO_2 + H_2O$$

$$H_2SnO_3 \xrightarrow{\Delta} SnO_2 + H_2O$$

Metastannic acid

Properties:

It is a white powder, insoluble in water. It is somewhat unreactive. However, it dissolves in concentrated H_2SO_4 forming stannic sulphate.

$$SnO_2 + 2H_2SO_4 \longrightarrow Sn(SO_4)_2 + 2H_2O$$

When the solution is diluted, stannic oxide is reprecipitated.

$$Sn(SO_4)_2 + 2H_2O \longrightarrow SnO_2 + 2H_2SO_4$$

It readily dissolves in alkalies forming stannates.

$$SnO_2 + 2KOH \longrightarrow K_2SnO_3 + H_2O$$

3.7.3 STANNOUS CHLORIDE ($SnCl_2$)

Preparation:

(i) Hydrated stannous chloride $SnCl_2.2H_2O$ is prepared by dissolving tin in hot concentrated hydrochloric acid and subjecting the solution to crystallisation.

$$Sn + 2HCl \xrightarrow{\Delta} SnCl_2 + H_2$$

Hydrated stannous chloride consists of two molecules of water as water of crystallisation ($SnCl_2.2H_2O$).

Anhydrous salt cannot be obtained by heating the hydrated salt as it undergoes hydrolysis and a white solid of tin hydroxy chloride is formed.

$$SnCl_2.2H_2O \longrightarrow Sn(OH)Cl + HCl + H_2O$$

(ii) Anhydrous stannous chloride is formed when dry HCl gas is passed over hot tin.

$$Sn + 2HCl(g) \longrightarrow SnCl_2 + H_2$$

It can also be obtained when a mixture of Sn and calculated quantity of mercuric chloride is heated.

$$Sn + HgCl_2 \longrightarrow SnCl_2 + Hg$$

Properties:

(i) It is a white crystalline solid. It is soluble in water, alcohol and ether.

(ii) In water, it is soon hydrolysed. However in presence of HCl (acid), hydrolysis is revered.

(iii) It forms a white precipitate with alkalies. The precipitate of stannous hydroxide, however, dissolves in excess of alkali.

$$SnCl_2 + 2NaOH \longrightarrow Sn(OH)_2 + 2NaCl$$

$$Sn(OH)_2 + 2NaOH \longrightarrow \underset{\text{Sodium stannite}}{Na_2SnO_2} + 2H_2O$$

(iv) It forms a dark brown precipitate of stannous sulphide on passing H_2S through its solution. The precipitate dissolves in yellow ammonium sulphide.

$$SnCl_2 + H_2S \longrightarrow SnS + 2HCl$$

$$SnS + \underset{\text{Yellow ammonium sulphide}}{(NH_4)_2S_2} \longrightarrow \underset{\text{Ammonium thiostannate}}{(NH_4)_2SnS_3}$$

(v) It is a strong reducing agent. Few examples are given below:

(a) It reduces mercuric chloride to mercurous chloride (white ppt) and finally to metallic mercury (dark grey or black).

$$2HgCl_2 + SnCl_2 \longrightarrow \underset{\text{Mercurous chloride}}{Hg_2Cl_2} + SnCl_4$$

$$Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg + SnCl_4$$

(b) It reduces ferric salts to ferrous salts and cupric salts into cuprous salts.

$$2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$$

$$2CuCl_2 + SnCl_2 \longrightarrow 2CuCl + SnCl_4$$

(c) It decolourises iodine and thus can be titrated with it.

$$SnCl_2 + 2HCl + I_2 \longrightarrow SnCl_4 + 2HI$$

(d) Organic nitro compounds are reduced to amino compounds.

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 6HCl + 3SnCl_2 \longrightarrow \underset{\text{Aniline}}{C_6H_5NH_2} + 3SnCl_4 + 2H_2O$$

(e) It reduces gold chloride to metallic gold.

$$2AuCl_3 + 3SnCl_2 \longrightarrow \underset{\text{Colloidal gold}}{2Au} + 3SnCl_4$$

$SnCl_4$ undergoes hydrolysis forming stannic acid which absorbs colloidal particle of gold and thus forms purple of cassius.

3.7.4 STANNIC CHLORIDE ($SnCl_4$)

Preparation:

$$\underset{\text{(fused)}}{Sn} + \underset{\text{dry}}{2Cl_2} \longrightarrow SnCl_4$$

Properties:

(i) It is a colourless fuming liquid having disagreeable smell.

(ii) It is hygroscopic and forms crystalline hydrates containing 3, 5, 6 and 8 molecules of water as water of crystallisation. The pentahydrate $SnCl_4.5H_2O$, is known as “butter of tin” or “oxymuriate of tin”.

(iii) It is soluble in water in which it undergoes hydrolysis.

$$SnCl_4 + 4H_2O \longrightarrow Sn(OH)_4 + 4HCl$$

It is also soluble in organic solvents showing that it is a covalent compound.

(iv) It dissolves in concentrated HCl forming chlorostannic acid. In presence of ammonium chloride, it forms ammonium salt of this acid.

$$SnCl_4 + 2HCl \longrightarrow \underset{\text{Chlorostannic acid}}{H_2SnCl_6}$$

$$SnCl_4 + 2NH_4Cl \longrightarrow \underset{\text{Ammonium chloro stannate}}{(NH_4)_2SnCl_6}$$

4 THE GROUP – 15 ELEMENTS (NITROGEN FAMILY)

4.1 GENERAL PROPERTIES AND STRUCTURES OF THE ELEMENTS

(i) The first element nitrogen differs from the rest. Nitrogen is a colourless, odourless, tasteless gas, which is diamagnetic and exists as N_2. The other elements are solids and exist as several allotropic forms. The N_2 molecule contains a triple bond $N \equiv N$. This bond is very stable, and the dissociation energy is consequently very high. Thus N_2 is inert at room temperature, though it does react with Li, forming the nitride Li_3N. Other isoelectronic species such as CO, CN^- and NO^+ are much more reactive than N_2, and this is because the bonds are partly polar, whilst in N_2 they are not.

Elemental form	**Melting point (°C)**	**Boiling point (°C)**
N_2	–210	–195.8
P_4	44	281
As	816	615
Sb	631	1587
Bi	271	1564

(ii) The majority of compounds formed by this group are covalent. A coordination number of 4 is obtained if the lone pair is donated to another atom or ion. An example is the ammonium ion NH_4^+.
It requires too much energy to remove all five outer electrons so M^{+5} ions are not formed. However, Sb and Bi can lose just three electrons, forming M^{+3} ions, but the ionisation energy is too high for the other elements to do so. Both SbF_3 and BiF_3 exist as ionic solids.
The M^{+3} ions are not very stable in solution. They can exist in fairly strong acid solutions, but are rapidly hydrolyzed in water to give the antimony oxide ion or bismuth oxide ion SbO^+ and BiO^+. This change is reversed by adding 5 M HCl.

$$Bi^{+3} \underset{HCl}{\overset{H_2O}{\rightleftharpoons}} [BiO]^+$$

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$

(iii) Strength of oxoacids of group VB elements
For an oxidation state of + 5, the strengths of various acids of group 15 elements follow the order, $HNO_3 > H_3PO_4 > H_3AsO_4 > H_3SbO_4$
For the oxyacids involving the same element in different oxidation states, the strength of an acid depends upon the number of unhydrogenated oxygen atoms attached to the central atom. For example, for the oxyacids of the type $(OH)_m\ ZO_n$, the acid strength varies directly with the value of n. Thus, nitric acid (HNO_3) is stronger than nitrous acid (HNO_2).
The acids H_3PO_2 , H_3PO_3 and H_3PO_4 are approximately of equal strength, because all these acids contain only one unhydrogenated oxygen atom each. The order of acid strength is $H_3PO_2 > H_3PO_3 > H_3PO_4$.

4.2 NITROGEN

4.2.1 PREPARATION OF NITROGEN

(i) $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

Since ammonium nitrite is very unstable, it cannot be kept as such. Hence nitrogen is usually prepared by heating a mixture of ammonium chloride and sodium nitrite.

$$NH_4Cl + NaNO_2 \xrightarrow{\Delta} NH_4NO_2 + NaCl$$

$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$$

(ii) Ammonium dichromate on heating decomposes to give nitrogen gas.

$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + 4H_2O + Cr_2O_3$$

$$2NH_3 + 3CuO \xrightarrow{\Delta} N_2(g) + 3Cu + 3H_2O$$

$$NH_2CONH_2 + 2HNO_2 \longrightarrow 2N_2 + CO_2 + 3H_2O$$

$$NaNO_2 + HCl \longrightarrow NaCl + HNO_2$$

4.2.2 ATOMIC AND PHYSICAL PARAMETERS OF NITROGEN

Ionisation enthalpy (kJ mol^{-1})	ΔH_1	1402
	ΔH_2	2856
	ΔH_3	4577
Electronegativity		3.0
Covalent radius/pm		70
Ionic radius/pm (N^{3-})		171

4.2.3 FIXATION OF ATMOSPHERIC NITROGEN IN CYANAMIDE FERTILIZER (THE CYANAMIDE PROCESS)

Nitrogen is also fixed as calcium cyanamide on heating it with calcium carbide at 1000°C in an electric furnace.

$$\underset{\text{calcium carbide}}{CaC_2} + N_2 \xrightarrow{\text{electric furnace}} \underset{\text{calcium cyanamide}}{CaCN_2} + C$$

The mixture of calcium cyanamide and carbon (trade name Nitrolim) is an important fertilizer. Calcium cyanamide may also be used as a source of ammonia. The ammonia so produced can be converted into useful fertilizers. Calcium cyanamide is decomposed by water to give ammonia.

$$CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

$$P_2O_5 + 6NH_3 + 3H_2O \longrightarrow 2(NH_4)_3PO_4$$

$$CaCl_2 + 8NH_3 \longrightarrow CaCl_2.8NH_3$$

By the hydrolysis of metal nitrides

$$AlN + NaOH + H_2O \xrightarrow{\text{boil}} NaAlO_2 + NH_3$$

4.3 AMMONIA

4.3.1 STRUCTURE OF AMMONIA

Ammonia is a covalent molecule. The ammonia molecule is formed due to the overlap of three sp^3 hybrid orbital of N and 1s orbital of each of the three hydrogen atoms. The fourth sp^3 hybrid orbital of N is occupied by a lone–pair. The H–N–H angle is 107.3°. The H–N–H bond angle is slightly less than the tetrahedral angle of 109°28′ due to the lone pair – bond pair repulsions, which tend to push the N–H bonds slightly inwards. In liquid and solid state, ammonia is associated due to hydrogen bonding.

4.3.2 REACTIONS OF AMMONIA

With halogens

Ammonia reacts with halogens and the nature of products depends upon the halogen and the reaction conditions.

(a) With chlorine

With limited amount of chlorine, ammonium chloride is formed but with excess of chlorine nitrogen trichloride is formed.

$$8NH_3 + 3Cl_2(\text{limited}) \longrightarrow 6NH_4Cl + N_2$$

$$NH_3 + 3Cl_2(\text{excess}) \longrightarrow NCl_3 + 3HCl$$

(b) With bromine

$$8NH_3 + 3Br_2 \longrightarrow 6NH_4Br + N_2$$

(c) With iodine

$$8NH_3.NI_3 \longrightarrow 5N_2 + 9I_2 + 6NH_4I$$

$$2NH_3 + CO_2 \xrightarrow[80\text{–}100\text{ atm.}]{200^\circ C} NH_2CONH_2 + H_2O$$

Action with heavy metal ions

With the metal ions of Al, Fe, Cr and Zn, it forms metal hydroxides, which are insoluble and form precipitates.

$$FeCl_3 + 3NH_4OH \longrightarrow 3NH_4Cl + \underset{\text{brown}}{Fe(OH)_3\downarrow}$$

$$CrCl_3 + 3NH_4OH \longrightarrow 3NH_4Cl + \underset{\text{green}}{Cr(OH)_3\downarrow}$$

$$AlCl_3 + 3NH_4OH \longrightarrow 3NH_4Cl + \underset{\text{white}}{Al(OH)_3\downarrow}$$

$$ZnCl_2 + 2NH_4OH \longrightarrow 2NH_4Cl + \underset{\text{white}}{Zn(OH)_2\downarrow}$$

Formation of complex compounds

It forms complex compounds with the soluble salts of copper, silver etc. With copper sulphate solution, it gives a deep blue coloured complex compound, tetramminecopper(II) sulphate.

$$CuSO_4 + 4NH_4OH \longrightarrow \underset{\text{tetramminecopper(II) sulphate}}{[Cu(NH_3)_4]SO_4} + 4H_2O$$

$$AgOH + 2NH_3 \longrightarrow \underset{\text{diammine silver(I) hydroxide}}{[Ag(NH_3)_2]OH}$$

$$\underset{\text{insoluble in water}}{AgCl} + 2NH_3 \longrightarrow \underset{\text{diammine silver(I) chloride (soluble in water)}}{[Ag(NH_3)_2]Cl}$$

4.4 OXIDES OF NITROGEN

Oxides of nitrogen provide a fascinating picture from the point of view of their varied structures and diverse chemical behaviour. They range from N_2O (oxidation state of nitrogen +1) through NO, N_2O_3, NO_2, N_2O_4 to N_2O_5 in which the oxidation state of nitrogen is +5. Nitric oxide(NO) is colourless, neutral, paramagnetic in which nitrogen has +2 oxidation state.

Preparation

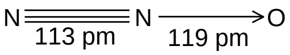
Some common methods of preparation of oxides of Group VB elements are described below. Oxides of nitrogen can be prepared by the methods given below.

Oxide of nitrogen	Preparation
(i) Nitrous oxide (N_2O)	By heating ammonium nitrate upto 240°C. $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$ N_2O is collected over hot water
(ii) Nitric oxide (NO)	(a) By the action of cold dil. HNO_3 on copper turnings (Laboratory method). $3Cu + 8\text{ dil. }HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$ (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. $4NH_3 + 5O_2 \xrightarrow[850^\circ C]{Pt} 4NO + 6H_2O$
(iii) Dinitrogen trioxide (N_2O_3)	(a) By the action of 50% HNO_3 on arsenious oxide.

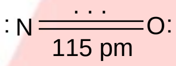
	$2HNO_3 + As_2O_3 + 2H_2O \longrightarrow NO + NO_2 + 2H_3AsO_4$ $\downarrow$ 250 K N_2O_3
(iv) Nitrogen dioxide (NO_2)	(a) By heating nitrates of heavy metals, e.g., lead nitrate. $2Pb(NO_3)_2 \xrightarrow{673K} 4NO_2 + 2PbO + O_2$ (b) By heating copper turnings with conc. HNO_3 $Cu + 4$ conc. $HNO_3 \longrightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$
(v) Dinitrogen pentoxide (N_2O_5)	(a) By dehydrating HNO_3 with phosphorus pentoxide $4HNO_3 + P_4O_{10} \longrightarrow 2N_2O_5 + 4HPO_3$

Structures

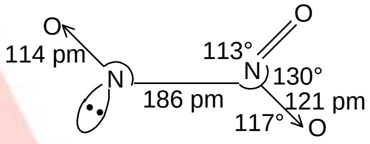
The oxides of nitrogen differ from those formed by P, As, Sb and Bi in their structures. The structures of nitrogen oxides are dictated by the tendency of nitrogen to form $p\pi - p\pi$ multiple bonds. The structures of nitrogen oxides are given in figure.



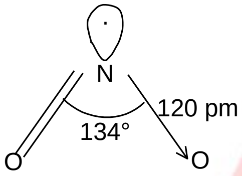
Nitrous oxide



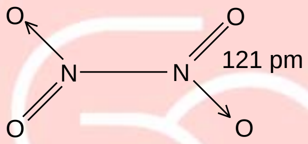
Nitric oxide



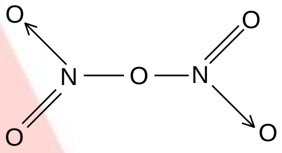
Dinitrogen trioxide



Nitrogen dioxide



Dinitrogen tetraoxide



Dinitrogen pentoxide

Nitric Oxide (NO)

NO has 11 valency electrons. It is impossible for them all to be paired and hence this is an odd electron molecule and the gas is paramagnetic. It is diamagnetic in the liquid and solid states, because the molecule dimerizes, forming O–N–N–O.

NO readily forms coordination complexes with transition metal ions. These complexes are called nitrosyls. Fe^{2+} and NO form the complex $[Fe(H_2O)_5NO]^{2+}$, which is responsible for the colour in the 'brown–ring test for nitrates. Most nitrosyl complexes are coloured. Another example is sodium nitroprusside $Na_2[Fe(CN)_5NO].2H_2O$.

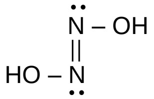
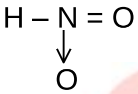
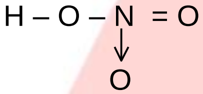
Nitrogen dioxide NO_2 and dinitrogen tetroxide N_2O_4

NO_2 is a red–brown poisonous gas and is produced on a large scale by oxidizing NO in the Ostwald process for the manufacture of nitric acid. In the laboratory, it is prepared by heating lead nitrate:

$$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$$

The gaseous products O_2 and NO_2 are passed through a U–tube cooled in ice. The NO_2 (boiling point 21°C) condenses. The $Pb(NO_3)_2$ must be carefully dried, since NO_2 reacts with water. The NO_2 is obtained as a brown liquid, which turns paler on cooling and eventually becomes a colourless solid. This is because NO_2 dimerizes into colourless N_2O_4. NO_2 is an odd electron molecule and is paramagnetic and very reactive. It dimerizes to N_2O_4, pairing the previously unpaired electrons. N_2O_4 has no unpaired electrons and is diamagnetic.

4.5 OXOACIDS OF NITROGEN

Oxoacids		Structure	Oxidation state of N	Basicity	pK$_a$	Nature
Name	Molecular formula					
Hyponitrous acid	$H_2N_2O_2$	 $HO-N=N-OH$	+ 1	2 (dibasic)	very weak	Highly explosive
Nitrous acid	HNO_2	 $H-\underset{\substack{\downarrow\\O}}{N}=O$	+ 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

Manufacture of HNO_3

1. Ostwald process

$$4NH_3 + 5O_2 \xrightarrow[\text{Catalyst}]{\text{Pt–Rh}} 4NO + 6H_2O$$

$$2NO + O_2 \longrightarrow 2NO_2$$

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

The nitric acid prepared is of 50% concentration.

2. Birkeland Eyde process

$$N_2 + O_2 \xrightarrow[\text{arc}]{\text{Electric}} 2NO$$

$$2NO + O_2 \xrightarrow{1000^{\circ}C} 2NO_2$$

$$2NO_2 + H_2O \longrightarrow HNO_3 + HNO_2$$

$$3HNO_2 \longrightarrow \underset{60\%}{HNO_3} + 2NO + H_2O$$

CHEMICAL PROPERTIES OF NITRIC ACID

Thermal stability

$$4HNO_3 \xrightarrow{\Delta} 2H_2O + 4NO_2 + O_2$$

$$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$$

Oxidising properties

$$2HNO_3\,(\text{conc.}) \longrightarrow H_2O + 2NO_2 + [O]$$

$$2HNO_3\,(\text{dilute}) \longrightarrow H_2O + 2NO + 3[O]$$

$$H_2S + 2HNO_3(\text{conc.}) \longrightarrow 2H_2O + 2NO_2 + S\downarrow$$

$$3H_2S + 2HNO_3(\text{dilute}) \longrightarrow 4H_2O + 2NO + 3S$$

$$2HNO_3(\text{conc.}) \longrightarrow H_2O + 2NO_2 + [O]$$

$$SO_2 + [O] + H_2O \longrightarrow H_2SO_4$$

$$SO_2 + 2HNO_3\,(\text{conc.}) \longrightarrow H_2SO_4 + 2NO_2\uparrow$$

$$2HNO_3(\text{dilute}) + 3SO_2 + 2H_2O \longrightarrow 3H_2SO_4 + 2NO$$

$$2FeSO_4 + H_2SO_4 + [O] \longrightarrow Fe_2(SO_4)_3 + H_2O$$

$$6FeSO_4 + 2HNO_3(\text{dil.}) + 3H_2SO_4(\text{dil.}) \longrightarrow 3Fe_2(SO_4)_3 + 2NO\uparrow + 4H_2O$$

Hydrobromic acid and hydroiodic acid to bromine and iodine respectively.

$$2HBr + 2HNO_3 \longrightarrow 2H_2O + 2NO_2\uparrow + Br_2\uparrow$$

$$2HI + 2HNO_3 \longrightarrow 2H_2O + 2NO_2\uparrow + I_2\uparrow$$

Non–metals like carbon, sulphur, iodine, phosphorus, etc are converted to their oxoacids by concentrated nitric acid, which in turn, is reduced to nitrogen dioxide.

$$C + 4HNO_3 \longrightarrow H_2CO_3 + H_2O + 4NO_2$$

$S + 6HNO_3 \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$

Iodine is oxidised to iodic acid (HIO_3).

$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$

$P + 5HNO_3 \longrightarrow H_3PO_4 + 5NO_2 + H_2O$

(a) Metals that are more electropositive than hydrogen

(i) Action on zinc

$Zn + 4HNO_3(\text{conc.}) \longrightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$

$4Zn + 10HNO_3(\text{dil.}) \longrightarrow 4Zn(NO_3)_2 + 5H_2O + N_2O$

$4Zn + 10HNO_3(\text{v. dil.}) \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$

$4Mg + 10HNO_3(\text{v. dil.}) \longrightarrow 4Mg(NO_3)_2 + NH_4NO_3 + 3H_2O$

(ii) Action on tin

$Sn + 4HNO_3(\text{conc.}) \longrightarrow \underset{\text{Metastannic acid}}{H_2SnO_3} + 4NO_2 + H_2O$

$4Sn + 10HNO_3(\text{dilute}) \longrightarrow \underset{\text{Stannous nitrate}}{4Sn(NO_3)_2} + NH_4NO_3 + 3H_2O$

(iii) Action on lead

$Pb + 4HNO_3\,(\text{conc.}) \longrightarrow Pb(NO_3)_2 + 2NO_2 + 2H_2O$

$3Pb + 8HNO_3(\text{dilute}) \longrightarrow 3Pb(NO_3)_2 + 2NO + 4H_2O$

(iv) Action on iron

$Fe + 6HNO_3(\text{conc.}) \longrightarrow Fe(NO_3)_3 + 3NO_2 + 3H_2O$

$4Fe + 10HNO_3(\text{dil.}) \longrightarrow 4Fe(NO_3)_2 + N_2O + 5H_2O$

$4Fe + 10HNO_3(\text{v. dil.}) \longrightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$

(b) Metals that are less electropositive than hydrogen

Action on copper

$Cu + 4HNO_3(\text{conc.}) \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

$3Cu + 8HNO_3(\text{v. dil.}) \longrightarrow 3Cu(NO_3)_2 + NO + 4H_2O$

Formation of aqua–regia

A mixture of conc. HCl and conc. HNO_3 (3:1 by volume) is called aqua–regia. It can dissolve noble metals like gold and platinum.

$HNO_3 + 3HCl \longrightarrow 2H_2O + 2Cl + NOCl$

$Au + 3Cl \longrightarrow AuCl_3\ ;\ AuCl_3 + Cl^- \longrightarrow [AuCl_4]^-$

$Pt + 4Cl \longrightarrow PtCl_4\ ;\ PtCl_4 + 2Cl^- \longrightarrow [PtCl_6]^{-2}$

4.6 PHOSPHORUS

Phosphorus is a very reactive element, so it does not occur free in nature. The ores of phosphorus which normally occur in nature are given as follows

(i) Phosphorite,	$Ca_3(PO_4)_2$
(ii) Fluorapatite	$3Ca_3(PO_4)_2.CaF_2$
(iii) Chlorapatite,	$3Ca_3(PO_4)_2.CaCl_2$

4.6.1 EXTRACTION OF PHOSPHORUS

Phosphorus is obtained by heating bone ash or phosphorite rock [$Ca_3(PO_4)_2$], with sand (SiO_2) and coke (C) in an electric furnace at about 1770 K. The reactions are as follows.

$2Ca_3(PO_4)_2 + 6SiO_2 \longrightarrow 6CaSiO_3 + P_4O_{10}$

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

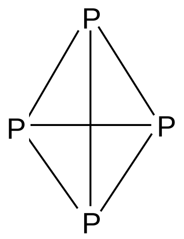
4.6.2 ALLOTROPES OF PHOSPHORUS

Phosphorus exists in the following five different allotropic forms.

(i) White (yellow) phosphorus is extremely reactive.

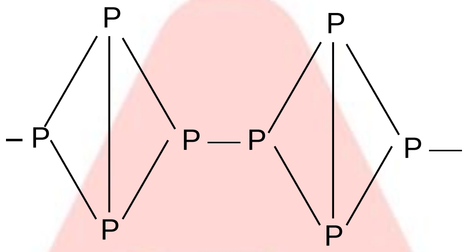
(ii) Below 800°C, its vapor density corresponds to the formula P_4. Above 1700°C, it exists as P_2.

(iii) Due to its low ignition temperature (~ 30°C), it undergoes oxidation in the presence of air which slowly raises its temperature and after a few moments it catches fire spontaneously. Due to this reason, it is stored under water.



Red Phosphorus

Red phosphorus is stable allotrope at room temperature. Red phosphorus is formed by heating white phosphorus in the absence of air at about 250°C. It is not poisonous. It is safe to handle because it does not burn spontaneously at room temperature.



Structure of red phosphorus

(i) Ignition temperature of red phosphorus is high (~ 265°C).
(ii) It sublimes on heating. It melts at 610°C under pressure giving yellow liquid, which on cooling gives white phosphorus.
(iii) It is insoluble in carbon disulphide.
(iv) Red phosphorus has a polymeric structure.

4.6.3 Properties of Phosphorus

Important chemical properties of phosphorus are

(i) Reaction with oxygen:

Yellow phosphorus readily catches fire in air giving dense white fumes of phosphorus pentoxide. Red phosphorus combines with oxygen only on heating. Both of them form either phosphorus trioxide or phosphorus pentoxide.

$$\underset{\text{Red phosphorus}}{P_4} + 3O_2 \xrightarrow{\text{heat}} \underset{\text{Phosphorus trioxide}}{P_4O_6}$$

$$\underset{\text{Red phosphorus}}{P_4} + 5O_2 \xrightarrow{\text{heat}} \underset{\text{Phosphorus pentoxide}}{P_4O_{10}}$$

(ii) Reaction with chlorine:

Phosphorus reacts with chlorine gas to form tri-and pentachlorides. Yellow phosphorus reacts violently at room temperature, whereas red phosphorus reacts on heating only.

$$P_4 + 6Cl_2 \longrightarrow \underset{\text{Phosphorus trichloride}}{4PCl_3}$$

$$P_4 + 10Cl_2 \longrightarrow \underset{\text{Phosphorus pentachloride}}{4PCl_5}$$

(iii) Reaction with alkalies (sodium/potassium hydroxide):

Yellow phosphorus dissolves in caustic soda on boiling under an inert atmosphere liberating phosphine.

$$\underset{\text{Yellow phosphorus}}{P_4} + 3NaOH + 3H_2O \xrightarrow{\text{boil}} \underset{\text{Phosphine}}{PH_3(g)} + \underset{\text{Sodium hypophosphite}}{3NaH_2PO_2}$$

(iv) Reaction with nitric acid: Phosphorus gets oxidised by nitric acid to phosphoric acid.

$$P_4 + 20HNO_3 \longrightarrow \underset{\text{Phosphoric acid}}{4H_3PO_4} + 20NO_2 + 4H_2O$$

(v) With metals: Phosphorus reacts with metals forming phosphides. For example

$$6Mg + P_4 \longrightarrow \underset{\text{Magnesium phosphide}}{2Mg_3P_2}$$

4.7 PHOSPHINE

(i) By hydrolysing metallic phosphides

Convenient methods of preparing phosphine are by the hydrolysis of metallic phosphides with water or dilute mineral acids.

$$Ca_3P_2 + 6H_2O \longrightarrow 2PH_3 + 3Ca(OH)_2$$
$$AlP + 3HCl \longrightarrow PH_3 + AlCl_3$$

(ii) Phosphine may also be obtained by heating phosphorus acid.

$$\underset{\text{phosphorus acid}}{4H_3PO_3} \xrightarrow{\text{heat}} 3H_3PO_4 + PH_3$$

With metallic salts: Formation of phosphides

Phosphine unlike ammonia does not precipitate hydroxides of metals on reacting with salt solutions. On the other hand, it precipitates metals like silver, copper etc., as phosphides when phosphine gas is passed through aqueous solutions of salts of these metals.

$$3CuSO_4 + 2PH_3 \longrightarrow \underset{\substack{\text{copper phosphide}\\ \text{(black ppt.)}}}{Cu_3P_2} + 3H_2SO_4$$

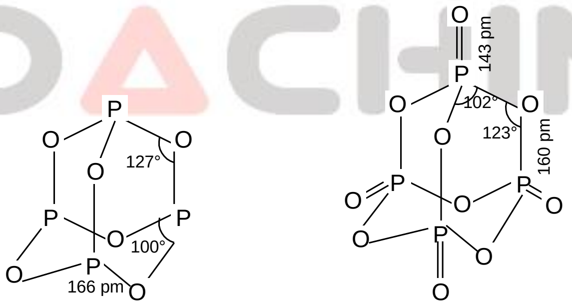
$$3AgNO_3 + PH_3 \longrightarrow \underset{\substack{\text{silver phosphide}\\ \text{(black ppt.)}}}{Ag_3P} + 3HNO_3$$

Uses of Phosphine

(i) It is used for producing smoke screens. Calcium phosphide is used in smoke screens. Phosphine obtained catches fire to give the needed smoke.

(ii) In Holme’s signals. A mixture of calcium carbide and calcium phosphide is taken in a container which is pierced and thrown into the sea. Phosphine liberated catches fire and lights up acetylene. Burning gases serve as a signal to the approaching ships.

4.8 OXIDES OF PHOSPHOROUS

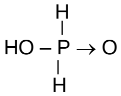
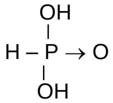
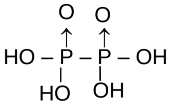
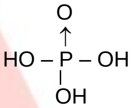
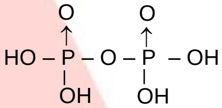
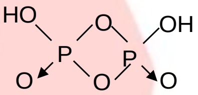


Phosphorus trioxide (P_4O_6) Phosphorus pentoxide (P_4O_{10})

Structures of some oxides of phosphorus

4.9 OXOACIDS OF PHOSPHORUS

Phosphorus forms a large number of oxoacids. All these acids are based on tetrahedral four coordinated phosphorus atom containing at least one P=O unit and one P–OH group. Condensed systems are formed by P–O–P linkage or P–P linkage. Some of the common oxo-acids of phosphorus are given on the next page.

Oxoacids		**Oxidation state of P**	**Basicity**	**Structure**
Name	Molecular formula			
Hypophosphorus acid	H_3PO_2	+ 1	1	 $\mathrm{HO-\overset{H}{\underset{H}{P}}\rightarrow O}$
Orthophosphorus acid	H_3PO_3	+ 3	2	 $\mathrm{H-\overset{OH}{\underset{OH}{P}}\rightarrow O}$
Hypophosphoric acid	$H_4P_2O_6$	+ 4	4	 $\mathrm{HO-\overset{\overset{O}{\uparrow}}{\underset{HO}{P}}-\overset{\overset{O}{\uparrow}}{\underset{OH}{P}}-OH}$
Orthophosphoric acid	H_3PO_4	+ 5	3	 $\mathrm{HO-\overset{\overset{O}{\uparrow}}{\underset{OH}{P}}-OH}$
Pyrophosphoric acid	$H_4P_2O_7$	+ 5	4	 $\mathrm{HO-\overset{\overset{O}{\uparrow}}{\underset{OH}{P}}-O-\overset{\overset{O}{\uparrow}}{\underset{OH}{P}}-OH}$
Metaphosphoric acid	HPO_3	+ 5	1	

Phosphorus mainly forms two series of oxoacids:

1. The phosphoric series of acids, in which the oxidation state of P is (V) and in which the compounds have oxidizing properties.
2. The phosphorous series of acids, which contain P in the oxidation state (III) and which are reducing agents.

In all of these, P is four co–ordinate and tetrahedrally surrounded wherever possible.

pπ–dπ back bonding gives rise to P=O bonds. The hydrogen atoms in OH groups are ionisable and are acidic, but the P–H bonds found in the phosphorous acids have reducing, not acidic, properties. Simple phosphate ions can condense (polymerise) together to give a wide range of more complicated isopolyacids or their salts.

The Phosphoric acid series

Orthophosphoric acid

The simplest phosphoric acid is H_3PO_4 (orthophosphoric acid). The acid contains three replaceable H atoms, and is tribasic. It undergoes stepwise dissociation.

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \quad ; \quad K_{a_1} = 7.5 \times 10^{-3}$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \quad ; \quad K_{a_2} = 6.2 \times 10^{-8}$$

$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-} \quad ; \quad K_{a_3} = 1 \times 10^{-12}$$

Three series of salts can be formed

1. Dihydrogen phosphates, for example sodium dihydrogen phosphate NaH_2PO_4 , which is slightly acidic in water
2. Monohydrogen phosphates, for example disodium hydrogen phosphate Na_2HPO_4, which is slightly basic in water.
3. Normal phosphates such as trisodium phosphate Na_3PO_4, which are appreciably basic in solution.

NaH_2PO_4 and Na_2HPO_4 are made industrially by neutralizing H_3PO_4 with soda ash (Na_2CO_3), but NaOH is required to make Na_3PO_4. All three salts exist in the anhydrous state and also in a number of hydrated forms, and they are used extensively.

Phosphoric acid also forms esters with alcohols:

$$\underset{\text{acid}}{(HO)_3P{=}O} + \underset{\text{alcohol}}{3EtOH} \longrightarrow \underset{\substack{\text{ester}\\\text{(triethy phosphate)}}}{(EtO)_3P{=}O} + \underset{\text{water}}{3H_2O}$$

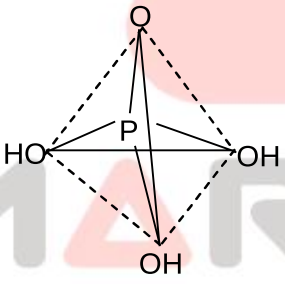
Phosphates are detected analytically by mixing a solution of the salt with dilute HNO_3 and ammonium molybdate solution. A yellow precipitate of a complex ammonium 12-molybdophosphate forms slowly, confirming the presence of phosphates. Arsenates form a similar precipate but only on heating the mixture.

The orthophosphates of group I metals (except Li) and NH_4^+ are soluble in water. Most of the other metal orthophosphates are soluble in dilute HCl or acetic acids. Titanium, zirconium and thorium phosphates are insoluble even in acids. Thus in qualitative analysis a solution of zirconyl nitrate is commonly added to remove any phosphate present in solution.

Phosphates can be estimated quantitatively by adding a solution containing Mg^{2+} and NH_4OH solution to a solution of the phosphate. Magnesium ammonium phosphate is precipitated quantitatively, and this is filtered, washed, ignited, and weighed as magnesium pyrophosphate $Mg_2P_2O_7$.

$$Mg^{2+} + NH_4^+ + PO_4^{3-} \longrightarrow MgNH_4PO_4$$

$$2MgNH_4PO_4 \longrightarrow Mg_2P_2O_7 + 2NH_3 + H_2O$$



H_3PO_4 orthophosphoric acid

Structure of orthophosphoric acid, H_3PO_4

Impure orthophosphoric acid H_3PO_4 is prepared in large amounts by treating phosphate rock with H_2SO_4. The $CaSO_4$ is hydrated to gypsum $CaSO_4 . 2H_2O$, which is filtered off, and the F^- is converted to $Na_2[SiF_6]$ and removed. The H_3PO_4 is concentrated by evaporation. Most of the H_3PO_4 made in this way is used to make fertilizer.

$$Ca_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 2H_3PO_4 + 3CaSO_4$$

$$[3(Ca_3(PO_4)_2). CaF_2] + 10H_2SO_4 + 16\,H_2O \longrightarrow 6H_3PO_4 + 10CaSO_4 + 2HF$$

Pure H_3PO_4 is made by the 'furnace process'. Molten P is burnt in a furnace with air and steam. First P_4O_{10} is formed by reaction between P and O, and then this is immediately hydrolysed.

$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$

$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

Phosphoric acid is hydrogen bonded in aqueous solution, and because of this the 'concentrated acid' is syrupy and viscous. Concentrated acid is widely used and contains about 85% by weight of H_3PO_4 (100% pure (anhydrous) H_3PO_4 is seldom used, but it can be prepared as colourless deliquescent crystals by evaporation at low pressure). Most of the acid (solution) made in this way is used in the laboratory, and in food (Kraft cheese Na_2HPO_4) and pharmaceutical preparations.

H_3PO_4 may also be made be the action of concentrated HNO_3 on P.

$P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$

Orthophosphoric acid loses water steadily on heating.

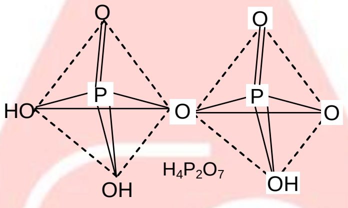
$$\underset{\text{orthophosphoric acid}}{H_3PO_4} \xrightarrow[220°C]{\text{gentle heat}} \underset{\text{pyrophosphoric acid}}{H_4P_2O_7} \xrightarrow[320°C]{\text{strong heat}} \underset{\text{metaphosphoric acid}}{(HPO_3)_n}$$

Polyphosphates

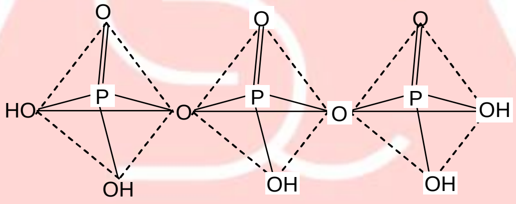
A very large number of polyphosphoric acids and their salts, the polyphosphates, arise by polymerising acidic $[PO_4]$ units forming isopolyacids. These consists of chains of tetrahedral, each sharing the O atoms at one or two corners of the $[PO_4]$ tetrahedron, giving simple unbranched chains, in a similar way to the formation of pyroxenes
by the silicates.

The hydrolysis of P_4O_{10} proceeds in stages, and an understanding of these stages leads to an understanding of the wide range of phosphoric acids.

$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4 \text{ (overall reaction)}$$

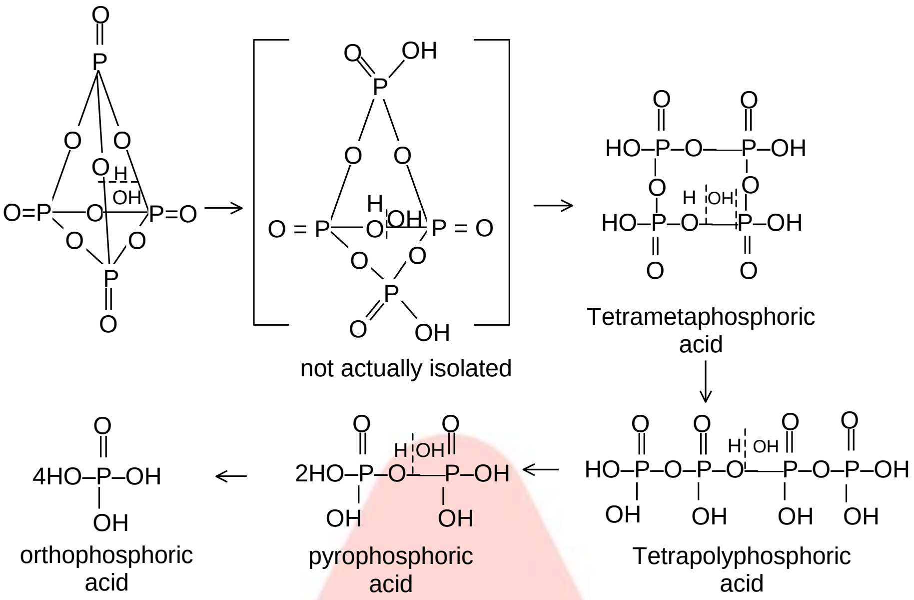


Structure of pyrophosphoric acid



$H_5P_3O_{10}$
tripolyphosphoric acid

Polyphosphates are straight chain compounds. The basicity of the various acids, that is the number of replaceable H atoms, can be found by drawing the structure and counting the number of OH groups. Thus, orthophosphoric acid is tribasic, pyrophosphoric acid is tetrabasic, tripolyphosphoric acid is pentabasic, tetrapolyphosphoric acid is hexabasic, and tetrametaphosphoric acid is tetrabasic.



Scheme for the hydrolysis of P_4O_{10}

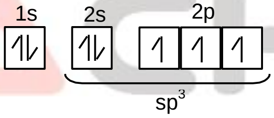
4.10 PENTAHALIDES OF PHOSPHORUS

The trigonal bipyramidal is not a regular structure. Electron diffraction on PF_5 gas shows that some bond angles are 90° and others are 120°, and the axial P–F bond lengths are 1.58 Å whilst the equatorial P–F lengths are 1.53 Å. In contrast nmr studies suggest that all five F atoms are equivalent. This paradox may be explained quite simply. Electron diffraction gives an instantaneous picture of the molecule, whilst nmr gives the picture averaged over several milliseconds. The axial and equatorial F atoms are thought to interchange their positions in less time than that needed to take the nmr. The interchange of axial and equatorial positions is called ‘pseudorotation’. PF_5 remains covalent and keeps this structure in the solid state. However, PCl_5 is close to the ionic–covalent borderline, and it is covalent in the gas and liquid states, but is ionic in the solid state. PCl_5 solid exists as $[PCl_4]^+$ and $[PCl_6]^-$ the ions have tetrahedral and octahedral structures respectively. In the solid, PBr_5 exists as $[PBr_4]^+$ Br^- and PI_5 appears to be $[PI_4]^+$ and I^- in solution.

4.11 INTERNAL π–BONDING USING d–ORBITALS

The compounds trimethylamine $(CH_3)_3N$ and trisilylamine $(SiH_3)_3N$ have similar formulae, but have totally different structures. In trimethylamine, the arrangement of electrons is as follows:

Electronic structure of nitrogen atom–ground state



Three unpaired electrons form bonds with CH_3 groups tetrahedral arrangement of 3 bond pairs and 1 lone pair (sp^3)

In trisilylamine, three sp^2 orbitals are used for σ bonding, giving a plane triangular structure. The lone pair of electrons occupy a p–orbitals at right angles to the plane triangle. This overlaps with empty d–orbitals on each of the three silicon atoms, and results in π–bonding, more accurately described as pπ–dπ bonding, because it is from a full p–orbital to an empty d–orbital. This shortens the bond lengths of N–Si bond. Since, the nitrogen no longer has a lone pair of electrons, the molecule has no donor properties. Similar pπ–dπ bonding is impossible in $(CH_3)_3N$ because C does not possess d–orbitals and hence this molecule is pyramidal. About 200 compounds are now thought to contain pπ–dπ bonds.

5 THE GROUP – 16 ELEMENTS (OXYGEN FAMILY)

5.1 GENERAL PHYSICAL PROPERTIES OF OXYGEN FAMILY ELEMENTS

Group VI(B) of the periodic table contains five elements namely oxygen, sulphur, selenium, tellurium and polonium. They are collectively called **chalcogens** or ore forming elements because many metal ores occur as oxides or sulphides. The first four members are non–metals while the last member polonium is a radioactive metal having very short half–life. Atoms of the elements have the outermost electronic configuration as $ns^2np_x^2np_y^1np_z^1$. Thus, there are two half filled p–orbitals which are used for bonding with other elements. Some properties of these elements are given in the following table:

PROPERTY	ELEMENT				
	Oxygen	**Sulphur**	**Selenium**	**Tellurium**	**Polonium**
Atomic number	8	16	34	52	84
Atomic mass	16.00	32.06	78.96	127.61	210
Atomic radius, pm	74	104	117	137	164
Oxidation states	2	2, 4, 6	2,4, 6	2, 4, 6	2, 4
Ionic radius, pm M^{2-}	140	184	198	221	–
M^{2+}	–	–	–	89	102
Ionisation energy, kJ mol^{-1}					
$[M \rightarrow M^+ + e^-]$	1358	999	940	869	–
Electronegativity	3.5	2.5	2.4	2.1	–
Density, kg/L	1.27	2.06	4.80	6.25	9.51
Melting point, K	55	392	490	723	527
Boiling point, K	90	718	958	1663	1235
Electron affinity, kJ mol^{-1}					
$[M + e^- \rightarrow M^-]$	– 142	–200	– 195	– 190	–
$[M + 2e^- \rightarrow M^{2-}]$	700	332	230	–	–
Outer electronic configuration	$2s^22p^4$	$3s^23p^4$	$4s^24p^4$	$5s^25p^4$	$6s^26p^4$

(i) Atomic and ionic radii

Atomic (covalent) radius increases as we go down the group.

O < S < Se < Te < Po

Ionic radius for dinegative ions (M^{2-}) also increases from oxygen to polonium. The order is,

$O^{2-} < S^{2-} < Se^{2-} < Te^{2-}$

(ii) Catenation

The self-linking property of atoms with identical atoms is called catenation. Oxygen shows a little tendency towards catenation, e.g., in peroxides, $[– O –O –]^{2-}$.

Sulphur shows a strong tendency towards catenation, e.g., in polysulphides S_n^{2-} sulphanes ($H – S_n – H$), polysulphuric acid ($HO_3S.S_n.SO_3H$), and in various allotropes. The S – S bond is very important in the biological systems. The S – S bonding is found in compounds such as, cysteine, some proteins and enzymes. The catenation tendency decreases markedly as we go down the group.

(iii) Density

Density of group VIB elements increases in going from oxygen to polonium, i.e., the density of group 16 elements follows the order,

O < S < Se < Te < Po

(iv) Melting points and Boiling points

The melting and boiling points show regular increase with the increase in atomic number. As we go down the group, the molecular size increases. As a result vander Waal forces increase and hence the melting and boiling points also increase.

(v) Electron Affinity vs Electron Gain Enthalpy

It has been recommended by IUPAC to replace the term Electron Affinity (E_{ae}) by a new term, Electron Gain Enthalpy ($\Delta_{eg}H$).

The electron gain enthalpy is the molar enthalpy change when an isolated gaseous atom or ion in its ground state, adds an electron to form the corresponding anion. Thus, the enthalpy change for the reaction,

$$X(g) + e^- \longrightarrow X^-(g)$$

is called the electron gain enthalpy ($\Delta_{eg}H$) of the element X. The $\Delta_{eg}H$ may be positive or negative (like the electron affinity).

Electron affinity (E_{ae}), or Electron gain enthalpy ($\Delta_{eg}H$) of oxygen and sulphur are given below:

$O(g) + e^- \longrightarrow O^-(g) \quad E_{ae}(O \rightarrow O^-) = -142 \text{ kJ mol}^{-1}$

$S(g) + e^- \longrightarrow S^-(g) \quad E_{ae}(S \rightarrow S^-) = -200 \text{ kJ mol}^{-1}$

$O^-(g) + e^- \longrightarrow O^{2-}(g) \quad E_{ae}(O^- \rightarrow O^{2-}) = +780 \text{ kJ mol}^{-1}$

$S^-(g) + e^- \longrightarrow S^{2-}(g) \quad E_{ae}(S^- \rightarrow S^{2-}) = +590 \text{ mol}^{-1}$

Thus, the electron affinities for $O \rightarrow O^{2-}$ and $S \rightarrow S^{2-}$ are positive.

The first electron affinity of oxygen is much smaller than those of the other elements.

Electron affinity becomes smaller as we go down the group, i.e., from sulphur to tellurium.

$$O < S > Se > Te > Po$$

(vi) Ionisation energy or ionisation enthalpy, Δ_iH

The ionisation energies of group VIB elements are quite high. Due to their high ionisation energies, it is extremely difficult to remove electrons from the atoms of these elements.

The ionisation energy decreases as we go from oxygen to polonium.

The first ionisation energies of lighter elements of group VIB (oxygen family) are lower than those of group VB, (nitrogen family).

(vii) Oxidation states

The outer electronic configuration of group VIB elements can be described as ns^2np^4. Being strongly electronegative, these elements complete their outer shells by gaining two electrons. Thus, all the elements of group 16 shows an oxidation state of –2. However, these elements also show other oxidation states as follows. Oxygen shows an oxidation state of + 2 in F_2O, and –1 in peroxides (O_2^{2-}). Other elements of group VIB exhibit oxidation states of + 2, + 4 and + 6 also. The oxidation states of + 4 and + 6 being more stable.

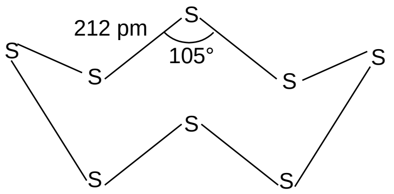
For sulphur, selenium and tellurium, the oxidation states of + 4 and + 6 are important. The + 4 state is more stable for Se, Te and Po, than + 6 state. This is due to the availability of d-orbitals in the valence shells of the atoms of these elements.

(viii) Molecular structure (or atomicity)

Oxygen forms stable diatomic (O_2) molecules, while sulphur, selenium, tellurium and polonium are octatomic molecules, viz., S_8, Se_8, Te_8 and Po_8 with puckered-ring structures. The puckered ring structure of sulphur is shown in figure. Under ordinary conditions, oxygen exists as a gas, while all other elements of this group are solids.

Explanation: This is because oxygen has a tendency to form $p\pi - p\pi$ multiple bonds. So, oxygen forms a diatomic (O = O) molecule. Due to weak Van der Waals' forces between the oxygen molecules, oxygen exists as a gas.

Because of their large atomic size, sulphur and other heavier elements of this group do not form stable $p_\pi - p_\pi$ bonds. So, these elements do not occur as diatomic molecules. Instead, S and other heavier elements of this group form M – M single bonds giving rise to polyatomic molecules. For example, sulphur forms octatomic (S_8) molecules. Due to stronger Van der Waals' forces between these polyatomic



Puckered ring structure of sulphur (S_8) molecule molecules, these elements (sulphur and others) exists as solid.

Allotropic forms of sulphur

Sulphur exists in several allotropic forms, the important ones are described below.

Rhombic or octahedral or α–sulphur

This is the common form of sulphur. It is pale yellow in colour. It melts at 114.5°C. Its specific gravity is 2.06. It is insoluble in water but readily soluble in CS_2. It is a crystalline variety and consists of S_8 structural units packed together into octahedral shape. This is the stable variety at ordinary temperature and all other forms gradually change into this form.

Monoclinic or prismatic or β–sulphur

This form is formed by melting sulphur in a dish and cooling till crust is formed. Two holes are made in the crust and liquid is poured out. On removing the crust, needle shaped crystals of monoclinic sulphur are obtained.

This form of sulphur is stable above 95.6°C. Crystals melt at 119°C. It is also soluble in CS_2. Below 95.6°C, it changes into rhombic form. Thus, 95.6°C is the transition temperature.

$$\text{Rhombic sulphur} \xrightleftharpoons{95.6^\circ C} \text{Monoclinic sulphur}$$

Plastic sulphur

This is obtained when boiling sulphur is passed into cold water. It is soft rubber like mass which hardens on standing and gradually changes into rhombic sulphur. It is amber–brown in colour and has specific gravity of 1.95. It is insoluble in CS_2 and has no sharp melting point. It consists of a completely random arrangement of chains of sulphur atoms.

(ix) Metallic character

The metallic character of group 16 elements increases with atomic number, i.e., as we go down the group. Thus, oxygen and sulphur are typical non-metals and are insulators; so Se and Te are semiconductors, and polonium is metallic in nature.

5.2 GENERAL CHEMICAL PROPERTIES

Oxygen is quite reactive. It reacts with almost every element, except lighter noble gases. Rest of the elements of this group are relatively less reactive. Oxygen differs from other elements of group 16 due to,

(a) its small size,

(b) high electronegativity,

(c) tendency to form $p_\pi - p_\pi$ double bonds,

(d) its inability to expand its valence shell due to the absence of d-orbitals in its valence shell.

However, oxygen resembles nitrogen and fluorine in the following respects.

(a) Like nitrogen and fluorine, oxygen forms strong hydrogen bonds.

(b) Like nitrogen, oxygen can also form stable $p_\pi - p_\pi$ bonds.

5.3 OXYGEN

Oxygen can be synthesised in the laboratory by the following methods:

(a) Thermal decomposition of metal oxides

$$2HgO \xrightarrow{450^\circ C} 2Hg + O_2$$

$$2Ag_2O \xrightarrow{350^\circ C} 4Ag + O_2$$

$$3MnO_2 \xrightarrow{\Delta} Mn_3O_4 + O_2$$

$$3Pb_3O_4 \xrightarrow{\Delta} 6PbO + O_2$$

(b) Thermal decomposition of oxygen rich salts

$$KNO_3 \xrightarrow{\Delta} 2KNO_2 + O_2$$

$$4K_2Cr_2O_7 \xrightarrow{400^{o}C} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

$$2KMnO_4 \xrightarrow{250^{o}C} K_2MnO_4 + MnO_2 + O_2$$

$$2KClO_3 \xrightarrow{400^{o}C} 2KCl + 3O_2$$

(c) Heating MnO_2, $KMnO_4$ or $K_2Cr_2O_7$ with concentration H_2SO_4

$$2MnO_2 + 2H_2SO_4 \longrightarrow 2MnSO_4 + 2H_2O + O_2$$

$$4KMnO_4 + 6H_2SO_4 \longrightarrow 2K_2SO_4 + 4MnSO_4 + 6H_2O + SO_2$$

$$2K_2Cr_2O_7 + 8H_2SO_4 \longrightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$$

Practically all the elements react with O_2 to form oxides, which may be classified according to their structure as normal oxides, peroxides or suboxides.

5.4 OZONE

Oxidising property

Ozone acts as a powerful oxidising agent due to the reaction,

$$O_3 \longrightarrow O_2 + [O]$$

$$4O_3 + PbS \longrightarrow 4O_2 + PbSO_4$$

$$O_3 + 2KI + H_2O \longrightarrow 2KOH + O_2 + I_2$$

$$2HCl + O_3 \longrightarrow O_2 + H_2O + Cl_2$$

$$O_3 + 2K_4[Fe(CN)_6] + H_2O \longrightarrow 2K_3[Fe(CN)_6] + 2KOH + O_2$$

Reducing property

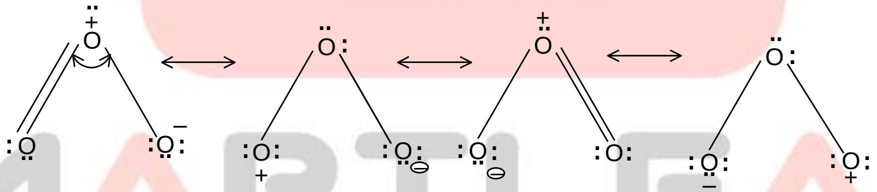
$$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$$

$$BaO_2 + O_3 \longrightarrow BaO + 2O_2$$

Structure of ozone

The structure of ozone is given in below figure. The bond length of 127.8 pm is intermediate between a single bond (bond length 148 pm) and a double bond (bond length 110 pm.) Ozone is, therefore, considered to be a resonance hybrid of the following canonical forms:

Structure of O_3



[Resonance structure of O_3]
bond length = 1.278 A°,
bond angle = 116°49'± 30'

Test for O_3

When O_3 comes in contact with the moist starch iodide paper, then the paper turns blue due to the oxidation of I^- ions and I_2, which gives blue colour with starch.

5.5 COMPOUNDS OF OXYGEN FAMILY

5.5.1 HYDRIDES

Shape and structure

All these hydrides (H_2M type) have angular structure. The central atom in these hydrides shows sp^3 hybridisation. Thus, there are two bond pairs and two lone pairs of electrons in the molecules of these hydrides. Due to stronger lone pair bond pair repulsions, the HMH angles in hydrides are less than the tetrahedral angle of 109° 28′. The bond angle in H_2M hydrides of group VIB elements decreases as we go from oxygen to tellurium in the group.

Hydride:	H_2O	H_2S	H_2Se	H_2Te
Bond angle:	104.5°	92.5°	91°	90°

Physical state

Thus, water has unusually high boiling point as compared to other hydrides of this group. The volatility of these hydrides follow the order

$H_2O < H_2S > H_2Se > H_2Te$

The existence of hydrogen bonds between water molecules is mainly responsible for its abnormally high melting and boiling points, (or for its low volatility).

Thermal stability

The thermal stability of hydrides of group 16 elements decreases with the increase in the size of the central atom.

$H_2O > H_2S > H_2Se > H_2Te$

Acidic nature

The hydrides of group VIB elements are weakly acidic. The acidic character of these hydrides increases with increasing atomic number. Thus, the acid strength of these hydrides increases as we move from O to Te because of the increase in the distance between central atom and hydrogen, which favour the release of hydrogen as proton.

	H_2O	<	H_2S	<	H_2Se	<	H_2Te
K_a	1.8×10^{-16}		1×10^{-7}		1.7×10^{-4}		2.3×10^{-3}

Reducing character

All hydrides of group VIB elements except H_2O, are reducing agents. The reducing power of these hydrides increases in going from H_2S to H_2Te, which may be due to increase in the size of the central atom and hence decrease in the M–H bond energy.

Some physical properties of hydrides of group VIB elements

Property	**H_2O H_2S**
Melting point / K Boiling point / K M – H distance / pm HMH angle (°) $\Delta_f H°$ / kJ mol^{-1} E(M – H) / kJ mol^{-1} Dissociation constant, K_a	**273188** **373213** **96 134** **104 92** **–286 20** **463347** **1.8×10^{-16} 1.3×10^{-7}**

5.5.2 HALIDES

Sulphur forms halides of the type, S_2X_2 (X = F, Cl, Br, I), SX_2 (X = F, Cl, Br), SX_4 (X = F, Cl) and SF_6. Selenium and tellurium form hexafluorides. Fluorides, chlorides and bromides of selenium and tellurium in the oxidation states of + 1, + 2 and + 4 are also known. Formulae of known halides of group VIB elements are summarised in table.

Element	**Fluorine**	**Chlorine**	**Bromine**	**Iodine**
Oxygen	F_2O	Cl_2O, ClO_2 Cl_2O_7	Br_2O	I_2O_5
Sulphur	SF_6, S_2F_{10} SF_4, S_2F_2	SCl_4, S_2Cl_2 S_2Cl_2	S_2Br_2	–
Selenium	SeF_6, SeF_4, Se_2Fe_2	$SeCl_4$, $SeCl_2$, Se_2Cl_2	$SeBr_4$, $SeBr_2$, Se_2Br_2	–
Tellurium	TeF_6, Te_2F_{10}, TeF_4	$TeCl_2$, $TeCl_4$	$TeBr_4$, $TeBr_2$	TeI_4
Polonium	PoF_6	$PoCl_4$, $PoCl_2$	$PoBr_4$, $PoBr_2$	PoI_4

Certain important features of halides of group VIB elements are described below.

(i) The stability and variety of halogen compounds formed by the elements of group 16 decreases with the increasing atomic number of the halogen, i.e., in the order

Fluoride > Chloride > Bromide > Iodide

This means, fluorides are the most stable, while iodides are the least stable of the halides of group VIB elements.

Sulphur, selenium and tellurium show maximum valency of six only in their fluorides. It is due to the small size and the most electronegative nature of fluorine atom.

The central atom in hexafluorides shows sp^3d^2 hybridisation. So, hexafluorides have octahedral structures.

(iii) The compounds of fluorine with oxygen are called oxygen fluorides. For example, the compound F_2O is actually written as OF_2 and is named as oxygen difluoride. This is because fluorine is more electronegative than oxygen.

The compounds of chlorine, bromine and iodine with oxygen are called halogen oxides, because oxygen is more electronegative than chlorine, bromine and iodine. For example, ClO_2 is named as chlorine dioxide, Cl_2O_7 is named as chlorine heptaoxide etc.

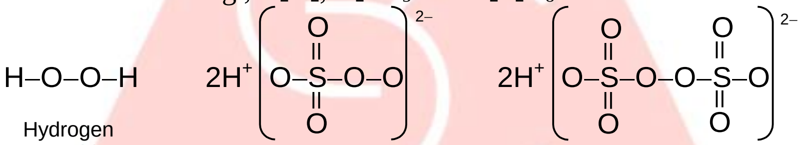
5.5.3 OXIDES

Normal oxides

These oxides contain only M–O bonds e.g., H_2O, MgO and Al_2O_3. The oxidation number of M can be deduced from the empirical formula M_xO_y taking the oxidation number of oxygen as –2.

Peroxides

These oxides contain more oxygen than would be expected from the oxidation number of M. Some are ionic and contain the peroxide anion O_2^{2-}, e.g., Na_2O_2 and BaO_2. Others are covalently bonded and contain –O–O– in the structure e.g., H_2O_2, H_2SO_5 and $H_2S_2O_8$.



Hydrogen peroxide

Peroxymonosulphuric acid

Peroxodisulphuric acid

Peroxo compounds are strong oxidising agents and are hydrolysed by water to give H_2O_2.

$$H_2SO_5 + H_2O \longrightarrow H_2SO_4 + H_2O_2$$

Superoxides e.g., KO_2, contain still more oxygen than would be expected.

Suboxides

These contain less oxygen than would be expected from the oxidation number of M.

They involve M–M bonds in addition to M–O bonds, for example carbon suboxide (O=C=C=C=O).

The oxides may also be classified as basic, acidic, amphoteric or neutral oxides depending on the products formed when they react with water.

Basic oxides

Metallic oxides are generally basic. The oxides of more electropositive metals having high lattice energy are ionic in nature e.g., Na_2O, MgO, La_2O_3 etc. These oxides have high melting points and when they react with water O^{2-} ion is converted into OH^- ion.

However many metal oxides with formulae M_2O_3 and MO_2 though ionic do not react with water e.g. Tl_2O_3, Bi_2O_3, ThO_2 etc. These oxides are also basic in nature because they react with acids to form salts.

Where a metal can exist in more than one oxidation slate and thus form more than one oxide e.g., CrO, Cr_2O_3, CrO_3, PbO, PbO_2, Sb_4O_6 and Sb_4O_{10}, the lowest oxidation state is the most ionic and the most basic. Thus, CrO is basic, Cr_2O_3 amphoteric and CrO_3 is acidic.

Amphoteric oxides

Many metals yield oxides, which are amphoteric and react with both strong acids and strong bases. This includes BeO, Al_2O_3, Ga_2O_3, SnO, PbO and ZnO.

$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3HO$$

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

$$PbO + 2HNO_3 \longrightarrow Pb(NO_3)_2 + H_2O$$

$$PbO + 2NaOH \longrightarrow Na_2PbO_2 + H_2O$$

Acidic oxides

Non–metal oxides are usually covalent compounds having low melting and boiling points. Many of them occur as discrete molecules e.g., CO_2, NO, SO_2, Cl_2O while some of them such as B_2O_3 and SiO_2 form infinite giant molecules having high melting points. They are all acidic. Many of them are anhydrides of acids.

$$B_2O_3 + 3H_2O \longrightarrow 2H_3BO_3$$

$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

N_2O_3 contains N(+III) and N_2O_5 contains N(+V). HNO_3 is a stronger acid than HNO_2.

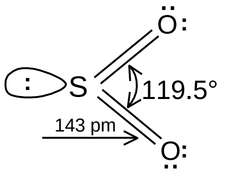
Neutral oxides

A few covalent oxides e.g., N_2O, NO and CO have neither acidic nor basic properties.

5.5.4 OXIDES OF SULPHUR, SELENIUM, TELLURIUM AND POLONIUM

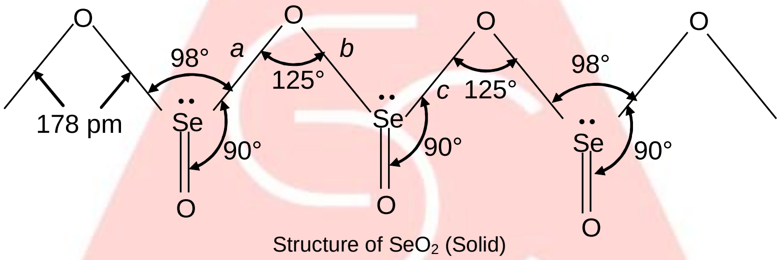
Dioxides

SO_2 being a discrete molecule exist in the gaseous state. Hybridisation of S in SO_2 in the gaseous state is sp^2 as shown in the figure. The double bond between sulphur and oxygen arises due to pπ–dπ overlap.



Structure of SO_2 in the gaseous state

Selenium and tellurium dioxides are solids having polymeric chain or layer structure. Structure of SeO_2 in the solid state is given in figure. It consists of a zig-zig chain. Hybridisation of Se in SeO_2 is sp^3. TeO_2 and PoO_2 are crystalline ionic solids.



Structure of SeO_2 (Solid)

Preparation of sulphur dioxide

(i) By roasting sulphides

$$\underset{\text{iron pyrite}}{4FeS_2} + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2(g)$$

(ii) By heating copper with concentrated H_2SO_4

$$Cu(s) + 2H_2SO_4\,(conc.) \xrightarrow{\text{heat}} CuSO_4 + 2H_2O + SO_2(g)$$

Properties of SO_2

Bleaching Action: Sulphur dioxide in presence of water, acts as a strong bleaching agent. In the presence of water, it reduced the colour matter to colourless product. Thus, it is used for bleaching coloured matter to colourless product. Thus, it is used for bleaching coloured wool, silk, sponges and straw. The bleaching action of sulphur dioxide in the presence of water is due to its reducing properties.

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + \underset{\text{nascent hydrogen}}{2H}$$

$$2H + X\text{ (coloured material)} \longrightarrow XH_2\text{ (colourless product)}$$

When the colourless product is allowed to stand in the air, it is reoxidised by the atmospheric oxygen to its original colour. So, bleaching with sulphur dioxide is temporary.

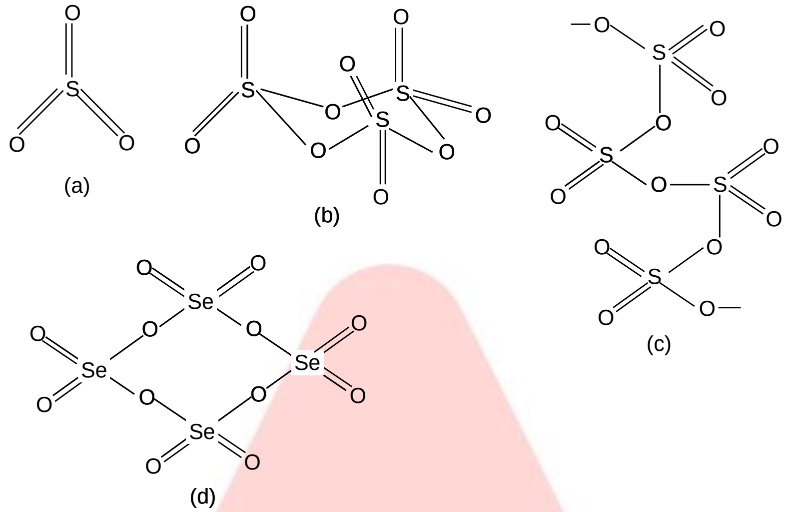
$$\text{Colourless vegetable product} + \underset{\text{from air}}{[O]} \longrightarrow \text{Coloured vegetable matter}$$

The bleaching action of chlorine, however, is due to its oxidising nature, and is permanent.

Trioxides

All the group 16 elements form trioxides, MO_3. Sulphur trioxide in the gas phase exists as planar triangular molecular species, although in the solid state it can exist as a linear chain or a cyclic trimer. Selenium trioxide (SeO_3) solid is a cyclic tetramer (Se_4O_{12}) as shown in figure. TeO_3 is a solid with a network structure in which TeO_6 octahedra share all vertices. SO_2 and SO_3 are the most important oxides from industrial point of view.

Structures of some oxides of sulphur and selenium are shown in figure.



Structures of (a) gaseous SO_3 (b) cyclic trimer of SO_3(s), (c) linear chain form of solid SO_3, and (d) cyclic tetrameric form of SeO_3(s)

Preparation of sulphur trioxide

Sulphur trioxide is prepared by the following method.

From SO_2: Sulphur trioxide is usually prepared in the laboratory by heating a mixture of sulphur dioxide and oxygen to about 450°C over platinised asbestos.

$$2SO_2(g) + O_2(g) \xrightarrow[450-500°C]{\text{Pt or } V_2O_5 \text{ catalyst}} 2SO_3(g)$$

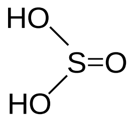
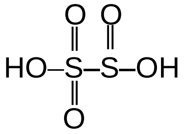
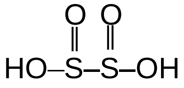
5.5.5 OXOACIDS OF SULPHUR

The oxoacids of sulphur are more numerous and more important than those of Se and Te. Many of the oxoacids of sulphur do not exist as free acids, but are known as anions and salts. Acids ending in –ous have S in the oxidation state (+IV), and form salts ending in –ite. Acids ending in –ic have S in the oxidation state (+VI) and form salts ending in –ate.

As discussed previously under bond lengths and pπ–dπ bonding, the oxoanions have strong π bonds and so they have little tendency to polymerise compared with the phosphates and silicates. To emphasize structural similarities the acids are listed in four series.

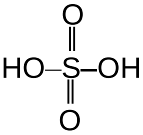
1. sulphurous acid series
2. sulphuric acid series
3. thionic acid series
4. peroxoacid series.

1. Sulphurous acid series

H_2SO_3 sulphurous acid		S(IV)
$H_2S_2O_5$ di- or pyrosulphurous acid	 $HO{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}\overset{\overset{O}{\|}}{S}{-}OH$	S(V), S(III)
$H_2S_2O_4$ dithionous acid	 $HO{-}\overset{\overset{O}{\|}}{S}{-}\overset{\overset{O}{\|}}{S}{-}OH$	S(III)

2. Sulphuric acid series

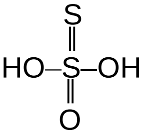
H_2SO_4 sulphuric acid



$$\mathrm{HO{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}OH}$$

S(VI)

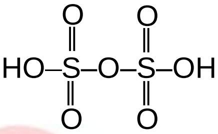
$H_2S_2O_3$ thiosulphuric acid



$$\mathrm{HO{-}\underset{\underset{O}{\|}}{\overset{\overset{S}{\|}}{S}}{-}OH}$$

S(VI),
S(–II)

$H_2S_2O_7$ di or pyrosulphuric acid

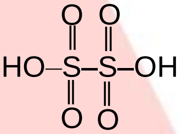


$$\mathrm{HO{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}O{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}OH}$$

S(VI)

3. Thionic acid series

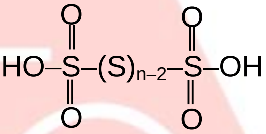
$H_2S_2O_6$ dithionic acid



$$\mathrm{HO{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}OH}$$

S(V)

$H_2S_nO_6$ polythionic acid
(n = 1 – 12)

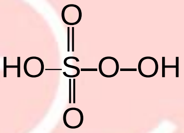


$$\mathrm{HO{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}(S)_{n-2}{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}OH}$$

S(V),
S(0)

4. Peroxoacid series

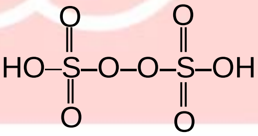
H_2SO_5 peroxomonosulphuric acid



$$\mathrm{HO{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}O{-}OH}$$

S(VI)

$H_2S_2O_8$ peroxodisulphuric acid



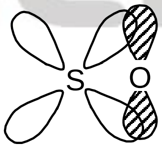
$$\mathrm{HO{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}O{-}O{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}OH}$$

S(VI)

Bond lengths and pπ–dπ bonding

The bonds between S and O, or Se and O, are much shorter than might be expected for a single bond. In some cases they may be formulated as localized double bonds. A σ bond is formed in the usual way. In addition a π bond is formed by the sideways overlap of a p–orbital on the oxygen with a d–orbital on the sulphur, giving a pπ–dπ interaction.

This pπ–dπ bonding is similar to that found in the oxides and oxoacids of phosphorous and is in contrast to the more common pπ–pπ type of double bond found in ethene.



pπ–dπ overlap

To obtain effective pπ–dπ overlap, the size of the d–orbital must be similar to the size of the p–orbital. Thus sulphur forms stronger π–bonds than the larger elements in the group. On crossing a period in the periodic table, the nuclear charge is increased and more s and p–electrons are added. Since these s and p–electrons shield the nuclear charge incompletely, the size of the atom and the size of the d–orbitals decreases from Si to P to S to Cl. The decrease in the size of the 3d–orbitals in this series of elements leads to progressively stronger pπ–dπ bonds. Thus, in the silicates there is hardly any pπ–dπ bonding. Thus, SiO_4 units polymerise into an enormous variety of structures linked by Si–O–Si σ–bonds. In the phosphates, π–bonding is stronger, but a large number of polymeric phosphates exist. In the oxoacids of sulphur, π–bonding is even stronger and has become a dominant factor. Thus, only a small amount of polymerization occurs and only a few polymeric compounds are known with S–O–S linkages. For chlorine, pπ–dπ bonding is so strong that no polymerization of oxoanions occurs.

In cases where there is more than one π bond in the molecule it may be more appropriate to explain the π bonding in terms of delocalized molecular orbitals covering several atoms.

Sulphuric acid, (H_2SO_4)

Manufacture of Sulphuric Acid by Contact Process

(i) Production of SO_2

Sulphur dioxide (SO_2) is obtained by burning sulphur or iron pyrites.

$$\underset{\text{sulphur}}{S} + O_2 \longrightarrow SO_2(g)$$

$$\underset{\text{iron pyrites}}{4FeS_2} + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2(g)$$

(ii) Catalytic oxidation of SO_2 to SO_3

Sulphur dioxide is oxidised by air in the presence of a catalyst to give sulphur trioxide.

$$2SO_2(g) + O_2(g) \overset{\text{catalyst}}{\rightleftharpoons} 2SO_3(g) \qquad \Delta H = -196.6\ kJ$$

(a) Air or oxygen required for the oxidation of sulphur dioxide must be in excess.

(b) The temperature must be low. A temperature between 350–450°C gives the maximum yield of the product.

(c) The pressure of about 2 atmospheres is used to carry out the above reaction.

(d) Platinised asbestos was used as a catalyst previously, but now-a-days it is replaced by must cheaper vanadium pentoxide (V_2O_5).

(e) The gases used (SO_2 and O_2) must be free of impurities, viz., dust particles, arsenious oxide etc., to prevent catalyst poisoning.

(iii) Conversion of sulphur trioxide into sulphuric acid. Sulphur trioxide is dissolved in concentrated sulphuric acid to produce oleum or fuming sulphuric acid.

$$SO_3(g) + \underset{\text{(conc.)}}{H_2SO_4} \longrightarrow \underset{\text{oleum}}{H_2S_2O_7}$$

(iv) Conversion of oleum to sulphuric acid

Oleum is diluted with a calculated amount of water to get sulphuric acid of desired concentration.

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

Chemical Properties of Sulphuric Acid

$$H_2SO_4 \xrightarrow{\Delta} H_2O + SO_3(g)$$

Reaction due to H^+:

$$NaOH + H_2SO_4 \longrightarrow \underset{\text{sodium hydrogen sulphate}}{NaHSO_4} + H_2O$$

Reaction due to sulphate ions:

$$BaCl_2(aq) + H_2SO_4(aq) \longrightarrow \underset{\text{barium sulphate}}{BaSO_4(s)} + 2HCl(aq)$$

$$(CH_3COO)_2Pb(aq) + H_2SO_4(aq) \longrightarrow \underset{\text{Lead sulphate}}{PbSO_4(s)} + 2CH_3COOH(aq)$$

Affinity for water

Charring of sugar is another example of dehydration by sulphuric acid.

$$\underset{\text{sugar}}{C_{12}H_{22}O_{11}} + H_2SO_4 \longrightarrow \underset{\text{brown}}{12C} + H_2SO_4.\ 11H_2O$$

$$\underset{\text{formic acid}}{HCOOH} + H_2SO_4 \longrightarrow CO + H_2SO_4.\ H_2O$$

$$\underset{\text{oxalic acid}}{(COOH)_2} + H_2SO_4 \longrightarrow CO + CO_2 + H_2SO_4.H_2O$$

Oxidising property

Hot concentrated sulphuric acid gives nascent oxygen and, therefore, acts as an oxidising agent.

$$H_2SO_4 \longrightarrow H_2O + SO_2 + \underset{\text{(nascent)}}{O}$$

$$2H_2SO_4 + C \longrightarrow 2SO_2 + 2H_2O + CO_2$$

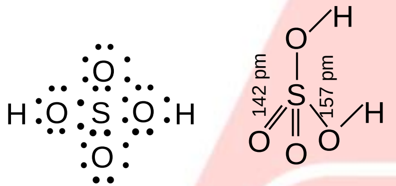
$$10H_2SO_4 + P_4 \longrightarrow 4H_3PO_4 + 10SO_2 + 4H_2O$$

$$H_2SO_4 + H_2S \longrightarrow 2H_2O + SO_2 + S$$

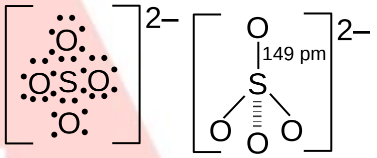
$$H_2SO_4 + 2HBr \longrightarrow 2H_2O + SO_2 + Br_2$$

$$2NaBr + 3H_2SO_4 \longrightarrow 2NaHSO_4 + 2H_2O + SO_2 + Br_2$$

Structure of Sulphuric acid and Sulphate ion



sulphuric acid



sulphate ion

5.5.6 SODIUM THIOSULPHATE $Na_2S_2O_3.5H_2O$ (Hypo)

Preparation:

(i) $Na_2SO_3 + S \xrightarrow{\text{Boil}} Na_2S_2O_3$

(ii) Springs reaction $Na_2S + I_2 + Na_2SO_3 \longrightarrow 2NaI + Na_2S_2O_3$

Reactions

(i) $\underset{\text{(efflorescent)}}{Na_2S_2O_3.5H_2O} \xrightarrow{215^\circ C} Na_2S_2O_3 + 5H_2O \xrightarrow{\Delta} Na_2SO_4 + Na_2S$

(ii) $Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + SO_2 + S + H_2O$

$Na_2S_2O_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + SO_2 + S$

(iii) $2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$

(iv) $Na_2S_2O_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2HCl + S$

(v) $2AgNO_3 + Na_2S_2O_3 \longrightarrow \underset{\text{White ppt}}{Ag_2S_2O_3} + 2NaNO_3$

$Ag_2S_2O_3 + H_2O \longrightarrow \underset{\text{Black ppt}}{Ag_2S} + H_2SO_4$

(vi) $AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$

(vii) $CuSO_4 + Na_2S_2O_3 \longrightarrow CuS_2O_3 + Na_2SO_4$

$2CuS_2O_3 + Na_2S_2O_3 \longrightarrow Cu_2S_2O_3 + Na_2S_4O_6$

$3Cu_2S_2O_3 + 2Na_2S_2O_3 \longrightarrow Na_4[Cu_6(S_2O_3)_5]$

6 THE GROUP – 17 ELEMENTS (HALOGEN FAMILY)

Fluorine (F), chlorine (Cl), Bromine (Br), Iodine (I) and astatine (At) are grouped together to form group 17 of the periodic table. Their salts are present in seawater and hence they are also known as **halogens** (Halos, in Greek, means sea salt producers). The group collectively is called **halogen family**.

The general electronic configuration of halogens is ns^2np^5. They are just one electron short of stable electronic configuration of inert gas elements. They have a very strong tendency to acquire stable configuration by accepting one electron. For this reason they exhibit non–metallic behaviour. Astatine, the last member of this group is a radioactive element with very short half–life.

6.1 GENERAL TRENDS IN PHYSICAL PROPERTIES

Some of the properties, of the elements of this group are given in the following table:

Element → **Property ↓**	**Fluorine**	**Chlorine**	**Bromine**	**Iodine**	**Astatine**
Covalent radius (pm)	72	99	114	113	–
Ionic radius (X^-) (pm	133	184	196	220	–
Ionisation energy (kJ mol^{-1})	1680	1256	1142	1008	–
Electronegativity	4.0	3.2	3.0	2.7	2.2
Melting point (K)	54.4	172	265.8	386.6	–
Boiling point (K)	84.9	239	332.5	458.2	–
Heat of dissociation $X_2 \longrightarrow 2X$, (kJ mol^{-1})	158.8	242.6	192.8	151.1	–

(i) Melting and boiling points

Melting and boiling points increase with the increase in atomic number. The enthalpy of fusion as well as enthalpy of vaporisation also increases as we go down the group. This indicates that the strength of intermolecular forces of attraction between the molecules increases with increase in atomic number.

(ii) Atomic and ionic radii

Atomic radii of the elements of this group are the smallest in their respective periods. Both the atomic radii and ionic radii for the anion X^- increase, regularly down the group because the electrons are added to higher and higher shells.

(iii) Ionisation energies

Ionisation energies of the all the halogens are very high. Therefore, they have very little tendency to loose electron. However, this tendency increases down the group because the nuclear force of attraction on valence electrons decreases. Iodine is capable of forming stable compounds in which it exists as I^+ ion.

(iv) Physical state

All the halogens are diatomic and exist as F_2, Cl_2, Br_2 and I_2. The intermolecular forces are very weak and their magnitude increases down the group. Thus, F_2, Cl_2 are gases, bromine is a volatile liquid and iodine is a volatile solid.

(v) Colour

Halogens are coloured. The colour of the halogen is due to absorption of certain wavelengths of visible light by their molecules resulting is the excitation of outer electron to higher energy orbitals. Fluorine being smaller in size absorbs shorter wavelengths corresponding to violet colour for excitation and appears pale yellow. Iodine on the other hand absorbs longer wavelengths corresponding to yellow colour for excitation and therefore appears violet. In between fluorine and iodine, the colour of chlorine is greenish yellow and of bromine is reddish brown. Thus, the colour deepens down the group.

(vi) Non–metallic character

All the halogens are non–metals because of their very high ionisation energies.

The non–metallic character, however, decreases with the increase in atomic number. Iodine shows some of the distinct metallic properties, e.g., it possesses metallic lustre and forms positive ions like I^+, I^{3+} etc.

(vii) Electron affinities

The halogens have strong tendency to accept electrons. Their electron affinities are highest in their respective periods. On moving down the group the electron affinity values generally decrease with the increase in size of the atom. The exception to this general rule is fluorine which has lower electron affinity than chlorine. It is due to the small size of fluorine atom, the incoming electron experiences repulsion due to existing electrons in the 2p subshell resulting in low value of electron affinity.

(viii) Oxidation states

The most common oxidation state of all the halogens is –1, as they attain stable configuration by accepting one electron. In fact this is the only oxidation state shown by fluorine because it is the most electronegative element known. Other elements of this group also show oxidation states of +1, +3, +5 and +7. Higher oxidation states of these elements are due to the presence of vacant and orbitals.

6.2 GENERAL TRENDS IN CHEMICAL PROPERTIES

All the halogens are very reactive and amongst them fluorine is the most reactive.

As we move down the group, reactivity decreases. This is due to the decrease in electronegativity.

In general, a halogen of low atomic number oxidises halide ions of higher atomic number i.e., F_2 displaces Cl_2, Br_2 and I_2 from their salts, Cl_2 displaces Br_2 and I_2 whereas Br_2 displaces I_2 from its salts.

$F_2 + 2X^- \longrightarrow 2F^- + X_2$ (X = Cl, Br, I)

$Cl_2 + 2X^- \longrightarrow 2Cl^- + X_2$ (X = Br, I)

$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$

6.3 FLUORINE

(a) Preparation of Fluorine

(i) Moisson's method

Materials for electrolytic bath: Alloy of Pt, Ir
Electrodes : Pt–Ir electrodes
Electrolyte: KHF_2 (1 part) + HF (5 part)
Temp. of the bath : –23°C

Reaction at the electrode:

$KHF_2 \longrightarrow KF + HF$

$KF \longrightarrow K^+ + F^-$

At cathode: $K^+ + e \longrightarrow K$

At anode: $F^- \longrightarrow F + e^-$

$2F \longrightarrow F_2\uparrow$

(ii) Dennis method

Electrolyte : KHF_2
Temperature : 240° – 250°C
Electrolytic cell : 'V' shaped copper tube
Electrode material : Graphite
Current : 5 (Amps)
Voltage : 12 volt

Reaction at the electrodes

$KHF_2 \longrightarrow KF + HF$

$KF \longrightarrow K^+ + F^-$

At cathode: $K^+ + e \longrightarrow K$ $2K + HF \longrightarrow 2KF + H_2\uparrow$

At anode : $2F^- - 2e \longrightarrow F_2$

(b) Properties

Physical properties

It is a pale greenish yellow gas having pungent odour and is highly poisonous. It is heavier than air. It is the most electronegative element (electronegativity 4.0) which condenses to yellow liquid at –188°C and yellow solid at –223°C.

Chemical properties

(i) It combines with most of the metals and non–metals to form fluorides.

$2Ag + F_2 \longrightarrow 2AgF$

$2Al + 3F_2 \longrightarrow 2AlF_3$

However, Cu does not appreciably react with F_2 due to deposition of CuF_2 layer. Hydrogen reacts violently with F_2 even in the dark

$H_2 + F_2 \longrightarrow H_2F_2$

Wood charcoal, phosphorus, arsenic, antimony, boron, silicon react with F_2 producing a flame.

$C + 2F_2 \longrightarrow CF_4$; $Si + 2F_2 \longrightarrow SiF_4$

$P_4 + 6F_2 \longrightarrow 4PF_3$; $2B + 3F_3 \longrightarrow 2BF_3$

(ii) Fluorine reacts vigorously with H_2O giving O_2 and O_3

$2H_2O + 2F_2 \longrightarrow 4HF + O_2$

$3H_2O + 3F_2 \longrightarrow 6HF + O_3$

(iii) Fluorine reacts with dilute alkali to form oxygen difluoride (OF_2) and with concentrated alkali to form O_2

$2NaOH + 2F_2 \longrightarrow OF_2 + 2NaF + H_2O$

$4NaOH + 2F_2 \longrightarrow 4NaF + 2H_2O + O_2$

(iv) It acts as a strong oxidising agent when it oxidises chlorates to perchlorates, iodates to periodates, bisulphates to peroxysulphates.

$$KClO_3 + F_2 + H_2O \longrightarrow KClO_4 + H_2F_2$$
$$KIO_3 + F_2 + H_2O \longrightarrow KIO_4 + H_2F_2$$
$$2NaHSO_4 + F_2 \longrightarrow Na_2S_2O_8 + H_2F_2$$

(iv) It attacks glass (SiO_2) at about 100°C. However dry F_2 reacts slowly.

$$SiO_2 + 2F_2 \longrightarrow SiF_4 + O_2$$

(vi) It reacts with NH_3 to form N_2 and H_2S burns in an atmosphere of F_2 to form SF_6

$$2NH_3 + 3F_2 \longrightarrow N_2 + 6HF$$
$$H_2S + 4F_2 \longrightarrow SF_6 + 2HF$$

6.4 CHLORINE

(a) Preparation of chlorine

1. Starting material

Powdered MnO_2 (Manganese dioxide) and concentrated HCl

Reaction: $2MnO_2 + 8HCl \longrightarrow 2MnCl_3 + Cl_2 + 4H_2O$

$$2MnCl_3 \longrightarrow 2MnCl_2 + Cl_2$$

$$\overline{2MnO_2 + 8HCl \longrightarrow 2MnCl_2 + 2Cl_2 + 4H_2O}$$

or, $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$

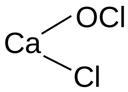
Chlorine thus produced becomes moisture free by passing through concentrated H_2SO_4

2. $2NaCl + 3H_2SO_4 + MnO_2 \longrightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + X_2$ (X = Cl, Br, I)

3. $K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$

4. $PbO_2 + 4HCl \longrightarrow PbCl_2 + Cl_2 + 2H_2O$

5. $2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 5Cl_2 + 8H_2O$

6. 

$Ca(OCl)Cl + 2HCl \longrightarrow CaCl_2 + Cl_2 + H_2O$

(b) Properties of Cl_2

Physical properties : Greenish yellow gas having a choking and irritating smell, 2.5 times heavier than air, liquefied to a yellow liquid by compressing it at 15°C. Electronegativity is 3.0 (Pauling's scale).

Chemical properties

(i) Arsenic catches fire in Cl_2 but P burns.

$$2As + 3Cl_2 \longrightarrow 2AsCl_3$$
$$2Sb + 3Cl_2 \longrightarrow 2SbCl_3$$
$$2P + 3Cl_2 \longrightarrow 2PCl_3$$
$$2P + 5Cl_2 \longrightarrow 2PCl_5$$

(ii) It reacts with water forming hydrochloric acid and hypochlorous acid. The chlorine water shows bleaching action due to oxidation by the nascent oxygen obtained by dissociation of hypochlorous acid.

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$
$$HOCl \longrightarrow HCl + [O]\uparrow$$

(iii) Cold and dilute solution of NaOH, KOH react with halogens Cl_2 , Br_2 , I_2 and producing hypohalites and halides. Concentrated, hot alkalies produce halides and halates with halogens Cl_2, Br_2 and I_2.

$$Cl_2 + 2NaOH \longrightarrow NaCl + \underset{\text{sodium hypochlorite}}{NaOCl} + H_2O$$

$$3Cl_2 + 6NaOH \longrightarrow 5NaCl + \underset{\text{sodium chlorate}}{NaClO_3} + 3H_2O$$

However, when chlorine is passed over dry slaked lime, bleaching powder is obtained

$$Ca(OH)_2 + Cl_2 \longrightarrow \underset{\text{Bleaching powder}}{Ca(OCl)Cl} + H_2O$$

(iv) Oxidation reactions of chlorine are:

$2CaO + 2Cl_2 \longrightarrow 2CaCl_2 + O_2\uparrow$

$8NH_3 + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$

(Excess)

$NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl$

(Excess)

$H_2S + Cl_2 \longrightarrow 2HCl + S$

Moist sulphur dioxide is oxidized to sulphuric acid

$SO_2 + Cl_2 + 2H_2O \longrightarrow 2HCl + H_2SO_4$

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

$2K_4[Fe(CN)_6] + Cl_2 \longrightarrow 2K_3[Fe(CN)_6] + 2KCl$

$2KBr + Cl_2 \longrightarrow 2KCl + Br_2$

$2KClO_3 + I_2 \longrightarrow 2KIO_3 + Cl_2\uparrow$

SO_2 bleaches by reduction as shown below:

$2H_2O + SO_2 \longrightarrow H_2SO_4 + 2[H]$

This is the main difference in bleaching action between Cl_2 and SO_2. Also bleaching by SO_2 is temporary but Cl_2 bleaches permanently.

$Ca(OCl)Cl + H_2SO_4 \longrightarrow CaSO_4 + CaCl_2 + 2HOCl$

$HOCl \longrightarrow HCl + [O]\uparrow$

$Ca(OCl)Cl + Na_3AsO_3 \longrightarrow Na_3AsO_4 + CaCl_2$

$Ca(OCl)Cl + 2FeSO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + CaCl_2 + H_2O$

(v) Addition reactions of chlorine are:

Chlorine reacts with SO_2, CO and unsaturated hydrocarbons forming addition products

$SO_2 + Cl_2 \longrightarrow SO_2Cl_2$

$CO + Cl_2 \longrightarrow COCl_2$(carbonyl chloride)

Phosgene

$CH_2{=}CH_2 + Cl_2 \longrightarrow CH_2Cl{-}CH_2Cl$

6.5 BROMINE

(a) Preparation of Bromine

Starting raw materials are

(i) KBr (ii) MnO_2 (iii) H_2SO_4 (concentrated)

$2KBr + MnO_2 + 3H_2SO_4 \longrightarrow 2KHSO_4 + MnSO_4 + Br_2\uparrow + 2H_2O$

This Br_2 is purified by distilling it over a mixture of KBr and ZnO.

(b) Properties of Br_2

Physical properties

It is a dark red, dense, heavy liquid at ordinary temperature, which boils at 59° C. And its vapours attack skin, eyes, nose and throat.

Chemical properties

Oxidising properties

$Br_2 + H_2S \longrightarrow 2HBr + S$

$Na_2SO_3 + Br_2 + H_2O \longrightarrow Na_2SO_4 + HBr + H_2SO_4$

$2HI + Br_2 \longrightarrow 2HBr + I_2$

$6FeSO_4 + 3Br_2 \longrightarrow Fe_2(SO_4)_3 + 2FeBr_3$

$8NH_3 + 3Br_2 \longrightarrow 6NH_4Br + N_2$

$KNO_2 + Br_2 + H_2O \longrightarrow 2HBr + KNO_3$

Change of red colour of Br_2 taken place when C_2H_2 or C_2H_4 (unsaturated compounds) are reacted with

$C_2H_4 + Br_2$ (red) $\longrightarrow C_2H_4Br_2$ (colourless)

Reducing properties

$Br_2 + 3F_2 \longrightarrow 2BrF_3$

$Br_2 + 5F_2 \longrightarrow 2BrF_5$

$Br_2 + Cl_2 \longrightarrow 2BrCl$

6.6 IODINE

(a) Preparation of I_2

1. Starting materials :

(i) KI (ii) MnO_2 (iii) concentrated H_2SO_4

Reaction: $(KI + H_2SO_4 \longrightarrow KHSO_4 + HI) \times 2$

$MnO_2 + H_2SO_4 \longrightarrow MnSO_4 + H_2O + O$

$2HI + O \longrightarrow H_2O + I_2$

$2KI + MnO_2 + 3H_2SO_4 \longrightarrow 2KHSO_4 + MnSO_4 + 2H_2O + I_2$

I_2 may be contaminated by ICl, IBr.
These are removed by KI by the following steps:

$ICl + KI \longrightarrow KCI + I_2$

$IBr + KI \longrightarrow KBr + I_2$

2. From chile saltpetre (caliche)

$2NaIO_3 + 5NaHSO_3 \longrightarrow 2Na_2SO_4 + 3NaHSO_4 + H_2O + I_2$

(b) Properties of I_2

Physical properties

It is a deep brown crystalline solid having specific gravity 4.9. It is almost insoluble in water but dissolves in non–aqueous solvents like chloroform and carbon tetrachloride.
However, it dissolves in an aqueous solution of potassium iodide because it reacts with KI forming KI_3

Chemical properties

Iodine reacts with non–metals like phosphorus, arsenic and antimony forming their respective tri–iodides.

$2P + 3I_2 \longrightarrow 2PI_3$

$2As + 3I_2 \longrightarrow 2AsI_3$

$2Sb + 3I_2 \longrightarrow 2SbI_3$

Burning of I_2 vapour takes place in the above reaction.

$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$

Oxidising properties

$KI + I_2 \longrightarrow KI_3$

$H_2S + I_2 \longrightarrow 2HI + S\downarrow$

Reducing properties

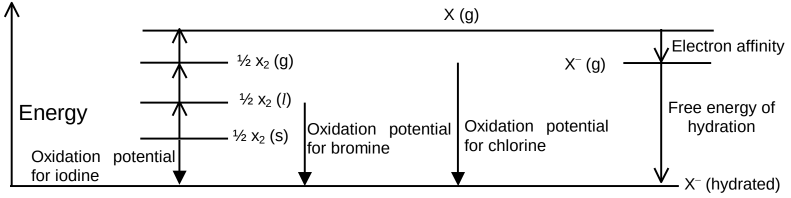
$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$

$I_2 + Cl_2 \longrightarrow 2ICl$

$I_2 + 3Cl_2 \longrightarrow 2ICl_3$

6.7 OXIDIZING POWER OF HALOGENS

Electron affinity is the tendency of the atoms to gain electrons. This reaches a maximum at chlorine. Oxidation may be regarded as the removal of electrons, so that an oxidizing agent gains electrons. Thus, the halogens act as oxidizing agents. The strength of an oxidizing agent (that is, its oxidation potential) depends on several energy terms and is best represented by a Born–Haber type of energy cycle. The oxidation potential is the energy change between the element in its standard state and in its hydrated ions. Thus, for iodine the change is from $I_{2(solid)}$ to $I^-_{(hydrated)}$. Thus the oxidation potential is equal to the sum of the energy put in as the enthalpies of fusion, evaporation and dissociation, less the energy evolved as the electron affinity and free energy of hydration.



In a similar cycle the oxidation potential for bromine can be calculated for the change from $\frac{1}{2}Br_{2(liquid)}$ to $Br^{-}_{(hydrated)}$. (Note that since in its standard state bromine is liquid, the free energy of fusion must be omitted. Similarly in calculating the oxidation potential for chlorine and fluorine, since they are gases, both the free energies of fusion and evaporation must be omitted).

Though the electron affinity of chlorine is the highest, it is not the strongest oxidizing agent. When all the terms in the energy cycle are summed, fluorine has the most negative ΔG° value, so fluorine is the strongest oxidizing agent. There are two main reasons for this:

1. F_2 has a low enthalpy of dissociation (arising from the weakness of the F–F bond).
2. F_2 has a high free energy of hydration (arising from the smaller size of the F^- ion).

Fluorine is a very strong oxidizing agent and it will replace Cl^- both in solution and also when dry. Similarly, chlorine gas will displace Br^- from solution. (This is the basis of the commercial extraction of bromine from sea water.) In general any halogen of low atomic number will oxidize halide ions of higher atomic number.

Iodine can replace Cl from $KClO_3$ because in ClO_3^-, Cl is in +7 oxidation state. Being strong electronegative element Cl cannot hold +7 oxidation state. Iodine being less electronegative it can hold the +7 charge very easily.

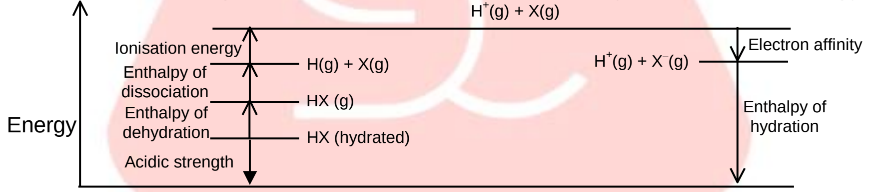
6.8 HALOGEN ACIDS

6.8.1 ACIDIC STRENGTH

It is at first paradoxical that HF is the weakest acid in water, since HF has a greater electronegativity difference than the other hydrides and therefore ahs more ionic character. However, acidic strength is the tendency of hydrated molecules to form hydrogen ions:

$$HX_{(hydrated)} \longrightarrow H^{+}_{(hydrated)} + X^{-}_{(hydrated)}$$

This may be represented in stages: dissociation, ionisation and hydration in an energy cycle.



The acid strength is equal to the sum of all the energy terms round the energy cycle in given above figure.

Acid strength = Free energy of dehydration
+ Free energy of dissociation
+ Ionisation energy of H^+
+ Electron affinity X^-
+ Free energy of hydration of H^+ and X^-

The factors, which make HF the weakest halogen acid in water, become apparent if the various thermodynamic terms are examined in more detail. The dissociation constant k for the change

$$HX_{(hydrated)} \rightleftharpoons H^{+}_{(hydrated)} + X^{-}_{(hydrated)}$$

is given by the equation:

$$\Delta G° = -RT \ln k$$

(where ΔG° is the Gibbs standard free energy, R the gas constant and T is absolute temperature). However, ΔG depends on the change in enthalpy ΔH and the change in entropy ΔS

$$\Delta G = \Delta H - T\Delta S$$

Consider first the total enthalpy change ΔH for the dissociation of $HX_{(hydrated)}$ into $H^{+}_{(hydrated)}$ and $X^{-}_{(hydrated)}$. The ΔH values for the various halogen acids are all negative, which means that energy, is evolved in the process, so the change is thermodynamically possible. However, the value for HF is small compared with the values for HCl, HBr and HI (which are all similar in magnitude). Thus, HF is only slightly exothermic in aqueous solution whereas the other evolve a considerable amount of heat.

The low total ΔH value for HF is the result of several factors.

1. The enthalpies of dissociation show that the H–F bond is much stronger than the H–Cl, H–Br or H–I bonds. Thus, the dissociation energy of HF is nearly twice that required to dissociate HI. (The strength of the HF bond is also shown by the short bond length of 1.0 Å compared with 1.7 Å in HI.
2. The heat of dehydration for the step $HX_{(hydrated)} \longrightarrow HX_{(gas)}$ is much higher for HF than for the others. This is because of the strong hydrogen bonding which occurs in aqueous HF solutions.
3. The unexpectedly low value for the electron affinity of F^- also contributes and though the enthalpy of hydration of F^- is very high, it is not enough to offset these other terms.

6.8.2 HYDROFLUORIC ACID (HF)

Chemical Properties:

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF\uparrow$$

HF etches glass. The reaction is

$$SiF_4 + 2HF \longrightarrow H_2SiF_6$$

Hence HF is stored in polythene coated bottle.

$$HF \rightleftharpoons H^+ + F^-$$

$$F^- + HF \rightleftharpoons HF_2^-$$

Conjugate base F^- bonds with HF by H–bonding thus statistically the effective number of molecules of H drops and registers acidity $K_a = 7.2 \times 10^{-4}$.

$$H_2F_2 + KOH \longrightarrow KHF_2 + H_2O$$

$$H_3BO_3 + 4HF \longrightarrow HBF_4 + 3H_2O$$

$$SiF_4 + 2HF \longrightarrow H_2SiF_6$$

$$BF_3 + HF \longrightarrow HBF_4$$

$$BaCl_2 + 2HF \longrightarrow BaF_2 + 2HCl$$

6.8.3 HYDROCHLORIC ACID

Preparation of HCl

Starting materials: NaCl, concentrated H_2SO_4 ; temperature ; 150°C

Reactions: $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl\uparrow$

$$NaCl + NaHSO_4 \longrightarrow Na_2SO_4 + HCl\uparrow$$

Purification of HCl is done by conc. H_2SO_4 not by CaO or P_2O_5 because both of them react with HCl.

Properties

Physical properties: Colourless gas with pungent smell. It is heavier than air, highly soluble in water.

Chemical properties

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2\uparrow + 2H_2O$$

$$PbO_2 + 4HCl \longrightarrow PbCl_2 + Cl_2\uparrow + 2H_2O$$

$$K_2Cr_2O_7 + 14HCl \xrightarrow{\text{ordinary test}} 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$$

$$2KMnO_4 + 16HCl \xrightarrow{\text{ordinary test}} 2KCl + 2MnCl_2 + 5Cl_2 + H_2O$$

$$AgNO_3 + HCl \longrightarrow \underset{\text{curdy white}}{AgCl\downarrow} + HNO_3$$

$$Hg_2(NO_3)_2 + 2HCl \longrightarrow \underset{\text{curdy white}}{Hg_2Cl_2\downarrow} + 2HNO_3$$

6.8.4 HYDROBROMIC ACID

Preparation of HBr :

$$\text{(Red) } 2P + 3Br_2 \longrightarrow 2PBr_3$$

$$PBr_3 + H_2O \longrightarrow HBr + H_3PO_3$$

Reaction of NaBr with H_2SO_4 does not give HBr because of the following reaction:

$$NaBr + H_2SO_4 \longrightarrow NaHSO_4 + HBr$$

$$H_2SO_4 \longrightarrow H_2O + SO_2 + O$$

$$2HBr + O \longrightarrow H_2O + Br_2\uparrow$$

Purification of HBr is done by $CaCl_2$ from moisture.

Properties:

HBr is colourless and having pungent odour shows the following reactions

$Zn + 2HBr \longrightarrow ZnBr_2 + H_2\uparrow$

$Na_2CO_3 + 2HBr \longrightarrow 2NaBr + CO_2 + H_2O$

$NaHCO_3 + HBr \longrightarrow NaBr + CO_2 + H_2O$

Reducing action:

$16HBr + 2KMnO_4 \longrightarrow 2KBr + 2MnBr_2 + 5Br_2 + 8H_2O$

$2HBr + H_2SO_4 \longrightarrow Br_2 + SO_2 + 2H_2O$

$K_2Cr_2O_7 + 14HBr \longrightarrow 2KBr + 2CrBr_3 + 3Br_2 + 7H_2O$

$HBr + O_2 \longrightarrow Br_2\uparrow + H_2O$

6.8.5 HYDROIODIC ACID

Preparation of HI:

1. $(\text{Red})\ 2P + 3I_2 + 6H_2O \longrightarrow 6HI + 2H_3PO_3$
2. $NaI + H_2SO_4 \longrightarrow NaHSO_4 + HI$
   $2HI + H_2SO_4 \longrightarrow I_2\uparrow + SO_2 + 2H_2O$
3. $SO_2 + 2H_2O + I_2 \longrightarrow H_2SO_4 + 2HI$
   $H_2SO_4 + BaI_2 \longrightarrow BaSO_4 + 2HI$

Chemical properties:

$4HI + O_2 \longrightarrow 2H_2O + I_2$

Reducing properties:

1. $2KMnO_4\uparrow + 3H_2SO_4 + 10HI \longrightarrow K_2SO_4 + 2MnSO_4 + 5I_2 + 8H_2O$
   Pink colourless
2. $K_2Cr_2O_7 + 6HI + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O$
3. $H_2O_2 + 2HI \longrightarrow 2H_2O + I_2$
4. $2HNO_3 + 2HI \longrightarrow I_2 + H_2 + 2H_2O + 2NO_2$
5. $2FeCl_3 + 2HI \longrightarrow 2FeCl_2 + 2HCl + I_2$
6. $2CuSO_4 + 4HI \longrightarrow Cu_2I_2 + 2H_2SO_4 + I_2$
7. $Pb(CH_3COO)_2 + 2HI \longrightarrow PbI_2\downarrow + 2CH_3COOH$

Reaction with KI in acid medium gives the detection test I^-.

$2KI + 2H_2SO_4 \longrightarrow K_2SO_4 + SO_2 + I_2 + 2H_2O$

Reducing Property of hydrogen halides

The stability of hydrogen halides decreases as we move down the group. The reducing property is in the order HF < HCl < HBr < HI. The ease of oxidation of halide ion is expected to increase in the order of increasing size of the halide ions F^-, Cl^-, Br^- and I^-. The electron to be removed from F^- is very near to nucleus and therefore it is most difficult to remove and easy for I^-. Therefore, HI should be strong reducing agent.

6.9 STRENGTH OF THE OXOACIDS

$HClO_4$ is an extremely strong acid, whilst HOCl is very weak acid. The dissociation of an oxoacids involves two energy terms:

1. Breaking an O–H bond to produce a hydrogen ion and an anion.
2. Hydrating both ions

Plainly the ClO_4^- ion is larger than the OCl^- ion, so the hydration energy of ClO_4^- is less than that of OCl^-. This would suggest that HOCl should ionise more readily than $HClO_4$. Since, we know the reverse to be true, the reason must be the energy required to break the O–H bond.

Oxygen is more electronegative than chlorine. In the series of oxoacids HOCl, $HClO_2$, $HClO_3$, $HClO_4$, an increasing number of oxygen atoms are bonded to the chlorine atom. The more oxygen atoms that are bonded, the more the electrons will be pulled away from the O–H bond and the more this bond will be weakened. Thus, $HClO_4$ requires the least energy to break the O–H bond and form H^+. Hence, $HClO_4$ is the strongest acid. In general, for any series of oxoacids, the acid with the most oxygen (that is the one with the highest oxidation number) is the most dissociated. Thus, the acid strengths decreases in the order $HClO_4 > HClO_3 > HClO_2 > HOCl$. In exactly the same way, H_2SO_4 is a stronger acid than H_2SO_3 and

HNO_3 is a stronger acid than HNO_2.

6.10 PSEUDOHALOGENS AND PSEUDOHALIDES

A few ions are known, consisting of two or more atoms of which at least one is N, that have properties similar to those of the halide ions. They are therefore called pseudohalide ions. Pseudohalide ions are univalent, and these form salts resembling the halide salts. For example, the sodium salts are soluble in water, but the silver salts are insoluble. The hydrogen compounds are acids like the halogen acids HX. Some of the pseudohalide ions combine to form dimmers comparable with the halogen molecules X_2. These include cyanogens $(CN)_2$, thiocyanogen $(SCN)_2$ and selenocyanogen $(SeCN)_2$.

Anion		Acid		Dimer	
CN^-	cyanide ion	HCN	hydrogen cyanide	$(CN)_2$	cyanogen
SCN^-	thiocyanate ion	HSCN	thiocyanic acid	$(SCN)_2$	thiocyanogen
$SeCN^-$	selenocyanate ion		$(SeCN)_2$		selenocyanogen
OCN^-	cyanate ion	HOCN	cyanic acid		
NCN^{2-}	cyanamide ion	H_2NCN	cyanamide		
N_3^-	azide ion	HN_3	hydrogen azide		

The best known pseudohalide is CN^{-1}. This resembles Cl^{-1}, Br^- and I^- in the following respects.

1. It forms an acid HCN.
2. It can be oxidized to form a molecule cyanogen $(CN)_2$.
3. It forms insoluble salts with Ag^+, Pb^{2+} and Hg^+.
4. Interpseudohalogen compounds ClCN, BrCN and ICN can be formed.
5. AgCN is insoluble in water but soluble in ammonia, as is AgCl.
6. It forms a large number of complexes similar to halide complexes, e.g. $[Cu(CN)_4]^{2-}$ and $[CuCl_4]^{2-}$ and $[Co(CN)_6]^{3-}$ and $[CoCl_6]^{3-}$

6.11 INTERHALOGEN COMPOUNDS

We know that halogen atoms have different electronegativity. Due to this difference in electronegativity the halogen atoms combine with each other and give rise to the formation of binary covalent compounds, which are called interhalogen compounds. These compounds are of four types: (i) AB type (+1), e.g. ClF, BrF, IF (detected spectroscopically), BrCl, ICl, IBr (ii) AB_3 type (+3), e.g. ClF_3, BrF_3, IF_3, ICl_3 (iii) AB_5 type (+5), e.g. ClF_5, BrF_5, IF_5 (iv) AB_7 type (+7), e.g. IF_7. The number given in the bracket indicates the oxidation number of A atom. A halogen atom is larger than B halogen atom, i.e. A atom is less electronegative than B atom. In interhalogen compounds, the halogen atoms having less electronegativity show positive oxidation state. It is for this reason that interhalogen compounds are named as the halides of less electronegative halogen atom. Thus ClF is called chlorine monofluoride and not fluorine monochloride, since the electronegativity of Cl atom is less than that of F atom.

Halogen atom A acts as the central atom with which odd number of B atoms are covalently bonded. The central atom A may be Cl, Br or I but never F, since F atom seldom achieves a positive oxidation state and also it can not expand its coordination number beyond 4.

With the exception of BrCl, ICl, IBr and ICl_3 all the remaining interhalogen compounds are halogen fluorides. Greater is the electronegativity difference, $(x_F - x_A)$ (A may be I or Br), greater is the number of fluorides given by atom A. For example iodine $(x_F - x_I = 4.0 - 2.5 = 1.5)$ gives four fluorides viz. IF, IF_3, IF_5, and IF_7 while Br atom $(x_F - x_{Br} = 4.0 - 2.8 = 1.2)$ gives only three fluorides namely BrF, BrF_3 and BrF_5. The formation of three fluorides by Cl-atom $(x_F - x_{Cl} = 4.0 - 3.0 = 1.0)$ is taken to be an exception. Actually Cl-atom should give less than three fluorides.

It has not been possible to prepare the inter-halogen compounds containing more than two halogen atoms (ternary inter-halogen compounds). The non-formation of ternary interhalogen compounds is due to the fact that these compounds so formed get decomposed into a mixture of stable binary interhalogen compounds and/or elemental halogens. Polyhalides such as MIBrF, MIClBr, $MIFCl_3$ etc, which contain three different halogen atoms have, how ever, been prepared.

General Methods of preparation

Following are the important general methods by which interhalogen compounds can be prepared.

(i) By the direct combination of halogens

All the interhalogens, except IF_7, can be prepared by the direct combination of the halogens under appropriate conditions. The following examples are noteworthy. For the preparation of AB_3 and AB_5 interhalogen compounds excess of halogen atom must be used in the reaction mixture.

$Cl_2 + F_2 \text{ (equal volumes) } \xrightarrow{250°} 2ClF$
$Cl_2 + 3F_2 \text{ (excess) } \xrightarrow{250°} 2ClF_3$
$I_2 + Cl_2 \text{ (liquid) (in equimolecular amount) } \rightarrow 2ICl$
$I_2 + 3Cl_2 \text{ (liquid and in excess) } \longrightarrow 2ICl_3$
$Br_2 \text{ (vapour) } + 3F_2 \text{ (diluted with } N_2) \longrightarrow 2BrF_3$
$I_2 + 3F_2 \text{ (in freon) } \xrightarrow{-78°C} 2IF_3$
$Br_2 + 5F_2 \text{ (excess) } \longrightarrow 2BrF_5$

(ii) From lower interhalogens

Higher interhalogens can be prepared by the interaction of lower interhalogens with halogens. This method is particularly used for the preparation of halogen fluorides. The following examples illustrate the method.

$ClF + F_2 \longrightarrow ClF_3$
$ClF_3 + F_2 \text{ (excess) } \xrightarrow{350°} CIF_5$
$BrF_3 + F_2 \text{ (excess) } \xrightarrow{200°} BrF_5$
$IF_5 + F_2 \xrightarrow{270°} IF_7$

(iii) Miscellaneous methods

Some miscellaneous methods have been illustrated by the following examples.

$6HCl + KIO_3 + 2KI \longrightarrow 2KCl + 3H_2O + 3ICl$
$Cl_2 + CIF_3 \xrightarrow{250–350°} 3CIF$
$KCl + 3F_2 \xrightarrow{200°} KF + ClF_5$
$3I_2 + 5AgF \longrightarrow 5AgI + IF_5$
$8F_2 + PbI_2 \longrightarrow PbF_2 + 2IF_7$

General Properties

(i) Physical state

The interhalogen compounds may be covalent gases (e.g. CIF, BrF, CIF_3, IF_7), liquids (e.g. BrF_3, BrF_5) or solids (e.g. ICl, IBr, IF_3, ICl_3).

(ii) Colour

Although many of the interhalogen compounds containing fluorine are colourless, yet those made up of heavier halogens are coloured. The colour becomes deeper with the increase of the molecular weight of the compound. In this behaviour these compounds resemble the halogens themselves.

(iii) Dimagnetic nature

Since all the valence electrons in interhalogen compounds are present as bonding or non-bonding (i.e., lone pairs) electron pairs, these compounds are diamagnetic in nature.

(iv) Heats of formation

All these compounds have low heats of formation. For example, these values for IBr and BrCl are –2.5 and –0.34 kcal/mole respectively. These are extremely volatile compounds. In general compounds containing fluorine are more volatile than those containing chlorine, bromine or iodine.

(v) Boiling points

For each type of interhalogen compounds, the boiling points increase with the increase in the electronegativity difference between *A* and *B* atoms.

(vi) Thermal stability

Thermal stability of AB type interhalogen compounds decreases with the decrease in electronegativity difference between A and B atoms. Thus the order of stability of some AB compounds is as

IF (=1.5) > BrF (1.2) > CIF (1.0) > ICI (0.5) > IBr (0.3) > BrCl(0.2)

In parentheses are given the electronegativity difference between A and B atoms.

The above order is also explained by saying that greater is the difference between the electronegativity values of A and B, the more polar is the A–B bond and hence greater is the thermal stability of AB compound.

(vii) Reactivity

AB type compounds are more reactive than A_2 and B_2 molecules, since A–B bond in AB compounds is weaker than A–A and B–B bonds in A_2 and B_2 molecules respectively. Thus AB type compounds convert the metals into a mixture of two halides. For example

$ICl + 2Na \longrightarrow NaI + NaCl$

The order of reactivity of some interhalogen compounds has been found as $ClF_3 > BrF_3 > IF_7 > BrF_5 > BrF$.

(viii) Hydrolysis

Hydrolysis gives halogen acid and oxy-halogen acid. The oxy-halogen acid is of larger (i.e., central) halogen atom. Examples are

$BrCl + H_2O \longrightarrow HCl$ (halogen acid) + HOBr (oxy–halogen acid)

$ICl + H_2O \longrightarrow HCl + HIO$

$ICl_3 + 2H_2O \longrightarrow 3HCl + HIO_2$

$IF_5 + 3H_2O \longrightarrow 5HF + HIO_3$

$BrF_5 + 3H_2O \longrightarrow 5HF + HBrO_3$

$IF_7 + 6H_2O \longrightarrow 7HF + H_5IO_6$

It may be noted that the oxidation state of A atom does not change during hydrolysis.

(ix) Reaction with non-metallic and metallic oxides

Non–metallic and metallic oxides are fluorinated by halogen fluorides to give the corresponding fluorides.

$4BrF_3 + 3SiO_2 \longrightarrow 3SiF_4 + 2Br_2 + 3O_2$

$4BrF_3 + 2WO_3 \longrightarrow 2WF_6 + 2Br_2 + 3O_2$

(x) Addition reactions

The diatomic interhalogens (AB type compounds) add at olefinic double bond sites.

$–CH = CH– + ICl \longrightarrow –CHI–CHCl–$

$CH_2 = CH_2 + BrCl \longrightarrow CH_2Br–CH_2Cl$

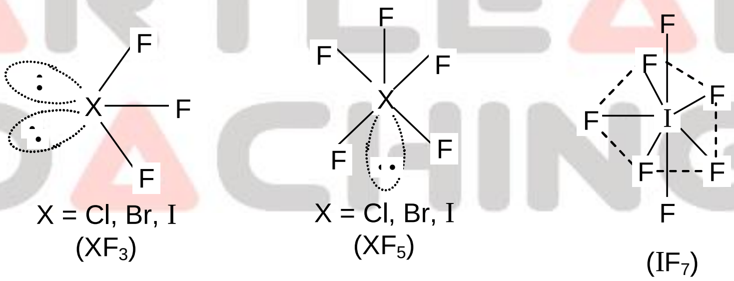
(xi) Reaction with alkali metal halides:

Reaction with alkali metal halides gives polyhalides like $NaIBr_2$, $CsIBrCl$, $KICl_4$ etc.

$IBr + NaBr \longrightarrow NaIBr_2$; $ICl + KCl \longrightarrow KICl_2$

$BrCl + CsI \longrightarrow CsIBrCl$; $ICl_3 + KCl \longrightarrow KICl_4$

The molecular structures of interhalogen compounds are very interesting and can be explained on the basis of VSEPR theory. The structure of some of these compounds are shown below.

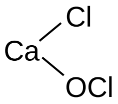


Hybridisation of X:	sp^3d	sp^3d^2	sp^3d^3
Geometry	T–shaped	square pyramidal	pentagonal bipyramidal

Structures of some interhalogen compounds

6.12 BLEACHING POWDER ($CaOCl_2.H_2O$)

Bleaching powder is also called calcium chlorohypochlorite because it is considered as a mixed salt of hydrochloric acid and hypochlorous acid.



Preparation:

$$Ca(OH)_2 + Cl_2 \xrightarrow{40^{o}C} Ca(OCl)Cl + H_2O$$

Properties

(a) It is a pale yellow powder. It has a strong smell of chlorine. It is soluble in water but a clear solution is never formed due to the presence of impurities.

(b) On long standing, it undergoes auto–oxidation into calcium chlorate and calcium chloride.

$$6CaOCl_2 \longrightarrow Ca(ClO_3)_2 + 5CaCl_2$$

(c) $2CaOCl_2 \xrightarrow{CoCl_2} 2CaCl_2 + O_2$

(d) In presence of a slight amount of a dilute acid, it loses oxygen.

$$2CaOCl_2 + H_2SO_4 \longrightarrow CaCl_2 + CaSO_4 + 2HClO$$

$$HClO \longrightarrow HCl + O$$

On account of the formation of nascent oxygen, it shows oxidising and bleaching properties.

(i) Oxidising properties

$$CaOCl_2 + H_2S \longrightarrow CaCl_2 + H_2O + S$$

$$CaOCl_2 + 2FeSO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + CaCl_2 + H_2O$$

$$CaOCl_2 + KNO_2 \longrightarrow CaCl_2 + KNO_3$$

$$3CaOCl_2 + 2NH_3 \longrightarrow 3CaCl_2 + 3H_2O + N_2$$

$$CaOCl_2 + 2KI + 2HCl \longrightarrow CaCl_2 + 2KCl + H_2O + I_2$$

$$Na_2AsO_3 + CaOCl_2 \longrightarrow CaCl_2 + Na_3AsO_4$$

(ii) Bleaching action

Coloured matter +[O] ⟶ colourless product.

(e) It loses its chlorine by the action of dilute acids (in excess) or CO_2.

$$CaOCl_2 + 2HCl \longrightarrow CaCl_2 + H_2O + Cl_2$$

$$CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_2$$

$$CaOCl_2 + CO_2 \longrightarrow CaCO_3 + Cl_2$$

The amount of chlorine obtained from a sample of bleaching powder by treatment with excess of dilute acids or CO_2 is called available chlorine. A good sample of bleaching powder contains 35–38% of available chlorine.

(f) Bleaching powder converts acetone or ethyl alcohol into $CHCl_3$

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

$$CH_3COCH_3 + 3Cl_2 \longrightarrow CCl_3COCH_3 + 3HCl$$

$$2CCl_3COCH_3 + Ca(OH)_2 \longrightarrow (CH_3COO)_2Ca + 2CHCl_3$$

7 THE GROUP – 18 ELEMENTS

The elements helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn) belong to group 18 of the periodic table. All these elements are gaseous under ordinary conditions of temperature and pressure. The last member of the group i.e. radon is obtained from radioactive disintegration of radium. All others are present in air in traces. They are also known as ***rare gases*** because they are found in very small amounts in nature. They are highly non–reactive and baring few exceptions, they don't take part in chemical reactions and are therefore, called ***inert gases*** or ***noble gases***. They always occur in free state because of the inert nature.

The valence shell electronic configuration of helium is $1s^2$ and for other members of this group is ns^2np^6. Thus, except helium, other noble gases have a closed octet of electrons in their outermost shell. This electronic configuration is very stable and is related to their chemical inertness.

Their physical properties show a regular gradation. Some of the physical properties are given in the following table:

Elements	Ionisation	Density at STP	Melting point	Boiling point (K)

	energy (kJ mol^{-1})	(g cm^{-3})	(K)	
Helium	2373	1.8×10^{-4}	–	4.2
Neon	2080	9.0×10^{-4}	24.6	27.1
Argon	1520	1.8×10^{-3}	83.8	87.2
Krypton	1351	3.7×10^{-3}	115.9	119.7
Xenon	1170	5.9×10^{-3}	161.3	165.0
Radon	1037	9.7×10^{-3}	202	211

7.1 GENERAL TRENDS IN PHYSICAL PROPERTIES

(i) State

All of them are mono atomic, colourless, odourless and tasteless gases.

(ii) Solubility

They are sparingly soluble in water. The solubility generally increases with increase in atomic number.

(iii) Boiling point and melting point

Due to weak intermolecular vander Waal's forces between them they possess very low boiling point and melting point in comparison to those of other substances of comparable atomic and molecular masses. However, the boiling point and melting point increase with increase in atomic number because vander Waal's forces become stronger with increase in size of the atoms or molecules. Therefore, among noble gases radon has the highest melting point and boiling point whereas helium has the least melting point and boiling point.

(iv) Liquefication

It is extremely difficult to liquefy these gases as there are only weak vander Waal's forces which hold atoms together. Since these forces increase with the increase in atomic size and population of electrons, ease of liquefication increases down the group from He to Rn.

(v) Atomic radii

It the case of noble gases, the atomic radii corresponds to vander Waal's radii. Therefore, these are quite large as compared with atomic radii of the other atoms belonging to the same period. As we go down the group, the vander Waal's radius increases due to the addition of new electronic shells and increase in screening effect.

(vi) Ionisation energies

The ionisation energies of noble gases are very high. This is due to the stable configurations of noble gases. However, the ionisation energies decrease with increase in atomic number from He to Rn due to increasing atomic size and decrease in effective nuclear charge.

(vii) Electron affinities

Due to the stable ns^2np^6 electronic configurations, noble gas atoms have no tendency to accept additional electron. Therefore, their electron affinities are almost zero.

(viii) Enthalpy of fusion and enthalpy of vapourization

In general, the enthalpies of fusion and the enthalpies of vaporization are low and increase down the group.

7.2 CHEMICAL PROPERTIES

The noble gases are generally inert and do not participate in chemical reactions due to

(i) very low electron affinities,
(ii) exceptionally high ionisation energies and
(iii) stable electronic configuration.

Prior to 1962, it was thought that the noble gases do not combine at all with other elements. However, in 1962 N. Barttlet used the highly oxidising compound PtF_6 to oxidise O_2.

$$O_2 + PtF_6 \longrightarrow O_2^+[PtF_6^-]$$

Moreover, the first ionisation energy for $O_2 \longrightarrow O_2^+$ is 1165 kJ mol^{-1} which is almost the same as the value of 1170 kJ mol^{-1} for $Xe \longrightarrow Xe^+$. It was predicted that xenon should react with PtF_6 in an analogous manner. Experiments revealed that when deep red PtF_6 vapour was mixed with equal volume of xenon, the gases combined immediately at room temperature to produce a yellow solid. Initially the yellow solid was wrongly formulated

as $Xe^+PtF_6^-$. Subsequently, it was found that the reaction is more complicated and the product was actually $[XeF]^+ [Pt_2F_{11}]^-$.

$$Xe + 2PtF_6 \longrightarrow [XeF]^+ [Pt_2F_{11}]^-$$

Once the reactivity of xenon was established, many more attempts were made to synthesize other compounds of noble gases. Now, many compounds of xenon and krypton are known with the fluorine and oxygen. The compounds of krypton are fewer, only the difluoride, KrF_2, has been synthesised. Compounds of He, Ne and Ar are not known. However, compounds of radon have been identified by radiotracer techniques but not isolated so far.

7.3 COMPOUNDS OF XENON: FLUORIDES, OXIDES AND OXOFLUORIDES

Xenon reacts directly only with F_2 forming three fluorides namely, XeF_2, XeF_4 and XeF_6. These can be obtained by the direct combination of xenon and fluorine at 400°C in a sealed nickel vessel and the products depend on the Xe/F_2 molar ratio.

$$Xe + F_2 \xrightarrow[400^oC]{\text{Ni tube}} XeF_2$$

(2 : 1)

$$Xe + 2F_2 \xrightarrow[\text{5–6 atm}]{\text{Ni tube, }400^oC} XeF_4$$

(1 : 5)

$$Xe + 3F_2 \xrightarrow[\text{50–60 atm}]{\text{Ni tube, }400^oC} XeF_6$$

(1 : 20)

The compounds XeF_2, XeF_4 and XeF_6 are all white solids, which sublime at room temperature. The lower fluorides form higher fluorides when heated with F_2 under pressure. They are extremely strong oxidising and fluorinating agents.

(i) They react quantitatively with hydrogen as follows

$$XeF_2 + H_2 \longrightarrow 2HF + Xe$$
$$XeF_4 + 2H_2 \longrightarrow 4HF + Xe$$

(ii) They oxidize Cl^- to Cl_2, I^- to I_2 and cerium(III) to cerium(IV)

$$XeF_2 + 2HCl \longrightarrow 2HF + Xe + Cl_2$$
$$XeF_4 + 4KI \longrightarrow 4KF + Xe + 2I_2$$
$$SO_4^{2-} + XeF_2 + Ce_2^{III}(SO_4)_3 \longrightarrow 2Ce^{IV}(SO_4)_2 + Xe + F_2$$

(iii) They fluorinate compounds:

$$XeF_4 + 2SF_4 \longrightarrow Xe + 2SF_6$$
$$XeF_4 + Pt \longrightarrow Xe + PtF_4$$

(iv) The fluorides differ in their reactivity with water. XeF_2 in soluble in water, but undergoes slow hydrolysis. Hydrolysis is more rapid with alkali.

$$2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$$

XeF_4 reacts violently with water, giving xenon trioxide XeO_3.

$$3XeF_4 + 6H_2O \longrightarrow 2Xe + XeO_3 + 12HF + 1\tfrac{1}{2}O_2$$

XeF_6 also reacts violently with water, but slow hydrolysis by atmospheric moisture gives the highly explosive solid XeO_3.

$$XeF_6 + 6H_2O \longrightarrow XeO_3 + 6HF$$

With small quantities of water, partial hydrolysis occurs, giving a colourless liquid xenon oxofluoride $XeOF_4$. The same product is formed when XeF_6 reacts with silica or glass:

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

$$2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$$

(v) XeO_3 is an explosive white hygroscopic solid. It reacts with XeF_6 and $XeOF_4$.

$$XeO_3 + 2XeF_6 \longrightarrow 3XeOF_4$$

$$XeO_3 + XeOF_4 \longrightarrow 2XeO_2F_2$$

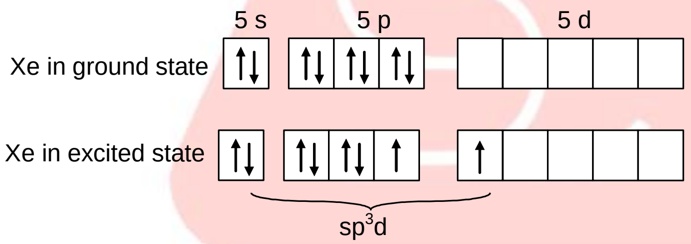
XeO_3 is soluble in water, but does not ionize. However, in alkaline solution above pH 10.5 it forms the xenate ion $[HXeO_4]^-$

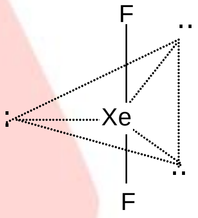
$$XeO_3 + NaOH \longrightarrow \underset{\text{Sodium xenate}}{Na^+ [HXeO_4]^-}$$

7.4 STRUCTURE AND BONDING

7.4.1 XENON DIFLUORIDE (XeF_2)

XeF_2 is a linear molecule F – Xe – F. Valence bond representation of XeF_2 may be explained, if one of the 5p electrons is promoted to the 5d orbital.





The structure of XeF_2

One 5s, three 5p and one 5d atomic orbitals hybridise to give five sp^3d hybridised orbitals. The two orbitals, which are singly occupied are used by two fluorine atoms to form bonds with xenon and the rest of the three are occupied by the lone pairs as shown.

7.4.2 XENON TETRAFLUORIDE (XeF_4)

$$Xe + 2F_2 \xrightarrow{400^\circ C,\ 5-6\ atm.} XeF_4$$

It reacts violently with water

$$3XeF_4 + 6H_2O \longrightarrow 2Xe + XeO_3 + 12HF + 3/2\ O_2$$

7.4.3 XENON HEXAFLUORIDE (XeF_6)

$$XeF_4 + O_2F_2 \xrightarrow{-130^\circ C} XeF_6 + O_2(g)$$

Properties

It is white solid, which sublimes at room temperature. It melts at 49.5°C to give yellow liquid.

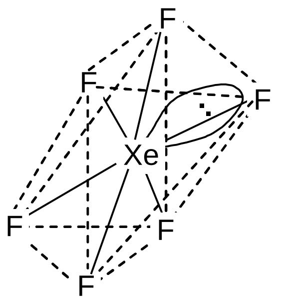
$$2XeF_6 + 3SiO_2 \longrightarrow 3SiF_4 + 2XeO_3$$

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

$$2XeF_6 \xrightarrow{\Delta} XeF_2 + XeF_4 + 3F_2$$

Structure of XeF_6

The Lewis structure of XeF_6 is given in figure. Xe uses six of its valence electrons in forming six σ-bonds with six F-atoms, while the remaining two electrons form a lone-pair. To accommodate, 7 electron-pair, therefore, Xe should exhibit sp^3d^3 hybridisation as shown below.



Structure of XeF_6: distorted octahedral

7.4.4 XENON TRIOXIDE (XeO_3)

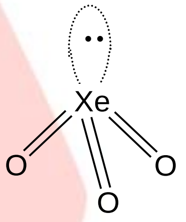
Xenon trioxide (XeO_3) may be prepared by the hydrolysis of XeF_4 or XeF_6.

$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$

$6XeF_4 + 12H_2O \longrightarrow 2XeO_3 + 4Xe + 3O_2 + 24HF$

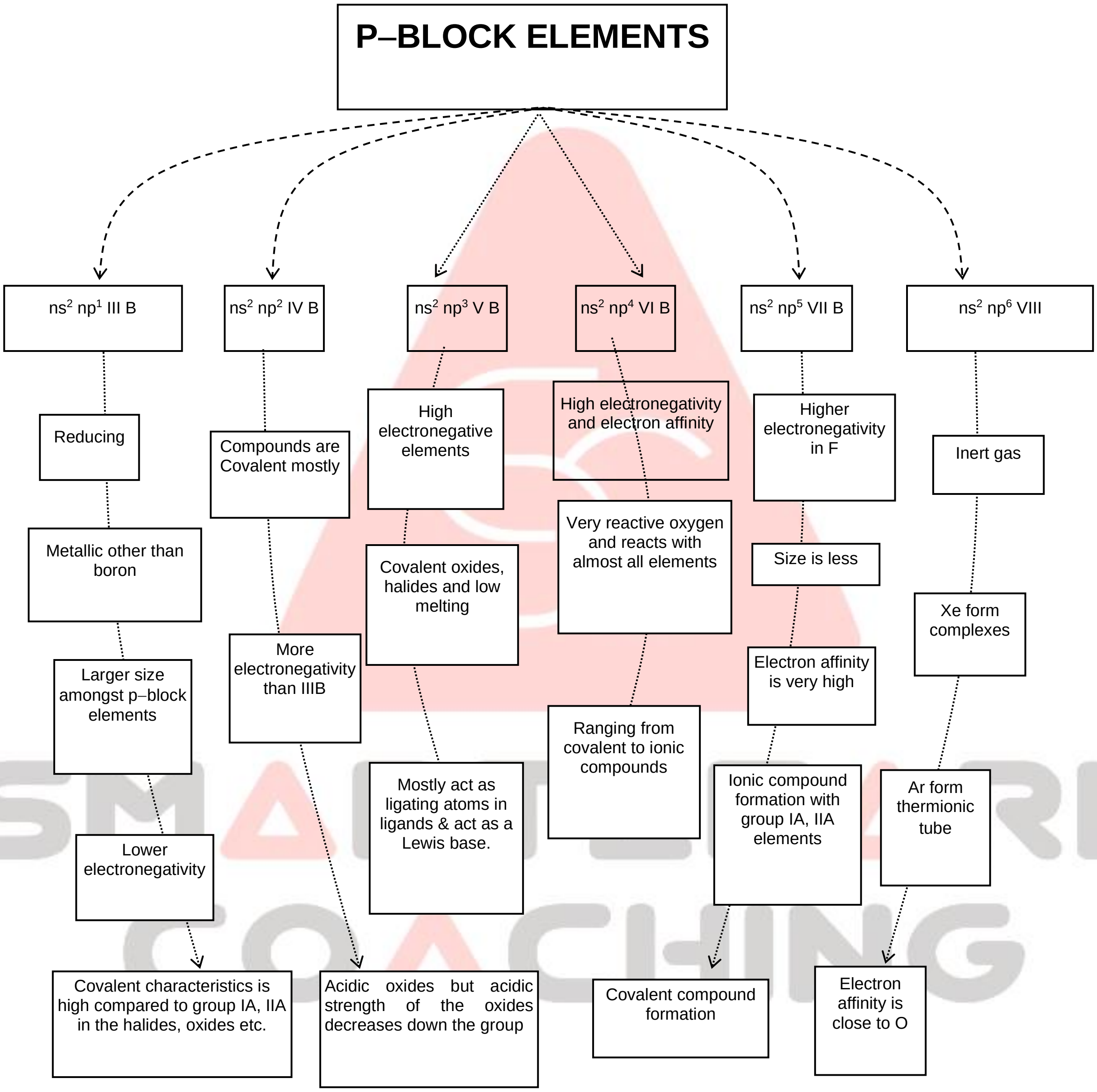
Structure of XeO_3

In XeO_3 , Xe exhibits sp^3 hybridisation. One of the hybrid orbitals is occupied by a lone pair, while other three are involved in the bond formation. This leads to a trigonal pyramidal structure of XeO_3.



Structure of XeO_3 (trigonal pyramidal)

MIND MAP



P–BLOCK ELEMENTS

- $ns^2\ np^1$ III B
  - Reducing
  - Metallic other than boron
  - Larger size amongst p–block elements
  - Lower electronegativity
  - Covalent characteristics is high compared to group IA, IIA in the halides, oxides etc.
- $ns^2\ np^2$ IV B
  - Compounds are Covalent mostly
  - More electronegativity than IIIB
  - Acidic oxides but acidic strength of the oxides decreases down the group
- $ns^2\ np^3$ V B
  - High electronegative elements
  - Covalent oxides, halides and low melting
  - Mostly act as ligating atoms in ligands & act as a Lewis base.
- $ns^2\ np^4$ VI B
  - High electronegativity and electron affinity
  - Very reactive oxygen and reacts with almost all elements
  - Ranging from covalent to ionic compounds
- $ns^2\ np^5$ VII B
  - Higher electronegativity in F
  - Size is less
  - Electron affinity is very high
  - Ionic compound formation with group IA, IIA elements
  - Covalent compound formation
- $ns^2\ np^6$ VIII
  - Inert gas
  - Xe form complexes
  - Ar form thermionic tube
  - Electron affinity is close to O