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p-Block Elements

- Elements having its last electron in p-subshell is called p-block elements.
 - 'He' has its last electron in its s-subshell but it is a p-block elements.
- p-block element starts from group 13 and ends with inert gas element of group 18.

GROUP - 13 (BORON FAMILY)

Element	Atomic number	Outer electronic configuration
B	5	$2s^2 2p^1$
Al	13	$3s^2 3p^1$
Ga	31	$4s^2 4p^1$
In	49	$5s^2 5p^1$
Tl	81	$6s^2 6p^1$

GENERAL PROPERTY

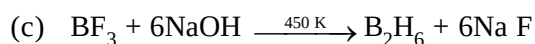
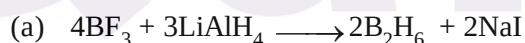
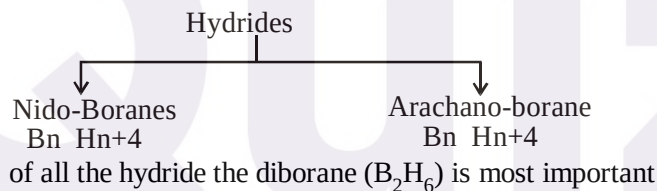
1. Atomic Radius : $B < Ga < Al < In < Tl$

The atomic radius of 'Ga' is found to be exceptionally less than that of Al. due to the poor screening of d-electrons in Ga.

2. Metallic Character : Boron is a typical non-metal but Al is metal.

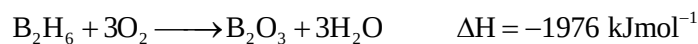
3. Oxidation - states : $\xrightarrow[\text{Stability of +1 state increases}]{Al < Ga < In < Tl}$

4. Hydrides :

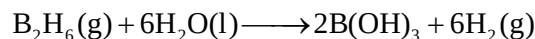


PROPERTY OF DIBORANE

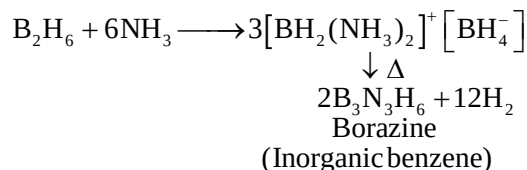
- (i) Combustion:



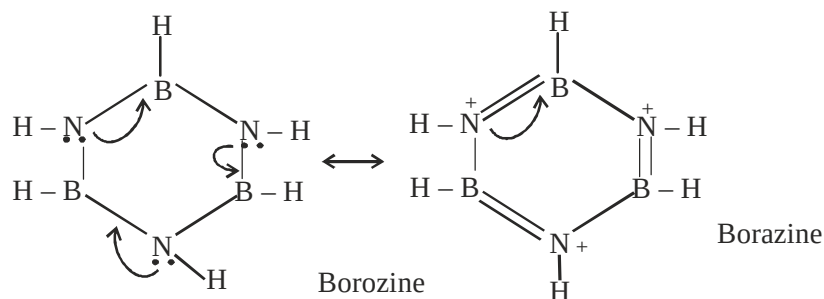
- (ii) Hydrolysis :



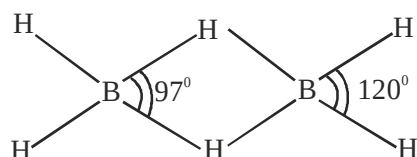
- (iii) Reaction with Ammonia :



Structure of inorganic benzene :

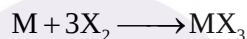


Structure of diborane :



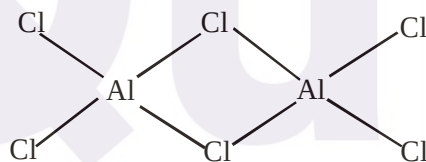
- The four terminal H and two borons are in one plane.
- Above and below this plane, there are two bridging H.
- The 4 terminal B-H bonds are regular 2C-2e bond while the two bridge H are 3C-2e bonds.

(b) Halides :

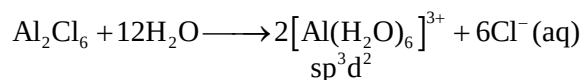


$\Rightarrow$ Tl(III) iodides are not known to exist.

Structure of $AlCl_3$: $AlCl_3$ exists in its dimeric state.

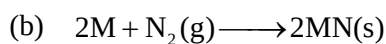
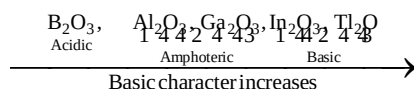
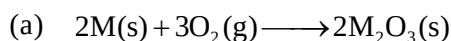


In polar solvent like H_2O , the covalent dimers dissociate into $[Al(H_2O)_6]^{3+}$ due to high heat of hydration.

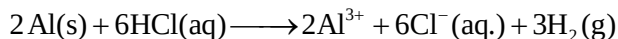


- White fumes are observed over the bottles of anhydrous $AlCl_3$. This is due to the partial hydrolysis of it in presence of moisture to liberate $HCl(g)$ which appears white.
- All group 13 element except B shows higher oxidation state. Boron does not show because of non-availability of vacant 'd' orbitals.

Reactivity towards air :

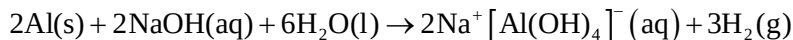


Reactivity towards Acids :



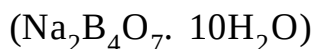
- But concentrated HNO_3 renders (Al) passive by forming a protective oxide-layer on surface.

Reactivity with Base :

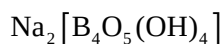


Sod. tetrahydroxo aluminate (III)

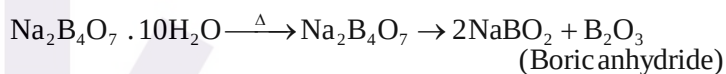
BORAX



Borax has tetranuclear units and in reality it exists as $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ with correct molecular formula as



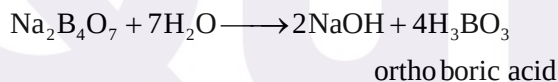
1. EFFECT OF HEAT ON BORAX :



Borax bead test : On heating borax it 1st loses water to swell up. On further heating it forms transparent liquid, which later solidifies into glass like material called as borax-bead. The meta borates of several transition metal has its own characteristic colour which is used to identify them in laboratory.

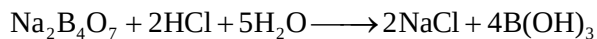
e.g. When Borax is heated in Bunshen flame with CoO , a blue colour of $\text{Co(BO}_2)_2$ bead is formed.

2. DISSOLUTION IN ALKALI :



BORIC ACID

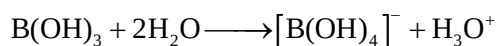
PREPARATION :



Boric acid

PROPERTIES :

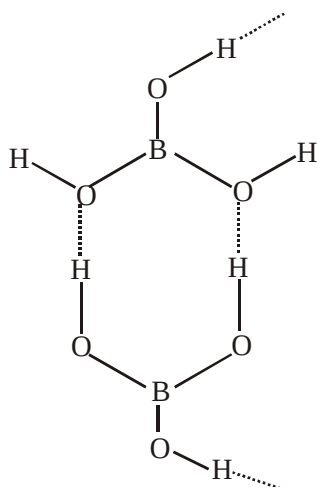
- (i) Sparingly soluble in normal water but soluble in hot water.
- (ii) Boric acid is a weak mono basic acid. It is not a protonic acid but acts as Lewis acid.



- (iii) Action of heat



Structure of Boric Acid :



GROUP 16

Carbon	Silicon	Germanium	Tin	Lead
$\Rightarrow \text{C}$	Si	Ge	Sn	Pb

Among all these elements, Si is the 2nd most abundant on earth and exist widely as Silicate and clay.

GENERAL PROPERTY :

1. Oxidation - state :

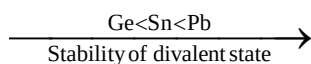
Carbon : Carbon in general forms covalent compounds having oxidation state of +4. But in few carbides carbon has ionic oxidation state as well as C^{4-} .

e.g. Be_2C , CaC_2 , SiC , Al_4C_3

2. Higher oxidation state:

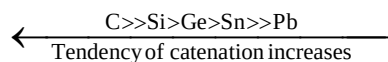
Except carbon all other elements forms compound of higher co-ordination number of 5 and 6.

e.g. SiF_5^- , SiF_6^{2-} , PbCl_6^{2-} etc.



Note : SiF_6^{2-} exists but SiCl_6^{2-} do not exists. This is since, smaller size of F will cause less amount of steric repulsion in it while due to the comparatively larger size of Cl, there will be high steric repulsion. In addition, the interaction of l-p of electron in F will be more with silicon than with Cl.

3. Catenation :



4. $p\pi - p\pi$ multiple bonds :

Due to small size and high concentration carbon has very strong tendency to form $p\pi - p\pi$ multiple bond

with itself, O, and N,

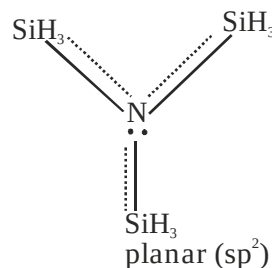
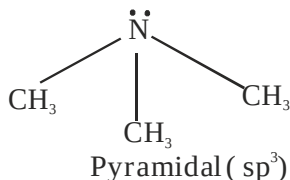
e.g. $C = C$, $C \equiv C$, $>C=O$, $C \equiv N$

$\Rightarrow$ other element of this group is reluctant to form $p\pi - p\pi$ bond.

5. $p\pi - d\pi$ bonding :

Carbon do not forms $p\pi - d\pi$ bond, because it don't have d orbital available. However Si and other elements of this group forms $p\pi - d\pi$ bond.

$\Rightarrow N(CH_3)_3$ is pyramidal whereas $N(SiH_3)_3$ is planar.



Allotropy: All the elements of this group except lead, shows allotropy.

ALLOTROPIC FORM OF CARBON :

- (i) Amorphous (ii) Crystalline
- Diamond and Graphites are the two crystalline forms .

1. Diamond :

- It has crystalline lattice.
- It has sp^3 hybridization of carbon to which other carbons are arranged tetrahedrally.
- The crystalline structure extends in space and produces rigidity in 3D structural form. The bonds are directional in nature.

2. Graphite :

Graphite has layer like structure in which layers are held together by vander waal forces. Each layer is composed of hexagonal rings of carbon with sp^2 hybridized state.

3. Fullerene :

It was discovered by H.W.kroto, E.smalley. R.F. curl in 1985. For this they were awarded with Nobel prize in 1996.

Preparation :

Heating of Graphite in an electric arc in the presence of inert gas such as the argon. Fullerene are the purest form of allotropes of carbon.

Structure :

C_{60} molecule has a shape like soccer ball and is called Buckminsterfullerenes. It has 20 six membered rings and 12 five membered rings. All the carbon atoms are equal and undergoes sp^2 hybridization.

Fullerene molecule has aromatic character because of its delocalised electron. Spherical fullerenes are also called Bucky balls.

Chemical :

(1) Oxides :

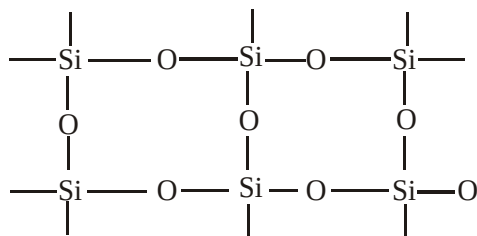
(a) Monoxide : All elements except silicon has monoxide.

CO , GeO , SnO , PbO

neutral acidic amphoteric alkaline

⇒ CO is colourless poisonous gas.

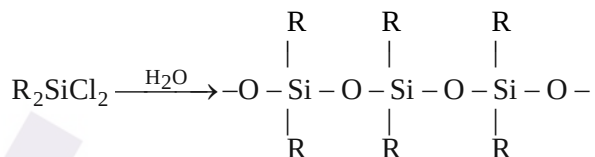
(b) Dioxide : $\overset{\text{Gas}}{\text{CO}_2}$, $\overset{1}{\text{SiO}_2}$, $\overset{4}{\text{GeO}_2}$, $\overset{4}{\text{SnO}_2}$, $\overset{4}{\text{PbO}_2}$
Solid



Giant network structure of SiO_2

(2) Silicones :

The synthetic material containing Si-O-Si linkage are called silicones. These are polymer having R_2SiO as repeating units.



GROUP - 15

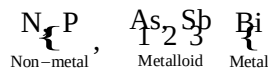
The elements of this group is called Pnictides. The word is derived from greek word 'Pniconides' which means 'Suffocation'.

(1) Oxidation state :

Only nitrogen forms few ionic compound in N^{3-} state, while all other elements gives rise to covalent compounds.

- Few ionic compounds of nitrogen - Mg_3N_2 , Ca_3N_2 etc.
- Since nitrogen do not have vacant d-orbital so it can't extend its covalency in excess of 4 e.g. NH_4^+ , R_4M^+ etc.
- On the otherhand other elements of this group exhibit higher covalency of five or even six eg. PCl_5 , AsF_5 , PF_6^- , SbF_6^-

(2) Metallic Character:



(3) Nature of Bonding :

Due to smaller size nitrogen forms $p\pi - p\pi$ multiple bonding with itself and with carbon and oxygen.

⇒ $\ddot{\text{N}} \equiv \ddot{\text{N}}$, Due to the triple bond N_2 has very high bond dissociation energy and it becomes inert and unreactive.

⇒ No other element of this group forms $p\pi - p\pi$ multiple bonding. This is due to why nitrogen exists at N_2 , whereas phosphorus exist as P_4 .

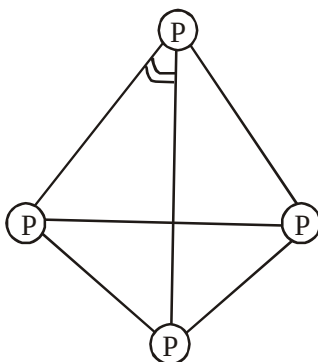
ALLOTROPE OF PHOSPHORUS :

Three allotropes

- (i) White phosphorus (ii) Red phosphorus (iii) Black phosphorus

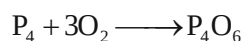
1. White phosphorus :

- (a) It exists as P_4 units. The four phosphorus atoms lie at the corner of a regular tetrahedron with $\angle PPP = 60^\circ$.



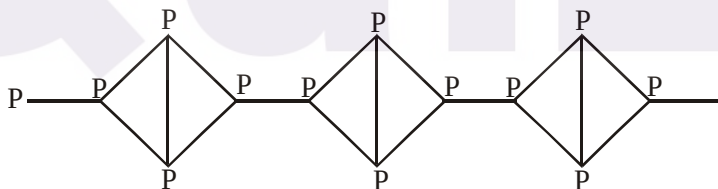
White Phosphorus

- (b) On exposure to light, white phosphorus turns yellow. Thus it is also called yellow phosphorus. It is highly toxic.
(c) It is very reactive and spontaneously catches fire in air with greenish glow.



2. Red phosphorus :

- (a) When white phosphorus is heated to 570 K in an inert atmosphere for several days, it gets converted into red phosphorus.
(b) Red phosphorus has higher m.pt than white phosphorus.
(c) Red phosphorus is amorphous and has a polymeric structure.



Polymeric Structure of Red Phosphorus

- (d) It is much less reactive than white phosphorus and is non-toxic.

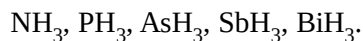
3. Black phosphorus :

Thermodynamically the most stable form of phosphorus is black phosphorus

- (a) It is obtained by heating white phosphorus at 470 K under high pressure.

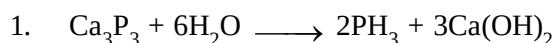
4. Hydrides :

All elements of this group form gaseous hydride of MH_3 type.



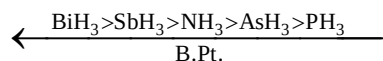
Stability of hydrides decreases

Few reactions given by hydrides:



2. $P_4 + 3K-OH + 3H_2O \longrightarrow PH_3 + 3KH_2PO_2$
3. $Zn_3M_2(s) + 6HCl(aq) \longrightarrow 2MH_3 + 3ZnCl_2(aq)$ $M = As \text{ or } Sb$.

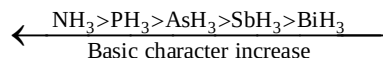
Boiling point :



From PH_3 to BiH_3 there is increase in B.pt. due to the increase in surface area.

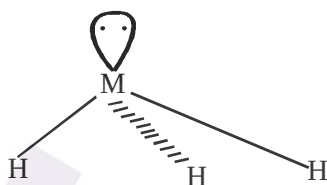
- But NH_3 has exceptionally large B.Pt. due to extensive H-bonding in it.

Basic Character :



Structure :

It has pyramidal structure

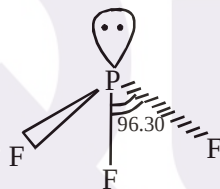


Halides :

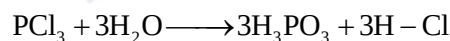
Two halides in general (a) MX_3 (b) MX_5

MX_3

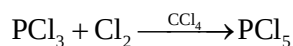
PF_3 / PCl_3 : It is pyramidal in gaseous state.



Properties : MX_3 fumes in moist air because of its reaction with H_2O producing HCl .

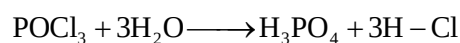
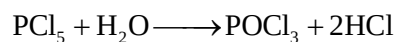


MX_5 :



PF_5 is molecular in both gaseous and solid states and has 'Trigonal bipyramidal' structure.

- PCl_5 fumes in air. It reacts with H_2O to give initially $POCl_3$ but with excess of H_2O , the product is H_3PO_4



- PCl_5 in gaseous and liquid phase is molecular while in solid phase it is ionic and exists as $[PCl_4]^+ [PCl_6]^-$.

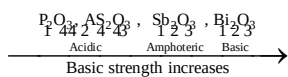
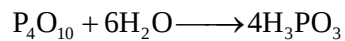
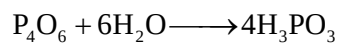
OXIDES

Two types of oxides -

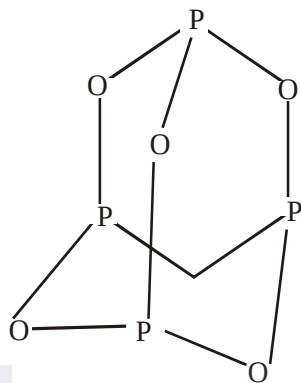
(a) M_2O_3

(b) M_2O_5

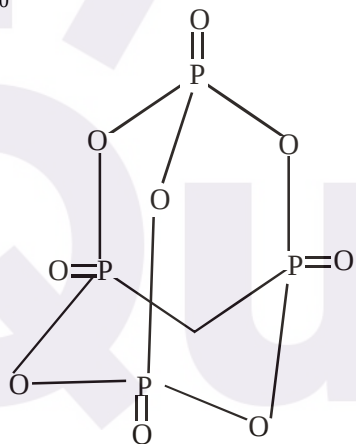
- Due to the formation of multiple bonding they have cage structure.
- The basic nature of these oxides increases with increase in atomic number. Because of its great affinity with water, P_4O_{10} is used as dehydrating agent.



Structure of P_4O_6 :

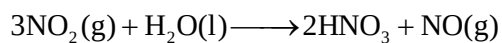
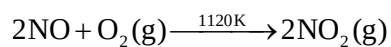
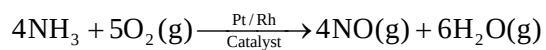


Structure of P_4O_{10} :

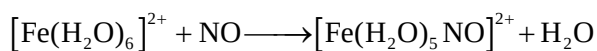
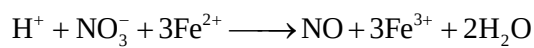


NITRIC ACID (HNO_3):

It is manufactured by contact process to use following reactions.

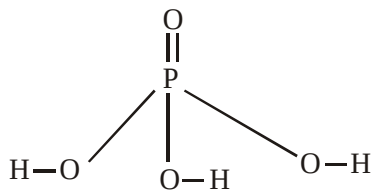


Nitrate ion Test :

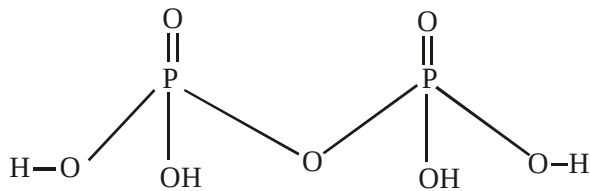


Brown ring

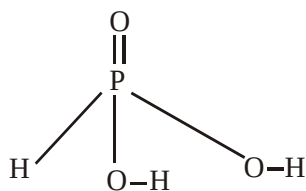
Oxo-Acids of Phosphorus :



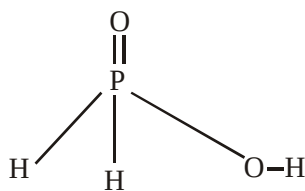
Ortho-phosphoric acid



Pyrophosphoric Acid



Phosphorous Acid



Hypophosphorus Acid

GROUP - 16

- They are called chalcogens, i.e. ore producers.

O, S, Se, Te, Po

⇒ Polonium is radioactive.

General Configuration : ns^2np^4 .

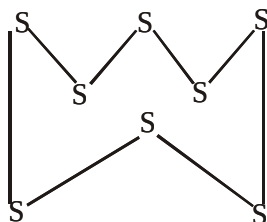
ALLOTROPES :

Sulphur forms numerous allotropes in which its two common allotropes are

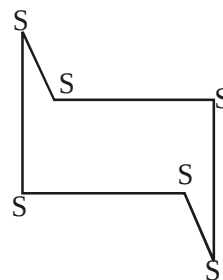
- (i) Yellow ortho rhombic (ii) α, β – monoclinic

- The stable form at room temperature is orthorhombic sulphur, which transforms to monoclinic sulphur at 369 K.

S_8 molecules are puckered up to give different crystal structure in two forms. The S_8 ring in the two form is puckered and gives crown ring structure.



(a) S_8



(b) S_6

- Few other Allotropic modification of sulphur containing upto 20 sulphur atom per ring have been synthesised.
- The ring takes chair form in S_6 .

Catena (S_n) :

Chain polymeric allotropes of sulphur is called catena. They have the general formula of S_n where $n = 2$ to 5 . They exist as liquid sulphur at higher temperature. At 1000 K S_2 is the most dominant species and S_2 is paramagnetic.

Oxidation state :

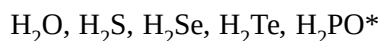
The important common oxidation states for group 16 elements are $-2, +4, +2, +6$ oxygen due to non availability of vacant d orbital does not show higher oxidation states.

Metallic Character :

Except Po* all other elements of this group are non metal. Metallic character increases down the group.

Hydrides :

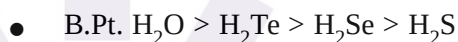
Type H_2X .



Thermal stability decreases $\rightarrow$

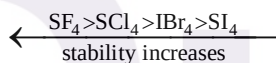
Bond dissociation energy decreases $\rightarrow$

acidic character increases $\rightarrow$

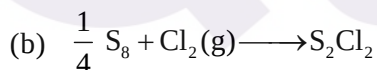
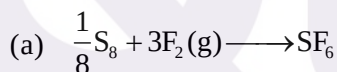


$\leftarrow$

Halides :



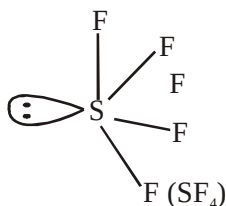
Preparation:



- SF_6 is inert, nontoxic gas. The inertness of SF_6 is due to the sterically protected sulphur atom which does not allow thermodynamically favourable reaction to take place. Due to this it rarely undergoes hydrolysis.
- But SeF_6 and SF_4 which is less sterically hindered undergoes hydrolysis.
- Because of the inertness of SF_6 and good dielectric property it is used as gaseous insulators.

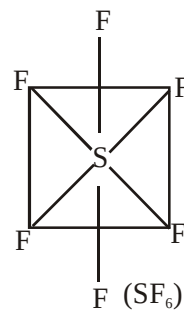
Structures

a) SF_4 : 'S' has sp^3d hybridization in SF_4



b) SF_6 : 'S' has sp^3d^2 hybridization in SF_6

Octahedral



- SeCl_4 , SeBr_4 , TeB_4 and TeI_4 exists as tetramer while TeF_4 has polymer structure.

Oxides

General formula is EO_2 and EO_3 . SO_2 is gas at room temperature and has an angular structure with bond angle 119° . It exists as discrete SO_2 molecule in gaseous state but SeO_2 in solid state has a layer structure. SO_3 in gas phase exists as planar triangular structure. In solid state SO_3 exists as linear cyclic trimeric or a polymeric chain.

Oxoacids of Sulphur

1. H_2SO_3 (Sulphurous acid)
2. H_2SO_4 (Sulphuric acid)
3. $\text{H}_2\text{S}_2\text{O}_7$ (Pyrosulphuric acid or oleum)
4. H_2SO_5 (Peroxomonosulphuric acid or caro's acid)
5. $\text{H}_2\text{S}_2\text{O}_8$ (Peroxdisulphuric acid or Marshall's acid)
6. $\text{H}_2\text{S}_2\text{O}_3$ (Thiosulphuric acid)
7. $\text{H}_2\text{S}_2\text{O}_6$ (Dithionic acid)

GROUP - 17 HALOGENS

Halo means salt producing. Most reactive non-metals are F, Cl, Br, I but At is radioactive.

ATOMIC AND PHYSICAL PROPERTIES:

Exists as diatomic molecules under ordinary condition.

F_2, Cl_2
Pale yellow
and greenish yellow
↓
react with
 H_2O

Br_2
Brown
E555F
Sparingly
soluble in
 H_2O but
soluble in
organic
solvents

I_2
Lustrous,
grayish black
crystalline
solid sublimes
to form deep
violet vapours

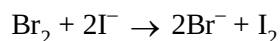
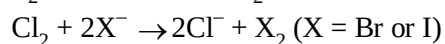
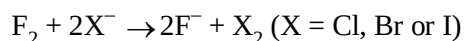
F–F bond energy is smaller than Cl–Cl but X–X bond energy after Cl_2 decrease due to increased size of X and less effective overlapping of atomic orbitals. F–F bond is weaker than Cl–Cl due to small size and large electron-electron repulsion of the lone pairs in F_2 .

OXIDATION STATE AND TRENDS IN CHEMICAL REACTIVITY :

F is the most electronegative its oxidation state is -1 in all compounds and is the strongest oxidising agent.

$\text{X}_2 + 2\text{e}^- \rightarrow 2\text{X}^-$ (accepts electrons : all are good oxidising agent).

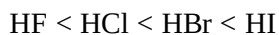
⇒ Oxidizing power decreases down the group. Any halogen of lower atomic number can oxidize the halide ion of higher atomic number.



- Interhalogen are compounds with formula AX_n where halogens combine among themselves. A and X both are halogens but X is more electronegative than A.

Hydrogen Halides : HX are Covalent molecular species. HX in aqueous form are called hydrohalic acids.

⇒ Acidic character in aqueous solution.

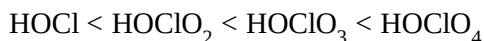


⇒ HF is a much weaker acid (Hydrogen bonding and high bond dissociation energy of H–F bond).

⇒ HF is corrosive and attacks glass, therefore used in etching of glass and manufacture of glass shells of T.V. tubes.

- Oxides OF_2 and O_2F_2 called oxygen fluorides. Because F is more electronegative.

Oxoacids:

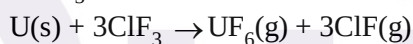


acidic strength increases

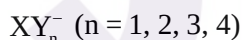
Inter-halogen compounds	AX_n :			
n =	(1, 3, 5 or 7)			
e.g.	AX	AX_3	AX_5	AX_7
	ClF	ClF_3	ClF_5	IF_7
	BrF	BrF_3	BrF_5	IF_7
	ICl	IF_3	IF_5	

⇒ Stability of inter-halogen compound increases as the size of the central atom increases. The more electronegative halogen is given a –ve oxidation state.

⇒ They are strong oxidising agents and covalent. AX_3 have T-shape structure. AX_5 have square pyramidal. ClF_3 is used as a fluorinating agent.



Polyhalide anions :



e.g.: $\text{I}_3^- \rightarrow$ linear triatomic iodide ion

Polyhalonium cations:

They are XY_{2n}^+ type

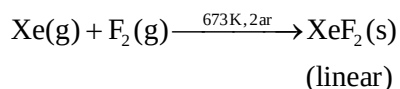
e.g. $\text{ClF}_2^+, \text{Cl}_2\text{F}^+, \text{BrF}_2^+, \text{IF}_2^+$ and ICF_2^+

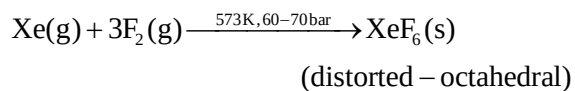
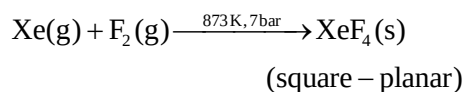
GROUP - 18

Noble Gases - ns^2np^6 , monoatomic, colourless, odourless, sparingly soluble in water because of weak dispersion interaction. He has lowest boiling point, diffuses through glass, rubber or plastic

⇒ Isolation : Except Rn all are present in atmosphere Ne, Ar, Kr and Xe are obtained as by products of liquification of air and separated by fractional distillation.

⇒ Xe–F compounds:





Properties of xenon fluorides

Hydrolysis :

- (a) $2\text{XeF}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{Xe}(\text{g}) + \text{HF}(\text{aq}) + \text{O}_2(\text{g})$
- (b) $\text{XeF}_2 + \text{PF}_5 \rightarrow [\text{XeF}]^+ + [\text{PF}_6]^-$ (fluoride donor)
- (c) $\text{XeF}_4 + \text{SbF}_5 \rightarrow [\text{XeF}_3]^+ [\text{SbF}_6]^-$
- (d) $\text{XeF}_6 + \text{MF} \rightarrow \text{M}^+ [\text{XeF}_7]^-$ (fluoride acceptor)

Xe–O compounds

- (a) $6\text{XeF}_4 + 12\text{H}_2\text{O} \rightarrow 4\text{Xe} + 4\text{XeO}_3 + 24\text{HF} + 3\text{O}_2$
- (b) $\text{XeF}_6 + \text{H}_2\text{O} \rightarrow \text{XeO}_3 + 6\text{HF}$ (Partial hydrolysis)
- (c) $\text{XeF}_6 + \text{H}_2\text{O} \rightarrow \text{XeOF}_4 + 2\text{HF}$
- (d) $\text{XeO}_3 \rightarrow$ colourless explosive solid, trigonal pyramidal structure. Xe has sp^3 hybridization.
- (e) $\text{XeOF}_4 \rightarrow$ colourless volatile liquid.
- (f) $\text{XeO}_3 + \text{OH}^- \rightarrow \text{HXeO}_4^- + \text{Xe} + \text{O}_2 + 2\text{H}_2\text{O}$
(disproportionation)