

## 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

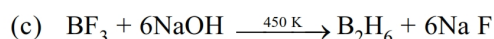
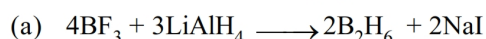
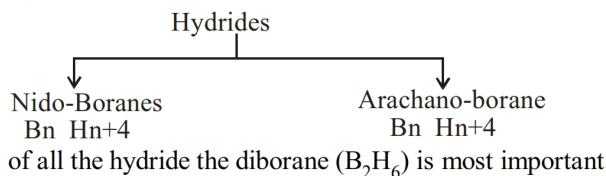
1. Atomic Radius :  $B < Ga < Al < In < Tl$

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

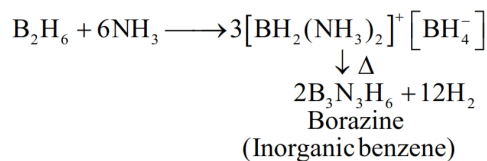
- (i) Combustion:



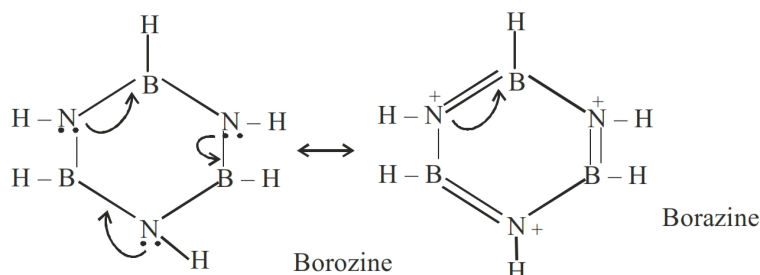
- (ii) Hydrolysis :



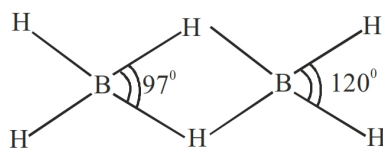
- (iii) Reaction with Ammonia :



Structure of inorganic benzene :

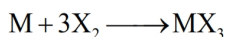


Structure of diborane :



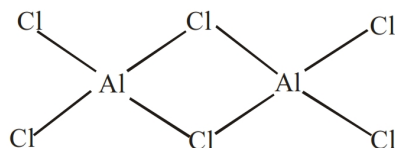
- The four terminal H and two borons are in one plane.
- Above and below this plane, there are two bridging H.
- The 4 terminal B-H bonds are regular 2C-2e bond while the two bridge H are 3C-2e bonds.

(b) Halides :

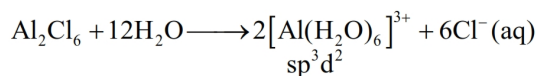


$\Rightarrow$  Tl(I) iodides are not known to exist.

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

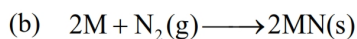
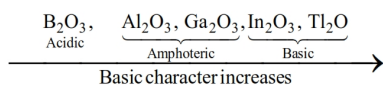
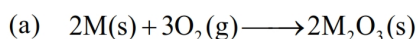


In polar solvent like  $H_2O$ , the covalent dimers dissociate into  $[Al(H_2O)_6]^{3+}$  due to high heat of hydration.

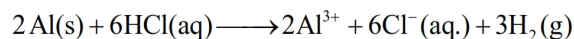


- White fumes are observed over the bottles of anhydrous  $AlCl_3$ . This is due to the partial hydrolysis of it in presence of moisture to liberate  $HCl(gas)$  which appears white.
- All group 13 element except B shows higher oxidation state. Boron does not show because of non-availability of vacant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

Reactivity towards air :

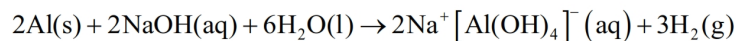


#### Reactivity towards Acids :



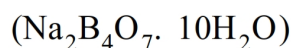
- But concentrated  $\text{HNO}_3$  renders (Al) passive by forming a protective oxide-layer on surface.

#### Reactivity with Base :

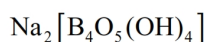


Sod. tetrahydroxo aluminate (III)

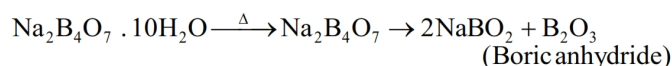
### BORAX



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



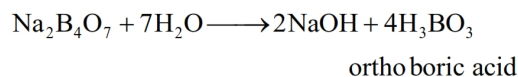
#### 1. EFFECT OF HEAT ON BORAX :



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.

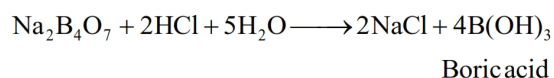
e.g. When Borax is heated in Bunshen flame with  $\text{CoO}$ , a blue colour of  $\text{Co(BO}_2)_2$  bead is formed.

#### 2. DISSOLUTION IN ALKALI :



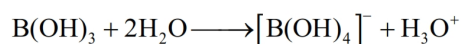
### BORIC ACID

#### PREPARATION :



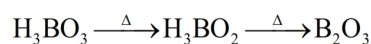
#### PROPERTIES :

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

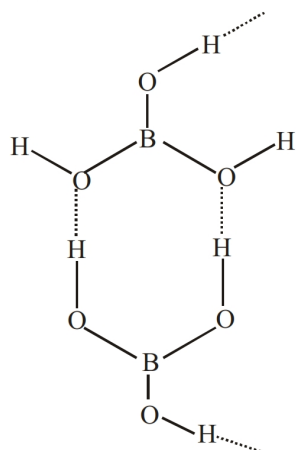


- Action of heat





Structure of Boric Acid :



## GROUP 16

Carbon	Silicon	Germanium	Tin	Lead
$\Rightarrow$ 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 :

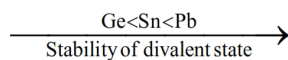
Carbon : Carbon in general forms covalent compounds having oxidation state of +4. But in few carbides carbon has ionic oxidation state as well as  $\text{C}^{4-}$ .

e.g.  $\text{Be}_2\text{C}$ ,  $\text{CaC}_2$ ,  $\text{SiC}$ ,  $\text{Al}_4\text{C}_3$

### 2. Higher oxidation state:

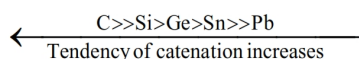
Except carbon all other elements forms compound of higher co-ordination number of 5 and 6.

e.g.  $\text{SiF}_5^-$ ,  $\text{SiF}_6^{2-}$ ,  $\text{PbCl}_6^{2-}$  etc.



Note :  $\text{SiF}_6^{2-}$  exists but  $\text{SiCl}_6^{2-}$  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,

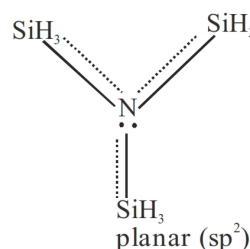
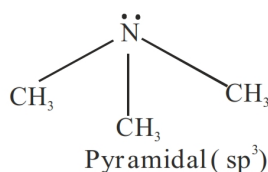
e.g.  $C = C$ ,  $C \equiv C$ ,  $>C = O$ ,  $C \equiv N$

$\Rightarrow$  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 :

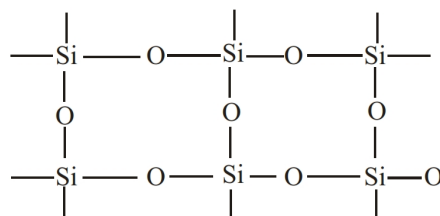
(a) Monoxide : All elements except silicon has monoxide.

$CO$ ,  $GeO$ ,  $SnO$ ,  $PbO$

neutral
acidic
amphoteric
alkaline

⇒ CO is colourless poisonous gas.

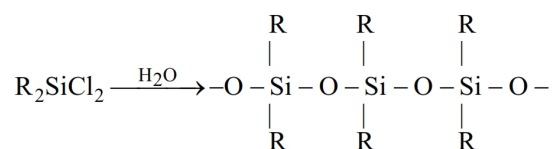
(b) Dioxide :  $\underbrace{\text{CO}_2}_{\text{Gas}}, \underbrace{\text{SiO}_2, \text{GeO}_2, \text{SnO}_2, \text{PbO}_2}_{\text{Solid}}$



Giant network structure of  $\text{SiO}_2$

(2) Silicones :

The synthetic material containing Si-O-Si linkage are called silicones. These are polymer having  $\text{R}_2\text{SiO}$  as repeating units.



## GROUP - 15

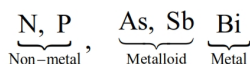
The elements of this group is called Pniconides. The word is derived from greek word 'Pniconides' which means 'Suffocation'.

(1) Oxidation state :

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

- Few ionic compounds of nitrogen -  $\text{Mg}_3\text{N}_2$ ,  $\text{Ca}_3\text{N}_2$  etc.
- Since nitrogen do not have vacant d-orbital so it can't extend its covalency in excess of 4 e.g.  $\text{NH}_4^+$ ,  $\text{R}_4\text{M}^+$  etc.
- On the otherhand other elements of this group exhibit higher covalency of five or even six eg.  $\text{PCl}_5$ ,  $\text{AsF}_5$ ,  $\text{PF}_6^-$ ,  $\text{SbF}_6^-$

(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.

⇒  $\text{N} \equiv \text{N}$ , Due to the triple bond  $\text{N}_2$  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  $\text{N}_2$ , whereas phosphorus exist as  $\text{P}_4$ .



## ALLOTROPES OF PHOSPHORUS :

Three allotropes

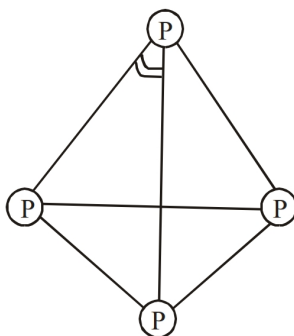
(i) White phosphorus

(ii) Red phosphorus

(iii) Black phosphorus

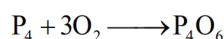
### 1. White phosphorus :

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



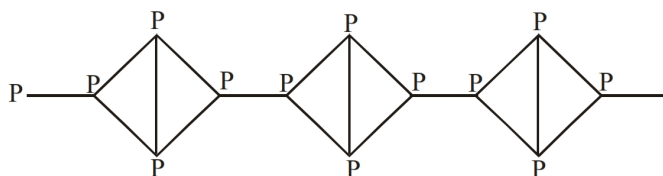
White Phosphorus

- (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.

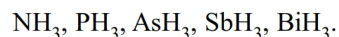
### 3. Black phosphorus :

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.



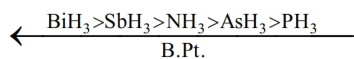
Stability of hydrides decreases

Few reactions given by hydrides:



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

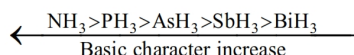
Boiling point :



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

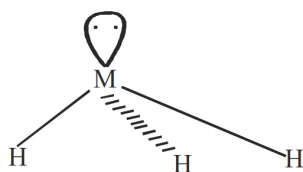
- But  $NH_3$  has exceptionally large B.Pt. due to extensive H-bonding in it.

Basic Character :



Structure :

It has pyramidal structure

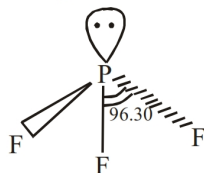


Halides :

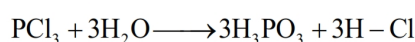
Two halides in general (a)  $MX_3$  (b)  $MX_5$

$MX_3$

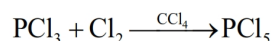
$PF_3 / PCl_3$  : It is pyramidal in gaseous state.



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

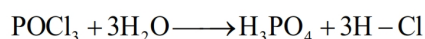
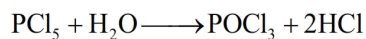


$MX_5$  :



$PF_5$  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  $[PCl_4]^+ [PCl_6]^-$ .

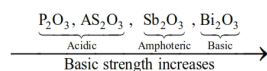
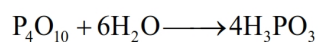
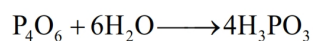
OXIDES

Two types of oxides -

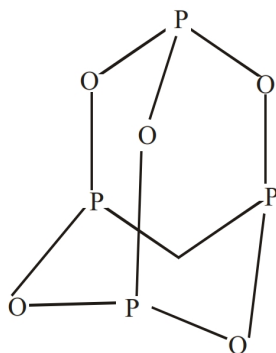
(a)  $M_2O_3$

(b)  $M_2O_5$

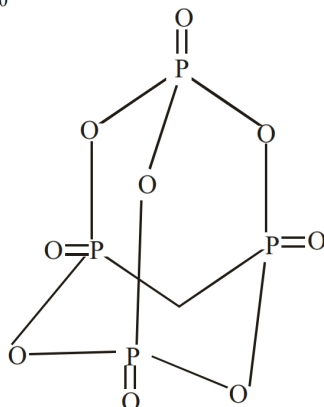
- Due to the formation of multiple bonding they have cage structure.
- The basic nature of these oxides increases with increase in atomic number. Because of its great affinity with water,  $P_4O_{10}$  is used as dehydrating agent.



Structure of  $\text{P}_4\text{O}_6$  :

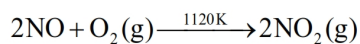
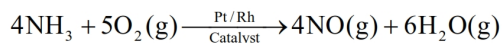


Structure of  $\text{P}_4\text{O}_{10}$  :

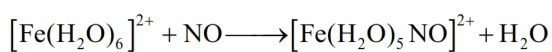
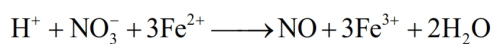


NITRIC ACID ( $\text{HNO}_3$ ):

It is manufactured by contact process to use following reactions.

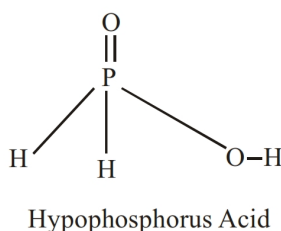
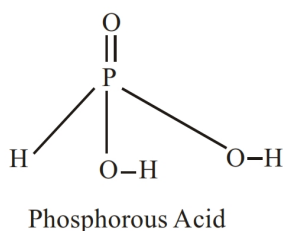
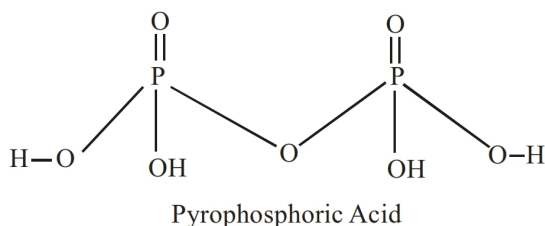
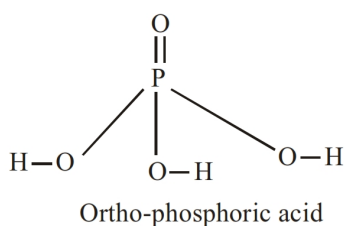


Nitrate ion Test :



Brown ring

### Oxo-Acids of Phosphorus :



## GROUP - 16

- They are called chalcogens, i.e. ore producers.  
O, S, Se, Te, Po  
⇒ Polonium is radioactive.

General Configuration :  $ns^2np^4$ .

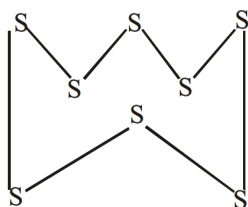
### ALLOTROPES :

Sulphur forms numerous allotropes in which its two common allotropes are

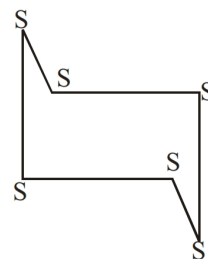
- (i) Yellow ortho rhombic (ii)  $\alpha, \beta$  – monoclinic

- 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  $1000\text{ K}$   $S_2$  is the most dominant species and  $S_2$  is paramagnetic.

### Oxidation state :

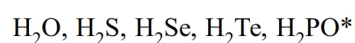
The important common oxidation states for group 16 elements are  $-2, +4, +2, +6$  oxygen due to non availability of vacant d orbital does not show higher oxidation states.

### 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  $\rightarrow$

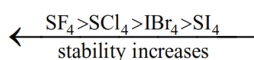
Bond dissociation energy decreases  $\rightarrow$

acidic character increases  $\rightarrow$

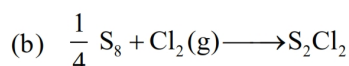
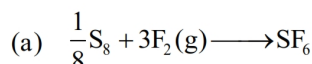
- B.Pt.  $H_2O > H_2Te > H_2Se > H_2S$

$\leftarrow$

### Halides :



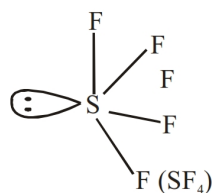
### Preparation:



- $SF_6$  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.

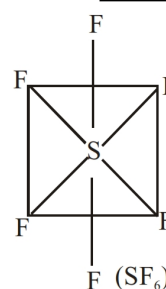
### Structures

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



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

Octahedral



- $\text{SeCl}_4$ ,  $\text{SeBr}_4$ ,  $\text{TeB}_4$  and  $\text{TeI}_4$  exists as tetramer while  $\text{TeF}_4$  has polymer structure.

### Oxides

General formula is  $\text{EO}_2$  and  $\text{EO}_3$ .  $\text{SO}_2$  is gas at room temperature and has an angular structure with bond angle  $119^\circ$ . It exists as discrete  $\text{SO}_2$  molecule in gaseous state but  $\text{SeO}_2$  in solid state has a layer structure.  $\text{SO}_3$  in gas phase exists as planar triangular structure. In solid state  $\text{SO}_3$  exists as linear cyclic trimeric or a polymeric chain.

### Oxoacids of Sulphur

1.  $\text{H}_2\text{SO}_3$  (Sulphurous acid)
2.  $\text{H}_2\text{SO}_4$  (Sulphuric acid)
3.  $\text{H}_2\text{S}_2\text{O}_7$  (Pyrosulphuric acid or oleum)
4.  $\text{H}_2\text{SO}_5$  (Peroxomonosulphuric acid or caro's acid)
5.  $\text{H}_2\text{S}_2\text{O}_8$  (Peroxodisulphuric acid or Marashall'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.

$\text{F}_2, \text{Cl}_2$   
Pale yellow  
and greenish yellow  
↓  
react with  
 $\text{H}_2\text{O}$

$\text{Br}_2$   
Brown  
□□□□  
Sparingly  
soluble in  
 $\text{H}_2\text{O}$  but  
soluble in  
organic  
solvents

$\text{I}_2$   
Lustrous,  
grayish black  
crystalline  
solid sublimes  
to form deep  
violet vapours

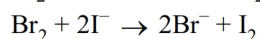
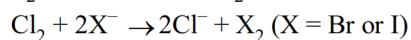
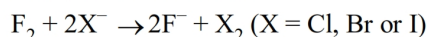
F-F bond energy is smaller than Cl-Cl but X-X bond energy after  $\text{Cl}_2$  decrease due to increased size of X and less effective overlapping of atomic orbitals. F-F bond is weaker than Cl-Cl due to small size and large electron-electron repulsion of the lone pairs in  $\text{F}_2$ .

### OXIDATION STATE AND TRENDS IN CHEMICAL REACTIVITY :

F is the most electronegative its oxidation state is -I 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).

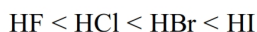
⇒ Oxidizing power decreases down the group. Any halogen of lower atomic number can oxidize the halide ion of higher atomic number.



- Interhalogen are compounds with formula  $\text{AX}_n$  where halogens combine among themselves. A and X both are halogens but X is more electronegative than A.

Hydrogen Halides :  $\text{HX}$  are Covalent molecular species.  $\text{HX}$  in aqueous form are called hydrohalic acids.

⇒ Acidic character in aqueous solution.

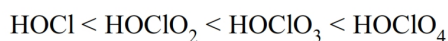


⇒ HF is a much weaker acid (Hydrogen bonding and high bond dissociation energy of H–F bond).

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

- Oxides  $\text{OF}_2$  and  $\text{O}_2\text{F}_2$  called oxygen fluorides. Because F is more electronegative.

#### Oxoacids:

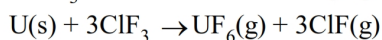


$\xrightarrow{\hspace{2cm}}$   
 acidic strength increases

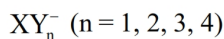
Inter-halogen compounds		$\text{AX}_n$ :		
	$n = (1, 3, 5 \text{ or } 7)$			
e.g.	AX	$\text{AX}_3$	$\text{AX}_5$	$\text{AX}_7$
	$\text{ClF}$	$\text{ClF}_3$	$\text{ClF}_5$	$\text{IF}_7$
	$\text{BrF}$	$\text{BrF}_3$	$\text{BrF}_5$	$\text{IF}_7$
	$\text{ICl}$	$\text{IF}_3$	$\text{IF}_5$	

⇒ 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.  $\text{AX}_3$  have T-shape structure.  $\text{AX}_5$  have square pyramidal.  $\text{ClF}_3$  is used as a fluorinating agent.



Polyhalide anions :



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

Polyhalonium cations:

They are  $\text{XY}_{2n}^+$  type

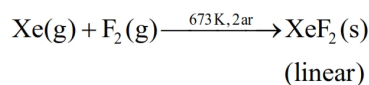
e.g.  $\text{ClF}_2^+, \text{Cl}_2\text{F}^+, \text{BrF}_2^+, \text{IF}_2^+$  and  $\text{ICF}_2^+$

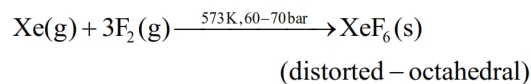
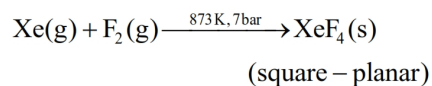
## GROUP - 18

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  $\text{sp}^3$  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)

