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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

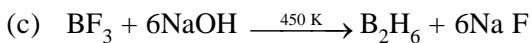
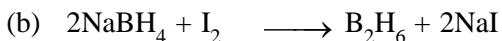
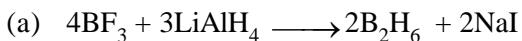
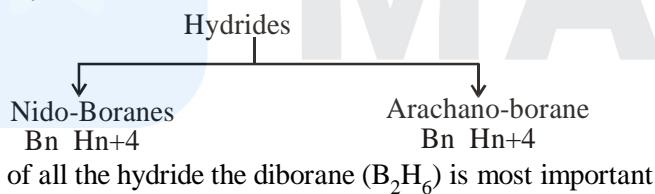
1. Atomic Radius : B < Ga < Al < In < Tl

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

4. Hydrides :



PROPERTY OF DIBORANE

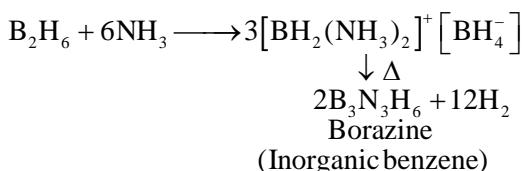
(i) Combustion:



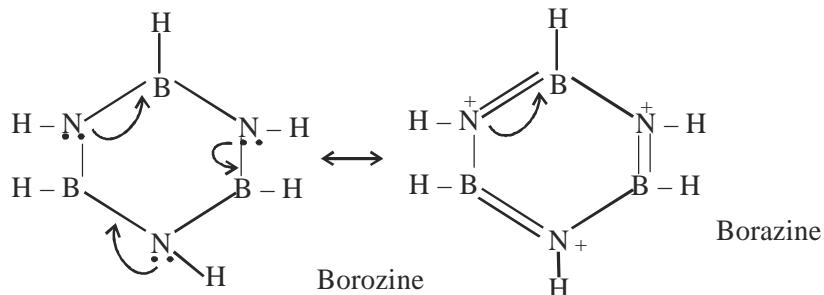
(ii) Hydrolysis :



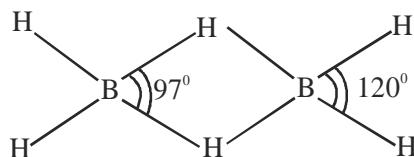
(iii) Reaction with Ammonia :



Structure of inorganic benzene :



Structure of diborane :



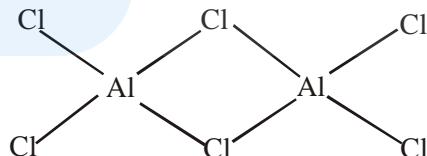
- The four terminal H and two borons are in one plane.
- Above and below this plane, there are two bridging H.
- The 4 terminal B–H bonds are regular 2C–2e bond while the two bridge H are 3C–2e bonds.

(b) Halides :

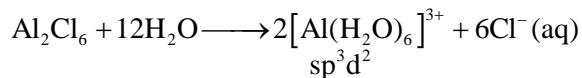


\Rightarrow Tl(11I) iodides are not known to exist.

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

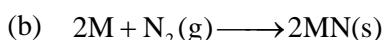
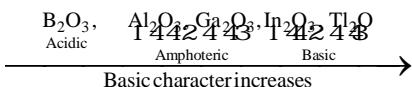
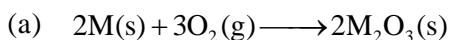


In polar solvent like H_2O , the covalent dimers dissociate into $[Al(H_2O)_6]^{3+}$ due to high heat of hydration.

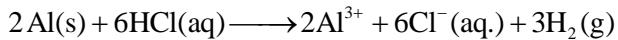


- White fumes are observed over the bottles of anhydrous $AlCl_3$. This is due to the partial hydrolysis of it in presence of moisture to liberate HCl (gas) which appears white.
- All group 13 element except B shows higher oxidation state. Boron does not show because of non-availability of vacant ‘d’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

Reactivity towards air :

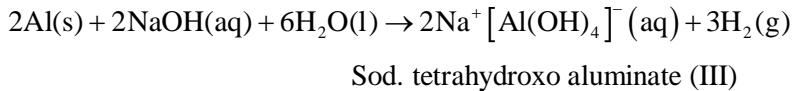


Reactivity towards Acids :



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

Reactivity with Base :

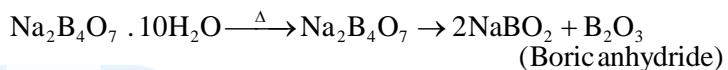


BORAX

$(\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O})$

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
 $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4]$

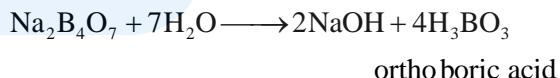
1. EFFECT OF HEAT ON BORAX :



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.

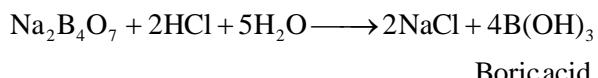
e.g. When Borax is heated in Bunshen flame with CoO , a blue colour of $\text{CO}(\text{BO}_2)_2$ bead is formed.

2. DISSOLUTION IN ALKALI :



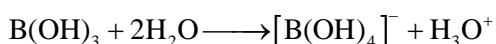
BORIC ACID

PREPARATION :



PROPERTIES :

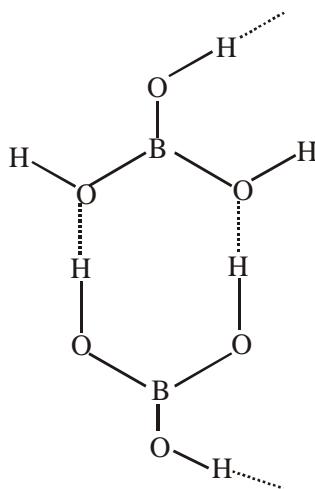
- Sparingly soluble in normal water but soluble in hot water.
- Boric acid is a weak mono basic acid. It is not a protonic acid but acts as Lewis acid.



- 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 :

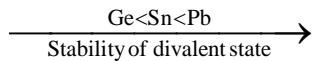
Carbon : Carbon in general forms covalent compounds having oxidation state of +4. But in few carbides carbon has ionic oxidation state as well as C^{4-} .

e.g. Be_2C , CaC_2 , SiC , Al_4C_3

2. Higher oxidation state:

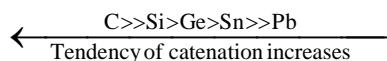
Except carbon all other elements forms compound of higher co-ordination number of 5 and 6.

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,

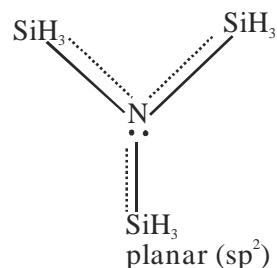
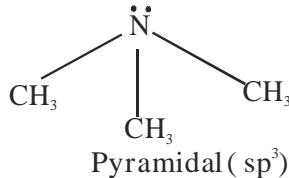


\Rightarrow other element of this group is reluctant to form $p\pi - p\pi$ bond.

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.

$\Rightarrow \text{N}(\text{CH}_3)_3$ is pyramidal whereas $\text{N}(\text{SiH}_3)_3$ 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 Buckminster fullerenes. 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 :

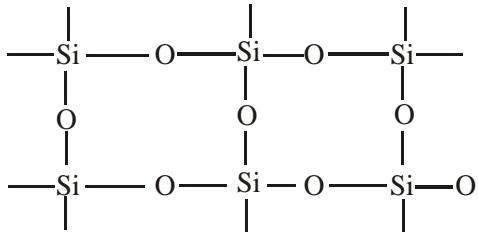
(1) Oxides :

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



neutral acidic amphoteric alkaline
 \Rightarrow CO is colourless poisonous gas.

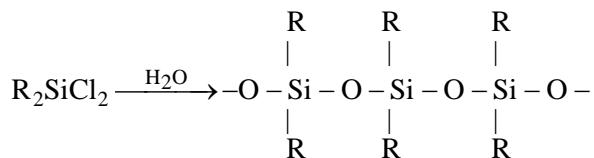
(b) Dioxide : $\begin{array}{c} \text{CO}_2 \\ \text{Gas} \end{array}, \begin{array}{c} \text{SiO}_4 \\ \text{Solid} \end{array}, \begin{array}{c} \text{GeO}_4 \\ \text{Solid} \end{array}, \begin{array}{c} \text{SnO}_4 \\ \text{Solid} \end{array}, \begin{array}{c} \text{PbO}_2 \\ \text{Solid} \end{array}$



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 Pniconides. 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 $\text{p}\pi - \text{p}\pi$ multiple bonding with itself and with carbon and oxygen.

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

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

ALLOTROPIES OF PHOSPHORUS :

Three allotropes

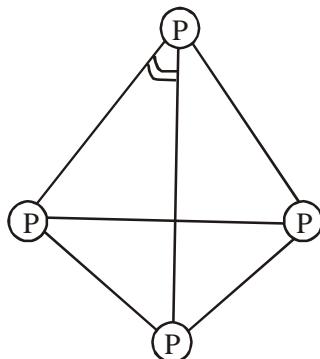
(i) White phosphorus

(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 $\angle PPP = 60^\circ$.



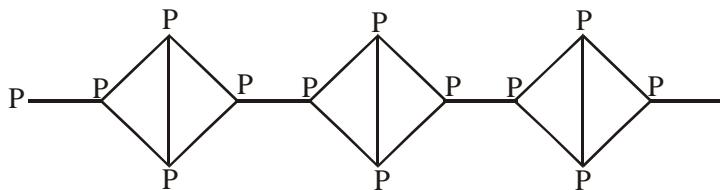
White Phosphorus

- (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.

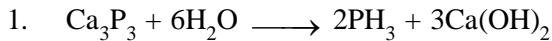
4. Hydrides :

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



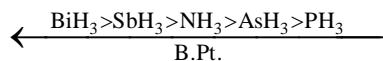
Stability of hydrides decreases

Few reactions given by Hydrides:



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

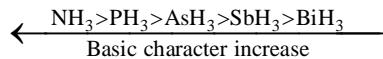
Boiling point :



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

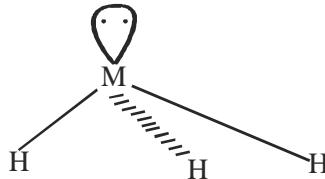
- But NH_3 has exceptionally large B.Pt. due to extensive H-bonding in it.

Basic Character :



Structure :

It has pyramidal structure

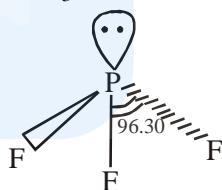


Halides :

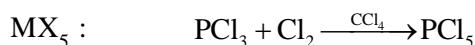
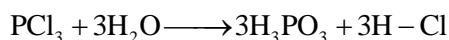
Two halides in general (a) MX_3 (b) MX_5

MX_3

PF_3 / PCl_3 : It is pyramidal in gaseous state.

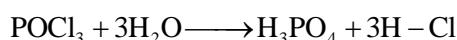
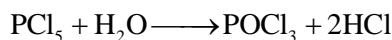


Properties : MX_3 fumes in moist air because of its reaction with H_2O producing HCl .



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



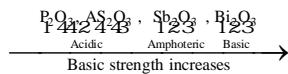
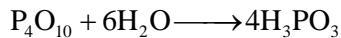
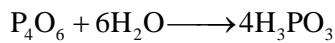
- PCl_5 in gaseous and liquid phase is molecular while in solid phase it is ionic and exists as $[PCl_4]^+ [PCl_6]^-$.

OXIDES

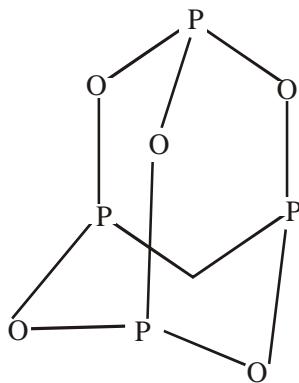
Two types of oxides - (a) M_2O_3

(b) M_2O_5

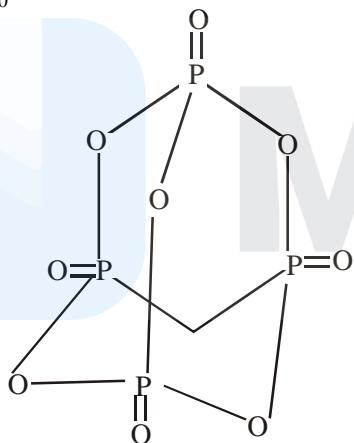
- Due to the formation of multiple bonding they have cage structure.
- The basic nature of these oxides increases with increase in atomic number. Because of its great affinity with water, P_4O_{10} is used as dehydrating agent.



Structure of P₄O₆ :

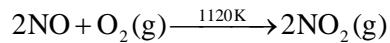
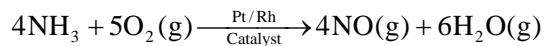


Structure of P₄O₁₀ :

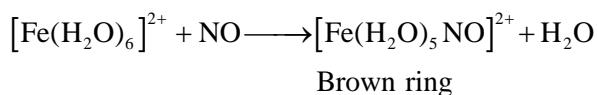
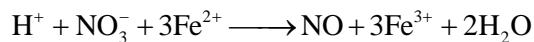


NITRIC ACID (HNO₃):

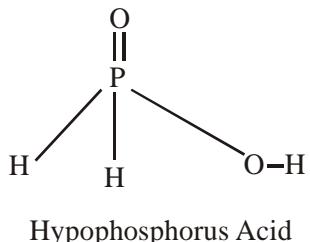
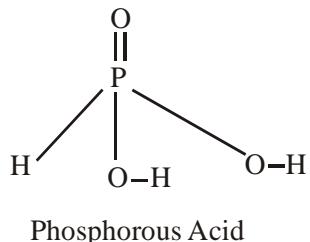
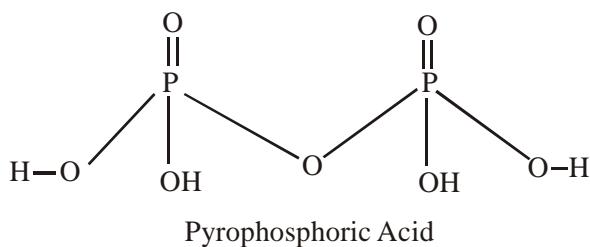
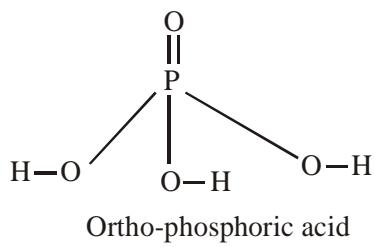
It is manufactured by contact process to use following reactions.



Nitrate ion Test :



Oxo-Acids of Phosphorus :



GROUP - 16

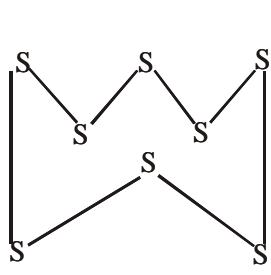
- They are called chalcogens, i.e. ore producers.
O, S, Se, Te, Po
⇒ Polonium is radioactive.

General Configuration : ns^2np^4 .

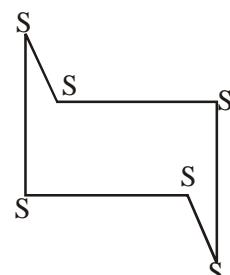
ALLOTROPES :

Sulphur forms numerous allotropes in which its two common allotropes are

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) S₈



(b) S₆

- 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 exists 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 shows higher oxidation states.

Metallic Character :

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

Hydrides :

Type H_2X .



Thermal stability decreases →

Band dissociation energy decreases →

acidic character increases →

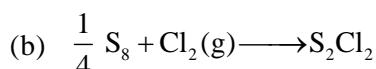
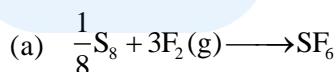
- B.Pt. $\text{H}_2\text{O} > \text{H}_2\text{Te} > \text{H}_2\text{Se} > \text{H}_2\text{S}$

↔

Halides :

$\text{SF}_4 > \text{SCl}_4 > \text{IBr}_4 > \text{SI}_4$
stability increases

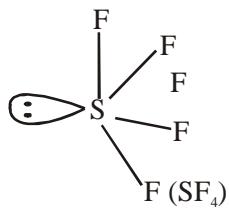
Preparation:



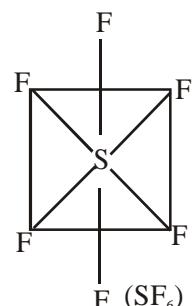
- SF_6 is inert, nontoxic gas. The inertness of SF_6 is due to the sterically protected sulphur atom which does not allow thermodynamically favourable reaction to take place. Due to this it rarely undergoes hydrolysis.
- But SeF_6 and SF_4 which is less sterically hindered undergoes hydrolysis.
- Because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



- 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. $\text{H}_2\text{S}_2\text{O}_8$ (Peroxodisulphuric 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 \downarrow react with H_2O	Br_2 Brown ESST	I_2 Lustrous, grayish black crystalline solid sublimes to form deep violet vapours
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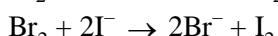
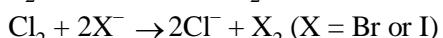
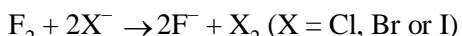
F–F bond energy is smaller than Cl–Cl but X–X bond energy after Cl_2 decrease due to increased size of X and less effective overlapping of atomic orbitals. F–F bond is weaker than Cl–Cl due to small size and large electron-electron repulsion of the lone pairs in F_2 .

OXIDATION STATE AND TRENDS IN CHEMICAL REACTIVITY :

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



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

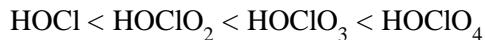


- Interhalogen are compounds with formula AX_n where halogens combine among themselves. A and X both are halogens but X is more electronegative than A.

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

- ⇒ Acidic character in aqueous solution.
 $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$
- ⇒ 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:



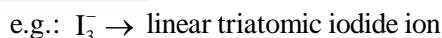
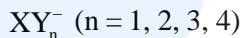
acidic strength increases

Inter-halogen compounds	AX_n :		
	$n = (1, 3, 5 \text{ or } 7)$		
e.g.	AX	AX_3	AX_5
	ClF	ClF_3	IF_7
	BrF	BrF_3	IF_7
	ICI	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 :



Polyhalonium cations:

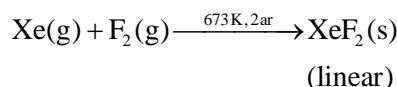
They are XY_{2n}^+ type

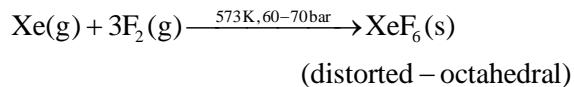
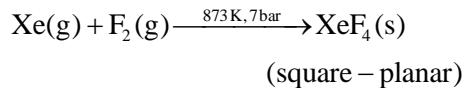


GROUP - 18

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 :

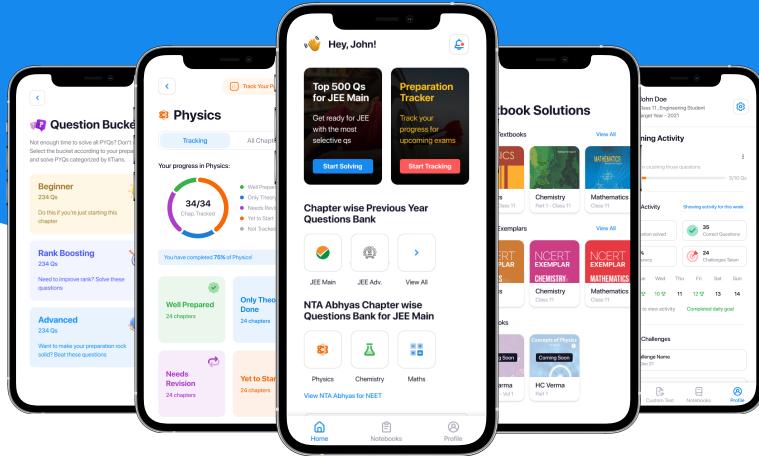
- (a) $2\text{XeF}_2\text{(g)} + 3\text{H}_2\text{O(l)} \longrightarrow 2\text{Xe(g)} + \text{HF(aq)} + \text{O}_2\text{(g)}$
- (b) $\text{XeF}_2 + \text{PF}_5 \rightarrow [\text{XeF}]^+ + [\text{PF}_6]^-$ (fluoride donor)
- (c) $\text{XeF}_4 + \text{SbF}_5 \rightarrow [\text{XeF}_3]^+ [\text{SbF}_6^-]$
- (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) XeO_3 → colourless explosive solid, trigonal pyramidal structure. Xe has sp^3 hybridization.
- (e) XeOF_4 → 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)



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