

## Allotropes of Sulphur

Sulphur forms numerous allotropes, of which the most important are as under-

- (1) Rhombic ( $\alpha$ -sulphur)
- (2) Monoclinic ( $\beta$  -sulphur)

Rhombic sulphur is stable at room temperature. It transforms to monoclinic sulphur on heating above 369 K.

### (1) Rhombic sulphur ( $\alpha$ -sulphur)

- (1) It is yellow in colour with m.p. 385.8 K and specific gravity 2.06.
- (2) Its crystals are obtained on evaporating the solution of roll sulphur in  $\text{CS}_2$ .
- (3) It is insoluble in water but dissolves to some extent in benzene, alcohol and ether.
- (4) It is readily soluble in  $\text{CS}_2$ .
- (5) It is stable below 369 K and transforms into  $\beta$  -sulphur above this temperature.

### (2) Monoclinic sulphur ( $\beta$ -sulphur)

- (1) Its m.p. is 393 K and specific gravity 1.98.
- (2) It is soluble in  $\text{CS}_2$ .
- (4) This form of sulphur is prepared by melting rhombic sulphur in a dish and cooling, till crust is formed. Two holes are made in the crust and the remaining liquid poured out. On removing the crust, colourless needle shaped crystals of  $\beta$  -sulphur are formed.
- (3) It is stable above 369 K and transforms into  $\alpha$  -sulphur below it.

At 369 K both the forms are stable. This temperature is called transition temperature.

Both rhombic and monoclinic sulphur have  $\text{S}_8$  molecules. These  $\text{S}_8$  molecules are packed to give different crystal structures. The  $\text{S}_8$  molecules in both the forms have puckered ring structure (crown shaped).

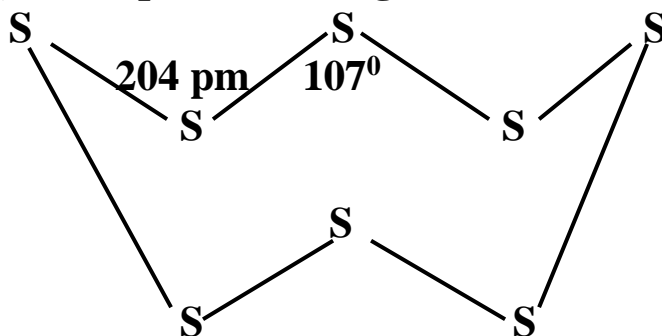


Fig.-  $\text{S}_8$  Molecule (puckered ring structure)

In the last two decades, several other modifications of sulphur containing 6 - 20 sulphur atoms per ring have been synthesized. In cyclo-S<sub>6</sub>, the ring adopts the chair form-

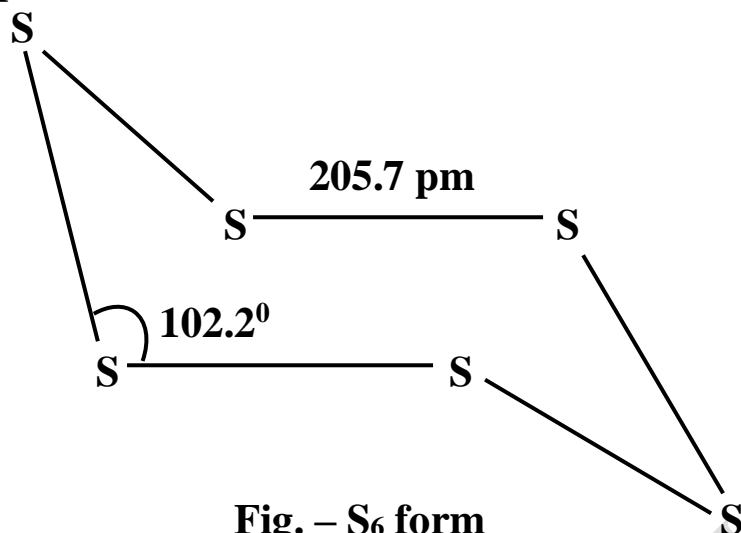


Fig. – S<sub>6</sub> form

At elevated temperatures (~1000 K), sulphur pre-dominantly contains S<sub>2</sub> molecules, which are paramagnetic in nature like O<sub>2</sub>.

**Q. Which form of sulphur shows paramagnetic behaviour ?**

**Ans.** In vapour state, sulphur partly exists as S<sub>2</sub> molecule which has two unpaired electrons in the antibonding  $\pi^*$  orbitals like O<sub>2</sub> and, therefore, exhibits paramagnetism.

### (1) Hydrides of Oxygen Family

All the elements of Group 16 form covalent hydrides of the type H<sub>2</sub>E (where, E = O, S, Se, Te, Po). All these hydrides are gaseous except H<sub>2</sub>O which is liquid at room temperature due to inter- molecular hydrogen bonding.



In all these hydrides, central atom is sp<sup>3</sup> hybridised with two bond pairs and two lone pair of electrons in its valence shell. Thus, these hydrides have angular (V- shaped) geometry.

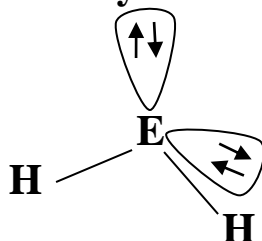


Fig.- Hydrides of O-family (Angular or V-shaped)

All these hydrides are covalent and are gaseous in nature at room temperature except H<sub>2</sub>O which is liquid due to strong inter-molecular hydrogen bonding.

The important properties of the hydrides of O-family are listed here-

### (1) Bond Angle

The bond angle of hydrides of O-family decreases on moving down the group and follows following order-

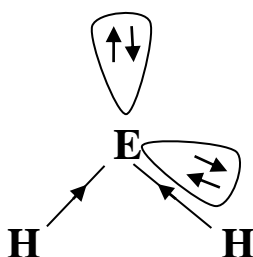


Fig.- Hydrides of O-family ((Angular or V-shaped))

In fact, bond angle of these hydrides depends upon the atomic size and electro-negativity of central atom. If the atomic size of central atom is smaller and its electro-negativity is larger, it attracts the bonded electron pair of E-H bond more strongly towards itself. Thus, distance between bonded electron pairs of E-H bonds gets decreased and therefore, repulsion amongst these electron pairs gets increased. Hence, the bond angle is relatively larger.

On moving down the group, the atomic size of central atom goes on increasing and electro-negativity goes on decreasing. Hence, the bond angle goes on decreasing.

Hydride	H <sub>2</sub> O	H <sub>2</sub> S	H <sub>2</sub> Se	H <sub>2</sub> Te	H <sub>2</sub> Po
Bond angle	104.5 <sup>0</sup>	92 <sup>0</sup>	91 <sup>0</sup>	90 <sup>0</sup>	-

### (2) Thermal Stability

The thermal stability of hydrides of N-family decreases on moving down the group and follows following order-



In fact, on moving down the group, the atomic size of central atom goes on increasing and therefore, their bond dissociation enthalpy and thermal stability goes on decreasing.

Hydride	H <sub>2</sub> O	H <sub>2</sub> S	H <sub>2</sub> Se	H <sub>2</sub> Te	H <sub>2</sub> Po
Bond dissociation Enthalpy (KJmol <sup>-1</sup> )	463	347	276	238	-

### (3) Reducing Nature

The reducing nature of hydrides of O-family increases on moving down the group and follows following order-



In fact, reducing nature of the hydrides depends upon their thermal stability and increases with decreases of thermal stability. On moving down the group, the atomic size of central atom goes on increasing and therefore, their bond dissociation enthalpy and thermal stability goes on decreasing. Hence, the reducing character of the hydrides goes on increasing. Here, water does not show reducing behavior, while H<sub>2</sub>S is a good reducing agent. H<sub>2</sub>Te is the strongest reducing agent amongst all the hydrides of O-family.

### (4) Acidic Nature

All the oxides of O-family are acidic in nature except H<sub>2</sub>O which is neutral. Acidic strength of hydrides of O-family goes on increasing on moving down the group and follows following order-



In fact, acidic strength of hydrides of O-family depends upon ease to which they ionize to give proton. The greater the ease to which a hydride ionizes to give proton, more is acidic strength of the respective hydride.

On moving down the group, the bond strength of E-H bonds goes on decreasing and therefore, the ease to which these hydrides ionize to give proton increases. Thus, the acidic strength of hydrides of O-family increases on moving down the group.

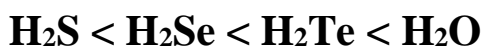
### (5) Boiling point

In general, boiling point increases with increase of the molecular mass of the compounds. Hence, the boiling point of the hydrides of oxygen family goes on increasing on moving down the group. However, the boiling point of H<sub>2</sub>O is found exceptionally higher than the boiling point of all the hydrides of O-family.

In fact, H<sub>2</sub>O involves intermolecular hydrogen bonding. Hence, additional intermolecular attraction operates amongst H<sub>2</sub>O molecules. Thus,

its boiling point becomes exceptionally higher than all the hydrides of O-family.

Thus, the order of boiling point of different hydrides of O-family will be as under-



Hydride	H <sub>2</sub> S	H <sub>2</sub> Se	H <sub>2</sub> Te	H <sub>2</sub> O
Boiling point (K)	213	232	269	373

## (2) Oxoacids of Sulphur

Sulphur forms following two series of oxo acids-

(1) Sulphurous series

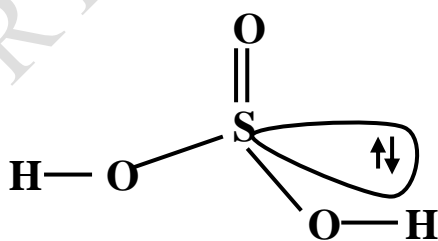
(2) Sulphuric series

In all these oxoacids, sulphur atom is sp<sup>3</sup> hybridized and contains at least one S=O and at least one S-OH bond. Here the hydrogen atoms of O-H bonds are ionizable and are acidic in nature. The number of such hydrogen atoms corresponds to the basicity of the acid. On the other hand, the hydrogen atoms attached directly to the sulphur atom are non-ionizable and is responsible for the reducing nature of the acid.

Oxo acids of Sulphur involves pπ-dπ bonds between oxygen and sulphur atoms.

Some important oxo acids of Sulphur along with their important properties are listed here-

### (1) Orthosulphurous acid (H<sub>2</sub>SO<sub>3</sub>)



Orthosulphurous acid

(S = +4)

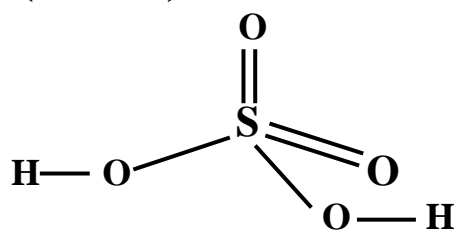
It is an unstable acid which is known only in solution phase. It is nothing but the aqueous solution of SO<sub>2</sub>.

It is a weak di-basic acid which ionizes in two steps and therefore, has two acidity constants.



It forms two types of salts of which one is acidic while, the other one is neutral. Here, since, sulphur is present in lower oxidation state, it shows reducing behaviour.

**(2) Orthosulphuric acid ( $H_2SO_4$ )**



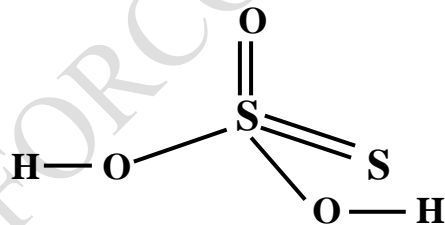
**Orthosulphuric acid**  
(S = +6)

It is a di-basic strong acid which shows strong oxidizing behaviour. It ionizes in two steps and therefore, has two acidity constants. It forms two types of salts of which one is acidic while, the other is neutral.

It shows strong affinity for water and therefore, it is used as dehydrating agent in organic reactions.

Because of its extensive use it is also called the king of chemicals.

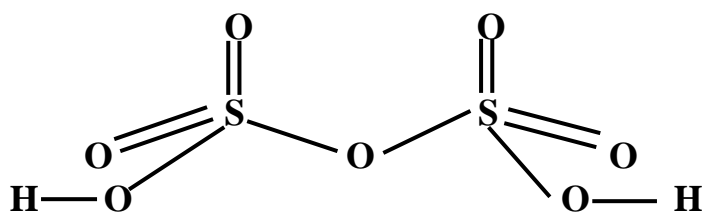
**(3) Thiosulphuric acid ( $H_2S_2O_3$ )**



**Thiosulphuric acid**  
(S = +2)

It is a di-basic strong acid which shows strong reducing behaviour. It ionizes in two steps and therefore, has two acidity constants. It forms two types of salts of which one is acidic while, the other is neutral.

**(4) Pyrosulphuric acid ( $H_2S_2O_7$ )**



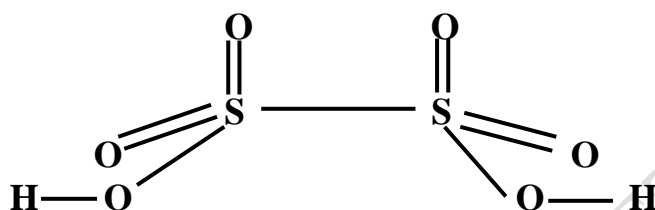
**Pyrosulphuric acid**  
(S = +6)

It is obtained by removal of a water molecule from two molecules of sulphuric acid. It is a di-basic acid which also shows strong oxidizing behaviour. It involves S-O-S bond.

Pyrosulphuric acid is nothing but concentrated sulphuric acid saturated with sulphur trioxide ( $\text{H}_2\text{SO}_4 + \text{SO}_3$ ). It is also called fuming sulphuric acid or oleum.

Sulphuric acid is usually preserved and transported as oleum. It is mixed with calculated amount of water to get sulphuric acid of desired concentration.

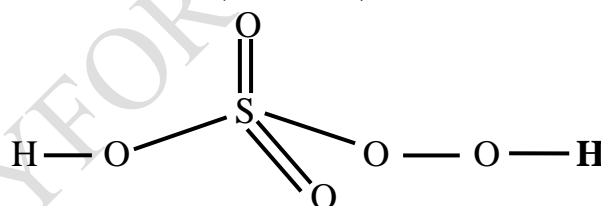
**(5) Disulphuric acid ( $\text{H}_2\text{S}_2\text{O}_6$ )**



**Disulphuric acid**  
(S = +5)

It is a di-basic acid which involves S - S bond. It is the only oxoacid of sulphur in which both the sulphur atoms remain bonded together directly.

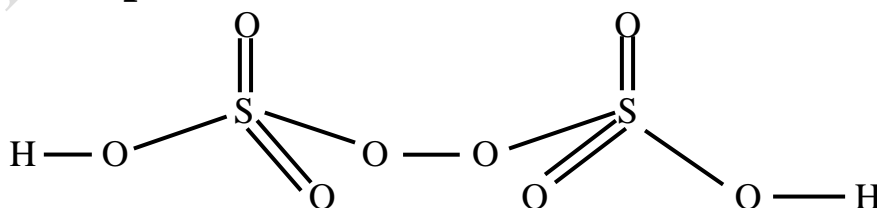
**(6) Peroxomonosulphuric acid ( $\text{H}_2\text{SO}_5$ )**



**Peroxomonosulphuric acid**  
(S = +6)

It is a di-basic peroxy acid which involves peroxide bond (-O - O- bond). It shows strong oxidizing behavior and is also called Caro's acid.

**(7) Peroxodisulphuric acid ( $\text{H}_2\text{S}_2\text{O}_8$ )**



**Peroxodisulphuric acid**  
(S = +6)

It is a di-basic peroxy acid which involves peroxide bond (-O – O-bond). It also shows strong oxidizing behavior and is also called Marshal's acid.

## Inter-halogen Compounds

Difference of the electro-negativities of different halogen atoms is relatively larger. Hence, they combine together to form compounds called inter-halogen compounds.

Some important types of inter-halogen compounds are listed here-

- (1) XY Type - ClF, BrCl, ICl etc.
- (2) XY<sub>3</sub> Type - ClF<sub>3</sub>, BrF<sub>3</sub>, ICl<sub>3</sub> etc.
- (3) XY<sub>5</sub> Type – ClF<sub>5</sub>, BrF<sub>5</sub>, ICl<sub>5</sub> etc.
- (4) XY<sub>7</sub> Type – IF<sub>7</sub>

Inter-halogen compounds are found to be more reactive as compared to their constituent halogens. It is because of lesser extent of overlapping in different sized orbitals of two halogens. Hence, the bond formed is relatively weaker.

The geometry of XY type of inter-halogen compounds is linear while, those of other inter-halogen compounds are as under-

(1) Geometry of ClF<sub>3</sub> molecule- In ClF<sub>3</sub> molecule, central Cl atom is sp<sup>3</sup>d hybridized and contains in all five electron pairs in its valence shell, of which three are bond pairs, while rest two are lone pairs. Here, lone pairs occupy equatorial positions, Hence, the molecule has T-shaped geometry. Here,

$$\begin{aligned} N &= \frac{1}{2}(V + M + A - C) \\ &= \frac{1}{2}(7 + 3 + 0 - 0) \\ &= 5 \text{ (sp}^3\text{d)} \end{aligned}$$

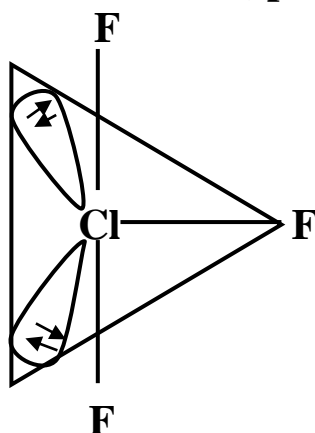


Fig.- Geometry of ClF<sub>3</sub> molecule (T-shaped)

- The geometry of BrF<sub>3</sub>, BrCl<sub>3</sub> and ICl<sub>3</sub> is identical to that of ClF<sub>3</sub>.



(2) **Geometry of ClF<sub>5</sub> molecule-** In ClF<sub>5</sub> molecule, central Cl atom is sp<sup>3</sup>d<sup>2</sup> hybridized and contains in all six electron pairs in its valence shell, of which five are bond pairs, while rest one is lone pair. Here, lone pair occupies one of the axial positions, Hence, the molecule has square pyramidal geometry. Here,

$$\begin{aligned} N &= \frac{1}{2}(V + M + A - C) \\ &= \frac{1}{2}(7 + 5 + 0 - 0) \\ &= 6 \text{ (sp}^3\text{d}^2\text{)} \end{aligned}$$

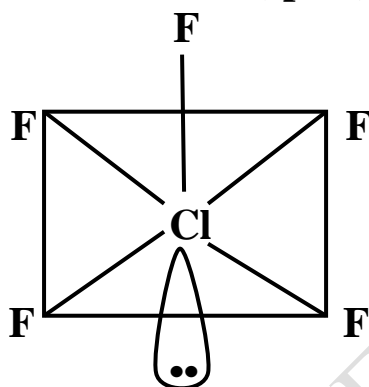


Fig.- Geometry of ClF<sub>5</sub> molecule (square pyramidal)

- The geometry of BrF<sub>5</sub> and BrCl<sub>5</sub> is identical to that of ClF<sub>5</sub>.

(3) **Geometry of IF<sub>7</sub> molecule-** In IF<sub>7</sub> molecule, central I atom is sp<sup>3</sup>d<sup>3</sup> hybridized and contains in all seven bonded electron pairs in its valence shell. Thus, there is no lone pair of electrons in valence shell of central iodine atom. Hence, the molecule has regular pentagonal bipyramidal geometry. Here,

$$\begin{aligned} N &= \frac{1}{2}(V + M + A - C) \\ &= \frac{1}{2}(7 + 7 + 0 - 0) \\ &= 7 \text{ (sp}^3\text{d}^3\text{)} \end{aligned}$$

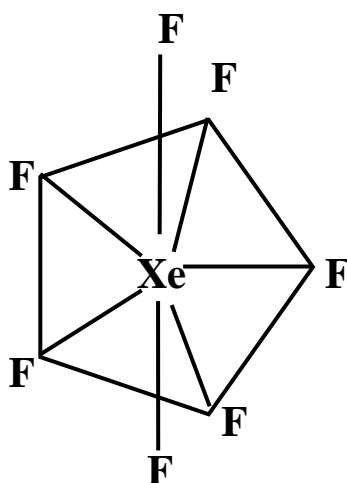


Fig.- Geometry of IF<sub>7</sub> molecule (pentagonal bipyramidal)

## Oxoacids of Halogens

Halogens form a number of oxoacids which are listed here-

(1) Hypohalous acid or Halic (I) acid

HFO	HClO	HBrO	HIO
Hypofluorous acid	Hypochlorous acid	Hypobromous acid	Hypoiodous acid

(2) Halous acid or Halic (III) acid

-	HOCIO	-	-
	Chlorous acid		

(3) Halic acid or Halic (V) acid

-	HOCIO <sub>2</sub>	HOBrO <sub>2</sub>	HOIO <sub>2</sub>
	Chloric acid	Bromic acid	Iodic acid

(4) Perhalic acid or Halic (VII) acid

-	HOCIO <sub>3</sub>	HOBrO <sub>3</sub>	HOIO <sub>3</sub>
	Perchloric acid	Perbromic acid	Periodic acid

Due to small atomic size and high electronegativity, fluorine forms only one oxoacid i.e. HOF called hypofluorous acid or fluoric (I) acid.

Most of these oxoacids cannot be isolated in pure state. They are stable only in aqueous solutions or in the form of their salts.

The acidic strength of a definite kind of oxoacids of different halogens decreases with decrease of the electronegativity of the halogens. For example, the order of acidic strength of different perchloric acids is as under-



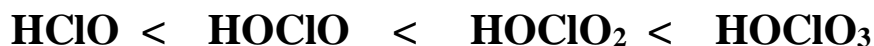
Here, perchloric acids (HOXO<sub>3</sub>) do not involve peroxide bond (-O-O-bond). Hence, they are not true peracids.

## Oxoacids of chlorine

Chlorine forms a number of oxoacids which are listed here-

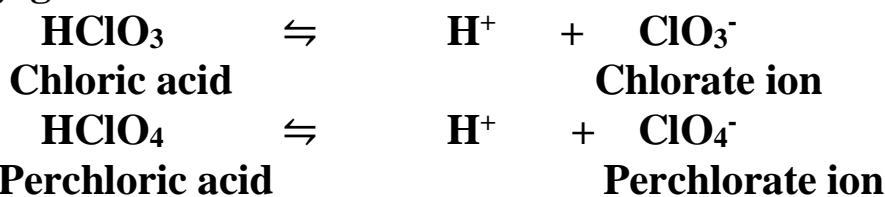
HClO	HOCIO	HOCIO <sub>2</sub>	HOCIO <sub>3</sub>
Hypochlorous acid	Chlorous acid	Chloric acid	Perchloric acid

The acidic strength of these oxoacids increases with increase of the oxidation number of the central chlorine atom. Thus, the order of acidic strength of different oxoacids of chlorine is as under-



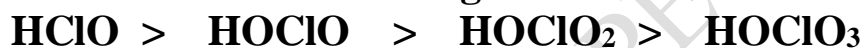
Here, perchloric acids (HOCIO<sub>3</sub>) is considered to be the strongest known acid of nature.

This order of acidic strength of different oxoacids of chlorine is explained in terms of the order of stability of their conjugate base. For example, the conjugate base of  $\text{HOClO}_2$  and  $\text{HOClO}_3$  are as under-



Here, in perchlorate ion the dispersal of negative charge occurs on four oxygen atoms, while in chlorate ion it occurs only on three oxygen atoms. Thus, perchlorate ion is more resonance stabilized as compared to chlorate ion. Hence, perchloric acid has more tendency to give proton and is the strongest acid. On the other hand, Chloric acid has relatively lesser tendency to give proton and therefore, it is relatively weaker acid.

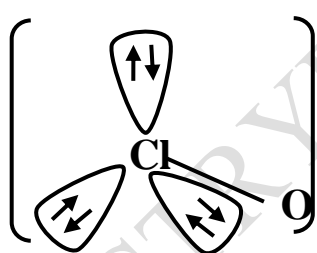
Different oxoacids of chlorine are oxidizing in nature. The oxidizing behavior of these oxoacids decreases with increase of the oxidation number of chlorine atom and follows following order-



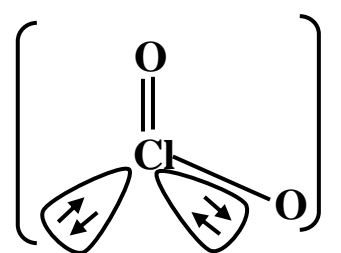
Here,  $\text{HClO}$  shows the strongest oxidizing nature.

### Structure of Different oxoacids of Chlorine-

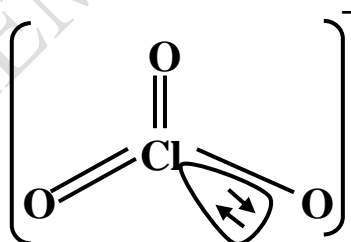
In its oxoacids, central chlorine atom is  $sp^3$  hybridized. The geometry of the conjugate base of these oxoacids are as under-



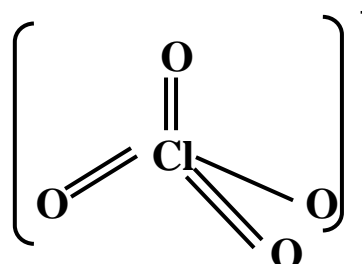
Hypochlorous ion  
(Linear)



Chlorous ion  
(Angular or V-shaped)



Chlorate ion  
(Trigonal pyramidal)



Perchlorate ion  
(Tetrahedral)

## Compounds of Xenon

Amongst inert gases, xenon is most reactive and combines with highly electronegative atoms like fluorine and oxygen in drastic conditions to form a few number of compounds. Some important compounds of xenon along with hybridization state of central xenon atom and geometry are listed here-

(1) **Geometry of XeF<sub>2</sub> molecule-** In XeF<sub>2</sub> molecule, central Xe atom is sp<sup>3</sup>d hybridized and contains in all five electron pairs in its valence shell, of which two are bond pairs, while rest three are lone pairs. Here, lone pairs occupy all the equatorial positions, while both the fluorine atoms occupy axial positions. Thus, XeF<sub>2</sub> molecule has linear geometry.

$$\begin{aligned} N &= \frac{1}{2}(V + M + A - C) \\ &= \frac{1}{2}(8 + 2 + 0 - 0) \\ &= 5 \text{ (sp}^3\text{d)} \end{aligned}$$

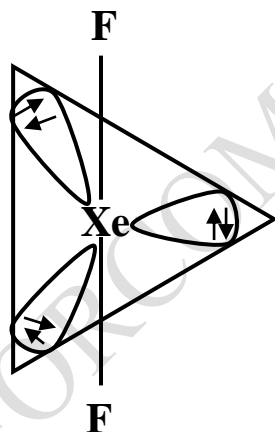


Fig.- Geometry of XeF<sub>2</sub> molecule (linear)

(2) **Geometry of XeF<sub>4</sub> molecule-** In XeF<sub>4</sub> molecule, central Xe atom is sp<sup>3</sup>d<sup>2</sup> hybridized and contains in all six electron pairs in its valence shell, of which four are bond pairs, while rest two are lone pairs. Here, lone pairs occupy both the axial positions, while fluorine atoms occupy all the equatorial positions. Thus, XeF<sub>4</sub> molecule has square planar geometry.

$$\begin{aligned} N &= \frac{1}{2}(V + M + A - C) \\ &= \frac{1}{2}(8 + 4 + 0 - 0) \\ &= 6 \text{ (sp}^3\text{d}^2\text{)} \end{aligned}$$

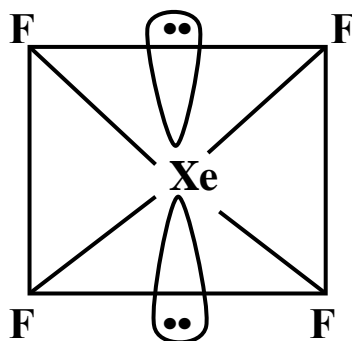


Fig.- Geometry of XeF<sub>4</sub> molecule (square planar)

(3) **Geometry of XeF<sub>6</sub> molecule-** In XeF<sub>6</sub> molecule, central Xe atom is sp<sup>3</sup>d<sup>3</sup> hybridized and contains in all seven electron pairs in its valence shell, of which six are bond pairs, while rest one is lone pair. Here, lone pair occupies one of the equatorial positions. Thus, XeF<sub>6</sub> molecule has distorted octahedral geometry.

$$\begin{aligned}
 N &= \frac{1}{2}(V + M + A - C) \\
 &= \frac{1}{2}(8 + 6 + 0 - 0) \\
 &= 7 \text{ (sp}^3\text{d}^3\text{)}
 \end{aligned}$$

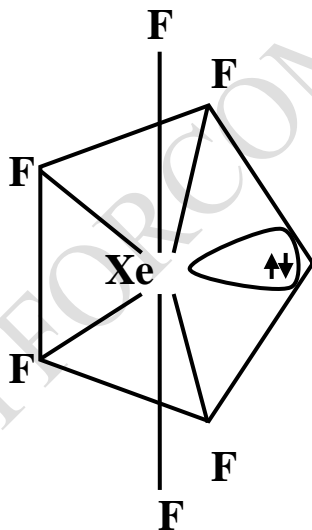


Fig.- Geometry of XeF<sub>6</sub> molecule (distorted octahedral)

(4) **Geometry of XeOF<sub>2</sub> molecule-** In XeOF<sub>2</sub> molecule, central Xe atom is sp<sup>3</sup>d hybridized and contains in all six electron pairs in its valence shell, of which four are bond pairs (three sigma, one pi), while rest two are lone pairs. Here, lone pairs and oxygen atom occupy equatorial positions, while both the fluorine atoms occupy axial positions. Thus, XeOF<sub>2</sub> molecule has T-shaped geometry.

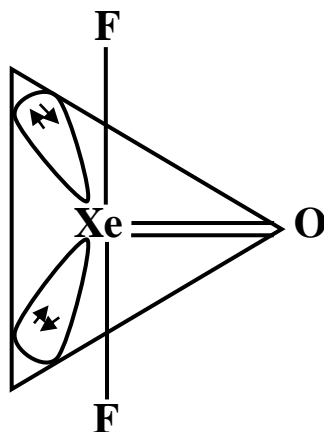


Fig.- Geometry of  $\text{XeOF}_2$  molecule (T-shaped)

(5) **Geometry of  $\text{XeOF}_4$  molecule-** In  $\text{XeOF}_4$  molecule, central Xe atom is  $sp^3d^2$  hybridized and contains in all seven electron pairs in its valence shell, of which six are bond pairs (five sigma, one pi), while rest one is lone pair. Here, lone pair and oxygen atom occupy axial positions, while fluorine atoms occupy equatorial positions. Thus,  $\text{XeOF}_4$  molecule has square pyramidal geometry.

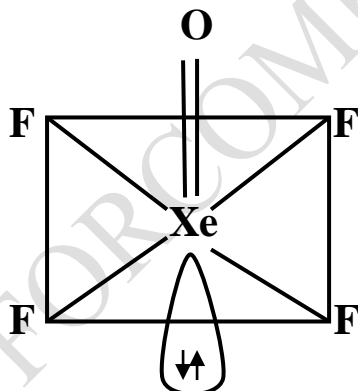


Fig.- Geometry of  $\text{XeOF}_4$  molecule (Square pyramidal)

(6) **Geometry of  $\text{XeO}_3$  molecule-** In  $\text{XeO}_3$  molecule, central Xe atom is  $sp^3$  hybridized and contains in all seven electron pairs in its valence shell, of which six are bond pairs (three sigma + three pi), while rest one is lone pair. Thus,  $\text{XeO}_3$  molecule has trigonal pyramidal (ammonia like) geometry.

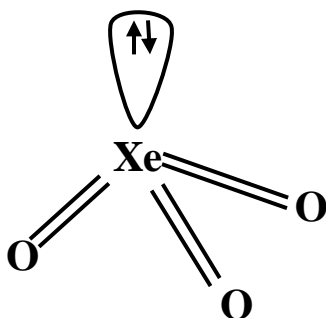


Fig.- Geometry of  $\text{XeO}_3$  molecule (Trigonal pyramidal)