HYDRIDES:

- Binary compounds of VI group element with hydrogen are called hydrides.
- VI group elements form hybrids of the type H_2M.
- All the hydrides of VI group elements are **covalent.**
- Except water other hydrides are **poisonous gases** with unpleasant or foul-smelling gases.
- Water is a liquid at room temperature.
- The affinity of the elements to form hydrides decreases from oxygen to polonium.
- The thermal stability of the hydrides decreases from H_2O to H_2Po due to the increase in bond length and decrease in bond energy with increase in atomic size.

  $H_2O > H_2S > H_2Se > H_2Te > H_2Po$
- Water can be prepared directly from hydrogen and oxygen but H_2S, H_2Se and H_2Te can be prepared by the action of acids on metal sulphides, selenides and tellurides.

  1) $FeS + H_2SO_4 \rightarrow H_2S + FeSO_4$

  2) $Al_2Se_3 + HCl \rightarrow H_2Se + AlCl_3$

  3) $Al_2Se_3 + H_2O \rightarrow H_2Se + Al(OH)_3$

Boiling points decreases from H_2O to H_2S and then increases

$H_2S < H_2Se < H_2Te < H_2Po < H_2O$

- **Volatility** increases from H_2O to H_2S and then decreases to H_2Po.

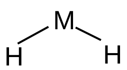
  $H_2S > H_2Se > H_2Te > H_2Po > H_2O$
- H_2O is a liquid due to the association of molecules through hydrogen bonds.
- The least volatility and high boiling point of water is due to hydrogen bonds.
- In other hydrides hydrogen bonding is not possible due to less electronegative central atom.
- **Reducing power** increases from H_2O to H_2Po due to decrease in bond energy.
- **Acidic character** increases from H_2O to H_2Po
- Enthalpy of formation : increases from top to bottom.

  H_2O and H_2S ΔH values are negative (exothermic)

  H_2Se, H_2Te, H_2Po ΔH value are positive (endothermic)
- **Thermal stability :** depends on bond strength between central and bonded atom.

  $H_2O \xrightarrow[\text{decreases}]{} H_2Po$

  due to decrease in bond energy, increase in bond length, increase in size of central atom decreases the bond strength.
- Heat of dissociation / enthalpy of decomposition : decreases and stability decreases .
- All the hydrides have bent structure.



- The $\angle$HMH bond angle in water is $104^\circ.31^1$ but in other hydrides it is almost equal to 90°. Order of bond angle $H_2O > H_2S > H_2Se > H_2Te > H_2Po$
- In H_2O oxygen is involved in sp^3 hybridisation but in other hydride pure 'p' orbitals are participated in bonding.
- Oxygen and sulphur form less stable polyoxides and polysulphides like H_2O_2, H_2S_2, H_2S-

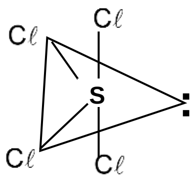
$_n$,(n=2 to10)

HALIDES :

- VI A group elements form monohalides of the type M_2X_2 ; dihalides of the type MX_2; tetrahalides of the type MX_4; and hexahalides of the type MX_6 (Where M = S, Se, Te ; X = halogen).
- The oxidation states of S, Se and Te in monohalides is +1, in dihalides is +2, in tetrahalides is +4 and in hexahalides is + 6.
- Since the electronegativity of fluorine is greater than oxygen the compounds of fluorine and oxygen are called **fluorides of oxygen** rather than oxides of fluorine.
- Except oxygen all the other VI A group elements form hexafluorides.
- Sulphur hexafluoride is formed by the direct reaction between sulphur and fluorine
  $S + 3F_2 \rightarrow SF_6$
- SF_6 is colourless, odourless, non – inflammable gas.
- SF_6 is highly stable and extremely inert compound. it is used as gas insulator.
- SF_6 is a covalent compound and have low boiling point.
- In SF_6 have octahedral shape.
- SF_6 have octahedral shape.
- All $\angle FSF$ are 90°
- SF_4 can be prepared indirectly by the reaction between sulphur and cobalt trifluoride.
  $S + 4CoF_3 \rightarrow SF_4 + 4CoF_2$
- SCl_4 can be prepared by the direction between sulphur and chlorine
  $S + 2Cl_2 \rightarrow SCl_4$
- SCl_4 is a unstable liquid.
- Tetrachlorides undergo hydrolysis to give the corresponding acids.
- SCl_4 gives sulphurous acid on hydrolysis.

$$SCl_4 + 4H_2O \rightleftharpoons S(OH)_4 + 4HCl$$
$$\downarrow$$
$$H_2SO_3 + H_2O$$

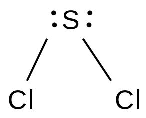
- SF_4 and SCl_4 acts both as Lewis acids and Lewis bases .
- SF_4 and SCl_4 have distorted trigonal bipyramidal structure with one corner of the equatorial position is occupied by lone pair.
- The hybridisation of sulphur in SF_4 and SCl_4 is sp^3d



- The best known dihlaide is SCl_2
- SCl_2 is a foul smelling red liquid
- When sulphur monochloride is saturated with chlorine sulphur dichloride is formed

$S_2Cl_2 + Cl_2 \rightarrow 2SCl_2$

- SCl_2 is angular in shape.
- In SCl_2 sulphur is in sp^3 hybridisation
- Due to the repulsion between two lone pairs and two bond pairs the $\angle$ ClSCl decreases to 103° from 109°28′

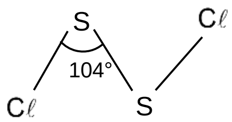


- Monohalides S_2F_2 and S_2Cl_2 are **dimers.**
- S_2F_2 and S_2Cl_2 can be prepared by the reaction between sulphur and halogens

  $2S + Cl_2 \rightarrow S_2Cl_2$
- S_2Cl_2 is used in the **vulcanization** of rubber.
- Structure of S_2Cl_2 is similar to H_2O_2 with bond angle 104°.

S – S = 2.05 Å

S – Cl = 1.99 Å



- S_2F_2 hydrolyses slowly and disproportionates

  $2S_2Cl_2 + 2H_2O \rightarrow 4HCl + SO_2 + 3S$
- Dihedral angle is 108°

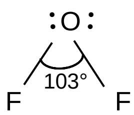
Halogen compounds of oxygen :

- Most of the halogen oxides are unstable and explosive in nature even at low pressures also.
- Iodine oxides are most stable oxygen compounds.
- **Oxygen difluoride (OF_2)** is prepared by passing fluorine gas through a very dilute solution of NaOH.

  $2NaOH + 2F_2 \rightarrow 2NaF + OF_2 + H_2O$
- OF_2 is a **pale yellow** coloured gas.
- OF_2 is more poisonous than F_2.
- OF_2 dissolves in water but does not given any oxy acid solution.

  $OF_2 + H_2O \rightarrow 2HF + O_2$
- OF_2 is an **angular** molecule in which oxygen is in sp^3 hybridisation $F\hat{O}F$ bond angle is 103° and

  O – F bond length is 1.45 Å

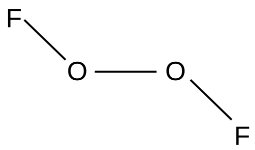


- **Dioxygen difluoride (O_2F_2) :** is prepared by passing silent electric discharge through a mixture of fluorine and oxygen at a very low temperature

  $F_2 + O_2 \xrightarrow{\text{silent electric discharge}} O_2F_2$

Structure :

- O_2F_2 has open book structure similar to H_2O_2
- Hybridisation of oxygen in O_2F_2 is sp^3
- The dihedral angle in O_2F_2 is 87°36′ where as $O\hat{O}F$ is 109°31′
- The O – O bond length is 1.27 Å



(OR)