

Inorganic chemistry II  
Second stage / Second semester

Seventh lecture

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Pro. Dr. Mohammed Hamid

**Elements of Group VIA or 16**

**(The Oxygen Family,  $ns^2np^4$ )**

**POSITION IN PERIODIC TABLE**

Group 16 or VIA of the extended form of periodic table consists of six elements oxygen (O), sulphur (S), selenium (Se), tellurium (Te), polonium (Po) and ununhexium (Uuh)". This family is known as oxygen family. These (except polonium and ununhexium) are the ore forming elements and thus called chalcogens. These are p-block elements as the last differentiating electron is accommodated on np shell. These elements have six electrons in their valency shell and thus placed in the VIth group.

The elements oxygen and sulphur are common while selenium, tellurium and polonium are comparatively rare. Oxygen is the most abundant element and is found both in free as well as in combined state. Oxygen makes up 20.9% by volume and 23% by mass of atmosphere. Most of the oxygen present in the atmosphere is produced by photosynthesis in plants. It also occurs in the form of ozone in the upper atmosphere which protects us from the harmful radiations of the sun. Oxygen makes up 46.6% by mass of the earth's crust. Sulphur is the sixteenth most abundant element and constitutes 0.034% by mass of the earth's crust. It occurs mainly in combined form. The member, polonium is radioactive in nature. The inclusion of these elements in the same subgroup is justified on the basis of same electronic configuration and similarities as well as gradation in their physical and chemical properties.

Like other groups, the first element oxygen differs from other elements of the group in several respects.

**1. Electronic Configuration**

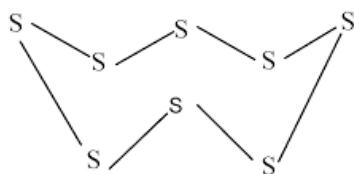
The distribution of electrons in various energy shells of the atoms of these elements is given as below:

Element	At.NO.	Electronic configuration	Inert gas core
O	8	$1s^2 2s^2 2p^4$	$[\text{He}] 2s^2 2p^4$
S	16	$1s^2 2s^2 2p^6 3s^2 3p^4$	$[\text{Ne}] 3s^2 3p^4$
Se	34	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$	$[\text{Ar}] 3d^{10} 4s^2 4p^4$
Te	52	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^4$	$[\text{Kr}] 4d^{10} 5s^2 5p^4$
Po	84	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^4$	$[\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^4$
Uuh	116	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5f^{14} 5d^{10} 6s^2 6p^6 6d^{10} 7s^2 7p^4$	$[\text{Rn}] 5f^{14} 6d^{10} 7s^2 7p^4$

All have six electrons in their outermost shell, i.e., they have electronic structure  $s^2p^4$ . The penultimate shell contains 2 electrons in oxygen, 8 electrons in sulphur and 18 electrons in Se, Te, Po and Uuh. This explains why oxygen differs from sulphur and these two from the remaining elements.

## 2. Physical Characteristics

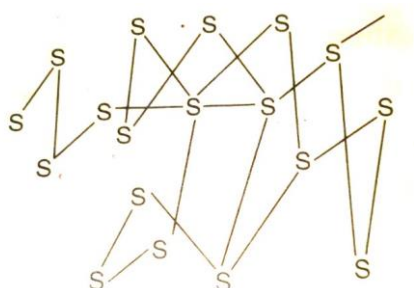
(a) Physical state: Oxygen is a gas while others are solids. Oxygen molecule is diatomic while the molecules of other elements are more complex. Sulphur, selenium and tellurium exist as staggered 8-atom rings. However, the tendency to exist in 8-atom rings is maximum with sulphur and decreases as we go down the group. In  $S_8$  molecule, every sulphur atom is in  $sp^3$  hybridized state involving both bonding and non bonding pairs of electrons.



Staggered ring structure of sulphur molecule,  $S_8$

[Oxygen atom has the tendency to form multiple bonds ( $p\pi-p\pi$  interaction) with other oxygen atom on account of small size while this tendency is missing in sulphur atom. The bond energy of oxygen-oxygen double bond ( $O=O$ ) is quite large (about three times that of oxygen-oxygen single bond,  $O-O = 34.9$  kcal mol) while sulphur-sulphur double bond ( $S=S$ ) is not so large (less than double of sulphur-sulphur single bond,  $S-S = 63.8$  kcal mol). As a result,  $-O-O-O-$  chains are less stable as compared to  $O=O$  molecule while  $-S-S-S-$  chains are more stable than  $S=S$  molecule. Therefore, at room temperature, while oxygen exists as a diatomic gas molecule, sulphur exists as  $S_8$  solid.]

The plastic sulphur which is formed by pouring liquid sulphur into water contains zig-zag long chains of sulphur atoms.



At temperatures above the boiling points, sulphur forms a red vapour, which turns to yellow as temperature is increased. In vapour there exist  $S_8$ ,  $S_6$  and  $S_2$  molecules. Above  $1000^\circ\text{C}$ , there exist only  $S_2$  molecule, which has structure like  $O_2$ .

(b) Metallic and non-metallic character: Metallic character increases with the increase of atomic number. Oxygen and sulphur are distinctly non-metallic. Selenium and tellurium show both non-metallic and metallic characters but polonium is definitely a metal.

(c) There is a gradual gradation in physical properties :

(i) Atomic and ionic radii: The atomic radii of the elements of group 16 are smaller than those of the corresponding elements of group 15. The atomic radii of the elements of this group increase gradually on moving down the group.

Element	O	S	Se	Te	Po
Atomic radii (pm)	66	104	117	137	146

[covalent radii (single bond)]

The smaller atomic radii of group 16 elements as compared with corresponding elements of groups 15 are due to the increased effective nuclear charge with increase in greater attraction towards nucleus. The attraction brings contraction in size. The gradual increase on moving down the group is due to the increase in the number of electron shells from member to member.

In the formation of anions, two electrons are being added to an atom. Therefore, the effective nuclear charge is reduced and hence, the electron cloud expands. Thus, the negative ions ( $M^{2-}$ ) are bigger in size than the corresponding atoms. Like atomic radii, ionic radii also increase gradually on moving down the group.

Element	O	S	Se	Te
Ionic radii (pm)	140	184	198	221

(ii) Ionisation energy: The ionisation enthalpies are high and thus the elements do not lose the electrons to form positive ions easily. The values decrease as the atomic number increases from O to Po and thus the tendency to form positive ion increases gradually, i.e., metallic nature increases.

	O	S	Se	Te	Po
Ionisation energy $\Delta_i H_1$ (kJ mol <sup>-1</sup> )	1314	1000	941	869	813
$\Delta_i H_2$	3388	2251	2045	1790	—

Decreases gradually

The ionisation energies of first three elements of group 16 are less than corresponding elements of group 15 in spite of the fact that nuclear charge increases. The abnormal behaviour is due to symmetrical and more stable electronic configuration of N, P and As as compared to O, S and Se respectively. However, the second ionisation values of group 16 elements are higher than those of group 15.

(iii) Electronegativity: Electronegativity decreases gradually. Oxygen is second most electronegative element after fluorine.

	O	S	Se	Te	Po
Electronegativity	3.5	2.44	2.48	2.01	1.76

Decreases gradually →

This decrease indicates a change from non-metallic to metallic character.

(iv) Melting and boiling points: The melting and boiling points increase gradually with increase in atomic number.

	O	S	Se	Te
Melting point (°C)	-219	119	217	450
	(Monoclinic)			
Boiling point (°C)	-183	445	688	990

(v) Electron affinity: Group 16 elements have high electron affinities. On moving from oxygen to sulphur, the EA<sub>1</sub> value increases and then decreases from S to Po.

Element	O	S	Se	Te	Po
EA, (kJ mol <sup>-1</sup> )	-141	-200	-195	-190	-183

The electron density in 2p energy shell in oxygen is high due to small size of oxygen atom and thus, there is some resistance to the incoming electron and thereby the EA of oxygen is comparatively low. Sulphur has maximum value and on moving from S to Po, the EA<sub>1</sub> values decrease due to increased size. the elements show allotropy:

(d) Allotropy: All the Element show Allotropic

Element	Allotropic forms
Oxygen	Ordinary oxygen and ozone
Sulphur	Rhombic, monoclinic, plastic, amorphous
Selenium	Red form (non-metallic), grey form (metallic form)
Tellurium	Crystalline and amorphous
Polonium	α and β forms (Both are metallic forms)

(e) Catenation : Oxygen and sulphur show the property of catenation. The property is more pronounced in sulphur. H-O-O-H, H-S-S-H, H-S-S-S-H, H-S-S S-S-H, the peroxides and polysulphides are fairly stable.

(f) Oxidation states: As the configuration of outer most shell is  $ns^2 np^4$ , these elements try to gain or share two electrons in order to attain inert gas configuration. Oxygen being highly electronegative shows -2 oxidation state in its compounds except in oxygen fluorides and most of the metal oxides are ionic and contain oxygen as dinegative anion. O<sup>2-</sup> Since the electronegativity decreases, the tendency to exhibit -2 oxidation state decreases as we go down in the group. However, positive oxidation states are exhibited by S, Se, Te and Po. In addition to +2 oxidation state, +4 and +6 oxidation states are observed. This is due to the availability of *d*-orbitals in these elements. Oxygen has no *d*-orbitals and hence cannot show +4 and +6 oxidation states while sulphur can have 2, 4 or 6 unpaired orbitals forming 2, 4 or 6 covalent bonds.

	3s	3p	3d	
Sulphur atom in ground state	$\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow$ $\uparrow$		Two unpaired electrons account for an oxidation state of + 2.
Sulphur atom in first excitation state	$\uparrow\downarrow$	$\uparrow$ $\uparrow$ $\uparrow$	$\uparrow$	Four unpaired electrons account for an oxidation state of + 4.
Sulphur atom in second excitation state	$\uparrow$	$\uparrow$ $\uparrow$ $\uparrow$	$\uparrow$ $\uparrow$	Six unpaired electrons account for an oxidation state of + 6.

Thus, oxygen is never more than divalent while other members may be divalent, tetravalent and hexavalent. The compounds having +4 oxidation state show both oxidising and reducing properties while compounds having +6 oxidation states are only oxidising.

(g) Multiple bonding: Oxygen atom has the tendency to form multiple bonds ( $p\pi-p\pi$  interaction) with the other oxygen atom on account of small size and high electronegativity. However, the rest of the elements do not form  $p\pi-p\pi$  multiple bonds due to their large size. Sulphur and higher members of group 16 possess vacant d-orbitals in their valence shell. They use these orbitals to form  $d\pi-p\pi$  bonds. However, this tendency is maximum and stronger in sulphur and decreases from sulphur onwards.

### 3. Trends in Chemical Reactivity

Oxygen is the most reactive element of the group despite it has high bond dissociation energy of oxygen molecule ( $493.4 \text{ kJ mol}^{-1}$ ) as nearly all its reactions are exothermic. Once initiated, these reactions continue spontaneously. Oxygen directly combines with almost all the metals except noble metals, all the non-metals except noble gases and halogens and many compounds under suitable conditions. The oxides are generally stable compounds. The elements such as W, Pt, Au, halogens and noble gases which do not directly combine with oxygen, form compounds with oxygen indirectly.

After oxygen, sulphur is quite reactive element especially at high temperatures which help in breaking of S-S bonds. Sulphur burns in air and reacts directly with carbon, phosphorus, arsenic and many metals. Oxidising acids oxidise it into  $\text{SO}_2$  and alkalis dissolve it to give sulphides and thiosulphates. It reacts with  $\text{H}_2$  and halogens. The sulphides are stable compounds and many metals are found in nature in the form of sulphides.

However, the reactivity of group 16 elements decreases from oxygen to polonium..

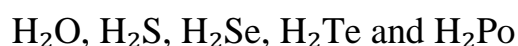


Selenium and tellurium combine with highly electropositive elements such as alkali and alkaline earth metals. Se and Te combine with oxygen, fluorine and chlorine. In general, the compounds of selenium and tellurium are less stable than oxygen and sulphur.

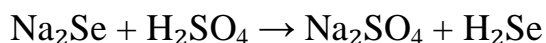
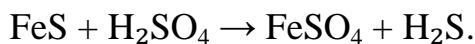
Some important trends in chemical reactivity of elements of group 16 are discussed here.

#### (a) Hydrides

All the elements of this group form the hydrides of type  $\text{H}_2\text{M}$  where,  $\text{M} = \text{O}, \text{S}, \text{Se}, \text{Te}$  and  $\text{Po}$ , i.e.,



H<sub>2</sub>O is obtained by burning hydrogen in the atmosphere of oxygen while H<sub>2</sub>S, H<sub>2</sub>Se and H<sub>2</sub>Te are obtained by the action of acids on sulphides, selenides and tellurides.



(i) Physical state: Water is colourless, odourless liquid while other hydrides are colourless, poisonous gases with bad odours.

(ii) Volatility: Water has low volatility (high boiling point) as hydrogen bonding brings association. H<sub>2</sub>S has high volatility as no hydrogen bonding is present. Volatility decreases from H<sub>2</sub>S to H<sub>2</sub>Te due to increase in molecular masses of the hydrides.

(iii) Covalent character: As the electronegativity difference between M and H decreases, the covalent character of these hydrides increases from H<sub>2</sub>O to H<sub>2</sub>Te. Water molecule is highly polar. It has high dielectric constant and hence acts as an excellent solvent for inorganic compounds.

(iv) Thermal stability: The thermal stability decreases as the atomic mass increases. Water dissociates at 2000°C while tellurium hydride, H<sub>2</sub>Te, decomposes at room temperature. This is due to an increase in M-H bond length.

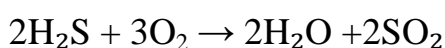
(v) Acidic nature: The hydrides are all weak acids and dissociate to varying degrees to give H<sup>+</sup> ions. The acidic strength increases from H<sub>2</sub>O to H<sub>2</sub>Te as it is evident from the values of dissociation constants.

	H <sub>2</sub> O	H <sub>2</sub> S	H <sub>2</sub> Se	H <sub>2</sub> Te
Dissociation constant (25°C)	1.0 x 10 <sup>-14</sup>	1.0 x 10 <sup>-7</sup>	1.7 x 10 <sup>-4</sup>	2.3 x 10 <sup>-3</sup>

The increasing trend can be explained on the basis of dissociation energies. The dissociation energies decrease as the bond length M-H increases from oxygen to tellurium. This facilitates the release of proton. The acidic nature can also be explained on the basis of charge density on M<sup>2-</sup> anion. The charge density on the M<sup>2-</sup> ion decreases as the size of M-atom increases from oxygen to tellurium. The decrease in charge density is responsible for the decrease in dissociation energies and thereby increasing the tendency to furnish proton.

(vi) Reducing nature: All hydrides except H<sub>2</sub>O act as reducing agents. The reducing nature increases as the atomic number of the central atom increases. This is due to weakening of M-H bond as the bond length increases with increase of size of M-atom.

(vii) Burning: H<sub>2</sub>S, H<sub>2</sub>Se, H<sub>2</sub>Te and H<sub>2</sub>Po burn in atmosphere of oxygen with blue flame forming dioxides.

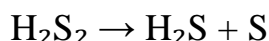
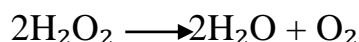


(viii) Shape: All these hydrides are V-shaped. In these hydrides, the central atom is  $sp^3$  hybridized. The bond angles are  $104.5^\circ$ ,  $92.5^\circ$ ,  $91^\circ$  and  $90^\circ$  in  $H_2O$ ,  $H_2S$ ,  $H_2Se$  and  $H_2Te$ , respectively.

This can be explained on the basis of decreasing electronegativity of central atom and decreasing tendency of  $sp^3$  hybridization.

### Other hydrides

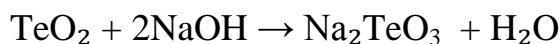
Oxygen and sulphur have a tendency to form polyoxides and polysulphides which are comparatively less stable. The two common examples are  $H_2O_2$  (hydrogen peroxide) and  $H_2S_2$  (hydrogen disulphide). They decompose on heating.



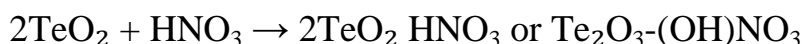
Hydrogen polysulphides ( $H-S_n-H$ ,  $n$  may be 2, 3, 4, 5) are heavy oily liquids which possess a more strong odour than  $H_2S$ .

### (b) Oxides

The most important oxides are of the type  $MO_2$  and  $MO_3$ .  $SO_2$  and  $SeO_2$  are acidic oxides and are soluble in water.  $TeO_2$  and  $PoO_2$  are insoluble in water. These are amphoteric oxides as they dissolve in both acids and bases.

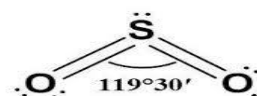
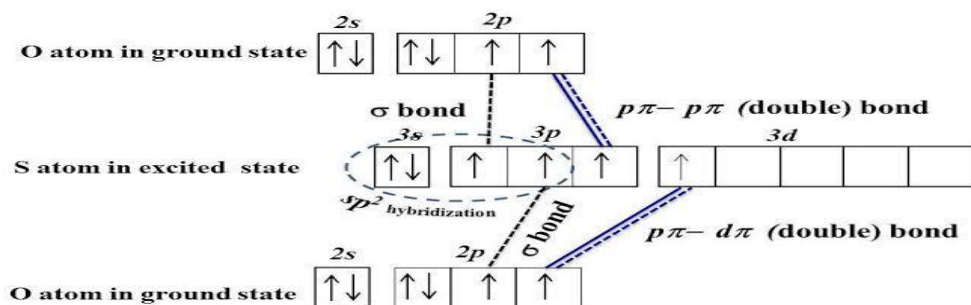


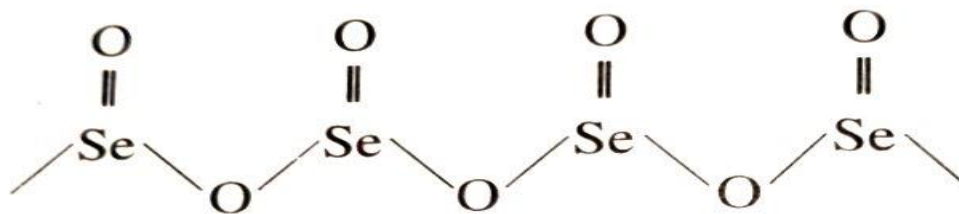
Sodium tellurite



Basic nitrate

$SO_2$  is a gas,  $SeO_2$  is a volatile solid and  $TeO_2$  is a white non-volatile solid. All the dioxides possess different structures.  $SO_2$  is an angular molecule with an O-S-O angle of  $119.5^\circ$ . The sulphur undergoes  $sp^2$  hybridization. Both the bonds have same bond lengths. This suggests resonance in the molecule.  $SeO_2$  has the same structure as  $SO_2$  in the gaseous state but the solid has a chain like structure which is not planar.



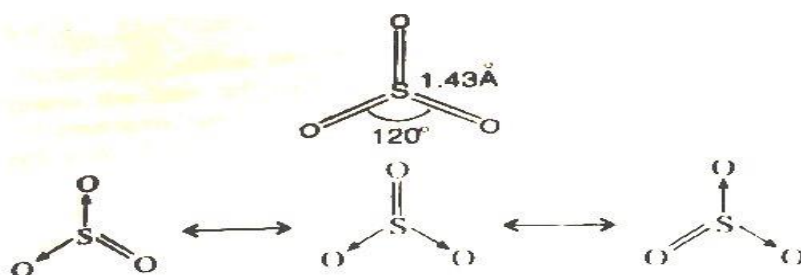


$\text{TeO}_2$  and  $\text{PoO}_2$  are crystalline ionic solids.

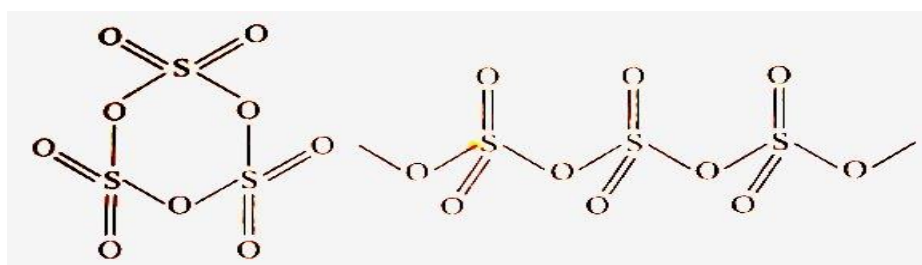
Trioxides:  $\text{SO}_3$ ,  $\text{SeO}_3$  and  $\text{TeO}_3$  are acidic in nature.



The acidic nature decreases on moving down the group.  $\text{SO}_3$  is a gas and has plane triangular structure. The structure of  $\text{SO}_3$  is similar to that of  $\text{SO}_2$  except for the fact that lone pair of electrons of sulphur atom is donated to third oxygen atom. According to another view, the true structure of  $\text{SO}$  molecule is considered to be resonance hybrid of the following structures.



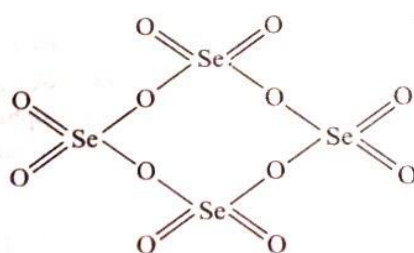
In the solid state,  $\text{SO}_3$  exists as a cyclic trimer or a linear chain



Cyclic trimer of  $\text{SO}_3$

Linear chain of  $\text{SO}_3$

Solid selenium trioxide is a cyclotetramer [ $\text{Se}_4\text{O}_{12}$ ]



(c) Oxyacids or oxoacids



Sulphur forms a number of oxyacids but selenium and tellurium form only two series of oxyacids, the-ous and -ic acids.

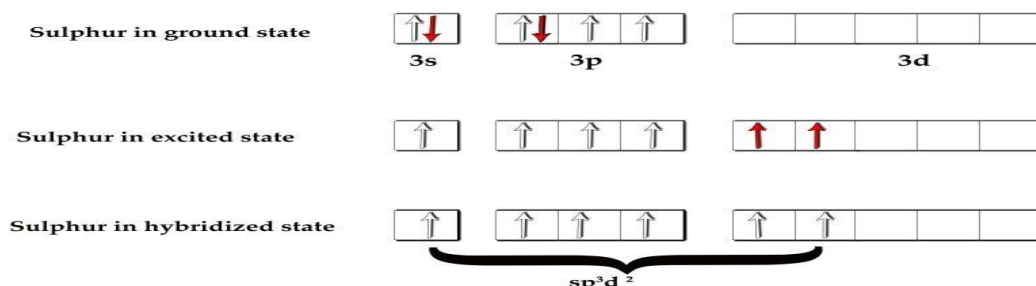
$H_2SO_3$	$H_2SeO_3$	$H_2TeO_3$
Sulphurous acid Salts Sulphite	Selenous acid Selenites	Tellurous acid Tellurites
$H_2SO_4$	$H_2SeO_4$	$H_2TeO_4$ or $H_2TeO_6$
Sulphuric acid Sulphates	Selenic acid Selenates	Telluric acid Tellurates

Oxyacids with S-S linkages are called thioacids and with O-O linkages are termed peroxy acids. Thionic acids have two-SO<sub>3</sub>H groups linked either directly or through a S-chain (polythionic acids).

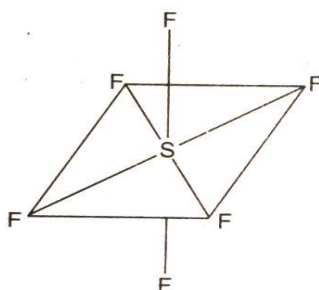
With increase oxidation number, the acid strength of oxyacid of an element increases, i.e., sulphuric acid is stronger than sulphurous acid. In the oxyacids of group 16 elements in same oxidation state, the acidic nature decreases from S to Te. The -ous acids act as reducing agents while -ic acids act as oxidizing agents. These properties decrease from S to Te. Oxyacids are dibasic in nature.

#### (d) Halides

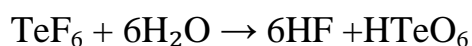
S, Se and Te form hexafluorides showing the maximum valency of six. They all involve  $sp^3d^2$  hybridization.



Thus, hexafluorides possess octahedral structure. These are colourless gases. SF<sub>6</sub> is extremely inert.

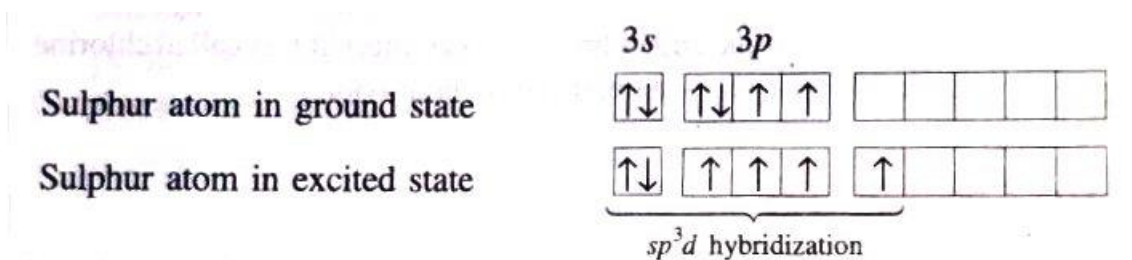


SeF<sub>6</sub> is slightly reactive while TeF<sub>6</sub> is hydrolysed by water.

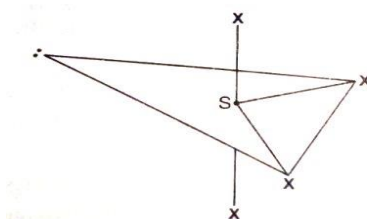


No other halogen forms the hexahalides due to larger size of Cl, Br and I

Many tetrahalides are known.  $\text{SF}_4$  is a gas,  $\text{SeF}_4$  is a liquid while  $\text{TeF}_4$  is a solid. S, Se, Te and Po form tetrachlorides and bromides while Te and Po form tetraiodides. All tetrahalides possess trigonal bipyramid structure with  $sp^3d$  hybridization.

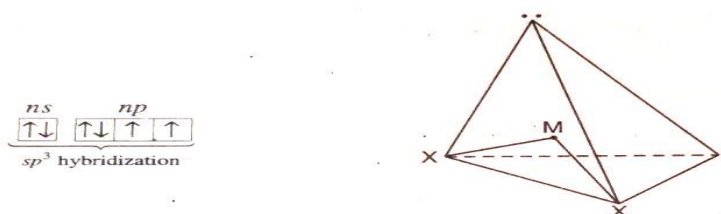


Four unpaired electrons form bonds with four halogen atoms and one position is occupied by lone pair.



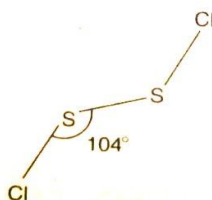
$\text{SF}_4$  is very reactive and is readily hydrolysed by water give  $\text{SO}_2$  and  $\text{HF}$  inspite of the fact that average bond energy in  $\text{SF}_4$  is greater than  $\text{SF}_6$ . This is due to the presence of empty  $3d$ -orbitals in sulphur atom in  $\text{SF}_4$ . It is used as fluorinating agent for many inorganic and organic compounds.

All the elements except selenium form stable dichlorides and dibromides, Di-jodides are not formed. Dihalides form tetrahedral molecules due to  $sp^3$  hybridization.



The bond angle is less than  $109^\circ 28'$  due to the presence of lone pairs. The bond angle is  $103^\circ$  in  $\text{SCl}_2$ ,  $101.5^\circ$  in  $\text{OF}_2$ , and  $98^\circ$  in  $\text{TeBr}_2$ .

Dimeric monohalides as  $\text{S}_2\text{F}_2$ ,  $\text{S}_2\text{Cl}_2$  and  $\text{S}_2\text{Br}_2$  are known. Their structure is similar to  $\text{H}_2\text{O}_2$ .



[Note: As fluorine is more electronegative than oxygen, the compounds of oxygen and fluorine are called fluorides. For example,  $\text{OF}_2$  is named oxygen difluoride. The compounds of oxygen and other halogens are called oxides as oxygen is more

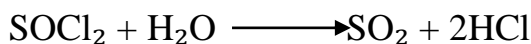
electronegative than chlorine, bromine and iodine. For example,  $\text{ClO}_2$  is called chlorine dioxide and  $\text{I}_2\text{O}_5$  is named iodine pentoxide.]

### (e) Oxyhalides

Only S and Se form oxyhalides. They are called thionyl and selenyl halides.



These react with water readily.



In addition, sulphuryl halides are also known.



These may be regarded as derivatives of  $\text{H}_2\text{SO}_4$  where both the OH groups have been replaced by two halogens atoms.

### ABNORMAL BEHAVIOUR OF OXYGEN

Oxygen differs from rest of the members of VIA group elements. The abnormal behaviour is attributed due to the following inherent characteristics :

- (i) Small size
- (ii) High electronegativity
- (iii) Non-availability of d-orbitals in the valency shell.

#### Points of difference

- (i) Oxygen is a gas while others are solids.
- (ii) It is diatomic molecule, while the rest are complex molecules, e.g.,  $\text{S}_8$ ,  $\text{Se}_8$  with puckered ring structure.
- (iii) Oxygen is highly non-metallic due to high value of electronegativity.
- (iv) Oxygen is more ionic in its compounds. The dinegative anion  $\text{O}^{2-}$  is quite common. The dinegative anions of other members are less common.
- (v) Oxygen exhibits an oxidation state of only -2 except in  $\text{OF}_2$  and peroxides. It does not show +4 and +6 oxidation states as shown by other members.
- (vi) Oxygen molecule is highly stable. The two atoms are held together by multiple bonds. The bonds are fairly strong and bond energy is quite high (117 kcal per mole). It is only at a high temperature that these bonds are broken and oxygen atoms react with other materials. Thus, ordinary oxygen is not active under ordinary conditions.
- (vii) Hydrogen bonding is present in water and many other compounds due to high electronegativity of oxygen. On account of this, water boils at higher temperature.

(viii) Oxygen molecule is paramagnetic in nature in gaseous, liquid and solid states. It is weakly attracted by a magnet. It has been explained by molecular orbital theory that oxygen molecule has two unpaired electrons.

(ix) Oxygen is the most abundant element in the earth's crust.

(x) Metals like Cu, Ag, Hg, etc., show lesser affinity with  $O_2$  to form oxide than with sulphur to form sulphide. It is due to polarizing power of  $Cu^{2+}$ ,  $Ag^+$ ,  $Hg^{2+}$  ion, owing to which they form strong bond with  $S^{2-}$

#### DISSIMILARITIES BETWEEN OXYGEN AND SULPHUR

Property	Oxygen	Sulphur
1. Electronic configuration	2 electrons in the penultimate orbit	8 electrons in the penultimate orbit
2. Physical state	Colourless, odourless gas	Pale yellow solid with faint odour
3. Abundance	Most abundant	Less abundant
4. Maximum covalency	2	6
5. Action of $HNO_3$	Not affected	Oxidised to $H_2SO_4$
6. Nature of hydride	$H_2O$ is neutral liquid under ordinary conditions. Hydrogen bonding is present.	$H_2S$ is acidic gas under ordinary conditions. No hydrogen bonding is present.
7. Molecule	Diatomic, $O_2$	Octatomic, $S_8$
8. Magnetic nature	Paramagnetic molecule	Diamagnetic molecule