BAL BHARATI PUBLIC SCHOOL

PITAMPURA

CHEMISTRY ,CLASS 12

SESSION 2020-2021

GROUP 16 P BLOCK ELEMENTS

(PART -1)

Electronic Configuration

Group 16 elements have 6 electrons in their valence shell and their general electronic configuration is ns^2np^4.

Element	Electronic Configuration
Oxygen	[He] $2s^2$ $2p^4$
Sulphur	[Ne] $3s^2$ $3p^4$
Selenium	[Ar] $3d^{10}$ $4s^2$ $4p^4$
Tellurium	[Kr] $4d^{10}$ $5s^2$ $5p^4$
Polonium	[Xe] $4f^{14}$ $5d^{10}$ $6s^2$ 6^4

Element	Symbol	Atomic No.	Electronic Configuration	Abundance In Earth's Crust (in ppm)
Oxygen	O	8	[He] $2s^2$ $2p^4$	4.66×10^5
Sulphur	S	16	[Ne] $3s^2$ $3p^4$	5.20×10^2
Selenium	Se	34	[Ar] $3d^{10}$ $4s^2$ $4p^4$	9.0×10^{-2}
Tellurium	Te	52	[Kr] $4d^{10}$ $5s^2$ $5p^4$	9.0×10^{-2}
Polonium			[Xe] $4f^{14}5d^{10}6s^2$ $6p^4$	2×10^{-3}

Fig. 3: Electronic Configuration of Group 16 Elements

	Oxygen	Sulfur	Selenium	Tellurium	Polonium
Ionization Energy (kJ/mol)	**1314**	**1000**	**941**	**869**	**812**
Ionic Radius (pm)	**140**	**184**	**198**	**221**	**230**

• Most abundant element in the group is oxygen .

• Least abundant element in the group is Po.

- These elements are collectively called as chalcogens since many metals occur as oxides and sulphides.
- Chalcogen means ore forming elements.

• Polonium was a radioactive metal (given by madam–curie).

• Oxygen is a gas, other elements are solids.

Electronic Configuration

The elements of Group16 have six electrons in the outermost shell and have ns 2 np 4 general electronic configuration.

Atomic and Ionic Radii

Due to increase in the number of shells, atomic and ionic radii increase from top to bottom in the group. The size of oxygen atom is, however, exceptionally small.

Ionisation Enthalpy

Ionisation enthalpy decreases down the group. It is due to increase in size. However, the elements of this group have **lower ionisation enthalpy values compared to those of Group15** in the corresponding periods. This is due to the fact that Group 15 elements have extra stable half filled p orbitals electronic configurations.

Electron Gain Enthalpy

The electron gain enthalpy decreases with increase in size of the central atom moving down the group. Oxygen molecule has a less negative electron gain enthalpy than sulfur. Oxygen is small in size all eight electrons are crowded in a small space any attempt to add on an electron increases electron electron repulsion.

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Thus oxygen has lesser inclination than sulfur atom to add on an electron **or we can say that** because of the compact nature of oxygen atom, it has less negative electron gain enthalpy than sulphur. However, from sulphur onwards the value again becomes less negative upto polonium.

Electronegativity

Next to fluorine, oxygen (on pauling scale oxygen EN is 3.5) has the highest electronegativity value amongst the elements. Within the group, electronegativity decreases with an increase in atomic number. This implies that the metallic character increases from oxygen to polonium.

Physical Properties

- Melting points and boiling point increases from oxygen to tellurium.

• Melting point and boiling point of polonium is less than tellurium but greater than selenium

• The large difference in the melting points and boiling points of oxygen (44.2 K and 90 K) to those of sulphur (3.87 K and 718 K) is because oxygen is a diatomic gas while sulphur exists as S_8 molecules.

• Metallic character increases from oxygen to polonium.

• Oxygen and sulphur are non metals, selenium and tellurium are metalloids, polonium is a pure metal.

• Oxygen is diatomic gas whereas sulphur exist as octa atomic S_8 molecules, which has puckered ring structure.

Chemical Properties : Oxidation states and trends in chemical reactivity

Oxidation states:

The group 16 elements have a configuration of ns^2 np^4 in their outer shell, they may accomplish noble gas configuration either by the gain of two electrons M^{-2}, or by sharing two electrons, in this manner shaping two covalent bonds. Thus, these elements indicate both negative and positive oxidation states.:

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- They show -2, +2, +4, +6 oxidation states. **Oxygen does not show +6 oxidation** state due to absence of d – orbitals.
- **Po does not show +6 oxidation state due to inert pair effect**.
- The stability of -2 oxidation state decreases down the group due to increase in atomic size and decrease in electronegativity.

- Oxygen shows high electro negativity. In all its metal oxides oxygen demonstrates a negative oxidation state of - 2. Despite - 2 oxidation states, oxygen shows - 1 oxidation state in peroxides and - 1/2 oxidation state in superoxides Oxygen shows positive oxidation state just in its compounds with fluorine, since fluorine is more electro-negative than oxygen. It shows +2 oxidation state in OF_2 and +1 in O_2F_2.

Remaining elements of the group, besides showing +2 oxidation states, also indicate +4 and +6 oxidation states due to the availability of d-orbitals in their particles.

- **The stability of +6 oxidation state decreases down the group and +4 oxidation state increases due to inert pair effect.**

	Element	Oxidation States
8O	Oxygen	-2,-1,+1,+2
$_{16}S$	Sulphur	-2,+2,+4,+6
$_{34}Se$	Selenium	-2,+2,+4,+6
$_{52}Te$	Tellurium	-2,+2,+4,+6
$_{84}Po$	Polonium	+2,+4

Anomalous behaviour of oxygen

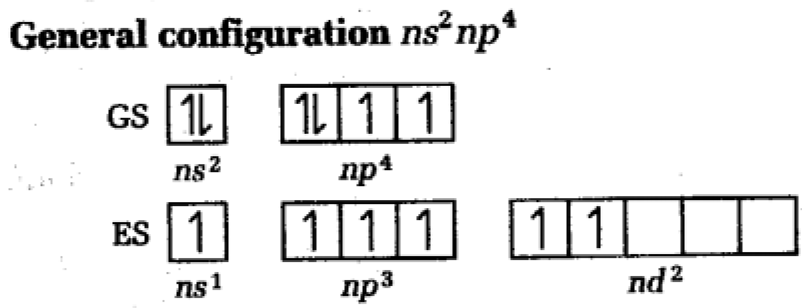
The anomalous behaviour of oxygen is because of its compact size, high electronegativity and nonavailability of d-orbitals in the valence shell. The basic differences are:

Atomicity:

Oxygen is gaseous and diatomic by nature, whereas the other elements of this group exist as solids.

Maximum Covalency:

Oxygen covalency is constrained to two, yet the covalency surpasses four in other elements because of the accessibility of d-orbitals in them.



Formation of M $^{-2}$ions:

Oxygen, because of its high electro-negativity, indicates negative oxidation state and does not demonstrate any positive oxidation state, aside from in OF_2 and O_2F_2.

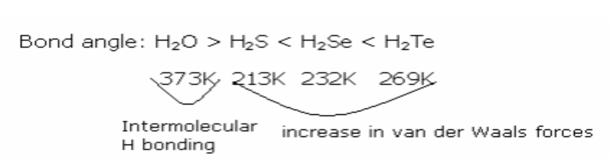
Hydrogen Bond Formation:

. **One typical example of effects of small size and high electronegativity is the presence of strong hydrogen bonding** in H2O which is not found in H2S.

REMEMBER

Since oxygen is second most electronegative element next to fluorine,
oxygen never exhibits positive oxidation states except in the compounds of fluorine.
Oxidation state : – 2, + 2, + 4,+6
Oxygen → (– 2) common (– 1) peroxides (–1/2 superoxides)
(+1) and (+2) in O2F2 and OF2 respectively.

.**Reactivity with hydrogen**: All group 16 elements form hydrides. Bent shape



Acidic nature: $H_2O < H_2S < H_2Se < H_2Te$ This is because the H-E bond length increases down the group. Therefore, the bond dissociation enthalpy decreases down the group.

Thermal stability: $H_2O < H_2S < H_2Se < H_2Te < H_2Po$ This is because the H-E bond length increases down the group. Therefore, the bond dissociation enthalpy decreases down the group.

Reducing character: $H_2O < H_2S < H_2Se < H_2Te < H_2Po$ This is because the H-E bond length increases down the group. Therefore, the bond dissociation enthalpy decreases down the group.

H_2O is a liquid while H_2S is a gas. This is because strong hydrogen bonding is present in water. This is due to small size and high electronegativity of O.

Reactivity with oxygen: EO_2 and EO_3 **Reducing character of dioxides decreases** down the group because oxygen has a strong positive field which attracts the hydroxyl group and removal of H^+ becomes easy.

Acidity also decreases down the group.

SO_2 is a gas whereas SeO_2 is solid. This is because SeO_2 has a chain polymeric structure whereas SO_2 forms discrete units.

Reactivity with halogens: EX_2 EX_4 and EX_6 The stability of halides decreases in the order $F^- > Cl^- > Br^- > I^-$. This is because E-X bond length increases with increase in size.

Among hexa halides, fluorides are the most stable because of steric reasons.

Dihalides are sp^3 hybridised, are tetrahedral in shape.

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Hexafluorides are only stable halides which are gaseous and have sp3 d^2 hybridisation and octahedral structure.

Examples of dihalides S_2F_2 , $S2Cl_2$, S_2Br_2 , Se_2Cl_2 and Se_2Br_2 . These dimeric halides undergo disproportionation as given below:

$$2Se_2Cl_2 \rightarrow SeCl_4 + 3Se$$

QUESTIONS RELATED TO THE TOPIC

1. H_2S is less acidic than H_2Te. Why?
2. Write the order of thermal stability of the hydrides of Group 16 elements.
3. Why is H_2O a liquid and H_2S a gas?
4. Why is dioxygen a gas but sulphur a solid?
5. Explain why SF4 is easily hydrolysed, whereas SF6 is resistant to hydrolysis ?
6. In group 16, the stability of + 6 oxidation state decreases and that of + 4 oxidation state increases down the group. Why ?
7. All the bonds in SF4 are not equivalent. Why
8. Explain why :

(a) H_2S is more acidic than H_2O. (b) Two S – O bonds in SO2 are identical.
(c) SF_6 is inert and stable but SF_4 is reactive. (d) Sulphur has greater tendency for catenation than oxygen.

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