Introduction

Element & atomic no.s		Electrons in penultimate shell	Electronic configuration
O – 8	→	(n–1) s^2	[He] $2s^2\ 2p^4$
S – 16	→	(n–1) $s^2\ p^6$	[Ne] $3s^2\ 3p^4$
Se – 34	→	(n–1) $s^2p^6\ d^{10}$	[Ar] $3d^{10}\ 4s^2\ 4p^4$
Te – 52	→	(n–1) $s^2p^6\ d^{10}$	[Kr] $4d^{10}5s^25p^4$
Po – 84	→	(n–1) $s^2p^6\ d^{10}$	[Xe] $4f^{14}5d^{10}6s^26p^4$

Properties :

- Most abundant element in the group is oxygen .
- Least abundant element in the group is Po.
- VI A group contains oxygen, sulphur, selenium, Tellurium and polonium belongs to p-block of periodic table.
- The first four elements are collectively called as **chalcogens** since many metals occur as oxides and sulphides.

  Ex : Pyrolusite – MnO_2 ; Haematite – Fe_2O_3

  Iron pyrites – FeS_2 ; Zinc blend – ZnS
- Chalcogen means **ore forming** elements.
- Polonium was a radioactive metal (given by madam–curie).
- Oxygen is a gas, other elements are solids.
- Atomic radius increase from oxygen to polonium.
- Ionisation potential decreases from oxygen to polonium.
- Electronegativity decreases gradually from oxygen to polonium.
- EN : Decreases [on pauling scale oxygen EN is 3.5 and most E.N in the group. Second most in the periodic table.]
- First electron affinity values are negative (exothermic)

  $O \xrightarrow[\text{increases}]{} S \xrightarrow[\text{decreases}]{} Te$

  E_1 : S > Se > Te > O
- Second electron affinity values are positive (endothermic)

  $O \xrightarrow[\text{decreases}]{} Te$ (with decreases in size repulsions decreases so E_2 decreases)
- Density increases from oxygen to polonium.
- 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 while sulphur, selenium and tellurium are octa atomic S_8, Se_8 and Te_8 molecules, which have puckered ring structure.

  $S\hat{S}S = 105^\circ$ S – S bond length = 2.21 Å
- All the elements except oxygen exhibit - 2, +2, +4 and + 6 oxidation states.
- 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 $\rightarrow$ (– 2) common
  (– 1) peroxides
  (–1/2 superoxides)
- (+1) and (+2) in O_2F_2 and OF_2 respectively.
- Sulphur

  – 2, + 2 is Ground state – $3s^2\ 3p^4$

  + 4 in 1st Excited state – $3s^2\ 3p^3\ 3d^1$

  + 6 in 2nd Excited state – $3s^2\ 3p^3\ 3d^2$

  Oxygen $\rightarrow$ maximum valency (3) in H_3O^+.

  Others $\rightarrow$ maximum valency (6)

  Oxygen cannot exhibit greater than 3 due to small size and absence of 'd' orbitals.

Allotropy (Polymorphism):

- All the VI A group elements exhibits allotropy due to
- Difference in crystal structure.
- Difference in atomicity.
- Difference in extent of polymerisation.
- The allotropic forms of oxygen are O_2 and O_3.

Oxygen :

O_2 is stable, Paramagnetic, contains two unpaired electrons and the structure is linear .

O_3 is unstable, doesn't contains any unpaired electrons hence diamagnetic and the structure is angular

- The structure $\ddot{O}=\ddot{O}$ cannot explain presence of 2 unpaired electrons in oxygen.

  So probable structure for oxygen is $:O\overset{\cdot\cdot}{=}O:$.

  (two, three e^- bonds are present in O_2)

- Among all 106 elements sulphur has highest number of allotropes.
- Se has 6 allotropes, 3 red non – metallic, 1 red amorphous, 2 grey metallic
- Te has 2 allotropes, 1 metallic, 1 non – metallic.
- Po has 2 allotropes both are metallic but differs in
  Crystal structure.
  □ - Cubic form, □ Rhombohedral – form.

Allotropes of sulphur are

1) α - sulphur or rhombic sulphur or octahedral sulphur.
2) β - sulphur or monoclinic or prismatic sulphur
3) γ - sulphur or monoclinic sulphur
4) χ - sulphur or plastic sulphur

- The most stable sulphur at room temperature is rhombic sulphur.
- Rhombic sulphur is insoluble in water but soluble in organic solvents like benzene, alcohol, ether etc.
- Monoclinic sulphur is stable above 368.5 K(95.5°c)
- At 95.5°c both rhombic and monoclinic sulphur are at equilibrium and this temperature is known as **Transition temperature** of sulphur.
- When liquid sulphur is poured in water plastic sulphur of χ - sulphur will be formed.
- The α, β, γ- sulphurs contain S_8 rings which are puckered rings or crown shape.
- Selenium has 6 – allotropes, of which three are red non metallic forms containing Se_8 rings, one amorphous red form and two grey metallic forms.
- Oxygen, sulphur shows catenation tendency. 'S' has maximum tendency.
- Sulphur can form chain with 10 'S' atoms, H_2S_n(n=2 to 10).
- Oxygen can form only peroxide chain H_2O_2.