
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 ² p ⁶ d ¹⁰	[Ar] 3d ¹⁰ 4s ² 4p ⁴
Te – 52 →	(n–1) s ² p ⁶ d ¹⁰	[Kr] 4d ¹⁰ 5s ² 5p ⁴
Po – 84 →	(n–1) s ² p ⁶ d ¹⁰	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁴

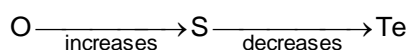
Properties :

- 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 – MnO₂ ; Haematite – Fe₂O₃

Iron pyrites – FeS₂ ; 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)



$$E_1 : \text{S} > \text{Se} > \text{Te} > \text{O}$$

- Second electron affinity values are positive (endothermic)
$$\text{O} \xrightarrow{\text{decreases}} \text{Te} \text{ (with decreases in size repulsions decreases so } E_2 \text{ decreases)}$$
 - 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
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exists as S₈ 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 S₈, Se₈ and Te₈ molecules, which have puckered ring structure.

$\angle \text{S-S-S} = 105^\circ$ 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 → (- 2) common
(- 1) peroxides
(-1/2 superoxides)

- (+1) and (+2) in O₂F₂ and OF₂ respectively.

- Sulphur

- 2, + 2 is Ground state – 3s² 3p⁴

+ 4 in 1st Excited state – 3s² 3p³ 3d¹

+ 6 in 2nd Excited state – 3s² 3p³ 3d²

Oxygen → maximum valency (3) in H₃O⁺.

Others → 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 O₂ and O₃.

Oxygen :

O₂ is stable, Paramagnetic, contains two unpaired electrons and the structure is linear .

O₃ is unstable, doesn't contains any unpaired electrons hence diamagnetic and the structure is angular

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

So probable structure for oxygen is $:\text{O}:::\text{O}:$

(two, three e⁻ bonds are present in O₂)

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- 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 .
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