# TDC Part I
# Paper I, Group B
# Inorganic Chemistry

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**TOPIC:- Group 16 & Allotropic forms**

# Group 16

The first two elements of this group, sometimes referred to as the "chalcogen" group, are familiar as oxygen, the colourless gas, vital for life and comprising about 21% of the earth's atmosphere and sulphur, a yellow non-metallic solid. The third element, selenium is not as well known, but is important in xerography processes. Tellurium is of less commercial importance, used in small amounts in metal alloys, tinting of glass and as catalysts in rubber industry. All isotopes of polonium (discovered by Marie Curie) are radioactive. Non-metallic character is maximum in oxygen and sulphur, weaker in selenium and tellurium whereas polonium is metallic. Some selected physical properties are shown in Table 17.

**Table 17: Physical properties of Group 16 elements**

| Property | O | S | Se | Te | Po |
|---|---|---|---|---|---|
| Atomic Number | 8 | 16 | 34 | 52 | 84 |
| Electronic Configuration | $[He]2s^2 2p^4$ | $[Ne]3s^2 3p^4$ | $[Ar]3d^{10} 4s^2 4p^4$ | $[Kr]4d^{10} 5s^2 5p^4$ | $[Xe]4f^{14} 5d^{10} 6s^2 6p^4$ |
| Covalent radius (pm) | 66 | 104 | 117 | 137 | 146 |
| Ionization Energy ($I^{st}$) ($KJmol^{-1}$) | 1314 | 1000 | 941 | 869 | 812 |
| Electron Affinity ($KJmol^{-1}$) | 141 | 200 | 195 | 190 | 180 |
| Electronegativity | 3.61 | 2.58 | 2.42 | 2.15 | 2.10 |
| Melting Point ($^0C$) | -218.8 | 112.8 | 217.0 | 452.0 | 250.0 |
| Boiling Point ($^0C$) | -183.0 | 444.7 | 685.0 | 990.0 | 962.0 |

## Allotropic forms

Oxygen exists primarily as the diatomic $O_2$ that is paramagnetic, but traces of triatomic $O_3$ (ozone) are found in the upper atmosphere and in the vicinity of electrical discharges. Ozone is diamagnetic and is formed when oxygen absorbs ultraviolet radiation from the sun

$$O_2 \xrightarrow{h\upsilon} 2O$$

$$O_2 + O \longrightarrow O_3$$

Ozone also absorbs ultraviolet radiation and decomposes back to oxygen

$$2O_3 \longrightarrow 3O_2$$

In the upper atmosphere a steady- state concentration of ozone is achieved which protects the earth's surface from ultraviolet radiation. Recently there has been a serious concern about the depletion of the ozone layer. Oxides of nitrogen (from high-flying aircraft) and chlorine atoms (from decomposition of chlorofluorocarbons used as aerosols, refrigerants etc.) catalyze the decomposition of ozone.

$$NO_2 + O_3 \longrightarrow NO_3 + O_2$$

$$NO_3 \longrightarrow NO + O_2$$

$$NO + O_3 \longrightarrow NO_2 + O_2$$

$$\text{Net } 2O_3 \longrightarrow 3O_2$$

$$\text{Chlorofluorocarbons} \xrightarrow{h\upsilon} Cl$$

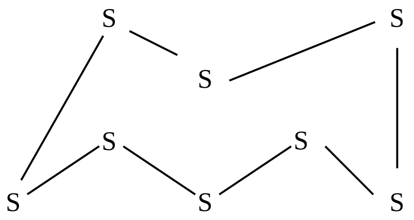
$$Cl + O_3 \longrightarrow ClO + O_2$$

$$ClO + O \longrightarrow Cl + O_2$$

$$\text{Net } O_3 + O \longrightarrow 2O_2$$

Ozone is a more powerful oxidizing agent than oxygen. Some diatomic and triatomic ions of oxygen are known e.g. $O_2^-$ (Superoxide), $O_2^{2-}$ (Peroxide), $O_3^-$ (Ozonide)

More allotropes are known for sulphur than for any other element. The most stable form at room temperature is orthorhombic or α-sulphur. This consists of $S_8$ molecules, arranged in a puckered ring




At $96^0$ C, orthorhombic sulphur is converted to monoclinic or β-sulphur in which the $S_8$ sings are arranged to give a different structure. Heating sulphur results in interesting changes in viscosity. At $119^0$C, a yellow liquid is obtained whose viscosity decreases up to $155^0$because of increased thermal motion. The viscosity increases sharply above $159^0$C till about $200^0$C, when it again decreases with the liquid acquiring a reddish tinge at high temperature. This variation in viscosity involves the tendency of S-S bonds to break and reform at high temperature. Above $159^0$C, the $S_8$ rings open giving chains, these react among themselves to give $S_{16}$ chains, $S_{24}$ chains and so on. At about $180^0$C, when the liquid has maximum viscosity, chains exceeding 200,000 sulphur atoms are known. The longer the chain, the greater is the viscosity. At higher temperatures, these chains breaks and the viscosity decreases. When molten sulphur is poured into cold water, a rubbery solid, plastic sulphur or γ-sulphur is obtained.