

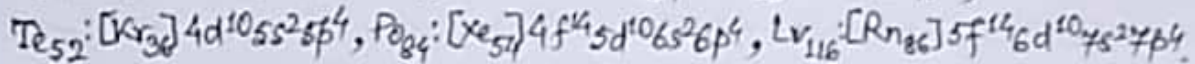
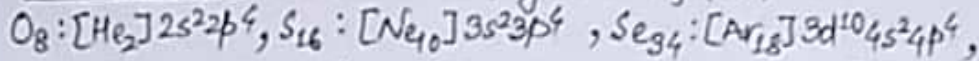
B.Sc. Part-III (Hons), Paper-06 (Inorganic Chemistry)

Group-B, Unit-1 General Chemistry of Group-16 elements (O, S, Se, Te, Po)

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Group-16 of modern periodic table includes Oxygen (O), Sulphur (S), Selenium (Se), Tellurium (Te), Polonium (Po) & Livermorium (Lv). These elements (except Po) are collectively known as Chalcogens (meaning Ore-forming elements).

1. Position in P.T.: Electronic configuration of Group-16 elements are -



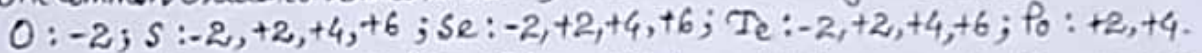
Outer electronic configuration: $ns^2 np^4$ (where $n = 2$ to 7); No. of valency electrons = 6

Group-10 + 2 + 4 = 16, Periods-2 to 7, Block-p.

So, they are placed in group-16 between group-15 (Nitrogen family) and group-17 (Halogens) of modern periodic table.

2. Oxidation states: The valence or outermost shell of Oxygen family (Group-16) has 6 electrons ($ns^2 np^4$) and they can attain stable configuration either by donating six electrons or gaining two electrons. So their oxidation states may range from -2 to +6.

The common oxidation states shown by these elements are given below:



* Oxygen also shows oxidation states: -1 (in peroxides); +1, +2 with fluorine (F).

* All elements (except O) show oxidation states +4 & +6 due to presence of vacant d-orbitals and so extend their coordination number to 4 & 6.

* Most stable and common oxidation states are -2 & +6.

3. Chemical activity/Compound formation: Oxygen and Sulphur are very reactive and in general the reactivity decreases: $\text{O} > \text{S} > \text{Se} > \text{Te} > \text{Po} > \text{Lv}$. Oxygen practically reacts with almost all the elements and its reactivity is slightly lesser than the reactivity of most reactive element (i.e. Fluorine) of group-17.

(i) Formation of hydrides: All elements of group-16 form volatile hydrides of formula H_2M (where $\text{M} = \text{O}, \text{S}, \text{Se}, \text{Te}$ or Po). e.g. $\text{H}_2\text{O}, \text{H}_2\text{S}, \text{H}_2\text{Se}, \text{H}_2\text{Te}$ & H_2Po . H_2O is obtained by combustion of H_2 while $\text{H}_2\text{S}, \text{H}_2\text{Se}, \text{H}_2\text{Te}$ are obtained by the action of acids on sulphides, selenides and tellurides respectively. H_2Po is less stable.

* Hydrides are volatile and order of volatility is $\text{H}_2\text{O} < \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$. H_2O is less volatile than H_2S due to intermolecular hydrogen bond. H_2O is liquid and H_2S is gas.

* The covalent character of these hydrides increases from H_2O to H_2Te or polarity in hydrides decreases from H_2O to H_2Te .

* The thermal stability of the hydrides decreases from H_2O to H_2Te due to decrease of bond enthalpy.

* The hydrides are all weak acids and their acidic nature increases from H_2O to H_2Te .

* All the hydrides (except H_2O) are reducing nature, which increases from H_2O to H_2Te .

* In all the hydrides, the central atom is sp^3 hybridised and V-shaped.

(ii) Formation of halides: The elements of group-16 form a number of halides showing +2, +4 & +6 oxidation states. e.g. $\text{OF}_2, \text{SF}_2, \text{S}_2\text{Cl}_2, \text{SF}_6, \text{Se}_2\text{F}_2, \text{SeF}_4, \text{TeF}_4, \text{TeF}_6$ etc.

• OF_2 is known as oxygen difluoride. Oxygen also forms compounds with other halogens

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but these are called Oxides of halogens and not halides e.g. Cl_2O , Cl_2O_3 , Cl_2O_5 etc.

Sulphur forms a large number of halides of type S_2X_2 ($\text{X} = \text{F}, \text{Cl}, \text{Br}$ or I), SX_2 ($\text{X} = \text{F}, \text{Cl}$ or Br), SF_4 ($\text{X} = \text{F}$ or Cl) and SF_6 .

Selenium & tellurium form hexafluorides as well as chlorides and bromides in oxidation states +1, +2 & +4

Sulphur hexafluoride (SF_6) is obtained by combustion of S in F_2 gas. It is extremely non-toxic and unreactive. In SF_6 , S atom is sp^3d^2 hybridised and octahedral shape. SF_6 is inert, stable and not hydrolysed while SeF_6 & TeF_6 undergo hydrolysis readily. SF_4 is prepared by fluorinating SbCl_5 with NaF . ($\text{SbCl}_5 + \text{NaF} \rightarrow \text{SF}_4 + \text{NaCl}$). In SX_4 , SeX_4 & TeX_4 , the central atoms show sp^3d hybridisation and therefore trigonal bipyramidal geometry with one of the equatorial position occupied by lone pair of electrons. SF_4 & SeF_4 are used as fluorinating agents.

(iii) Formation of Oxides: All elements (except O) form Oxides of type MO_2 , on burning in air. $\text{M} + \text{O}_2 \rightarrow \text{MO}_2$ (where $\text{M} = \text{S}, \text{Se}, \text{Te}, \text{Po}$)

Sulphur forms a number of Oxides: SO (sulphur monoxide), SO_2 , SO_3 , S_2O_7 (Sulphur heptoxide) etc. S, Se & Te form trioxides also. All (except Se) form monoxide (SO , TeO , PoO)

The acidic character as well as stability of dioxides decrease down the group. SO_2 & SeO_2 are acidic while TeO_2 & PoO_2 are amphoteric. SO_2 is a gas, SeO_2 is volatile covalent solid while TeO_2 & PoO_2 are white crystalline ionic solids. Their trioxides (SO_3 , SeO_3 , TeO_3) are acidic nature which decrease from SO_3 to TeO_3 . SO_3 is planar triangular while $\text{SO}_3(\text{s})$ is cyclic trimer structure. TeO_3 possesses a solid network structure.

(iv) Formation of Oxyacids: Sulphur forms a large number of oxyacids in different oxidation states, e.g. Thiosulphurous acid ($\text{H}_2\text{S}_2\text{O}_3$), Hyposulphurous acid ($\text{H}_2\text{S}_2\text{O}_4$), Sulphuric acid (H_2SO_4), Sulphurous acid (H_2SO_3), Pyrosulphurous acid ($\text{H}_2\text{S}_2\text{O}_5$), Dithionic acid ($\text{H}_2\text{S}_2\text{O}_6$), Pyrosulphuric acid ($\text{H}_2\text{S}_2\text{O}_7$), Peroxy monosulphuric acid or Caro's acid (H_2SO_5), Peroxy disulphuric acid or Marshall's acid ($\text{H}_2\text{S}_2\text{O}_8$). Of which most common and important/useful acid is sulphuric acid (H_2SO_4), called King of chemicals or Oil of vitriol.

The dioxides (XO_2) dissolve in water to give oxo acids of type H_2XO_3 , e.g. H_2SO_3 (Sulphurous acid), H_2SeO_3 (Selenous acid) & H_2TeO_3 (Tellurous acid). Similarly, trioxides (XO_3) gives oxo-acids of type H_2XO_4 with $\text{H}_2\text{O} + \text{XO}_2 + \text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{H}_2\text{SO}_3$; $\text{H}_2\text{O} + \text{SO}_3 \rightarrow \text{H}_2\text{SO}_4$. The strength & stability of the oxo-acids decrease from S to Te; $\text{H}_2\text{SO}_3 > \text{H}_2\text{SeO}_3 > \text{H}_2\text{TeO}_3$ (same o-state). The strength & stability of oxyacids increase with the increase of o-state of same element, i.e., $\text{H}_2\text{S}_2\text{O}_3 < \text{H}_2\text{SO}_3 < \text{H}_2\text{SO}_4$.

(v) Formation of oxy halides: Only S & Se form oxyhalides, e.g. SOCl_2 , SOBr_2 , SO_2Cl_2 (Thionyl & Sulphonyl halide); SeOCl_2 , SeOBr_2 , SeO_2Cl_2 (Selenonyl halide). They liberate SO_2 gas, on hydrolysis, e.g. $\text{SOCl}_2 + \text{H}_2\text{O} \rightarrow \text{SO}_2 \uparrow + 2\text{HCl}$. Sulphur forms sulphonyl halide (SO_2X_2)

(vi) Formation of Carbides: All these elements form compounds with C, e.g. CS_2 , CSe_2 & CTe_2 . These are covalent compounds and neutral, except CO_2 which is acidic. CO , CO_2 are gases, CS_2 is liquid and CSe_2 & CTe_2 are solids.