

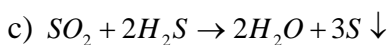
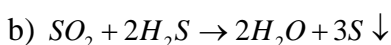
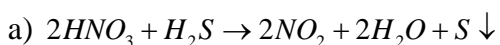
VIA Group Elements (Subtopic-I)

General characteristics, Hydrides, Oxides and Halides

- Group VI A of periodic table consists of five elements O, S, Se, Te and Po
- The first four elements are collectively known as chalcogens (ore forming elements), since many metals occur as oxides (or) sulphides in nature.
- The outer electronic configuration of these elements is ns^2np^4 .
- Sulphur exists mainly as sulphides and sulphates. Such as gypsum $CaSO_4 \cdot 2H_2O$ Epsom salt $MgSO_4 \cdot 7H_2O$ barite $BaSO_4$ and sulphides such zinc blend ZnS , galena Pbs etc
- Existence of oxygen as a diatomic molecule is due to ability of atom to form stable $P\pi - P\pi$ multiple bonds whereas Sulphur and other elements of this group are incapable of $P\pi - P\pi$ overlap.
- **Magnetic Property:** Molecular oxygen in the gaseous, liquid, and solid states is paramagnetic while molecules of other elements are diamagnetic in nature.
- **Electron affinity** values decrease from S to Te. Electron affinity of $O < S$ due to small size of Oxygen atom.
- Oxygen exists as a diatomic molecule (O_2), sulphur, Selenium, Tellurium exist as octatomic molecules. (S_8, Se_8, Te_8).
- **Oxidation states:**
- The common oxidation state of these elements is -2 , because they have S^2P^4 configuration in their outer most orbits.
- Oxygen shows positive oxidation states in fluorides. Oxidation state of oxygen in O_2F_2 is $+1$ and in OF_2 is $+2$.
- The oxidation state of oxygen in peroxide is -1 and in a super oxide is $-\frac{1}{2}$.
- **Allotropic forms of Sulphur:** It exists in several allotropic forms.
- **Rhombic or octahedral or α - Sulphur:** This is the common crystalline form of Sulphur, Pale yellow in colour (m.pt $114.5^\circ C$), specific gravity 2.06). It is insoluble in water but readily soluble in carbon disulphide. It consists of S_8 structural units packed together into octahedral shape. This is the stable variety at ordinary temperature and all other forms

gradually change into this form. This form is prepared by evaporating sulphur solution in CS_2 .

- **Mono clinic or Prismatic or β Sulphur:** This form of Sulphur is stable above 95.6°C . The needle shaped crystals are amber yellow in colour (m.pt. 119°C , Specific gravity of 1.96). It is also soluble in carbon disulphide. Below 95.6°C . It changes into rhombic form. Thus 95.6°C (or) 368.5K is the transition temperature of $S_{(R)} \rightarrow S_{(M)}$.
- **Plastic Sulphur:** Boiling Sulphur on pouring into cold water gives plastic sulphur. It is soft rubber like mass which hardens on standing and gradually changes into rhombic sulphur. It is amber brown in colour and has specific gravity of 1.95. It is insoluble in CS_2 and has no sharp melting point. It consists of a completely random arrangement of chains of sulphur atoms. It is also referred as super cooled sulphur liquid.
- **Colloidal or δ - sulphur:** By passing H_2S through a solution of an oxidizing agent. (e.g. nitric acid, pot. Permanganate, etc.). or water; or by treating sodium thiosulphate solution with dil. HCl , a white turbidity of colloidal S is formed.

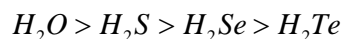


On heating or long standing colloidal sulphur changes into the ordinary form.

- In Puckered S_8 rings S – S bond length 2.12Å & $\angle \text{S} - \text{S} - \text{S}$ bond angle 105° .
- Sulphur persists with the S_8 units, just above the boiling point of sulphur (160°C). Further increase in temperature leads to the dissociation of S_8 units successively into S_6 units (Engel's sulphur), S_4 and S_2 units.
- When liquid sulphur above 160°C is poured into water, plastic sulphur or λ sulphur is formed.
- **Catenation Capacity**
- Oxygen and Sulphur show catenation tendency.
- Catenation is maximum in sulphur upto 10 atoms (H_2S_n) ($n = 2 - 10$)
- **Hydrides**
- VIA group elements can form hydrides of the formula H_2M (M = VIA group element).

➤ The ease of formation and thermal stability decrease from H_2O to H_2Po (as M-H bond energy decreases)

➤ The thermal stability Order:



Water dissociates at about 2273K, H_2S at 673-873 K, H_2Se at 433 K and H_2Te at ordinary room temperatures. H_2Po is unstable at room temperature

➤ M-H bond length in the hydrides increases from H_2O to H_2Po .

➤ The aqueous solutions of these hydrides behave as weak acids. The acidic strength increases from H_2O to H_2Te

➤ The reducing property increases from H_2O to H_2Po .

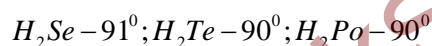
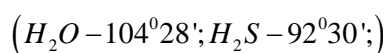
➤ Covalent character increases from H_2S to H_2Te . Order: $H_2O < H_2S < H_2Se < H_2Te$

➤ When compared to other hydrides, water has abnormal high boiling point. This is due to intermolecular hydrogen bonding in water.

➤ Boiling point order: $H_2S < H_2Se < H_2Te < H_2O$

➤ Order of volatile nature is $H_2S > H_2Se > H_2Te > H_2O$

➤ The bond angle decreases from H_2O to H_2Po .



➤ VIA group elements can form two types of oxides.

(a) Dioxides eg: SO_2 , SeO_2

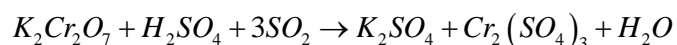
(b) Trioxides eg: SO_3 , SeO_3

➤ Order of acidic strength: $SO_2 > SeO_2 > TeO_2$ and $SO_3 > SeO_3 > TeO_3$

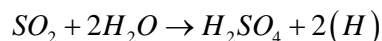
➤ SO_2 acts as a Lewis base due to the presence of lone-pair of electrons.

➤ It acts as mild reducing agent in acid solutions and a strong reducing agent in basic solutions.

➤ SO_2 reduces acidified $K_2Cr_2O_7$ into Cr(III) sulphate.

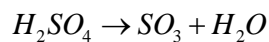


➤ SO_2 is a bleaching agent. It bleaches the vegetable colouring matter by reduction. In this process it is oxidised to H_2SO_4 . This bleaching process is temporary.

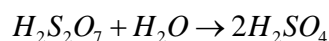
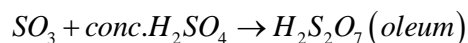


Coloured matter + 2(H) → colourless matter.

- SO_3 is the anhydride of sulphuric acid or sulphuric anhydride.

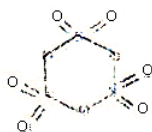


- Commercially it is not possible to react SO_3 directly H_2O . Hence SO_3 dissolved in conc. H_2SO_4 to give oleum ($H_2S_2O_7$). Then it is dissolved in water to get H_2SO_4 .

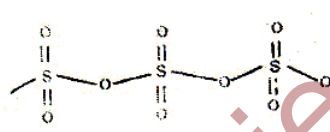


Oleum is also called fuming sulphuric acid or pyrosulphuric acid.

- **Structure of solid SO_3 :** It possesses either cyclic trimer (α -form) structure an infinite helical chains. (β and γ form)



γ -form



β -form

1. α -form contains three S – O – S bonds
 2. Each sulphur is bonded to four oxygen atoms
 3. Each oxygen is bonded to two sulphur atoms
 4. Each sulphur contains two doubly bonded oxygen atoms
- In γ -form 3 molecules of SO_3 polymerise to give cyclic structure. γ form SO_3 is a cyclic trimer
 - α form is the most stable form and is made of cross linked chains.
 - The acid strength of 'ous' oxyacids of VIA group follows the order:
 $H_2SO_3 > H_2SeO_3 > H_2TeO_3$

- The trioxides of VIA group elements dissolve in water to give 'ic' acids of the type H_2MO_4 .
 $H_2SO_4 > H_2SeO_4 > H_2TeO_4$

- Dioxides act as both oxidizing and reducing agents.

- Structure of OF_2 is angular.

$\angle FOF$ bond angle in OF_2 is 103° O – F bond length in OF_2 is 1.45 \AA .

- O_2F_2 has open book like structure.

- In O_2F_2 molecule bond angle $\angle FOO = 190^\circ 31'$

Dihedral angle = $87^\circ 30'$.

O – O bond length = 1.27 \AA .

O – F bond length = 1.58 \AA

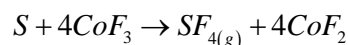
- SF_6 is a colourless, odourless, non-flammable gas.

- In SF_6 , sulphur atom is sp^3d^2 hybridized.

All F – S – F angles are 90° . The shape of SF_6 molecule is octahedral

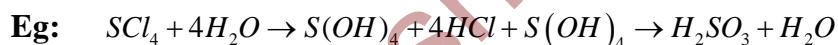
- Sulphur reacts with fluorine (diluted with nitrogen to form SF_4 and SF_6).

- SF_4 is also prepared by reaction between Cobalt trifluoride with Sulphur.



- SF_4 is highly reactive gas and a good fluorinating agent.

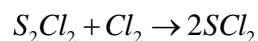
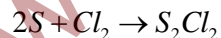
- Tetra halides undergo hydrolysis to give the corresponding 'ous' acids. (except SF_4)



- SF_4 and SCl_4 are Lewis acids since they can accept lone pairs of electrons readily to form hexa halides using halide ions.

- Tetra halide (SF_4, SCl_4) molecules have trigonal bipyramidal structure with one corner of equatorial position occupied by a lone pair of electrons (sea-saw structure)

- Sulphur on heating with chlorine gives S_2Cl_2 . This on saturation with chlorine gives SCl_2



- In SCl_2 , the lone pairs distort the tetrahedral angle from $109^\circ 28'$ to 103°

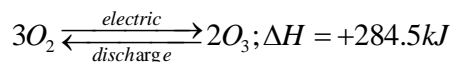
- SCl_2 molecule has angular shape.

- The structure of S_2Cl_2 is similar to H_2O_2 with the bond angle 104° . Hybridization is sp^3 in S_2Cl_2 & dihedral bond angle is $108^\circ 18'$.
- In S_2Cl_2 , S – S bond length is 205pm or 2.05Å , S – Cl bond length 199pm or 1.99Å

VI A GROUP ELEMENTS (SUBTOPIC-II)

Ozone and Sulphuric acid

- Formation of ozone is an endothermic, reversible reaction.



- In Brodie's and Siemens process only around 5- 10% conversion of O_2 to O_3 is possible
- The obtained gas is a mixture of $O_2 + O_3$ it is called Ozonised oxygen
- Electrolysis of acidulated water with platinum electrodes gives O_3 at anode. The gases liberated at the anode contain about 95% O_3 and 5% O_2 .

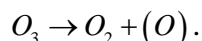
➤ **Physical properties**

- It decolourises organic colouring matter by oxidation.

➤ **Chemical properties**

➤ **Oxidising properties**

- Oxidising power of O_3 is weaker than F_2 but stronger than H_2O_2 or $KMnO_4$.
- Ozone decomposes to give nascent oxygen.



Thus in all oxidation reactions if one mole of ozone is consumed, one mole oxygen is formed. (In presence of HCl)

In the above reactions, (h & i), the three oxygen atoms of ozone are utilized. Hence these are considered as special oxidation reactions.

➤ **Structure**

- Ozone is an angular molecule with a bond angle of $116^\circ 49'$ structure.
- O – O bond length is 1.28Å . Ozone has two resonating structures.

It is a diamagnetic molecule.

Uses of ozone

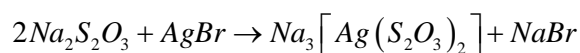
- A mixture of O_3 and C_2N_2 is known as (cyanogens) and is used as Rocket fuel.

Sodium Thiosulphate

- Hydrated Sodium Thiosulphate ($Na_2S_2O_3 \cdot 5H_2O$) is called Hypo.

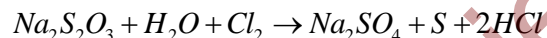
Chemical properties

- Hypo with a dilute solution of $AgNO_3$ gives a white precipitate which changes to yellow, brown and finally black due to the formation of Ag_2S .
- With concentrated solution of Hypo, $AgNO_3$ gives no precipitate. This is because silver thiosulphate (a white ppt) formed in the reaction is easily soluble in excess of Hypo forming a complex, $Na_3[Ag(S_2O_3)_2]$ (sodium argentorhiosulphate)
- Silver halides dissolve in hypo solution to give sodium argentothiosulphate.

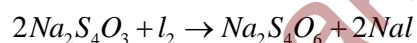


This reaction is made use in photography. This is known as fixing in photography.

- Hypo removes excess chlorine in moist condition. So hypo is used as an antichlor.



- Hypo reduces Iodine to form sodium tetrathionate. In $Na_2S_4O_6$ oxidation number of sulphur is +2.5.



Oxyacids of Sulphur

- The hybridisation of 'S' in all oxyacids is sp^3 .
- Oxyacids of Sulphur with S – S linkage are called thioacids.
- Salt of Caro's acid is called permonosulphate and salt of Marshall's acid is perdisulphate or persulfate.
- Distillation of $H_2S_2O_8$ with water gives H_2SO_5 which on further hydrolysis gives H_2O_2 .
Basicity of all Oxo acids of Sulphur is 2.
- Hybridization of sulphur in SO_3^{-2} , SO_4^{-2} , $S_2O_3^{-2}$, $S_2O_4^{-2}$ ions is sp^3 .

- Because of its wide applications in industry, it is called 'King of chemicals'. It was also called as oil of vitriol.
- A suitable catalyst is to be used to increase the rate of formation of SO_3 .

Catalyst used	Name of the process
1) Platinized asbestos	1) Baudisch process
2) Vanadium pentoxide	2) Baudisch process
3) Finely divided Pt Deposited on $MgSO_4$	3) Grillo's process
4) Fe_2O_3 and CuO	4) Mannheim process

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