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**Section: Senior**

**Group-16**

**Date: 15-06-2020**

**General properties:**

- ❖ O, S are non-metals, Se, Te are metalloids and Po is metal and is radioactive.
- ❖ Oxygen is anomalous due to its smaller size, higher electronegativity and the lack of suitable *d* orbitals.
- ❖ Oxygen can use *p* orbitals to form strong bonds.
  - The tendency to form bond decreases down the group.
  - CO<sub>2</sub> (O = C = O) is stable, CS<sub>2</sub> less stable, CSe<sub>2</sub> polymerises rather than form double bonds and CTe<sub>2</sub> is unknown.
- ❖ Sulphur shows a much greater tendency to form chains and rings (alone and with nitrogen) than the other elements.
  - Oxygen does not undergo catenation which can be attributed to weak O – O bond.
- ❖ Se is reluctant to attain the highest oxidation state of (+VI) shown by S due to poor shielding inner *d*-electrons.
  - HNO<sub>3</sub> oxidizes S to H<sub>2</sub>SO<sub>4</sub> (S +VI) but only oxidizes Se to H<sub>2</sub>SeO<sub>3</sub> (Se +VI).

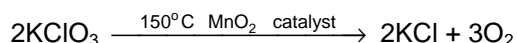
**Oxidation states:**

- ❖ Most common oxidation state is -2.
- ❖ O: -2, -1, +1(O<sub>2</sub>F<sub>2</sub>), +2(OF<sub>2</sub>)
- ❖ S, Se & Te +2, +4, +6
- ❖ Po: +2, +4

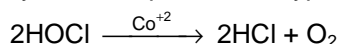
**EXTRACTION AND USES OF THE ELEMENTS:**

**Extraction and separation of dioxygen:**

- ❖ Oxygen is produced by distillation of liquid air
- ❖ O<sub>2</sub> is prepared in the laboratory by thermal decomposition of KClO<sub>3</sub> (with MnO<sub>2</sub> as catalyst), though the product often contains traces of Cl<sub>2</sub> or ClO<sub>2</sub>.



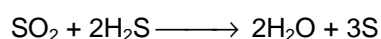
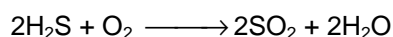
- Small amounts of O<sub>2</sub> as an emergency breathing supply in aircraft are produced by heating NaClO<sub>3</sub>.
- O<sub>2</sub> can also be made by the catalytic decomposition of hypochlorites:



- O<sub>2</sub> can also be prepared by electrolysis of water with a trace of H<sub>2</sub>SO<sub>4</sub> or barium hydroxide solution.

**Extraction of Sulphur:**

- ❖ Major deposits of S were formed by anaerobic bacteria which metabolize CaSO<sub>4</sub> to form H<sub>2</sub>S and S. These underground deposits of S are mined by the Frasch process.
- ❖ H<sub>2</sub>S from natural gas can be converted into sulphur.



**Structure and allotropy of elements**

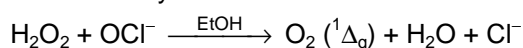
**Oxygen:**

- ❖ Oxygen occurs in two non-metallic forms, dioxygen O<sub>2</sub> and ozone O<sub>3</sub>.

- ❖ Dioxygen is paramagnetic and contains two unpaired electrons.
- ❖ Liquid dioxygen is pale blue in colour, and the solid is also blue.
- ❖ The colour arises from electronic transitions which excite the ground state (a triplet state) to a singlet state. This transition is 'forbidden' in gaseous dioxygen.
- ❖ In liquid or solid dioxygen a single photon may collide with two molecules simultaneously and promote both to excited states, absorbing red-yellow-green light, so O<sub>2</sub> appears blue.
- ❖ The origin of the excited singlet states in O<sub>2</sub> lies in the arrangement of electrons in the antibonding  $\pi^*2p_y$  and  $\pi^*2p_z$  molecular orbitals, and is shown below:

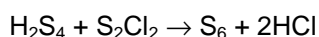
	$\pi^*p_y$	$\pi^*p_z$		State	Energy (kJ)
Second excited state (electrons have opposite spins)	$\uparrow$	$\downarrow$	Singlet	$^1\Sigma_g^+$	157
First excited state (electrons paired)	$\uparrow\downarrow$		Singlet	$^1\Delta_g$	92
Ground state (electrons have parallel spins)	$\uparrow$	$\uparrow$	Triplet	$^3\Sigma_g^-$	0

- ❖ Singlet O<sub>2</sub> is excited, and is much more reactive than normal ground state triplet dioxygen.
- ❖ Singlet dioxygen can be generated photochemically by irradiating normal dioxygen in the presence of a sensitizer such as fluorescein, methylene blue or some polycyclic hydrocarbons.
- ❖ Singlet dioxygen can also be made chemically:

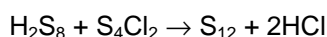
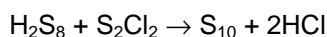


### Sulphur:

- ❖ The different allotropes of sulphur arise partly from the extent to which S has polymerized, and partly from the crystal structures adopted.
- ❖ The two common crystalline forms are  $\alpha$  or rhombic sulphur which is stable at room temperature, and  $\beta$  or monoclinic sulphur which is stable above 95.5°C.
  - These two forms change reversibly with slow heating or slow cooling.
- ❖ A third modification known as  $\gamma$ -monoclinic sulphur is nacreous (Having a play of lustrous rainbow colours).
  - It can be made by chilling hot concentrated solutions of S in solvents such as CS<sub>2</sub>, toluene or EtOH.
- ❖ All three forms contain puckered S<sub>8</sub> rings with a crown conformation, and differ only in the overall packing of the rings in the crystal. This affects their densities.
- ❖ Engel's sulphur ( $\epsilon$ -sulphur) is unstable and contains S<sub>6</sub> rings arranged in the chair conformation.
  - It is made by pouring Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution into concentrated HCl and extracting the S with toluene.
  - It can also be made as follows:



- ❖ Several other rings S<sub>7</sub>, S<sub>9</sub>, S<sub>10</sub>, S<sub>11</sub>, S<sub>12</sub>, S<sub>18</sub> and S<sub>20</sub> have been made by Schmidt and his group.
  - They are usually obtained by 1 : 1 reactions in dry ether between hydrogen polysulphides and polysulphur dichlorides with the required number of S atoms, for example:



- ❖ Plastic or  $\chi$  sulphur is obtained by pouring liquid sulphur into water.

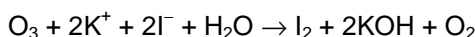
### Action of heat on Sulphur

- ❖ Sulphur melts to form a mobile liquid.
  - As the temperature is raised the colour darkens.
  - At 160°C the S<sub>8</sub> rings break, and the diradicals so formed polymerize, forming long chains of upto a million atoms.

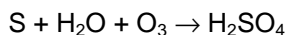
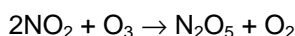
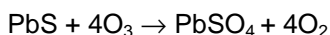
- The viscosity increases sharply, and continues to rise up to 200°C.
- At higher temperatures chains break, and shorter chains and rings are formed, which makes the viscosity decrease upto 444°C, the boiling point.
- The vapour at 200°C consists mostly of S<sub>8</sub> rings, but contains 1-2% of S<sub>2</sub> molecules.
- At 600°C the gas mainly consists of S<sub>2</sub> molecules.
- The S<sub>2</sub> molecule is paramagnetic and blue coloured like O<sub>2</sub>, and presumably has similar bonding.
- S<sub>2</sub> gas is stable up to 2200°C.

#### Chemistry of Ozone:

- ❖ O<sub>3</sub> is an unstable, dark blue diamagnetic gas.
- ❖ The colour is due to intense absorption of red light ( $\lambda = 557$  and  $602$  nm).
- ❖ It also absorbs strongly in the UV region ( $\lambda = 255$  nm).
- ❖ O<sub>3</sub> has a characteristic sharp smell, often associated with sparking electrical equipment.
- ❖ O<sub>3</sub> is also used as a disinfectant. It is used to purify drinking water, since it destroys bacteria and viruses. Its advantage over chlorine for this purpose is that it avoids the unpleasant smell and taste of chlorine, since any excess of O<sub>3</sub> soon decomposes to O<sub>2</sub>.
- ❖ The amount of O<sub>3</sub> in a gas mixture may be determined by passing the gas into a KI solution buffered with a borate buffer (pH 9.2). The iodine that is liberated is titrated with sodium thiosulphate.



- ❖ O<sub>3</sub> is thermodynamically unstable, and decomposes to O<sub>2</sub>. The decomposition is exothermic.
- ❖ O<sub>3</sub> is an extremely powerful oxidizing agent, second only to F<sub>2</sub> in oxidizing power, and reacts much more readily than dioxygen.



#### Bonds Lengths and $p\pi > d\pi$ bonding:

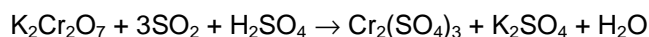
- ❖ The bonds between S and O or Se and O, are much shorter than might be expected for a single bond.
- ❖ A  $\sigma$  bond is formed in the usual way. In addition a  $\pi$  bond is formed by the sideways overlap of a p-orbital on the oxygen with a d orbital on the sulphur, giving a  $p\pi-d\pi$  interaction.
- ❖ Sulphur forms stronger  $\pi$  bonds than the larger elements in the group.
- ❖ The decrease in the size of the 3d orbitals in this series(Si to Cl) of elements leads to progressively stronger  $p\pi-d\pi$  bonds.
  - In silicates there is hardly any  $p\pi-d\pi$  bonding. SiO<sub>4</sub> units polymerize into an enormous variety of structures linked by Si – O – Si  $\sigma$  bonds.
  - In the phosphates,  $\pi$  bonding is stronger, but a large number of polymeric phosphates exist.
  - In the oxoacids of sulphur,  $\pi$  bonding is even stronger and has become a dominant factor. Thus only a small amount of polymerization occurs, and only a few polymeric compounds are known with S – O – S linkages.
  - For chlorine,  $p\pi-d\pi$  bonding is so strong that no polymerization of oxoanions occurs.

#### Oxides of sulphur

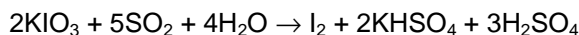
##### SO<sub>2</sub> :

- ❖ The SO<sub>2</sub> in solution is almost completely present as various hydrated species such as SO<sub>2</sub>.6H<sub>2</sub>O and the solution contains only a minute amount of sulphurous acid H<sub>2</sub>SO<sub>4</sub>.
- ❖ SO<sub>2</sub> may be detected in the laboratory.

- 1) By its smell. It has a suffocating smell.
- 2) Because it turns a filter paper moistened with acidified potassium dichromate solution green, due to the formation of  $\text{Cr}^{+3}$ .

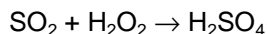


- 3) Because it turns starch iodate paper blue (due to starch and  $\text{I}_2$ )



❖ Quantitative methods for measuring  $\text{SO}_2$  in the atmosphere (concern over **acid rain**):

- 1) Oxidation to  $\text{H}_2\text{SO}_4$  followed by determination of the  $\text{H}_2\text{SO}_4$  by titration (or conductimetric titration)



- 2) Reaction with  $\text{K}_2[\text{HgCl}_4]$  to give a mercury complex which reacts with the dye pararosaniline, and is estimated calorimetrically.



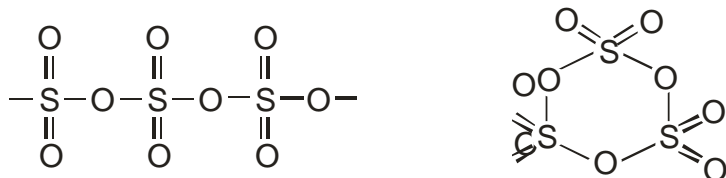
- 3) Burning in a hydrogen flame in a flame photometer, and measuring the spectrum of  $\text{S}_2$ .

❖  $\text{SO}_2$  is used to make :  $\text{Na}_2\text{SO}_3 + \text{S} \xrightarrow{\text{heat}} \text{Na}_2\text{S}_2\text{O}_3$   
(sodium thiosulphate)

❖  $\text{SO}_2$  gas forms discrete V-shaped molecules, and this structure is retained in the solid state.

**$\text{SO}_3$  :**

- ❖ Prepared by reacting  $\text{SO}_2$  with  $\text{O}_2$  using  $\text{V}_2\text{O}_5$  as the catalyst
- ❖ The  $\text{SO}_3$  reacts with water vapour and causes the formation of a dense mist of  $\text{H}_2\text{SO}_4$  droplets, which are difficult to condense and pass out of the absorber into the atmosphere.
- ❖ To avoid this, it has been found best to dissolve  $\text{SO}_3$  in 98–99%  $\text{H}_2\text{SO}_4$  in ceramic packed towers, to give oleum or fuming sulphuric acid.
- ❖ At room temperature,  $\text{SO}_3$  is solid and exists in three distinct forms.
- ❖  $\gamma\text{-SO}_3$  is ice-like and is a cyclic trimer  $(\text{SO}_3)_3$ , melting point  $16.8^\circ\text{C}$ .



Structure of  $\text{SO}_3$  chains and  $\text{SO}_3$  cyclic trimer

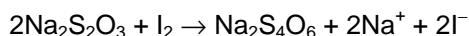
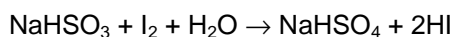
- ❖ If  $\text{SO}_3$  is kept for a long time, or if a trace of water is present, either  $\beta\text{-SO}_3$  or  $\alpha\text{-SO}_3$  is formed.
- ❖ Both look like asbestos, and comprise bundles of white silky needles.
- ❖  $\beta\text{-SO}_3$  (melting point  $32.5^\circ\text{C}$ ) is made up of infinite helical chains of tetrahedral  $[\text{SO}_4]$  units each sharing two corners.
- ❖ This structure is similar to that of chain phosphates.
- ❖  $\alpha\text{-SO}_3$  (melting point  $62.2^\circ\text{C}$ ) is the most stable form, and is made of chains cross-linked into sheets.

### Oxoacids of Sulphur:

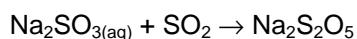
- ❖ 1) Sulphurous acid series, 2) Sulphuric acid series, 3) Thionic acid series, 4) Peroxoacid series

S.No	Oxoacid of Sulphur	Structure	Oxidation state
1)	Sulphurous acid series:		
	H <sub>2</sub> SO <sub>3</sub> sulphurous acid	$\begin{array}{c} \text{HO} - \text{S} - \text{OH} \\ \parallel \\ \text{O} \end{array}$	S(+IV)
	H <sub>2</sub> S <sub>2</sub> O <sub>5</sub> di- or pyrosulphurous acid	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{HO} - \text{S} - \text{S} - \text{OH} \\ \parallel \\ \text{O} \end{array}$	S(+V), S(+III)
	H <sub>2</sub> S <sub>2</sub> O <sub>4</sub> dithionous acid	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{HO} - \text{S} - \text{S} - \text{OH} \end{array}$	S(+III)
2)	Sulphuric acid series:		
	H <sub>2</sub> SO <sub>4</sub> sulphuric acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{HO} - \text{S} - \text{OH} \\ \parallel \\ \text{O} \end{array}$	S(+VI)
	H <sub>2</sub> S <sub>2</sub> O <sub>3</sub> thiosulphuric acid	$\begin{array}{c} \text{S} \\ \parallel \\ \text{HO} - \text{S} - \text{OH} \\ \parallel \\ \text{O} \end{array}$	S(+VI), S(-II)
	H <sub>2</sub> S <sub>2</sub> O <sub>7</sub> di- or pyrosulphuric acid	$\begin{array}{c} \text{O} \quad \quad \text{O} \\ \parallel \quad \quad \parallel \\ \text{HO} - \text{S} - \text{O} - \text{S} - \text{OH} \\ \parallel \quad \quad \parallel \\ \text{O} \quad \quad \text{O} \end{array}$	S(+VI)
3)	Thionic acid series:		
	H <sub>2</sub> S <sub>2</sub> O <sub>6</sub> dithionic acid	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{HO} - \text{S} - \text{S} - \text{OH} \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \end{array}$	S(+V)
	H <sub>2</sub> S <sub>n</sub> O <sub>6</sub> polythionic acid (n = 1–12)	$\begin{array}{c} \text{O} \quad \quad \text{O} \\ \parallel \quad \quad \parallel \\ \text{HO} - \text{S} - (\text{S})_n - \text{S} - \text{OH} \\ \parallel \quad \quad \parallel \\ \text{O} \quad \quad \text{O} \end{array}$	S(+V), S(0)
4)	Peroxoacid series		
	H <sub>2</sub> SO <sub>5</sub> peroxomonosulphuric acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{HO} - \text{S} - \text{O} - \text{OH} \\ \parallel \\ \text{O} \end{array}$	S(+VI)
	H <sub>2</sub> S <sub>2</sub> O <sub>8</sub> peroxodisulphuric acid	$\begin{array}{c} \text{O} \quad \quad \text{O} \\ \parallel \quad \quad \parallel \\ \text{HO} - \text{S} - \text{O} - \text{O} - \text{S} - \text{OH} \\ \parallel \quad \quad \parallel \\ \text{O} \quad \quad \text{O} \end{array}$	S(+VI)

- ❖ The main use of Na<sub>2</sub>SO<sub>3</sub> is as a bleach for wood pulp in the paper making industry.
- ❖ Sulphides and hydrogen sulphites both contain S in the oxidation state (+IV) and are moderately strong reducing agents.
- ❖ Sulphates are determined by reaction with I<sub>2</sub>, and determination of the excess I<sub>2</sub> with sodium thiosulphate.



- ❖ On heating solid hydrogen sulphites, or treating their solutions with SO<sub>2</sub>, disulphites are formed.

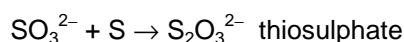
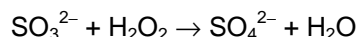


- ❖  $\text{Na}_2\text{S}_2\text{O}_5$  is called sodium disulphite, but in the past it has been called sodium pyrosulphite and sodium metabisulphite.

- ❖ The free acid  $\text{H}_2\text{S}_2\text{O}_5$  is not known. Adding acid to disulphites gives  $\text{SO}_2$

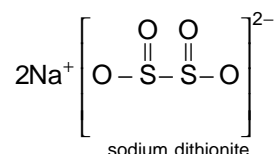
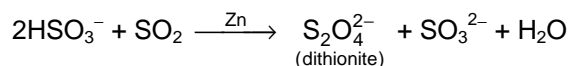


- ❖ On oxidation sulphites form sulphates, and with sulphur they form thiosulphates.



- ❖ Reduction of sulphite solution plus  $\text{SO}_2$  with Zn dust, or electrolytically, yields dithionites.

- ❖ These contain S in the oxidation state (+III).



- ❖  $\text{Na}_2\text{S}_2\text{O}_4$  is a powerful reducing agent, which has a variety of industrial uses.

- ❖ In NaOH solution  $\text{Na}_2\text{S}_2\text{O}_4$  is used to absorb dioxygen in gas analysis.

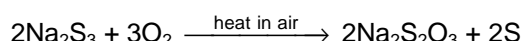
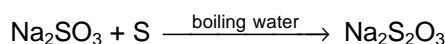
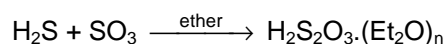
- ❖ Concentrated  $\text{H}_2\text{SO}_4$  has quite strong oxidizing properties.

- When NaBr is dissolved in concentrated  $\text{H}_2\text{SO}_4$  HBr is formed but in addition some  $\text{Br}^-$  ions are oxidized to  $\text{Br}_2$ .
- Cu dissolve in concentrated  $\text{H}_2\text{SO}_4$  due to its oxidizing properties.

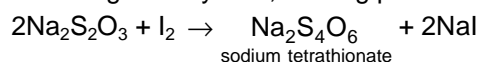
- ❖ Concentrated  $\text{H}_2\text{SO}_4$  absorbs water avidly, and is an effective drying agent for gases.

- It is used as a drying agent in desiccators.
- It dehydrates  $\text{HNO}_3$ , forming the nitronium ion  $\text{NO}_2^+$ , which is very important in the nitration of organic compounds.
- $\text{H}_2\text{SO}_4$  removes water so strongly from some organic compounds that they char, and only the carbon remains.

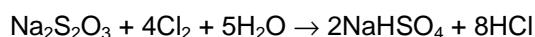
- ❖ Thiosulphuric acid  $\text{H}_2\text{S}_2\text{O}_3$  cannot be formed by adding acid to a thiosulphate because the free acid decomposes in water into a mixture of S,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{S}_n$ ,  $\text{SO}_2$  and  $\text{H}_2\text{SO}_4$ .



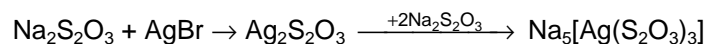
- Hydrated sodium thiosulphate  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  is called 'hypo'.
- It forms very large colourless hexagonal crystals, melting point  $48^\circ\text{C}$ .



- $\text{Na}_2\text{S}_2\text{O}_3$  is used in the bleaching industry to destroy any excess  $\text{Cl}_2$  on fabrics after they have been through a bleach bath (antichlor).
- $\text{Na}_2\text{S}_2\text{O}_3$  is sometimes used to remove the taste from heavily chlorinated drinking water.
- Since  $\text{Cl}_2$  is a stronger oxidizing agent than  $\text{I}_2$ , hydrogensulphate ions are formed rather than tetrathionate ions.



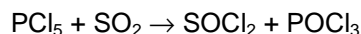
- Hypo is used in photography for 'fixing' films and prints.
- Hypo forms a soluble complex with silver salts, thus dissolving any unchanged silver salts in the photographic emulsion.
- When there is no photographic emulsion left, the film or print can safely be exposed to light.



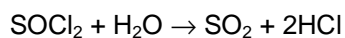
## OXOHALIDES:

### Thionyl compounds:

- ❖ Thionyl chloride  $\text{SOCl}_2$  is a colourless fuming liquid, boiling point  $78^\circ\text{C}$ , and is usually prepared as follows:



- ❖ Most thionyl compounds are readily hydrolysed by water, though  $\text{SOF}_2$  only reacts slowly.



### Sulphuryl compounds:

- ❖ Sulphuryl chloride  $\text{SO}_2\text{Cl}_2$  is a colourless fuming liquid, boiling point  $69^\circ\text{C}$ , and is made by direct reaction of  $\text{SO}_2$  and  $\text{Cl}_2$  in the presence of a catalyst.
- ❖ Sulphuryl fluoride is a gas and is not hydrolysed by water, but the chloride fumes in moist air and is hydrolysed by water.

## HALIDES:

- ❖  $\text{SF}_6$  is a colourless, odourless, non-flammable gas, which is insoluble in water and extremely inert. It does not undergo hydrolysis. It is used as a gaseous dielectric (insulator) in high voltage transformers and switchgear.
- ❖  $\text{SeF}_6$  is slightly more reactive and  $\text{TeF}_6$  is hydrolysed by water. This is possibly due to the larger size of Te which permits the larger coordination number necessary in the first stage of hydrolysis.

