INORGANIC CHEMISTRY

Topic: 2

Group VI A elements.

LONG ANSWER QUESTIONS

1. Write the general properties of group VI A elements in detail.

Ans: The important physical properties of the elements of group 16 are recorded as shown below:

Some general properties of the elements of group 16

Property	Oxygen	Sulphur	Selenium	Tellurium	Polonium
Atomic radius (A^o)	0.73	1.09	1.16	1.35	-
Ionic (M^{2+}) radius (A^o)	1.40	1.85	1.98	2.21	-
Ionization energy (kJ mol^{-1})	1314	1000	941	869	-
Electronegativity	3.5	2.5	2.4	2.1	2.0
Electron affinity (k.J mol^{-1})	141.4	208.8	195.5	190.0	-
Melting point (K)	54	392	490	723	527
Boiling Point (K)	90	718	958	1263	1235
Oxidation state	- 2	- 2, + 2 + 4, + 6	- 2, + 2 + 4,+6	- 2, + 2 + 4,+6	- 2, + 4
Density (g cm^{-3}) (in solid state)	1.14	2.07	4.79	6.25	9.4

The general trends in characteristic properties are discussed below:

1. Atomic and ionic radii:

The atomic and ionic radii of the elements of this group increase on going down the group. This is due to the increase in the number of electron shells.

2. Ionization energies:

The ionization energies of the elements of oxygen family are less than those of nitrogen family. As we move down the group from oxygen to polonium, the ionization energy decreases.

Explanation:

We expect that the ionization energy of oxygen should be more than that of N because of decrease in size. However, oxygen has unexpectedly low ionization energy than N. This is due to the reason that nitrogen has completely half filled orbitals and the configuration is stable because half filled and completely filled configurations have extra stability. But the configuration of O is less stable and therefore, has less ionization energy.

$$N(Z = 7) : 1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$$

(Half filled, stable)

$$O(Z = 8) : 1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$$

Less stable

As one moves down a group there is increase in nuclear charge. But at the same time the atomic size as well as the number of inner electrons, which shield the valence electrons from the nucleus increase. The overall effect of increase in atomic size and the shielding effect is much more than effect of increase in nuclear charge. Consequently, the outermost electron is less and less tightly held by the nucleus as we move down the group and hence ionization energy decreases.

3. Melting and boiling points:

The melting and boiling points increase with the increase in atomic number as we go down the group.

Explanation:

When we move down the group, the molecular size increases. As a result, the magnitude of the van der Waals forces also increases with increase in atomic number and therefore melting point also increases. The melting point of polonium is, however, small.

4. Electronegativity:

Oxygen is the second most electronegative element, the first being fluorine. The electronegativity decreases on going down the group. This is due to increase in size of the atoms.

5. Metallic and non-metallic character:

The first four elements namely oxygen, sulphur, selenium and tellurium are non-metals. The non-metallic character is stronger in O and S and weaker in Se and Te. On the other hand, last element is markedly metallic. However, it is radioactive and is only short-lived. .

6. Electron affinity:

The elements of this family have high electron affinities. The values decrease down the group from sulphur to polonium. Oxygen unexpectedly has low electron affinity. This is attributed to the small size of oxygen atom so that its electron cloud is distributed over a small region of space and therefore, it repels the incoming electron. Thus, the electron affinity of oxygen is unexpectedly less in the family.

7. Catenation:

Catenation is the tendency of an atom to form bonds with identical atoms. In this group only sulphur has a strong tendency for catenation. Oxygen also shows this tendency to a limited extent. Thus the polyoxides and polysulphides of the following types are known:

H_2O_2, H - O - O - H

Polyoxides

H_2S_2, H-S-S-H

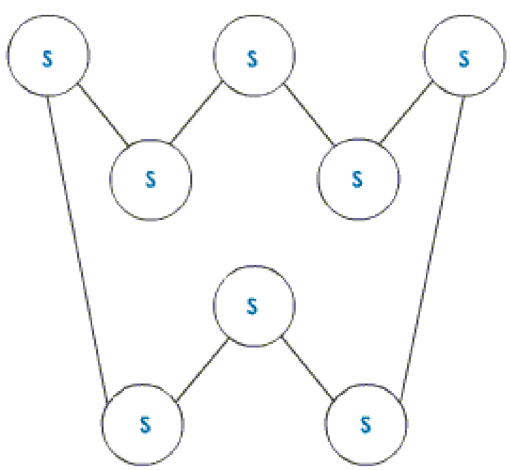
H_2S_3, H-S-S-S-H

H_2S, H-S-S-S-S-H

Polysulphides

8. Elemental state:

Oxygen exists as diatomic molecule. Under normal conditions oxygen exists as a gas. In oxygen molecule there is pp-pp overlap between two oxygen atoms forming double bond, O = O. The intermolecular forces in oxygen are weak van der Waals forces and therefore, oxygen exists as a gas. On the other hand the other elements of family do not form stable pp-pp bonds and do not exist as M_2 molecules. On the other hand the other atoms are linked by single bonds and form polyatomic complex molecules. For e.g., sulphur and selenium molecules have eight atoms per molecule (S_8 and Se_8) and have puckered ring structure. The puckered ring structure of S is as shown below.



The Puckered ring structure of S_8 molecule

9. Allotropy:

All the elements of the group exhibit allotropy. For e.g., oxygen exists as O_2 and O_3 (ozone). Sulphur exists in a number of allotropic forms such as rhombic, monoclinic, plastic sulphur. All these allotropic forms of sulphur are non-metallic. Selenium has two common forms-red and grey. Similarly tellurium and polonium occur in allotropic forms.

2. How oxides of sulphur prepared?

Oxides of Sulphur :

Two of the important oxides of sulphur are sulphur dioxide and sulphur trioxide.

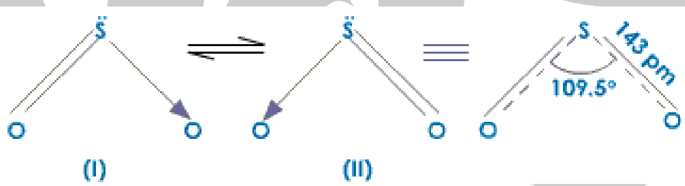
1. Sulphur dioxide:

Sulphur dioxide is formed by burning sulphur in air or roasting metal sulphides in the presence of air.

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

Sulphur dioxide is a colorless gas with an irritating and suffocating smell. It is a bent molecule. In fact, it is a hybrid of structures I and II as shown below:



A large amount of SO_2 gas is released into the atmosphere from coal and oil based power plants, oil-refinery operations and copper-smelting plants. It is also accompanied by some oxides of nitrogen. The emission of these gases causes severe environmental pollution. These gases also dissolve in rain water and make it acidic. The rain containing these dissolved compounds is called acid rain. Acid rain slowly corrodes the historical monuments and it also destroys various bacteria and nutrients. It dissolves large number of compounds present in the soil. These compounds are carried into the rivers and ultimately in the oceans and play havoc with aquatic animals. Methods are being devised by scientists to control the levels of SO_2 emissions from industrial plants.

2. Sulphur trioxide

Sulphur trioxide is formed by any of the following methods.

(i) Catalytic oxidation of sulphur dioxide

$$2SO_2(g) + O_2(g) \xleftrightarrow{V_2O_6,\ 700\ K} 2S_3(g)$$

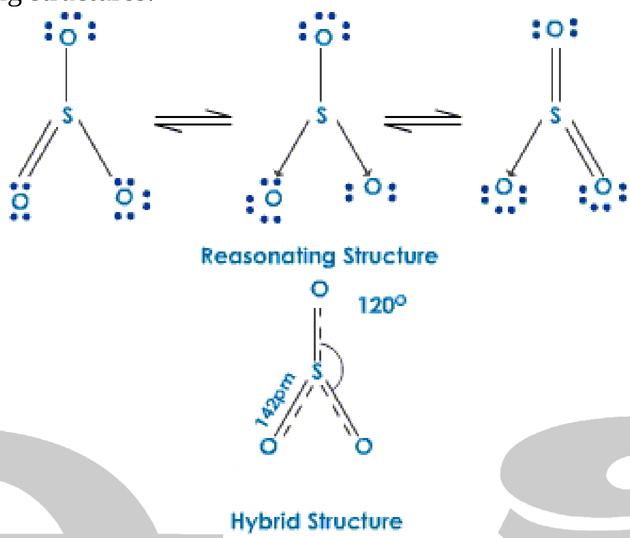
(ii) Heating of ferric sulphate

$$Fe_2(SO_4)_3 \xrightarrow{Heat} Fe_2O_3 + 3SO_3$$

(iii) Dehydration of H_2SO_4

$$H_2SO_4 \xrightarrow{P_2O_5} SO_3 + H_2O \text{ Heat}$$

Monomeric SO_3 has a planar structure with three oxygen atoms occupying the corners of equilateral triangle. Each S-O bond length is 144 pm. SO_3 molecule can be considered as the hybrid of the following structures:



Resonating structure and hybrid structure

3. What are the halides of S? How are they prepared? Give their structures.

SF_6: Sulphur hexafluoride is formed by the direct reaction between sulphur and fluorine

$$S + 3F_2 \rightarrow SF_6$$

SF_6 is colourless, odourless, non – inflammable gas.
SF_6 is highly stable and extremely inert compound. it is used as gas insulator.
SF_6 is a covalent compound and have low boiling point.
In SF_6 have octahedral shape.
SF_6 have octahedral shape.
All ∠FSF are 90°

SF_4: SF_4 can be prepared indirectly by the reaction between sulphur and cobalt trifluoride.

$$S + 4CoF_3 \rightarrow SF_4 + 4CoF_2$$

SCl_4:

SCl_4 can be prepared by the direction between sulphur and chlorine

$$S + 2Cl_2 \rightarrow SCl_4$$

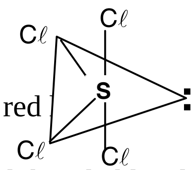
SCl_4 is a unstable liquid.
Tetrachlorides undergo hydrolysis to give the corresponding acids.
SCl_4 gives sulphurous acid on hydrolysis.

$$SCl_4 + 4H_2O \rightarrow S(OH)_4 + 4HCl$$
$$\downarrow$$
$$H_2SO_3 + H_2O$$

SF_4 and SCl_4 acts both as Lewis acids and Lewis bases .

SF_4 and SCl_4 have distorted trigonal bipyramidal structure with one corner of the equatorial position is occupied by lone pair.

The hybridisation of sulphur in SF_4 and SCl_4 is sp^3d



SCl_2:

The best known dihlaide is SCl_2 . SCl_2 is a foul smelling red

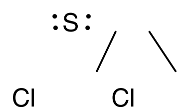
When sulphur monochloride is saturated with chlorine sulphur dichloride is formed

$$S_2Cl_2 + Cl_2 \rightarrow 2SCl_2$$

SCl_2 is angular in shape.

In SCl_2 sulphur is in sp^3 hybridisation

Due to the repulsion between two lone pairs and two bond pairs the $\angle$ ClSCl decreases to 103° from 109°28′



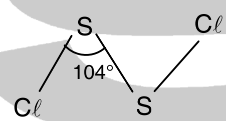
Monohalides S_2F_2 and S_2Cl_2 are dimers.

S_2F_2 and S_2Cl_2 can be prepared by the reaction between sulphur and halogens

$$2S + Cl_2 \rightarrow S_2Cl_2$$

S_2Cl_2 is used in the vulcanization of rubber.

Structure of S_2Cl_2 is similar to H_2O_2 with bond angle 104°.



S – S = 2.05 Å

S – Cl = 1.99 Å

S_2F_2 hydrolyses slowly and disproportionates

$$2S_2Cl_2 + 2H_2O \rightarrow 4HCl + SO_2 + 3S$$

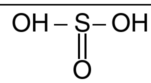
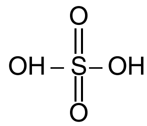
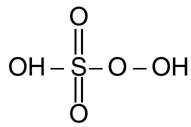
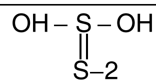
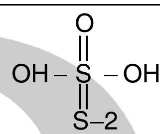
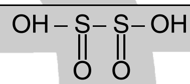
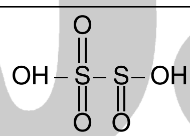
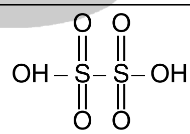
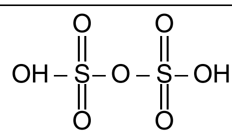
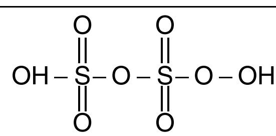
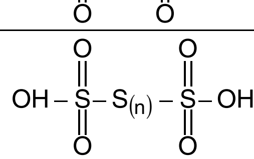
Dihedral angle is 108°

4. What are the series of oxoacids of S? Write their structure.

Oxyacids of sulphur : All are dibasic acids

- H_2SO_3 → Sulphurous acid
- H_2SO_4 → Sulphuric acid
- H_2SO_5 → Per – oxo – monosulphuric acid or Caro’s acid
- $H_2S_2O_2$ → Thiosulphurous
- $H_2S_2O_3$ → Thiosulphuric
- $H_2S_2O_4$ → Dithionous acid or hyposulphurous acid
- $H_2S_2O_5$ → Pyro – sulphurous acid
- $H_2S_2O_6$ → Dithionic acid or hyposulphuric acid
- $H_2S_2O_7$ → Pyro sulphuric acid or oleum / disulphuric acid
- $H_2S_2O_8$ → Per – oxo – disulphuric acid or marshals acid
- $H_2S_{n+2}O_6$ → Poly thionic acid [n = 1 – 10

OXYACIDS OF SULPHUR :

Formula	Structure	Oxidation Number	No.of (p-d) bonds	Average oxidation state of sulphur	Basicity
H_2SO_3		+ 4	1		2
H_2SO_4		+ 6	2		2
H_2SO_5		+ 6	2		2
$H_2S_2O_2$		– 2, + 4	1		2
$H_2S_2O_3$		– 2, + 6	2		2
$H_2S_2O_4$		(+3, +3)	2	+ 3	2
$H_2S_2O_5$		(+ 5, + 3)	3	+ 4	2
$H_2S_2O_6$		(+ 5, + 5)	4	+ 5	2
$H_2S_2O_7$		(+ 6, + 6)	4	+ 6	2
$H_2S_2O_8$		(+ 6, + 6)	4	+ 6	2
$H_2S_{n+2}O_6$		(+ 5, + 5)	4	+ 5	2

5. Explain the preparation of ozone by Siemens' method and write its properties of Ozone.

Ans: When a silent electric discharge is passed through dry oxygen, ozone is formed. Oxygen is never converted into ozone completely and we always obtain a mixture of oxygen and ozone. This mixture is called ozonized oxygen.

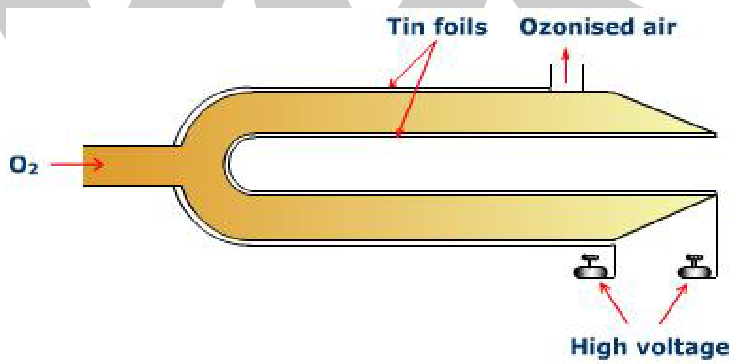
$$3O_2 \xrightarrow[\text{discharge}]{\text{electric}} 2O_3 \qquad \Delta H = +284.5\text{kJ}$$

'Ozoniser', is the apparatus used to prepare ozone by the passage of silent electrical discharge. Two types of ozonizers are used:

Siemens' ozoniser

It consists of two co-axial glass tubes fused together. Tin foil is used to coat the inner-side of the inner tube and the outer-side of the outer tube. The inner and outer tin coatings are connected to the terminals of an induction coil, which produces current of high voltage. A slow current of pure and dry oxygen is passed through the annular space. On subjecting oxygen to silent electrical discharge, ozonised oxygen containing 10-15% ozone is formed. By taking the following precautions, the yield of ozone can be increased in the ozonised oxygen:

- Only pure and dry oxygen should be used.
- The ozoniser should be perfectly dry.
- A fairly low temperature (around 0°C) should be maintained.
- There should be no sparking.



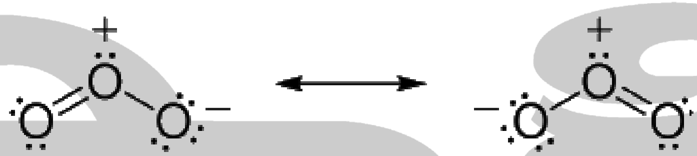
Ozone (O_3 or trioxygen) is a triatomic molecule, consisting of three oxygen atoms. It is an allotrope of oxygen that is much less stable than the diatomic allotrope (O_2). Ozone in the lower atmosphere is an air pollutant with harmful effects on the respiratory systems of animals and will burn sensitive plants; however, the ozone layer in the upper atmosphere is beneficial, preventing potentially damaging electromagnetic radiation from reaching the Earth's surface. Ozone is present in low concentrations throughout the Earth's atmosphere. It has many industrial and consumer application

Physical properties:

- Ozone is a pale blue gas, slightly soluble in water and much more soluble in inert non-polar solvents.
- It is dangerous to allow this liquid to warm to its boiling point, because both concentrated gaseous ozone and liquid ozone can detonate.
- At temperatures below –193 °C, it forms a violet-black solid.
- Ozone is diamagnetic, which means that its electrons are all paired. In contrast, O_2 is paramagnetic, containing two unpaired electron

Structure:

The O – O distances are 127.2 pm. The O – O – O angle is 116.78°. The central atom is *sp*² hybridized with one lone pair. Ozone is a polar molecule with a dipole moment of 0.53 D. The bonding can be expressed as a resonance hybrid with a single bond on one side and double bond on the other producing an overall bond order of 1.5 for each side.



Chemical properties:

Ozone is a powerful oxidizing agent, far stronger than O_2. It is also unstable at high concentrations, decaying to ordinary diatomic oxygen (with a half-life of about half an hour in atmospheric conditions):

$$2\ O_3 \rightarrow 3\ O_2$$

This reaction proceeds more rapidly with increasing temperature and increased pressure. Deflagration of ozone can be triggered by a spark, and can occur in ozone concentrations of 10 wt% or higher.

1. With metals

Ozone will oxidize most metals (except gold, platinum, and iridium) to oxides of the metals in their highest oxidation state. For example:

$$2\ Cu^{+} + 2\ H_3O^{+} + O_3 \rightarrow 2\ Cu^{2+} + 3\ H_2O + O_2$$

2. With nitrogen and carbon compounds

Ozone also oxidizes nitric oxide to nitrogen dioxide:

$$NO + O_3 \rightarrow NO_2 + O_2$$

This reaction is accompanied by chemiluminescence. The NO_2 can be further oxidized:

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

The NO_3 formed can react with NO_2 to form N_2O_5:

Solid nitryl perchlorate can be made from NO_2, ClO_2, and O_3 gases:

$$2\ NO_2 + 2\ ClO_2 + 2\ O_3 \rightarrow 2\ NO_2ClO_4 + O_2$$

Ozone does not react with ammonium salts but it oxidizes with ammonia to ammonium nitrate:

$$2\ NH_3 + 4\ O_3 \rightarrow NH_4NO_3 + 4\ O_2 + H_2O$$

Ozone reacts with carbon to form carbon dioxide, even at room temperature:

$$C + 2\ O_3 \rightarrow CO_2 + 2\ O_2$$

3. With sulfur compounds

Ozone oxidizes sulfides to sulfates. For example, lead(II) sulfide is oxidised to lead(II) sulfate:

$$PbS + 4\ O_3 \rightarrow PbSO_4 + 4\ O_2$$

Sulfuric acid can be produced from ozone, water and either elemental sulfur or sulfur dioxide:

$$S + H_2O + O_3 \rightarrow H_2SO_4$$
$$3\ SO_2 + 3\ H_2O + O_3 \rightarrow 3\ H_2SO_4$$

In the gas phase, ozone reacts with hydrogen sulfide to form sulfur dioxide:

$$H_2S + O_3 \rightarrow SO_2 + H_2O$$

In an aqueous solution, however, two competing simultaneous reactions occur, one to produce elemental sulfur, and one to produce sulfuric acid:

$$H_2S + O_3 \rightarrow S + O_2 + H_2O$$
$$3\ H_2S + 4\ O_3 \rightarrow 3\ H_2SO_4$$

4. Other substrates

All three atoms of ozone may also react, as in the reaction of tin (II) chloride with hydrochloric acid and ozone:

$$3\ SnCl_2 + 6\ HCl + O_3 \rightarrow 3\ SnCl_4 + 3\ H_2O$$

Iodine perchlorate can be made by treating iodine dissolved in cold anhydrous perchloric acid with ozone:

$$I_2 + 6\ HClO_4 + O_3 \rightarrow 2\ I(ClO_4)_3 + 3\ H_2O$$

5. Combustion

Ozone can be used for combustion reactions and combusting gases; ozone provides higher temperatures than combusting in dioxygen (O_2). The following is a reaction for the combustion of carbon subnitride which can also cause higher temperatures:

$$3\ C_4N_2 + 4\ O_3 \rightarrow 12\ CO + 3\ N_2$$

Ozone can react at cryogenic temperatures. At 77 K (−196 °C), atomic hydrogen reacts with liquid ozone to form a hydrogen superoxide radical, which dimerizes:

$$H + O_3 \rightarrow HO_2 + O$$
$$2\ HO_2 \rightarrow H_2O_4$$

6. Reduction to ozonides

Reduction of ozone gives the ozonide anion, O_3^- . Derivatives of this anion are explosive and must be stored at cryogenic temperatures. Ozonides for all the alkali metals are known. KO_3, RbO_3, and CsO_3 can be prepared from their respective superoxides:

$$KO_2 + O_3 \rightarrow KO_3 + O_2$$

Although KO_3 can be formed as above, it can also be formed from potassium hydroxide and ozone:

$$2\ KOH + 5\ O_3 \rightarrow 2\ KO_3 + 5\ O_2 + H_2O$$

NaO_3 and LiO_3 must be prepared by action of CsO_3 in liquid NH_3 on an ion exchange resin containing Na^+ or Li^+ ions:

$$CsO_3 + Na^+ \rightarrow Cs^+ + NaO_3$$

A solution of calcium in ammonia reacts with ozone to give to ammonium ozonide and not calcium ozonide:

$$3\ Ca + 10\ NH_3 + 6\ O_3 \rightarrow Ca{\cdot}6NH_3 + Ca(OH)_2 + Ca(NO_3)_2 + 2\ NH_4O_3 + 2\ O_2 + H_2$$

Applications

Ozone can be used to remove manganese from water, forming a precipitate which can be filtered:

$$2\ Mn^{2+} + 2\ O_3 + 4\ H_2O \rightarrow 2\ MnO(OH)_2\ (s) + 2\ O_2 + 4\ H^+$$

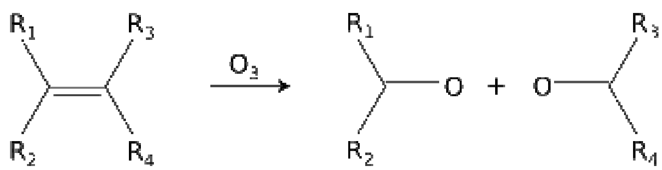
Ozone will also detoxify cyanides by converting it to cyanate, which is a thousand times less toxic.

$$CN^- + O_3 \rightarrow CNO^- + O_2$$

Ozone will also completely decompose urea:

$$(NH_2)_2CO + O_3 \rightarrow N_2 + CO_2 + 2\,H_2O$$

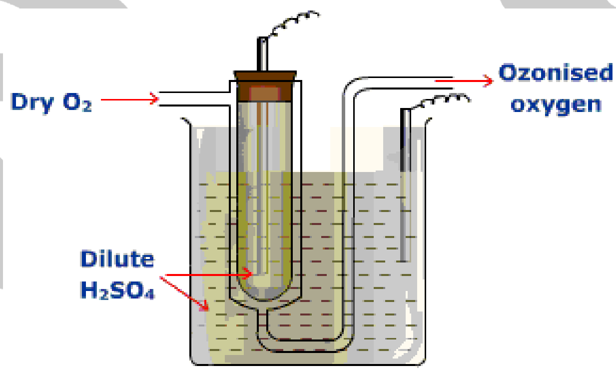
Ozone will cleave alkenes to form carbonyl compounds in the ozonolysis process.



6. Explain the preparation of Ozone by Brodie's method. Write its reduction reactions.

Brodie's ozoniser

In principle, this ozoniser is like the Siemen's ozoniser but dilute sulphuric acid replaces the tin foil. Two carbon electrodes are dipped in the acid and connected to an induction coil. A current of dry oxygen is passed through the space between the tubes. Ozonised oxygen containing about 5% O_3 comes out at the other end. If the apparatus is kept cool, the proportion of ozone may go up 20-25%.



Reduction properties:

Ozone reduces peroxides to oxides and in turn gets reduced to oxygen. For example, with H_2O_2 and BaO_2, it gives H_2O and BaO respectively.

$$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$$

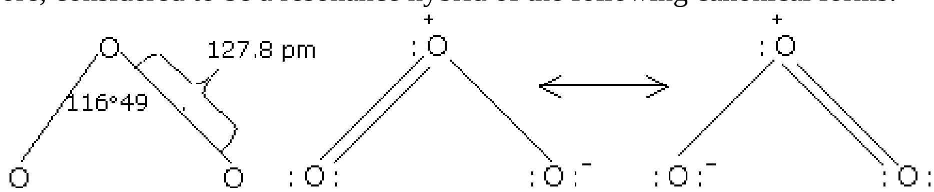
$$\underset{\text{barium peroxide}}{BaO_2} + O_3 \longrightarrow BaO + 2O_2$$

7. Write the structure of Ozone and explain its uses.

Structure of Ozone:

In the structure of ozone, the bond length of 127.8 pm is intermediate

between a single bond (bond length 148 pm) and a double bond (bond length 110 pm). Ozone is, therefore, considered to be a resonance hybrid of the following canonical forms:



Uses of ozone

Ozone is used

- For air purification at the crowded places like cinema halls and tunnel railways. Due to its strong oxidizing power it also destroys the foul smell in slaughter houses.
- In sterilizing drinking water by oxidizing all germs and bacteria.
- For preservation of meat in cold storages.
- For bleaching delicate fabrics such as silk, ivory, oils, starch and wax.
- It helps to locate a double bond in any unsaturated organic compound by ozonolysis.

8. How do you prepare hypo in laboratory / Write the chemical properties of hypo.

A method of preparing sodium thiosulphate is to react sodium sulphite with sulphur.

Method: 1

Dissolve 3g sodium sulphite (Na_2SO_3) in 15 cm^3 hot water and add 1g sulphur (S_8). boil the suspension until nearly all the sulphur has reacted. Filter hot (using a glass filter funnel plugged with a small piece of cotton. Ensure that the tip of the funnel is heated as well as the container for the filtrate) and evaporate the filtrate until crystallization starts. Cool and filter the crystals by suction. Dry the product in a warm oven (keep below 48^0C).

Equation

Na_2SO_3 (s) + 1/8 S_8 (s) $\xrightarrow{H_2O/100^0C}$ $Na_2S_2O_3$ (s)

Method: 2

$Na_2S_2O_3.5_2O$: It is manufactured by saturating a solution of sodium carbonate with SO_2 which gives a solution of sodium sulfite,

$$Na_2CO_3 + SO_2 + H_2O — Na_2SO_3 + CO_2 + H_2O$$

The resulting solution is boiled with powdered sulfur as, $Na_2SO_3 + S \xrightarrow{373K} Na_2S_2O_3$

The solution is then cooled to get crystals of sodium thiosulfate.

Physical properties:

(i) Sodium thiosulfate is a colorless crystalline solid. In the hydrated form, it is called hypo.

(ii) It melts at 320 *K* and loses its water molecules of crystallization on heating to 490*K*.

Chemical properties:

(i) Action with halogens: It reacts with halogens as,

(a) Chlorine water oxidizes sodium thiosulphate to sodium sulphate and sulphur is precipitated,

$$Na_2S_2O_3 + Cl_2 + H_2O \longrightarrow 2HCl + Na_2SO_4 + S$$

This property enables it to act as an antichlor in bleaching *i.e.* it destroys the unreacted chlorine in the process of bleaching.

(b) Bromine water also oxidizes sodium thiosulfate to sodium sulfate and sulfur,

$$Na_2S_2O_3 + Br_2 + H_2O \longrightarrow Na_2SO_4 + 2HBr + S$$

(c) With iodine it forms a soluble compound called sodium tetrathionate,

$$2Na_2S_2O_3 + I_2 \longrightarrow \underset{\text{Sod. tetrathionate}}{Na_2S_4O_6} + 2NaI$$

Therefore, hypo is commonly used to remove iodine stains from the clothes.

(ii) *Action of heat* : Upon heating, sodium thiosulfate decomposes to form sodium sulfate and sodium pentasulfide,

$$4Na_2S_2O_3 \xrightarrow{\text{Heat}} 3Na_2SO_4 + \underset{\text{Sodium pentasulphate}}{Na_2S_5}$$

(iii) *Action with acids* : Sodium thiosulphate reacts with dilute hydrochloric acid or Sulfuric acid forming sulfur dioxide and sulfur. The solution turns milky yellow due to sulfur.

$$Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + SO_2 + H_2O + S$$

(iv) *Action with silver halides* : Sodium thiosulfate forms soluble complex when treated with silver chloride or silver bromide,

$$2Na_2S_2O_3 + 2AgBr \longrightarrow \underset{\text{Sodium disthiosulphate}}{Na_3Ag(S_2O_3)_2} + NaBr$$

argentate (I)complex

This property of hypo is made use in photography.

Uses of sodium thiosulfate:

(i) It is largely used in photography as a fixing agent.

(ii) It is used as a preservative for fruit products such as jams and squashes.

(iii) It is used as an antichlor in bleaching.

(iv) It is used as a volumetric agent for the estimation of iodine.

(v) It is used in medicine.

9. Write any four uses of hypo with chemical equations.

(i) With iodine it forms a soluble compound called sodium tetrathionate,

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(iii) Chlorine water oxidizes sodium thiosulphate to sodium sulphate and sulphur is precipitated,

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This property enables it to act as an antichlor in bleaching *i.e.* it destroys the unreacted chlorine in the process of bleaching

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(i) It is largely used in photography as a fixing agent.

(ii) It is used as a preservative for fruit products such as jams and squashes.

(iii) It is used as an antichlor in bleaching.

(iv) It is used as a volumetric agent for the estimation of iodine.

(v) It is used in medicine.

10. Explain the preparation of Suphuric acid using contact process.
Ans:

<u>Manufacture of Sulphuric Acid</u>

Introduction to manufacture of sulfuric acid:

Manufacture of sulfuric acid industrially is done by the CONTACT PROCESS. Manufacture of sulfuric acid using the contact process involves the

- production of sulfur dioxide
- oxidation of sulfur dioxide to form sulfur trioxide
- dissolution of sulfur trioxide in dilute sulfuric acid to obtain a very high concentrated form of sulfuric acid called ole-um
- dilution of ole-um to obtain sulfuric acid

The above mentioned four steps in manufacture of sulfuric acid are enumerated below.

Explanation of the Steps of Contact Process:

a) Production of sulfur dioxide

Sulfur dioxide can be industrially produced by

- either burning Louisiana sulfur, which is 99.5% pure in purified air (oxygen). The chemical reaction is $S + O_2 \rightarrow SO_2$
- or roasting of iron pyrites (FeS_2), that is, oxidation of iron pyrites in the presence of air. The chemical reaction is $4FeS_2 + 11O_{22} + 2Fe_2O_3 \rightarrow 8SO$

Before carrying out the oxidation of sulfur dioxide into sulfur trioxide, the mixture of air and sulfur dioxide is purified of all impurities like dust particles, moisture, and arsenic oxide, because the presence of these substances will inhibit the oxidation process.

b) Oxidation of sulfur dioxide into sulfur trioxide

- The clean dried mixture of sulfur dioxide and air is passed into a tower containing vanadium pent-oxide or platinum placed on perforated shelves. This tower is known as the converter.
- The mixture of sulfur dioxide and air is heated before passing it into the converter.
- The vanadium pent-oxide (or platinum) placed in the converter acts as a catalyst for the oxidation of sulfur dioxide to sulfur trioxide.
- Sulfur trioxide is formed by the following chemical reaction : $S_2O_2 + O_2 \rightarrow S_2O_3$

- The above reaction if exothermic and thus without supplying heat, the temperature of the converter is maintained at 450 degrees Celsius.

b) Explanation of the Steps of Contact Process:

i) Absorption of sulfur trioxide in water to form Ole-um

The sulfur trioxide obtained above is cooled and passed into the absorption tower, where it is absorbed by dilute H_2SO_4 to form Ole-um, also known as pyrosulfuric acid. The reaction is as follows:-

$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$ (ole-um)

2) Dilution of Ole-um to obtain concentrated sulfuric acid

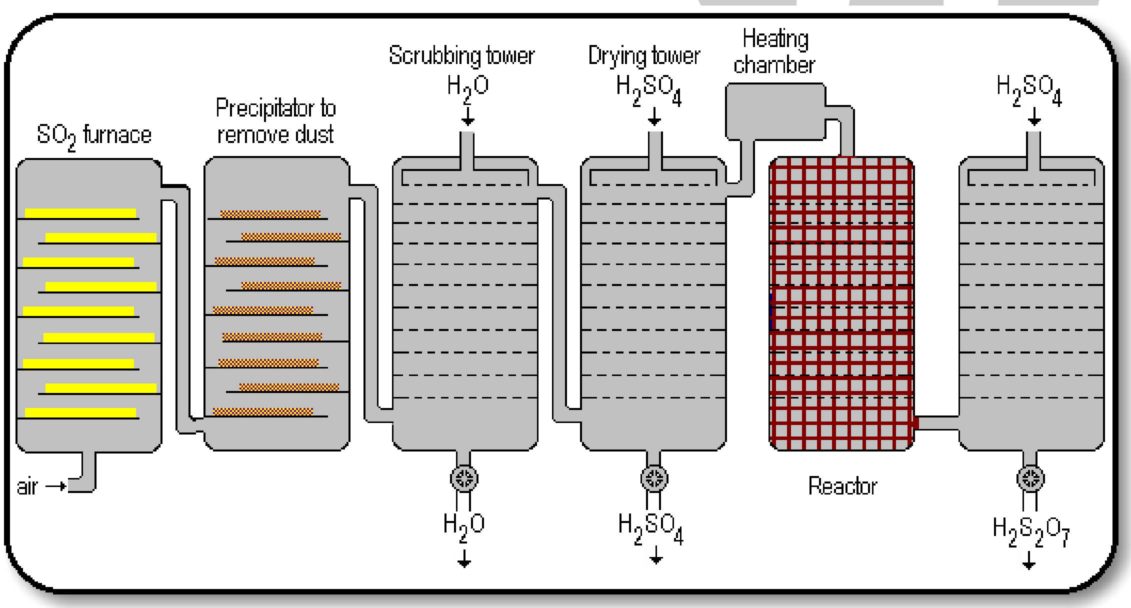
Calculated amount of water is added to ole-um obtained above to obtain sulfuric acid of the desired concentration. Reaction:-

$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$

11. Explin variou steps involved in the industrial preparation of sulphuric acid by contact process.

Sulphuric acid:

Sulphuric acid, H_2SO_4, is one of the most important industrial chemicals. It is an oily liquid having a boiling point of 335 ºC, which evolves much heat on dilution with water. Millions of tons of sulphuric acid are made every year by the CONTACT PROCESS, which converts raw sulphur, oxygen and water to sulphuric acid.



Step 1: Melted sulphur is burned in a furnace, using air, producing sulphur dioxide, SO_2.

Step 2: The SO_2 gas is passed through a tower called a precipitator in order to remove dust and other impurities which might interfere with the catalyst.

Step 3: The SO_2 is then washed with water, in a scrubbing tower.

Step 4: The SO_2 is then dried in a drying tower.

Step 5: After passing through a heating chamber, the SO_2, which is still mixed with air, is passed through a reactor. There, using vanadium pentoxide, V_2O_5, as catalyst, the SO_2 is converted to sulphur trioxide, SO_3.

$$2\,SO_2 + O_2 \xrightarrow{V_2O_5} 2\,SO_3$$

Step 6: Finally, the SO_3 is absorbed in concentrated sulphuric acid, giving the so-called oleum or pyrosulphuric acid. This is the diluted with water to give about 98% pure H_2SO_4.

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$

SHORT ANSWER QUESTIONS

1. Discuss the following properties of VIA group elements. a) Ionization potential b) Electron affinity.

Ans:

Some general properties of the elements of group 16

Property	Oxygen	Sulphur	Selenium	Tellurium	Polonium
Ionization energy (kJ mol^{-1})	1314	1000	941	869	-
Electron affinity (k.J mol^{-1})	141.4	208.8	195.5	190.0	-

1. Ionization energies:

The ionization energies of the elements of oxygen family are less than those of nitrogen family. As we move down the group from oxygen to polonium, the ionization energy decreases.

Explanation:

We expect that the ionization energy of oxygen should be more than that of N because of decrease in size. However, oxygen has unexpectedly low ionization energy than N. This is due to the reason that nitrogen has completely half filled orbitals and the configuration is stable because half filled and completely filled configurations have extra stability. But the configuration of O is less stable and therefore, has less ionization energy.

$$N(Z = 7): 1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$$

(Half filled, stable)

$$O(Z = 8): 1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$$

Less stable

As one moves down a group there is increase in nuclear charge. But at the same time the atomic size as well as the number of inner electrons, which shield the valence electrons from the nucleus increase. The overall effect of increase in atomic size and the shielding effect is much more than effect of increase in nuclear charge. Consequently, the outermost electron is less and less tightly held by the nucleus as we move down the group and hence ionization energy decreases.

2. Electron affinity:

The elements of this family have high electron affinities. The values decrease down the group from sulphur to polonium. Oxygen unexpectedly has low electron affinity. This is attributed to the small size of oxygen atom so that its electron cloud is distributed over a small region of space and therefore, it repels the incoming electron. Thus, the electron affinity of oxygen is unexpectedly less in the family.

2. What are the different oxidation states of S? Explain +6 state in terms of the electronic configuration of S.

Ans: Sulphur

– 2, + 2 is Ground state – $3s^2\ 3p^4$

+ 4 in 1st Excited state – $3s^2\ 3p^3\ 3d^1$

+ 6 in 2nd Excited state – $3s^2\ 3p^3\ 3d^2$

Oxygen → maximum valency (3) in H_3O^+.

Others → maximum valency (6)

Oxygen cannot exhibit greater than 3 due to small size and absence of ‘d’ orbitals

3. Write a short notes on allotropy of Chalcogens?

Ans: **Allotropy:**

All the elements of the group exhibit allotropy. For e.g., oxygen exists as O_2 and O_3 (ozone). Sulphur exists in a number of allotropic forms such as rhombic, monoclinic, plastic sulphur. All these allotropic forms of sulphur are non-metallic. Selenium has two common forms-red and grey. Similarly tellurium and polonium occur in allotropic forms

4. What are the halides of chacogens? How do you prepare them in laboratory?

Ans: **HALIDES :**

VI A group elements form monohalides of the type M_2X_2 ; dihalides of the type MX_2; tetrahalides of the type MX_4; and hexahalides of the type MX_6 (Where M = S, Se, Te ; X = halogen).

The oxidation states of S, Se and Te in monohalides is +1, in dihalides is +2, in tetrahalides is +4 and in hexahalides is + 6. Since the electronegativity of fluorine is greater than oxygen the compounds of fluorine and oxygen are called fluorides of oxygen rather than oxides of fluorine. Except oxygen all the other VI A group elements form hexafluorides.

Sulphur hexafluoride is formed by the direct reaction between sulphur and fluorine

$$S + 3F_2 \rightarrow SF_6$$

SF_4 can be prepared indirectly by the reaction between sulphur and cobalt trifluoride.

$$S + 4CoF_3 \rightarrow SF_4 + 4CoF_2$$

SCl_4 can be prepared by the direction between sulphur and chlorine

$$S + 2Cl_2 \rightarrow SCl_4$$

The best known dihlaide is SCl_2 . SCl_2 is a foul smelling red liquid .When sulphur monochloride is saturated with chlorine sulphur dichloride is formed

$$S_2Cl_2 + Cl_2 \rightarrow 2SCl_2$$

Halogen compounds of oxygen :

Most of the halogen oxides are unstable and explosive in nature even at low pressures also.

Iodine oxides are most stable oxygen compounds. Oxygen difluoride (OF_2) is prepared by passing fluorine gas through a very dilute solution of NaOH.

$$2NaOH + 2F_2 \rightarrow 2NaF + OF_2 + H_2O$$

Dioxygen difluoride (O_2F_2) : is prepared by passing silent electric discharge through a mixture of fluorine and oxygen at a very low temperature

$$F_2 + O_2 \xrightarrow{\text{silent electric discharge}} O_2F_2$$

5. What are the main oxides of suophur? How are they prepared?

Ans: VI group elements form two types of oxides, dioxides of the type MO_2 and trioxides of the type MO_3.

The main oxides of suphur are SO_2 and SO_3.

Dioxide:

Dioxides can be prepared directly by burning the elements in air

$$\text{Ex . } S + O_2 \rightarrow SO_2$$

SO_2 can also be prepared by heating metal sulphides (sulphide ores) in air.

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$

.

Trioxides :

Sulphur trioxide can be prepared by reacting SO_2 and O_2 in the presence of catalyst like Pt or V_2O_5 or $NOSO_3$.

$$2SO_2 + O_2 \xrightarrow{\text{Catalyst}} 2SO_3 \quad H = -196 \text{ kJ}$$

SO_3 is the anhydride of H_2SO_4

$$SO_3 + H_2O \rightarrow H_2SO_4.$$

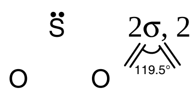
It is called Sulphuric anhydride.

6. What are the structures of SO_2 and SO_3 ?

Ans:

- The structure of SO_2 is a resonance hybride of two structures
  Shape : Angular ; Hybridisation : sp^2 ; bond angle

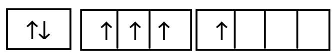
  is less than 120° (119.5°) $\neq 0$. (dipole moment is not zero)

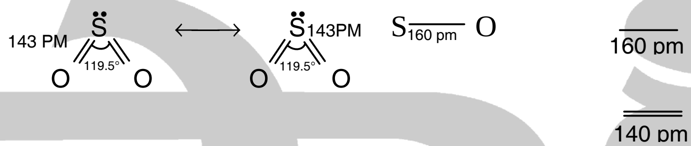


2σ, 2 . bonds $\begin{bmatrix} 1\pi - p\pi - d\pi \\ 1\pi - p\pi - p\pi \end{bmatrix}$

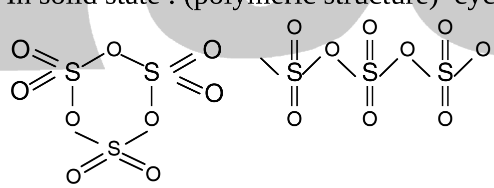
excited : $3s^2\ 3p^4$

$3s^2\ 3p^3\ 3d^1$





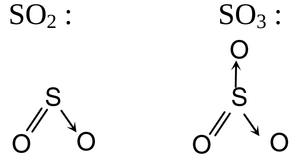
- SO_3 has planar triangular structure
  In solid state : (polymeric structure) cyclic (˜) or chain(. or)



Cyclic form Chain form(. - form)

In aqueous state SO_3 exists as [SO_4^{2-} - tetrahedral]

SO_2 : SO_3 :



7. Mention various halides of O2. Write equations for their formation.

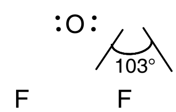
Ans:

Halogen compounds of oxygen : Most of the halogen oxides are unstable and explosive in nature even at low pressures also. Iodine oxides are most stable oxygen compounds.

Oxygen difluoride (OF_2) is prepared by passing fluorine gas through a very dilute solution of NaOH.

$$2NaOH + 2F_2 \rightarrow 2NaF + OF_2 + H_2O$$

OF_2 is an angular molecule in which oxygen is in sp^3 hybridisation $F\hat{O}F$ bond angle is 103° and
O – F bond length is 1.45 Å

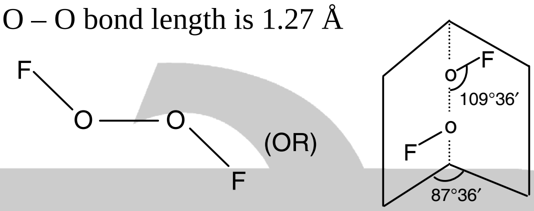


Dioxygen difluoride (O_2F_2) : is prepared by passing silent electric discharge through a mixture of fluorine and oxygen at a very low temperature

$$F_2 + O_2 \xrightarrow{\text{silent electric discharge}} O_2F_2$$

Structure :
O_2F_2 has open book structure similar to H_2O_2
Hybridisation of oxygen in O_2F_2 is sp^3
The dihedral angle in O_2F_2 is 87°36′ where as $O\hat{O}F$ is 109°31′

The O – O bond length is 1.27 Å



8. Mention the halides of 'S', How they are formed?
Ans:
HALIDES :

Sulphur hexafluoride is formed by the direct reaction between sulphur and fluorine

$$S + 3F_2 \rightarrow SF_6$$

SF_4 can be prepared indirectly by the reaction between sulphur and cobalt trifluoride.

$$S + 4CoF_3 \rightarrow SF_4 + 4CoF_2$$

SCl_4 can be prepared by the direction between sulphur and chlorine

$$S + 2Cl_2 \rightarrow SCl_4$$

SCl_4 is a unstable liquid.Tetrachlorides undergo hydrolysis to give the corresponding acids. SCl_4 gives sulphurous acid on hydrolysis.

The best known dihlaide is SCl_2. SCl_2 is a foul smelling red liquid. When sulphur monochloride is saturated with chlorine sulphur dichloride is formed

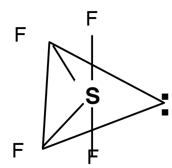
$$S_2Cl_2 + Cl_2 \rightarrow 2SCl_2$$

SCl_2 is angular in shape.

9. Give the structures 0f i) SF_4 ii) SF_6 .
Ans: **SF_6 :**
SF_6 is colourless, odourless, non – inflammable gas.

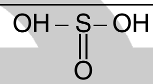
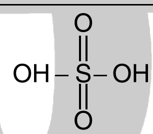
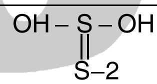
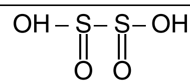
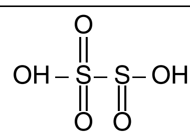
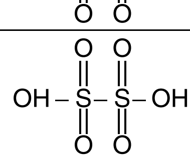
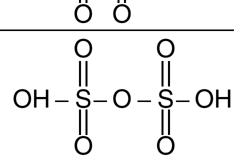
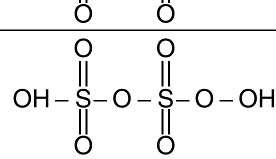
SF_6 is highly stable and extremely inert compound. it is used as gas insulator.
SF_6 is a covalent compound and have low boiling point.
In SF_6 have octahedral shape.
SF_6 have octahedral shape.
All ∠FSF are 90°

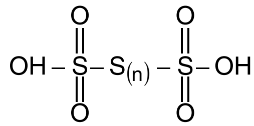
SF_4 : SF_4 and SCl_4 acts both as Lewis acids and Lewis bases. SF_4 and SCl_4 have distorted trigonal bipyramidal structure with one corner of the equatorial position is occupied by lone pair. The hybridisation of sulphur in SF_4 and SCl_4 is sp^3d



10. Write the names and formulae of all the oxyacids of 'S'.

OXYACIDS OF SULPHUR:

Formula	**Structure**	***Name***
H_2SO_3		Sulphurous acid
H_2SO_4		Sulphuric acid
$H_2S_2O_2$		Tiosulphuric acid
$H_2S_2O_4$		Dthionous acid
$H_2S_2O_5$		Pyro Sulphurous acid
$H_2S_2O_6$		Dithionic acid
$H_2S_2O_7$		Pyrosuphuric acid
$H_2S_2O_8$		Peroxythionic acid

$H_2S_{n+2}O_6$		Pyrothionic acid

11. Write the chemical reactions that takes place in contact process.

Ans: Explanation of the Steps of Contact Process:

a) Production of sulfur dioxide

Sulfur dioxide can be industrially produced by

1. either burning Louisiana sulfur, which is 99.5% pure in purified air (oxygen). The chemical reaction is $S + O_2 \rightarrow SO_2$
2. or roasting of iron pyrites (FeS_2), that is, oxidation of iron pyrites in the presence of air. The chemical reaction is

$$4FeS_2 + 11O_{22} + 2Fe_2O_3 \rightarrow 8SO_2$$

b) Oxidation of sulfur dioxide into sulfur trioxide

- Sulfur trioxide is formed by the following chemical reaction : $S_2O_2 + O_2 \rightarrow S_2O_3$
- The above reaction if exothermic and thus without supplying heat, the temperature of the converter is maintained at 450 degrees Celsius.

1) Absorption of sulfur trioxide in water to form Ole-um

The sulfur trioxide obtained above is cooled and passed into the absorption tower, where it is absorbed by dilute H_2SO_4 to form Ole-um, also known as pyrosulfuric acid. The reaction is as follows:-

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7 \text{ (ole-um)}$$

2) Dilution of Ole-um to obtain concentrated sulfuric acid

Calculated amount of water is added to ole-um obtained above to obtain sulfuric acid of the desired concentration. Reaction:-

$$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$$

VERY SHORT ANSWER QUESTIONS

1. What are elements of VIA group? Write their outer shell electronic configuration.

Ans: The elements of Group 16 are:

elements	**symbol**	**electron configuration**
oxygen	O	$[He]2s^2 2p^4$
sulfur	S	$[Ne]3s^2 3p^4$
selenium	Se	$[Ar]3d^{10} 4s^2 4p^4$
tellurium	Te	$[Kr]4d^{10} 5s^2 5p^4$
polonium	Po	$[Xe]4f^{14} 5d^{10} 6s^2 6p^4$

2. Why are group 16 elements called chalcogens?

Ans: The first four elements are collectively called as chalcogens since many metals occur as oxides and sulphides.

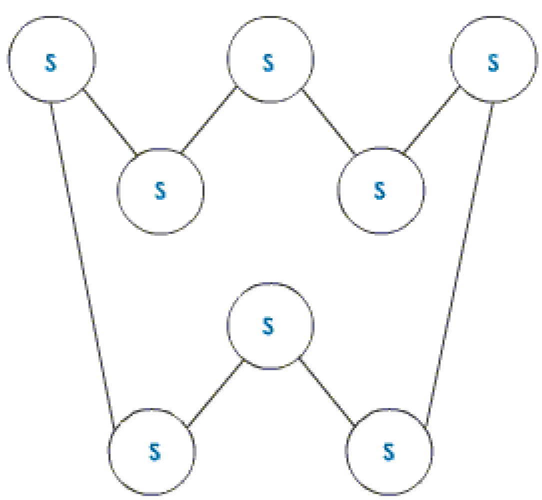
Ex : Pyrolusite – MnO_2 ; Haematite – Fe_2O_3

Iron pyrites – FeS_2 ; Zinc blend – ZnS

Chalcogen means ore forming elements.

3. Write the structure of sulphur molecule at low temperature.

Ans: Sulphur molecules have eight atoms per molecule (S_8 and Se_8) and have puckered ring structure. The puckered ring structure of S is as shown below.



4. Explain the oxidation states of ‘S’ in terms of its electronic configuration.

Ans:

The oxidation state of the elements of group 16 are shown below:

Property	Oxygen	Sulphur	Selenium	Tellurium	Polonium
Oxidation state	- 2	- 2, + 2 + 4, + 6	- 2, + 2 + 4,+6	- 2, + 2 + 4,+6	- 2, + 4

5. What are the oxidation states of Oxygen? Why it will not shwo higher oxidation states?

Ans: Oxygen shows oxidation states of -2 to +2. It cannot show higher oxidation states as it has no d-orbitals.

6. What is allotropy? Give the allotropes of Oxygen.

Ans:

Allotropy (Polymorphism): It is the property of an element existing in different crystalline forms having same chemical properties and different physical properties. The allotropic forms of oxygen are O_2 and O_3.

7. Write the names of allotropes of S.

Ans: 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

8. How does the stability of hydrides of chalcogens vary. Explain.

Ans:

Thermal stability: depends on bond strength between central and bonded atom.

$$H_2O \xrightarrow[\text{decreases}]{} H_2Po$$

Due to decrease in bond energy, increase in bond length, increase in size of central atom decreases the bond strength.

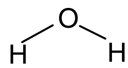
$$H_2O > H_2S > H_2Se > H_2Te > H_2Po$$

9. At room temperature H_2O is a liquid whereas H_2S is a gas, explain.

Ans: H_2O contain hydrogen bonds therefore it is a liquid; whereas H_2S doesn’t contain hydrogen bonds therefore it is a gas.

10. Explain the shape of water molecule.

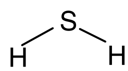
All the hydrides have bent structure. Water has V shape structure.



The ∠HOH bond angle in water is $104^{\circ}.31^{1}$

11. What is the structure of H_2S

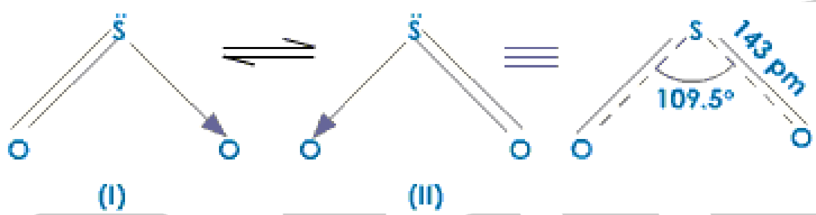
Ans: The H_2S has bent structure. Water has V shape structure.



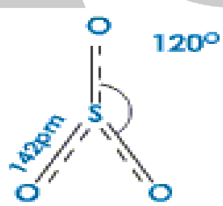
The ∠HSH bond angle is 90°.

12, Write the shapes of SO_2 and SO_3 .

Ans: Structure of SO_2.



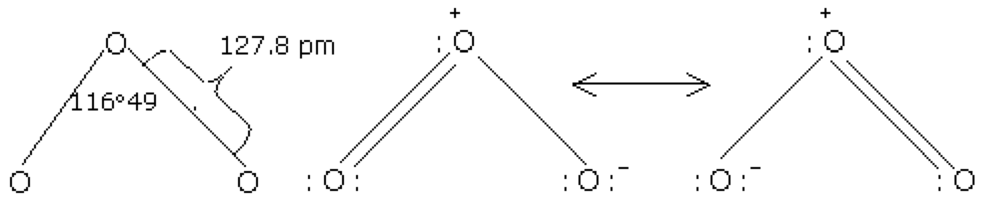
Structure of SO_3:



Hybrid Structure

13. Write the structural formula of O_3. Why is it important in atmosphere?

In the structure of ozone, the bond length of 127.8 pm is intermediate between a single bond (bond length 148 pm) and a double bond (bond length 110 pm). Ozone is, therefore, considered to be a resonance hybrid of the following canonical forms:



Ozone absorbs radiation strongly in the ultraviolet region of the atmospheric spectrum between 220-290 nm. This protects the Earth and its inhabitants from the harmful ultraviolet radiation of the Sun. Without this protective layer, more ultraviolet radiation would reach the surface of the Earth and cause damage to plant, animal and human life.

14, What happens when silver reacts with O_3? Give balanced equation.

Silver metal when warmed with ozone gets blackened due to reduction of the oxide formed in the initial stages of the reaction.

$$2Ag + O_3 \longrightarrow \underset{\text{silver oxide}}{Ag_2O} + O_2$$

$$Ag_2O + O_3 \longrightarrow 2Ag + 2O_2$$

15. What is tailing of Mercury?

Ans: When ozone is passed through mercury, it loses its meniscus and sticks to the glass due to the formation of mercurous oxide. This is called tailing of mercury. The meniscus can be restored by shaking it with water.

$$O_3 \longrightarrow O_2 + O$$

$$2Hg + O \longrightarrow Hg_2O$$

$$O_3 + 2Hg \longrightarrow O_2 + \underset{\text{Mercurious oxide}}{Hg_2O}$$

16. Locate oxidant and reductant in the reaction between H_2O_2 and O_3.

Ans: Ozone reduces peroxides to oxides and in turn gets reduced to oxygen. For example, with H_2O_2 gives H_2O and BaO respectively.

$$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$$

Ozone is reductant and H_2O_2 oxidant.

17. How is hypo useful in photgraphy?

Ans: **Action with silver halides**: Sodium thiosulfate forms soluble complex when treated with silver chloride or silver bromide,

$2Na_2S_2O_3 + 2AgBr \longrightarrow Na_3Ag(S_2O_3)_2$ + NaBr

Sodium disthiosulphate argentate (I)complex

This property of hypo is made use in photography.

18. Which of the catalyst used in contact process is least poisoned?

Ans: Vanadium pentaoxide(V_2O_5).

19. In the contact process what happens if air is used in the catalytic chamber instead of pure oxygen.

Ans: If air is used in catalytic chamber it will poison the catalyst therefore oxygen is used.

20. Which is more reactive SF_6 or TeF_6?

Ans: SF_6 exptionally stable for steric reasons. Therefore TeF_6 is more stable .