11. GROUP 16 ELEMENTS (VI A GROUP ELEMENTS)

Synopsis

ent & Electrons in atomic no.s		penultimate shell	Electronic configuration
O – 8	→	(n–1) s^2	[He] $2s^2$ $2p^4$
S – 16	→	(n–1) s^2 p^6	[Ne] $3s^2$ $3p^4$
Se – 34	→	(n–1) s^2p^6 d^{10}	[Ar] $3d^{10}$ $4s^2$ $4p^4$
Te – 52	→	(n–1) s^2p^6 d^{10}	[Kr] $4d^{10}5s^2$$5p^4$

Properties :

- Most abundant element in the group is oxygen .
- Least abundant element in the group is Po.
- VI A group contains oxygen, sulphur, selenium, Tellurium and polonium belongs to p-block of periodic table.
- 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.
- Polonium was a radioactive metal (given by madam–curie).
- Oxygen is a gas, other elements are solids.
- Atomic radius increase from oxygen to polonium.
- Ionisation potential decreases from oxygen to polonium.
- Electronegativity decreases gradually from oxygen to polonium.
- EN : Decreases [on pauling scale oxygen EN is 3.5 and most E.N in the group. Second most in the periodic table.]
- First electron affinity values are negative (exothermic)
  $O \xrightarrow[\text{increases}]{} S \xrightarrow[\text{decreases}]{} Te$
  E_1 : S > Se > Te > O
- Second electron affinity values are positive (endothermic)
  $O \xrightarrow[\text{decreases}]{} Te$ (with decreases in size repulsions decreases so E_2 decreases)
- Density increases from oxygen to polonium.
- Melting points and boiling point increases from oxygen to tellurium.
- Melting point and boiling point of polonium is less than tellurium but greater than selenium.
- The large difference in the melting points and boiling points of oxygen (44.2 K and 90 K) to those of sulphur (3.87 K and 718 K) is because oxygen is a diatomic gas while sulphur exists as S_8 molecules.
- Metallic character increases from oxygen to polonium.
- Oxygen and sulphur are non metals, selenium and tellurium are metalloids, polonium is a pure metal.
- Oxygen is diatomic gas while sulphur, selenium and tellurium are octa atomic S_8, Se_8 and Te_8

molecules, which have puckered ring structure.

$S\hat{S}S = 105°$ S – S bond length = 2.21 Å

- All the elements except oxygen exhibit - 2, +2, +4 and + 6 oxidation states.
- Since oxygen is second most electronegative element next to fluorine, oxygen never exhibits positive oxidation states except in the compounds of fluorine.
- Oxidation state : – 2, + 2, + 4,+6

  Oxygen → (– 2) common
  (– 1) peroxides
  (–1/2 superoxides)
- (+1) and (+2) in O_2F_2 and OF_2 respectively.
- 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.

  Allotropy (Polymorphism):
- All the VI A group elements exhibits allotropy due to
- Difference in crystal structure.
- Difference in atomicity.
- Difference in extent of polymerisation.
- The allotropic forms of oxygen are O_2 and O_3.

  Oxygen :

  O_2 is stable, Paramagnetic, contains two unpaired electrons and the structure is linear .

  O_3 is unstable, doesn't contains any unpaired electrons hence diamagnetic and the structure is angular
- The structure $\ddot{O}{=}{=}\ddot{O}$ cannot explain presence of 2 unpaired electrons in oxygen.

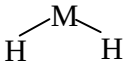
  So probable structure for oxygen is $:O\overset{\cdot\cdot\cdot}{\underset{\cdot\cdot\cdot}{}}O:$. (two, three e^- bonds are present in O_2)
- Among all 106 elements sulphur has highest number of allotropes.
- Se has 6 allotropes, 3 red non – metallic, 1 red amorphous, 2 grey metallic
- Te has 2 allotropes, 1 metallic, 1 non – metallic.
- Po has 2 allotropes both are metallic but differs in

  Crystal structure. α - Cubic form, β Rhombohedral – form.
- **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.
- Rhombic sulphur is insoluble in water but soluble in organic solvents like benzene, alcohol, ether etc.

- Monoclinic sulphur is stable above 368.5 K(95.5°c)
- At 95.5°c both rhombic and monoclinic sulphur are at equilibrium and this temperature is known as **Transition temperature** of sulphur.
- When liquid sulphur is poured in water plastic sulphur of χ - sulphur will be formed.
- The α, β, γ - sulphurs contain S_8 rings which are puckered rings or crown shape.
- Selenium has 6 – allotropes, of which three are red non metallic forms containing Se_8 rings, one amorphous red form and two grey metallic forms.
- Oxygen, sulphur shows catenation tendency. 'S' has maximum tendency.
- Sulphur can form chain with 10 'S' atoms, H_2S_n(n=2 to 10).
- Oxygen can form only peroxide chain H_2O_2.

HYDRIDES :

- Binary compounds of VI group element with hydrogen are called hydrides.
- VI group elements form hybrids of the type H_2M.
- All the hydrides of VI group elements are **covalent.**
- Except water other hydrides are **poisonous gases** with unpleasant or foul smelling gases.
- Water is a liquid at room temperature.
- The affinity of the elements to form hydrides decreases from oxygen to polonium.
- The thermal stability of the hydrides decreases from H_2O to H_2Po due to the increase in bond length and decrease in bond energy with increase in atomic size.
  $H_2O > H_2S > H_2Se > H_2Te > H_2Po$
- Water can be prepared directly from hydrogen and oxygen but H_2S, H_2Se and H_2Te can be prepared by the action of acids on metal sulphides, selenides and tellurides.
  1) $FeS + H_2SO_4 \rightarrow H_2S + FeSO_4$
  2) $Al_2Se_3 + HCl \rightarrow H_2Se + AlCl_3$
  3) $Al_2Se_3 + H_2O \rightarrow H_2Se + Al(OH)_3$
- **Boiling points** decreases from H_2O to H_2S and then increases
  $H_2S < H_2Se < H_2Te < H_2Po < H_2O$
- **Volatility** increases from H_2O to H_2S and then decreases to H_2Po.
  $H_2S > H_2Se > H_2Te > H_2Po > H_2O$
- H_2O is a liquid due to the association of molecules through hydrogen bonds.
- The least volatility and high boiling point of water is due to hydrogen bonds.
- In other hydrides hydrogen bonding is not possible due to less electronegative central atom.
- **Reducing power** increases from H_2O to H_2Po due to decrease in bond energy.
- **Acidic character** increases from H_2O to H_2Po
- Enthalpy of formation : increases from top to bottom.
  H_2O and H_2S ΔH values are negative (exothermic)
  H_2Se, H_2Te, H_2Po ΔH value are positive (endothermic)
- **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.
- Heat of dissociation / enthalpy of decomposition : decreases and stability decreases .
- All the hydrides have bent structure.



- The ∠HMH bond angle in water is 104°.31[1] but in other hydrides it is almost equal to 90°. Order of bond angle $H_2O > H_2S > H_2Se > H_2Te > H_2Po$
- In H_2O oxygen is involved in sp^3 hybridisation but in other hydride pure 'p' orbitals are participated in bonding.
- Oxygen and sulphur form less stable polyoxides and polysulphides like H_2O_2, H_2S_2, H_2S_n,(n=2 to10)

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

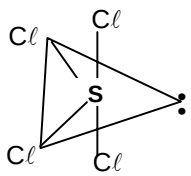
  $S + 4CoF_3 \rightarrow SF_4 + 4CoF_2$
- SCl_4 can be prepared by the direction between sulphur and chlorine

  $S + 2Cl_2 \rightarrow SCl_4$
- SCl_4 is a unstable liquid.
- Tetrachlorides undergo hydrolysis to give the corresponding acids.
- SCl_4 gives sulphurous acid on hydrolysis.

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

  $\downarrow$

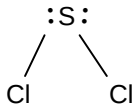
  $H_2SO_3 + H_2O$
- SF_4 and SCl_4 acts both as Lewis acids and Lewis bases .
- SF_4 and SCl_4 have distorted trigonal bipyramidal structure with one corner of the equatorial position is occupied by lone pair.
- The hybridisation of sulphur in SF_4 and SCl_4 is sp^3d



- 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

  $S_2Cl_2 + Cl_2 \rightarrow 2SCl_2$

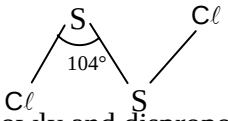
- SCl_2 is angular in shape.
- In SCl_2 sulphur is in sp^3 hybridisation
- Due to the repulsion between two lone pairs and two bond pairs the $\angle$ CISCl decreases to 103° from 109°28′



- 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

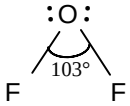
  $2S_2Cl_2 + 2H_2O \rightarrow 4HCl + SO_2 + 3S$
- Dihedral angle is 108°

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 a **pale yellow** coloured gas.
- OF_2 is more poisonous than F_2.
- OF_2 dissolves in water but does not given any oxy acid solution.

  $OF_2 + H_2O \rightarrow 2HF + O_2$
- 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

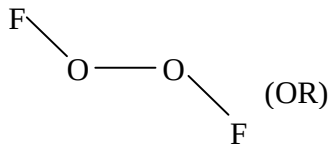


- **Dioxygen difluoride (O_2F_2) :** is prepared by passing silent electric discharge through a mixture of fluorine and oxygen at a very low temperature

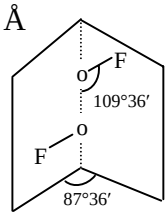
  $F_2 + O_2 \xrightarrow{\text{silent electric discharge}} O_2F_2$

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 $\hat{OOF}$ is 109°31′
- The O – O bond length is 1.27 Å



(OR)



OXIDES :

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

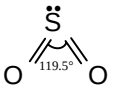
Dioxides :

- O_3 may be treated as **Oxygen dioxide (OO_2).**
- Dioxides can be prepared directly by burning the elements in air
  Ex . $S + O_2 \rightarrow SO_2$
- SO_2 can also be prepared by heating metal sulphides (sulphide ores) in air.
  $4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$
  $2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$
- SO_2 is highly soluble in water and forms hydrated SO_2
- SO_2 can be condensed to liquid which is used as a solvent.
- SO_2 acts as a **lewis base** due to presence of lone pairs of electrons.
- SO_2 acts as a **reducing agent** in both in acid and in alkaline medium.
- SO_2 reduces $K_2Cr_2O_7$ in to chromium sulphate
  $K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \rightarrow K_2SO_4 + Cr_2(SO_4) + H_2O$
- SO_2 acts as a **bleaching agent** in the presence of moisture.
- The bleaching action of SO_2 is due to **reduction.**
  $SO_2 + 2\ H_2O \rightarrow H_2SO_4 + 2\ (H)$
- During bleaching SO_2 will be oxidised to H_2SO_4
- Coloured matter + 2(H) $\rightarrow$ Colourless product
- SO_2 bleaching is temporary bleaching
- Acidic nature decreases from SO_2 to PoO_2.
- Trioxides are more acidic than corresponding dioxides.

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 $NOSO_3$.
  $2SO_2 + O_2 \xrightarrow{\text{Catalyst}} 2SO_3\ \Delta H = -196$ kJ
- SO_3 is the anhydride of H_2SO_4
  $SO_3 + H_2O \rightarrow H_2SO_4$.
- It is called **Sulphuric anhydride.**
- SO_2 is angular in shape.

- Sulphur in SO_2 is in sp^2 hybridisation .
- Number of pairs = $\frac{6+0}{2}$ =3 (2BP + 1LP)
- Sulphur atom is in double bonds with oxygen atoms.
- One oxygen of SO_2 form a **pπ - pπ bond** and another oxygen atom form pπ - dπ bond with sulphur atom.
- 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°) $\mu \neq 0$. (dipole moment is not zero)

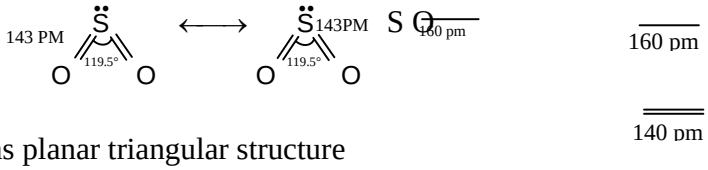


2σ, 2π bonds $\begin{bmatrix} 1\pi - p\pi - d\pi \\ 1\pi - p\pi - p\pi \end{bmatrix}$

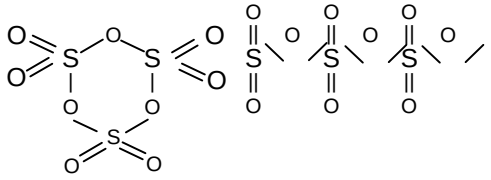
excited :$3s^2\ 3p^4$

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





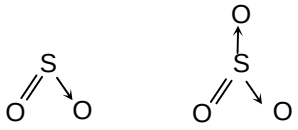
- SO_3 has planar triangular structure
  In solid state : (polymeric structure) cyclic (α–) or chain(β or γ)



Cyclic form Chain form(α - form)

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

SO_2 : **SO_3 :**



Oxyacids

'Ous' acids	'ic' acids
$MO_2 + H_2O \rightarrow$ ous acids	$MO_3 + H_2O \rightarrow$ ic acids
H_2SO_3	H_2SO_4
H_2SeO_3	H_2SeO_4
H_2TeO_3	H_2TeO_4

- Acidic nature – decreases for sulphur oxyacids to tellurium oxyacids
- – ic acids > – ous acids
- – ous acids and their salts act as reducing agents
- – ic acids and their salts act as oxidising agents

Acidic nature :

$H_2SO_3 > H_2SeO_3 > H_2TeO_3$

$H_2SO_4 > H_2SeO_4 > H_2TeO_4$

- 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

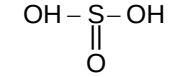
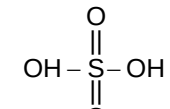
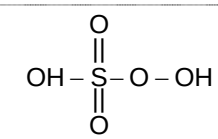
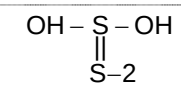
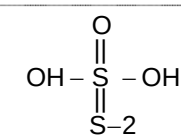
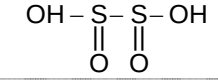
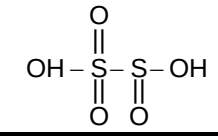
$H_2S_2O_6$ → Dithionic acid or hyposulphuric acid

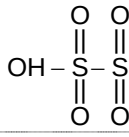
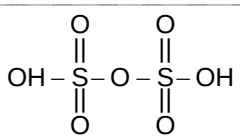
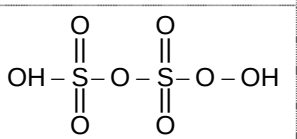
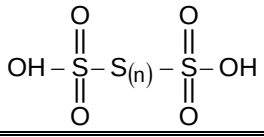
$H_2S_2O_7$ → Pyro sulphuric acid or oleum / disulphuric acid

$H_2S_2O_8$ → 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)π 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

OZONE :

- Ozone was first discovered by **Van Marum** in 1785
- The name ozone was given by **Schonbein.**
- **Sorret** assigned the formula of ozone as O_3.
- Ozone is present in the upper layers of atmosphere which is formed by the action of U.V. light on oxygen.
- Ozone layer in upper atmosphere is protecting the life on the earth from bad effect of U.V. radiations coming from the sun.

Preparation :

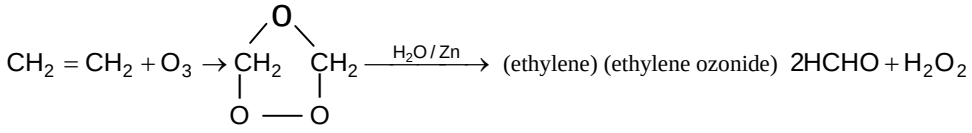
- Conversion of oxygen to ozone is endothermic

  $3O_2 \rightleftarrows 2O_3$ $\Delta H = +284.5$ kJ
- Ozone is prepared by subjecting cold, dry oxygen to silent electric discharge.
- Instruments used for the preparation of ozone are called ozonizers.
- The difference between Siemen's ozoniser and Brodie's ozonizers is only in medium.
- In **Siemen's ozoniser** silent electric discharge is produced by passing electric current through tin foils.
- In **Brodie's ozoniser** silent electric discharge is produced by passing electric current through copper wires dipped in sulphuric acid solution.
- The ozonised oxygen coming out of the ozonizer contain 10% ozone.
- Ozone is manufactured by **Siemen – Halske** method.
- Electrolysis of acidified water with high current density using platinum electrodes gives 95% ozone and 5% oxygen at anode.
- Chemically ozone can be prepared by heating oxygen to 2500°C and quenching it.

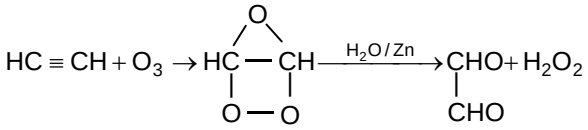
Properties :

- Ozone is a **Pale blue** pungent smelling, gas.
- In high concentration ozone is poisonous and produces headache and nausea if inhaled in large quantities.
- Ozone is heavier than air.
- Ozone is slightly soluble in water.

- Ozone is highly soluble in turpentine oil, glacial acetic acid or carbon tetrachloride.
- Ozone is respiratory irritant.
- Thermodynamically ozone is unstable and decomposes
  $2O_3 \rightarrow 3O_2$ $\Delta H = -284.5$ kJ mol^{-1}
- Two volumes ozone convert's into three volumes of oxygen.
- Decomposition of ozone is **exothermic.**
- The nascent oxygen liberated during the decomposition ozonen is used in oxidation.
- Black lead sulphide is oxidised to white lead sulphate by ozone.
  $PbS + 4\ O_3 \rightarrow PbSO_4 + 4\ O_2$
- Halogen acids are oxidised to the corresponding halogens
  $2HCl + O_3 \rightarrow Cl_2 + H_2O + O_2$
- Ozone liberates iodine from moist KI
  $2KI + H_2O + O_3 \rightarrow 2KOH + I_2 + O_2$
- White shining silver is blackened by ozone due to first oxidation to Ag_2O and then reduction to Ag.
  $2Ag + O_3 \rightarrow Ag_2O + O_2$
  $Ag_2O + O_3 \rightarrow 2Ag + 2O_2$
- In the oxidation of SO_2 to SO_3 and $SnCl_2$ to $SnCl_4$ all the three oxygen atoms are utilised in oxidation and no oxygen gas is liberated.
  $3SO_2 + O_3 \rightarrow 3SO_3$
  $3SnCl_2 + 6HCl + O_3 \rightarrow 3SnCl_4 + 3H_2O$
- When ozone is passed through mercury tailing effect takes place.
- The phenomenon of lasing luster, meniscus and consequent sticking nature to glass by mercury is called **tailing effect.**
- Tailing effect of mercury is due to oxidation of mercury to **mercurous oxide**
  $2Hg + O_3 \rightarrow Hg_2O + O_2$
- When the tailed mercury is washed with water the mercury regains its original properties.
- Ozone bleaches the vegetable colour by oxidation.
- Ozone can also act as reducing agent.
- Ozone reduces hydrogen peroxide to water
  $H_2O_2 + O_3 \rightarrow H_2O + 2O_2$
- Ozone reduces barium peroxide to barium oxide
  $BaO_2 + O_3 \rightarrow BaO + 2O_2$
- Ozone reduces silver oxide to silver
  $Ag_2O + O_3 \rightarrow 2Ag + 2O_2$
- Reduction of H_2O_2 and Ag_2O with O_3 is **mutual reduction** reaction.
- Ozone forms addition compounds with organic compounds containing double and triple bonds called ozonides.
- The ozonides undergo reductive hydrolysis in the presence of water and zinc metal forming carbonyl compounds.
- Formation of ozonide and subsequent reductive hydrolysis forming carbonyl compounds is called **ozonolysis** reaction .

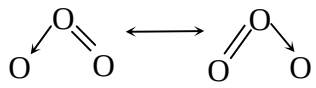


(formaldehyde)



(Acetylene) (Acetyleneozonide) (Glyoxal)

- Ozone is diamagnetic substance
- Ozone is angular in shape
- The bond angle in ozone is 116° 49′
- The O–O bond length in ozone is 128 pm (1.28 A°) which is intermediate of O – O single bond length (1.48 A°) and double bond length (1.21 A°)
- Ozone is a resonance hybrid of two structures



- The hybridisation of central oxygen in ozone is sp^2
- The bond order in ozone is 1.5

Uses :

- Ozone is used in purifying the drinking water by destroying bacteria and virus.
- Ozone is used in improving the quality of air in crowded places like underground railways, mines, cinema halls etc.
- Ozone is used in bleaching oils, oil paintings, ivory articles.
- Ozone is used in the manufacture of artificial silk and synthetic camphor.
- Ozone is used in the detection and determination of number of double and triple bonds in unsaturated organic compounds.
- A mixture of ozone and cyanogen ($O_3 + C_2N_2$) is used as **rocket fuel.**

Sodium thiosulphate :

- Anhydrous sodium thiosulphate $Na_2S_2O_3\ 5H_2O$ is known as **hypo**
- Hypo can be prepared by boiling sodium sulphite solution with sulphur

  $Na_2SO_3 + S \rightarrow Na_2S_2O_3$
- When sulphur is boiled with caustic soda hypo will be formed along with sodium sulphide and sodium pentasulphide

  $6NaOH + 12S \rightarrow Na_2S_2O_3 + 2Na_2S_5 + 3H_2O$
- Sodium pentasulphide can be converted into hypo by atmospheric oxidation

  $2Na_2S_5 + 3O_2 \rightarrow 2Na_2S_2O_3 + 6S$
- When SO_2 gas is passed into sodium sulphide solution hypo will be formed

  $2Na_2S + 3SO_2 \rightarrow 2Na_2S_2O_3 + S$

Properties :

- Hypo is an **effloresent substance**
- Hypo can form **super saturated solution .**
- When heated to 488 K it loses water of cyrstalisation.
- At high temperatures hypo decomposes to sulphur dioxide, sodium sulphide and sulphur.
- With dilute acids hypo liberates SO_2 gas and colloidal sulphur will be formed

  $S_2O_3^{2-} + 2H^+ \rightarrow SO_2 + S + H_2O$
- With dilute solution of hypo silver nitrate gives first a white precipitate which immediately turns to yellow, brown and finally black due to the formation of black silver sulphide

  $Na_2S_2O_3 + 2Ag\ NO_3 \rightarrow Ag_2S_2O_3 + 2NaNO_3$

  $Ag_2S_2O_3 + H_2O \rightarrow Ag_2S + H_2SO_4$
- With concentrated solution of hypo, silver nitrate first gives a white precipitate of silver thiosuphate which dissolves due to the conversion into complex

  $Na_2S_2O_3 + 2AgNO_3 \rightarrow Ag_2S_2O_3 + 2NaNO_3$

  $Ag_2S_2O_3 + 3Na_2S_2O_3 \rightarrow 2Na_3\ [Ag(S_2O_3)_2]$
- Silver halides dissolve in hypo solution due to the formation of sodium argento thiosulphate complex

  $AgBr + 2S_2O_3^{2-} \rightarrow [Ag\ (S_2O_3)_2]^{3-} + Br^-$

  $AgBr + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$ …(1)
- Chlroine oxidises hypo to sodium sulphate

  $Na_2S_2O_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl + S$ …(2)
- Iodine oxidises hypo to sodium tetrathionate

  $Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$……(3)

Uses :

- Hypo is used in photography as a fixing agent due to its complexing property with silver bromide (reaction 1)
- Hypo is used in textile industry as antichlor to remove excess Cl_2 used in bleaching (reaction 2)
- In the laboratory hypo is used in iodometric titration for the estimation of copper etc (reaction 3)
- In metallurgy hypo is used in the extraction of gold and silver.
- Hypo is used as antiseptic in medicine.

SULPHURIC ACID (H_2SO_4) :

- Sulphuric acid is a very important chemical used in industry.
- Because of its wide applications in industry, it is called 'King of chemicals'. It was also called as 'OIL OF VITREOL'.
- There are two important methods of manufacturing sulphuric acid.
  1) Lead chamber process
  2) Contact process

  CONTACT PROCESS :
- The steps involved are :
  i) Burning of sulphur (or) sulphide ores (like iron pyrites) in air to get SO_2

  $S + O_2 \rightarrow SO_2$

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

ii) Conversion of SO_2 to SO_3 catalytically

$2SO_2 + O_2 \xrightarrow[\Delta]{Catalyst} 2SO_3$

iii) SO_3 is absorbed in 98% H_2SO_4 to get oleum

$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$

- Oleum is diluted with water to get sulphuric acid of desired concentration
  $H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$
- The key step in the process is catalytic oxidation of SO_2 with O_2 to give SO_3 in presence of catalyst V_2O_5, The process is reversible

$2SO_{2(g)} + O_{2(g))} \rightleftharpoons 2SO_{3(g)}; \Delta H = -189kJ$

- Forward reaction is : Exothermic and $\Delta n = -ve$
- According to Lechatlier's principle to favour forward process the following conditions are to be maintained.
  I. High pressure is preferred. But actually 2 atm pressure is maintained. This is because acid resistant towers that can withstand high pressures cannot be built.
  II. Low temperatures are preferred. At low temperature the kinetic energy of reactants is less and hence in industry low temperatures are not advisable. So optimum temperatures are used. A temperature of 673-723 K is generally used.
  III. A suitable catalyst is to be used to increase the rate of formation of SO_3

CATALYST USED	**NAME OF THE PROCESS**
- Platinized asbestos	Baudische process
- Vanadium pentoxide	Baudische process
- Finely divided deposited on $MgSO_4$	Grillo's process
- A mixture of Fe_2O_3 and CuO	Mannheim process

- The type of catalysis in contact process is heterogenous catalysis.
- All the gases used in this process must be extremely pure as the catalysts are easily poisoned
  Ex: Pt gets poisoned by As_2O_3

  Now-a-days excess of oxygen is being used in the gaseous mixture.
- Important parts and their functions in contact process apparatus are :
  PYRITE BURNERS : S (or) Sulphide ore is burned.
  DUSTING TOWER : Dust particles in gaseous mixture are settled down.
  COOLING PIPES : Gases are cooled and dust particles are settled completely.
  SCRUBBING TOWERS : Water falling from top of tower cleans up going gases.
  DRYING TOWER : Gases are dried.
  ARSENIC PURIFIER : As_2O_3 (Main impurity) is removed by using gelatinous $Fe(OH)_3$.
  TESTING BOX : The purity of gases is tested.
  PREHEATER : Gases are heated to 673-723 K
  CONTACT TOWER : Gases are made to react in presence of catalyst. SO_3 is obtained.
  ABSORPTION TOWER : SO_3 is absorbed in conc.H_2SO_4 to get Oleum.
- Baudische process is combined with Mannheium process to get acid in greater amount.

ADVANTAGES OF CONTACT PROCESS :

- Acid obtained is very pure (96-98%)
- Gases can be tested and if impurities are present, reactants can be recycled.

- The reactants are relatively cheap