

s & p Block Elements part 3

(2) **Chemical Fertilizers** : The chemical substances which are added to the soil to keep up the fertility of soil are called fertilizers.

Types of fertilizers : Chemical fertilizers are mainly of four types,

(i) **Nitrogenous fertilizers** : e.g. Ammonium sulphate $(NH_4)_2SO_4$, Calcium cyanamide $CaCN_2$, Urea NH_2CONH_2 etc.

(ii) **Phosphatic fertilizers** : e.g. $Ca(H_2PO_4)_2 \cdot H_2O$ (Triple super phosphate), Phosphatic slag etc.

(iii) **Potash fertilizers** : e.g. Potassium nitrate (KNO_3) , Potassium sulphate (K_2SO_4) etc.

(iv) **Mixed fertilizers** : These are made by mixing two or more fertilizers in suitable proportion. e.g. **NPK** (contains nitrogen, phosphorus and potassium).

NPK is formed by mixing ammonium phosphate, super phosphate and some potassium salts.

Oxygen Family.

Oxygen is the first member of group 16 or VIA of the periodic table. It consists of five elements Oxygen (O), sulphur (S), selenium (Se), tellurium (Te) and polonium (Po). These (except polonium) are the ore forming elements and thus called **chalcogens**.

Electronic configuration

Elements	Electronic configuration ($ns^2 np^4$)
${}_8O$	$1s^2, 2s^2 2p^4$ or $[He]2s^2 2p^4$
${}_{16}S$	$1s^2, 2s^2 2p^6, 3s^2 3p^4$ or $[Ne]3s^2 3p^4$
${}_{34}Se$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^4$ or $[Ar]3d^{10} 4s^2 4p^4$
${}_{52}Te$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10}, 5s^2 5p^4$ or $[Kr]4d^{10} 5s^2 5p^4$
${}_{84}Po$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10} 4f^{14}, 5s^2 5p^6 5d^{10}, 6s^2 6p^4$ or $[Xe]4f^{14} 5d^{10} 6s^2 6p^4$

Physical properties

(1) **Physical state** : Oxygen is gas while all other are solids.

(2) **Atomic radii** : Down the group atomic radii increases because the increases in the number of inner shells overweighs the increase in nuclear charge.

(3) **Ionisation energy** : Down the group the ionisation energy decrease due to increase in their atomic radii and shielding effect.

(4) **Electronegativity** : Down the group electronegativity decreases due to increase in atomic size.

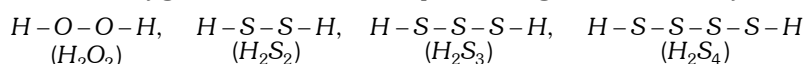
(5) **Electron affinity** : Element of this group have high electron affinity electron affinity decreases down the group.

(6) **Non – metallic and metallic character** : These have very little metallic character because of their higher ionisation energies.

(7) **Nature of bonding** : Compound of oxygen with non metals are predominantly covalent. S, Se, and Te because of low electronegativities show more covalent character.

(8) **Melting and boiling points** : The m. pt. and b. pt increases on moving down the group.

(9) **Catenation** : Oxygen has some but sulphur has greater tendency for catenation.



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(10) Allotropy

Oxygen –	O₂ and O₃
Sulphur –	Rhombic, monoclinic, plastic sulphur
Selenium –	Red (non-metallic) grey (metallic)
Tellurium –	Non-metallic and metallic (more stable)
Polonium –	α and β (both metallic)

(11) **Oxidation states** : Oxygen → - 2 and -1 oxidation state. These element shows +2, +4 and +6 oxidation state.

Chemical properties

(1) **Hydrides** : H₂O, H₂S, H₂Se, H₂Te and H₂Po, H₂O - colourless and odourless. H₂S, H₂Se, H₂Te and H₂Po - colourless, unpleasant smell.

Increasing order of reducing power of hydrides : H₂O < H₂S < H₂Se < H₂Te

Increasing order of bond angles in hydrides : H₂Te < H₂Se < H₂S < H₂O

The order of stability of hydrides : H₂O > H₂S > H₂Se > H₂Te

The order of increasing acidic nature of hydrides : H₂O < H₂S < H₂Se < H₂Te

(2) **Oxides** : These elements form monoxides (MO), dioxides (MO₂) increasing order of acidic nature of oxides is TeO₃ < SeO₃ < SO₃.

(3) **Oxyacids** : H₂SO₃, H₂SO₄, H₂S₂O₃, H₂SO₅, H₂S₂O₈, H₂S₂O₇, H₂S₂O₆

(4) **Halides** : Oxygen : OF₂, Cl₂O, Br₂O

Sulphur : S₂F₂, S₂Cl₂, SF₂, SCl₂, SBr₂, SF₄, SCl₄ and SF₆

Selenium and tellurium : SeF₆ and TeF₆

Oxygen and its compounds

Oxygen is the most abundant element in the earth crust (46.5%). It was discovered by **Karl Scheele** and **Joseph Priestley**. It occurs in three isotopic forms :

${}^8\text{O}^{16}$
(Abundance: 99.76%)

${}^8\text{O}^{17}$
(Abundance: 0.037%)

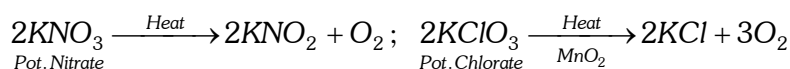
${}^8\text{O}^{18}$
(Abundance: 0.204%)

Out of the three isotopes, ${}^8\text{O}^{18}$ is radioactive.

(1) **Occurrence** : In free state, it occurs in air and constitutes 21% by volume of air.

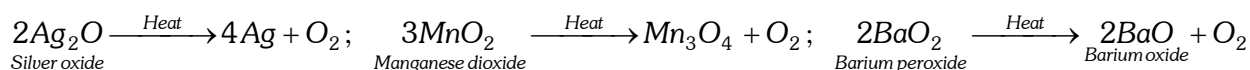
(2) **Preparation of Dioxygen** : Oxygen is prepared by the following methods.

(i) **By the decomposition of oxygen rich compounds** : e.g.

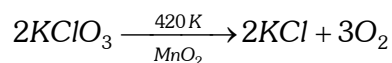


(ii) **By heating dioxides, Peroxides and higher oxides** : e.g.

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(iii) **Laboratory Method** : In the laboratory, O_2 is prepared by thermal decomposition of potassium chlorate.



Note : * In the absence of MnO_2 catalyst, the decomposition takes place at 670-720 K. Therefore, MnO_2 acts as a catalyst and also lowers the temperature for the decomposition of KClO_3 .

(iv) O_2 can also be prepared by the action of water on sodium peroxide as, $2\text{Na}_2\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{NaOH} + \text{O}_2$.

(v) **Industrial preparation** : The main sources for the industrial preparation of dioxygen are air and water.

(a) *From air* : O_2 is prepared by fractional distillation of air. During this process, N_2 with less boiling point (78 K) distills as vapour while O_2 with higher boiling point (90 K) remains in the liquid state and can be separated.

(b) *From water* : O_2 can also be obtained by the electrolysis of water containing a small amount of acid or alkali, $2\text{H}_2\text{O} \xrightleftharpoons{\text{Electrolysis}} 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$.

(3) **Physical properties of O_2** : It is a colourless, tasteless and odourless gas. It is slightly soluble in water and its solubility is about 30 cm^3 per litre of water at 298 K.

Physical properties of atomic and molecular oxygen

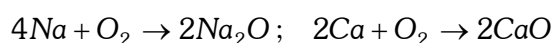
Atomic properties	Molecular properties
Atomic radius (pm) - 73	Bond length (pm) - 120.7
Ionic radius O^{2-} (pm) - 140	Bond energy (kJ mol^{-1}) - 493
Electronegativity - 3.5	Density at S.T.P. (g cm^{-3}) - 1.429
Ionisation energy (kJ mol^{-1}) - 1310	Melting point (K) - 54.4
Electron affinity (kJ mol^{-1}) - 140	Boiling point (K) - 90.2

(4) **Chemical properties of O_2** : It does not burn itself but helps in burning. It is quite stable in nature and its bond dissociation energy is very high. Therefore, it is not very reactive as such, $\text{O}_2 \rightarrow \text{O} + \text{O}$.

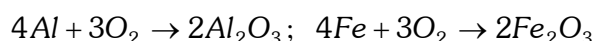
Therefore, dioxygen reacts at higher temperatures. However, once the reaction starts, it proceeds of its own. This is because the chemical reactions of dioxygen are exothermic and the heat produced during the reaction is sufficient to sustain the reactions.

(i) **Action with litmus** : Like dihydrogen, it is also neutral and has no action on blue or red litmus.

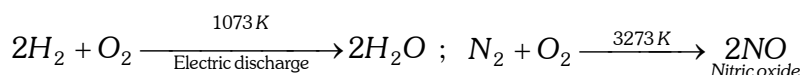
(ii) **Reaction with metals** : Active metals like Na , Ca react at room temp. to form their respective oxides.



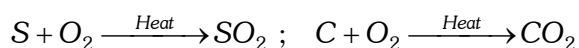
It reacts with Fe , Al , Cu etc. metals at high temperature



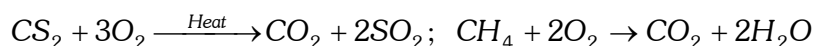
(iii) **Action with Non-metals** : It form oxides.



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(iv) **Reaction with compounds** : Dioxygen is an oxidising agent and it oxidises many compounds under specific conditions. e.g. $4HCl + O_2 \xrightarrow[CuCl_2]{700K} 2H_2O + 2Cl_2$; $4NH_3 + 5O_2 \xrightarrow[Pt]{1073K} 4NO + 6H_2O$



(5) Uses of dioxygen

- (i) It is used in the oxy-hydrogen or oxy-acetylene torches which are used for welding and cutting of metals.
- (ii) It is used as an oxidising and bleaching agent,
- (iii) Liquid O_2 is used as rocket fuel.
- (iv) It is used in metallurgical processes to remove the impurities of metals by oxidation.

(6) Compounds of Oxygen

Oxides : A binary compound of oxygen with another element is called oxide. On the basis of acid-base characteristics, the oxides may be classified into the following four types,

(a) **Basic oxides** : Alkali, alkaline earth and transition metals form basic oxides - Na_2O, MgO, Fe_2O_3 etc. their relative basic character decreases in the order : alkali metal oxides > alkaline earth metal oxides > transition metal oxides.

(b) **Acidic oxides** : Non-metal oxides are generally acidic - $CO_2, SO_2, SO_3, NO_2, N_2O_5, P_4O_{10}, Cl_2O_7$ etc.

(c) **Amphoteric oxides** : Al_2O_3, SnO_2 etc.

(d) **Neutral oxides** : H_2O, CO, N_2O, NO etc.

Trends of oxides in the periodic Table : On moving from left to the right in periodic table, the nature of the oxides change from basic to amphoteric and then to acidic. For example, the oxides of third period has the following behaviour,

Na_2O strongly basic	MgO basic	Al_2O_3 amphoteric	SiO_2 weakly acidic	P_4O_{10} acidic	SO_2 strongly acidic	Cl_2O_7 very strongly acidic
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Basic to acidic character increase

However, on moving down a group, acidic character of the oxides decreases. For example in the third group, the acidic character of oxides decreases as:

B_2O_3 acidic	Al_2O_3 amphoteric	Ga_2O_3 (weakly basic)	In_2O_3, Tl_2O_3 basic
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Acidic character decrease

On the basis of oxygen content the oxides may be classified into the following types,

Normal oxides : These contain oxygen atoms according to the normal oxidation number i.e. - 2. For example, $MgO, H_2O, CaO, Li_2O, Al_2O_3$ etc.

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Polyoxides : These contain oxygen atoms more than permitted by the normal valency. Therefore, these contain oxygen atoms in oxidation state different than -2 .

Peroxides : These contain O_2^{2-} ion having oxidation number of oxygen as -1 . For example, $H_2O_2, Na_2O_2, BaO_2, PbO_2$ etc.

Superoxides : These contain O_2^- ion having oxidation number of oxygen as $-1/2$. For example, KO_2, PbO_2 , etc.

Suboxides : These oxides contain less oxygen than expected from the normal valency. For example, N_2O .

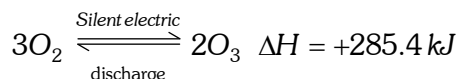
Mixed oxides : These oxides are made up of two simple oxides. For example, red lead $Pb_3O_4 (2PbO_2 + PbO_2)$, magnetic oxide of iron, $Fe_3O_4 (FeO + Fe_2O_3)$ and mixed oxide of manganese, $Mn_3O_4 (MnO_2 + 2MnO)$.

Ozone or trioxygen

Ozone is an allotrope of oxygen. It is present in the upper atmosphere, where it is formed by the action of U. V. radiations on O_2 , $3O_2 \xrightarrow[\text{Ozone}]{U.V.\text{radiation}} 2O_3$.

O_3 protects us from the harmful U. V. radiations which causes skin cancer. Now a days, ozone layer in the stratosphere is depleting due to NO released by supersonic aircrafts and chlorofluoro carbons (CFC'S) i.e. freon which is increasingly being used in aerosols and as a refrigerant.

Preparation : Ozone is prepared by passing silent electric discharge through pure, cold and dry oxygen in a specially designed apparatus called ozoniser. The formation of ozone from oxygen is an endothermic reaction.



Ozone is prepared in the laboratory by the following two types of ozonisers,

(a) Siemen's ozoniser, (b) Brodie's ozoniser

For the better yield of ozone : (a) Only pure and dry oxygen should be used. (b) The ozoniser must be perfectly dry. (c) A fairly low temperature ($\approx 273 \text{ K}$) must be maintained. (d) The electric discharge must be sparkless.

Physical properties : Ozone is a light blue coloured gas, having pungent odour. It is heavier than air. Its vapour density is 24. It is slightly soluble in water.

Chemical properties : The important chemical properties of ozone are discussed below,

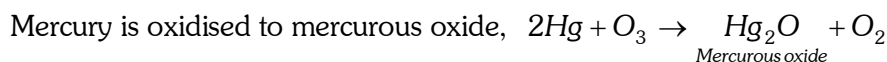
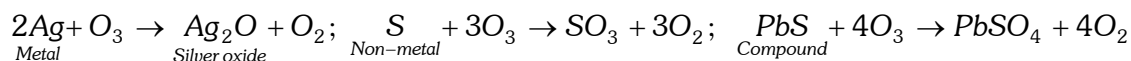
(1) **Decomposition** : Pure ozone decomposes on heating above 475 K to form O_2 gas.



(2) **Oxidising agent** : Ozone is one of the most powerful oxidising agent with the liberation of dioxygen. In fact, ozone is a stronger oxidising agent than molecular oxygen because ozone has higher energy content and decomposes to give atomic oxygen as: $O_3 \rightarrow O_2 + \underset{\text{Atomic oxygen}}{O}$

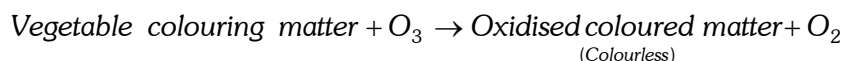
Therefore, ozone oxidises a number of non-metals and other reducing agents. e.g.

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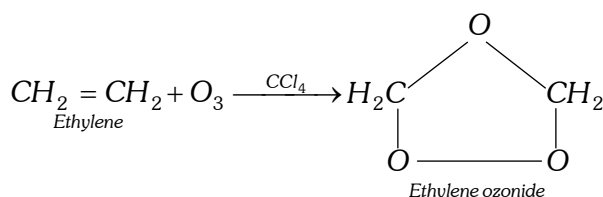
During this reaction mercury loses its meniscus and starts sticking to the sides of the glass. This is known as tailing of mercury. Mercurous oxide formed in this reaction dissolves in mercury and starts sticking to the glass surface.

(3) **Bleaching agent** : Due to the oxidising action of ozone, it acts as a mild bleaching agent as well as a sterilizing agent. It acts as a bleaching agent for vegetable colouring matter.

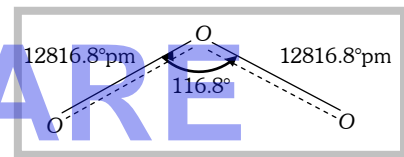


For example, ozone bleaches indigo, ivory, litmus, delicate fabrics etc.

(4) **Formation of ozonides** : Ozone reacts with alkenes in the presence of CCl_4 to form an ozonide. e.g.



Structure of O_3 : The structure of O_3 molecule is angular as shown in fig. The $\text{O}-\text{O}-\text{O}$ bond angle is 116.8° and $\text{O}-\text{O}$ bond length is 128 pm.



Uses of ozone

- (1) O_3 is used for disinfecting water for drinking purposes because ozone has germicidal properties.
- (2) It is used for purifying air of crowded places such as cinemas, under ground railway, auditoriums, tunnels, mines etc.
- (3) It is used in industry for the manufacture of KMnO_4 , artificial silk, synthetic camphor etc.

Sulphur and its compounds

Sulphur is the second member of oxygen family and belongs to group-16 (VI A) of the periodic table.

(1) **Occurrence** : Sulphur occurs in the earth's crust to the extent of 0.05%. It occurs in the free state as well as in combined state. Sulphure occurs mainly as sulphides and sulphates. eg.

Sulphide Ores		Sulphate Ores	
Iron pyrites (fool's gold)	- FeS_2	Gypsum	- $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Galena	- PbS	Epsom salt	- $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Copper pyrites	- CuFeS_2	Barytes	- BaSO_4
Cinnabar	- HgS	Zinc blende	- ZnS

(2) **Extraction of sulphur** (Frasch process) : Sulphur is generally extracted from underground deposits by drilling three concentric pipes upto the beds of sulphur (700 – 1200 feet deep).

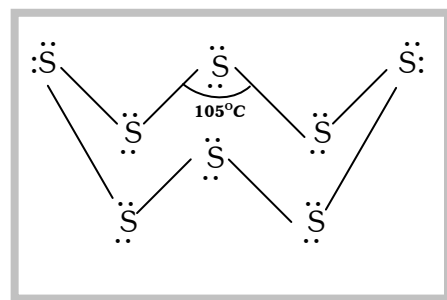
(3) **Allotropy in sulphur** : Sulphur exists in four allotropic forms,

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(i) **Rhombic or octahedral or α -sulphur** : It is a bright yellow solid, soluble in CS_2 and stable at room temp. All other varieties of sulphur gradually change into this form on standing.

(ii) **Monoclinic sulphur or prismatic or β -sulphur**: It is prepared by melting the sulphur and then cooling it till a crust is formed. On removing the crust, needle shaped crystals of monoclinic sulphur separate out. It is dull yellow in colour, soluble in CS_2 and stable only above 369K. Below this temperature it changes into rhombic form.

Thus, at 369K both these varieties co-exist. This temperature is called transition temperature and the two sulphurs are called enantiotropic substances. It also exist as molecules similar to that of rhombic sulphur but the symmetry of the crystals is different.



(iii) **Plastic or amorphous or γ -sulphur** : It is a super cooled liquid insoluble in CS_2 , soft and amorphous. It consists of long zig-zag chains of S-atoms.

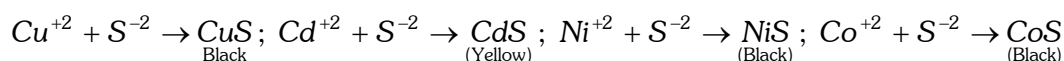
(iv) **Colloidal or δ -sulphur** : It is prepared by passing H_2S through a solution of an oxidizing agent or water or by treating sodium thiosulphate with dil. HCl .

(4) **Properties of sulphur** : It burns in air with, a blue flame forming SO_2 , gives sulphur hexafluoride with F_2 and sulphur mono chloride with Cl_2 , sulphides with metals like Na, Ca, Zn, Hg, Fe, Cu etc., reduces HNO_3 to NO_2 and H_2SO_4 to SO_2 . With $NaOH$ solution on heating, $S_8 + 12NaOH \longrightarrow 4Na_2S + 2Na_2S_2O_3 + 6H_2O$. It gives sodium sulphide and sodium thiosulphate, with excess of sulphur, $2Na_2S + S_8 \longrightarrow 2Na_2S_5$.

(5) **Uses of sulphur** : It is used in the manufacture of matches, gun powder (mixture of charcoal, sulphur and potassium nitrate), explosives and fire works SO_2, H_2SO_4, CS_2 and dyes, sulphur drugs and ointment for curing skin diseases and in the vulcanization of rubber.

Compounds of Sulphur

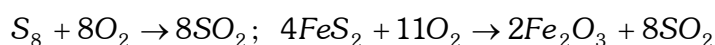
(1) **Hydrogen Sulphide** : It is prepared in the laboratory by the action of dil. H_2SO_4 on ferrous sulphide in kipp's apparatus, $FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S$. It is colourless gas having foul smell resembling that of rotten eggs. It reacts with many cations (of group II and IV) to give coloured sulphides,



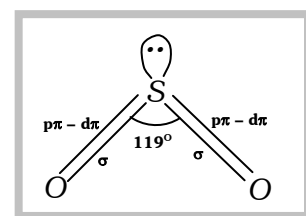
The solubility of sulphides can be controlled by the H^+ ions concentration and therefore, H_2S finds extensive use in qualitative analysis of cation radicals.

(2) **Oxides of sulphur** : Sulphur forms several oxides of which sulphur dioxide (SO_2) and sulphur trioxide (SO_3) are most important.

(i) **Sulphur dioxide (SO_2)** : It is prepared by burning sulphur or iron pyrites in air.



In laboratory, it is prepared by heating copper turnings with conc. H_2SO_4

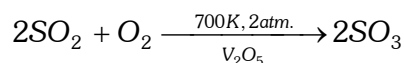


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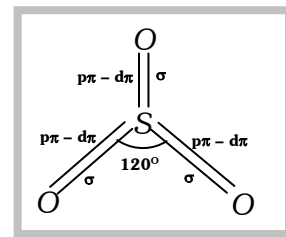
It is a colourless gas with irritating and suffocating smell.

SO_2 molecule has a bent structure with a $\text{O}-\text{S}-\text{O}$ bond angle of 119° . Sulphur is sp^2 hybridized.

(ii) **Sulphur trioxide (SO_3)** : It is formed by the oxidation of SO_2 .



In the gaseous phase, it exists as planar triangular molecular species involving hybridization of the S-atom. It has three $\text{S}-\text{O}$ σ bonds and three $\text{S}-\text{O}$ π bonds. The $\text{O}-\text{S}-\text{O}$ bond angle is of 120° .



(3) **Oxyacids of sulphur** : Sulphur forms many oxyacids. Some of these are,

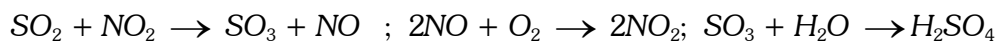
Formula	Name	Important properties	Structural formula
H_2SO_3 (+4)	Sulphurous acid	Free acid does not exist diprotic, strong reducing agent	$\begin{array}{c} \text{O} \\ \parallel \\ \text{O} = \text{S} - \text{OH} \\ \\ \text{OH} \end{array}$
H_2SO_4 (+6) (Oil of vitriol)	Sulphuric acid	Stable diprotic, dehydrating agent	$\begin{array}{c} \text{O} \\ \parallel \\ \text{O} = \text{S} - \text{OH} \\ \\ \text{OH} \end{array}$
$\text{H}_2\text{S}_2\text{O}_3$ (-2 and +6)	Thiosulphuric acid	Free acid does not exist but its salts e.g. $\text{Na}_2\text{S}_2\text{O}_3$ All quite stable reducing agent	$\begin{array}{c} \text{S} \\ \parallel \\ \text{O} = \text{S} - \text{OH} \\ \\ \text{OH} \end{array}$
$\text{H}_2\text{S}_2\text{O}_4$ (+3)	Dithionous acid		$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{HO} - \text{S} - \text{S} - \text{OH} \end{array}$
$\text{H}_2\text{S}_2\text{O}_6$ (+5)	Dithionic acid	Free acid is moderately stable but its salts are quite stable.	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{O} = \text{S} - \text{S} = \text{O} \\ \quad \\ \text{OH} \quad \text{OH} \end{array}$
$\text{H}_2\text{S}_2\text{O}_7$ (+6) (Oleum)	Disulphuric acid (Pyrosulphuric acid)	Strong oxidising agent	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{O} = \text{S} - \text{O} - \text{S} = \text{OH} \\ \quad \\ \text{OH} \quad \text{OH} \end{array}$
H_2SO_5 (+6) (Caro's acid)	Peroxomonosulphuric acid (Its salts known as persulphates)	Stable crystalline solid, powerfull oxidising agent	$\begin{array}{c} \text{O} \\ \parallel \\ \text{HO} = \text{S} - \text{OOH} \\ \\ \text{O} \end{array}$
$\text{H}_2\text{S}_2\text{O}_8$ (+6) (Marshals acid)	Peroxodisulphuric acid (its salts are known as disulphates)	Strong oxidising agent.	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{O} = \text{S} - \text{O} - \text{O} - \text{S} = \text{O} \\ \quad \\ \text{OH} \quad \text{OH} \end{array}$

(4) **Sulphuric acid (H_2SO_4)** : H_2SO_4 is a very stable oxyacid of sulphur. It is often called king of chemicals, since it is one of the most useful chemicals in industry.

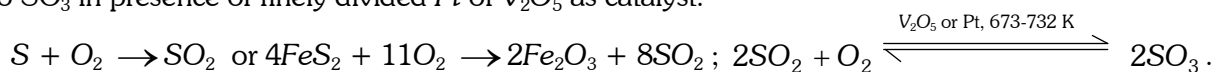
Manufacture of sulphuric acid : H_2SO_4 can be manufactured by following process,

(1) **Lead chamber process** : In this process, SO_2 is oxidized to SO_3 by the oxides of nitrogen and the SO_3 thus formed is dissolved in steam to form H_2SO_4 .

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(2) **Contact process** : In the contact process, SO_2 obtained by burning of S or iron pyrites is catalytically oxidized to SO_3 in presence of finely divided Pt or V_2O_5 as catalyst.

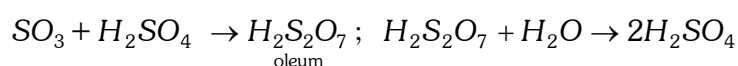


V_2O_5 is, however, preferred since is much cheaper than Pt and is also not poisoned by arsenic impurities.

The favorable conditions for maximum yield of SO_3 are,

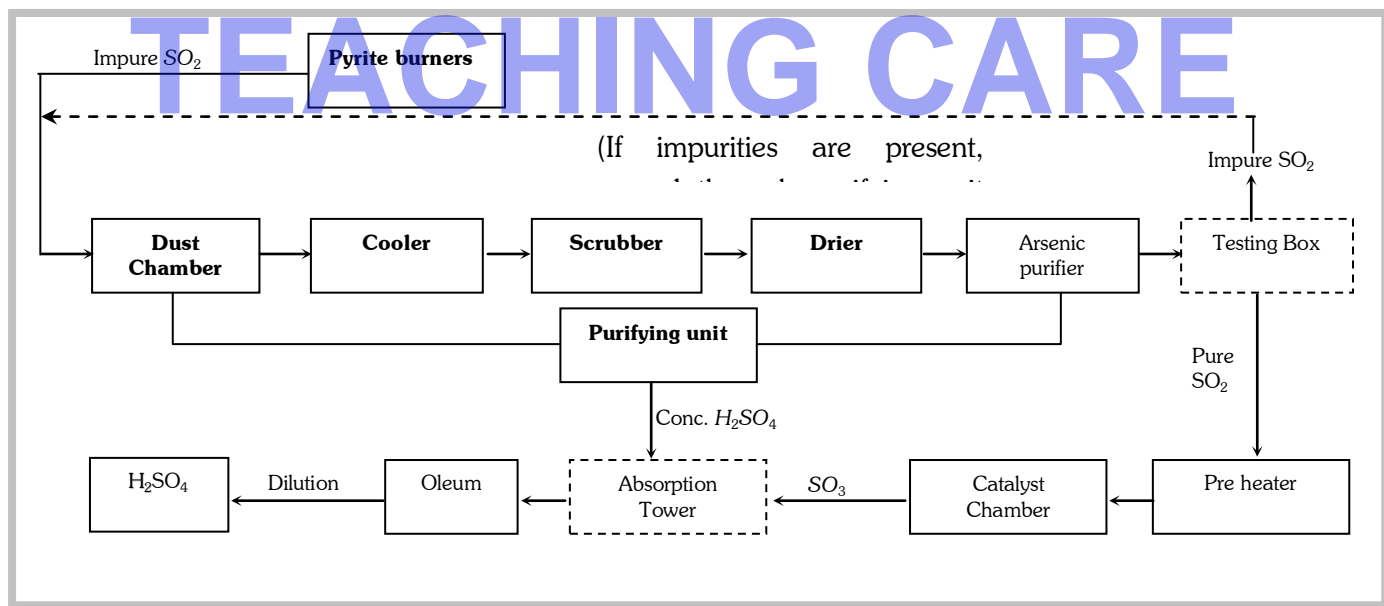
(i) High concentration of SO_2 and O_2 . (ii) Low temperature of 673 to 723 K, (iii) High pressure about 2 atmospheres.

SO_3 thus obtained is absorbed in 98% H_2SO_4 to form oleum which on dilution with water gives H_2SO_4 of desired concentration.



Contact process is preferred over lead chamber process (gives 98% pure H_2SO_4) since it gives H_2SO_4 of greater purity (100%).

Flow sheet diagram of it's preparation is as follows



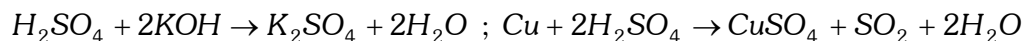
Structure : H_2SO_4 is a covalent compound and has tetrahedral (S is sp^3 - hybridized) structure.

Properties : H_2SO_4 has high b.p. (611K) and is also highly viscous due to H-bonding. It has strong affinity for H_2O and a large amount of heat is evolved when it is mixed with water.

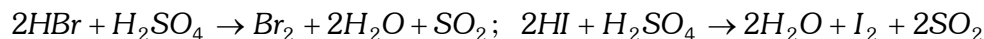
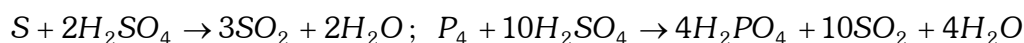
(1) H_2SO_4 is a strong dibasic acid. It neutralizes alkalis, liberates CO_2 from carbonates and bicarbonates.

(2) It reacts with more electropositive (than hydrogen) metals to evolve H_2 and produces SO_2 on heating with less electropositive metals than hydrogen .eg.,

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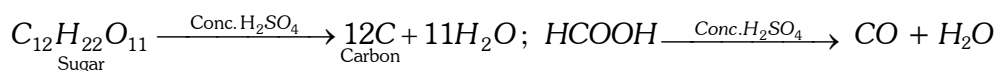
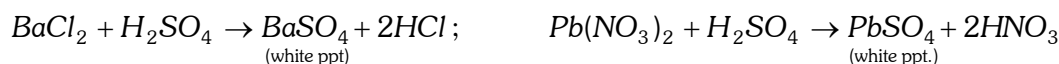
(3) It is a strong oxidizing agent and oxidises as follows,



(4) It reacts with number of salts. It liberates HCl from chlorides, H_2S from sulphides, HNO_3 from nitrates.

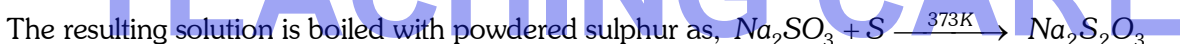
(5) It acts as a strong dehydrating agent, as it dehydrates, sugar to sugar charcoal (carbon), formic acid to CO , oxalic acid to $CO + CO_2$ and ethyl alcohol to ethylene.

(6) It is also a good sulphonating agent and used for sulphonation of aromatic compounds. eg.,



Uses : H_2SO_4 is used (i) in the preparation of fertilizers like $(NH_4)_2 SO_4$ and super phosphate of lime, (ii) in lead storage batteries (iii) in preparation of dyes, paints and explosives (iv) in textile and paper industry (v) for tanning (vi) as a dehydrating agent.

(5) **Sodium thiosulphate** $Na_2S_2O_3 \cdot 5H_2O$: It is manufactured by saturating a solution of sodium carbonate with SO_2 which gives a solution of sodium sulphite, $Na_2CO_3 + SO_2 + H_2O \rightarrow Na_2SO_3 + CO_2 + H_2O$



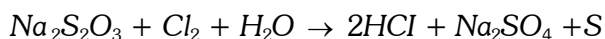
The solution is then cooled to get crystals of sodium thiosulphate.

Physical properties : (1) Sodium thiosulphate is a colourless crystalline solid. In the hydrated form, it is called hypo. (2) It melts at 320 K and loses its water molecules of crystallization on heating to 490K.

Chemical properties

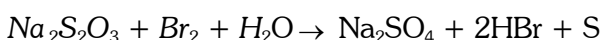
(1) **Action with halogens :** It reacts with halogens as,

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

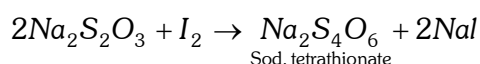


This property enables it to act as an antichlor in bleaching i.e. it destroys the unreacted chlorine in the process of bleaching.

(ii) Bromine water also oxidizes sodium thiosulphate to sodium sulphate and sulphur,



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



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

(2) **Action of heat :** Upon heating, sodium thiosulphate decomposes to form sodium sulphate and sodium pentasulphide, $4Na_2S_2O_3 \xrightarrow{\text{Heat}} 3Na_2SO_4 + \underset{\text{Sodium pentasulphide}}{Na_2S_5}$

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

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(4) **Action with silver halides** : Sodium thiosulphate forms soluble complex when treated with silver chloride or silver bromide, $2\text{Na}_2\text{S}_2\text{O}_3 + 2\text{AgBr} \rightarrow \text{Na}_3\text{Ag}(\text{S}_2\text{O}_3)_2 + \text{NaBr}$.

Sodium dithiosulphate
argentate (I) complex

This property of hypo is made use in photography.

Uses of sodium thiosulphate

- (1) It is largely used in photography as a fixing agent.
- (2) It is used as a preservative for fruit products such as jams and squashes.
- (3) It is used as an antichlor in bleaching.
- (4) It is used as a volumetric agent for the estimation of iodine.
- (5) It is used in medicine.

Halogen Family.

Fluorine is the first member of group 17 or VIIA of the periodic table. It consists of five elements Fluorine (F), Chlorine (Cl), bromine (Br), iodine (I) and astatine (At). These are known as halogen because their salts are found in sea water. Halogen is a greek word meaning a sea salt.

Electronic configuration

Elements	Electronic configuration ($ns^2 np^5$)
${}_9\text{F}$	$1s^2, 2s^2 2p^5$ or $[\text{He}]2s^2 2p^5$
${}_{17}\text{Cl}$	$1s^2, 2s^2 2p^6, 3s^2 3p^5$ or $[\text{Ne}]3s^2 3p^5$
${}_{35}\text{Br}$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^5$ or $[\text{Ar}]3d^{10} 4s^2 4p^5$
${}_{53}\text{I}$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10}, 5s^2 5p^5$ or $[\text{Kr}]4d^{10} 5s^2 5p^5$
${}_{85}\text{At}$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10} 4f^{14}, 5s^2 5p^6 5d^{10}, 6s^2 6p^5$ or $[\text{Xe}]4f^{14} 5d^{10} 6s^2 6p^5$

Physical properties

(1) **Physical state** : Halogens exist as diatomic covalent molecules.

F_2 – gas, Cl_2 – gas, Br_2 – corrosive liquid, I_2 – volatile solid.

(2) **Melting and boiling points** : They increase with increase in atomic number.

(3) **Ionization energy** : The I.E. decreases on moving down the group.

(4) **Electron affinity** : $F < Cl > Br > I$ or $Cl > F > Br > I$.

(5) **Electronegativity** : $F > Cl > Br > I$.

(6) **Bond energy**

Element	$F - F$	$Cl - Cl$	$Br - Br$	$I - I$
Bond length (Å)	1.42	1.99	2.28	2.67
Bond dissociation energy (kcal / mole)	38	57	45.5	35.6

(7) **Colour** : F – Light yellow, Cl – Greenish yellow, Br – Reddish brown, I – Deep violet.

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(8) **Oxidation state** : All exhibit -1 Oxidation state Except fluorine other element also show +3, +5, +7 oxidation state.

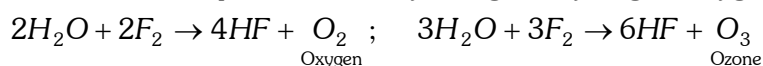
(9) **Oxidising power** : $F_2 > Cl_2 > Br_2 > I_2$.

(10) **Solubility** : Halogen being non polar in nature do not dissolve in water $2F_2 + 2H_2O \rightarrow 4HF + O_2$, $3F_2 + 3H_2O \rightarrow 6HF + O_3$ (fluorine highly soluble) Cl_2 and Br_2 are fairly soluble. I_2 is a least soluble in water.

Chemical properties

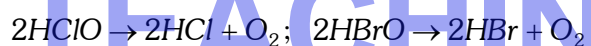
(1) **Reactivity** : The halogen are most reactive elements due to their low bond dissociation energy, high electron affinity and high enthalpy of hydration of halide ion. $F > Cl > Br > I$

(2) **Reaction with H_2O** : Halogens readily decomposes water. This tendency decreases on moving down the group. Fluorine decomposes water very energetically to give oxygen and ozone,



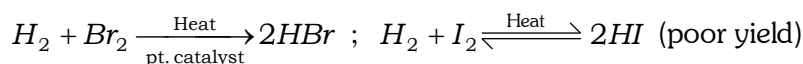
Fluorine gives fumes in moist air. This is due to the formation of HF, which is a liquid and can absorb moisture to form liquid droplets and therefore, gives fumes with moist air. Chlorine and bromine react less vigorously, $Cl_2 + H_2O \rightarrow HCl + \underset{\text{Hypochlorous acid}}{HClO}$; $Br_2 + H_2O \rightarrow HBr + \underset{\text{Hypobromous acid}}{HBrO}$

In the presence of sunlight, $HClO$ (hypochlorous acid) $HBrO$ (hypobromous acid) liberate oxygen.



Iodine is only slightly soluble in water. However, it dissolves in 10% aqueous solution of KI due to the formation of I_3^- ions. $I_2 + KI \rightleftharpoons KI_2$ or $I_2 + I^- \rightleftharpoons \underset{\text{Complex ion}}{I_3^-}$

(3) **Reaction with hydrogen** : Form covalent halides.



Acidic strength in aqueous solution is in the order, $HI > HBr > HCl < HF$.

Reducing character of hydrides follow the order, $HI > HBr > HCl > HF$.

Boiling point $HF > HI > HBr > HCl$. Thermal stability, $H-F > H-Cl > H-Br > H-I$.

HCl is also called Muriatic acid.

(4) **Hydrides** : All the halogens combine directly with hydrogen to form halogen acids but their reactivity progressively decreases from fluorine to iodine, $H_2 + X_2 \rightarrow 2HX$ ($X = F, Cl, Br$ or I).

(i) **Boiling points or volatility** : In other words volatility decreases in the order : $HCl > HBr > HI > HF$ as the boiling points increase in the order: HCl (189K) < HBr (206K) < HI (238K) < HF (292.5K).

(ii) **Thermal stability** : Thermal stability of the hydrides decrease from HF to HI i.e., $HF > HCl > HBr > HI$.

(iii) **Acidic strength** : The acidic strength of halogen acids decreases from HI to HF i.e, $HI > HBr > HCl > HF$.

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(iv) **Reducing properties** : Since the stability of hydrides decreases from HF to HI , their reducing properties increase in the order $HF < HCl < HBr < HI$.

(v) **Dipole moments** : The dipole moments of hydrogen halides decrease in the order : $HF > HCl > HBr > HI$ as the electro negativity of the halogen atom decreases from F to I.

HX	HF	HCl	HBr	HI
Dipole moment (D)	1.74	1.07	0.78	0.38

(5) **Oxides** : Halogens (except F_2) do not combine readily with oxygen. However, a number of compounds of halogens with oxygen have been prepared by indirect methods. Only two compounds of fluorine with oxygen, i.e. oxygen difluorine (OF_2) and oxygen fluoride (O_2F_2) are known. Chlorine forms largest number of oxides i.e. Cl_2O , ClO_2 , Cl_2O_6 and Cl_2O_7 while iodine forms the least, i.e. I_2O_5 . Bromine, however, forms three oxides (Br_2O , BrO_2 & BrO_3). In all these compounds, bonds are largely covalent. All the oxides of halogens are powerful oxidizing agents. These compounds are very reactive and are unstable towards heat. The stability of oxides is greatest for iodine while bromine oxides are the least stable. For a particular halogen, higher oxides are more stable than the lower ones.

Iodine-oxygen bond is stable due to greater polarity of the bond (due to larger electro negativity difference between I and O) while in chlorine-oxygen bond, the stability is gained through multiple bond formation involving the d-orbital of chlorine atom. Bromine lacks both these characteristics and hence forms least stable oxides.

Oxides of chlorine, bromine and iodine are acidic and the acidic character increases as the percentage of oxygen increases in them.

Iodine also forms I_2O_4 and I_4O_9 compounds which are believed not to be true oxides but are basic iodyliodate, IO (IO_3) and normal iodine triiodate, I (IO_3)₃ having tripositive iodine as the cation.

OF_2 is V-shaped having bond angle 103° , Cl_2O is also V-shaped with bond angle 111° while ClO_2 is angular with-bond angle 118° . It is paramagnetic due to odd number of electrons having three-electron bond. It is regarded as a mixed anhydride of chloric and chlorous acids. $2ClO_2 + H_2O \rightarrow HClO_2 + HClO_3$

(6) **Oxoacids of halogens** : Fluorine does not form any oxoacid since it is the strongest oxidizing agent. Chlorine, bromine and iodine mainly form four series of oxoacids namely hypohalous acid (HXO), halous acid (HXO_2) halic acid (HXO_3) and perhalic acid (HXO_4) as given below :

Oxidation state	Chlorine	Bromine	Iodine	Thermal stability and acid strength
+1	$HClO$	$HBrO$	HIO	<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> ↑ Increases ↓ </div> <div style="text-align: center;"> ↑ Decreases ↓ </div> </div>
+3	$HClO_2$	-	-	
+5	$HClO_3$	$HBrO_3$	HIO_3	
+7	$HClO_4$	$HBrO_4$	HIO_4	
Acidity decreases →				

(i) **Hybridized ion** : In all these oxoacids, the halogen atom is sp^3 -hybridized.

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(ii) **Acidic character** : All these acids are monobasic containing an—OH group. The acidic character of the oxoacids increases with increase in oxidation number, i.e., $HClO < HClO_2 < HClO_3 < HClO_4$ and the strength of the conjugate bases of these acids follows the order, $ClO^- > ClO_2^- \rightarrow ClO_3^- > ClO_4^-$.

(iii) **Oxidising power and thermal stability** : The oxidizing power of these acids decreases as the oxidation number increases, i.e., $HClO < HClO_2 < HClO_3 < HClO_4$. Stability of oxoacids of chlorine in the increasing order is, $HClO < HClO_2 < HClO_3 < HClO_4$ and the increasing stability order of anions of oxoacids of chlorine is, $ClO^- < ClO_2^- < ClO_3^- < ClO_4^-$.

As the number of oxygen atoms in an ion increases there will be a greater dispersal of negative charge and thus greater will be the stability of ion formed. For different halogen having the same oxidation number, the thermal stability decreases with increase in atomic number i.e., it is in the order $HClO > HBrO > HIO$ and $ClO^- > BrO^- > IO^-$. However, in HXO_3 is most stable. The stability order being $HClO_3 < HBrO_3 < HIO_3$.

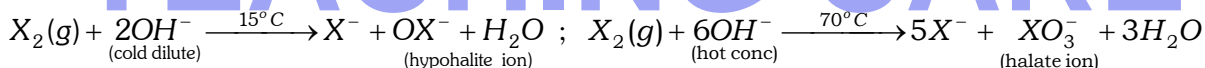
(iv) Perhalates are strong oxidizing agents, the oxidizing power is in the order, $BrO_4^- > IO_4^- > ClO_4^-$.

Thus BrO_4 is the strongest oxidizing agent (though its reaction is quite slow) and ClO_4^- is the weakest.

(v) The acidity of oxoacids of different halogens having the same oxidation number decreases with increase in the atomic size of the halogen i.e. $HClO_4 > HBrO_4 > HIO_4$.

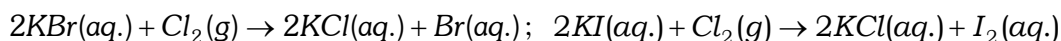
(7) **Reaction with alkalis** : $2F_2 + 2NaOH \xrightarrow{\text{(cold dilute)}} 2NaF + OF_2 + H_2O$; $2F_2 + 4NaOH \xrightarrow{\text{(hot conc.)}} 4NaF + O_2 + 2H_2O$

Halogen other than fluorine (Cl_2, Br_2, I_2) react with $NaOH$ as follows,



(8) **Bleaching action of halogen** : Cl_2 acts as bleaching agent, its bleaching action is permanent Cl_2 water can also act as ink remover.

(9) **Reaction with other halides**



(10) **Inter halogen compounds** : The compounds of one halogen with the other are called interhalogens or interhalogen compounds. The main reason for their formation is the large electronegativity and the size differences between the different halogens. Taking A as the less electronegative and B as the more electronegative halogen, they are divided into the following four types the less electronegative halogen (A) is always written first.

AB	AB ₃	AB ₅	AB ₇
ClF	ClF ₃ , BrF ₃	BrF ₅ , IF ₅	IF ₇
BrF, BrCl, ICl	IF ₃ , ICl ₃		
IBr, IF			

These interhalogen compounds are unstable and more reactive

(i) **General properties**

(a) Largest halogen always serves the central atom.

(b) The highest interhalogen compound i.e. IF_7 is obtained with iodine, the largest halogen attached to the smallest one

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(c) The bonds in interhalogen compounds are essentially covalent.

(d) Thermal stability decreases as the size difference decreases and increases as the polarity of the bond increases. Thus ClF is thermally more stable as compared to IBr .

(e) They ionize in solution or in the liquid state, $2ICl \rightleftharpoons I^+ + ICl_2^-$; $2ICl_3 \rightleftharpoons ICl_2^+ + ICl_4^-$

(f) Hydrolysis of interhalogen compounds always produces a halide ion derived from smaller halogen and oxyhalide derived from larger halogen, $ICl + H_2O \rightarrow Cl^- + OI^- + 2H^+$; $BrF_5 + 3H_2O \rightarrow 5F^- + BrO_3^- + 6H^+$

(g) They are strong oxidizing agents.

(h) Largest number of interhalogens are formed by fluorine due to its smaller size and higher electronegativity or oxidizing power.

(ii) **Structure** : Interhalogen compounds are,

(a) AB type i.e. ICl , IBr , IF etc, are linear

(b) AB_3 type i.e. IF_3 , ClF_3 , BrF_3 have distorted trigonal bipyramidal (dsp^3 -hybridization) structures of T-shape due to two lone pairs in equatorial positions ICl_3 is dimeric, I_2Cl_6 and has a planar structure.

(c) AB_5 types i.e. BrF_5 , IF_5 have distorted octahedral (d^2sp^3 -hybridization) shapes or square pyramidal due to a lone pair one of the axial positions.

(d) AB_7 type i.e. IF_7 , have pentagonal bipyramidal (d^3sp^3 -hybridization) structures.

(11) **Polyhalides** : $KI + I_2 \rightarrow KI_3 = K^+ + I_3^-$; $Cl_3^-, Br_3^-, I_3^-, ICl_2^-, IBr_2^-, ICl_4^-, BrF_4^-, I_5^-, IF_6^-$ and I_7^-

(12) **Pseudohalogen and pseudohalides**

Pseudohalogen	Pseudohalide
Cyanogen - $(CN)_2$	Cyanide - CN^-
Oxocyanogen - $(OCN)_2$	Cyanate - OCN^-
Thiocyanogen - $(SCN)_2$	Thiocyanate - SCN^-
Selenocyanogen - $(SeCN)_2$	Selenocyanate - $SeCN^-$

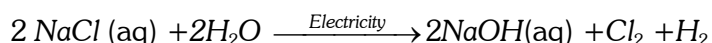
(13) **Freons** : Freon -11 is CCl_3F ; Freon -12 is CCl_2F_2 and it is marketed under the popular brand names such as '**Freon**' and '**Genetron**'; Freon -113 is CCl_2F . $CClF_2$; Freon -114 is $CClF_2$. $CClF_2$; Freon -115 is $CClF_2$. CF_3 . These cause ozone depletion.

Preparation of halogens

(1) **Preparation of fluorine** : F_2 is prepared by electrolysis of a solution of KHF_2 (1 Part) in HF (5 part) in a vessel (Modern method) made of $Ni - Cu$ alloy or $Ni - Cu - Fe$ alloy called the monel metal using carbon electrodes. During the electrolysis following reactions occur, $KHF_2 \rightleftharpoons KF + HF$; $KF \rightleftharpoons K^+ + F^-$.

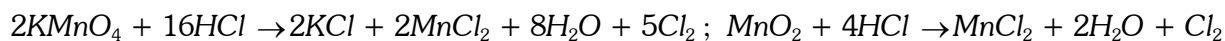
At cathode : $K^+ + e^- \rightarrow K$; $2K + 2HF \rightarrow 2KF + H_2 \uparrow$; At anode : $F^- \rightarrow F + e^-$; $F + F \rightarrow F_2$

(2) **Preparation of chlorine** : On the industrial scale, Cl_2 is prepared by the electrolysis of concentrated aqueous solution of $NaCl$. In this process, $NaOH$ and H_2 are by products.

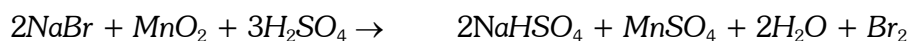


In the laboratory, Cl_2 can be prepared by adding conc HCl on $KMnO_4$ or MnO_2 .

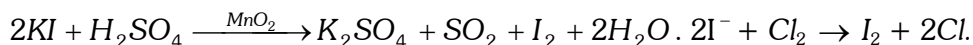
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(3) **Preparation of Bromine** : In laboratory it is prepared by heating NaBr with MnO₂ and Conc H₂SO₄.



(4) **Preparation of Iodine** (Lab method) : By heating a mixture of MnO₂, H₂SO₄ and an iodide



I₂ is commercially prepared from sea weeds.

Uses of Halogens

(1) **Uses of Fluorine** : (i) It is used as an oxidising agent and fluorinating agent. (ii) Fluorine and its compounds such as NF₃, OF₂ are used as rocket fuels. (iii) It is used in the manufacture of a plastic known as Teflon (CF₂-CF₂)_n which is resistant to the action of all acids, alkalies and even boiling aqua regia. (iv) It is used in the manufacture of fluorocarbons like freon which is used as an excellent refrigerant and in air conditioning. (v) It is used for the preparation of uranium hexafluoride, which is used for the separation of isotopes of U(235) and U(238).

(2) **Uses of Chlorine** : (i) Chlorine is used in sterilization of drinking water. (ii) Large quantities of chlorine are used industrially for the bleaching of cotton, paper, wood, textiles, etc. (iii) It is used in making insecticides like D.D.T., germicides, dyes, drugs, etc. (iv) It is used for preparing vinyl chloride which is a starting material for making the plastic PVC. (v) It is used in the manufacture of chlorinated organic solvents like CHCl₃, CCl₄, which are used for dry cleaning and degreasing machinery. (vi) It is used in the preparation of HCl, bleaching powder, chlorates, perchlorates, sodium hypochlorite which are important industrial compounds.

(3) **Uses of Bromine** : (i) Bromine is used in the preparation of ethylene bromide, which is mixed with tetraethyl lead (TEL) and added to the petrol as an anti-knocking agent. (ii) In the manufacture of AgBr used in photography. (iii) In the manufacture of dyes, drugs, etc. (iv) It is used in the manufacture of benzyl bromide which is an effective tear gas. (v) It is used as a laboratory reagent.

(4) **Uses of Iodine** : (i) Iodine is used as a laboratory reagent. (ii) It is used in making medicines and dyes. Tincture of iodine is an antiseptic. (iii) AgI is used in photographic emulsions. (iv) It is used in the preparation of iodized salt. Iodized salt is used to prevent the occurrence of common goiter.

Noble Gases.

Helium is the first member of group 18 or zero of the periodic table. It consists of six elements helium (He), Neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn). Zero group occupies the intermediate position between the elements of VIIA (17th) and IA (1st) groups. These are collectively called as inactive gases or inert gases. However, these are now called noble gases as some compounds of these gases have been obtained under certain specific conditions.

Electronic configuration

Elements	Electronic configuration (ns ² np ⁶)
₂ He	1s ²
₁₀ Ne	1s ² , 2s ² 2p ⁶
₁₈ Ar	1s ² , 2s ² 2p ⁶ , 3s ² 3p ⁶
₃₆ Kr	1s ² , 2s ² 2p ⁶ , 3s ² 3p ⁶ 3d ¹⁰ , 4s ² 4p ⁶

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$_{54}\text{Xe}$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10} 4f^{14}, 5s^2 5p^6$
$_{86}\text{Rn}$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10} 4f^{14}, 5s^2 5p^6 5d^{10}, 6s^2 6p^6$

(1) **Atomic radii** : The atomic radii of noble gases increases on moving down the group and their atomic radii correspond to the van der Waal's radii.

(2) **Boiling points** : The m.pt. and b.pt. increases from *He* to *Rn*, because of increase in magnitude of Vander Waal's forces.

(3) **Polarizability** : The polarizability increases down the group, $He < Ne < Ar < Kr < Xe$

(4) **Ionisation energy and electron affinity** : Noble gases have stable $ns^2 np^6$ fully filled electronic configuration, so these have no tendency to add or lose electron. Therefore, ionisation energy of noble gases is very high. On the other hand their electron affinity is zero.

(5) **Heat of vapourisation** : They possess very low values of heat of vapourisation, because of presence of very weak Vander Waal's forces of attraction between their monoatomic molecules. However the value of heat of vapourisation increases with atomic number down the group and this shows that there is an increasing polarizability of the larger electronic clouds of the elements with higher atomic number.

(6) **Solubility in water** : They are slightly soluble in water. Their solubility generally increases with the increase in atomic number down the group.

(7) **Adsorption by charcoal** : All of them except helium are adsorbed by coconut charcoal at low temperature. The extent of adsorption increases down the group.

(8) **Characteristic spectra** : All of them give characteristic spectra, by which they can be identified.

(9) **Liquification of gases** : It is difficult to liquify noble gases as their atoms are held by weak Vander Waal's forces. Ease of liquification increases down the group from *He* to *Rn*. Helium has the lowest boiling point (4.18 K) of any known substance. The ease of liquification increases down the group due to increase in intermolecular forces.

The elements helium (*He*), neon (*Ne*), argon (*Ar*), krypton (*Kr*), xenon (*Xe*) and radon (*Rn*), constitute zero group of the periodic table. These are gases at ordinary temperature and do not have chemical reactivity and therefore, these are called inert gases.

(10) **Occurrence** : Due to the inert nature of noble gases, they always occur in the free state. Except radon, all these gases are present in atmosphere in the atomic state.

Element	<i>He</i>	<i>Ne</i>	<i>Ar</i>	<i>Kr</i>	<i>Xe</i>
Abundance (Volume %)	5.2×10^{-4}	1.8×10^{-3}	9.3×10^{-1}	1.4×10^{-3}	8.7×10^{-6}

He is also present in natural gas to the extent of 2 to 7%.

(11) Isolation

(i) **Helium** : It is commercially obtained from natural gas. The natural gas contains hydrocarbons (methane etc.), CO_2 , H_2S and *He* as the main constituents.

The natural gas is compressed to about 100 atm and cooled to 73K. *He* remains unliquefied while other gases get liquefied. About 99% pure *He* is prepared by this method.

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(ii) **Argon, Neon, Krypton and Xenon** : These gases are prepared by the fractionation distillation of liquid air. Fractional distillation of air gives O_2 , N_2 and mixture of noble gases. The individual gases may be obtained by adsorption of air on coconut charcoal. The charcoal adsorbs different gases at different temperatures and can be collected.

(iii) **Radon** : It can be obtained by radio active disintegration of radium (226), ${}_{88}\text{Ra}^{226} \rightarrow {}_{86}\text{Rn}^{222} + {}_2\alpha^4$.

(12) Compounds of Xenon

In 1962, N. Bartlett noticed that PtF_6 is a powerful oxidizing agent which combines with molecular oxygen to form ionic compound, dioxygenyl hexafluoro platinate (v) $O_2^+[\text{PtF}_6]^-$, $O_{2(g)} + \text{PtF}_{6(g)} \rightarrow O_2^+[\text{PtF}_6]^-$, This indicates that PtF_6 has oxidized O_2 to O_2^+ . Now, oxygen and xenon have some similarities,

(i) The first ionization energy of Xe gas (1170kJ mol^{-1}) is fairly close to that of oxygen (1166kJ mol^{-1}).

(ii) The molecular diameter of oxygen and atomic radius of Xe are similar (4\AA)

On this assumption, Bartlett reacted Xenon and PtF_6 in gas phase and a orange yellow solid of the composition Xe PtF_6 was obtained, $\text{Xe}_{(g)} + \text{PtF}_{6(g)} \rightarrow \text{Xe}^+[\text{PtF}_6]_{(s)}^-$.
Orange yellow

Some important stable compounds of Xe are,

+2	+4	+6
XeF_2	XeF_4 , XeOF_2	XeF_6 , XeOF_4 , XeO_3

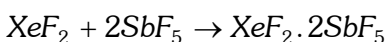
Fluorides : Xenon forms three compounds with fluorine. These are : Xenon difluoride (XeF_2), Xenon tetrafluoride (XeF_4) and Xenon hexafluoride (XeF_6).

(i) **Xenon difluoride** (XeF_2) is formed when a mixture of Xenon and fluorine in the ratio 1 : 3 by volume is passed through a nickel tube at 673 K, $\text{Xe} + \text{F}_2 \xrightarrow{\text{Ni, 673K}} \text{XeF}_2$

Structure : XeF_2 has trigonal bipyramid geometry due to sp^3d -hybridization of Xe. Three equatorial positions are occupied by lone pairs of electrons giving a linear shape to the molecule.

Properties : XeF_2 is a colourless crystalline solid, reacts with H_2 to give Xe and HF. It is hydrolysed completely by water, $2\text{XeF}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Xe} + \text{O}_2 + 4\text{HF}$.

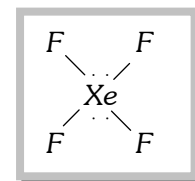
It also forms addition compounds with reactive pentafluorides like SbF_5 , TaF_5 etc.



It is a mild fluorinating agent and hence reacts with benzene to give fluorobenzene.

(ii) **Xenon tetrafluoride** (XeF_4) is prepared by heating a mixture of xenon and fluorine in the ratio 1 : 5 in a nickel vessel at 673 K and then suddenly cooling it in acetone. XeF_4 is also formed when an electric discharge is passed through a mixture of xenon and excess of fluorine, $\text{Xe} + 2\text{F}_2 \xrightarrow{\text{Ni, 673K}} \text{XeF}_4$

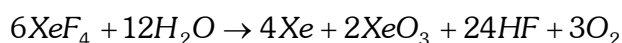
Structure : XeF_4 has square planar shape due to sp^3d^2 hybridization of Xe giving octahedral geometry with two trans positions occupied by lone pairs of electrons.



Properties : XeF_4 is a colourless, crystalline solid, soluble in anhydrous HF, reacts with

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H_2 to form Xe and HF and reacts with water to give highly explosive solid, XeO_3 . (complete hydrolysis),

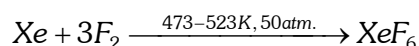


Partial hydrolysis yields $XeOF_2$, $XeF_4 + H_2O \xrightarrow{193K} XeOF_2 + 2HF$

It also forms addition compounds with SbF_5 , $XeF_4 + SbF_5 \rightarrow [XeF_3]^+[SbF_6]^-$.

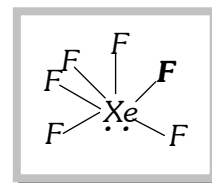
It also acts as a strong fluorinating agent.

(iii) **Xenon hexafluoride** (XeF_6) is prepared by heating a mixture of xenon and fluorine in the ratio 1 : 20 at 473—523 K under a pressure of 50 atmospheres.

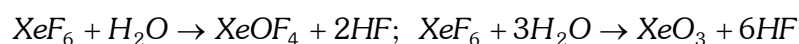


Structure : XeF_6 has pentagonal bipyramid geometry due to sp^3d^3 hybridization. One trans position is occupied by a lone pair giving a distorted octahedral shape.

Properties : It is colourless, crystalline solid, highly soluble in anhydrous HF giving solution which is a good conductor of electricity, $HF + XeF_6 \rightarrow XeF_5^+ + HF_2^-$.



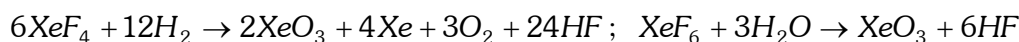
It is the most powerful fluorinating agent and reacts with H_2 to give Xe and HF . Partial hydrolysis of XeF_6 yields $XeOF_4$ an complete hydrolysis yields xenon trioxide, XeO_3 .



It forms addition compounds with alkali metal fluorides (except LiF) of the formula $XeF_6 \cdot MF$ where M represents the alkali metal.

Oxides : Xenon forms two oxides such as xenon trioxide (XeO_3) and xenon tetraoxide (XeO_4).

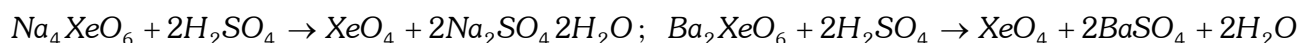
(i) **Xenon trioxide** (XeO_3) is prepared by complete hydrolysis of XeF_4 and XeF_6



Structure : XeO_3 has tetrahedral geometry due to sp^3 hybridization of Xe . One of the hybrid orbitals contains a lone pair of electrons giving a trigonal pyramidal shape. The molecule has three $Xe = O$ double bonds containing $p\pi - d\pi$ overlapping.

Properties : It is a colourless solid, highly explosive and powerful oxidizing agent.

(ii) **Xenon tetraoxide** (XeO_4) is prepared by the action of conc. H_2SO_4 on sodium or barium xenate (Na_4XeO_6 ; Ba_2XeO_6) at room temperature,



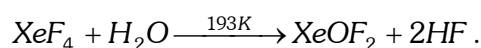
XeO_4 is purified by vacuum sublimation at 195 K.

Structure : XeO_4 has tetrahedral structure due to sp^3 hybridization of Xe . There are four $Xe-O$ double bonds containing $p\pi - d\pi$ overlapping.

Properties : It is quite unstable gas and decomposes to xenon and oxygen, $XeO_4 \rightarrow Xe + 2O_2$.

Oxyfluorides : Xenon forms three types of oxy fluorides such as xenon oxydifluoride ($XeOF_2$), xenon oxytetrafluoride $XeOF_4$ and xenon dioxydifluoride (XeO_2F_2).

(i) **Xenon oxydifluoride** ($XeOF_2$) is formed by partial hydrolysis of XeF_4 at 193 K,



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Structure : XeOF_2 has trigonal bipyramid geometry due to sp^3d -hybridization of Xe. Two equatorial positions are occupied by lone pairs of electrons giving a T-shape to the molecule. There is one Xe–O double bond containing $p\pi - d\pi$ overlapping.

(ii) **Xenon oxytetrafluoride** (XeOF_4) is prepared by partial hydrolysis of XeF_6 ; $\text{XeF}_6 + \text{H}_2\text{O} \rightarrow \text{XeOF}_4 + 2\text{HF}$.

It can also be prepared by the reaction of SiO_2 with XeF_6 , $2\text{XeF}_6 + \text{SiO}_2 \rightarrow 2\text{XeOF}_4 + \text{SiF}_4$.

Structure : XeOF_4 has octahedral geometry due to sp^3d^2 hybridization of Xe. One trans position is occupied by a lone pair giving pyramid shape to the molecule. There is one Xe–O double bond containing $p\pi - d\pi$ overlapping.

Properties : It is a colourless volatile liquid which melts at 227 K. It reacts with water to give XeO_2F_2 and XeO_3 , $\text{XeOF}_4 + \text{H}_2\text{O} \rightarrow \text{XeO}_2 + 2\text{HF}$, $\text{XeO}_2\text{F}_2 + \text{H}_2\text{O} \rightarrow \text{XeO}_3 + 2\text{HF}$.

It is reduced by H_2 to Xe, $\text{XeOF}_4 + 3\text{H}_2 \rightarrow \text{Xe} + \text{H}_2\text{O} + 4\text{HF}$

(iii) **Xenon dioxydifluoride** (XeO_2F_2) is formed by partial hydrolysis of XeOF_4 or XeF_6

$\text{XeOF}_4 + \text{H}_2\text{O} \rightarrow \text{XeO}_2\text{F}_2 + 2\text{HF}$; $\text{XeF}_6 + 2\text{H}_2\text{O} \rightarrow \text{XeO}_2\text{F}_2 + 4\text{HF}$

It can also be prepared by mixing XeO_3 and XeOF_4 at low temperature (195K). The product is purified by fractional distillation, $\text{XeO}_3 + \text{XeOF}_4 \xrightarrow{195\text{K}} 2\text{XeO}_2\text{F}_2$

Structure : XeO_2F_2 has trigonal bipyramid geometry due to sp^3d -hybridization of Xe. One equatorial position is occupied by a lone pair of electrons giving a see-saw structure (shape) to the molecule. There are two Xe–O double bonds containing $p\pi - d\pi$ overlapping.

Properties : It is a colourless solid which melts at 303 K. It is easily hydrolysed to give XeO_3

$\text{XeO}_2\text{F}_2 + \text{H}_2\text{O} \rightarrow \text{XeO}_3 + 2\text{HF}$

(13) Uses of noble gases

(i) He is used for filling of balloons and air ships because of its non-inflammability and high power (which is 92.6% to that of hydrogen).

(ii) Oxygen-helium (1 : 4) mixture is used for treatment of asthma and for artificial respiration in deep sea diving because unlike nitrogen, helium is not soluble in blood even under high pressure.

(iii) Helium is also used for creating inert atmosphere in chemical reactions.

(iv) Liquid helium is used as a cryogenic fluid to produce and maintain extremely low temperatures for carrying out researches and as a coolant in atomic reactors and super conducting magnets.

(v) It is also used in low temperature gas thermometry and as a shield gas for arc welding.

(vi) Argon is used for creating inert atmosphere in chemical reactions, welding and metallurgical operations and for filling in incandescent and fluorescent lamps. It is also used in filling Geiger-Counter tubes and thermionic tubes.

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(vii) Krypton and xenon are also used in gas filled lamps. A mixture of krypton and xenon is also used in some flash tubes for high speed photography.

(viii) Radon is used in radioactive research and therapeutics and in the non-surgical treatment of cancer and other malignant growths.

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