

GROUP-15 ELEMENTS NITROGEN FAMILY

The elements of this group are : Nitrogen (N), Phosphorus (P), Arsenic (As), Antimony (Sb), Bismuth (Bi) and Moscovium (Mc).

Nitrogen and phosphorus are non-metals Arsenic and Antimony are metalloids and Bismuth and Moscovium are metals.

Occurance :

Nitrogen:

Atmosphere → 78% by volume of the atmosphere.

Earth crust → It occurs as

1. Sodium nitrate (NaNO_3) → Chile saltpetre.
2. Potassium nitrate (KNO_3) → Indian saltpetre
3. It is also found in proteins in plants and animals.

Phosphorus

It mainly occurs in the earth crust as **phosphate rock**. It consist mainly of

(1) **Hydroxy apatite** → $\text{Ca}_9 (\text{PO}_4)_6 \text{Ca}(\text{OH})_2$

(2) **Fluorapatite** → $\text{Ca}_9 (\text{PO}_4)_6 \text{Ca}(\text{F})_2$

(3) Phosphorus is also an essential constituent of animal and plant matter. It is present in bones and also in living cells. Phosphoproteins are present in milk and eggs.

Arsenic , antimony and Bismuth: Present as sulphide minerals

Moscovium [Mc- At. No.=115 , Mass No= 289] → It is a synthetic radioactive element. Electronic configuration $[\text{Rn}]5f^{14}6d^{10}7s^27p^3$

Physical Properties:

Electronic configuration : The general electronic configuration is – $ns^2 np^3$

Atomic radii:

Atomic radii of these elements increase in moving down the group from N → Bi

Ionisation energy: The ionization energy decreases on moving down from N → Bi due to gradual increase in atomic size.

The 15th group elements have high values of ionization energy due to the extra stability of half filled p-orbitals and smaller size.

Electronegativity: Electronegativity of these elements decreases from N→ Bi due to increase in atomic size.

Melting and boiling points:

The **boiling points** of these elements increase from top to bottom. But the **melting point** first increases from N to As This is due to increase in magnitude of inter-particle force due to increase in atomic size. Melting point then decrease from As→Bi.. This is because of decrease in the magnitude of inter-metallic bond strength.

Oxidation state

1. The commonly observed oxidation states these elements are –3, +3 and +5. The tendency to show -3 oxidation state decreases down the group.
2. Antimony and bismuth mainly display an oxidation state of +3 or +5.
3. The stability of +3 oxidation state increases while that of +5 oxidation state decreases on moving down the group. This is due to **inert pair effect**
 1. N also shows +1, +2 and +4 oxidation states when it reacts with oxygen.
 2. P also shows +1 and +4 oxidation states in some oxoacids.

[All oxidation states of N from +1 to +4 disproportionate in acid solution

Eg $3\text{HNO}_2 \rightarrow \text{HNO}_3 + \text{H}_2\text{O} + 2\text{NO}$

P also disproportionate in all intermediate oxidation states]

[Inert pair effect: Within a group, the higher oxidation state becomes progressively less stable as the atomic number increases. This is because of the fact that the *s*-electrons of the valence shell do not participate in bond formation. This effect is called inert pair effect. On moving down the group, the *s*-electrons of the valence shell become more penetrating. That is they are held more tightly and hence, show reluctance for participation in bonding.]

Catenation

Elements of group 15 also exhibit catenation, but less extend than group 14.

Catenation tendency of N is less than that of P. This is because single N-N bond is weaker than the single P-P bond because of high inter electronic repulsion of the non-bonding electrons in N due to small bond length.

Allotropy: All elements of this group except nitrogen and bismuth show allotropy.

Phosphorus exists as : **White, red and black phosphorus**

Arsenic exists as : **Yellow and grey**

Antimony exists as : **Yellow and grey**

Tendency to form $p\pi$ - $p\pi$ multiple bonds

Nitrogen has the tendency to form $p\pi$ - $p\pi$ multiple bonds due to its small size. Nitrogen therefore exists as a diatomic molecule, N_2 . In N_2 molecule the two nitrogen atoms are linked by triple bond ($N \equiv N$) and posses high bond strength (941.4 KJ/mol). Thus N_2 molecule is chemically less reactive.

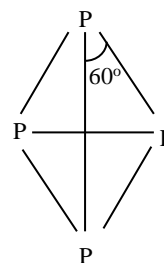
On the other hand, P, As and Sb form tetrahedral molecules in their elemental state with formula M_4 .

Eg: P_4

Here each phosphorus atom is linked to three other atoms. This is because phosphorus and other heavier atoms do not form $p\pi$ - $p\pi$ multiple bonds due to their large size.

[But phosphorus can form $d\pi$ - $p\pi$ bond. Eg. $R_3P=O$ or $R_3P=CH_2$.

P and As can also form $d\pi$ - $d\pi$ bond. Therefore their compounds eg $P(C_2H_5)_3$ can link to transition metals as ligands.]



Q. Nitrogen do not form penta and hexa co-ordinated derivatives. [Or Nitrogen shows a maximum covalency of 4] Why?

Even though nitrogen contains five valence electrons, the maximum number of bonds formed by nitrogen is four. (eg: NH_4^+). This is due to the absence of *d*-orbital in nitrogen. But other members can form penta or hexa co-ordinated compounds due to the presence of *d*-orbitals in their valence shell. (Eg. PCl_5 , AsF_5 , PF_6^- etc)

Chemical Characteristics

Hydrides

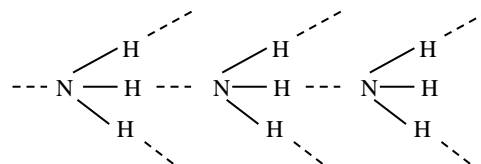
The elements of group 15 form hydrides of general formula MH_3 . All these are covalent in nature.

| | | | | |
|---------|-----------|---------|---------|------------|
| NH_3 | PH_3 | AsH_3 | SbH_3 | BiH_3 |
| Ammonia | Phosphine | Arsine | Stibine | Bismuthine |

1. The **stability** of these hydrides decreases in the order. $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$. This is because the strength of M-H bond decreases down the group due to increase in the size of central atom.

2. **The reducing power** decreases in the order. $BiH_3 > SbH_3 > AsH_3 > PH_3 > NH_3$. The least stable hydride (BiH_3) acts as the strongest reducing agent

3. **Boiling points** NH_3 molecules are associated by intermolecular H-bonds. As a result, its boiling point is very high. But in PH_3 there is no inter-molecular hydrogen bonding. So its boiling point is low.



But from moving from PH_3 to BiH_3 , boiling point increases. This is due to increase in the magnitude of *van der Waals forces* due to increase in molecular size.



4. Due to the presence of lone pair electrons in the central atom, they act as good **Lewis bases**. The basic character decreases down the group. $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$

This is because in NH_3 , due to its small size the lone pair electrons are distributed in a small region and electron density is high. But as the size increases the electron density decreases. Therefore the electron donor capacity decreases down the group.

5. **Structure:** These hydrides have a pyramidal structure with the central atom under sp^3 hybridization. The bond angle decreases down the group

| | | | | |
|------------|---------------|---------------|----------------|----------------|
| | NH_3 | PH_3 | AsH_3 | SbH_3 |
| Bond angle | 107.8° | 93.6° | 91.8° | 91.3° |

In NH_3 , the electron pairs are present in the second orbit. This causes greater repulsive interaction between the electron pairs around nitrogen. But in PH_3 , the electron pairs are present in the large 3^{rd} orbit. This reduces the repulsive interaction between the electron pairs there by decreasing the bond angle.

Halides

All the elements of group 15 form two series of halides:

- (i) Trihalides of the type MX_3 Eg: NF_3 , PCl_3 ,
- (ii) Pentahalides of the type MX_5 Eg: PCl_5 , PBr_5 -----

- The trihalides are mainly covalent molecules except BiF_3 . [**BiF_3 is ionic.**]. The ionic character increases down the group.
- All trihalides except that of N are stable. In case of nitrogen only NF_3 is stable
- These trihalides have a pyramidal structure [sp^3 hybridised].
- Except nitrogen other elements of this group form **pentahalides**. **Nitrogen cannot form pentahalides**. This is because it cannot expand its covalency beyond 4 due to the non-availability of d-orbital in the valence shell.
- The penta halides are more covalent than trihalides**. This is because higher the oxidation state, more will be the polarizing power, which in turn increases the covalent character.

Oxides

- The elements of group 15 form two types of oxides: **E_2O_3** and **E_2O_5** .
- But N forms a number of oxides with oxidation states from +1 to +5 { N_2O , NO , NO_2 , N_2O_3 , N_2O_5 }
- The oxide in the higher oxidation state is more acidic than lower oxidation state
- The acidic character decreases down the group.
- All the oxides of nitrogen (except NO and N_2O) and phosphorus are strongly acidic. Oxides of arsenic are weakly acidic, oxides of antimony are amphoteric and those of bismuth are weakly basic.

| | | | |
|------------------------|-------------------------|-------------------------|-------------------------|
| P_2O_3 | As_2O_3 | Sb_2O_3 | Bi_2O_3 |
| Acidic | Acidic | Amphoteric | Basic |

- The oxides of P, As and Sb forms cage like structure and exist as dimers [Eg P_4O_{10}] This is due to the reason that they cannot form $\text{p}\pi\text{-p}\pi$ multiple bonding.

Reaction with metals

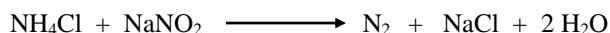
These elements combine with metals to form binary compounds with -3 oxidation state.

Eg. Ca_3N_2 (Calcium nitride), Ca_3P_2 (Calcium phosphide), Zn_3Sb_2 (Zinc antimonide)
 Mg_3Bi_2 (Magnesium bismuthide)

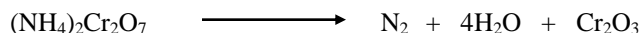
NITROGEN

Preparation

- N_2 is prepared in the laboratory by heating a mixture of ammonium chloride and sodium nitrite.

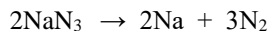
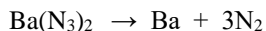


- It can also be obtained by heating ammonium dichromate.



This reaction is violent and accompanied by flashes of light. Therefore this reaction forms the basis of **chemical volcano**.

- (3) Pure nitrogen can be obtained by thermal decomposition of sodium or barium azide.



Manufacture

By liquifaction and fractional distillation of air. Liquid nitrogen distills out first leaving behind liquid oxygen

Properties

It is a colourless gas. It is slightly soluble in water. Its boiling point is 78K. It is neither combustible nor a supporter of life.

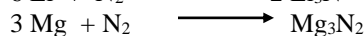
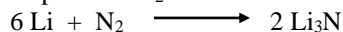
It exists in two isotopes- ^{14}N and ^{15}N

Chemical Properties

N_2 is chemically unreactive at ordinary temperature. The inert nature is due to the high bond energy of $\text{N}\equiv\text{N}$ (946 KJ/mol). But at high temperature it gives some reactions.

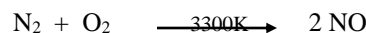
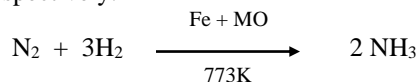
(i) With reactive metals

At high temperature N_2 combines with some metal to form the respective nitrides.



(2) With non- metals

Non-metals like H_2 and O_2 react with nitrogen at high temperature to produce ammonia and nitric oxide respectively.

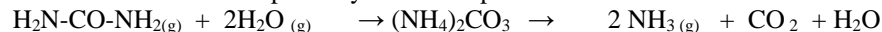


Uses of Nitrogen

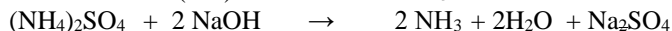
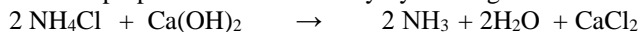
- (1) In the manufacture of NH_3 , nitric acid, calcium cyanamide etc.
- (2) To provide inert atmosphere in industry and in laboratory.
- (3) Liquid nitrogen is used as a refrigerant to preserve biological materials and freezing food materials and in cryosurgery.

AMMONIA

1. Ammonia is formed in atmosphere by the decomposition of urea.

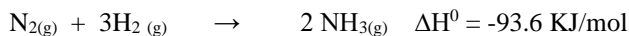


2. Ammonia is prepared in the laboratory by treating ammonium salts with caustic soda or lime



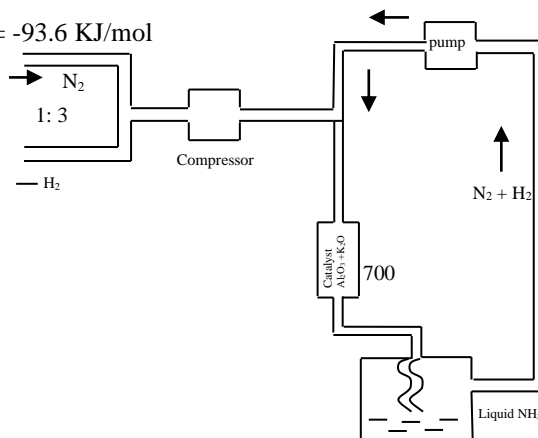
Manufacture

Ammonia is manufactured by Haber process. It is represented by the equation



According to *Le Chatelier's* principle the favourable conditions are high pressure and low temperature. The optimum conditions are a pressure of about 200 atm, a temperature of 700K and the use of catalyst such as iron oxide with small amounts of K_2O and Al_2O_3 as promoters. Earlier iron was used as catalyst with molybdenum as promoter.

A mixture of pure nitrogen and hydrogen in the ratio 1:3 by volume is compressed to 200 atm and then passed over the catalyst at 700K. Ammonia formed is



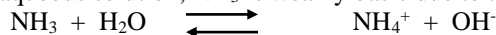
condensed to liquid ammonia. The unreacted nitrogen and H₂ are again used.

Properties

Ammonia is a colourless gas with a pungent odour. In liquid and solid state its molecules are associated by hydrogen bonding. Therefore it has high melting and boiling points.

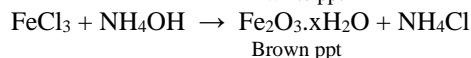
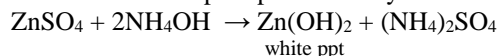
It has a **pyramidal** structure

- (1) In aqueous solution, NH₃ is weakly basic due to the production of OH⁻ ions.

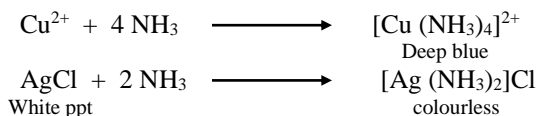


It forms ammonium salts like NH₄Cl, (NH₄)₂SO₄ etc with acids.

As a weak base it precipitates the hydroxides of many metals from their salt solutions.



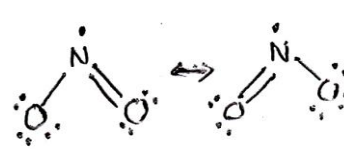
- (2) Due to the presence of a lone pair of electron on nitrogen, NH₃ acts as a Lewis base. It forms co-ordinate compounds with many metal ions.

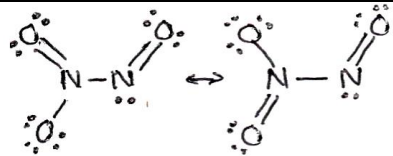
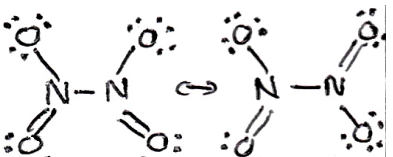
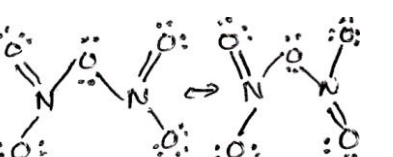


Uses

- (1) NH₃ is used to manufacture many fertilizers (eg: Urea, ammonium nitrate etc)
- (2) In the manufacture of some inorganic nitrogen compounds such as nitric acid.
- (3) Liquid ammonia is used as a refrigerant.

Oxides of Nitrogen

| | O. N | Structure | Preparation | |
|---|---------|--|--|--|
| <u>N₂O</u> Nitrous Oxide, [Dinitrogen oxide] <i>(laughing gas)</i> Nitrogen(I)oxide | +1 | $\begin{array}{c} :\text{N} \equiv \text{N} - \ddot{\text{O}}: \leftrightarrow \\ :\ddot{\text{N}} = \text{N} = \ddot{\text{O}}: \end{array}$ (Linear) | NH ₄ NO ₃ → N ₂ O + 2H ₂ O | It is colourless, neutral. It is used as an anaesthetic |
| <u>NO</u> Nitric oxide, [Nitrogen monoxide] Nitrogen(II)oxide | +2 | $:\ddot{\text{N}} = \ddot{\text{O}}: \leftrightarrow :\text{N} = \ddot{\text{O}}:$ | 2NaNO ₂ + 2FeSO ₄ + 3H ₂ SO ₄ → Fe ₂ (SO ₄) ₃ + 2NaHSO ₄ + 2H ₂ O + 2NO. | It is a colourless, neutral gas. It is paramagnetic. It is used to prepare nitric acid |
| <u>NO₂</u> Nitrogen dioxide Nitrogen(IV)oxide | +4 |  Angular | 2 Pb(NO ₃) ₂ → 2 PbO + 4 NO ₂ + O ₂ | Brown gas, Acidic |

| | | | | |
|--|----|---|---|-------------------------------------|
| <u>N₂O₃</u> Dinitrogen trioxide Nitrogen(III)oxide | +3 |  Planar | $2\text{NO} + \text{N}_2\text{O}_4 \xrightarrow{250\text{K}} 2\text{N}_2\text{O}_3$ | Blue solid , Acidic |
| <u>N₂O₄</u> Dinitrogen tetroxide Nitrogen(IV)oxide | +4 |  Planar | $2\text{NO}_2 \xrightarrow{\text{Cool}} \text{N}_2\text{O}_4$ | Colourless solid/ liquid, Acidic |
| <u>N₂O₅</u> Dinitrogen pentoxide Nitrogen(V)oxide | +5 |  Planar | $4\text{HNO}_3 + \text{P}_4\text{O}_{10} \rightarrow 2\text{N}_2\text{O}_5 + 4\text{HPO}_3$ | Colourless solid, Acidic |

Oxoacids of nitrogen

Nitrogen forms many oxoacids –

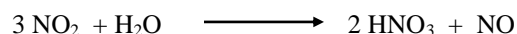
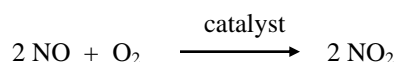
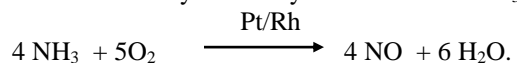
1. Hyponitrous acid (H₂N₂O₂) 2. Nitrous acid. (HNO₂) 3. Nitric acid (HNO₃)

HNO₃ (Nitric acid)

Nitric acid is the most important oxoacid formed by nitrogen

Manufacture [Ostwald's Process]

HNO₃ is manufactured by the catalytic oxidation of NH₃. The sequence of reaction are

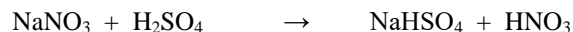


Ammonia is mixed with air (1:10 ratio) and passed through a metal gauze made of 90% platinum and 10% rhodium at a temperature of 500K and a pressure of 9 bar. The nitric oxide (NO) formed is cooled below 420K. The NO react with unreacted O₂ to give NO₂. Then NO₂ is dissolved in water to give nitric acid.

The nitric acid thus obtained can be concentrated up to 68% by distillation and concentrated up to 98% by dehydration with concentrated H₂SO₄.

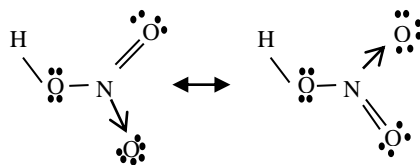
Laboratory Preparation of HNO₃

It is prepared in the laboratory by heating NaNO₃ (or KNO₃) with con.H₂SO₄.



Structure

In gaseous state HNO₃ exists as a planar molecule with the following structure.



Properties

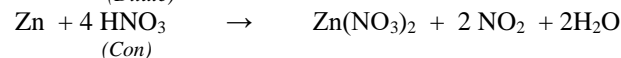
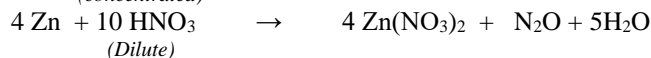
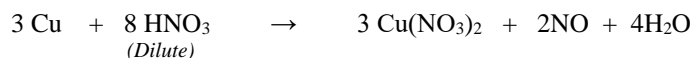
Physical properties

Pure nitric acid is a colourless liquid. The impure nitric acid is generally yellow due to the presence of NO_2 . HNO_3 containing dissolved NO_2 is called fuming nitric acid. The specific gravity of pure HNO_3 at 298 K is 1.504 and its boiling point is 359 K.

Chemical properties

(1) Action on metals

Con. HNO_3 is a strong oxidizing agent and attacks most of the metals except gold and platinum. The HNO_3 is reduced to different compounds depending upon the concentration of the acid and nature of the material undergoing oxidation. The principal products are nitric oxide (NO) when dilute acid is used, and NO_2 , when concentrated acid is used.



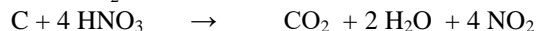
(2) With non-metals

Con. HNO_3 also oxidizes many non-metals and their compounds.

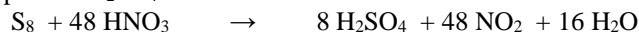
(i) Iodine to iodic acid



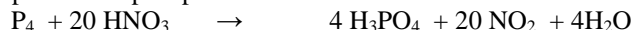
(ii) Carbon to CO_2



(iii) Sulphur to H_2SO_4



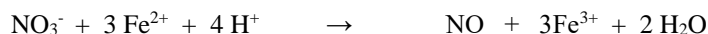
(iv) Phosphorous to phosphoric acid



Brown ring test for nitrates.

Brown ring test for nitrates depend on the ability of Fe^{2+} to reduce nitrates to nitric oxide. Nitric oxide (NO) reacts with excess Fe^{2+} to form a brown coloured complex $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^{2+}$

This test is usually carried out by adding dilute ferrous sulphate solution to an aqueous solution containing nitrate ion. Then con sulphuric acid is carefully added along the sides of the test tube. A brown ring at the interface of two liquid layers indicate the presence of nitrate ion.



Uses of HNO_3

1. Used in the manufacture of ammonium nitrate for fertilizers and other nitrates in explosives and pyrotechnics.
2. Used in the preparation of nitroglycerine, trinitrotoluene etc.
3. Also used in pickling of stainless steel and etching of metals.
4. As an oxidizer in rocket fuels.

Phosphorus

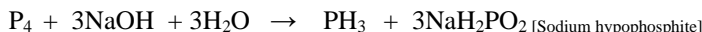
Allotropy of Phosphorus :

There are three allotropic forms of phosphorus

- (1) **White phosphorus** (2) **Red phosphorus** (3) **Black phosphorus**

White phosphorus The most common allotrope of phosphorus is white phosphorus

- (1) It is a translucent white waxy solid.
- (2) It is highly toxic
- (3) It is formed by the condensation from the gaseous or liquid state
- (4) It is insoluble in water but soluble in CS₂ and benzene
- (5) White phosphorous is less stable and highly reactive than other solid phases under normal conditions. This is because of the angular strain in the P₄ molecule where the angles are only 60°. It spontaneously ignites in air giving dense white fumes of P₄O₁₀. Hence it is stored under water
(P₄ + 5O₂ → P₄O₁₀)
- (6) It glows in dark. This phenomenon is known as **Chemiluminescence**.
- (7) It consists of discrete P₄ molecules. The four P atom occupy the corner of a regular tetrahedron. Each phosphorous atom is covalently linked to 3 other phosphorous atom .
- (8) It dissolves in boiling NaOH giving PH₃.

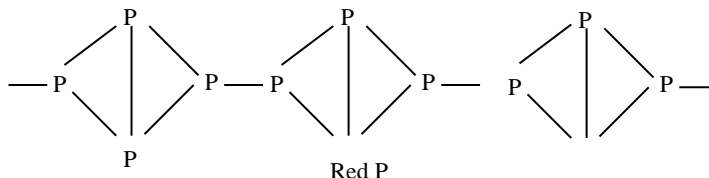
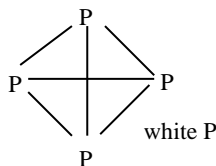


Red Phosphorous :

- (1) Red phosphorous is obtained by heating white phosphorous at 573 K in an inert atmosphere for several days. It is more stable and less reactive
- (2) It posses iron grey lustre.
- (3) It does not glow in dark.
- (4) It is insoluble in water as well as in CS₂.
- (5) It has greater density and higher melting point than white phosphorus.
- (6) It is amorphous and has a polymeric structure. The P₄ units are linked to one another to form a linear chain .
- (7) It is non toxic and odourless

Black Phosphorous

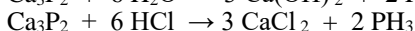
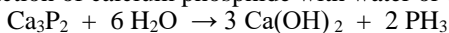
- (1) Black phosphorous is the most stable form of phosphorus
- (2) It has two forms- **α-black phosphorous** and **β-black phosphorous**.
- (3) **α-black phosphorous** obtained by heating red P in a sealed tube at 803K. It can be sublimed in air. It has opaque, monoclinic or rhombohedral crystals. It does not oxidize in air.
- (4) **β-black phosphorous** is obtained by heating white phosphorus at 473 K under high pressure. It consists of an extended layer structure in which each P is bound to 3 neighbors by single bonds. It does not burn in air up to 673K.



Phosphine

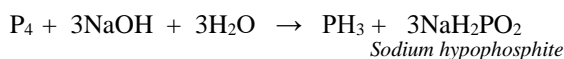
Preparation:

Reaction of calcium phosphide with water or dilute HCl

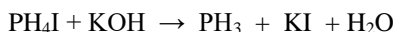


Lab preparation

By heating white phosphorus with con.NaOH in an inert atmosphere of CO₂.



It is purified by absorption in HI to form phosphonium iodide (PH₄I) which on treatment with KOH gives pure phosphine.



Properties

1. It is a colourless gas with rotten fish smell.
2. It is highly poisonous.
3. It has a pyramidal structure. P is in sp³ hybridisation. Bond angle is 93°
4. It explodes in contact with traces of oxidizing agents like HNO₃, Cl₂ and Br₂ vapours
5. The solution of phosphine in water decomposes in presence of light giving red P and H₂.
6. Phosphine gets absorbed in copper sulphate or mercuric chloride solution giving corresponding phosphides

$$3 \text{CuSO}_4 + 2 \text{PH}_3 \rightarrow \text{Cu}_3\text{P}_2 + 3 \text{H}_2\text{SO}_4$$

$$3 \text{HgCl}_2 + 2 \text{PH}_3 \rightarrow \text{Hg}_3\text{P}_2 + 6 \text{HCl}$$
7. **Phosphine is weakly basic and like ammonia**, gives phosphonium compounds with acids. This is due to the presence of lone pair electron in P and it acts as Lewis base.

$$\text{PH}_3 + \text{HI} \rightarrow \text{PH}_4\text{I}$$

Uses

The spontaneous combustion of phosphine is used in **Holme's signals**. Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea. Then the gas evolved burns and serves as a signal. It is also used in **smoke screens**.

Phosphorus Halides

Phosphorus forms two types of halides → Trihalides (PX₃) and Pentahalides (PX₅)

Phosphorus Trichloride [PCl₃]

Preparation

- (1) It is obtained by passing dry chlorine over heated white phosphorus.

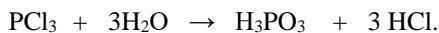
$$\text{P}_4 + 6 \text{Cl}_2 \rightarrow 4 \text{PCl}_3$$
- (2) It is also obtained by the action of thionyl chloride with white phosphorus.

$$\text{P}_4 + 8 \text{SOCl}_2 \rightarrow 4 \text{PCl}_3 + 4 \text{SO}_2 + 2 \text{S}_2\text{Cl}_2$$

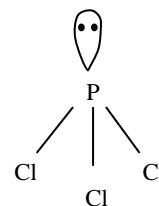
Properties

PCl₃ is a colourless oily liquid. It has a pyramidal structure. P atom is sp³ hybridised

1. PCl₃ is a colourless liquid with a boiling point of 349 K. It is easily hydrolysed by water. Therefore it fumes in moist air because of its reaction with water producing HCl.



All trihalides except NX₃ can be hydrolyzed by water. But NX₃ is not hydrolysed.. This is due to the non-availability of vacant d-orbitals in nitrogen.



2. PCl₃ reacts with organic compounds containing -OH group such as acids and alcohols.

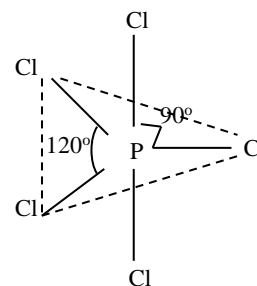
$$3 \text{CH}_3\text{-CH}_2\text{-OH} + \text{PCl}_3 \rightarrow 3 \text{CH}_3\text{-CH}_2\text{-Cl} + \text{H}_3\text{PO}_3$$

$$3 \text{CH}_3\text{-COOH} + \text{PCl}_3 \rightarrow 3 \text{CH}_3\text{-CO-Cl} + \text{H}_3\text{PO}_3$$

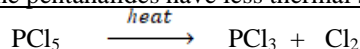
Phosphorus pentachloride [PCl₅]

The most important pentahalide of this group is **PCl₅**. It is an industrial intermediate for various phosphorus compounds.

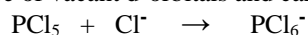
In PCl₅, phosphorus atom is under sp³d hybridisation. In liquid and gaseous state it has a **triangular bipyramidal** geometry. The three equatorial P-Cl bonds are equivalent, but the two axial bonds are longer than equatorial bonds. This is due to the fact that the axial bonds face more repulsion compared to equatorial bonds. Therefore PCl₅ is unstable.



The pentahalides have less thermal stability than trihalides.

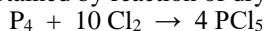


They act as Lewis acids. This is because the central atom can easily accept the halide ion due to the presence of vacant d-orbitals and can extend the co-ordination number.

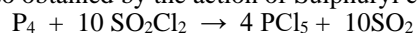


Preparation

- (1) It is obtained by reaction of dry chlorine with white phosphorus.

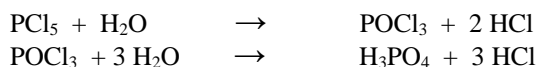


- (2) It is also obtained by the action of Sulphuryl chloride with white phosphorus.



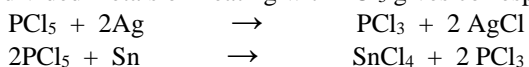
Reactions

1. PCl_5 reacts with water to give POCl_3 . If water is in excess, the product is H_3PO_4 .

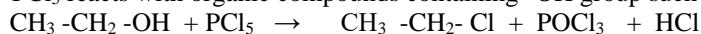


During this reaction HCl is produced. Hence PCl_5 fumes in moist air.

2. Finely divided metals on heating with PCl_5 gives corresponding chlorides.



3. PCl_5 reacts with organic compounds containing -OH group such as acids and alcohols.



In the solid state PCl_5 exists as an ionic solid. $[\text{PCl}_4]^+[\text{PCl}_6]^-$. Here the cation $[\text{PCl}_4]^+$ is tetrahedral and the anion $[\text{PCl}_6]^-$ is octahedral

Oxoacids of Phosphorus

Phosphorus forms numerous oxoacids. All of which are based on tetrahedral four co-ordinated phosphorus containing at least one P=O unit and one P-OH group.

| | Structure | O.N | Preparation |
|---|-----------|-----|---|
| H_3PO_2 Hypophosphorous acid [Phosphinic acid] | | +1 | White P_4 + Alkali |
| H_3PO_3 Orthophosphorous acid [Phosphonic acid] | | +3 | $\text{P}_2\text{O}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{PO}_3$ |
| H_3PO_4 Orthophosphoric acid [Phosphoric acid] | | +5 | $\text{P}_4\text{O}_{10} + 6\text{H}_2\text{O} \rightarrow 4 \text{H}_3\text{PO}_4$ |

| | | | |
|--|--|----|---|
| H₄P₂O₅ Pyrophosphorous | | +3 | PCl ₃ + H ₃ PO ₃ |
| H₄P₂O₇ Pyrophosphoric | | +5 | Heating phosphoric acid $2\text{H}_3\text{PO}_4 + \text{heat} \rightarrow \text{H}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O}$ |
| H₄P₂O₆ Hypophosphoric acid | | +4 | Red P ₄ + Alkali |
| (HPO₃)_n Metaphosphoric acid | | +5 | Phosphorus acid + Br ₂ , heat in a sealed tube |

Reducing character [H₃PO₂ is a reducing agent. Why?]

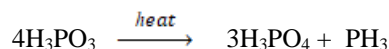
The oxoacids of phosphorous which contain P-H bonds are reducing agents. Thus hypophosphorous acid is a strong reducing agent. It reduces AgNO₃ to metallic silver



Disproportionation

Oxoacids in which the P in the +3 oxidation state disproportionate into higher and lower oxidation states.

For example **orthophosphorous** acid on heating disproportionate to give orthophosphoric and phosphine



Basicity [H₃PO₄ is a tribasic acid. Why?]

Only hydrogen attached with oxygen in P-OH form in an oxoacid is ionisable and cause basicity. Thus H₃PO₃ contain two such P-OH bonds and hence its basicity is two. H₃PO₄ contain three such P-OH bonds and hence its basicity is three.

GROUP-16 ELEMENTS [OXYGEN FAMILY]

The group 16 elements are Oxygen [O], Sulphur (S), Selenium (Se), Tellurium (Te) and Polonium (Po).

These elements are called **chalcogens** or ore forming elements.

[The word ***chalcogen*** is derived from the Greek word for *brass*. This points to the association of sulphur and its congeners with copper. Most copper minerals contain either oxygen or sulphur]

Occurance

Oxygen: It is the most abundant element in the earth crust. It constitutes 46.6% by mass of earth crust. It forms 20.946% of air as the free element by volume.

Sulphur: It occurs in earth crust to the extent of 0.03 - 0.1%. It occurs mainly as *sulphides* and *sulphates*. It also occurs in elemental form in underground beds.

Eg **Gypsum** \rightarrow $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ **Epsom salt** \rightarrow $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ **Baryte** \rightarrow BaSO_4 .
Galena \rightarrow PbS , **Zinc blende** \rightarrow ZnS , **Copper pyrites** \rightarrow CuFeS_2

It is also present as H_2S in volcanoes, natural gas and crude oil. It also occurs in organic matter such as eggs, proteins, garlic, onion, mustard, hair, wool etc.

Selenium and **tellurium** are less abundant in earth. They occur as *selenides* and *tellurides* in sulphide ores. Polonium occurs as decay products of thorium and uranium minerals.

Trends in physical properties

1. **Electronic configuration** : ns^2np^4 (where $n = 2 - 6$)

2. Atomic and ionic radii

The atomic and ionic radii increase down the group due to increase in the number of shells.

3. Melting point and boiling points:

The m.p and b.p increases down the group. On moving down the group the molecular size increases. As a result the magnitude of vander Waal's forces increases.

The large difference in m.p and b.p between oxygen and sulphur can be explained on the basis of atomicity. Oxygen exists as a diatomic molecule (O_2) but sulphur exists as polyatomic molecule (S_8).

4. Ionization energy

Ionization energy decreases from *O* to *Po* due to the increase in atomic size. Group 16 elements have lower ionization enthalpy than that of Group 15 elements. This is due to the fact that group 15 elements have extra stable half filled p-orbital electronic configuration.

5. Metallic character.

The metallic character increases down the group. The oxygen and sulphur are typical non-metals and are insulators. Se and Te are semi-conductors and polonium is metallic.

6. Electron gain enthalpy

Electron gain enthalpy becomes less negative from S to Po. Electron gain enthalpy becomes less negative from S to Po. Oxygen has less negative electron gain enthalpy than sulphur due to compact nature of oxygen atom.

7. Electro negativity

The electronegativity of these elements is relatively high. Oxygen has highest electronegativity in the group. (*Oxygen is the second most electronegative element in the periodic table.*) The value of electronegativity decreases with increases in atomic number down the group.

8. Catenation

In this group 'S' has strong tendency of catenation due to strong S-S bonds. Some examples are H_2S_2 , H_2S_4 etc. Oxygen also shows this tendency to a limited extent. Eg: $\text{H}-\text{O}-\text{O}-\text{H}$

9. Multiple bond formation

These elements can form multiple bonds with carbon, nitrogen and oxygen. The tendency to form multiple bonds decreases from S to Te

10. Allotropy The elements of this group exhibit allotropy

11. Oxidation state

Oxygen mainly exhibits the oxidation state of -2 in its compounds due to its high electronegativity. In addition to -2 , oxygen also exhibits an oxidation state of -1 in H_2O_2 , zero in O_2 and $+2$ in OF_2 . It cannot extend its oxidation state beyond 2 due to the non-availability of d-orbitals.

The oxidation states of S, Se and Te are -2 , $+2$, $+4$ and $+6$. The oxidation states $+4$ and $+6$ are particularly important for S, Se and Te. This is due to the availability of vacant d-orbitals.

The $+4$ oxidation state is relatively more stable for Se, Te and Po than their $+6$ state (Due to inert pair effect). S, Se and Te show $+4$ oxidation state with oxygen and $+6$ oxidation state with F.

Chemical properties

Hydrides

1. All the elements form bivalent hydrides H_2E . Eg: H_2O , H_2S , H_2Se , H_2Te and H_2Po . The most important of these hydrides is water.
2. All these hydrides have angular shape and central atom is sp^3 hybridised state.
3. The **boiling points** of these hydrides increases from H_2S to H_2Te . This is due to increase in *Vander Waal's* interactions due to increase in molecular size. Water has high boiling point because in H_2O , the molecules are associated through hydrogen bonding.
4. **Acidic character** : Acidic character increases from H_2O to H_2Te . This is due to decrease in bond dissociation enthalpy down the group.
5. **Thermal stability**: Thermal stability decreases from H_2O to H_2Po . This is due to decrease in bond dissociation enthalpy down the group.
6. **Reducing character** : All hydrides except water possess reducing property. The reducing property increases from H_2O to H_2Te . This is due to decrease in bond dissociation enthalpy down the group.

Oxides

1. All the group 16 elements form dioxides with the general formula EO_2 and EO_3 . where E = S, Se, Te or Po. Both type of oxides are acidic in nature.
2. O_3 and SO_2 is a gas but SeO_2 is a solid. Reducing property decreases from SO_2 to TeO_2 . Here SO_2 is reducing agent while TeO_2 is oxidizing agent.
3. S, Se and Te also form trioxides. (SO_3 , SeO_3 , TeO_3)

Halides

The elements of group 16 form a number of halides of the type EX_6 , EX_4 and EX_2 . (X → halogen)

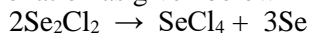
The stability of these hydrides decreases in the order $F > Cl > Br > I$

Hexa halides → They have octahedral structure. (sp^3d^2 hybridization.) Among hexahalides only hexa fluorides are stable. All hexa fluorides are gaseous in nature. SF_6 is highly stable due to steric reasons.

Tetra halides → They have trigonal bipyramidal geometry (sp^3d hybridization.) in which one of the equatorial position is occupied by lone pair. (*see-saw geometry*). SF_4 is a gas, SeF_4 is a liquid and TeF_4 is a solid

Dihalides → All elements of group 16 except Se form dichlorides and dibromides and have tetrahedral structure. They are formed by sp^3 hybridisation.

Monohalides → They are dimeric in nature. Eg. S_2F_2 , S_2Cl_2 , S_2Br_2 and Se_2Br_2 . They undergo disproportionation as given below



Sulphur

Allotropes of Sulphur:

Sulphur exists in several forms such as Rhombic (α) sulphur, Monoclinic (β) sulphur, and Plastic (γ) sulphur

(a) **Rhombic sulphur** (α -Sulphur)

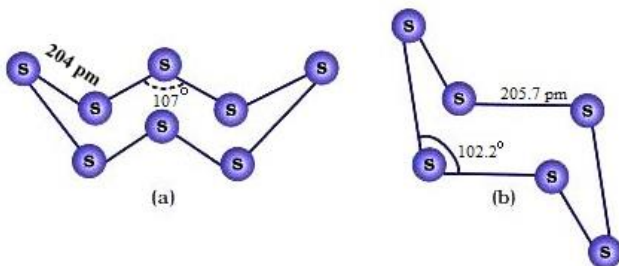
- It is the most stable and common form of sulphur at room temperature.
- It is obtained by evaporating a solution of sulphur in CS_2
- It has bright yellow colour
- Its melting point is 385.8 K and specific gravity is 2.06.
- It is insoluble in water but soluble in carbon disulphide. It dissolves to some extent in benzene, alcohol etc
- It exists as S_8 molecule. The eight sulphur atoms in S_8 molecule form a puckered ring and has a crown shape. The hybridization of sulphur in S_8 molecule is sp^3

(b) **Monoclinic sulphur** (β -sulphur)

- Monoclinic sulphur is obtained by heating rhombic sulphur above 369 K.
- It is dull yellow in colour and has a long needle shaped crystal
- Its melting point is 393 K and specific gravity is 1.98.
- It is soluble in carbon disulphide but insoluble in water.
- It slowly changes into rhombic sulphur. At 369 K both α and β forms are stable.
- It also exists as S_8 molecules which have puckered ring structure. It however, differs from the rhombic sulphur only in the packing arrangement.

Several other modifications of sulphur containing 6-20 sulphur atoms per ring have been synthesized. In **cyclo- S_6** , the ring adopts the chair form.

Above 1000 K, S_2 species predominates. Like dioxygen (O_2), S_2 is **paramagnetic**.



Uses of Sulphur

1. Most of the sulphur produced is used for the manufacture of H_2SO_4
2. It is largely used for the manufacture of carbon disulphide.
3. It is used in rubber industry for the vulcanisation of rubber.
4. Used in the manufacture of safety matches, fire works, dyes and explosive.
5. It is used in the manufacture of large number of drugs (sulpha drugs)

Halides of sulphur

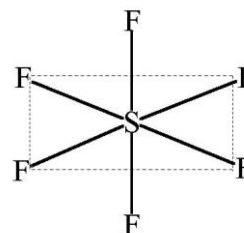
Sulphur hexafluoride (SF_6)

SF_6 is an inert non toxic gas . It has an octahedral structure. Here 'S' atom is in sp^3d^2 hybridization. It is prepared by combustion of sulphur in a stream of fluorine..



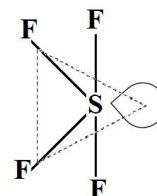
SF_6 is extremely un-reactive. Because of its chemical inertness and good dielectric strength, it is used as a gaseous insulator in high voltage generators and switch gears.

The chemical inertness SF_6 is due to the presence of sterically protected sulphur atom. Therefore it does not undergo hydrolysis. But less sterically hindered SF_4 and SeF_6 can undergo hydrolysis.



Sulphur tetrafluoride (SF_4)

SF_4 has trigonal bipyramidal geometry with one of the equatorial position occupied by a lone pair of electron. (*See-saw geometry*) Here sulphur is in sp^3d hybridization.

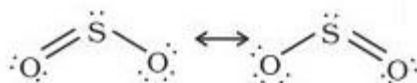


Oxides of sulphur

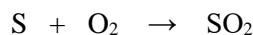
Sulphur dioxide (SO_2)

SO_2 is a colourless gas with a pungent smell. It is highly soluble in water. It boils at 263K. It liquefies at 2 atm.

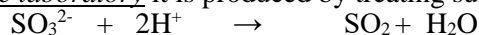
Structure: The molecule has an angular structure with a bond angle 119° . It is a resonance hybrid of the following canonical structures.



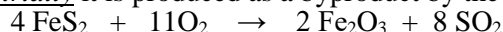
Preparation: SO_2 is prepared by the direct reaction of sulphur and oxygen. Here 6-8% of SO_3 is also formed.



In the laboratory it is produced by treating sulphite with dil H_2SO_4 .



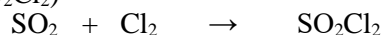
Industrially it is produced as a byproduct by the roasting of sulphide ores.



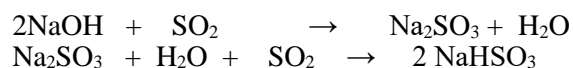
Properties:

1. SO_2 dissolves in H_2O to form sulphurous acid (H_2SO_3)
$$\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3$$

2. SO_2 reacts with Cl_2 in presence of charcoal to form sulphuryl chloride (SO_2Cl_2)

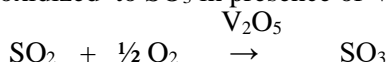


3. It readily reacts with NaOH solution to form sodium sulphite which then reacts with more SO_2 to form sodium hydrogen sulphite

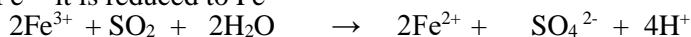


This behavior of SO_2 is similar to that of CO_2

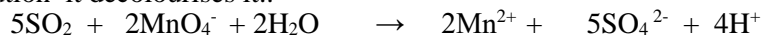
4. SO_2 is oxidized to SO_3 in presence of V_2O_5 catalyst.



5. SO_2 acts as a reducing agent. When it is passed through an aqueous solution of Fe^{3+} it is reduced to Fe^{2+}



6. **Test for SO_2 gas:** When it is passed through a solution of acidified KMnO_4 solution it decolourises it..

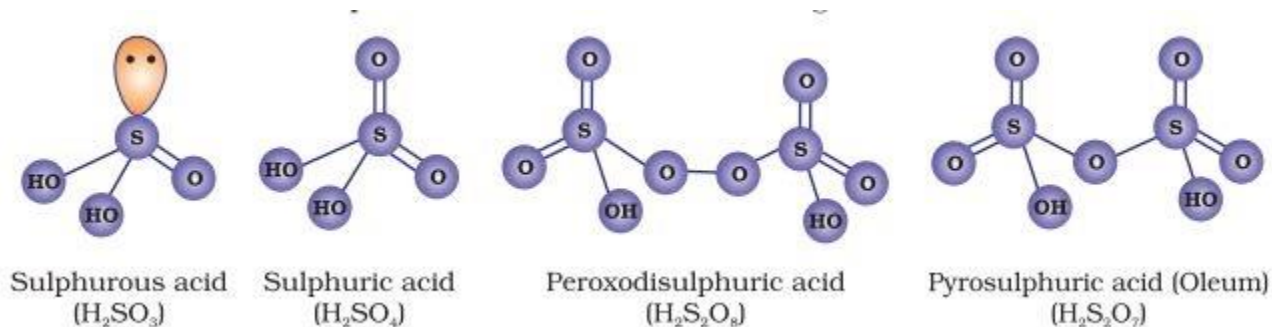


Uses:

1. It is used in the refining of petroleum and sugar. 2. In bleaching wool and silk. 3. As an anti-chlor, disinfectant and preservative 4. In the manufacture of sulphuric acid, sodium hydrogen sulphate etc. As a solvent for many organic and inorganic chemicals.

Oxoacids of sulphur

Sulphur forms many oxoacids. The principal acids formed by sulphur are



Of these *sulphurous* and *thiosulphuric acids* are unstable and cannot be isolated. They are present in aqueous solutions or in the form of their salts.

Sulphuric acid (Oil of vitriol)

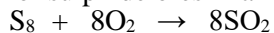
Sulphuric acid is the most important industrial chemical. So it is called *king of chemicals*. It is manufactured by two processes.

1) **Lead chamber process**

2) **Contact process.**

Contact process: It involves 3 stages.

(1) Burning of sulphur or sulphide ores in air to generate SO_2



(2) Conversion of SO_2 to SO_3 by reaction with oxygen in presence of V_2O_5 catalyst (or Platinised asbestos).



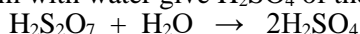
By Le Chatlier's principle, the yield can be improved by using high pressure and low temperature.

The plant is operated at a pressure of 2 bar and a temperature of 720K. Pure and dry SO₂ free from moisture, dust and *arsenic* (catalyst poison) are used.

(3) Absorption of SO₃ in H₂SO₄ to give **oleum** (H₂S₂O₇)

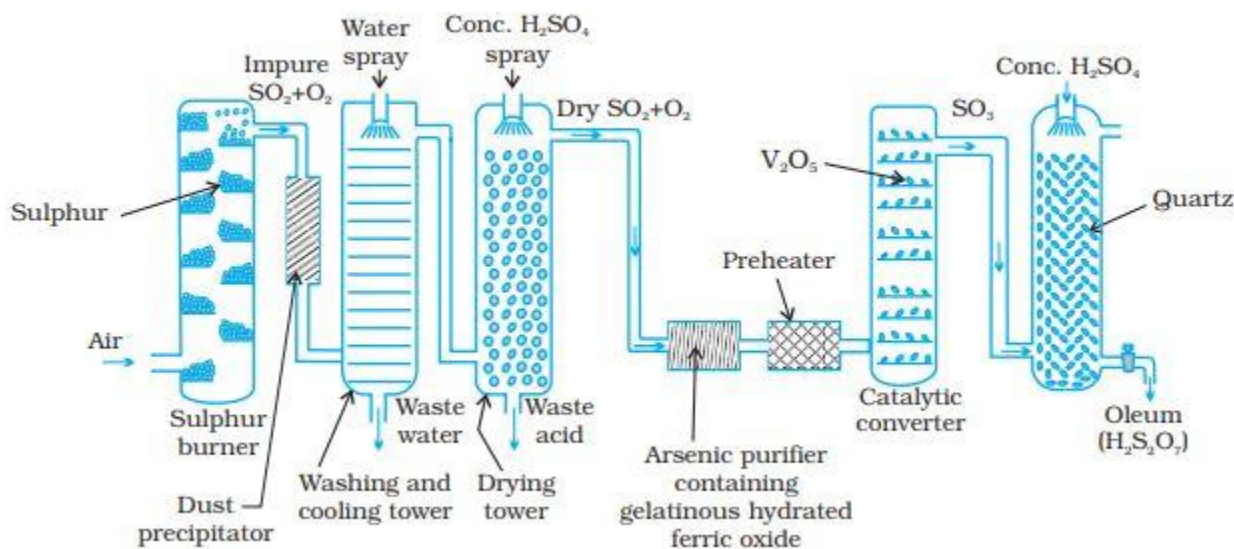


Dilution of oleum with water give H₂SO₄ of the desired concentration.



The sulphuric acid obtained by contact process is generally 96-98% pure.

Flow diagram of manufacture of H₂SO₄

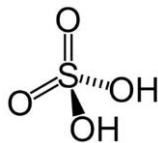


Properties of H₂SO₄

H₂SO₄ is a colourless, dense oily liquid (specific gravity 1.84g/cm³). It freezes at 283K and boils at 611K. It dissolves in water to produce a large quantity of heat. Therefore care must be taken in diluting H₂SO₄. The concentrated acid must be added slowly to cooled water with constant stirring.

Structure:

H₂SO₄ has a tetrahedral structure



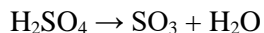
Chemical reactions:

The chemical reactions of sulphuric acid are due to the following characteristics.

(1) Low volatility (2) strong acidic character (3) strong affinity for water and (4) ability to act as an oxidizing agent.

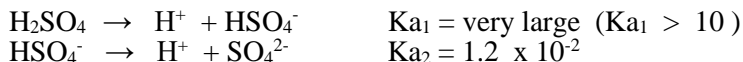
(1) Dissociation :

On strong heating H_2SO_4 dissociates to SO_3 and water.



(2) Acidic properties:

In aqueous solution, sulphuric acid behaves as a strong dibasic acid.

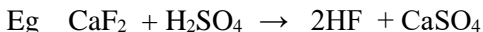
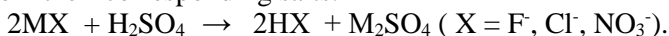


[The larger value of K_a means that H_2SO_4 is easily dissociated into H^+ and HSO_4^-]

Therefore sulphuric acid form two series of salts (a) Normal sulphate Eg: Sodium sulphate (Na_2SO_4), Copper sulphate etc. (b) Acid sulphate: Eg: Sodium bisulphate (NaHSO_4).

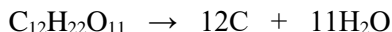
(3) Displacement reactions:

Because of its low volatility, sulphuric acid can be used to manufacture more volatile acids from their corresponding salts.



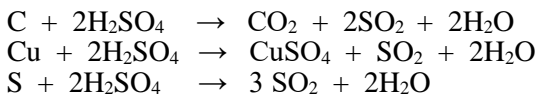
(4) Dehydrating property:

Concentrated H_2SO_4 is a strong dehydrating agent. Many wet gases can be dried by passing through sulphuric acid. Sulphuric acid removes water from organic compounds. That is why carbohydrates undergo charring on treatment with H_2SO_4



(5) Oxidising Property

Hot concentrated sulphuric acid is a moderately strong oxidizing agent. (It is intermediate between phosphoric and nitric acids). It oxidises both metals and non metals, getting itself reduced to SO_2 .



Uses of H_2SO_4

1. It is mainly used for the manufacture of fertilizers like ammonium sulphate, super phosphate etc.
2. Petroleum refining
3. Manufacture of pigments, paints and dyestuff intermediates.
4. Detergent industry
5. Metallurgical applications [Electroplating and Galvanising]
6. Storage batteries.
7. Manufacture of nitrocellulose products
8. As a laboratory reagent.

Sulphuric acid is the most important industrial chemical. It is used in the manufacture of large number of chemicals. Therefore a nation's industrial strength can be judged by the quantity of H_2SO_4 it produces and consumes.

Anomalous behaviour of oxygen

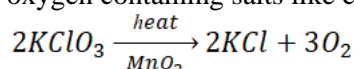
- 1) O₂ is a gas at ordinary temperature while others are solids.
- 2) Oxygen is a diatomic molecules while other members are poly atomic.
- 3) Oxygen generally shows the oxidation state of -2 but others are capable of exhibiting +2, +4 and +6 in addition to -2.
- 4) Molecular oxygen is paramagnetic while other elements are diamagnetic.
- 5) Oxygen is capable of forming Pπ – Pπ bond.

The anomalous properties are due to (a) smaller size (b) high value of ionization energy and electro negativity and (c) non availability of vacant d-orbitals in the valence shell.

Dioxygen (O₂)

Preparation

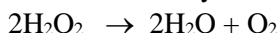
1. By heating oxygen containing salts like chlorates, nitrates, permanganates etc



2. By thermal decomposition of oxides of metal low in the electrochemical series



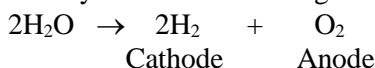
3. By decomposition of H₂O₂ by catalysts like finely divided metals and MnO₂.



4. On large scale

(i) It is prepared by the liquefaction and fractional distillation of air. First CO₂ and water vapour are removed. The remaining gases are liquified and fractionally distilled to get N₂ and O₂.

(ii) By the electrolysis water containing small amounts of acid



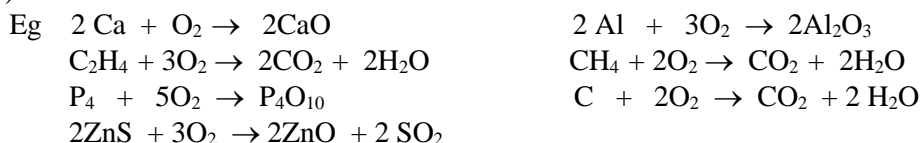
Properties

Physical properties

1. It is colourless, odourless gas
2. 3 Isotopes → O¹⁶, O¹⁷ and O¹⁸
3. Molecular oxygen is paramagnetic
4. It is soluble in water to a small extent (3.08 cm³ in 100cm³) at 298 K
5. It is liquefied at 90K (Pale blue liquid) and solidified at 55K

Chemical properties

Oxygen directly reacts with nearly all metals (Except Au, Pt) and non-metals (Except noble gases). These reactions are exothermic. But they need some external heating to initiate the reaction. This is due to high bond dissociation energy of oxygen □ oxygen double bond (493.4 kJ/mol)



Some compounds also catalytically oxidized.



Uses

- (1) O₂ is used in normal respiration and combustion processes
- (2) O₂ is used in oxyacetylene welding

- (3) In the manufacture of steel
- (4) Liquid oxygen is used as rocket fuel
- (5) Oxygen cylinder widely used in hospitals, mountaineering, high altitude flying etc.

Oxides

A binary compound of oxygen with another element is called oxide. Oxide can be simple (MgO, Al₂O₃) or mixed (Pb₃O₄, Fe₃O₄)

Simple oxides

Simple oxides can be classified as *acidic*, *basic*, *amphoteric* or *neutral*

(1) Acidic oxide

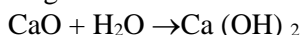
An oxide that combines with water to give an acid is termed acidic oxide (Eg: SO₂, Cl₂O₃, CO₂, N₂O₅ etc)



Usually non-metal oxides and oxides of metals in high oxidation state are acidic (CrO₃, V₂O₅ etc)

(2) Basic oxide

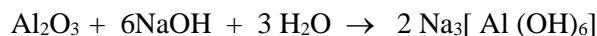
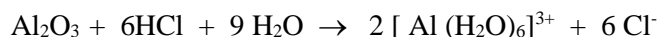
An oxide which gives a base with water are known as basic oxide (N₂O, CaO, BaO)



Usually metallic oxides are basic

(3) Amphoteric oxide

Amphoteric oxide shows the characteristics of both acidic as well as basic oxide. They react with acid as well as with alkalis Eg: Al₂O₃



(4) Neutral Oxide

Some oxides are neither acidic or basic. Such oxides are known as neutral oxide Eg: CO, NO and N₂O

Ozone

Ozone is the allotropic form of oxygen. It is formed in the upper atmosphere (height of 20 kms) from oxygen in the presence of UV – light. It protects the earth from harmful UV radiations

Preparation

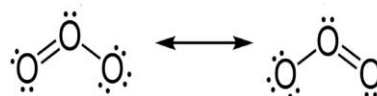
O₃ is prepared by passing a slow dry stream of oxygen through a silent electrical discharge. Here 10% oxygen is converted to ozone. The product is called *ozonised oxygen*. The formation of ozone is an endothermic reaction. Silent electric discharge is used to prevent the decomposition of O₃



The apparatus used is called **ozoniser**. Most commonly used ozoniser is **Siemen's ozoniser**

Structure

Ozone is a resonance hybrid of the following structures. The two oxygen - oxygen bond lengths are identical (128pm) and the molecule is angular with bond angle 117°



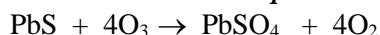
Properties

- (1) Ozone is a pale blue gas, dark blue liquid and violet black solid
- (2) In small concentration it is harmless. When inhaled in small quantities it produces headache and nausea
- (3) Ozone is thermodynamically unstable. The decomposition of ozone into oxygen results in the liberation of heat (ΔH is negative). It is also associated with an increase in entropy (ΔS +ve)
Thus the conversion of ozone to oxygen has large negative Gibbs energy change.
Therefore the high concentration of ozone can be dangerous explosive

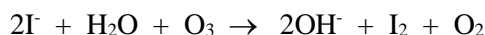
Oxidising properties

Ozone easily decomposes to liberate atom of nascent oxygen ($O_3 \rightarrow O_2 + O$) Therefore it is powerful oxidising agent.

(a) It oxidise black lead sulphide to white lead sulphate



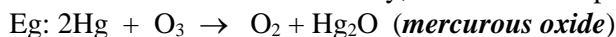
(b) It oxidise iodide to iodine



Estimation of O_3 gas

O_3 reacts with excess of potassium iodide solution liberating iodine. The iodine liberated is titrated against standard solution of sodium thiosulphate

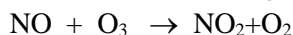
(c) Ozone oxidises metals like mercury, silver etc to respective oxides



During the reaction mercury loses its mobility and sticks to glass. This process is called **tailing of mercury**

(d) Reaction with nitrogen oxide

Nitric oxide combines with O_3 very rapidly to form NO_2



This is the reason why nitrogen oxide emitted from the exhaust system of super sonic jet aeroplanes deplete the ozone layer

Chemical which depletes ozone layer is **freon** which is used in aerosol sprays and as refrigerant.

Uses

- (1) It is used as a germicide, disinfectant and for sterilizing water
- (2) Due to the formation of nascent oxygen, O_3 acts as a bleaching agent for starch, oils, ivory, flour etc
- (3) It acts as an oxidising agent in the manufacture of $KMnO_4$.

GROUP -17 ELEMENTS
THE HALOGEN FAMILY

The group 17 elements are Fluorine, Chlorine, Bromine, Iodine and Astatine. Astatine is radio active. They are collectively called halogens meaning **salt producer**. [*Halo* means *salt* and *gens* means born]

Occurance and extraction-

Halogens are very reactive elements and hence do not occur in the free elemental state in nature.

| | | |
|----------|---|--|
| Fluorine | → | Fluorine is mainly found as insoluble fluorides. Eg. Fluorspar (CaF_2), Cryolite (Na_3AlF_6) and Fluoroapatite [$3\text{Ca}_3(\text{PO}_4)_2\text{CaF}_2$]. It also present in small amount in soil, plants and teeth and bones of animals. |
| Chlorine | → | In Sea water, salt wells and salt beds as NaCl, KCl, MgCl_2 . The deposits of dried up seas contain NaCl and <i>carnallite</i> . ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) |
| Bromine | → | In sea water and salt lakes as NaBr, KBr, MgBr_2 etc |
| Iodine | → | Certain forms of marine life contain iodine in their system. For example sea weeds contain up to 0.5% of iodine. Chile saltpetre also contains iodine in the form of sodium iodate (NaIO_3) (0.2%) |

Trends in physical properties

1. Electronic configuration

The halogens have a general electronic configuration of **ns^2np^5** in their valence shells.

2. Atomic size

Halogens have the smallest atomic size due to its maximum effective nuclear charge. The atomic size increases down the group.

3. Melting point and boiling points:

The m.p and b.p increases down the group. On moving down the group the molecular size increases. As a result the magnitude of vander Waal's forces increases.

4. Ionization energy

These elements possess large value of ionization energy. Ionization energy decreases from F to I due to the increase in atomic size.

5 Electron gain enthalpy. (Electron affinity)

These elements have maximum negative electron gain enthalpy values. This is due to the fact that these elements have small size and only one electron less than the stable noble gas configuration.

Electron gain enthalpy of the elements becomes less negative from Cl to I. The negative electron gain enthalpy of *Fluorine is less than that of chlorine*. This is due to its small size. When an electron is added to the small sized 2p orbital of fluorine atom, there arise strong inter-electronic repulsion. Therefore the incoming electron does not experience much attraction.

The order is $\text{Cl} > \text{F} > \text{Br} > \text{I}$

6. Electro negativity

The electronegativity of these elements is relatively high. Fluorine is the most electronegative in the periodic table. The value of electronegativity decreases with increase in atomic number down the group.

7. Physical state and colour

Fluorine and chlorine are gases, bromine is liquid and iodine is solid. All halogens are coloured. This is due absorption of radiation in visible region and excitation of outer electron to higher energy levels. By absorbing different wavelength they show different colours.

| | | |
|----------|---|-------------------|
| Fluorine | → | Yellow , |
| Chlorine | → | Greenish yellow , |
| Bromine | → | Reddish brown |
| Iodine | → | Violet |

Trends in chemical properties

Halogens are most reactive elements. The reactivity decreases from fluorine to iodine.

Bond dissociation enthalpy: The bond dissociation enthalpy of F_2 is smaller than that of Cl_2 . The low bond dissociation of F_2 molecule is due to relatively large electron –electron repulsion among the lone pairs in F_2 molecule. This is due to its small size.

The bond dissociation enthalpies from chlorine onwards show the expected trend



Oxidation states

Halogens have only one electron less than the next noble gas. Therefore they have a strong tendency to gain or share one electron. Fluorine, being the most electronegative element can only gain electron and hence shows -1 oxidation state. It cannot show higher oxidation states since it does not contain d-orbitals.

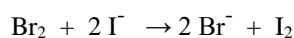
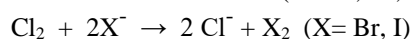
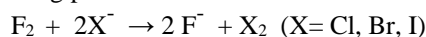
The other elements show oxidation states -1 , $+1$, $+3$, $+5$, and $+7$. This is due to the presence of vacant d-orbitals. The higher oxidation states of Cl_2 , Br_2 , and I_2 are shown with highly electronegative F and O atoms.

But in oxides and oxyacids these can exhibit $+4$ and $+6$ oxidation states also.

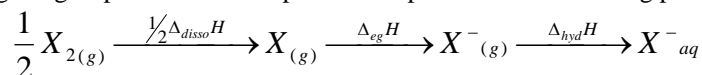
Oxidising power

Halogens are strong oxidizing agents. The ready acceptance of an electron is the reason for the strong oxidizing nature. Among halogens fluorine is the strongest oxidizing agent

Fluorine oxidizes other halide ions in solution or even in the solid state. In general, a halogen of low atomic number will oxidize halides of higher atomic number
The oxidizing power decrease in the order $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$.



The decreasing oxidizing power is explained due to the decrease in electrode potential on descending the group. The electrode potential depends on the following parameters



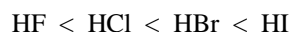
Reaction with hydrogen

Halogens combine with hydrogen to form hydrogen halides. These are covalent diatomic gaseous molecules. HF is a liquid due to intermolecular hydrogen bonding. HCl, HBr, and HI are colourless gases.

The stability of these hydrides decreases from HF to HI. This is due to decrease in bond dissociation enthalpy in the order $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$

The reducing character of hydrogen halides increases down the group due to the weakening of H – X bond. The order is $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$

The aqueous solutions of hydrogen halides are known as hydrohalic acids. The strength of hydrohalic acids increases as follows.



[Since H – I bond is weakest, HI is the strongest acid. H – F bond is strongest, hence it is the weakest acid.]

Hydrofluoric acid (HF) is corrosive and extreme care has to be taken while working with HF.

HF attacks glass and hence it is used for etching glass and manufacture of glass shell of television tubes.

Reactivity towards oxygen

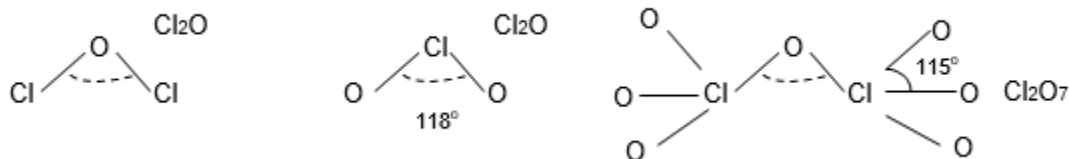
All the halogens form different types of oxides.

1. **Fluorine** forms two oxides **OF_2** and **O_2F_2** .
2. These compounds are called oxygen fluorides because of the higher electronegativity of fluorine. Both are strong fluorinating agents.
3. Only OF_2 is thermally stable at 298K.

4. O_2F_2 oxidises plutonium to PuF_6 . This reaction is used for removing plutonium as PuF_6 from spent nuclear fuel.
5. The stability of oxides formed by halogen $\text{I} > \text{Cl} > \text{Br}$
6. The higher oxides of halogen are more stable than lower oxides.

Chlorine, bromine and iodine form oxides with oxidation states from +1 to +7

The important oxides of **Chlorine** are Cl_2O (+1), ClO_2 (+4), Cl_2O_6 (+6) and Cl_2O_7 (+7)



The important oxides of **bromine** are Br_2O (+1), BrO_2 (+4) and BrO_3 (+6). These are the least stable halogen oxides.

The important oxides of **iodine** are I_2O_4 (+4), I_2O_5 (+5) and I_2O_7 (+7). I_2O_5 is an important oxidizing agent and is used in the estimation of carbon monoxide.

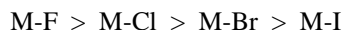
The oxides are unstable and reactive compounds. The oxides are powerful **oxidizing** and they dissociate into their elements on heating or by applying shocks. Cl_2O and ClO_2 are extensively used as bleaching agent for paper pulp and textiles and to disinfect sewage and drinking water.

Reactivity towards metals.

Halogens react with metals to form metal halides.



The halides of metals like Na, K, Mg etc with low ionization energies are ionic in nature. They have high melting and boiling points. The ionic character of the M-X bond decreases in the order



But halides of metals like tin, lead etc with high ionization potential are covalent in nature. They have low melting and boiling points.

If a metal exhibits more than one oxidation state, the halide in the higher oxidation state will be more covalent than the one with lower oxidation state.

Eg: SnCl_4 , PbCl_4 , SbCl_5 , UF_6 etc are more covalent than SnCl_2 , PbCl_2 , SbCl_3 , UF_4 etc.

Reactivity of halogen with other halogen

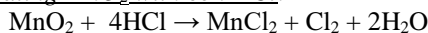
Halogen also combine among themselves to form a number of compounds known as **interhalogen compounds** of the type XX' , XX'_3 , XX'_5 and XX'_7 where X is larger halogen and X' is smaller halogen

CHLORINE (discovered by Sheele)

Davy established its elementary nature and also suggested its name to account its colour-(*Chloros* means *greenish yellow*.)

Preparation

1. By heating MnO_2 with con HCl .



(But usually a mixture of NaCl and H_2SO_4 is used in place of HCl .)

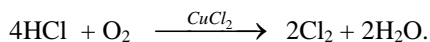


2. By the action of HCl on KMnO_4 .



Manufacture of Chlorine

1. Deacon's process By oxidation of HCl gas by atmospheric O₂ in presence of CuCl₂ catalyst at 723K.



2. Electrolytic process

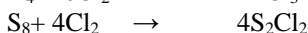
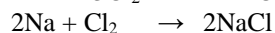
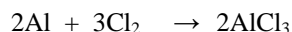
By the electrolysis of brine (con NaCl soln). Cl₂ is liberated at anode.

Physical properties

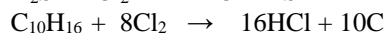
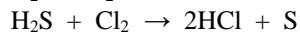
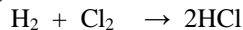
It is a greenish yellow gas with pungent suffocating odour. It is soluble in water. It can be easily liquefied into greenish yellow liquid.

Chemical properties.

1. Cl₂ reacts with a number of metals and non-metals.

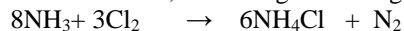


2. Cl₂ combines with compounds containing hydrogen to form HCl, because of its great affinity for hydrogen.

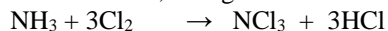


3. With ammonia

- (a) With excess ammonia, chlorine gives nitrogen and ammonium chloride



- (b) With excess chlorine, nitrogen trichloride is formed. (NCl₃ is an explosive)

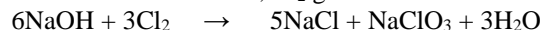


4. With NaOH

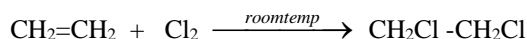
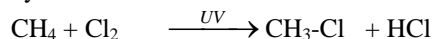
- (a) With cold dilute alkali, chlorine gives chloride and hypochloride.



- (b) With hot concentrated alkali, Cl₂ give chloride and chlorate.



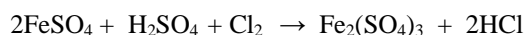
5. With hydrocarbons



6. Oxidising property

Chlorine water on standing it loses its yellow colour due to the formation of HCl and HOCl. The hypochlorous acid (HOCl) thus formed gives nascent oxygen which is responsible for oxidizing and bleaching properties of chlorine.

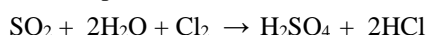
- (a) It oxidizes ferrous to ferric



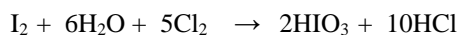
- (b) It oxidizes sulphite to sulphate.



- (c) SO₂ to sulphuric acid



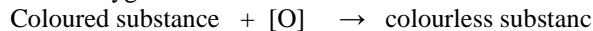
(d) Iodine to iodic acid



7. **Bleaching agent:** Chlorine is a powerful bleaching agent. Its bleaching action is due to oxidation reaction as follows



The nascent oxygen thus liberated converts coloured matter to colourless matter.



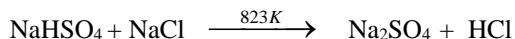
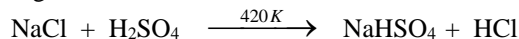
Uses

1. To bleach wood pulp for manufacture of paper.
2. In the extraction of gold and Pt
3. Manufacture of dyes, drugs and organic compounds such as CCl_4 , CHCl_3 , DDT, refrigerants etc
4. For sterilizing drinking water.
5. Preparation of poisonous gases such as *phosgene* (COCl_2), *tear gas* (CCl_3NO_2), *mustard gas* ($\text{Cl}-\text{CH}_2\text{CH}_2-\text{S}-\text{CH}_2\text{CH}_2-\text{Cl}$).

HYDROGEN CHLORIDE (HCl) - Glauber

Preparation

Heating NaCl with concentrated H_2SO_4 .

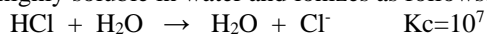


The HCl thus produced is dried by passing over con. H_2SO_4 .

Properties

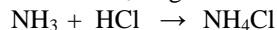
It is colourless and pungent smelling gas. It is easily liquefiable and highly soluble in water.

1. It is highly soluble in water and ionizes as follows.



It is a strong acid in water. Aqueous solution of HCl is called hydrochloric acid.

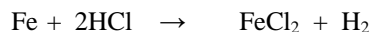
2. It reacts with NH_3 to give white fumes NH_4Cl .



3. It decomposes salts of weaker acids eg: carbonates, hydrogen carbonates, sulphites etc.

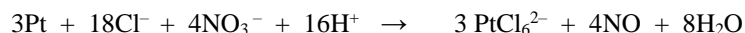


4. With powdered iron: It reacts with powdered iron producing H_2 and FeCl_3 .



Aqua regia

A mixture of 3 parts of con HCl and one part of con. HNO_3 is known as aqua regia. It is used for dissolving noble metals (gold and Pt)



Uses

1. In the manufacture of chlorine, NH_4Cl , and glucose.
2. For extraction glue from bones and purifying bone black.
3. As a laboratory reagent and in medicine.

Oxoacids

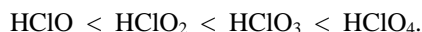
Several oxoacids are formed by halogens. Fluorine forms only one oxoacid, *hypofluorous acid* (HOF)

The other halogens form several oxoacids. The oxoacids of halogens are shown below.

| | F | Cl | Br | I |
|--|--------------------------|---------------------------------------|-------------------------------------|-------------------------------------|
| <i>Halic(I) acid</i> (<i>Hypohalous acid</i>) | HOF (Hypoflurousacid) | HOCl (Hypochlorous acid) | HOBr (Hypobromous acid) | HOI (Hypoiodous acid) |
| <i>Halic (III) acid</i> (<i>Halous acid</i>) | — | HOClO Chlorous acid | — | — |
| <i>Halic (V) acid</i> (<i>Halic acid</i>) | — | HOClO ₂ Chloric acid | HOBrO ₂ Bromic acid | HOIO ₂ Iodic acid |
| <i>Halic (VII) acid</i> (<i>Per halic acid</i>) | — | HOClO ₃ Perchloric acid | HOBrO ₃ Perbromicacid | HOIO ₃ Periodic acid. |

The acidic strength of oxoacids

(1) The acidic strength of oxoacids of a particular halogen atom increases with increase in oxidation number. For example the acidic strength of oxoacids chlorine increase in the order.



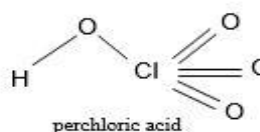
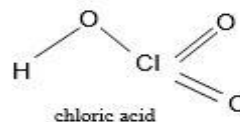
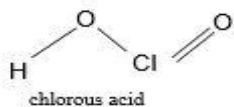
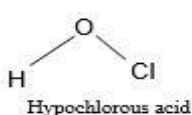
This can be explained on the basis of Lowry bronsted concept. The conjugate bases formed from the above acids are ClO^- , ClO_2^- , ClO_3^- and ClO_4^- . Now more the number of oxygen atoms in the ion, greater is the dispersal of the negative charge and hence more is the stability of the resulting ion. Hence ClO_4^- is the most stable ion and the corresponding acid (HClO_4) is the strongest acid.

(2) The strength of halic acids with the same oxidation state of the halogen decrease in the sequence.



Greater the size of the halogen lesser will be its electronegativity and hence lesser will be the acidic character.

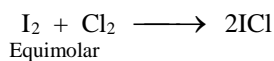
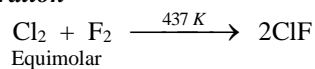
The structure of different oxoacids of chlorine

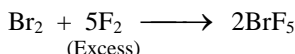
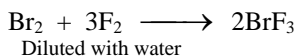
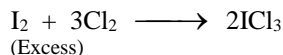
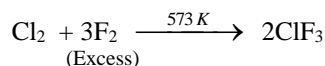


Interhalogen compounds

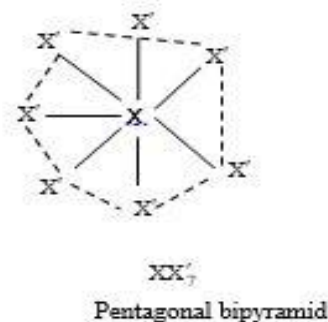
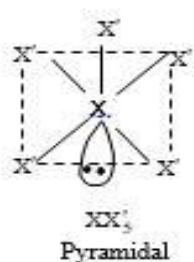
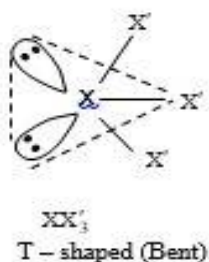
Halogens form compounds among themselves known as inter-halogen compounds. The different classes of interhalogen compounds are XX' , $\text{X X}'_3$, $\text{X X}'_5$ and $\text{X X}'_7$ where X is heavier halogen and X' is smaller halogen. Except BrCl , ICl , IBr and ICl_3 , the other interhalogen compounds are the fluorides: ClF , ClF_3 , ClF_5 , BrF , BrF_3 , BrF_5 , IF_3 , IF_5 and IF_7

Preparation



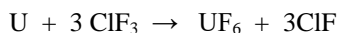


1. The interhalogen compounds are strong oxidizing agents.
2. These are all covalent molecules and **diamagnetic** in nature.
3. They are generally more reactive than halogens. (except fluorine). This is because X-X' bond in interhalogens is weaker than X-X bond in halogens.
4. They are essentially covalent.
5. The stability of the interhalogen compounds increases as the size of the central atom increases.
6. In these compounds the smaller atom is assigned a negative oxidation state.
7. Their structure can be explained on the basis of VSEPR theory. The XX'_3 compounds are **bent T shaped**, XX'_5 compounds are **square pyramidal** and XX'_7 compounds are **pentagonal bipyramid**. The structures of some of the compound are



Uses

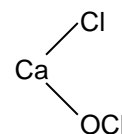
1. These compounds are used as non-aqueous solvents.
2. These are very useful fluorinating agents.
3. ClF_3 and BrF_3 are used for the production of UF_6 in the enrichment of uranium.



Bleaching powder.

Bleaching powder is a mixture of calcium hypochlorite and basic calcium chloride. It has the composition **$\text{Ca}(\text{OCl})_2 \cdot \text{CaCl}_2 \cdot 2\text{H}_2\text{O}$**

Bleaching powder is prepared by passing chlorine over slaked lime.



Uses:

1. It is used as a bleaching agent for cotton, linen and wood pulp.
2. As a disinfectant and germicide especially in the sterilization of drinking water.
3. For the manufacture of chloroform.

Anomalous behaviour of fluorine

1. Ionisation enthalphy, electronegativity, bond enthalpy etc are higher for fluorine than expected from the trend of other halogens.
2. But the ionic and covalent radii, m.p, b.p and electron gain enthalphy are lower than that expected.
3. Most of the reactions of fluorine are exothermic
4. Fluorine forms only one oxoacid while others forms a number of oxoacids.
5. Hydrogen fluoride is a liquid due to hydrogen bonding but other hydrogen halides are gases

The anomalous properties of fluorine are due to its small size, highest electronegativity, low F-F bond dissociation enthalpy and non-availability of d-orbitals in valence shell.

Group 18 Elements: Noble gases

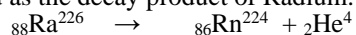
Group-18 elements – helium, neon, argon, krypton, xenon and radon are collectively called **noble gases**. They have their valence shell orbitals completely filled. Therefore they are chemically unreactive. They form very few compounds. Therefore they are also called **noble gases**.

Occurance:

All noble gases except radon occur in the atmosphere. Their total abundance is approximately 1% by volume. Of these **argon** is the major component. **He** is present in natural gas. He is the second most abundant element in the universe. He and sometimes Ne are found in minerals of radioactive origin. Eg. Pitchblende, monazite etc.

Xenon and **radon** are the rarest elements in the group.

Radon is obtained as the decay product of Radium.



Physical properties

- (1) **Electronic configuration:** All noble gases except He has the stable electronic configuration ns^2np^6 . Helium has only two electrons and has the electronic configuration $1s^2$.
- (2) **M.P and B.P:** All the noble gases are mono-atomic. The only type of inter-atomic attraction in these elements is weak dispersion interaction. Therefore they have low melting and boiling points. B.P increases down the group.

Helium has the lowest boiling point of any known substance. **He has the unusual property of diffusing through commonly used laboratory materials such as glass, rubber or plastics.**

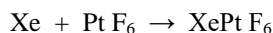
- (3) **Atomic radi:** In case of noble gas, the atomic radii are *vander Waal's radii*. It increases down the group.
- (4) **Ionisation energy:** Due to stable electronic configuration, the ionization energies of noble gases are very high. It decreases down the group.
- (5) **Election gain enthalpy:** Due to stable noble gas configuration they have no tendency to accept electron Therefore they have large positive values of electron gain enthalpy.

Chemical Properties:

Noble gases are least reactive. It is due to the following reasons

1. Noble gases (except He) have completely filled ns^2np^6 electronic configuration in the valence shell.
2. They have high ionization enthalpy and positive electron gain enthalpy.

The first compound of noble gases was isolated by **Neil Bartlett** in 1962. First he prepared a red compound $\text{O}_2^+\text{Pt F}_6^-$. Then he realized that the first ionization energy of molecular oxygen (1175 kJ/mol) is almost same as that of Xenon (1170 kJ/mol). Then he succeeded in isolating a red crystalline solid compound XePt F_6 by mixing PtF_6 and Xe



After that several compounds of xenon are known. No true compounds of He, Ne or Ar are yet known.

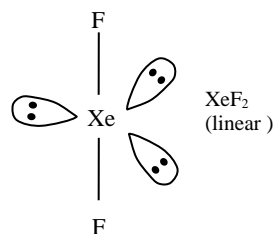
[RnF_2 is the only isolated compound of Rn and KrF_2 is the only isolated compound of Kr]

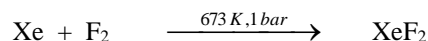
Xenon-fluorine compounds

Xenon forms 3 fluorides, **XeF_2** , **XeF_4** and **XeF_6** .

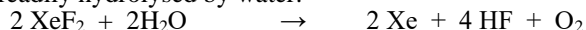
Xenon difluoride (XeF_2)

It is prepared by heating of a mixture of xenon and fluorine in the ratio 2:1 at 673K.





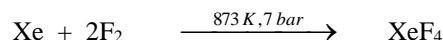
XeF_2 is readily hydrolysed by water.



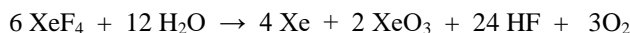
In XeF_2 , Xe has sp^3d hybridization and has a **linear structure**.

Xenon tetra fluoride (XeF_4)

It is prepared by heating of a mixture of xenon and fluorine in ratio 1:5 at 873K at 7 bar.



XeF_4 is hydrolysed by water forming explosive XeO_3 .

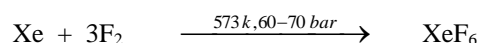


In XeF_4 , Xe has sp^3d^2 hybridization and has **square planar** geometry.

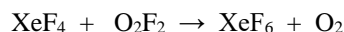
Xenon hexa fluoride (XeF_6)

Preparation:

- (1) It is prepared by heating of a mixture of xenon and fluorine in ratio 1:20 at 573K at 60-70 bar.

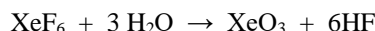


- (2) It is also prepared by interacting XeF_4 and O_2F_2



Hydrolysis

XeF_6 is readily hydrolysed by water forming explosive XeO_3 .



In XeF_6 , Xe has sp^3d^3 hybridization and has a **distorted octahedral** structure.

XeF_2 , XeF_4 and XeF_6 are powerful fluorinating agents.

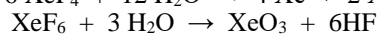
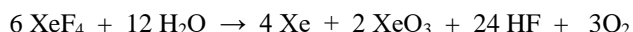
XeF_2 , XeF_4 , XeF_6 are colourless crystalline solids.

F

Xenon-Oxygen compounds

XeO_3

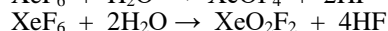
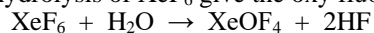
It is prepared by hydrolysis of XeF_4 and XeF_6



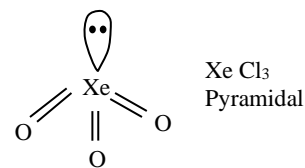
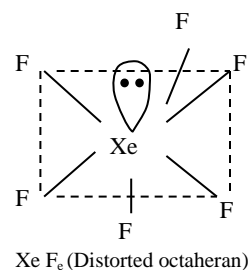
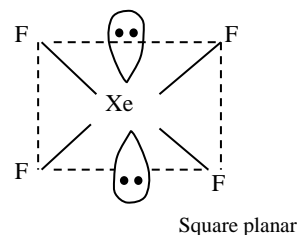
XeO_3 is a colourless highly explosive solid. It has a **trigonal pyramidal** molecular structure, (sp^3). It is a powerful oxidising agent in aqueous solution.

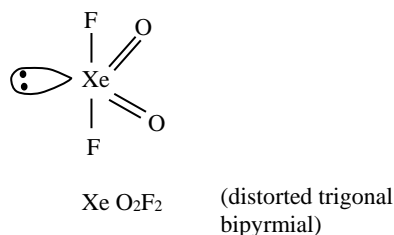
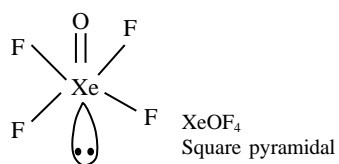
XeOF_4 and XeO_2F_2

Partial hydrolysis of XeF_6 give the oxy fluorides XeOF_4 and XeO_2F_2 .



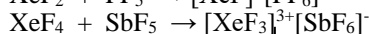
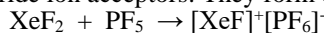
XeOF_4 is a colourless volatile liquid. It has a square pyramidal structure.



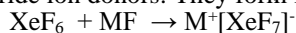


Reaction of Xenon fluorides with fluoride ion acceptors and fluoride ion donors.

1. With fluoride ion acceptors: They form cationic species.



2. With fluoride ion donors: They form fluoroanions.



Uses:

Helium:

- (1) Helium is a non-flammable and light gas. Hence it is used in filling balloons and air ships
- (2) It is also used in gas cooled nuclear reactors.
- (3) It is used as a cryogenic agent for carrying out various experiments at low temperature.
- (4) They are used to produce powerful super conducting magnets in NMR spectrometer and MRI systems (clinical diagnosis)

Neon:

Neon is used discharge tubes and fluorescent bulbs for advertisement display purposes. It is also used in beacon lights for safe air navigation as the light can penetrate through fog.

Argon: Along with nitrogen it is used to fill electric lamps .It is also used to provide inert atmosphere in high temperature metallurgical operations.

Xenon: Used in high speed photography

Radon: Used for treatment of cancer.

