

The elements in which the last electron enters in the valence p-sub shell are called the p-block elements. They include elements of the groups 13 to 18. Their general outer electronic configuration is ns^2np^{1-6} (except He which has $1s^2$ configuration). They include metals, non-metals and metalloids.

Group 15 Elements

Group 15 includes nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi). As we go down the group, the metallic character increases. Nitrogen and phosphorus are non-metals, arsenic and antimony metalloids and bismuth is a typical metal. The valence shell electronic configuration of these elements is ns^2np^3 . The s orbital in these elements is completely filled and p orbitals are half-filled, making their electronic configuration extra stable.

Covalent and ionic radii increase down the group. There is a considerable increase in covalent radius from N to P. However, from As to Bi only a small increase in covalent radius is observed. This is due to the presence of completely filled d or f orbitals in heavier members. Ionisation enthalpy decreases down the group due to gradual increase in atomic size. Because of the extra stable half-filled p orbitals and smaller size, the ionisation enthalpy of the group 15 elements is much greater than that of group 14 elements.

Oxidation states and trends in chemical reactivity

The common oxidation states of these elements are -3 , $+3$ and $+5$. The tendencies to exhibit -3 oxidation state decreases down the group due to increase in size and metallic character. The last member of the group, bismuth does not form any compound in -3 oxidation state. The stability of $+5$ oxidation state decreases and that of $+3$ state increases (due to inert pair effect) down the group. Nitrogen exhibits $+1$, $+2$, and $+4$ oxidation states also when it reacts with oxygen. Phosphorus also shows $+1$ and $+4$ oxidation states in some oxoacids. Nitrogen is restricted to a maximum covalency of 4 since only four orbitals (one s and three p) are available for bonding.

Anomalous properties of nitrogen

Nitrogen differs from the rest of the members of this group due to its smaller size, high electro negativity, high ionisation enthalpy and non-availability of d orbitals. Some of the anomalous properties shown by nitrogen are:

1. Nitrogen has the ability to form **$p\pi-p\pi$ multiple** bonds with itself and with other elements like C and O. Other elements of this group do not form **$p\pi-p\pi$** bonds.
2. Nitrogen exists as a diatomic molecule with a triple bond (one s and two p) between the two atoms. So its bond enthalpy is very high. While other elements of this group are poly atomic with single bonds.
3. The single N–N bond is weak. So the catenation tendency is weaker in nitrogen.
4. Due to the absence of d orbitals in its valence shell, the maximum covalency of nitrogen is four
5. N cannot form **$d\pi-p\pi$ bond**. While Phosphorus and arsenic can form **$d\pi-d\pi$ bond** with transition metals and with C and O.

Hydrides of Group 15 Elements

All the elements of Group 15 form hydrides of the type EH_3 (where E = N, P, As, Sb or Bi). The hydrides show regular gradation in their properties. The bond dissociation enthalpy of E – H decreases from NH_3 to BiH_3 . So the thermal stability decreases from NH_3 to BiH_3 and the reducing character increases. Ammonia is only a mild reducing agent while BiH_3 is the strongest reducing agent amongst all the hydrides. Basicity decreases in the order $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$. The melting point of these hydrides increases from top to bottom. This is due to increase in the atomic size of the central atom which increases the van der Waal's force of attraction. NH_3 has the highest melting and boiling points due to inter molecular hydrogen bonding. All these hydrides have pyramidal geometry.

Q₁. Though nitrogen exhibits $+5$ oxidation state, it does not form pentahalides. Give reason.

Nitrogen with $n = 2$, has s and p orbitals only. It does not have d orbitals to expand its covalence beyond four. That is why it does not form pentahalide.

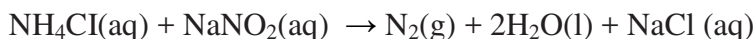
Q2. PH_3 has lower boiling point than NH_3 . Why?

Unlike NH_3 , PH_3 molecules are not associated through inter molecular hydrogen bonding in liquid state. That is why the boiling point of PH_3 is lower than NH_3 .

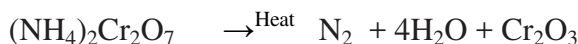
Dinitrogen (N_2)

Preparation: Dinitrogen is produced commercially by the liquefaction and fractional distillation of air.

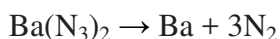
In the laboratory, dinitrogen is prepared by treating an aqueous solution of ammonium chloride with sodium nitrite.



It can also be obtained by the thermal decomposition of ammonium dichromate.

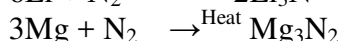
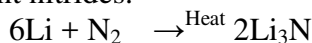


Very pure nitrogen can be obtained by the thermal decomposition of sodium or barium azide.

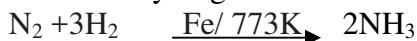


Properties

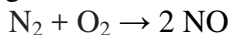
Dinitrogen is inert at room temperature because of the high bond enthalpy of $\text{N} \equiv \text{N}$ bond. At higher temperatures, it directly combines with some metals to form ionic nitrides and with non-metals to form covalent nitrides.



It combines with hydrogen at about 773 K in the presence of a catalyst (Haber's Process) to form ammonia:



Dinitrogen combines with dioxygen at very high temperature (at about 2000 K) to form nitric oxide



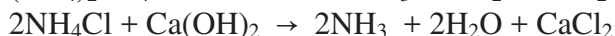
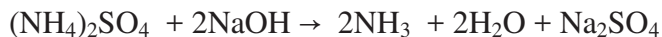
Uses: 1. The main use of dinitrogen is in the manufacture of ammonia and other industrial chemicals containing nitrogen (e.g., calcium cyanamide).

2. It also used to create an inert atmosphere in metallurgy.

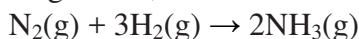
3. Liquid dinitrogen is used as a refrigerant to preserve biological materials, food items and in cryosurgery.

Ammonia

Preparation: In laboratory, ammonia is obtained by treating ammonium salts with caustic soda (NaOH) or slaked lime.



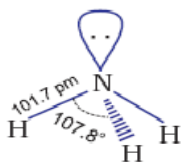
On a large scale, ammonia is manufactured by Haber's process.



In accordance with Le Chatelier's principle, high pressure of about 200 atm, a temperature of about 773 K and the catalyst such as iron oxide with small amounts of K_2O and Al_2O_3 are employed to increase the rate of this reaction.

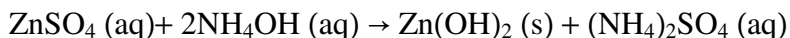
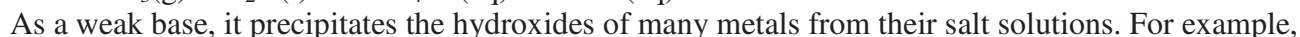
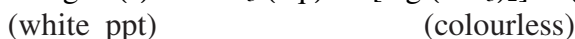
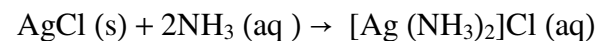
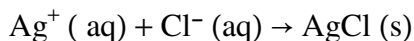
Properties

Ammonia is a colourless gas with pungent smell. It is highly soluble in water because of its ability to form inter molecular hydrogen bond with water. Liquid ammonia has high melting and boiling points because of inter molecular hydrogen bonding.



The ammonia molecule has a *trigonal pyramidal geometry*. It has three bond pairs and one lone pair of electrons.

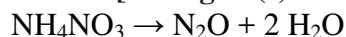
Its aqueous solution is weakly basic due to the formation of OH^- ions.


$$\text{Cu}^{2+}(\text{aq}) + 4 \text{NH}_3(\text{aq}) \rightarrow [\text{Cu}(\text{NH}_3)_4]^{2+}(\text{aq})$$


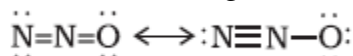
Uses: Ammonia is used i) to produce various nitrogenous fertilizers (ammonium nitrate, urea, ammonium phosphate and ammonium sulphate) ii) in the manufacture of nitric acid iii) liquid ammonia is used as a refrigerant.

Nitrogen forms a number of oxides in different oxidation states. They are:

1. **Nitrous Oxide [Nitrogen (I) Oxide]:** It is prepared by heating ammonium nitrate.



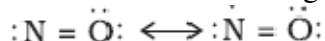
It is a colourless, neutral gas. Its structure is:



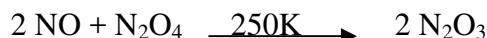
2. **Nitric Oxide [Nitrogen (II) Oxide]:** It is prepared by treating sodium nitrite with acidified ferrous sulphate.



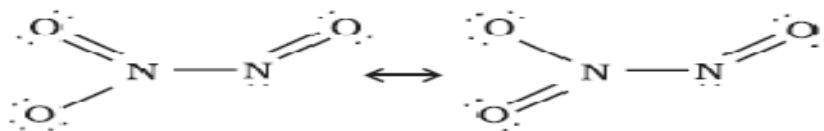
It is a colorless neutral gas. Its structure is:



3. **Dinitrogen trioxide [Nitrogen (III) oxide]:** It is prepared by treating nitric oxide with dinitrogen tetroxide



It is a blue solid with acidic nature. Its structure is:



4. **Nitrogen dioxide [Nitrogen (IV) oxide]:** It is prepared by heating lead nitrate at about 673K.



It is an acidic brown gas. Its structure is:



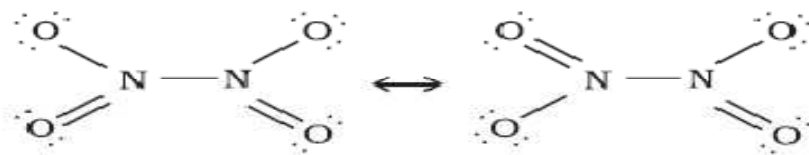
5. **Dinitrogen tetroxide [Nitrogen (IV) oxide]:** It is prepared by cooling NO_2 .



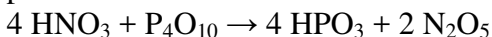
Heat

It is a colourless solid or liquid with acidic character. Its structure is:

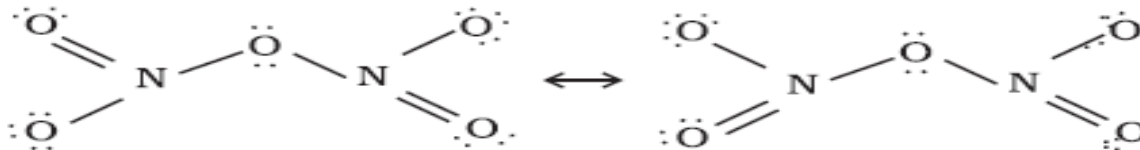




6. **Dinitrogen pentoxide [Nitrogen (V) oxide]:** It is prepared by nitric acid with phosphorus pentoxide.

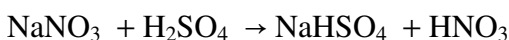


It is a colourless solid with acidic character. Its structure is:



Nitric Acid (HNO₃)

Preparation: In the laboratory, nitric acid is prepared by heating KNO₃ or NaNO₃ and concentrated H₂SO₄ in a glass retort.

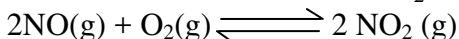


On a large scale it is prepared by **Ostwald's process**. It involves three steps:

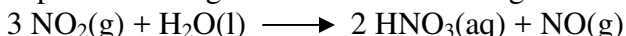
1. The catalytic oxidation of NH₃ by atmospheric oxygen in presence of platinum/ rhodium gauge (wire) catalyst.



2. The nitric oxide is converted to NO₂

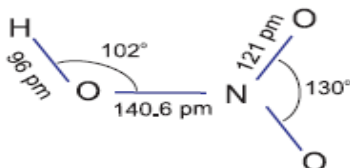


3. Absorption of nitrogen dioxide in water to get nitric acid.

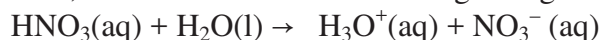


The aqueous HNO₃ can be concentrated by distillation up to 68% by mass. Further concentration to 98% can be achieved by dehydration with concentrated H₂SO₄. 98% HNO₃ is known as *fuming nitric acid*.

Properties: It is a colourless liquid. In the gaseous state, HNO₃ exists as a planar molecule with the structure as shown below:



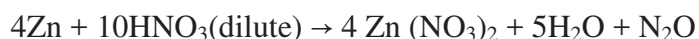
In aqueous solution, nitric acid behaves as a strong acid giving hydronium and nitrate ions.



Concentrated nitric acid is a strong oxidising agent and attacks most metals except noble metals such as gold and platinum. The products of oxidation depend upon the concentration of the acid, temperature and the nature of the material undergoing oxidation.



Zinc reacts with dilute nitric acid to give N₂O and with concentrated acid to give NO₂.

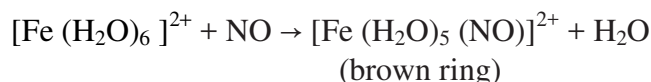
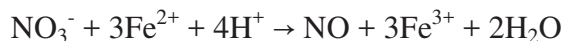


Some metals (e.g., Cr, Al) do not dissolve in concentrated nitric acid because of the formation of a passive film of oxide on the surface.

Concentrated nitric acid also oxidises non-metals and their compounds. Iodine is oxidised to iodic acid, carbon to carbon dioxide, sulphur to H_2SO_4 , and phosphorus to phosphoric acid.



Brown Ring Test: It is a test used for the detection of nitrates. The test is carried out by adding dilute ferrous sulphate solution to an aqueous solution containing nitrate ion, and then carefully adding concentrated sulphuric acid along the sides of the test tube. A brown ring at the interface between the solution and sulphuric acid layers indicate the presence of nitrate ion in solution.



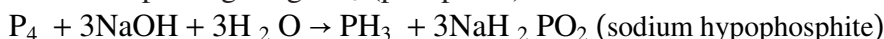
Uses: It is used i) in the manufacture of ammonium nitrate for fertilizers and other nitrates for use in explosives and pyrotechnics. ii) for the preparation of nitroglycerin, trinitrotoluene and other organic nitro compounds. iii) in the *pickling of stainless steel*, etching of metals and as an oxidiser in rocket fuels.

Phosphorus

The allotropic forms of phosphorus:

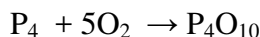
Phosphorus exists mainly in three allotropic forms – white (yellow) phosphorus, red phosphorus and black phosphorus

1. **White phosphorus:** It is a translucent white waxy solid. It is poisonous, insoluble in water but soluble in carbon disulphide and glows in dark (chemiluminescence). It dissolves in boiling NaOH solution in an inert atmosphere giving PH_3 (phosphine).

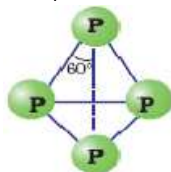


White phosphorus is less stable and therefore, more reactive. This is because in white phosphorus, the P-P-P bond angles are only 60° . So it has greater angular strain and highly unstable.

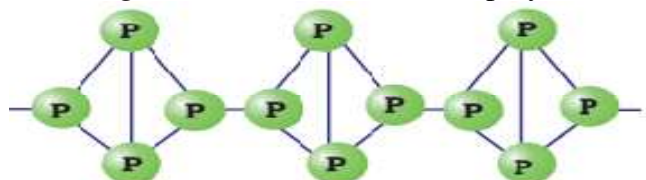
It readily catches fire in air to give dense white fumes of P_4O_{10} .



It consists of discrete tetrahedral P_4 molecule



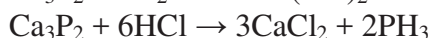
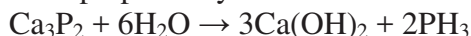
2. **Red phosphorus:** It is obtained by heating white phosphorus at 573K in an inert atmosphere for several days. Red phosphorus has iron grey lustre. It is odourless, non-poisonous and insoluble in water as well as in carbon disulphide. Chemically, red phosphorus is much less reactive than white phosphorus. It does not glow in the dark. It contains polymeric chains of P_4 tetrahedra.



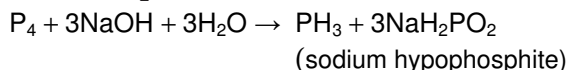
3. **Black phosphorus:** It has two forms- α -black phosphorus and β -black phosphorus. α -black phosphorus is formed when red phosphorus is heated in a sealed tube at 803K. It does not oxidise in air. β -Black phosphorus is prepared by heating white phosphorus at 473K under high pressure. It does not burn in air up to 673K

Phosphine (PH₃)

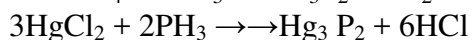
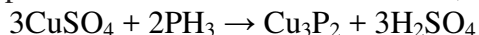
Preparation: It is prepared by the reaction of calcium phosphide with water or dilute HCl.



In the laboratory, it is prepared by heating white phosphorus with concentrated NaOH solution in an inert atmosphere of CO₂.



Properties: It is a colourless gas with rotten fishy smell and is highly poisonous. It is slightly soluble in water. The solution of PH₃ in water decomposes in presence of light giving red phosphorus and H₂. When absorbed in copper sulphate or mercuric chloride solution, the corresponding phosphides are obtained.



Like NH₃, Phosphine is weakly basic and gives phosphonium compounds with acids.



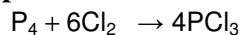
Uses: Phosphine is technically used to produce Holme's signal. Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea. The gases evolved burn and serve as a signal. It is also used in smoke screens.

Phosphorus Halides

Phosphorus forms two types of halides- PX₃ and PX₅

Phosphorus trichloride (PCl₃)

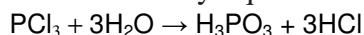
Preparation: It is obtained by passing dry chlorine over heated white phosphorus.



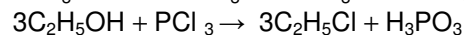
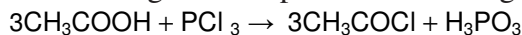
It is also obtained by the action of thionyl chloride with white phosphorus.



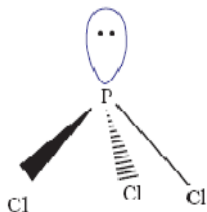
It is a colourless oily liquid and hydrolyses in the presence of moisture.



It reacts with organic compounds containing –OH group such as CH₃COOH, C₂H₅OH.

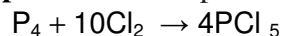


Structure: It has a pyramidal shape as shown, in which phosphorus is sp³ hybridized.

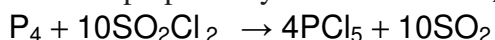


Phosphorus Pentachloride (PCl₅)

Preparation: Phosphorus pentachloride is prepared by the reaction of white phosphorus with excess of dry chlorine.

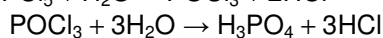
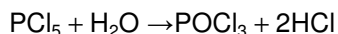


It can also be prepared by the action of SO₂Cl₂ on phosphorus.



Properties

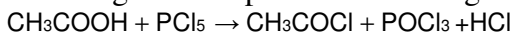
PCl₅ is a yellowish white powder and in moist air, it hydrolyses to POCl₃ and finally gets converted to Phosphoric acid.

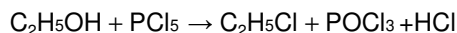


When heated, it sublimates but decomposes on strong heating.



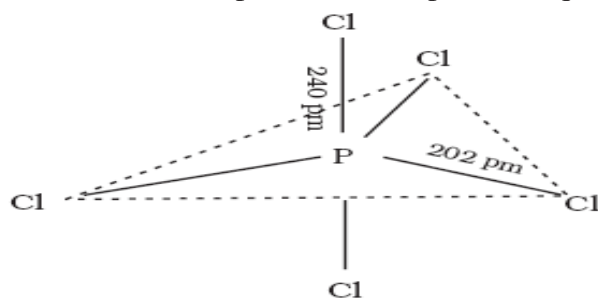
It reacts with organic compounds containing –OH group to give chloro derivative.





Structure:

In gaseous and liquid phases, it has a trigonal bipyramidal structure. The three equatorial P–Cl bonds are equivalent, while the two axial bonds are longer than equatorial bonds. This is due to the fact that the axial bond pairs suffer more repulsion as compared to equatorial bond pairs.

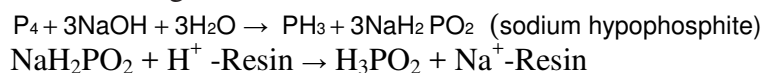


In the solid state it exists as an ionic solid, $[\text{PCl}_4]^+[\text{PCl}_6]^-$ in which the cation, $[\text{PCl}_4]^+$ is tetrahedral and the anion, $[\text{PCl}_6]^-$ is octahedral.

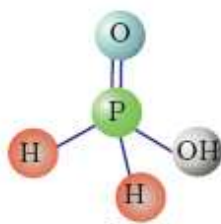
Oxoacids of Phosphorus: Phosphorus forms a number of oxoacids.

1. **H_3PO_2 [Hypophosphorus Acid (Phosphinic Acid)]**

It is prepared by heating white phosphorus with concentrated NaOH solution followed by passing through cation exchange resin.



Structure:



It is a strong reducing agent due to the presence of a P-H bond. It is monobasic even though it contains three hydrogen atoms. This is because the hydrogen atoms directly bonded to the P atom will not dissociate.

2. **H_3PO_3 [Orthophosphorus Acid (Phosphonic Acid)]**

It is prepared by the action of water on P_2O_3



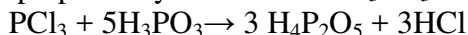
It is dibasic because of the presence of two –OH groups.

Structure:



3. **$\text{H}_4\text{P}_2\text{O}_5$ [Pyrophosphorus Acid]**

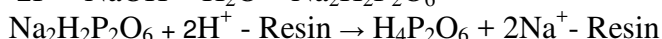
It is prepared by the action of H_3PO_3 on PCl_3



It is also dibasic because of the presence of two –OH groups.

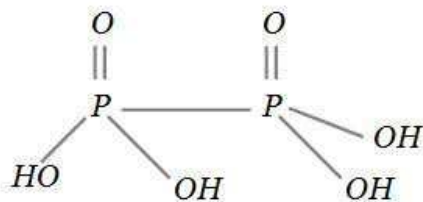
4. **$\text{H}_4\text{P}_2\text{O}_6$ [Hypophosphoric Acid]**

It is prepared by the action of an alkali on red Phosphorus followed by passing through cation exchange resin.



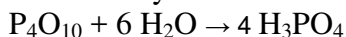
It is a tetra basic acid.

Structure:



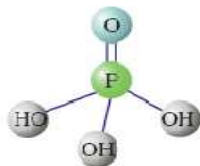
5. **H₃PO₄ [Orthophosphoric Acid]**

It is obtained by the action of water on phosphorus pentoxide (P₄O₁₀)



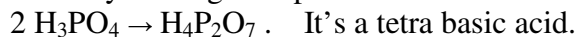
It is also called Phosphoric acid. It's a tribasic acid and has a tetrahedral shape.

Structure:

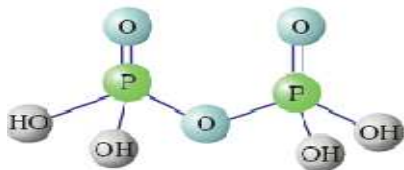


6. **H₄P₂O₇ [Pyrophosphoric Acid]**

It is obtained by heating Phosphoric acid at about 250°C.

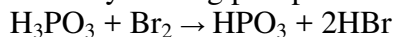


Structure:

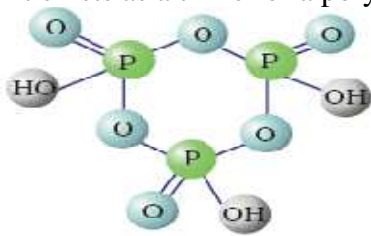


7. **(HPO₃)_n [Metaphosphoric acid]**

It is obtained by heating phosphorus acid with Br₂ vapours in a sealed tube.

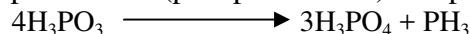


Structure: It exists as a trimer or a polymer as follows:



Cyclotrimetaphosphoric acid, (HPO₃)₃ Polymetaphosphoric acid, (HPO₃)_n

The oxoacids of phosphorus in +3 oxidation state undergo disproportionation (i.e. simultaneously oxidised and reduced). For example, orthophosphorous acid (or phosphorous acid) on heating disproportionates to give orthophosphoric acid (phosphoric acid) and phosphine.



Group 16 Elements

The members of this group are oxygen (O), sulphur (S), selenium (Se), tellurium (Te) and polonium (Po). They are also called chalcogens (means ore producing). Oxygen and sulphur are non-metals, selenium and tellurium are metalloids, while polonium is a radioactive metal.

Ionisation enthalpy of these elements decreases down the group. It is due to increase in size. However, the elements of this group have lower ionisation enthalpy values compared to those of Group 15 elements. This is due to the fact that Group 15 elements have extra stable half-filled p orbitals electronic

configurations.

Oxygen atom has less negative electron gain enthalpy than sulphur because of the compact nature of its shells due to which the electronic repulsion is greater.

Oxidation states: The elements of Group 16 exhibit a number of oxidation states (-2,+2,+4 & +6). The stability of -2 oxidation state decreases down the group. Since electronegativity of oxygen is very high, it shows only -2 oxidation state (except in the case of OF₂ where its oxidation state is +2). Other elements of the group exhibit +2, +4 & +6 oxidation states. But +4 and +6 are more common. Sulphur, selenium and tellurium usually show +4 oxidation state in their compounds with oxygen and +6 with fluorine. Down the group, the stability of +6 oxidation state decreases and that of +4 oxidation state increases (due to inert pair effect).

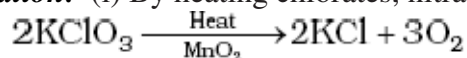
Hydrides of 16th group elements

All the elements of Group 16 form hydrides of the type H₂E (E = S, Se, Te, Po). Their acidic character increases from H₂O to H₂Te. This is due to the decrease in bond (H–E) dissociation enthalpy down the group. So the thermal stability also decreases down the group. All the hydrides except water possess reducing property and this character increases from H₂S to H₂Te.

Dioxygen (O₂)



Preparation: (i) By heating chlorates, nitrates and permanganates.



(ii) By the thermal decomposition of the oxides of metals low in the electrochemical series and higher oxides of some metals.



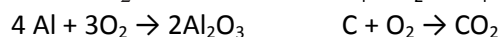
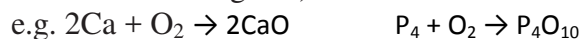
(iii) By the decomposition of Hydrogen peroxide (H₂O₂) in presence of manganese dioxide.



(iv) On large scale it can be prepared from water or air. Electrolysis of water leads to the release of hydrogen at the cathode and oxygen at the anode. It is also obtained by the fractional distillation of air.

Properties:

Dioxygen directly reacts with metals and non-metals (except with some metals like Au, Pt etc and with some noble gases).



Uses: 1) oxygen is used in oxyacetylene welding, in the manufacture of many metals, particularly steel.

2) Oxygen cylinders are widely used in hospitals, high altitude flying and in mountaineering.

3) Liquid O₂ is used in rocket fuels.

Oxides

Oxides are binary compounds of oxygen with other elements. There are two types of oxides – simple oxides (e.g., MgO, Al₂O₃) and mixed oxides (Pb₃O₄, Fe₃O₄)

Simple oxides can be further classified on the basis of their acidic, basic or amphoteric character. An oxide that combines with water to give an acid is called acidic oxide (e.g., SO₂, Cl₂O₇, CO₂, N₂O₅).

Generally, non-metal oxides are acidic but oxides of some metals in higher oxidation states also have acidic character (e.g., Mn₂O₇, CrO₃, V₂O₅ etc.).

The oxide which gives an alkali on dissolved in water is known as basic oxide (e.g., Na₂O, CaO, BaO). Generally, metallic oxides are basic in nature.

Some metallic oxides exhibit a dual behaviour. They show the characteristics of both acidic and basic oxides. Such oxides are known as amphoteric oxides. They react with acids as well as alkalies.

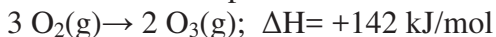
E.g.: Al₂O₃, Ga₂O₃ etc.

There are some oxides which are neither acidic nor basic. Such oxides are known as neutral oxides. Examples of neutral oxides are CO, NO and N₂O.

Ozone (O₃)

Ozone is an allotropic form of oxygen.

Preparation: When a slow dry stream of oxygen is passed through a silent electric discharge, oxygen is converted to ozone. The product is known as ozonised oxygen.



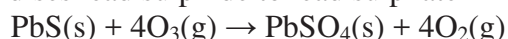
Since the formation of ozone from oxygen is an endothermic process, a silent electric discharge should be used, unless the ozone formed undergoes decomposition.

Properties: Pure ozone is a pale blue gas, dark blue liquid and violet-black solid. Ozone has a characteristic smell.

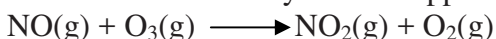
Ozone is thermodynamically unstable with respect to oxygen since its decomposition into oxygen results in the liberation of heat (ΔH is negative) and an increase in entropy (ΔS is positive). So the Gibbs energy change (ΔG) for this process is always negative ($\Delta G = \Delta H - T\Delta S$).

Due to the ease with which it liberates nascent oxygen ($\text{O}_3 \rightarrow \text{O}_2 + \text{O}$), it acts as a powerful oxidising agent.

For e.g., it oxidises lead sulphide to lead sulphate

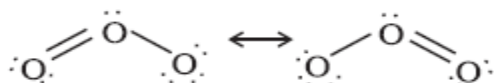


Oxides of nitrogen (particularly nitric oxide) combine very rapidly with ozone and deplete it. Thus nitrogen oxides emitted from the exhaust systems of supersonic jet aeroplanes, slowly depleting the concentration of the ozone layer in the upper atmosphere.



Estimation of ozone: When ozone reacts with an excess of potassium iodide solution buffered with a borate buffer, iodine is liberated. The liberated iodine can be titrated against a standard solution of sodium thiosulphate. This is a quantitative method for estimating O₃ gas.

Structure: O₃ has an angular structure. It is a resonance hybrid of the following two forms:



Uses: It is used as a germicide, disinfectant and for sterilising water. It is also used for bleaching oils, ivory, flour, starch, etc. It acts as an oxidising agent in the manufacture of potassium permanganate.

Allotropes of Sulphur

Sulphur forms a large number of allotropes. Among these **yellow rhombic** (α -sulphur) and **monoclinic** (β -sulphur) forms are the most important. The stable form at room temperature is rhombic sulphur, which transforms to monoclinic sulphur when heated above 369 K.

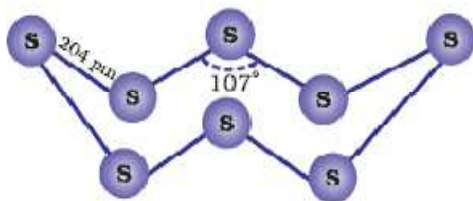
1. Rhombic sulphur (α -sulphur)

It is prepared by evaporating the solution of roll sulphur in CS₂. It is insoluble in water but readily soluble in CS₂.

2. Monoclinic sulphur (β -sulphur)

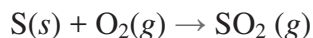
It is prepared by melting rhombic sulphur in a dish and cooling, till a crust is formed. Two holes are made in the crust and the remaining liquid is poured out. On removing the crust, colourless needle shaped crystals of β -sulphur are formed. It is stable above 369 K and transforms into α -sulphur below it. At 369 K both the forms are stable. This temperature is called **transition temperature**.

Both rhombic and monoclinic sulphur have S₈ molecules. The S₈ ring in both the forms is puckered and has a crown shape.

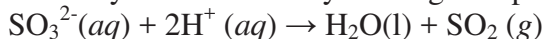


Sulphur Dioxide (SO₂)

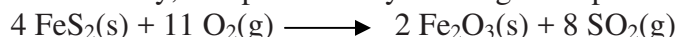
Preparation: 1. Sulphur dioxide is formed when sulphur is burnt in air or oxygen:



2. In the laboratory it is obtained by treating a sulphite with dilute sulphuric acid.

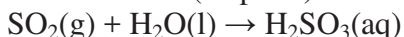


3. Industrially, it is produced by roasting of sulphide ores.

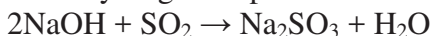


Properties: Sulphur dioxide is a colourless gas with pungent smell and is highly soluble in water.

With water, it forms a solution of sulphurous acid which is a dibasic acid and form two types of salts with alkalies – normal salt (sulphite) and acid salt (bisulphate or hydrogen sulphite).



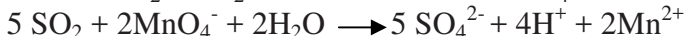
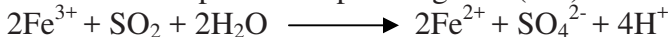
With sodium hydroxide solution, it forms sodium sulphite, which then reacts with more sulphur dioxide to form sodium hydrogen sulphite.



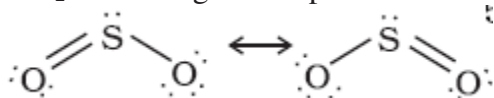
SO₂ is oxidised to sulphur trioxide by oxygen in the presence of vanadium pentoxide (V₂O₅) catalyst.



Moist sulphur dioxide behaves as a reducing agent. It converts iron(III) ions to iron(II) ions and decolourises acidified potassium permanganate(VII) solution (This used as a test for SO₂).



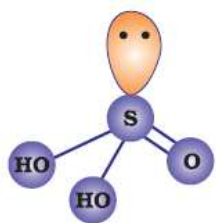
Structure: SO₂ has an angular shape. It is a resonance hybrid of the following two canonical forms:



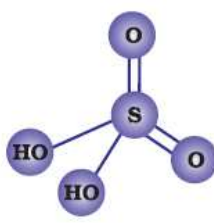
Uses: Sulphur dioxide is used (i) in refining petroleum and sugar (ii) in bleaching wool and silk and (iii) as an anti-chlor, disinfectant and preservative (iv) for the production of Sulphuric acid, sodium hydrogen sulphite and calcium hydrogen sulphite (v) Liquid SO₂ is used as a solvent to dissolve a number of organic and inorganic chemicals.

Oxoacids of sulphur

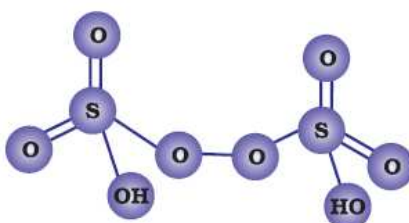
Sulphur forms a large no. of oxoacids like Sulphurous acid (H₂SO₃), Dithionous acid (H₂S₂O₄), Sulphuric acid (H₂SO₄), Pyrosulphuric acid (Oleum, H₂S₂O₇), Peroxomonosulphuric acid (Caro's acid, H₂SO₅), Peroxodisulphuric acid (Marshall's acid, H₂S₂O₈) etc. structure of some oxoacids are:



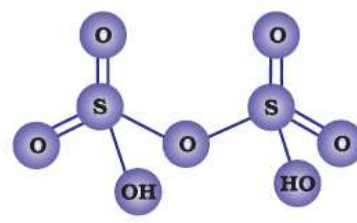
Sulphurous acid
(H₂SO₃)



Sulphuric acid
(H₂SO₄)



Peroxodisulphuric acid
(H₂S₂O₈)



Pyrosulphuric acid (Oleum)
(H₂S₂O₇)

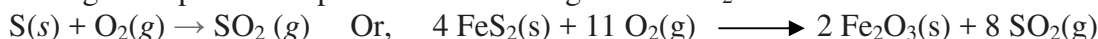
Sulphuric Acid (H₂SO₄)

The most important oxoacid of sulphur is sulphuric acid which is also known as the 'King of Chemicals'.

Manufacture:

Sulphuric acid is manufactured by the **Contact Process** which involves three steps:

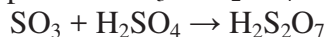
(i) burning of sulphur or sulphide ores in air to generate SO₂.



(ii) conversion of SO₂ to SO₃ by the reaction with oxygen in the presence of a catalyst (V₂O₅)



(iii) absorption of SO_3 in H_2SO_4 to give *Oleum* ($\text{H}_2\text{S}_2\text{O}_7$).



(iv) Dilution of oleum with water gives H_2SO_4 of the desired concentration.



Properties

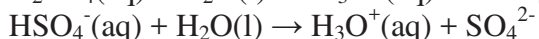
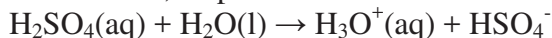
Sulphuric acid is a colourless, dense, oily liquid. It dissolves in water with the evolution of a large quantity of heat. Hence, for diluting the acid, the concentrated acid must be added slowly into water with constant stirring.

Chemical properties: The chemical reactions of sulphuric acid are due to the following reasons:

- (a) its low volatility
- (b) strong acidic character
- (c) strong affinity for water and
- (d) its ability to act as an oxidising agent.



In aqueous solution, sulphuric acid ionises in two steps.



So it is dibasic and forms two series of salts: normal sulphates and acid sulphates.

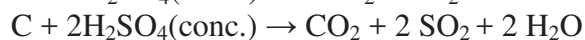
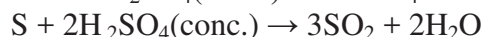
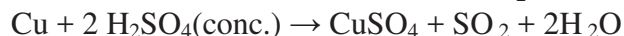
Because of its low volatility sulphuric acid can be used for the manufacture of more volatile acids from their corresponding salts.



Concentrated sulphuric acid is a strong dehydrating agent and drying agent. Many wet gases can be dried by passing them through sulphuric acid. Sulphuric acid removes water from organic compounds



Hot concentrated sulphuric acid is a moderately strong oxidising agent. It oxidises both metals and non-metals and the acid itself reduces to SO_2 .



Uses: The important uses of Sulphuric acid are:

1) In the manufacture of fertilizers 2) in petroleum refining 3) in the manufacture of pigments, paints and dyestuff intermediates 4) in detergent industry 5) in metallurgical applications 6) as electrolyte in storage batteries 7) in the manufacture of nitrocellulose products and 8) as a laboratory reagent.

Group 17 Elements

Fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At) are the members of Group 17. They are collectively known as the halogens (means salt producers). They are highly reactive non-metallic elements. All these elements have seven electrons in their outermost shell (ns^2np^5) and so they do not readily lose their electron. So they have very high ionisation enthalpy.

Halogens have maximum negative electron gain enthalpy in the corresponding periods. This is due to the fact that the atoms of these elements have only one electron less than stable noble gas configurations. Electron gain enthalpy of these elements decreases down the group. However, the negative electron gain enthalpy of fluorine is less than that of chlorine. It is because, in fluorine the incoming electron goes to the 2p subshell, but in Cl it enters in to the 3p subshell. Due to the compactness of 2p subshell compared to 3p subshell, the electron – electron repulsion is greater in fluorine than in chlorine. So F does not easily gains electron.

Halogens have very high electronegativity. The electronegativity decreases down the group. Fluorine is the most electronegative element in the periodic table.

All halogens have characteristic colour. For example, F_2 has yellow, Cl_2 -greenish yellow, Br_2 -red and I_2 , violet colour. This is due to absorption of radiations in visible region which results in the excitation of outer electrons to higher energy level.

The bond dissociation enthalpy of F_2 is low. This is due to the relatively large electron-electron repulsion among the lone pairs in F_2 molecule.

All the halogens are highly reactive. They react with metals and non-metals to form halides. The reactivity of the halogens decreases down the group.

Halogens are strong oxidising agents since they readily accept electron. F_2 is the strongest oxidising halogen and it oxidises other halide ions in solution or in the solid phase.

Oxidation states

All the halogens exhibit -1 oxidation state. Chlorine, bromine and iodine also show $+1$, $+3$, $+5$ and $+7$ oxidation states in their oxides, oxy acids and in inter halogen compounds. Due to the absence of vacant d orbitals and the maximum electronegativity, fluorine exhibits only -1 oxidation state.

Anomalous behavior of fluorine

Due to the small size, highest electronegativity, low F-F bond dissociation enthalpy, and non availability of d orbitals in valence shell, fluorine shows properties different from other halogens.

Some of the anomalous properties of fluorine are:

1. Ionisation enthalpy, electronegativity, enthalpy of bond dissociation and electrode potentials are higher for fluorine than expected.
2. Ionic and covalent radii, m.p. and b.p. and electron gain enthalpy are quite lower than expected.
3. Most of the reactions of fluorine are exothermic (due to the small and strong bond formed by it with other elements).
4. F forms only one oxoacid while other halogens form a number of oxoacids.
5. Hydrogen fluoride is a liquid due to strong hydrogen bonding. While the hydrogen halides of other elements are gases.

Hydrides of halogens

Halogens react with hydrogen to give hydrogen halides which dissolve in water to form hydrohalic acids. The acidic strength of these acids varies in the order: $HF < HCl < HBr < HI$. The stability of these halides decreases down the group due to decrease in bond dissociation enthalpy from HF to HI.

Chlorine (Cl_2)

Preparation: It can be prepared by any one of the following methods:



- (i) By heating manganese dioxide with concentrated hydrochloric acid.



Conc. HCl can be replaced by a mixture of common salt and concentrated H_2SO_4



- (ii) By the action of HCl on potassium permanganate.



Manufacture of chlorine

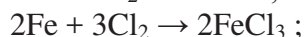
- (i) **Deacon's process:** By oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of $CuCl_2$ (catalyst) at 723 K.



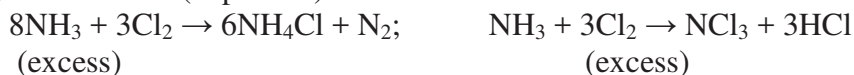
- (ii) **Electrolytic process:** Chlorine is obtained by the electrolysis of brine solution (concentrated NaCl solution). During electrolysis chlorine is liberated at the anode.

Properties: It is a greenish yellow gas with pungent and suffocating odour. It is soluble in water.

It reacts with a number of metals and non-metals to form chlorides.



With excess ammonia, chlorine gives nitrogen and ammonium chloride whereas with excess chlorine, nitrogen trichloride (explosive) is formed.



With cold and dilute alkalies chlorine produces a mixture of chloride and hypochlorite but with hot and concentrated alkalies it gives chloride and chlorate.

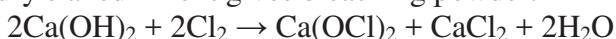


(cold and dilute)



(hot and conc.)

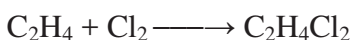
With dry slaked lime it gives bleaching powder.



Chlorine reacts with hydrocarbons and gives substitution products with saturated hydrocarbons and addition products with unsaturated hydrocarbons.



Methane Methyl chloride

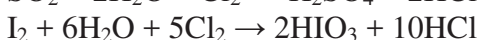
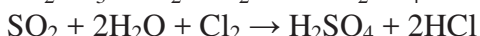


Ethene 1,2-Dichloroethane

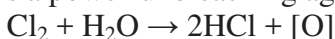
Chlorine water on standing loses its yellow colour due to the formation of HCl and HOCl.

Hypochlorous acid (HOCl) so formed is unstable and dissociates to give nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.

(i) It oxidises ferrous to ferric, sulphite to sulphate, sulphur dioxide to sulphuric acid and iodine to iodic acid.



(ii) It is a powerful bleaching agent; bleaching action is due to oxidation.



It bleaches vegetable or organic matter in the presence of moisture. Its bleaching action is permanent.

Uses: It is used

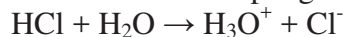
- (i) for bleaching wood pulp, bleaching cotton and textiles,
- (ii) in the extraction of gold and platinum
- (iii) in the manufacture of dyes, drugs and organic compounds such as CCl_4 , CHCl_3 , DDT, refrigerants, etc.
- (iv) in sterilising drinking water and
- (v) preparation of poisonous gases such as phosgene (COCl_2), tear gas (CCl_3NO_2), mustard gas ($\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$).

Hydrogen Chloride (HCl)

Preparation: It is prepared in the laboratory, by heating sodium chloride with concentrated sulphuric acid.



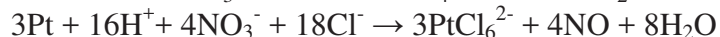
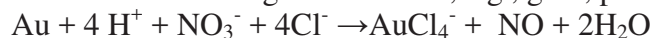
Properties: It is a colourless and pungent smelling gas. It is extremely soluble in water and ionises as:



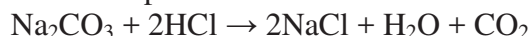
Its aqueous solution is called hydrochloric acid, which is a strong acid in water. It reacts with NH_3 and gives white fumes of NH_4Cl .

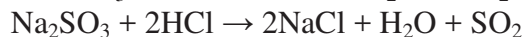
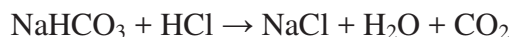


When three parts of concentrated HCl and one part of concentrated HNO_3 are mixed, aqua regia is formed which is used for dissolving noble metals, e.g., gold, platinum.



Hydrochloric acid decomposes salts of weaker acids like carbonates, hydrogen carbonates, sulphites, etc.



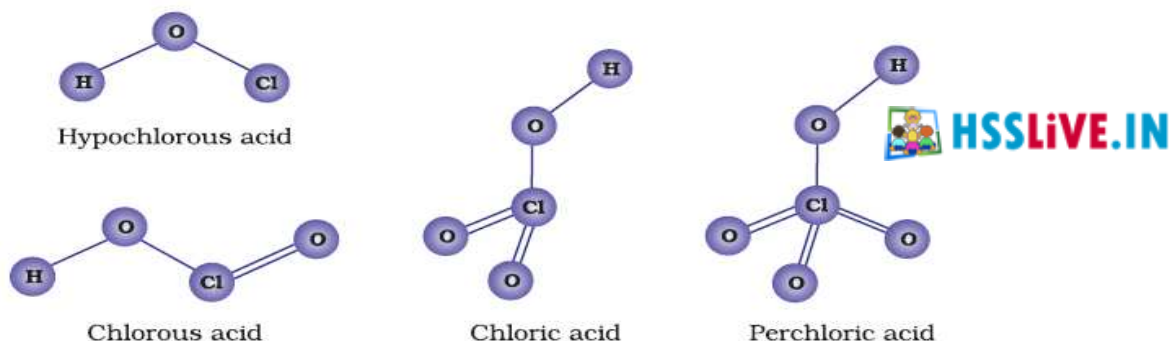


Uses: It is used (i) in the manufacture of chlorine, NH_4Cl and glucose (from corn starch),
(ii) for extracting glue from bones and purifying bone black,
(iii) in medicine and as a laboratory reagent.

Oxoacids of Halogens

Due to high electronegativity and small size, fluorine forms only one oxoacid, HOF known as fluoric (I) acid or hypofluorous acid. The other halogens form several oxoacids like Hypohalous acid (HOX), halous acid (HOXO), halic acid (HOXO₂) and perhalic acid (HOXO₃). They are stable only in aqueous solutions or in the form of their salts.

Chlorine forms 4 types of oxoacids – hypochlorous acid (HOCl), Chlorous acid (HOClO or HClO₂), Choric acid (HOClO₂ or HClO₃) and perchloric acid (HOClO₃ or HClO₄). The structures of them are:

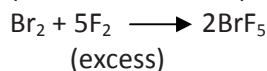
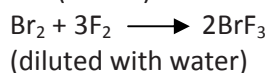
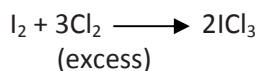
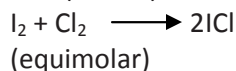
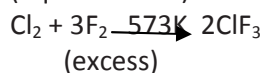
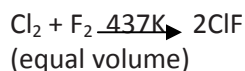


Interhalogen Compounds

When two different halogens react with each other, interhalogen compounds are formed. They can be assigned general compositions as AX, AX₃, AX₅ and AX₇, where both A and X are halogens. A is larger and more electropositive than X. As the size of the central atom (A) increases, the stability of the compound also increases.

Preparation

The interhalogen compounds can be prepared by the direct combination or by the action of halogen on lower interhalogen compounds.



Properties:

These are all covalent molecules and are diamagnetic in nature. They are volatile solids or liquids except ClF which is a gas at 298 K. Their physical properties are intermediate between those of constituent halogens. The interhalogen compounds are more reactive than halogens (except fluorine). This is because A–X bond in interhalogens is weaker than X–X bond in halogens except F–F bond.

The types of inter halogen compounds and their structures are as follows:

Type	Examples	Structure
AX	ClF, BrF, IF, BrCl, BrI	Linear
AX ₃	ClF ₃ , BrF ₃ , IF ₃ , ICl ₃ , IBr ₃ etc.	Bent T-shaped
AX ₅	ClF ₅ , BrF ₅ , IF ₅	Square pyramidal
AX ₇	IF ₇	Pentagonal bipyramidal

Uses: These compounds can be used as non aqueous solvents. Interhalogen compounds are very useful fluorinating agents.

Group 18 Elements

Group 18 consists of six elements- helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn). All these are gases and chemically unreactive. So they are called inert gases or noble gases.

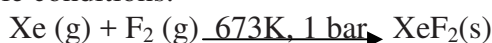
All noble gases have general electronic configuration ns^2np^6 (except helium which has $1s^2$). Due to stable electronic configuration these gases have very high ionisation enthalpy and electron gain enthalpy.

Even though these elements are chemically inert, Kr and Xe form some compounds with oxygen and fluorine under special conditions.

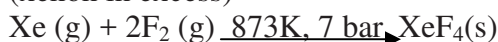
In noble gases, there is only weak van der Waals force of attraction. So they have low melting and boiling point.

(a) Xenon-fluorine compounds

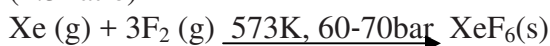
Xenon forms three binary fluorides, XeF_2 , XeF_4 and XeF_6 by the direct reaction of elements under suitable conditions.



(xenon in excess)

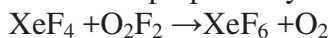


(1:5 ratio)



(1:20 ratio)

XeF_6 can also be prepared by the interaction of XeF_4 and O_2F_2 at 143K.

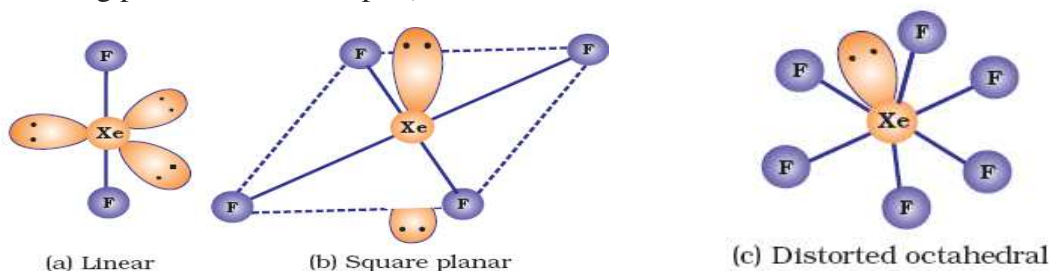


XeF_2 , XeF_4 and XeF_6 are colourless crystalline solids. They are powerful fluorinating agents. They are readily hydrolysed even by traces of water. For example, XeF_2 is hydrolysed to give Xe, HF and O_2 .



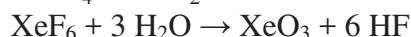
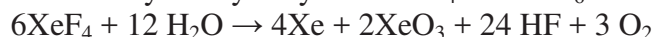
Structures

XeF_2 and XeF_4 have linear and square planar structures respectively. XeF_6 has seven electron pairs (6 bonding pairs and one lone pair) and thus, have a distorted octahedral structure

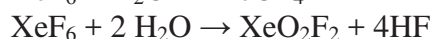
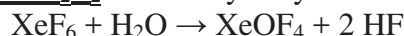


(b) Xenon-oxygen compounds

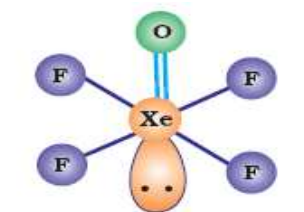
1. **XeO_3** : It is obtained by the hydrolysis of XeF_4 and XeF_6 with water.



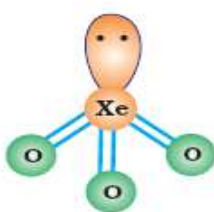
2. **XeOF_4 & XeO_2F_2** : Partial hydrolysis of XeF_6 gives oxyfluorides, XeOF_4 and XeO_2F_2 .



XeO_3 is a colourless explosive solid and has a pyramidal molecular structure. XeOF_4 is a colourless volatile liquid and has a square pyramidal molecular structure.

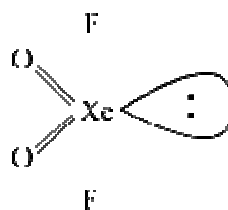


(d) Square pyramidal



(e) Pyramidal

Xenon dioxy difluoride



See saw structure

Uses of noble gases:

Helium is used in filling balloons for meteorological observations. It is also used in gas-cooled nuclear reactors. Liquid helium is used as cryogenic agent for carrying out various experiments at low temperatures. It is used as a diluent for oxygen in modern diving apparatus because of its very low solubility in blood.

Neon is used in discharge tubes and fluorescent bulbs for advertisement display purposes. Neon bulbs are used in botanical gardens and in green houses.

Argon is used to provide an inert atmosphere in high temperature metallurgical processes and for filling electric bulbs. It is also used in the laboratory for handling substances that are air-sensitive.

Xenon and Krypton are used in light bulbs designed for special purposes.

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