Class 12 Chemistry Chapter 7 p-Block elements

Group-15 Elements

- Group-15 is also known as pnictogens or nitrogen family. It contains nitrogen (N), phosphorous (P), arsenic (As), antimony (Sb), bismuth (Bi) and moscovium (Mc).
- As we move from up to down the group metallic characters increases. As N and P are non-metals, As and Sb are metalloids, Bi and Mc are metals.

Occurrence:

- 78% by volume of the atmosphere is comprises by molecular nitrogen.
- In the earth's crust, nitogen found as $NaNO_3$ or Chile saltpeter and KNO_3 or Indian saltpetre.
- Nitrogen in main component of amino acids.
- Phosphorous in main component of rocks, it is found as apatite i.e. fluorapatite.
- Phosphorous is present in bones as well as in tooth enamel. It is present in milk and eggs as phosphoprotein.
- As, Sb and Bi are found mainly as sulphide compounds in nature. Mc is a synthetic radioactive element with atomic number 115, atomic mass 289. It's half-life is very short.

Table: Atomic and Physical Properties of Group 15 Elements

Property	N	P	As	Sb	Bi
Atomic Number	7	15	33	51	83
Atomic mass/g mol^{-1}	14.01	30.97	74.92	121.75	208.98
Electronic configuration	$[He]2s^2 2p^3$	$[Ne]3s^2 3p^3$	$[Ar]3d^{10} 4s^2 4p^3$	$[Kr]4d^{10} 5s^2 5p^3$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^3$
Ionisation enthalpy-I	1402	1012	947	834	703
II	2856	1903	1798	1596	1610
III	4577	2910	2736	2443	2466
Electronegativity	3.0	2.1	2.0	1.9	1.9
Covalent radius	70	110	121	141	148

(pm^a)					
Ionic radius (pm)	171^b	212^b	222^b	76^b	102^b
Melting point (K)	63	317	1089	904	544
Boiling Point (K)	77.2	554	888	1860	1837
Density (g cm^{-3})	0.879	1.823	5.77	6.69	9.80

Electronic Configuration

- The valence shell electronic configuration of nitrogen family is $ns^2\ np^3$. The s-orbital is fully filled and p-orbitals are half-filled, which stabilize the electronic configuration.

Atomic and Ionic radius

- As we move down the group covalent and ionic radii increase in size. There is a significant increase in covalent radius from N to P.
- From Arsenic to Bismuth a small increase in covalent radius is noticed. This is owing to the presence of completely filled d or f orbitals in higher members.

Ionization enthalpy

- As we move down the group Ionisation enthalpy decreases due to gradual increase in atomic size. As a consequence of the extra stable half-filled p-orbitals electronic configuration and smaller size, the ionisation enthalpy of the group 15 elements is much greater than that of group 14 elements in the parallel periods.
- The order of successive ionisation enthalpies is $\Delta_iH_1 < \Delta_iH_2 < \Delta_iH_3$.

Electronegativity

- As we move down the group the electronegativity value decreases with increase in atomic size.

Physical properties

- All the elements of 15-group are polyatomic.
- N_2 is a diatomic gas while all others are solids. As we move down the group metallic character increases. N and P are non-metals, As and Sb

metalloids and Bi is a metal, because of decrease in ionisation enthalpy and increase in atomic size.

- The boiling points increase as we move from top to bottom in the group but the melting point increases up to As and then decreases up to Bi. All the elements show allotropy except N.

Chemical properties:

Oxidation states and trends in chemical reactivity

- The common oxidation states of Nitrogen family are –3, +3 and +5.
- The tendency to show -3 oxidation state decreases as we move down the group because of increase in size and metallic character.
- Bi barely forms any compound in –3 oxidation state.
- The stability of +5 oxidation state decreases as we move down the group. The only known Bi (V) compound is BiF_5. The stability +3 state increases due to inert pair effect as we move down the group.
- In addition to +5 oxidation state, nitrogen exhibits + 1, + 2, + 4 oxidation states also when it reacts with oxygen.
- Nitrogen does not have d-orbitals to accommodate electrons from other elements to form bonds so it does not form compounds in +5 oxidation state with halogens.
- Phosphorus also shows +1 and +4 oxidation states in some oxoacids.
- All oxidation states from +1 to +4 tend to disproportionate in acid solution in case of nitrogen.
- Example:

$$3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$$

- All intermediate oxidation states disproportionate into +5 and –3 both in alkali and acid in case of phosphorus.
- On the other hand +3 oxidation state in case of As, Sb and Bi becomes increasingly stable with respect to disproportionation.
- Nitrogen is restricted to a maximum covalency of 4 as only four i.e. one s and three p-orbitals are available for bonding.

- The heavy elements of group-15 have vacant d-orbitals in the outermost shell which is used for bonding and through this they can expand their covalence for example in PF^{-6}.

Anomalous properties of nitrogen

- Nitrogen is different from the rest of the members of 15-group due to having small size, high electronegativity, high ionisation enthalpy and unavailability of d-orbitals.
- Nitrogen has exceptional ability to form pπ-pπ multiple bonds with itself and with other elements having small size and high electronegativity (like C, O).
- Nitrogen exists as a diatomic molecule with a triple bond ($N\equiv N$) i.e. one sigma and two pie bond between the two atoms. Its bond enthalpy is 941.4 kJ mol–1 which is very high.
- Heavier elements of this group do not form pπ-pπ bonds as their atomic orbitals are so large and because of that they cannot have effective overlapping.
- On the other hand, phosphorus, arsenic and antimony form single bonds as P–P, As–As and Sb–Sb while Bi forms metallic bonds in elemental state.
- The single N–N bond is weaker than the single P–P bond because of high inter-electronic repulsion of the non-bonding electrons, due to the small bond length. Consequently the catenation tendency is weaker in nitrogen.
- Another reason which affects the chemistry of nitrogen is the absence of d-orbitals in its valence shell. Besides restricting its covalency to four, nitrogen cannot form dπ –pπ bond as the heavier elements can example: $R_3P = O$ or $R_3P = CH_2$ (here R is a alkyl group).
- P and As can make dπ –dπ bond with transition metals in case they act as ligands for example: $P(C_2H_5)_3$ and $As(C_6H_5)_3$.

1. Reactivity towards hydrogen:

- All the elements of nitrogen family form hydrides of the type EH_3 where E = N, P, As, Sb or Bi.

- The hydrides show regular progression in their properties. The stability of hydrides decreases from ammonium hydride to bismuth hydride by observing their bond dissociation enthalpy. As a result, the reducing character of the hydrides increases.
- Ammonia is a mild reducing agent while BiH_3 is the strongest reducing agent amongst all the hydrides.
- Basicity decreases in the order

  $$\mathbf{NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3}$$

  Due to high electronegativity and small size of nitrogen, NH_3 shows hydrogen bonding in both solid and liquid state. As a result of this, it has higher melting and boiling points than that of PH_3.

Table: Properties of Hydrides of Group-15 Elements

Property	**NH_3**	**PH_3**	**AsH_3**	**SbH_3**	**BiH_3**
M.p. (K)	195.2	139.5	156.7	185	-
B.p. (K)	238.5	185.5	210.6	254.6	290
(E-H) Distance (pm)	101.7	141.9	151.9	170.7	-
HEH Angle (°)	107.8	93.6	91.8	91.3	-
$\Delta_f H^\ominus$ (k J mol^{-1})	-46.1	13.4	66.4	145.1	278
$\Delta_{diss} H^\ominus$ (E-H)(k J mol^{-1})	389	322	297	255	-

2. Reactivity towards oxygen:
    - All 15 group's elements form two types of oxides: E_2O_3 and E_2O_5.
    - The oxides with higher oxidation state are more acidic than that of lower oxidation state. Their acidic character decreases as we move down the group.

- The oxides of the type E_2O_3 of nitrogen and phosphorus are purely acidic; arsenic and antimony are amphoteric and bismuth's oxides are mostly basic.

3. Reactivity towards halogens:

   - The group-15 elements react to form two series of halides: EX_3 and EX_5.
   - Nitrogen does not form pentahalide due to unavailability of the d-orbitals in its valence shell.
   - Pentahalides are more covalent than trihalides. Because in pentahalides +5 oxidation state exists while in the case of trihalides +3 oxidation state exists.
   - As elements in +5 oxidation state have high polarising power than in +3 oxidation state, the covalent character of bonds is more in pentahalides.
   - All the trihalides of group-15 elements except those of nitrogen are stable.
   - In case of nitrogen, only NF_3 is stable. Except for BiF_3 all trihalides are predominantly covalent in nature.

4. Reactivity towards metals:

   - All group-15 elements react with metals to form their binary compounds showing –3 oxidation state, for example: calcium nitride (Ca_3N_2), calcium phosphide (Ca_3P_2), sodium arsenide (Na3As), zinc antimonide (Zn_3Sb_2) and magnesium bismuthide (Mg_3Bi_2).

Dinitrogen (N_2)

Preparation:

- Dinitrogen is made by the liquefaction and fractional distillation of air.
- Liquid dinitrogen having boiling point77.2 K, first distils out leaving behind liquid oxygen which have boiling point 90 K.

- In the laboratory, N_2 is prepared by reaction of an aqueous solution of NH_4Cl with $NaNO_3$.

$$NH_4Cl\ (aq) + NaNO_2\ (aq) \rightarrow N_2\ (g) + 2H_2O(l) + NaCl\ (aq)$$

- Small amounts of nitric oxide and nitric acid formed as by product in reaction; these impurities are eliminated by passing the gas through aqueous sulphuric acid containing potassium dichromate.
- Ntrogen obtained by the thermal decomposition of $(NH_4)_2Cr_2O_7$.

$$(NH_4)_2C \quad \text{Heat} \qquad + 4H_2O + Cr_2O_3$$

- Very pure nitrogen is prepared by the thermal decomposition of sodium or barium azide.

$$Ba(N_3)_2 \rightarrow Ba + 3N_2$$

Properties:

- Dinitrogen (N_2) is a colourless, odourless, tasteless and non-toxic gas.
- There are two stable isotopes of it : ^{14}N and ^{15}N.
- It has a less solubility in water and low f.p. and b.p.
- It is inert at room temperature because of the high bond energy of N≡N bond.
- It's reactivity increase rapidly with rising the temperature. At higher temperatures, it readily combines with some metals to form mainly ionic nitrides and with non-metals, covalent nitrides. A few reactions are as follows:

$$6Li + N_2 \xrightarrow{\text{Heat}} 2Li_3N$$

$$3Mg + N_2 \xrightarrow{\text{Heat}} Mg_3N_2$$

- Dinitrogen combines with hydrogen at about 773 K in the presence of a catalyst to form ammonia which is known as Haber's Process:

773 K

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g);\ \Delta_f H^{\ominus} = -46.1\ kJmol^{-1}$$

- N_2 combines with O_2 at very high temperature) to form nitric oxide, NO.

$$N_2 + O_2(g) \overset{Heat}{\rightleftharpoons} 2NO\,(g)$$

Uses:

- The main use of N_2 is in the manufacture of ammonia and other industrial chemicals containing nitrogen such as calcium cyanamide.
- It is used to create an inert atmosphere (example in iron and steel industry, inert diluent for reactive chemicals).
- Liquid N_2 is used as a refrigerant to preserve biological materials, food items and in cryosurgery.

Ammonia

Preparation:

- NH_3 is present in slight amount in air and soil where it is formed by the decay of nitrogenous organic matter. Example: urea.

$$NH_2CONH_2 + 2H_2O \rightarrow (NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$$

- On small scale ammonia can be prepared from ammonium salts which decompose on treating with caustic soda or $Ca(OH)_2$.

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + 2H_2O + CaCl_2$$
$$(NH_4)_2SO4 + 2NaOH \rightarrow 2NH_3 + 2H_2O + Na_2SO_4$$

- on a large scale ammonia is manufactured by Haber's process.

$$N_2(g) + 3H\,(g) \rightleftharpoons 2NH_3\,(g);\ \Delta_f H^{\ominus} = -46.1\ kJ\ mol^{-1}$$

- According to Le Chatelier's principle, high pressure favours the ammonia formation. The optimum conditions are a pressure of 200 × 105 Pa, a temperature of approximately 700 K and the use of a catalyst such as

FeO with small amounts of K_2O and Al_2O_3 to increase the rate of achievement of equilibrium.

- Previously, Fe was used as a catalyst with Mo as a promoter.

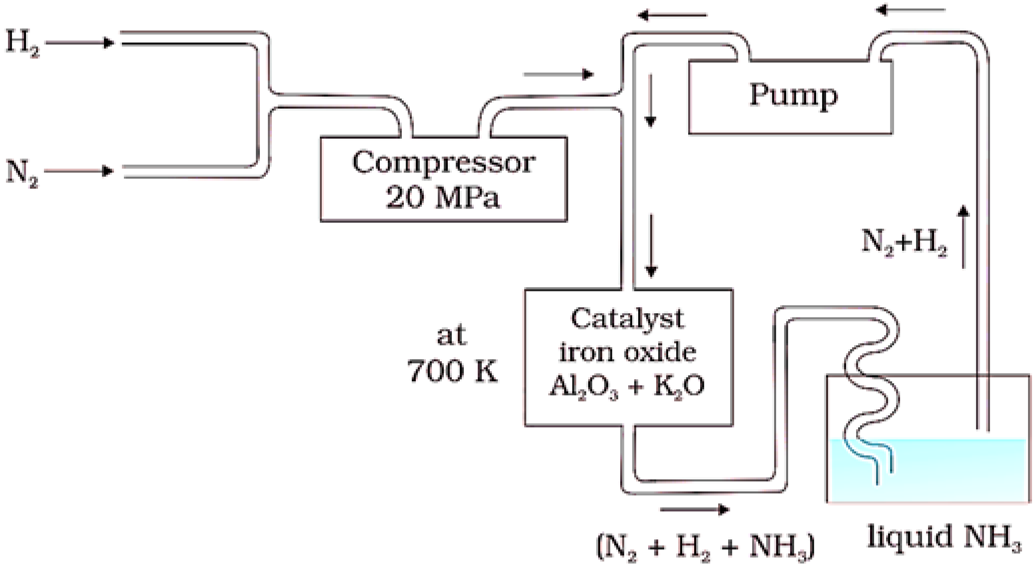


Figure: Flow chart for the manufacture of ammonia

Properties:

- NH_3 is a colourless gas with a pungent odour.
- The freezing and boiling points are 198.4 and 239.7 K respectively.
- In the solid and liquid states, it is linked by hydrogen bonds as in the case of water and which is responsible for its higher m.p. and b.p.
- It is trigonal pyramidal and the nitrogen atom at the apex. Ammonia has three bond pairs and one lone pair of electrons.

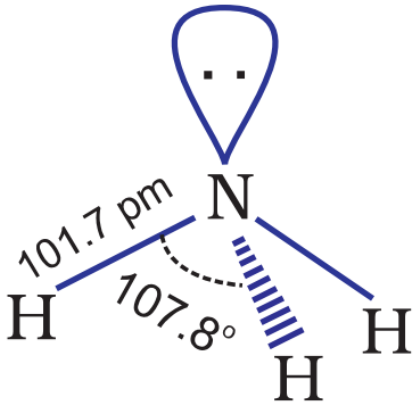


Figure: structure of ammonia

- Ammonia gas is highly soluble in water. Its aqueous solution is weakly basic due to the generation of OH^- ions.

$$NH_3\,(g) + H_2O(l) \rightleftharpoons NH_4^+\,(aq) + OH^-(aq)$$

- With acids ammonia makes ammonium salts, example: NH_4Cl, $(NH_4)_2SO_4$. As a weak base, it precipitates the hydroxides of many metals from their salt solutions. Examples:

$$ZnSO_4\,(aq) + 2NH_4OH\,(aq) \rightarrow Zn(OH)_2\,(s) + (NH_4)_2SO_4\,(aq)$$

(White ppt)

$$FeCl_3\,(aq) + NH_4OH\,(aq) \rightarrow Fe_2O_3.\,X\,H_2O\,(s) + NH_4Cl\,(aq)$$

(Brown ppt)

- Ammonia is a Lewis base due to presence of a lone pair of electrons on the nitrogen atom.
- It donates the electron pair and forms linkage with metal ions and the formation of such complex compounds used in detection of metal ions for example: Cu^{2+}, Ag^+ :

$$Cu^{2+}\,(aq) + 4NH_3\,(aq) \rightleftharpoons [Cu(NH_3)_4\,]^{2+}(aq)$$

(blue) (deep blue)

$$Ag^+\,(aq) + Cl^-\,(aq) \rightarrow AgCl\,(s)$$

(colourless) (white ppt)

$$AgCl\,(s) + 2NH_3\,(aq) \rightarrow [Ag(NH_3)_2]Cl\,(aq)$$

(white ppt) (colourless)

Uses:

- Ammonia is used to produce various nitrogenous fertilisers such as ammonium nitrate, urea, ammonium phosphate and ammonium sulphate, etc.

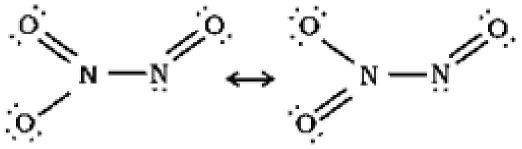
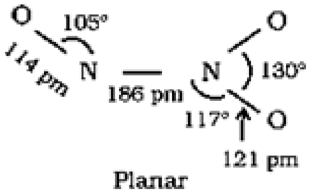
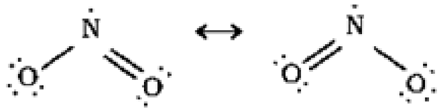
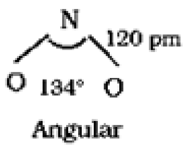
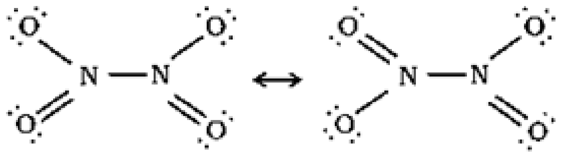
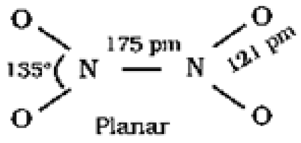
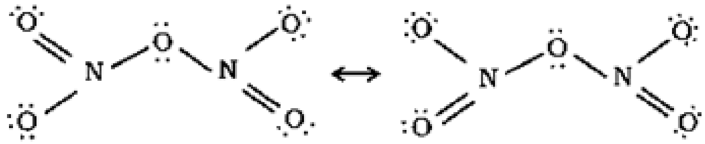
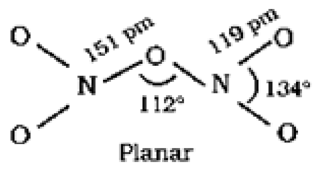
- It is used in the manufacture of some inorganic nitrogen compounds, the most important one being HNO_3.
- Liquid ammonia is as used as a refrigerant.

Oxides of nitrogen

Table: Oxides of nitrogen

Name	Formula	Oxidation state of nitrogen	Methods of preparation	Physical appearance and chemical nature
Dinitrogen oxide	N_2O	+1	$NH_4NO_3 \xrightarrow{Heat} NO_2 + 2H_2O$	Colourless gas, Neutral
Nitrogen monoxide	NO	+2	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$	Colourless gas, neutral
Dinitrogen trioxide	N_2O_3	+3	$2NO + N_2O_4 \xrightarrow{250\,K} 2N_2O_3$	Blue solid, acidic
Nitrogen dioxide	NO_2	+4	$2Pb(NO_3)_2 \xrightarrow{673K} 4NO_2 + 2PbO + O_2$	Brown gas, Acidic
Dinitrogen tetroxide	N_2O_4	+4	$2NO_2 \underset{Heat}{\overset{Cool}{\rightleftharpoons}} N_2O_4$	Colorless solid/ liquid, acidic
Dinitrogen pentoxide	N_2O_5	+5	$4HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + 2N_2O_5$	Colorless solid, acidic

Table: Structure of oxides of nitrogen

Formula	Resonance Structures	Bond Parameters
N_2O	$\ddot{N}=N=\ddot{O} \longleftrightarrow :N\equiv N-\ddot{O}:$	N − N − O 113 pm 119 pm Linear
NO	$:N=\ddot{O}: \longleftrightarrow :\dot{N}=\ddot{O}:$	N − O 115 pm
N_2O_3		
NO_2		
N_2O_4		
N_2O_5		

Nitric acid

- Nitrogen forms oxoacids. Examples: $H_2N_2O_2$, HNO_2 and HNO_3.

Preparation

- In the laboratory, HNO_3 is prepared by heating KNO_3 or $NaNO_3$ and conc. Sulphuric acid in a glass retort.

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$

- On a large scale nitric acid is prepared mostly by Ostwald's process. Ostwald's process is based on catalytic oxidation of NH_3 by atmospheric oxygen.

$$4NH_3(g) + \underset{\text{(from air)}}{5O_2(g)} \xrightarrow[\text{500 K, 9 bar}]{\text{Pt / Rh gauge catalyst}} 4NO(g) + 6H_2O(g)$$

- Nitric oxide thus formed reacts with oxygen giving NO_2.

$$2NO\ (g) + O_2\ (g) \rightleftharpoons 2NO_2\ (g)$$

- NO_2 reacts with H_2O and form HNO_3.

$$3NO_2\ (g) + H_2O\ (l) \rightarrow 2HNO_3\ (aq) + NO\ (g)$$

- Thus formed NO is recycled and the aqueous HNO_3 can be concentrated by distillation upto approximately 68% by mass.
- Further concentration to 98% can be achieved by dehydration with concentrated sulphuric acid.

Properties:

- It is a colourless liquid which have f.p. 231.4 K and b.p. 355.6 K.
- Laboratory grade HNO_3 contains approximately 68% of the HNO_3 by mass.

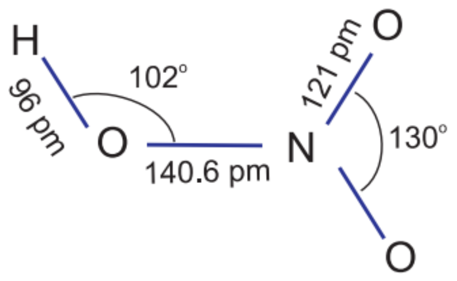


Figure: Structure of nitric acid

- It has a specific gravity of 1.504. In the gaseous state, nitric acid exists as a planar molecule. In aqueous solution, HNO_3 behaves as a strong acid giving H_3O^+ ion and NO_3^- ions.

$$HNO_3\ (aq) + H_2O\ (l) \rightarrow H_3O^+\ (aq) + NO_3^-\ (aq)$$

- Conc. HNO_3 is a strong oxidising agent and attacks most metals except noble metals such as Au and Pt.

$$3Cu + 8HNO_3\ (dil) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$Cu + 4HNO_3\ (conc.) \rightarrow 3Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

- Zn reacts with dil. $HNO_3$to give N_2O and with concentrated acid to give NO_2.

$$4Zn + 10HNO_3(dilute) \rightarrow 4\ Zn\ (NO_3)_2 + 5H_2O + N_2O$$

$$Zn + 4HNO_3(conc.) \rightarrow Zn\ (NO_3)_2 + 2H_2O + 2NO_2$$

- Some metals like chromium, aluminium do not dissolve in conc. HNO_3 because of the formation of a passive film of oxide on the surface of metal. Concentrated nitric acid also oxidises non–metals.
- Iodine is oxidised to iodic acid, carbon to CO_2, sulphur to sulphuric acid and phosphorus to phosphoric acid.

$$I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

$$C + 4HNO_3 \rightarrow CO_2 + 2H_2O + 4NO_2$$

$$S_8 + 48HNO_3 \rightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$$

$$P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

- **Brown Ring Test:** The familiar brown ring test for nitrates depends on the ability of Fe^{2+} to reduce nitrates to nitric oxide, which reacts with Fe^{2+} to form a brown coloured complex.
- The test is usually carried out by adding dil. ferrous sulphate solution to an aqueous solution containing nitrate ion, and then carefully adding concentrated H_2SO_4 along the sides of the test tube.
- A brown ring generation at interface between sulphuric acid and the solution layers indicates the presence of nitrate ion in solution.

$$NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow NO + 3Fe^{3+} + 2H_2O$$

$$[Fe(H_2O)_6]^{2+} + NO \rightarrow \underset{\text{(brown)}}{[Fe\ (H_2O)_5\ (NO)]^{2+}} + H_2O$$

Uses:

- The main use of HNO_3 is in the manufacture of ammonium nitrate for fertilisers and other nitrates for use in explosives and pyrotechnics.
- HNO_3 is used for the preparation of trinitrotoluene.
- It is used in etching of metals and pickling of stainless steel, and as an oxidising agent in rocket fuels.

Phosphorous allotropic forms

- Phosphorus is found in various allotropic forms, the important ones being white, red and black.
- **White phosphorus**: it is a translucent white waxy solid. It consists of discrete tetrahedral P_4-molecule.

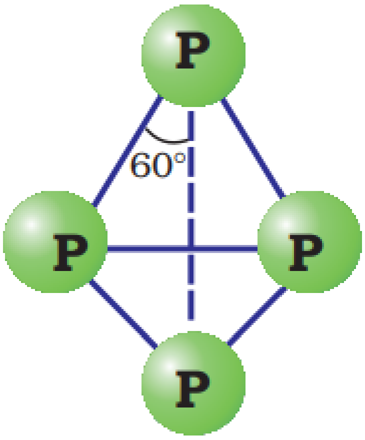


Figure: White phosphorous

- It is poisonous, insoluble in water but soluble in CS_2 and glows in dark. It dissolves in boiling sodium hydroxide solution in an inert atmosphere giving PH_3.

$$P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$$

(sodium hypophosphite)

- White phosphorus is less stable and it is very reactive because of angular strain in the P_4 molecule where the angles are only 60°. It tends to catch fire readily in air to give dense white fumes of P_4O_{10}.

$$P_4 + 5O_2 \rightarrow P_4O_{10}$$

- **Red phosphorus**: It is preparaed by heating white phosphorus at 573K in an inert atmosphere for several days.
- When red P is heated under high pressure black phosphorus is formed.
- It possesses iron grey lustre. It is odourless, non-poisonous and insoluble in water as well as in CS_2.

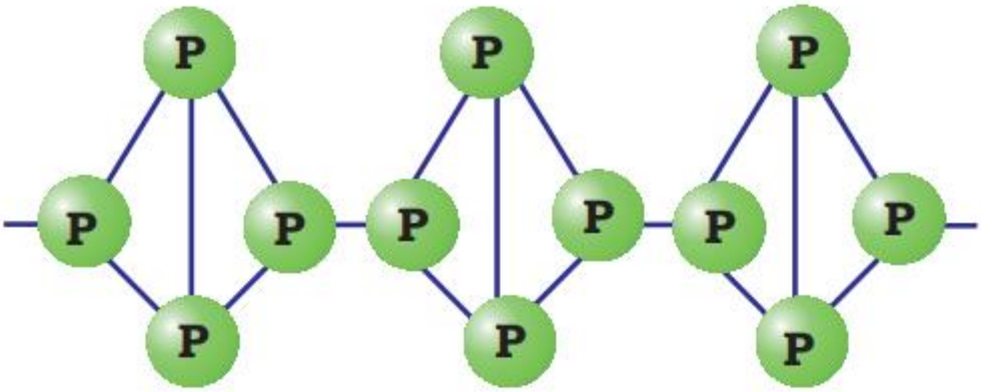


Figure: Red phosphorous

- Chemically, red P is less reactive than white phosphorus.
- It does not glow in the dark. It is polymeric and consist of chains of P_4 tetrahedral linked together.
- **Black phosphorus**:
- Black phosphorus has two forms α and β-black phosphorus.
- α-Black phosphorus is preparaed by heating red phosphorus in a sealed tube at 803K.
- It can be sublimed in air and it has opaque monoclinic or rhombohedral crystals.
- It does not oxidise in air.
- When white phosphorus is heated at 473 K under high pressure β-Black phosphorus forms.

Phosphine

Preparation:

- Phosphine is prepared by the reaction of calcium phosphide with water or dil. Hydrochloric acid.

$$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$$
$$Ca_3P_2 + 6HCl \rightarrow 3CaCl_2 + 2PH_3$$

- Phosphine is prepared by heating white phosphorus with conc. NaOH solution in presence of CO_2.

$$P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + \underset{\text{(sodium hypophosphite)}}{3NaH_2PO_2}$$

- In pureest form it is non-inflammable but becomes inflammable due to the presence of P_2H_4 or P_4 vapours.
- To purify it is absorbed in HI to form phosphonium iodide (PH_4I) which on treating with KOH gives off phosphine.

$$PH_4I + KOH \rightarrow KI + H_2O + PH_3$$

Properties:

- It is a colourless gas with rotten fish smell and it is highly poisonous.
- Phosphine explodes in contact with contact of nitric acid, chlorine and bromine vapours.
- It is slightly soluble in water. The solution of PH_3 in water decomposes in presence of light and gives red phosphorus and H_2 gas.
- When it is absorbed in $CuSO_4$ or $HgCl_2$ solution, the corresponding phosphides are obtained.

$$3CuSO_4 + 2PH_3 \rightarrow Cu_3P_2 + 3H_2SO_4$$

$$3HgCl_2 + 2PH_3 \rightarrow Hg_3P_2 + 6HCl$$

- Phosphine is weakly basic and gives phosphonium compounds with acids, example:

$$PH_3 + HBr \rightarrow PH_4Br$$

Uses:

- Containers containing CaC_2 and Ca_3P_2 are sliced and thrown in the sea when the gases evolved burn and serve as a signal.

Phosphorus trichloride

- Phosphorus forms two types of halides:
  1. PX_3 (here X = F, Cl, Br, I)
  2. PX_5 (here X = F, Cl, Br).

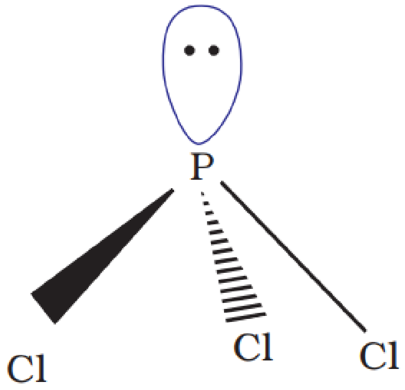


Figure: Phosphorus trichloride

Preparation:

- It is prepared by passing dry Cl_2 over heated white phosphorus.

$$P_4 + 6Cl_2 \rightarrow 4PCl_3$$

- It is prepared by the reaction of $SOCl_2$ with white phosphorus.

$$P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_3 + 2S_2Cl_2$$

Properties:

- It is an oily liquid and which hydrolyses in moisture.

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

- It reacts with organic compounds containing –OH group such as CH_3COOH, C_2H_5OH.

$$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$$
$$3C_2H_5OH + PCl_3 \rightarrow 3C_2H_5Cl + H_3PO_3$$

Phosphorous pentachloride

- It has a pyramidal shape and phosphorus is sp^3 hybridised.

Preparation:

- PCl_5 can be produced by the reaction of white phosphorus with excess of dry chlorine.

$$P_4 + 10Cl_2 \rightarrow 4 PCl_5$$

- PCl_5 is prepared by the reaction of SO_2Cl_2 and phosphorus.

$$P_4 + 10SO_2Cl_2 \rightarrow 4PCl_5 + 10SO_2$$

Properties:

- Phosphorous pentachloride is a yellowish white powder and it hydrolyses to $POCl_3$ in moist air and finally gets converted to phosphoric acid.

$$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$$
$$POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$$

- It sublimes on heating but decomposes on stronger heating.

$$PCl_5 \xrightarrow{\text{Heat}} PCl_3 + Cl_2$$

- It reacts with compounds containing hydroxyl group converting them to chloro-derivatives.

$$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$$

$$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$$

- Metal powder on heating with PCl_5 gives chlorides.

$$2Ag + PCl_5 \rightarrow 2AgCl + PCl_3$$

$$Sn + 2PCl_5 \rightarrow SnCl_4 + 2PCl_3$$

- It is used in the synthesis of some organic compounds, for example C_2H_5Cl, CH_3COCl.

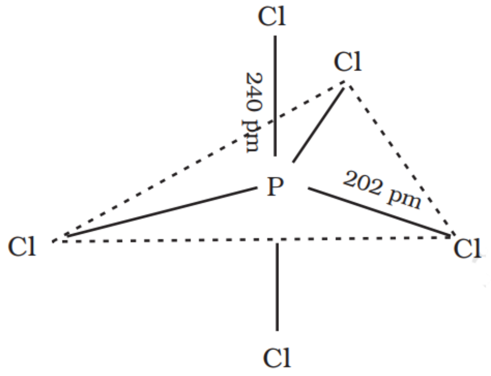


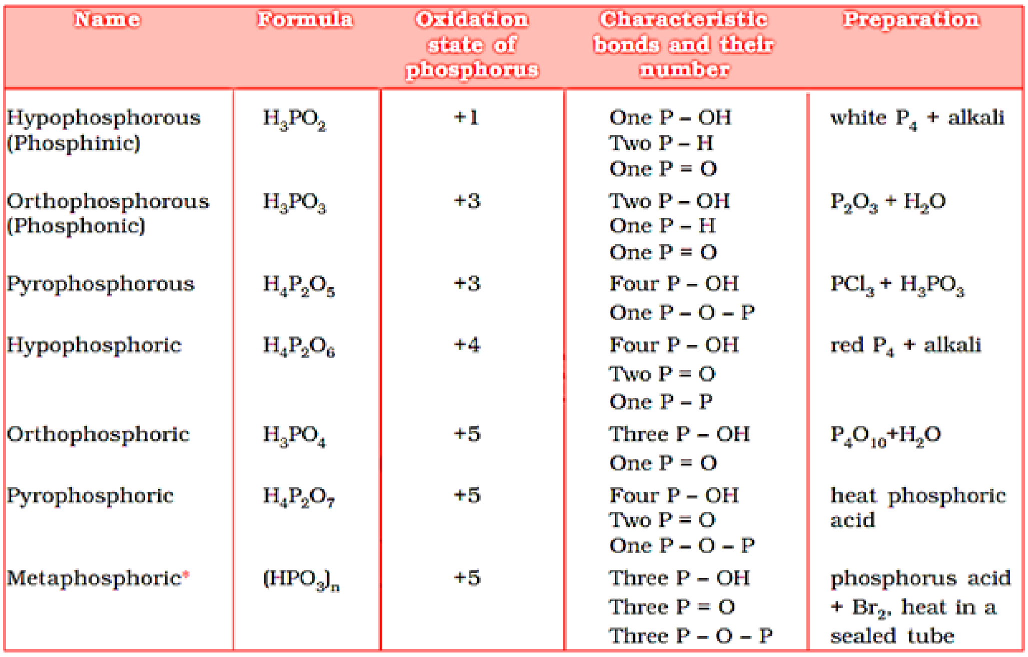
Figure: phosphorous pentachloride

- It has a trigonal bipyramidal structure In gaseous and liquid phases,.
- The three equatorial P–Cl bonds are equivalent, and axial bond pairs suffer more repulsion as compared to equatorial bond pairs so two axial bonds are longer than equatorial bonds.

Oxoacids of phosphorous

- Phosphorus makes different type of oxoacids.
- The important oxoacids of phosphorus with their formulas, methods of preparation and the presence of some characteristic bonds in their structures are as follosw:

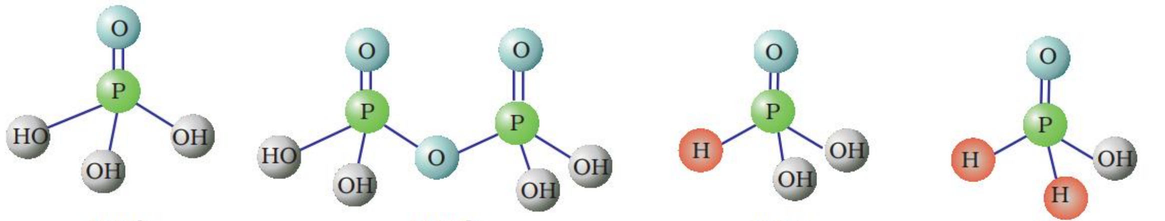
Table: Oxoacids of phosphorous



Name	Formula	Oxidation state of phosphorus	Characteristic bonds and their number	Preparation
Hypophosphorous (Phosphinic)	H_3PO_2	+1	One P – OH Two P – H One P = O	white P_4 + alkali
Orthophosphorous (Phosphonic)	H_3PO_3	+3	Two P – OH One P – H One P = O	$P_2O_3 + H_2O$
Pyrophosphorous	$H_4P_2O_5$	+3	Four P – OH One P – O – P	$PCl_3 + H_3PO_3$
Hypophosphoric	$H_4P_2O_6$	+4	Four P – OH Two P = O One P – P	red P_4 + alkali
Orthophosphoric	H_3PO_4	+5	Three P – OH One P = O	P_4O_{10}+H_2O
Pyrophosphoric	$H_4P_2O_7$	+5	Four P – OH Two P = O One P – O – P	heat phosphoric acid
Metaphosphoric*	$(HPO_3)_n$	+5	Three P – OH Three P = O Three P – O – P	phosphorus acid + Br_2, heat in a sealed tube

- The compositions of the oxoacids are interrelated in terms of loss or gain of water molecule or O-atom.
- In oxoacids phosphorus is in Td geometry, surrounded by other atoms.
- All oxoacids contain at least one P=O bond and one P–OH bond.
- The oxoacids has P=O and P–OH bonds, either P–P (example: $H_4P_2O_6$) or P–H (example: H_3PO_2) bonds but not both.
- These acids in +3 oxidation state of phosphorus tend to disproportionate to higher and lower oxidation states. Eg.: ortho-phophorous acid on heating disproportionates to give ortho-phosphoric acid and phosphine.

$$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$$

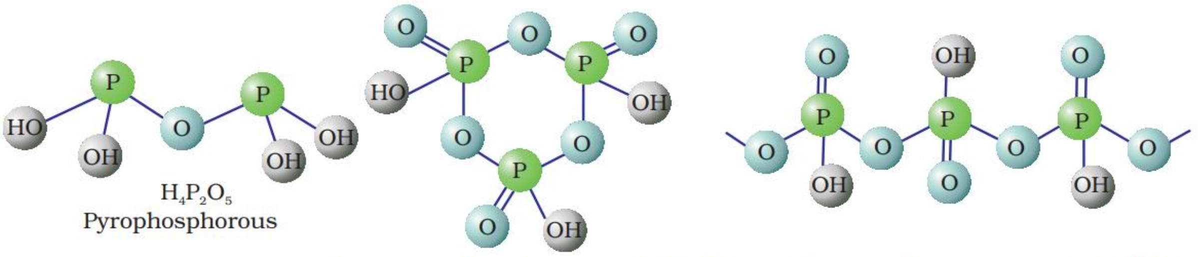


H_3PO_4 Orthophosphoric acid

$H_4P_2O_7$ Pyrophosphoric acid

H_3PO_3 Orthophosphorous acid

H_3PO_2 Hypophosphorous acid



$H_4P_2O_5$ Pyrophosphorous

Cyclotrimetaphosphoric acid, $(HPO_3)_3$

Polymetaphosphoric acid, $(HPO_3)_n$

Figure: structures of some important oxoacids of phosphorus

- The acids with P–H bond have strong reducing properties.
- Hypo-phosphorous acid is a good reducing agent as it contains two P–H bonds and reduces, for example, $AgNO_3$ to metallic Ag.

$$4\ AgNO_3 + 2H_2O + H_3PO_2 \rightarrow 4Ag + 4HNO_3 + H_3PO_4$$

- These P–H bonds are not ionisable to give H^+ and do not play any role in basicity.
- H_3PO_3 is dibasic and H_3PO_4 is tribasic, as the structure of H_3PO_3 has two P–OH bonds and H_3PO_4 three P-OH bonds.

Group-16 elements

- Oxygen (O), sulphur (S), selenium (Se), tellurium (Te), polonium (Po) and livermorium (Lv) constitute Group 16 of the periodic table.
- Group-16 elements are recognized as group of chalcogens.

Occurrence

- Oxygen is the most abundant on earth.
- Oxygen contributes about 46.6% by mass of earth's crust.
- Dry air contains 20.94% O_2 by volume.
- The abundance of sulphur in the earth's crust is only 0.03-0.1%.
- Sulphur exists primarily as sulphates, for example: gypsum ($CaSO_4 .2H_2O$), baryte ($BaSO_4$) and sulphides such as galena (PbS), zinc blende (ZnS), epsom salt ($MgSO_4 .7H_2O$), and copper pyrites ($CuFeS_2$).
- Traces of sulphur occur as H_2S in volcanoes.
- Organic materials such as proteins, garlic, mustard, onion, hair and wool contain sulphur.
- Se and Te are also found as metal selenides and tellurides in sulphide ores.
- Po occurs in nature as a decay product of thorium (Th) and uranium (U) minerals.
- Lv is a synthetic radioactive element and the atomic number is 116, atomic mass 292.
- Lv has been produced only in a very small amount and has very short half-life. This limits the proper study of Lv.

Table: Some Physical Properties of Group 16 Elements

Property	O	S	Se	Te	Po
Atomic Number	8	16	34	52	84
Atomic mass (g mol^{-1})	16.00	32.06	78.96	127.60	210.00
Electronic configuration	$[He]2s^22p^4$	$[Ne]3s^23p^4$	$[Ar]3d^{10}4s^24p^4$	$[Kr]4d^{10}5s^25p^4$	$[Xe]4f^{14}5d^{10}6s^26p^4$
Covalent radius (pm)^a	66	104	117	137	146
Ionic radius,	140	184	198	221	230

E^{2-} (pm)					
Electron gain enthalpy $\Delta_{eg}H$ kJ mol^{-1}	-141	-200	-195	-190	-174
Ionisation enthalpy (Δ_iH_1) (kJ mol^{-1})	1314	1000	941	869	813
Electronegativity	3.50	2.58	2.55	2.01	1.76
Density (g cm^{-3}) (298 K)	1.32	2.06	4.19	6.25	-
Melting point (K)	55	393	490	725	520
Boiling point (K)	90	718	958	1260	1235
Oxidation states	-2,-1,1,2	-2,2,4,6	-2,2,4,6	-2,2,4,6	2,4

Electronic configuration

- The elements of Group-16 have 6 e$^-$ in the outermost shell and have ns^2 np^4 general electronic configuration.

Atomic and ionic radii

- Due to increase in the number of shells, atomic and ionic radii increase as we move from top to bottom in the group.

Ionisation enthalpy

- Ionisation enthalpy decreases as we move down the group because of increase in size.
- The elements of this group have lower ionisation enthalpy values compared to those of Group-15 in the corresponding periods as Group-15 elements have extra stable half-filled p-orbitals electronic configurations.

Electronegativity

- Oxygen has very high electronegativity value.
- In the group-16, electronegativity decreases with an increase in atomic number. This indicates that the metallic character increases as we move from oxygen to polonium.

Physical properties

- O and Sr are non-metals, Se and Te metalloids, whereas Po is a metal.
- Polonium is radioactive and half-life is 13.8 days.
- All these elements show allotropy.
- The m.p. and b.p. increase with an increase in atomic number as we move down the group.
- The large difference between the m.p. and b.p. of oxygen and sulphur can be explained on the basis of their atomicity; oxygen exists as diatomic molecule (O_2) whereas sulphur exists as polyatomic molecule (S_8).

Chemical property

Oxidation states and trends in chemical reactivity

- The elements of Group-16 show different oxidation states.
- The oxidation state -2 shown by these elements, and its stability decreases down the group.
- Po barely shows –2 oxidation state.
- The electronegativity of oxygen is very high, it shows only negative oxidation state as –2 except in the case of OF_2 where its oxidation state is +2.
- Other elements of the group exhibit + 2, + 4, + 6 oxidation states but + 4 and + 6 are more common.
- S, Se and Te usually show +4 oxidation state in their compounds with oxygen and +6 with fluorine.
- The stability of +6 oxidation state decreases as we move down the group and stability of +4 oxidation state increases due to inert pair effect.
- Bonding in +4 and +6 oxidation states is mainly covalent.

Anomalous behaviour of oxygen

- The anomalous behaviour of oxygen, like other members of p-block present in II period is due to its high electronegativity and small size.
- One typical example of effects of small size and high electronegativity is the presence of strong hydrogen bonding in H_2O which is not exists in H_2S.
- The absence of d-orbitals in oxygen limits its covalency to four and hardly exceeds two.
- In case of other elements of the group-16, the valence shells can be expanded and covalence exceeds four.

i) Reactivity with hydrogen:

- Group-16 elements form hydrides of the type H_2E.
- Their acidic character increases as we move from H_2O to H_2Te.
- The increase in acidic character is explained in terms of decrease in bond enthalpy for the dissociation of H–E bond as we move down the group.
- Because of the decrease in enthalpy for the dissociation of H–E bond down the group, the thermal stability of hydrides also decreases as we move from H_2O to H_2Po.
- All the hydrides except H_2O possess reducing property and this character increases from H_2S to H_2Te.

Table: Properties of Hydrides of Group 16 Elements

Property	**H_2O**	**H_2S**	**H_2Se**	**H_2Te**
m.p.(K)	273	188	208	222
b.p. (K)	373	213	232	269
H-E distance (pm)	96	134	146	169
HEH angle (°)	104	92	91	90
Δ_f H(kJ mol^{-1})	-286	-20	73	100
Δ_{diss} H (H–E)(kJ mol^{-1})	463	347	276	238
Dissociation constant	1.8×10^{-16}	1.3×10^{-7}	1.3×10^{-4}	2.3×10^{-3}

ii) Reactivity with oxygen:

- Allgroup-16 elements form oxides of the EO_2 and EO_3 types.
- Ozone (O_3) and sulphur dioxide are gases while selenium dioxide is solid.
- Reducing property of dioxide decreases from SO_2 to TeO_2.
- Besides EO_2 type, S, Se and Te also form EO_3 type oxides which are SO_3, SeO_3, TeO_3. These oxides are acidic in nature.

iii) Reactivity towards the halogens:

- Elements of Group-16 form a large number of halides of the type, EX_6, EX_4 and EX_2 ; here E = element of the group and X = halogen.
- The stability of the halides decreases in the order:

$$\mathbf{F^- > Cl^- > Br^- > I^-}$$

- Hexa fluorides are the only stable halides amongst hexa halides,.
- All hexa fluorides are gaseous in nature. They have octahedral structure. SF_6 is remarkably stable for steric reasons.
- Amongst tetrafluorides, SF_4 is a gas, SeF_4 is a liquid and TeF_4 is a solid.
- This geometry is termed as see-saw geometry.
- All elements except oxygen form dichlorides and dibromides. These dihalides are formed by sp^3-hybridisation and thus, have Td structure. The famous monohalides are dimeric in nature.
- Examples: S_2F_2, S_2Cl_2, S_2Br_2, Se_2Cl_2 and Se_2Br_2. The disproportionation reaction of these is as follows:

$$2Se_2Cl_2 \rightarrow SeCl_4 + 3Se$$

Dioxygen

Preparation

- O_2 is obtained in the laboratory by the following ways:

1. On heating the oxygen containing salts such as chlorates, nitrates and permanganates.

$$2KClO_3 \xrightarrow[MnO_2]{Heat} 2KCl + 3O_2$$

2. By thermal decomposition of the metal oxides :

$$2Ag_2O\ (s) \rightarrow 4Ag\ (s) + O_2\ (g)$$
$$2HgO\ (s) \rightarrow 2Hg\ (l) + O_2\ (g)$$
$$2Pb_3O_4\ (s) \rightarrow 6PbO\ (s) + O_2\ (g)$$
$$2PbO_2\ (s) \rightarrow 2PbO\ (s) + O_2\ (g)$$

3. Hydrogen peroxide is readily decomposed into H_2O and O_2 by catalysts such as powdered metals and MnO_2.

$$2H_2O_2\ (aq) \rightarrow 2H_2O(l) + O_2\ (g)$$

- On large scale oxygen is prepared from water or air. Electrolysis of H_2O leads to the release of H_2 gas at the cathode and oxygen at the anode.

Properties

- O_2 is a colourless and odourless gas.
- Its solubility in water is to the extent of 3.08 cm^3 in 100 cm^3 water at 293 K which is sufficient for the vital support of marine and aquatic life.
- O_2 liquefies at 90 K and freezes at 55 K.
- Oxygen atom has three stable isotopes: ^{16}O, ^{17}O and ^{18}O.
- Dioxygen directly reacts with nearly all metals and non-metals except some metals (e.g., gold, platinum) and some noble gases.
- Some of the combustion reactions of dioxygen with metals, non-metals and other compounds are given below:

$$2Ca + O_2 \rightarrow 2CaO$$
$$4Al + 3O_2 \rightarrow 2Al_2O_3$$
$$P_4 + 5O_2 \rightarrow P_4O_{10}$$
$$C + O_2 \rightarrow CO_2$$
$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$
$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

- Some compounds are catalytically oxidised. For example:

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$
$$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$

Uses:

- Oxygen is used in oxyacetylene welding, in the manufacture of many metals, particularly steel.
- Oxygen cylinders are widely used in hospitals, high altitude flying and in mountaineering.
- The combustion of fuels, example: hydrazines in liquid oxygen, provides tremendous thrust in rockets.

Simple oxide

- A binary compound of an element and oxygen is known as oxide. O_2 reacts with all elements of the periodic table and form oxides.
- Oxides can be simple for example: MgO, Al_2O_3 or mixed (Pb_3O_4, Fe_3O_4.
- Simple oxides can be classified in acidic, basic or amphoteric oxides.
- An oxide that combines with water to give an acid is termed acidic oxide (example: SO_2, Cl_2O_7, CO_2, N_2O_5). The SO_2 combines with water to give H_2SO_3, an acid.

$$SO_2 + H_2O \rightarrow H_2SO_3$$

- When a oxide gives a base with water is termed as basic oxides (e.g., Na_2O, CaO, BaO).
- Calcium oxide combines with H_2O and gives $Ca(OH)_2$.

$$CaO + H_2O \rightarrow Ca(OH)_2$$

- Generally metallic oxides are basic but some show dual behaviour. Such oxides are known as amphoteric oxides. Example: Al_2O_3, which reacts with acids as well as alkalies.

$$Al_2O_3\,(s) + 6HCl\,(aq) + 9H_2O\,(l) \rightarrow 2[Al(H_2O)_6]^{3+}\,(aq) + 6Cl^-\,(aq)$$
$$Al_2O_3\,(s) + 6NaOH\,(aq) + 3H_2O\,(l) \rightarrow 2Na_3[Al(OH)_6](aq)$$

- Some oxides are neither acidic nor basic. Such oxides are known as neutral oxides. Examples: CO, NO and N_2O.

Ozone

- Ozone is an allotropic form of oxygen.

- Ozone is formed from atmospheric oxygen in the presence of sunlight at the height of 20 kilometres,.
- The earth's surface is protected by ozone layer from an excessive concentration of ultraviolet (UV) radiations.

Preparation

- When oxygen is passed through an electrical discharge, conversion of oxygen into ozone happens. The product is ozonised oxygen.

$$3O_2 \rightarrow 2O_3;\ \Delta H^{\ominus}(298\text{ K}) = +142\text{ kJ mol}^{-1}$$

- The formation of O_3 from O_2 is an endothermic process.
- If concentrations of $O_3 > 10\%$ are required, a battery of ozonisers can be used, and pure ozone is condensed in a vessel surrounded by liquid O_2.

Properties

- O_3 is a pale blue gas, dark blue in liquid state and violet-black in solid state. O_3 has a distinctive smell.
- If the concentration > 100 ppm, breathing becomes uncomfortable and causes headache or nausea.
- Ozone is thermodynamically unstable with respect to oxygen since its decomposition into oxygen results in the liberation of heat (ΔH = -ve) and an increase in entropy (ΔS = +ve).
- These two effects reinforce each other, resulting ΔG = –ve for its conversion into oxygen. O_3 in high concentration is explosive.
- Due to the ease with which it liberates atoms of nascent oxygen ($O_3 \rightarrow O_2 + O$), it acts as a powerful oxidising agent.
- Ozone oxidises PbS to lead sulphate and iodide ions to iodine.

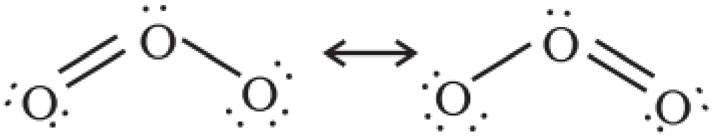
$$PbS(s) + 4O_3(g) \rightarrow PbSO_4(s) + 4O_2(g)$$
$$2I^-(aq) + H_2O(l) + O_3(g) \rightarrow 2OH^-(aq) + I_2(s) + O_2(g)$$

- When O_3 reacts with an excess of KI solution buffered with a borate buffer, iodine is liberated which can be titrated against a standard solution of sodium thiosulphate. It is used to estimate O_3 gas.
- The nitrogen monoxide combines very rapidly with ozone. So that nitrogen oxides emitted from the exhaust systems of supersonic jet

aeroplanes may be slowly deplete the ozone layer in the upper atmosphere.

$$NO\ (g) + O_3\ (g) \rightarrow NO_2\ (g) + O_2\ (g)$$

- Another threat to this ozone layer is posed by the use of freons which are used in aerosol sprays and as refrigerants.
- The two O-O bond lengths in the ozone molecule are identical (128 pm) and the molecule is angular as expected with a bond angle of about 117°. Resonance in O_3 is as follows:



Uses:

- O_3 helps in formation of germicide, disinfectant and for sterilising water.
- O_3 is also used for bleaching oils, flour, starch, and ivory.
- Ozone acts as an oxidising agent for the production of $KMnO_4$.

Sulphur allotropic forms

- Sulphur forms various allotropes of which the yellow rhombic i.e. α-sulphur and monoclinic i.e. β –sulphur form.
- The rhombic sulphur is stable form at room temperature. Rhombic sulphur transforms into monoclinic sulphur if heated at 369 K temperature.

Rhombic sulphur (α-sulphur)

- This allotrope is yellow in colour and its m.p. is 385.8 K and the specific gravity is 2.06.
- The evaporation of roll sulphur in carbon disulphide results crystals of rhombic sulphur.
- It is insoluble in protic solvent like water but dissolves little in benzene, alcohol and ether. It is readily soluble in CS_2.

Monoclinic sulphur (β-sulphur)

- The m.p. of monoclinic sulphur is 393 K and specific gravity is 1.98.
- It is soluble in CS_2.

- Colourless needle shaped crystals of **β**-sulphur is prepared by melting rhombic sulphur.
- The α-sulphur is stable below 369 K and transforms into β-sulphur above this.
- At 369 K both the forms are stable. This temperature is termed as transition temperature.
- The rhombic and monoclinic sulphur have S_8 molecules. Both has a crown shape.
- At elevated temperatures approximately 1000 K, S_2 is the dominant species and is paramagnetic in nature.

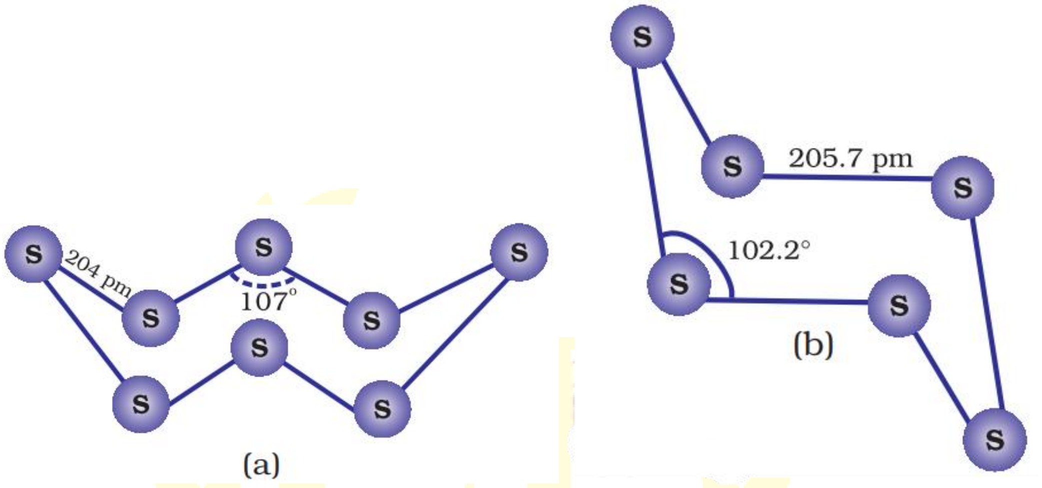


Figure: The structures of (a) S_8 ring in rhombic sulphur and (b) S_6 form

Sulphur dioxide

Preparation

- SO_2 is formed together with sulphur trioxide when sulphur is burnt in presence of air:

$$S\ (s) + O_2\ (g) \rightarrow SO_2\ (g)$$

- In the lab it is readily prepared by treating a sulphite with dil. H_2SO_4.

$$SO_3^{2-}\ (aq) + 2H^+\ (aq) \rightarrow H_2O\ (l) + SO_2\ (g)$$

- Industrially sulphur dioxide is produced as a by-product of the roasting of sulphide ores. The gas after drying is liquefied under high pressure and stored in steel cylinders.

$$4FeS_2\,(s) + 11O_2\,(g) \rightarrow 2Fe_2O_3\,(s) + 8SO_2\,(g)$$

Properties

- SO_2 is a colourless gas with pungent smell and it is soluble in H_2O.
- SO_2 liquefies at room temperature under a pressure of two atmospheres and boils at 264 K.
- When SO_2 passed through water, forms a solution of sulphurous acid.

$$SO_2\,(g) + H_2O\,(l) \rightleftharpoons H_2SO_4\,(aq)$$

- It reacts easily with NaOH solution, forming sodium sulphite. Then sodium sulphite reacts with more SO_2 to form sodium hydrogen sulphite ($NaHSO_3$).

$$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$$
$$Na_2SO_3 + H_2O + SO_2 \rightarrow 2NaHSO_3$$

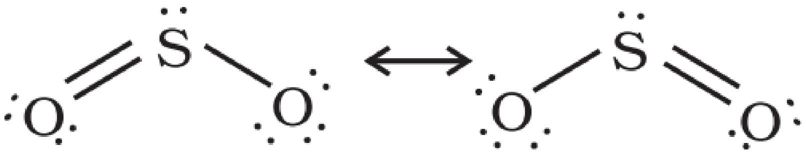
- The reaction of SO_2 with water and alkalies, it behaves very similar to that of CO_2.
- SO_2 reacts with Cl_2 in the presence of charcoal to give SO_2Cl_2.
- It is oxidised to SO_3 by oxygen in the presence of vanadium oxide catalyst.

$$SO_2(g) + Cl_2\,(g) \rightarrow SO_2Cl_2(l)$$
$$2SO_2\,(g) + O_2\,(g) \xrightarrow{V_2O_5} 2SO_3\,(g)$$

- SO_2 behaves as a reducing agent when it is moist. Example: it converts Fe(III) ions to Fe(II) ions and decolourises acidified $KMnO_4$ (VII) solution.

$$2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$$
$$5SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$$

- The molecule of SO_2 is angular. It is a resonance hybrid of the two canonical forms:

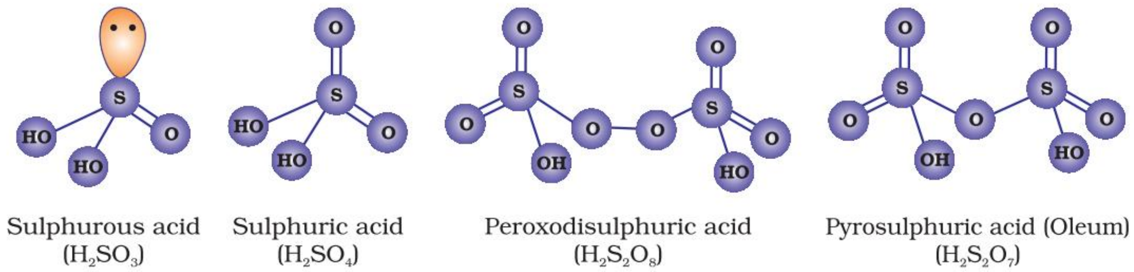


Uses:

- Sulphur dioxide is used
  1. In refining petroleum and sugar
  2. In bleaching wool and silk
  3. As a disinfectant and preservative. H_2SO_4, sodium hydrogen sulphite and calcium hydrogen sulphite are manufactured from SO_2.
  4. Liquid SO_2 is used as a solvent to dissolve different organic and inorganic chemicals.

Oxoacids of sulphur

- Sulphur forms a different oxoacids such as H_2SO_3, $H_2S_2O_3$, $H_2S_2O_4$, $H_2S_2O_5$, $H_2S_xO_6$ (Here x = 2 to 5), H_2SO_4, $H_2S_2O_7$, H_2SO_5, $H_2S_2O_8$.
- Some of these acids are unstable and cannot be isolated as they are known in aqueous solution or in the form of their salts.



Sulphurous acid (H_2SO_3)

Sulphuric acid (H_2SO_4)

Peroxodisulphuric acid ($H_2S_2O_8$)

Pyrosulphuric acid (Oleum) ($H_2S_2O_7$)

Figure: Structures of some important oxo-acids of sulphur

Sulphuric Acid

Manufacture

- H_2SO_4 is one of the most important industrial chemicals worldwide.
- H_2SO_4 is prepared industrially by the contact Process which is as follows:
  1. Burning of sulphur ores in air to produce SO_2.
  2. Conversion of SO_2 to SO_3 by the reaction with oxygen in the presence of a catalyst like V_2O_5.

3. Absorption of SO_3 in H_2SO_4 to give Oleum i.e. $H_2S_2O_7$.

- The main step in the manufacture of H_2SO_4 is the catalytic oxidation of SO_2 with O_2 to give SO_3 in the presence of V_2O_5.

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g) \quad \Delta_r H^\ominus = -196.6\,\text{kJmol}^{-1}$$

- The reaction is exothermic, reversible.
- Low temperature and high pressure are the favourable conditions for maximum yield.
- The plant is operated at a pressure of 2 bar and a temperature of 720 K. The sulphur trioxide gas from the catalytic converter is absorbed in concentrated H_2SO_4 to yield oleum.
- Dilution of oleum with H_2O gives sulphuric acid.
- In the industry two steps are carried out simultaneously to reduce the cost.

$$SO_3 + H_2SO_4 \rightarrow \underset{\text{(Oleum)}}{H_2S_2O_7}$$

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

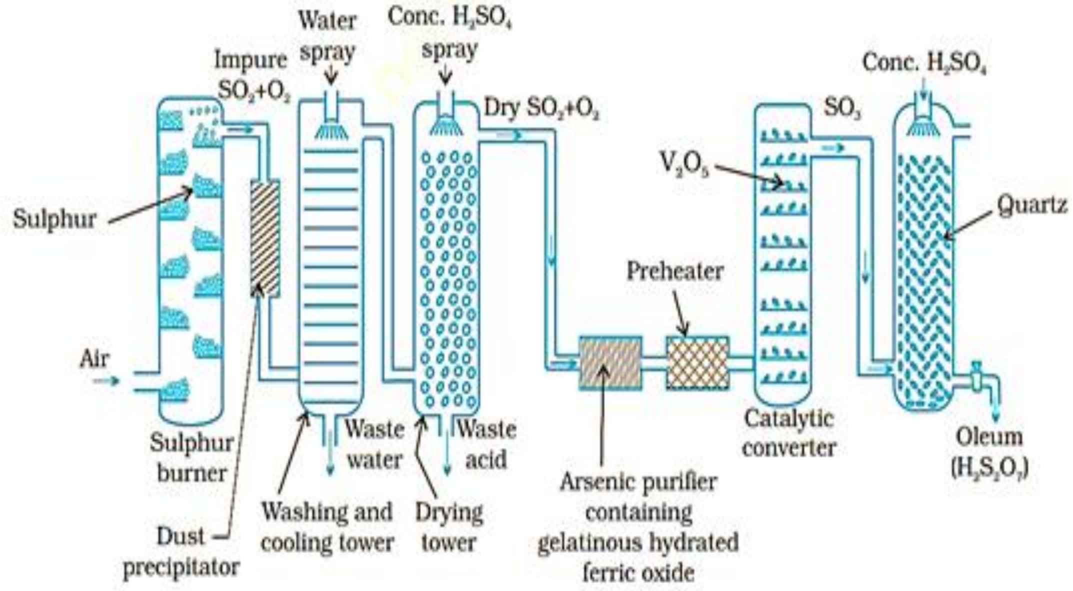


Figure: Flow diagram for the manufacture of sulphuric acid

Properties

- H_2SO_4 is a colourless, dense, and oily liquid. It has specific gravity of 1.84 at 298 K.
- H_2SO_4 freezing point is 283 K and boiling point 611 K.
- Conc. H_2SO_4 should add into water very slowly with continuous stirring.
- The sulphuric acid shows following characteristics:

1. Low volatility
2. Strong acidic character
3. Strong affinity for water and
4. Ability to act as an oxidising agent. H_2SO_4 ionises in two steps In aqueous solution-

$$H_2SO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HSO_4^-(aq);\ K_{a_1} = \text{very large}\ (K_{a_1} > 10)$$

$$HSO_4^-(aq) + H_2O(l) \rightarrow H_3O^+(aq) + SO_4^{2-}(aq)\ ;\ K_{a_2} = 1.2 \times 10^{-2}$$

- The high value of K_{a1} means that sulphuric acid is largely dissociated into HSO_4^- and H^+.
- Sulphuric acid is less volatile so it can be used to manufacture more volatile acids from their corresponding salts.

$$2MX + H_2SO_4 \rightarrow 2HX + M_2SO_4 \text{ (here M is metal and X= F, Cl, } NO_3\text{)}$$

Uses

- Sulphuric acid is a significant chemical reagent.
- $H_2SO_4$is needed for the manufacture of hundreds of other compounds and also in many industrial processes.
- The bulk of H_2SO_4 produced is used in the manufacture of fertilisers like $(NH_4)_2SO_4$.
- Other uses are in:
    1. Petroleum refining
    2. manufacture of paints, pigments and dyestuff intermediates
    3. detergent industry
    4. storage batteries
    5. metallurgical applications examples: cleansing metals before enamelling, electroplating and galvanising
    6. in the manufacture of nitrocellulose products and
    7. as a laboratory reagent.

Group- 17 elements

- Fluorine (F), chlorine (Cl), bromine (Br), iodine (I), astatine (At) and tennessine (Ts) are members of Group-17.
- Group- 17 elements are also termed as the halogens.
- These are highly reactive non-metallic elements.
- There is a regular progression in their physical and chemical properties. At and Ts are radioactive elements.

Occurrence

- F and Cl are plentiful in nature while Br and I are less so.
- F is present mainly as insoluble fluorides such as CaF_2, Na_3AlF_6 and $3Ca_3(PO_4)_2.CaF_2$ and small quantities are present in soil, bones and teeth of animals and river water, plants.
- Sea water contains NaCl, NaBr and NaI, KCL, KBr and, $MgCl_2$, $MgBr_2$, MgI_2 and also $CaCl_2$, $CaBr_2$, CaI_2 but mainly NaCl solution 2.5% by mass.
- Certain forms of marine life contain iodine (I) in their body; various seaweeds, for example, contain upto 0.5% of iodine and Chile saltpetre contains upto 0.2% of sodium iodate.
- Ts is a synthetic radioactive element. Its atomic number is 117, atomic mass is 294. Its half-life is in milliseconds only.

Table: Atomic and physical properties of halogens

Property	**F**	**Cl**	**Br**	**I**	**A**
Atomic number	9	17	35	53	85
Atomic mass(g mol^{-1})	19.00	35.45	79.90	126.90	21
Electronic configuration	$[He]2s^2 2p^5$	$[Ne]3s^2 3p^5$	$[Ar]3d^{10} 4s^2 4p^5$	$[Kr]4d^{10} 5s^2 5p^5$	$[Kr]4f^{14} 5d$
Covalent radius/pm	64	99	114	133	-
Ionic radius X^- (pm)	133	184	196	220	-
Ionisation enthalpy (kJ mol^{-1})	1680	1256	1142	1008	-

Electron gain enthalpy (kJ mol^{-1})	-333	-349	-325	-296	-
Electronegativity	4	3.2	3.0	2.7	2.
$\Delta_{Hyd}H(X^-)$ (kJ mol^{-1})	515	381	347	305	-
	F_2	Cl_2	Br_2	I_2	-
Melting point (K)	54.4	172.0	265.8	386.6	-
Boiling point (K)	84.9	239.0	332.5	458.2	-
Density (g cm^3)	1.5	1.66	3.19	4.94	-
Distance X (pm)	143	199	228	266	-
Bond dissociation enthalpy (kJ mol^{-1})	158.8	242.6	192.8	151.1	-
E^e/V^e	2.87	1.36	1.09	0.54	-

Electronic configuration

- Halogen have 7 electrons in their outermost shell which is one electron short ($ns^2\ np^5$) of the next noble gas.

Atomic and ionic radius

- The halogens have the smallest atomic radius in their respective periods because of maximum Z_{eff}.
- Atomic and ionic radii increase from F to I because of increase in number of quantum shells.

Ionisation enthalpy

- The halogens have almost no tendency to lose any electron. They show high ionisation enthalpy.
- Due to increase in atomic size, ionisation enthalpy decrease as we move down the group.

Electron gain enthalpy

- Halogens have maximum -ve electron gain enthalpy in the corresponding periods. Because the atoms of these elements have only one e^- less than stable noble gas configurations.
- Electron gain enthalpy of the elements of the group becomes less -ve as we move down the group.
- The -ve electron gain enthalpy of F is less than that of Cl; due to small size of F-atom.
- Consequently, there are strong inter-electronic repulsions in the relatively small 2p orbitals of F and thus, the incoming electron does not experience much attraction.

Electronegativity

- Halogens have very high electronegativity. The electronegativity decreases down the group.
- F is the most electronegative element nn the periodic table.

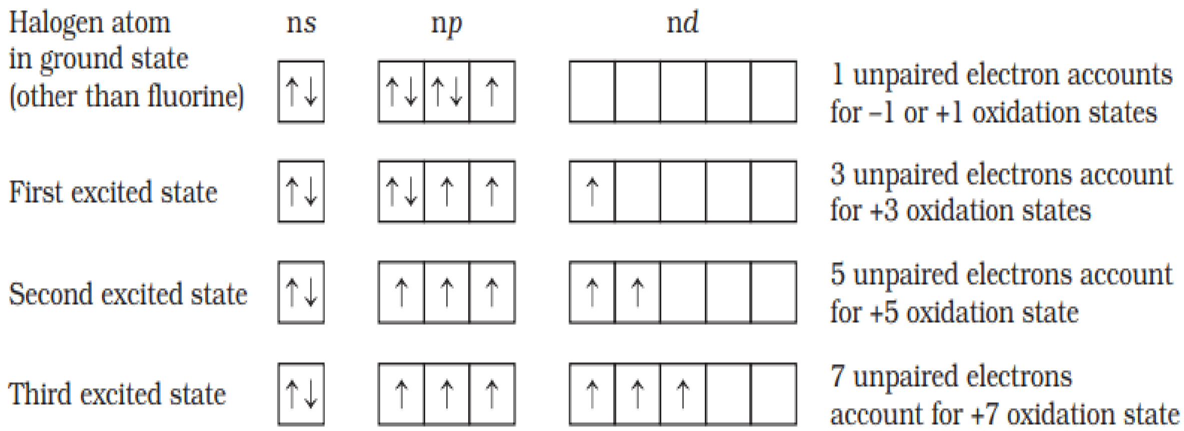
Physical properties

- Halogens display variations in their physical properties.
- F and Cl are gases, Br is a liquid and I is a solid.
- Their m.p. and b.p. gradually increase with the atomic number.
- All group-17 elements are coloured; due to absorption of radiations in visible region. Due to this outer electrons get excited to the higher energy level.
- They display different colours by absorbing different quanta of radiation,. E.g., F_2 has yellow, Cl_2 has greenish yellow, Br_2 has red and I_2 has violet colour.
- F and Cl react with water. Br and I are sparingly soluble in water but are soluble in various organic solvents like $CHCl_3$, CCl_4, CS_2 and hydrocarbons to give coloured solutions.
- F_2 have lower enthalpy of dissociation as compared to that of Cl_2 whereas X-X bond dissociation enthalpies from chlorine onwards show following trend: $Cl – Cl > Br – Br > I – I$.
- A reason for this anomaly is the relatively large electron-electron repulsion among the lone pairs in F_2 molecule where they are much closer to each other than in case of Cl_2.

Chemical properties

Oxidation states and trends in chemical reactivity:

- All the halogens exhibit –1 oxidation state. However, chlorine, bromine and iodine exhibit + 1, + 3, + 5 and + 7 oxidation states also as explained below:



1 unpaired electron accounts for –1 or +1 oxidation states

3 unpaired electrons account for +3 oxidation states

5 unpaired electrons account for +5 oxidation state

7 unpaired electrons account for +7 oxidation state

- The higher oxidation states of Cl, Br and I are realised mainly when the halogens are in combination with the small and highly electronegative F and O-atoms. Examples: in interhalogens, oxides and oxoacids.
- The oxidation states of +4 and +6 occur in the oxides and oxoacids of Cl and Br.
- The F-atom has no d-orbitals in its valence shell and so cannot expand its octet.
- Being the most electronegative, it exhibits only –1 oxidation state.
- All the halogens are highly reactive. They form halides on reacting with metals and non-metals.
- The reactivity of the halogens decreases as we move down the group. They readily accept an electron to complete octet, it is the reason for the strong oxidising nature of halogens.
- F_2 is the strongest oxidising halogen and it oxidises other halide ions in solution or even in the solid phase.
- A halogen oxidises halide ions of higher atomic number.

$$F_2 + 2X^- \rightarrow 2F^- + X_2 \text{ (X = Cl, Br or I)}$$
$$Cl_2 + 2X^- \rightarrow 2Cl^- + X_2 \text{ (X = Br or I)}$$
$$Br_2 + 2I^- \rightarrow 2Br^- + I_2$$

- The decreasing oxidising ability of the halogens in aqueous solution as we move down the group is evident from their standard electrode potentials which are dependent on the parameters shown below:

$$\frac{1}{2}X_2(g) \xrightarrow{1/2\,\Delta_{diss}H^\ominus} X(g) \xrightarrow{\Delta_{eg}H^\ominus} X^-(g) \xrightarrow{\Delta_{hyd}H^\ominus} X^-(aq)$$

- Oxidizing power of halogens:

$2F_2 (g) + 2H_2O (l) \rightarrow 4H+ (aq) + 4F^- (aq) + O_2 (g)$
$X_2(g) + H_2O (l) \rightarrow HX (aq) + HOX (aq)$ (here X is Cl/Br)
$4I^- (aq) + 4H^+ (aq) + O_2 (g) \rightarrow 2I_2 (s) + 2H_2O (l)$

Anomalous behaviour of fluorine

- For F ionisation enthalpy, electrode potentials and electronegativity are higher than expected from the trends set by other halogens.
- The ionic and covalent radii, m.p. and b.p., bond dissociation enthalpy and enthalpy of electron gain are much lower than expected.
- The irregular behaviour of fluorine is due to its small size, highest electronegativity, low F-F bond dissociation enthalpy, and non-availability of d-orbitals in valence shell.
- Most of the reactions of fluorine are exothermic.
- HF is in liquid state because of strong H-bonding. H-bond is formed in HF due to small size and high due to small size and high electronegativity of F.

1. Reactivity towards hydrogen:

- All halogens react with hydrogen to give H-X but affinity for hydrogen decreases as we move from fluorine to iodine.

- H-X dissolves in H_2O to form hydrohalic acids.
- The strength of halo acids is as follows:

HF < HCl < HBr < HI

- The stability of these halides decreases as we move down the group due to decrease in (H–X) bond dissociation enthalpy in the order:

H–F > H–Cl > H–Br > H–I

2. Reactivity towards oxygen:

- Halogens form many oxides with oxygen but almost all are unstable.
- Fluorine forms two oxides OF_2 and O_2F_2. At 298 K OF_2 is thermally stable.
- These oxides are essentially oxygen fluorides because of the electronegativity of fluorine is higher than oxygen. Both are strong fluorinating agents. O_2F_2 oxidises Pu to PuF_6.
- Cl, Br and I form oxides in which the oxidation states of these halogens range from +1 to +7.
- The decreasing order of stability of halo-oxides:

I > Cl > Br

- The oxides of iodine are more stable due to greater polarisability of bond between iodine and oxygen.
- There is multiple bond formation take place between Cl and oxygen due to accessibility of d–orbitals. It makes them more stable.
- Br lacks both the characteristics hence stability of oxides of bromine is very less.
- Chlorine oxides such as Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7 are highly reactive oxidising agents and tend to explode.
- Chlorine dioxide is used as a bleaching agent for paper pulp a, textiles and also in water treatment.
- The bromine oxides exist only at low temperatures. Example: Br_2O, BrO_2, BrO_3 are the least stable halogen oxides. They are very powerful oxidising agents.

- The iodine oxides such as I_2O_4, I_2O_5, I_2O_7 are insoluble solids and decompose on heating.
- I_2O_5 is a very good oxidising agent and is used in the estimation of CO.

3. Reactivity towards metals:

- Halogens and metals give metal halides. Example, Br_2 reacts with Mg to give magnesium bromide.

$$Mg\ (s) + Br_2\ (l) \rightarrow MgBr_2\ (s)$$

- The order of ionic character of the halides is as follows:

$$MF > MCl > MBr > MI$$

Here M = monovalent metal.

- The halides with higher oxidation state are covalent than the one with lower oxidation state. Example: $SbCl_5$, $SnCl_4$, $PbCl_4$, and UF_6 are more covalent than $SnCl_2$, $PbCl_2$, $SbCl_3$ and UF_4 respectively.

4. Reactivity of halogens towards other halogens:

- Halogens combine with themselves to form a number of compounds termed inter-halogens of the types XX', XX_3', XX_5' and XX_7' here X is a larger size halogen and X′ is smaller size halogen.

Chlorine

- In 1774 Chlorine was discovered by Scheele by observing the reaction of HCl with MnO_2.

Preparation

- It is prepared by the following methods:

1. By heating MnO_2 with conc. HCl.

$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$$

$$4NaCl + MnO_2 + 4\ H_2SO_4 \rightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$$

2. By the action of hydrochloric acid on $KMnO_4$.

$$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

Manufacture of chlorine

1. Deacon's process:

- Chlorine is manufactured by oxidation of HCl gas through atmospheric oxygen in the presence of a catalyst i.e. $CuCl_2$ at 723 K.

$$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$

2. Electrolytic process:

- Chlorine is obtained by the electrolysis of concentrated NaCl solution known as brine. Chlorine is liberated at anode.

Properties

- It is a greenish yellow gas with pungent and suffocating odour.
- It is liquefied into greenish yellow solution. It is soluble in water.
- Chlorine reacts with following metals and non-metals to form chlorides-

$$2Al + 3Cl_2 \rightarrow 2AlCl_3;$$
$$2Na + Cl_2 \rightarrow 2NaCl;$$
$$2Fe + 3Cl_2 \rightarrow 2FeCl_3;$$
$$P_4 + 6Cl_2 \rightarrow 4PCl_3$$
$$S_8 + 4Cl_2 \rightarrow 4S_2Cl_2$$

- Chloride reacts with compounds containing hydrogen to form HCl.

$$H_2 + Cl_2 \rightarrow 2HCl$$
$$H_2S + Cl_2 \rightarrow 2HCl + S$$
$$C_{10}H_{16} + 8Cl_2 \rightarrow 16HCl + 10C$$

- With cold bases chlorine produces a mixture of chloride and hypochlorite but with hot bases produces chloride and chlorate.

$$2NaOH + Cl_2 \rightarrow NaCl + NaOCl + H_2O$$

(Cold and dil.)

$$6NaOH + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$$

(Hot and concentrate)

- Chlorine gives bleaching powder reacting with dry slaked lime.

$$2Ca(OH)_2 + 2Cl_2 \rightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$$

The composition of bleaching powder is $Ca(OCl)_2 .CaCl_2 .Ca(OH)_2 .2H_2O$.

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

$$\underset{\text{Methane}}{CH_4} + Cl_2 \xrightarrow{UV} \underset{\text{Methyl chloride}}{CH_3Cl} + HCl$$

$$\underset{\text{Ethene}}{C_2H_4} + Cl_2 \xrightarrow{\text{Room temp.}} \underset{\text{1,2-Dichloroethane}}{C_2H_4Cl_2}$$

- The yellow colour of chlorine water fades on standing for long-time due to the formation of HCl and HOCl.
- Hypochlorous acid so formed, gives nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.
- Chlorine oxidises ferrous into ferric and sulphite into sulphate.
- Chlorine oxidises SO_2 to SO_3 and I_2 to iodate.
- In the presence of water they form H_2SO_4 and iodic acid respectively.

$$2FeSO_4 + H_2SO_4 + Cl_2 \rightarrow Fe_2(SO_4)_3 + 2HCl$$
$$Na_2SO_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl$$
$$SO_2 + 2H_2O + Cl_2 \rightarrow H_2SO_4 + 2HCl$$
$$I_2 + 6H_2O + 5Cl_2 \rightarrow 2HIO_3 + 10HCl$$

- Chlorine show bleaching action due to oxidation. The organic matter is bleached in the presence of moisture. Bleaching effect of chlorine is permanent.

$$Cl_2 + H_2O \rightarrow 2HCl + O$$

Coloured substance + O → Colourless substance

Uses

1. It is used for bleaching the wood pulp which is required for the manufacture of paper and rayon), bleaching cotton and textiles.
2. It is used for in the extraction of gold and platinum.
3. It is used for in the manufacture of dyes, drugs and organic compounds such as CCl_4, $CHCl_3$, DDT, refrigerants, etc.
4. It is used for in sterilising drinking water.
5. It is used for preparation of poisonous gases such as phosgene ($COCl_2$), tear gas (CCl_3NO_2), mustard gas ($ClCH_2CH_2SCH_2CH_2Cl$).

Hydrogen Chloride

- Glauber prepared HCl in 1648 by heating NaCl with conc. H_2SO_4.

Preparation

- HCl can be made by heating NaCl with conc. H_2SO_4.

$$\mathrm{NaCl + H_2SO_4 \xrightarrow{420\,K} NaHSO_4 + HCl}$$

$$\mathrm{NaHSO_4 + NaCl \xrightarrow{823\,K} Na_2SO_4 + HCl}$$

Properties

- It is a colourless gas with pungent smell.
- It is easily liquefied to a colourless liquid and freezes to a white crystalline solid. HCl is soluble in water.

$$\mathrm{HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)} \quad K_a = 10^7$$

- Its aqueous solution is called hydrochloric acid. High Ka indicates that it is a strong acid. HCl reacts with ammonia and gives NH_4Cl.

$$NH_3 + HCl \rightarrow NH_4Cl$$

- When HCl and conc.HNO_3 are mixed in 3:1, aquaregia is formed which is used for dissolving noble metals, e.g., Au, Pt.

$$\mathrm{Au + 4H^+ + NO_3^- + 4Cl^- \rightarrow AuCl_4^- + NO + 2H_2O}$$

$$\mathrm{3Pt + 16H^+ + 4NO_3^- + 18Cl^- \rightarrow 3PtCl_6^{2-} + 4NO + 8H_2O}$$

- Hydrochloric acid decomposes salts of weak acids, for e.g., carbonates, hydrogen-carbonates, sulphites, etc.

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$$
$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$$
$$Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2$$

Uses

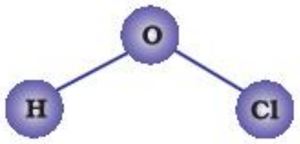
- It is used to produce chlorine, NH_4Cl and glucose.
- It is used for removing glue from the bones.
- It is used in medicine and as a laboratory reagent.

Oxoacids of Halogens

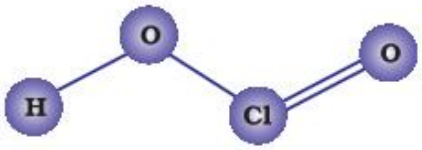
- As being electronegativity with small size, fluorine forms an oxoacid, HOF (hypofluorous acid).
- The other halogens form several oxoacids. They are stable in aqueous solutions or in their salts.

Table: Oxoacids of halogens

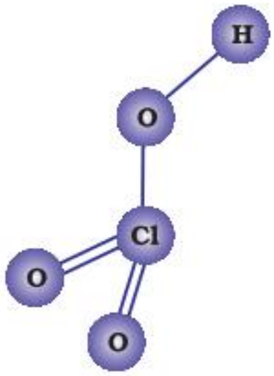
Halic (I) acid	HOF	HOCl	HOBr	HOI
Halic (III) acid	-	HOClO	-	-
Halic (V) acid	-	$HOClO_2$	$HOBrO_2$	$HOIO_2$
Halic (VII) acid	-	$HOClO_3$	$HOBrO_3$	$HOIO_3$



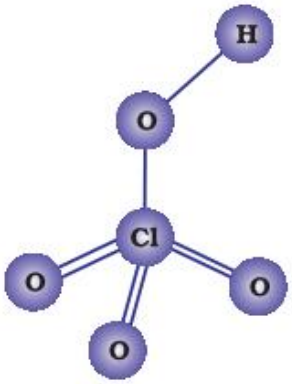
Hypochlorous acid



Chlorous acid



Chloric acid



Perchloric acid

Figure: The structures of oxoacids of chlorine

Interhalogen compounds

- Interhalogen compounds can be preparedby the reaction of different halogens.
- They can be assigned general compositions as XX′, XX_3' , XX_5' and XX_7'
  Here X = halogen of larger size
  X′ = halogen of smaller size.
- As the ratio between radii of X and X′ increases, the number of atoms per molecule also increases. Thus, iodine (VII) fluoride should have maximum number of atoms as the ratio of radii between I and F should be maximum and its formula is IF_7.

Preparation

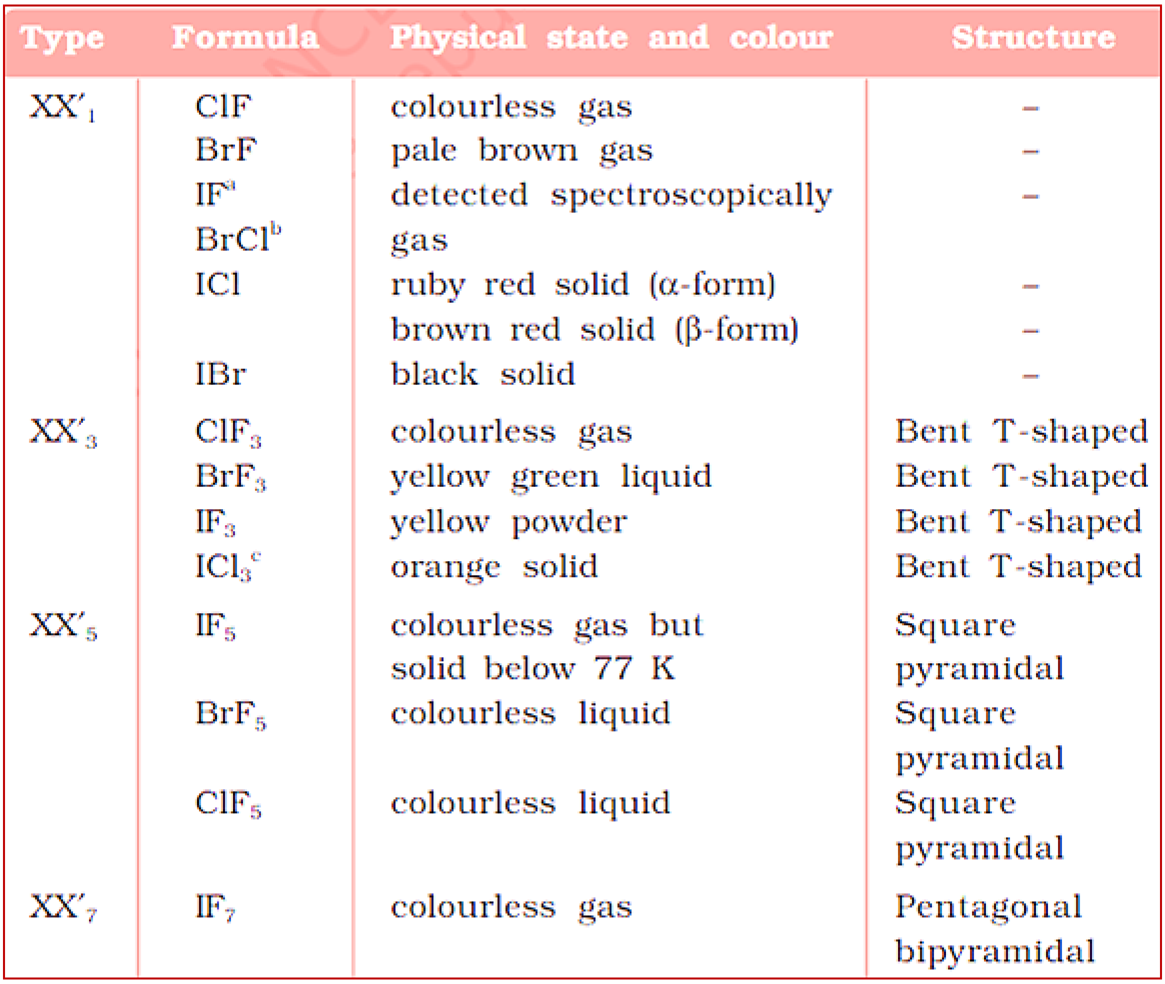
- The inter-halogen compounds can be prepared by the direct combination or by the action of halogen on lower interhalogen compounds.
- The product formed depends upon some specific conditions; As follows:

$$\underset{\text{(equal volume)}}{Cl_2 + F_2} \xrightarrow{437\,K} 2ClF; \qquad I_2 + \underset{\text{(excess)}}{3Cl_2} \rightarrow 2ICl_3$$

$$Cl_2 + \underset{\text{(excess)}}{3F_2} \xrightarrow{573\,K} 2ClF_3; \qquad \underset{\text{(diluted with water)}}{Br_2 + 3F_2} \rightarrow 2BrF_3$$

$$\underset{\text{(equimolar)}}{I_2 + Cl_2} \rightarrow 2ICl; \qquad Br_2 + \underset{\text{(excess)}}{5F_2} \rightarrow 2BrF_5$$

Table: Some Properties of Interhalogen Compounds



Type	Formula	Physical state and colour	Structure
XX'_1	ClF	colourless gas	–
	BrF	pale brown gas	–
	IF^a	detected spectroscopically	–
	$BrCl^b$	gas	
	ICl	ruby red solid (α-form) brown red solid (β-form)	– –
	IBr	black solid	–
XX'_3	ClF_3	colourless gas	Bent T-shaped
	BrF_3	yellow green liquid	Bent T-shaped
	IF_3	yellow powder	Bent T-shaped
	ICl_3^c	orange solid	Bent T-shaped
XX'_5	IF_5	colourless gas but solid below 77 K	Square pyramidal
	BrF_5	colourless liquid	Square pyramidal
	ClF_5	colourless liquid	Square pyramidal
XX'_7	IF_7	colourless gas	Pentagonal bipyramidal

- These are diamagnetic in nature and covalent too. They are volatile solids or liquids at 298 K temperature except ClF which is a gas.
- The interhalogen compounds are very reactive than halogens.Due to the weakness of X–X′ bond in interhalogens as compare to X–X bond in halogens.
- All these undergo hydrolysis giving halide ion derived from the smaller halogen and a hypohalite, halite, halate and perhalate anion derived from the larger halogen.

$$XX' + H_2O \rightarrow HX' + HOX$$

- The XX_3 compounds show the bent 'T' shape, XX_5 compounds square pyramidal and IF_7 has pentagonal bipyramidal structures according to VSEPR theory.

Uses

- These compounds can be used as non-aqueous solvents.

- Interhalogen compounds are very useful fluorinating agents. Trifluoro chlorine and Trifluoro bromine are used for the production of UF_6 in the enrichment of ^{235}U.

$$U(s) + 3ClF_3\,(l) \rightarrow UF_6\,(g) + 3ClF\,(g)$$

Group 18 elements

- Group 18 consists of these elements: He, Ne, Ar, Kr, Xe, Ra and Og.
- All these are gases and chemically unreactive.
- All these gases except radon and Og occur in the atmosphere.
- Their atmospheric abundance in dry air is approximately 1% by volume of which argon is the major constituent.
- Xe and Ra are the rarest elements of the group. Ra is obtained as a decay product of ^{226}Ra.

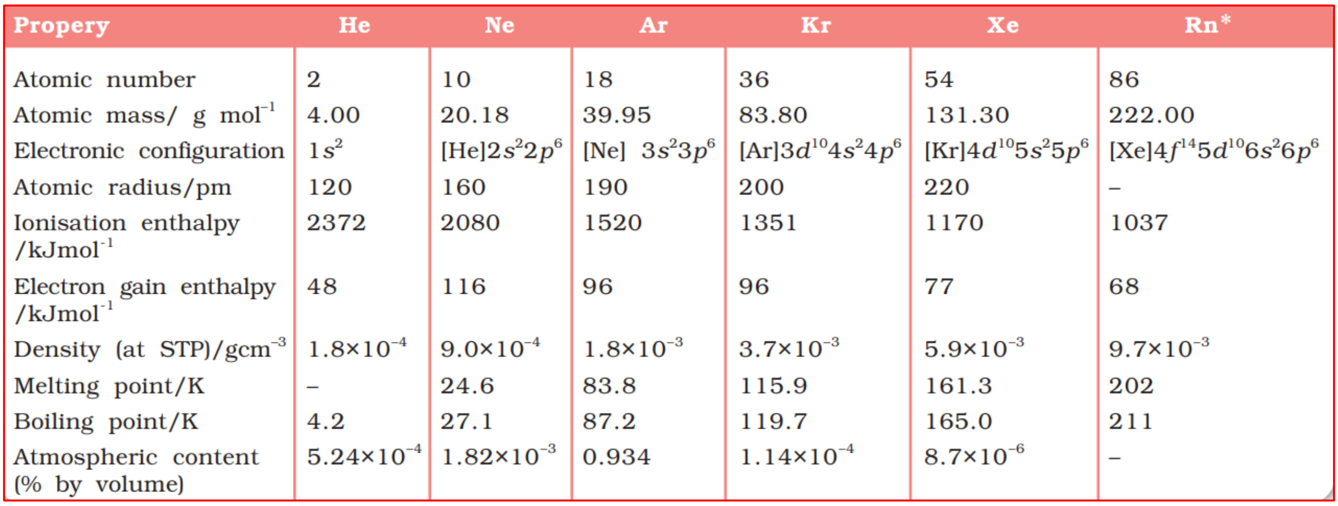
$$^{226}_{88}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\text{He}$$

- Og has been synthetically produced by collision of $^{249}Cf_{98}$ atoms and $^{48}Ca_{20}$ ions.

$$^{249}_{98}\text{Cf} + {}^{48}_{20}\text{Ca} \longrightarrow {}^{294}_{118}\text{Og} + 3n$$

- Og atomic number is 118, atomic mass is 294.
- Its half-life is 0.7 milliseconds.

Table: Atomic and Physical Properties of Group 18 Elements



Propery	He	Ne	Ar	Kr	Xe	Rn*
Atomic number	2	10	18	36	54	86
Atomic mass/ g mol^{-1}	4.00	20.18	39.95	83.80	131.30	222.00
Electronic configuration	$1s^2$	$[He]2s^22p^6$	$[Ne]\ 3s^23p^6$	$[Ar]3d^{10}4s^24p^6$	$[Kr]4d^{10}5s^25p^6$	$[Xe]4f^{14}5d^{10}6s^26p^6$
Atomic radius/pm	120	160	190	200	220	–
Ionisation enthalpy /kJmol^{-1}	2372	2080	1520	1351	1170	1037
Electron gain enthalpy /kJmol^{-1}	48	116	96	96	77	68
Density (at STP)/gcm^{-3}	1.8×10^{-4}	9.0×10^{-4}	1.8×10^{-3}	3.7×10^{-3}	5.9×10^{-3}	9.7×10^{-3}
Melting point/K	–	24.6	83.8	115.9	161.3	202
Boiling point/K	4.2	27.1	87.2	119.7	165.0	211
Atmospheric content (% by volume)	5.24×10^{-4}	1.82×10^{-3}	0.934	1.14×10^{-4}	8.7×10^{-6}	–

Electronic Configuration

- All noble gases have general electronic configuration $ns^2\ np^6$.
- Many of the properties of noble gases including their inactive nature are ascribed to their closed shell structures.

Ionisation Enthalpy

- These gases shoe high ionisation enthalpy.
- It decreases as we move down the group with increase in atomic size.

Atomic Radii

- Atomic radii increase as we move down the group with increase in atomic number.

Electron Gain Enthalpy

- Since noble gases have complete octet, they have no tendency to accept the electron, have large +ive values of electron gain enthalpy.

Physical Properties

- All the noble gases are monoatomic, colourless. They are odourless and tasteless.
- They are sparingly soluble in water.
- They have very low m.p. and b.p. owing to weak dispersion forces.

- He has an unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.

Chemical Properties

- The noble gases are least reactive.
- Their inertness to chemical reactivity is credited to these reasons:
  1. The noble gases except He ($1s^2$) have fully filled ns^2np^6 electronic configuration.
  2. They have high ionisation enthalpy and more +ive electron gain enthalpy.
- The compounds of krypton are fewer. Only the difluoride like KrF_2 has been known.
- Compounds of Ra have not been isolated but only identified i.e. RnF_2 by radiotracer technique

(a) Xenon-fluorine compounds

- Xe forms binary fluorides for example- XeF_2, XeF_4 and XeF_6 by the direct reaction of elements under appropriate experimental conditions.

$$\underset{\text{(xenon in excess)}}{Xe\,(g) + F_2\,(g)} \xrightarrow{673\,K,\ 1\,bar} XeF_2(s)$$

$$\underset{\text{(1:5 ratio)}}{Xe\,(g) + 2F_2\,(g)} \xrightarrow{873\,K,\ 7\,bar} XeF_4(s)$$

$$\underset{\text{(1:20 ratio)}}{Xe\,(g) + 3F_2\,(g)} \xrightarrow{573\,K,\ 60-70\,bar} XeF_6(s)$$

- The interaction of XeF_4 and O_2F_2 gives XeF_6 at 143K.

$$XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$$

- XeF_2, XeF_4 and XeF_6 are colourless crystalline solids and sublime easily at 298 K. They are powerful fluorinating agents.
- They are hydrolysed even by water. Example:

$$2XeF_2\,(s) + 2H_2O\,(l) \rightarrow 2Xe\,(g) + 4HF\,(aq) + O_2\,(g)$$

- The structures of the xenon fluorides can be deduced from VSEPR. XeF_2 have linear and XeF_4 have square planar structure. XeF_6 has seven e^- pairs and would, thus, have a distorted Oh structure as found experimentally in the gas phase.

- Xenon fluorides react with F^- acceptors to form cationic species and fluoride ion donors to form fluoro-anions.

$$XeF_2 + PF_5 \rightarrow [XeF]^+ [PF_6]^- ; \quad XeF_4 + SbF_5 \rightarrow [XeF_3]^+ [SbF_6]^-$$
$$XeF_6 + MF \rightarrow M^+ [XeF_7]^- \ (M = Na, K, Rb \text{ or } Cs)$$

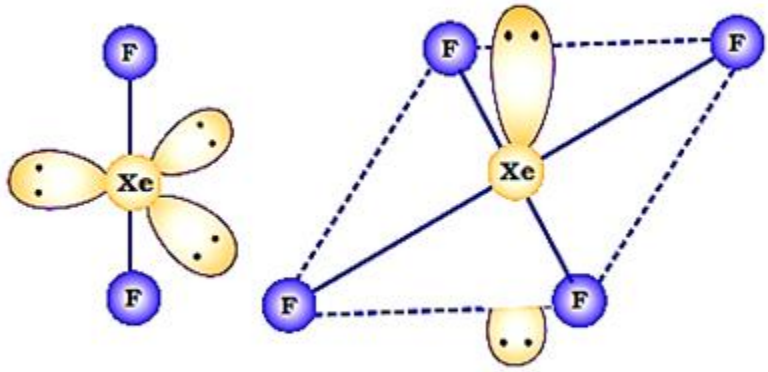
(b) **Xenon-oxygen compounds**

- Hydrolysis of hexafluoro xenon and tetrafluoro xenon with H_2O gives XeO_3.

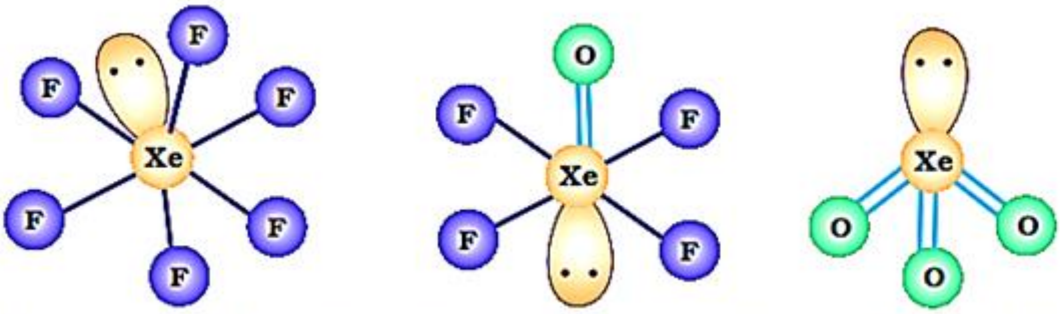
$$6XeF_4 + 12\ H_2O \rightarrow 4Xe + 2Xe0_3 + 24\ HF + 3\ O_2$$
$$XeF_6 + 3\ H_2O \rightarrow XeO_3 + 6\ HF$$

- Fractional hydrolysis of XeF_6 gives $XeOF_4$ and XeO_2F_2.

$$XeF_6 + H_2O \rightarrow XeOF_4 + 2\ HF$$
$$XeF_6 + 2\ H_2O \rightarrow XeO_2F_2 + 4HF$$



(a) Linear (b) Square planar



(c) Distorted octahedral (d) Square pyramidal (e) Pyramidal

Figure: The structures of (a) XeF_2 (b) XeF_4 (c) XeF_6 (d) $XeOF_4$ and (e) XeO_3

- Xenon trioxide is a colourless explosive solid and it has a pyramidal structure.
- $XeOF_4$ is a colourless volatile liquid. It has a square pyramidal structure.

Uses

- Xenon is used in blowing balloons for meteorological observations.
- It is also used in nuclear reactors which are gas-cooled. Liquid He finds use as cryogenic agent for carrying out various experiments at low temperatures.
- It is used to produce and sustain powerful superconducting magnets which form an essential part of m Magnetic Resonance Imaging systems for clinical diagnosis.
- It is used as a diluent for oxygen in diving apparatus as it is very less soluble in blood.
- For advertisement display purposes neon is used in fluorescent bulbs.
- Ne bulbs are used in green houses.
- Argon is used mainly to provide an inert atmosphere in high temperature metallurgical processes and for filling electric bulbs.
- They are used in light bulbs designed for special purposes.