The p-Block Elements

General Trends of Group 15 Elements

Group 15 Elements

- Nitrogen (N), Phosphorus (P), Arsenic (As), Antimony (Sb) and Bismuth (Bi)

Occurrence

- **Nitrogen**
  - Comprises 78% of the atmosphere (by volume)
  - Occurs as sodium nitrate ($NaNO_3$) and potassium nitrate (KNO_3) in earth's crust
  - Found in the form of proteins in plants and animals
- **Phosphorus**
- Occurs in minerals of the apatite family $Ca_9(PO_4)_6.CaX_2$ (X = F, Cl or OH), which are the main components of phosphate rocks
- Essential constituent of animal and plant matter
- Present in bones as well as in living beings
- Phosphoproteins are present in milk and eggs.
- Arsenic, antimony and bismuth are found mainly as sulphide minerals.

Atomic Properties

- General valence shell electronic configuration is ns^2np^3
- Covalent and ionic radii increase down the group
- Ionisation enthalpy decreases down the group due to gradual increase in atomic size. Order of successive ionisation enthalpies: $\Delta_iH_1 < \Delta_iH_2 < \Delta_iH_3$
- Electronegativity decreases down the group, with increase in atomic size

Physical Properties

- Polyatomic
- N_2 is a diatomic gas; all others are solids
- Metallic character increases down the group

- N and P: non-metals; As and Sb: metalloids; Bi: metal
- Boiling points increase down the group
- Melting point increases up to arsenic, and then decreases up to bismuth
- All the elements show allotropy (except nitrogen)

Chemical Properties

- Common oxidation states are −3, +3 and +5
- Stability of +5 oxidation state decreases down the group
- Tendency to exhibit −3 oxidation state decreases down the group
- Reason: Increase in size and metallic character
- Nitrogen can exhibit +1, +2, +4 oxidation states
- Phosphorus exhibits +1 and +4 oxidation states in some oxoacids
- All oxidation states from +1 to + 4 of nitrogen tend to disproportionate in acid solution
- Example:

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

- Nearly all intermediate oxidation states of phosphorus disproportionate into +5 and −3, both in alkali and acid

- **Reactivity with hydrogen**
- All form hydrides of the type EH_3 (E = N, P, As, Sb or Bi)
- Basicity order: $NH_3 > PH_3 > AsH_3 > SbH_3 \geq BiH_3$
- **Reactivity with oxygen**
- All form two types of oxides: E_2O_3 and E_2O_5
- Acidic character of oxides decreases down the group
- **Reactivity towards halogens**

- React to form two series of halides: EX_3 and EX_5
- Nitrogen does not form pentahalides due to non-availability of the *d*-orbitals in its valence shell
- **Reactivity towards metals**
- All react with metals to form their binary compounds, exhibiting −3 oxidation state
- Example: Ca_3N_2, Ca_3P_2, Na_3As, Zn_3Sb_2 and Mg_3Bi_2

Anomalous Behaviour of Nitrogen

- Nitrogen differs from the rest of the elements of this group
- Reason: Smaller size, high electronegativity, high ionisation enthalpy and non-availability of *d*-orbitals
- Unique ability to form $p\pi - p\pi$ multiple bond with itself and some other elements
- Exists as diatomic molecules with a triple bond; hence, its bond enthalpy is very high (941.4 $kJ\ mol^{-1}$). On the other hand, P, As and Sb form single bonds as P−P, As−As and Sb−Sb; bismuth forms metallic bonds
- The single N−N bond is weaker than P−P bond.
- Reason: Due to small bond length, the interelectronic repulsion of the non-bonding electrons in nitrogen is high

Ammonia (NH3)

The composition of ammonia was determined by Claude Berthollet in 1785.

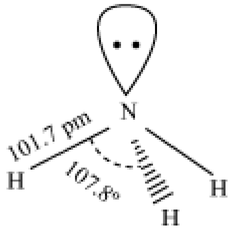
Occurrence

In the free state, ammonia is found in air and natural water.

In the combined state, it is obtained by destructive distillation of coal or wood. Also, it is found on the sides of craters and fissures of lava of volcanoes.

Structure

- It has a trigonal pyramidal structure with nitrogen atom at the apex.



- It has three bond pairs and one lone pair of electrons.

Forms

- Dry ammonia gas (gaseous ammonia)
- Liquid ammonia (liquified ammonia)
- Liquor ammonia fortis (saturated solution of ammonia in water)
- Laboratory bench reagent (dilute solution of liquor ammonia)

Preparation of ammonia

Ammonia can be prepared by the following methods.

- Ammonium salts on warming with caustic alkali produce salt, water and ammonia gas as shown in the reactions below:

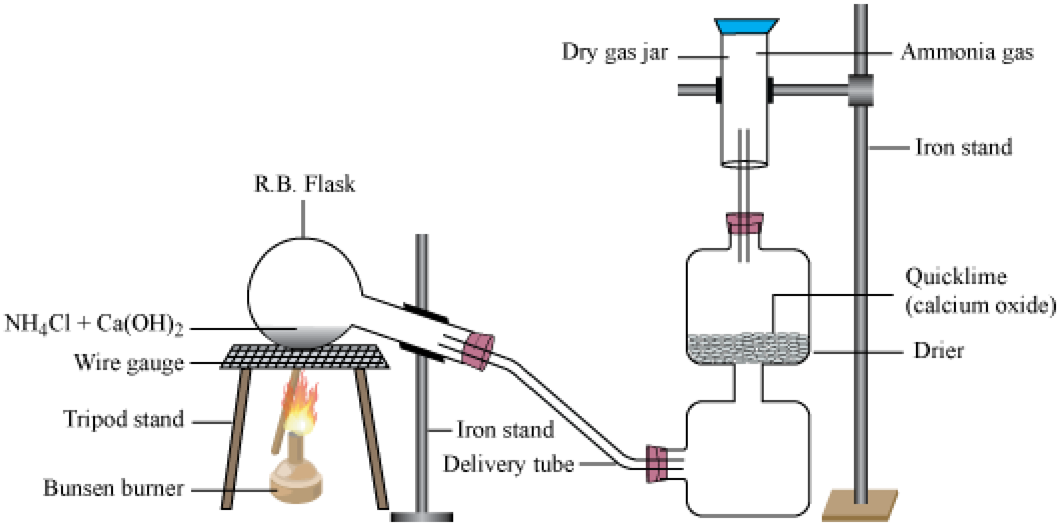
$$2\ NH_4Cl + Ca(OH)_2 \xrightarrow{\Delta} CaCl_2 + 2H_2O + 2\ NH_3$$

$$(NH_4)_2SO_4 + 2\ NaOH \xrightarrow{\Delta} Na_2SO_4 + 2H_2O + 2\ NH_3$$

- Ammonia is formed by the decay of nitrogenous organic matter such as urea.

$$NH_2CONH_2 + 2H_2O \longrightarrow (NH_4)_2CO_3 \longleftrightarrow 2NH_3 + H_2O + CO_2$$

- On a small scale, ammonia is obtained from ammonium salts, which decompose when treated with caustic soda or lime. It forms a metal salt, water, and ammonia gas.



In this method, the mixture of ammonium chloride and dry calcium hydroxide is placed in a round-bottomed flask. It is clamped to an iron stand so that its neck is tilting downwards. This stops water vapours formed by condensation to trickle back into the hot flask.

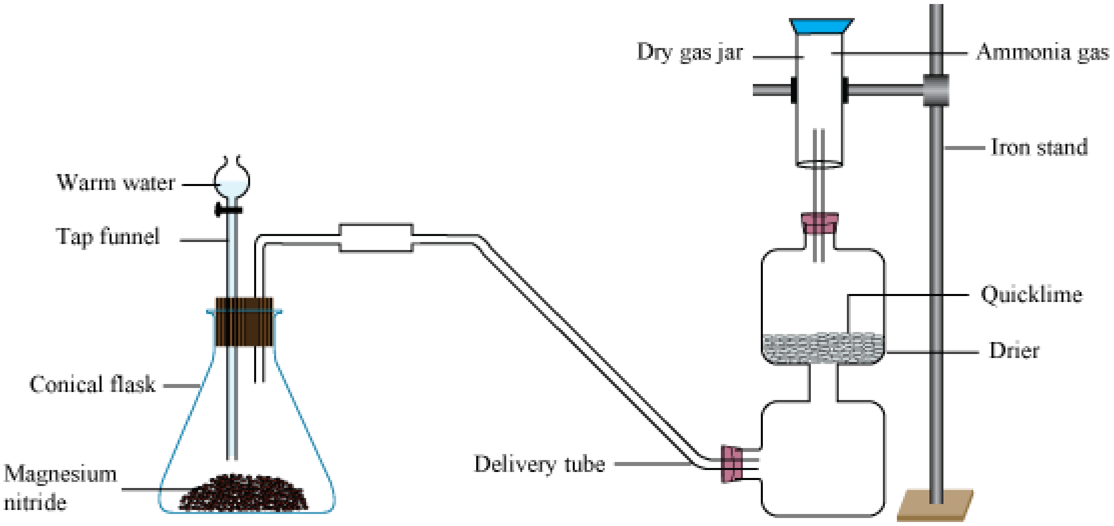
$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + 2H_2O + CaCl_2$$

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3 + 2H_2O + Na_2SO_4$$

The ammonia gas contains water vapours as impurities. The water vapour has to be removed as the ammonia gas is extremely soluble in water. Thus, it is passed through drier containing quicklime.

The vapour density of ammonia is 8.5. Therefore, it is lighter than air. Thus, it is collected by downward displacement of the air. Also, since ammonia gas is extremely soluble in water, it cannot be collected over water.

- Ammonia can also be prepared by treating metal nitrides like magnesium, sodium and aluminium with warm water.



In this method, magnesium nitride is placed in a conical flask. Warm water is allowed to trickle on it. This evolves moist ammonia gas.

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$$

The ammonia gas contains water vapours as impurities. The water vapour has to be removed as ammonia gas is extremely soluble in water. Hence, it is passed through drier containing quicklime.

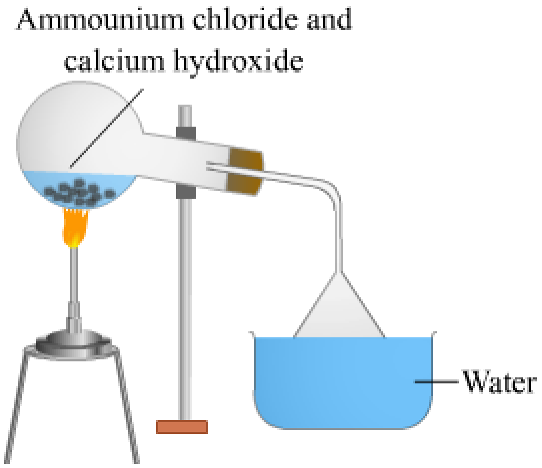
The vapour density of ammonia is 8.5. Therefore, it is lighter than air. Thus, it is collected by downward displacement of air. Also, since ammonia gas is extremely soluble in water, it cannot be collected over water.

The following reactions take place when water reacts with sodium and magnesium nitride.

$$Na_3N + 3H_2O \rightarrow 3NaOH + NH_3$$
$$AlN + 3H_2O \rightarrow Al(OH)_3 + NH_3$$

- **Preparation of Aqueous ammonia**

By dissolving ammonia in water, an aqueous solution of ammonia is obtained. Take water in a container and dip a small portion of the mouth of the funnel in water.



The level of the water decreases when ammonia dissolves in water at a higher rate than that of its production.

The water rushes into the funnel due to the decrease in the pressure above water level and this results in loss of contact between water and the rim of the funnel.

The funnel comes in contact with water again as the water is pushed down by the ammonia produced. This is how ammonia dissolves in water without a back suction.

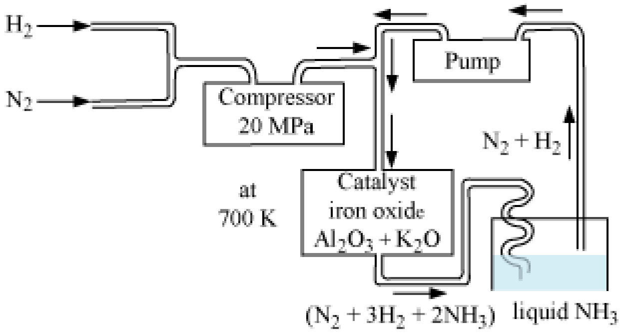
- **On large scale, ammonia is obtained by Haber's process.**

A mixture of hydrogen and nitrogen gases in the ratio 3:1 is taken in the compressor. It is then compressed from 200 atm to 900 atm pressure and passed over the heated catalyst in catalyst chamber. The mixture is maintained at a temperature between 450 – 500°C. In the condenser, the hot mixture of ammonia gas and unreacted hydrogen and nitrogen gases coming out of catalyst chamber are led to cooling pipes.

$$N_{2(g)} + 3H_{2(g)} \longleftrightarrow 2NH_{3(g)}; \Delta_f H^{\ominus} = -46.1\,\text{kJ mol}^{-1}$$

The reaction is reversible and exothermic in nature.

Catalysts such as iron oxide with small amounts of molybdenum are used to increase the rate of attainment of equilibrium.



- High pressure favours the formation of NH_3.
- **Optimum condition** :
- Pressure = 200×10^5 Pa(about 200 atm)
- Temperature ~ 700 K
- Finely divided iron as catalyst and molybdenum or Al_2O_3 as promoter increase the rate of reaction

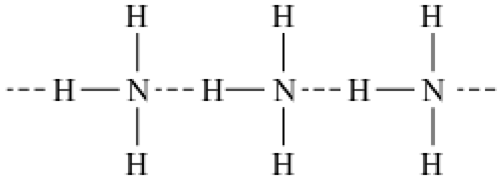
The produced ammonia gas is collected by either **liquefaction** as ammonia has higher boiling point than nitrogen and hydrogen hence, it condenses easily, or **absorption** in water as ammonia is highly soluble in water. The unused mixture of hydrogen and nitrogen gases are recompressed and then recycled into catalyst chamber.

Properties of ammonia

1. It is a colourless non-poisonous gas with a characteristic pungent odour. It is lighter than air and extremely soluble in water because of hydrogen bonding.

2. It can be liquefied when cooled to $10\ ^{o}C$ under pressure of 6 atm. It forms white crystals on cooling.

3. Ammonia has higher melting point and boiling point, latent heat of vaporisation or fusion because of its ability to form hydrogen bonding with itself. Since it has third highest electronegativity so it can form hydrogen bonds with itself and also with water.



$$\cdots H-\underset{H}{\overset{H}{N}}\cdots H-\underset{H}{\overset{H}{N}}\cdots H-\underset{H}{\overset{H}{N}}\cdots$$

4. It has basic nature because of the presence of a lone pair of electrons.

5. It acts as a reducing agent
$3CuO + 2NH_3 \rightarrow 3 Cu + N_2 + 3H_2O$

6. It is lighter than air with the vapour density of 8.5.

7. Inhaling this gas causes irritation to the eyes and respiratory system.

8. It is highly soluble in water.

Uses

1. Due to high dielectric constant, ammonia is a good solvent for ionic compounds.
2. It is used as a cleaning agent for removing grease in dry cleaning.
3. It is used in the manufacturing of artificial silk.
4. It is used as a laboratory reagent.

Oxides of Nitrogen & Preparation and Properties of Nitric Acid

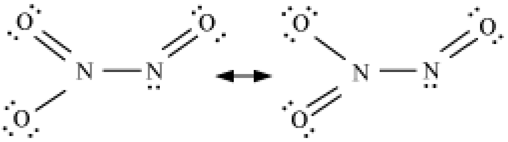
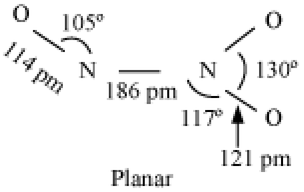
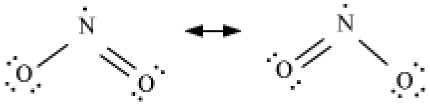
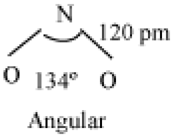
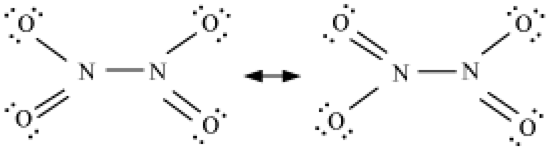
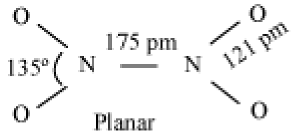
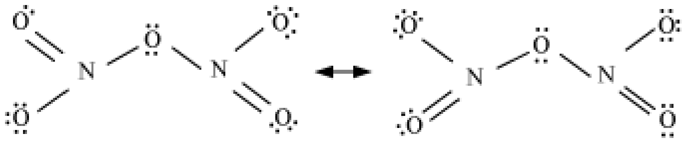
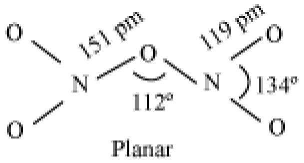
Oxides of Nitrogen

- Forms a number of oxides in different oxidation states
- The given table lists the names, formulae, preparation, and physical appearances of oxides of nitrogen.

Name	Formula	Oxidation state of nitrogen	Common methods of preparation	Physical appearance and chemical nature
Dinitrogen oxide [Nitrogen (I) oxide]	N_2O	+ 1	$NH_4NO_3 \xrightarrow{\text{Heat}} N_2O + 2H_2O$	Colourless gas, neutral
Nitrogen monoxide [Nitrogen (II) oxide	NO	+ 2	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$	Colourless gas, neutral
Dinitrogen trioxide [Nitrogen (III) oxide]	N_2O_3	+ 3	$2NO + N_2O_4 \xrightarrow{250\text{ K}} 2N_2O_3$	Blue solid, acidic

Nitrogen dioxide [Nitrogen (IV) oxide]	NO_2	+ 4	$2Pb(NO_3)_2 \xrightarrow{673K} 4NO_2 + 2PbO$	Brown gas, acidic
Dinitrogen tetroxide [Nitrogen (IV) oxide]	N_2O_4	+ 4	$2NO_2 \xleftrightarrow[\text{Heat}]{\text{Cool}} N_2O_4$	Colourless solid/liquid, acidic
Dinitrogen pentoxide [Nitrogen (V) oxide]	N_2O_5	+ 5	$4HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + 2N_2O_5$	Colourless solid, acidic

- Structures and bond parameters of oxides of nitrogen are given in the following table.

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

Question:

Do you know why NO_2 dimerises?

Answer:

It is a typical odd molecule with odd number of valence electrons. Hence, it dimerises to form stable N_2O_4 molecule with even number of electrons.

Oxoacids of Nitrogen

- Hyponitrous acid – $H_2N_2O_2$
- Nitrous acid – HNO_2
- Nitric acid – HNO_3

Nitric acid (HNO_3)

- In laboratory – By heating KNO_3 or $NaNO_3$ with concentrated H_2SO_4 in glass retort

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

Let us see the laboratory preparation of nitric acid by means of the following video.

- On large scale – By Ostwald's process

Steps involved:

- Catalytic oxidation of NH_3

$$4NH_{3(g)} + \underset{\text{(from air)}}{5O_{2(g)}} \xrightarrow[\text{500K, 9bar}]{\text{Pt/Rh gauge catalyst}} 4NO_{(g)} + 6H_2O_{(g)}$$

- $2NO_{(g)} + O_{2(g)} \longleftrightarrow 2NO_{2(g)}$
- $3NO_{2(g)} + H_2O_{(l)} \longrightarrow 2HNO_{3(aq)} + NO_{(g)}$
- NO formed is recycled and aqueous HNO_3 can be concentrated upto ~ 68% (by mass) by distillation.
- 98% concentration of HNO_3 is attained by dehydration with concentrated H_2SO_4.

Properties

- Colourless liquid (f.p. = 231.4 K and b.p. = 355.6 K)
- Laboratory grade HNO_3 – 68% of the HNO_3 by mass and has specific gravity of 1.504
- Behaves as a strong acid in aqueous solution

$$HNO_{3(aq)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + NO^-_{3(aq)}$$

- Strong oxidising agent – Can oxidise most metals (except noble metals such as Au and Pt)
- With copper:

$3Cu + 8HNO_3\text{(dilute)} \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

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

- With zinc:

$$4Zn + 10HNO_3(\text{dilute}) \rightarrow 4Zn(NO_3)_2 + 5H_2O + N_2O$$
$$Zn + 4HNO_3(\text{conc}) \rightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$$

- Cr and Al do not dissolve in concentrated HNO_3.

  Reason – Formation of passive film of oxide on the surface

- Oxidation of non-metals:

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$
$$C + 4HNO_3 \longrightarrow CO_2 + 2H_2O + 4NO_2$$
$$S_8 + 48HNO_3(\text{conc.}) \longrightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$$
$$P_4 + 20HNO_3(\text{conc.}) \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

Brown Ring Test

Test for nitrates

Depends upon the ability of Fe^{2+} to reduce nitrate to nitric oxide (NO)

NO then reacts with Fe^{2+} to form a brown-coloured complex.

$$NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow NO + 3Fe^{3+} + 2H_2O$$
$$[Fe(H_2O)_6]^{2+} + NO \rightarrow \underset{\text{(brown)}}{[Fe(H_2O)_5(NO)]^{2+}} + H_2O$$

Procedure

Dilute $FeSO_4$ solution is added to an aqueous solution of nitrate ion.

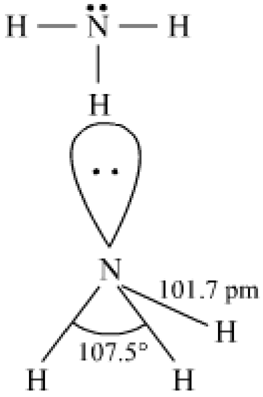
After that, concentrated H_2SO_4 is added along the sides of the test tube.

Result

A brown ring is observed at the interface between the solution and H_2SO_4 layers → Indicates the presence of nitrate ion in the solution

Hydrides and Halides of Nitrogen

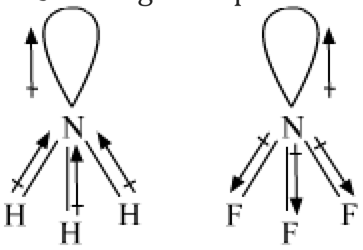
Nitrogen in ammonia molecule is *sp*^{3} hybridised but due to the presence of lone pair of electron, its structure is distorted and it acquires the pyramidal structure. The bond angle N-H is about 107◦.



Nitrogen forms trihalides such as NF_3, NCl_3 or NI_3. Lewis structure of NF_3 is similar to that of NH_3. There is significant difference between NF_3 and NCl_3 as NF_3 is inert but NCl_3 is highly explosive and on decomposition it gives N_2 and Cl_2.

$$2\ NCl_3 \rightarrow N_2 + 3\ Cl_2$$

Even though the structures of NH_3 and NF_3 are similar but their dipole moments are quite different. NH_3 has higher dipole moment than NF_3.



This is because, in case of NH_3 the orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the N–H bonds, whereas in NF_3 the orbital dipole is in the direction opposite to the resultant dipole moment of the three N–F bonds. The orbital dipole because of lone pair decreases the effect of the resultant N–F bond moments, which results in the low dipole moment of NF3.

Phosphorus - Allotropic Forms & Preparation and properties of Phosphine

- **Allotropic Forms of Phosphorus**
- **White phosphorus**
- A translucent white waxy solid
- Poisonous

- Insoluble in water, but soluble in carbon disulphide (CS_2)
- Glows in dark (chemiluminescence)
- Dissolves in boiling NaOH in an inert atmospheric to give PH_3

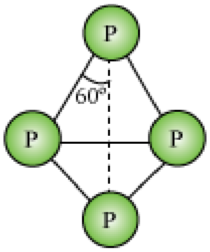
$$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + \underset{\text{Sodium hypophoshite}}{3NaH_2PO_2}$$

  - Readily catches fire in air to give dense fumes of P_4O_{10}

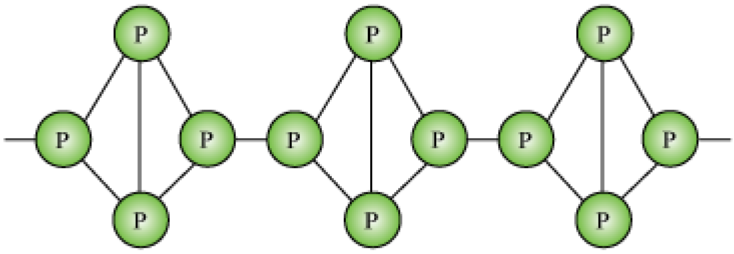
$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$

Less stable and is therefore more reactive than the other solid phases. Reason: Angular strain in the P_4 molecule where the angles are only 60°

  - Consists of discrete tetrahedral P_4 molecule



- **Red Phosphorus**
  - Obtained by heating white phosphorus at 573 K in an inert atmosphere for several days
  - Possesses iron grey lustre
  - Odourless and non-poisonous
  - Insoluble in water as well as in carbon disulphide
  - Less reactive than white phosphorus
  - Does not glow in dark
  - On heating under high pressure, a series of phase of black phosphorus is formed.
  - Polymeric, consisting of chains of P_4 tetrahedra (shown in the figure below)



- **Black phosphorus**
- Two forms – α-black phosphorus and β-black phosphorus
- **α-black phosphorus**
- Formed when red phosphorus is heated in a sealed tube at 803 K
- Can be sublimed in air
- Has opaque monoclinic or rhombohedral crystals
- Does not oxidise in air
- **β-black phosphorus**
    - Formed by heating white phosphorus at 473 K under high pressure
    - Does not burn in air up to 673 K

Phosphine (PH_3)

- **Preparation**
- By the reaction of calcium phosphide with water or dilute HCl

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

- In laboratory – By heating white phosphorus with conc. NaOH solution in an inert atmosphere of CO_2

$$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + \underset{\text{Sodium hypophoshite}}{3NaH_2PO_2}$$

- When pure – Non inflammable

When impurities (P_2H_4 or P_4 vapours) are present – Inflammable

- Impurities can be removed by their absorption in HI to form PH_4I, which on treating with KOH, gives PH_3.

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

- **Properties**
- Colourless gas with rotten fish smell
- Highly poisonous
- Explodes when in contact with traces of oxidising agents such as HNO_3, Cl_2, and Br_2 vapours
- Slightly soluble in water
- Solution of PH_3 in water decomposes in presence of light to give red phosphorus and H_2.
- A weak base
- Gives phosphorium compounds with acids

$$PH_3 + HBr \longrightarrow PH_4Br$$

- Phosphides are formed when absorbed in $CuSO_4$ or $HgCl_2$ solution.

$$3CuSO_4 + 2PH_3 \longrightarrow Cu_3P_2 + 3H_2SO_4$$
$$3HgCl_2 + 2PH_3 \longrightarrow Hg_3P_2 + 6HCl$$

- **Uses**
- Spontaneous combustion of PH_3 is used in Holme's signal. Containers containing CaC_2 and Ca_3P_2 are pierced and thrown in the sea when the gases evolved burn and serve as a signal.
- In smoke screens

Phosphorus Halides & Oxoacids of Phosphorus

Phosphorus Halides

- Two types – PX_3 (X =F, Cl, Br, I)

PX_5 (X = F, Cl, Br)

Phosphorus Trichloride (PCl_3)

- **Preparation**

- By passing dry Cl_2 over heated white phosphorus

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

- By the action of thionyl chloride with white phosphorus

$$P_4 + 8SOCl_2 \longrightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$$

- **Properties**

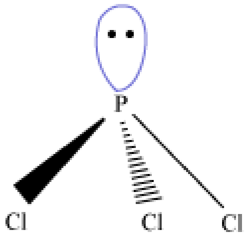
- Colourless oily liquid
- Hydrolyses in the presence of moisture

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

- Reacts with organic compounds containing –OH group such as CH_3COOH, C_2H_5OH

$$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$$
$$3C_2H_5OH + PCl_3 \rightarrow 3CH_3Cl + H_3PO_3$$

- **Structure**
- Has a pyramidal shape
- Phosphorus (P) is sp^3 hybridised.



Phosphorus Pentachloride (PCl_5)

- **Preparation**

- By the reaction of white phosphorus (P_4) with excess of dry chlorine

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

- By the action of SO_2Cl_2 on phosphorus

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

- **Properties**

- Yellowish white powder
- In moist air, it hydrolyses to $POCl_3$ and finally gets converted to phosphoric acid.

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

- Sublimes when heated, but decomposes on stronger heating

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

- Converts the organic compounds containing −OH group to chloro derivation

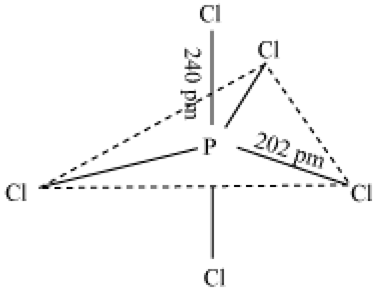
$$C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl + POCl_3 + HCl$$
$$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$$

- On heating with finely divided metals, it gives corresponding chlorides.

$$2Ag + PCl_5 \longrightarrow 2AgCl + PCl_3$$
$$Sn + 2PCl_5 \longrightarrow SnCl_4 + 2PCl_3$$

- **Structure**

- Trigonal bipyramidal shape in gaseous and liquid phase



Three equatorial bonds are equivalent while the two axial bonds are longer than equatorial bonds.

Reason – More repulsion is suffered by axial bonds as compared to equatorial bonds.

- In solid state – Exists as ionic solid

  $[PCl_4]^+[PCl_6]^-$

  Cation, $[PCl_4]^+$ → Tetrahedral

  Anion, $[PCl_6]^-$ → Octahedral

  Oxoacids of Phosphorus

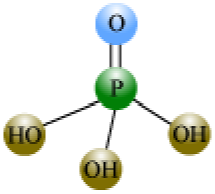
- The given table lists oxoacids of phosphorus with their formulae, oxidation states of phosphorus, characteristic bonds, and their preparation.

Name	Formula	Oxidation state of phosphorus	Characteristic bonds and their number	Preparation
Hypophosphorous	H_3PO_2	+1	One P – OH Two P – H One P = O	white P_4 + alkali
Orthophosphorous	H_3PO_3	+3	Two P – OH One P – H One P = O	$P_2O_3 + H_2O$
Pyrophosphorous	$H_4P_2O_5$	+3	Two P – OH Two P – H Two P = O	$PCl_3 + H_3PO_3$

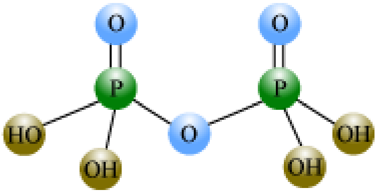
Hypophosphoric	$H_4P_2O_6$	+4	Four P − OH Two P = O One P − P	red P_4 + alkali
Orthophosphoric	H_3PO_4	+5	Three P − OH One P = O	P_4O_{10} + H_2O
Pyrophosphoric	$H_4P_2O_7$	+5	Four P − OH Two P = O One P − O − P	heat phosphoric acid
Metaphosphoric	$(HPO_3)_n$	+5	Three P − OH Three P = O Three P − O − P	phosphorus acid + Br_2, heat in a sealed tube

- **Structures**

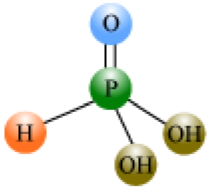
  Structures of some important oxoacids of phosphorus are as follows:



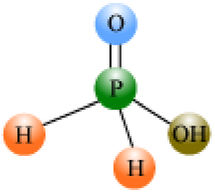
H_3PO_4
Orthophosphoric acid



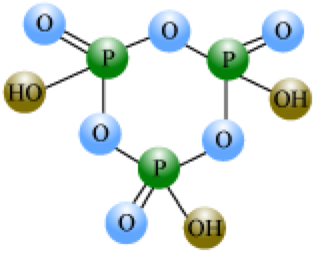
$H_4P_2O_7$
Pyrophosphoric acid



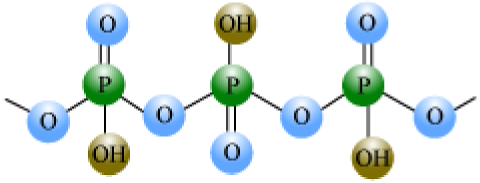
H_3PO_3
Orthophosphorous acid



H_3PO_2
Hypophosphorous acid



Cyclotrimetaphosphoric acid, $(HPO_3)_3$



Polymetaphosphoric acid, $(HPO_3)_n$

- Phosphorus is tetrahedrally surrounded by other atoms.
- Contains at least one P = O and one P – OH bond

  In the oxoacids in which P has oxidation state of less than +5, it contains either P – P (example: $H_4P_2O_6$) or P – H bond (example: H_3PO_2) along with P = O and P – OH bonds.

- **Chemical Properties**

- Acids in +3 oxidation state of P, disproportionate to higher and lower oxidation states

  Example:

$$\underset{\text{Phosphorus acid}}{4H_3PO_3} \longrightarrow \underset{\text{Phosphoric acid}}{3H_3PO_4} + \underset{\text{Phosphine}}{PH_3}$$

- Acids containing P – H bond have strong reducing properties. For example, hypophosphorus acid is a strong reducing agent as it contains two P – H bonds. It reduces $AgNO_3$ to metallic Ag.

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

- P – H bonds are not ionisable.
- P – OH bonds are ionisable and cause basicity.

- H_3PO_3 is dibasic as it contains two –OH bonds.

- H_3PO_4 is tribasic as it contains three –OH bonds.

General Trends of Group 16 Elements

Group 16 Elements

- Oxygen (O), Sulphur (S), Selenium (Se), Tellurium (Te) and Polonium (Po)
- Also known as chalcogens

Occurrence

- **Oxygen**
- Most abundant of all the elements on earth
- Forms about 46.6% by mass of earth's crust
- Dry air contains 20.946% oxygen by volume
- **Sulphur**
- Abundance in earth's crust is 0.03 – 0.1%
- Exists as sulphates such as gypsum ($CaSO_4.2H_2O$), epsom salt ($MgSO_4.7\ H_2O$), baryte ($BaSO_4$); as sulphides such as galena (PbS), zinc blende (ZnS), copper pyrite ($CuFeS_2$)
- Also occurs as hydrogen sulphide in volcanoes
- Present in organic materials such as eggs, proteins, garlic, onion, mustard, hair and wool
    - Selenium and tellurium – Found as metal selenides and tellurides in sulphide ores
    - Polonium – Decay product of thorium and uranium minerals

Atomic Properties

- General valence shell electronic configuration is ns^2np^4.
- Atomic and ionic radii increase down the group.
- Ionisation enthalpy decreases down the group.
- Oxygen has lesser negative electron-gain enthalpy than sulphur because due to small size of oxygen atom, the incoming electron faces a high inter-electronic repulsion due to which its addition becomes difficult and less energy is released. While in the case of sulphur atom, due to its large size, inter-electronic repulsion is less and incoming electron added with an ease, hence it has high

negative electron gain enthalpy than oxygen. But from sulphur onwards, the value becomes less negative up to polonium.

- Within the group, electronegativity decreases with an increase in atomic number.

Physical Properties

- Oxygen and sulphur: Non-metals
- Selenium and tellurium: Metalloids
- Polonium: Metal (Radioactive; half-life = 13.8 days)
- All these elements exhibit allotropy.
- M.p and b.p. increase down the group

Chemical Properties

- Oxidation states

  O = −2, −1, +1, +2

  Te, S, Se = − 2, +2, +4, +6

  Po = +2, +4

- Stability of −2 oxidation state decreases down the group.
- Oxygen shows only negative oxidation state as −2. (Exception: OF_2, where oxygen is in +2 state)

  Reason: Electronegativity of oxygen is very high.

- Bonding in +4 and +6 oxidation states are primarily covalent.
- **Reactivity with hydrogen**
- All elements of this group form hydrides of the type H_2E (E = O, S, Se, Te).
- Acidic strength order:

  $H_2O < H_2S < H_2Se < H_2Te$

- Order of reducing character:

  $H_2S < H_2Se < H_2Te$

- **Reactivity with oxygen**
- All these elements form oxides of the EO_2 and EO_3 type. (E = S, So, Te or Po).
- Both types of oxides are acidic in nature.
- **Reactivity with halogens**
- Form halides of the type EX_6, EX_4 and EX_2

  Where,E is the element of this group and X is the halogen.

Anomalous Behaviour of Oxygen

- It is different from the rest of the members of the group due to its
- Small size
- High electronegativity
- Strong hydrogen bonding is present in H_2O, which is not found in H_2S.
- Absence of *d*-orbitals in oxygen limits its covalence to four, and in practice, rarely exceeds two. On the other hand, other elements of the group can expand their covalence beyond four.

Dioxygen

Preparation

- By heating chlorates, nitrates and permanganates

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

- By the thermal decomposition of oxides of metals which are present low in the electrochemical series

$$2Ag_2O_{(s)} \longrightarrow 4Ag_{(s)} + O_{2(g)}$$
$$2HgO_{(s)} \longrightarrow 2Hg_{(l)} + O_{2(g)}$$

- By the thermal decomposition of higher oxides of some metals such as lead

$$2Pb_3O_{4(s)} \longrightarrow 6PbO_{(s)} + O_{2(g)}$$
$$2PbO_{2(s)} \longrightarrow 2PbO_{(s)} + O_{2(g)}$$

- Decomposition of hydrogen peroxide (H_2O_2) in the presence of catalysts such as finely divided metals and MnO_2

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

- By electrolysis of water – produces H_2 at the cathode and O_2 at the anode
- Industrially, it is obtained from air by first removing CO_2 and H_2O vapour, and then liquefying and fractionally distilling the remaining gases to give N_2 and O_2.

Physical Properties

- Colourless and odourless gas
- Soluble in water – to the extent of 3.08 cm^3, in 100 cm^3 water, at 293 K – sufficient for the vital support of marine and aquatic life
- Liquefies at 90 K
- Freezes at 55 K
- Three stable isotopes – ^{16}O, ^{17}O and ^{18}O
- Paramagnetic in nature
- Bond dissociation enthalpy of O = O double bond is high (493.4 kJ mol^{-1})

Chemical Properties

- Reacts with nearly all metals (except metals like Au and Pt) , non-metals and some noble gases
- Combination with other elements is often strongly exothermic
- Some reactions of O_2 with metals, non-metals and other compounds are as follows:

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

- Some compounds are catalytically oxidised.

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

Uses

- In normal respiration and combustion
- As an oxidant (in liquid state) for propelling rockets
- In oxyacetylene welding
- In the manufacture of many metals (particularly steel)
- Oxygen cylinders are used in hospitals, high altitude flying and mountaineering.

Simple Oxides & Preparation and Properties of Ozone

Oxides

- Binary compounds of oxygen with another element
- Can be simple (example – MgO, Al_2O_3) or mixed (example – Pb_3O_4, Fe_3O_4)

Simple Oxides

- Classified as acidic, basic, amphoteric, or neutral oxides
- **Acidic oxides** – Combine with water to give an acid
- Example – SO_2, Cl_2O_7, CO_2, N_2O_5

$$\underset{}{SO_2 + H_2O \longrightarrow} \underset{\text{(Acid)}}{H_2SO_3}$$

- Non-metal oxides are acidic in nature.
- Oxides of some metals in higher oxidation state also have acidic character. (Example − Mn_2O_7, CrO_3, V_2O_5)
- **Basic oxides –** Combine with water to give bases
- Examples − Na_2O, CaO, BaO

$$CaO + H_2O \longrightarrow \underset{\text{(base)}}{Ca(OH)_2}$$

- Metallic oxides are basic in nature.
- **Amphoteric oxides –** Show the characteristics of both acidic as well as basic oxides
- React with both acids and alkalies
- Example – Al_2O_3

$$Al_2O_{3(s)} + 6HCl_{(aq)} + 9H_2O_{(l)} \longrightarrow 2\left[Al(H_2O)_6\right]^{3+}_{(aq)} + 6Cl^-_{(aq)}$$
$$Al_2O_{3(s)} + 6NaOH_{(aq)} + 3H_2O_{(l)} \longrightarrow 2Na_3\left[Al(OH)_6\right]_{(aq)}$$

- **Neutral oxides –** Neither acidic nor basic
- Examples − CO, NO, N_2O

Ozone

- An allotropic form of oxygen
- Very reactive; cannot remain for long in the atmosphere at sea level
- Formed from atmospheric oxygen (at a height of about 20 km) in the presence of sunlight
- Ozone layer protects the earth’s surface from UV radiations.
- **Preparation**
- When a slow dry stream of oxygen is passed through a silent electric discharge, formation of O_3 (10%) takes place.

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

- Pure ozone can be condensed in a vessel surrounded by liquid O_2.
- **Physical properties**
- Pure ozone − Pale blue gas, dark blue liquid, and violet-black solid
- Has a characteristic smell
- In small concentrations, it is harmless.
- If concentration is above about 100 parts per million, then breathing becomes uncomfortable. It results in headache and nausea.
- Thermodynamically unstable with respect to O_2

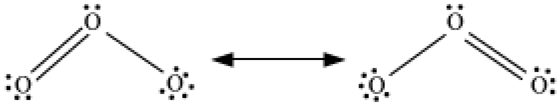
  Reason − Decomposition of O_3 to O_2 results in the liberation of heat (ΔH = − ve) and an increase in entropy (ΔS = + ve), leading to large negative value of ΔG.
- **Chemical properties**
- Powerful oxidising agent because it liberates nascent oxygen atoms ($O_3 \rightarrow O_2 + O$)

$$PbS_{(s)} + 4O_{3(g)} \longrightarrow PbSO_{4(s)} + 4O_{2(g)}$$
$$2I^-_{(aq)} + H_2O_{(l)} + O_{3(g)} \longrightarrow 2OH^-_{(aq)} + I_{2(s)} + O_{2(g)}$$

- Nitrogen oxide (particularly nitric oxide, NO) combines rapidly with ozone.

$$NO_{(g)} + O_{3(g)} \longrightarrow NO_{2(g)} + O_{2(g)}$$

- Therefore, nitrogen oxides emitted from supersonic jet aeroplanes may deplete the concentration of O_3 layer in the atmosphere.
- Freons used in aerosol sprays and as refrigerant also deplete ozone layer.
- Ozone reacts with excess of KI (buffered with a borate buffer of $pH = 9.6$) to produce I_2, which can be titrated against standard sodium thiosulphate solution. It is the quantitative method for estimating O_3 gas.
- **Structure**
- Two main resonating forms:

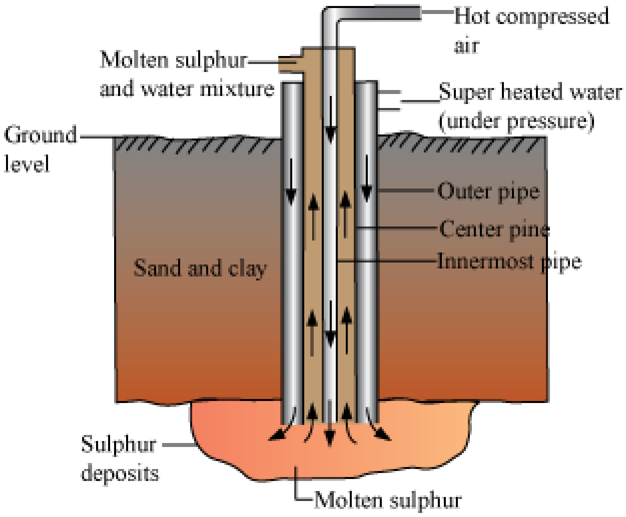


- In resonance hybrid of these two forms, the two O–O bond lengths are identical (128 pm) with a bond angle of about 117°.
- **Uses**
- As a germicide and disinfectant
- For sterilising water
- For bleaching oils, ivory, flour, starch, etc.
- As an oxidising agent in the manufacture of $KMnO_4$

Sulphur - Allotropic forms & Preparation and Properties of Sulphur Dioxide

Extraction of Sulphur

Sulphur is extracted by Frasch process. It is found at depths of more than 150 to 300 metres below the earth's surface. Compressed superheated water is pressed into a pipe, which reaches up to the sulphur deposits. The sulphur here melts. Introducing hot air through another pipe brings it up. The molten sulphur and water is collected in a tank wherein sulphur is cooled and evaporated.



Allotropic forms of Sulphur

Rhombic sulphur (α-sulphur)

- Yellow in colour
- Melting point = 385.8 K
- Specific gravity = 2.06
- On evaporating the solution of roll sulphur in CS_2, crystals of α-sulphur are obtained.
- Insoluble in water, but dissolves to some extent in benzene, alcohol, and ether;

  readily soluble in CS_2

  Monoclinic Sulphur (β-sulphur)

- Melting point = 393 K
- Specific gravity = 1.98
- Soluble in CS_2
- **Preparation**
- By melting rhombic sulphur in a dish and cooling till crust is obtained

  Two holes are made in the crust.

  The remaining liquid is then poured out.

  On removing the crust, colourless needle-shaped crystals of β-sulphur are obtained.

  Stability of α and β-Sulphur

- β-sulphur is stable above 369 K.

- Below 369 K, β-sulphur transforms into α-sulphur.

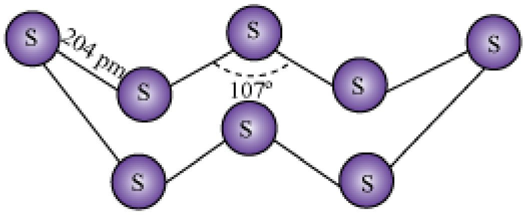
- α-sulphur is stable below 369 K.

- Above 369 K, α-sulphur transforms into β-sulphur.

- At 369 K, both the allotropes are stable and this temperature is called transition temperature.

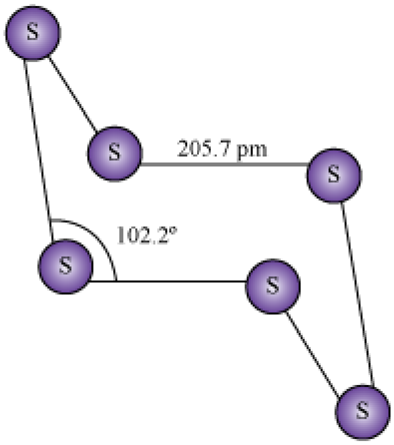
  Structures of Allotropes of Sulphur

- Both α-and β- forms of sulphur have S_8 molecules.
- S_8 molecules are packed to give different crystal structures.
- In both the forms (α-and β-), S_8 ring is puckered and has crown shape.
- Structure of S_8 ring in α-sulphur:



Other Modifications of sulphur

- Sulphur containing 6-20 sulphur atoms per ring has been synthesised.
- In cyclo-S_6, the ring adopts the chair form as shown below.



- At elevated temperatures (~ 1000 K), S_2 is the dominant species and is paramagnetic.

Chemical properties of sulphur

- **Action of air:** When sulphur is heated in air above 444°C, it catches fire and burns with a pale blue flame forming sulphur dioxide gas.

$$S\ (s) + O_2\ (g) \xrightarrow{>444^\circ C} SO_2\ (g)$$
$$2S\ (s) + 3O_2\ (g) \xrightarrow{>444^\circ C} 2SO_3\ (g)$$

- **Action of hydrogen:** When hydrogen gas is passed over boiling sulphur, it reacts to form a foul smelling hydrogen sulphide gas.

$$H_2\ (s) + S\ (l) \rightarrow H_2S\ (g)$$

- **Reaction with carbon:** When sulphur vapours are passed through red hot coke or charcoal, they react to form vapours of carbon disulphide.

$C\ (s) + 2S\ (g) \rightarrow CS_2\ (l)$

Uses of sulphur

The various uses of sulphur are:

- It is used in refining petroleum and sugar.
- It is used in bleaching wool and silk.
- It is used as an anti-chlor, disinfectant, and preservative.
- It is used in the manufacture of sulphuric acids, sodium hydrogen sulphate, and calcium hydrogen sulphate.
- Liquid SO_2 is used as a solvent to dissolve a number of organic and inorganic compounds.

Sulphur Dioxide

Preparation

- When sulphur is burnt in air or oxygen

$$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$$

- In laboratory – By treating sulphite with dilute H_2SO_4

$$SO_3^{2-}{}_{(aq)} + 2H^+{}_{(aq)} \longrightarrow H_2O_{(l)} + SO_{2(g)}$$

- Industrially produced as a by-product of the roasting of sulphide ores

$$4FeS_{2(s)} + 11O_{2(g)} \longrightarrow 2Fe_2O_{3(s)} + 8SO_{2(g)}$$

Properties

- Colourless gas with pungent smell
- Soluble in water
- Liquefies at room temperature under a pressure of 2 atm
- Boils at 263 K
- When passed through water, it produces sulphurous acid.

$$SO_{2(g)} + H_2O_{(l)} \longleftrightarrow H_2SO_{3(aq)}$$

- Reaction with NaOH

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

- Reaction with Cl_2

$$SO_{2(g)} + Cl_{(g)} \xrightarrow{\text{Char coal}} \underset{\text{Sulphuryl chloride}}{SO_2Cl_{2(l)}}$$

- Reaction with O_2

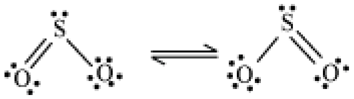
$$2SO_{2(g)} + O_{2(g)} \xrightarrow{V_2O_5} 2SO_{3(g)}$$

- Moist sulphur dioxide behaves as a reducing agent.
- For example:

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

Structure

- Angular in shape
- It is a resonance hybrid of the following two canonical forms:



Uses

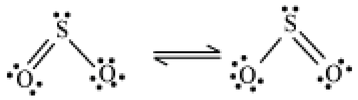
- In refining petroleum and sugar
- In bleaching wool and silk
- As an anti-chlor, disinfectant, and preservative
- In the manufacture of sulphuric acids, sodium hydrogen sulphate, and calcium hydrogen sulphate
- Liquid SO_2 is used as a solvent to dissolve a number of organic and inorganic compounds.

Occurrence

Sulphur dioxide was was first prepared in 1774 by Priestley by heating mercury with sulphuric acid. It occurs in free state in fumes of volcanic vents. It is also found in exhaust of engines and in industrial belts where coal and petroleum are used.

Structure

- Sulphur dioxide is angular in shape.



Preparation of sulphur dioxide gas

- When sulphur is burnt in excess of air or oxygen, sulphur dioxide is formed.

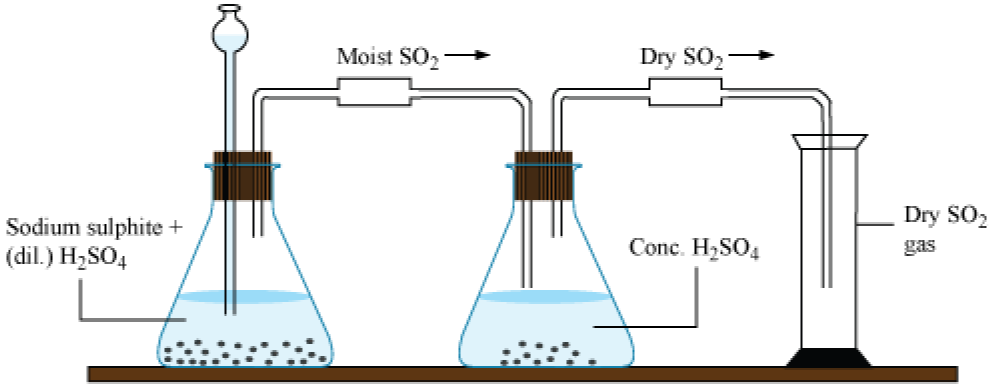
$$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$$

- Industrially produced as a by-product of the roasting of sulphide ores

$$4FeS_{2(s)} + 11O_{2(g)} \longrightarrow 2Fe_2O_{3(s)} + 8SO_{2(g)}$$

- In laboratory, sulphur dioxide is prepared by treating sulphites of active metal with dilute sulphuric acid.

  The metal sulphite (i.e., sodium sulphite) is placed in a conical flask. Dilute sulphuric acid is poured from the thistle funnel.



  To remove impurities such as water vapours, the gas evolved is passed through sulphuric acid.

$$SO_3^{2-}{}_{(aq)} + 2H^+{}_{(aq)} \longrightarrow H_2O_{(l)} + SO_{2(g)}$$

$$Na_2SO_4 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + SO_2$$
$$NaHSO_4 + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O + 2SO_2$$

The gas being heavier than air gets collected by its upward displacement.

- Sulphur dioxide can also be prepared by heating copper turnings with concentrated sulphuric acid:

$$Cu(s) + 2H_2SO_4(aq) \rightarrow CuSO_4(aq) + SO_2(g) + 2H_2O(l)$$

Physical Properties of sulphur dioxide gas

- It is a colourless gas with pungent smell.
- It is soluble in water.
- It liquefies at room temperature under a pressure of 2 atm.
- It boils at 263 K.
- The vapour density of sulphur dioxide is 32. Thus, it is heavier than air.
- Physiological nature: Sulphur dioxide causes headache when inhaled in small amount while it might prove fatal in large amounts. Thus, it is poisonous in nature.

Chemical Properties of sulphur dioxide gas

Sulphur dioxide is neither combustible nor does it support combustion. Also, it has both acidic and bleaching properties. Some other chemical properties are given below:

- When passed through water, it produces unstable sulphurous acid.

$$SO_{2(g)} + H_2O_{(l)} \longleftrightarrow H_2SO_{3(aq)}$$

- It reacts with alkalis such as sodium hydroxide. When sulphur is present in limited amount, it forms their respective soluble sulphites and water, but when sulphur is present in excess, it forms their respective metal hydrogen sulphites.

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

- Reaction with dry chlorine

$$SO_{2(g)} \quad + \quad Cl_{(g)} \quad \xrightarrow{\text{Char coal}} \quad \underset{\text{Sulphuryl chloride}}{SO_2Cl_{2(l)}}$$

Sulphur dioxide reduces chlorine water to hydrochloric acid.

$$SO_{2(g)} + Cl_{2(g)} + 2H_2O \longrightarrow HCl_{(l)} + H_2SO_4$$

- Reaction with oxygen

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{V_2O_5} 2SO_{3(g)}$$

- Moist sulphur dioxide behaves as a reducing agent.

For example:

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

Comparison of bleaching action of chlorine and sulphur dioxide

- **Role of moisture**

It is essential for both sulphur dioxide and chlorine.

$$Cl_2 + H_2O \rightarrow 2HCl + [O]$$
$$SO_2 + H_2O \rightarrow 2H_2SO_4 + [O]$$

- **Chemical process involved**

In bleaching action of chlorine, oxidation occurs while in bleaching action of sulphur dioxide, reduction takes place.

- **Nature of bleaching action**

In bleaching action of chlorine, permanent action occurs while in bleaching action of sulphur dioxide, temporary effect occurs.

- **Bleaching strength**

Chlorine is a strong bleaching agent. It damages fibres of delicate objects. Hence, it is used for bleaching jute, wood pulp, etc.

Sulphur dioxide acts as a strong bleaching agent. It does not damage the fibres of delicate objects. Hence, it is used for bleaching wool, silk, hair, etc.

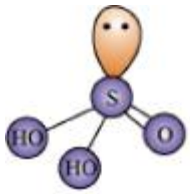
Uses of sulphur dioxide

- It is used in refining petroleum and sugar.
- It is used in bleaching delicate fibres such as wool and silk.
- It is used as an anti-chlor, disinfectant, and preservative.
- It is used in the manufacture of sulphuric acid. It is catalytically oxidised to sulphur trioxide, which is then dissolved in water to form sulphuric acid.
- It is also used in the manufacture of sodium hydrogen sulphate and calcium hydrogen sulphate.
- Liquid SO_2 is used as a solvent to dissolve a number of organic and inorganic compounds.
- It is also used in refrigeration industry as it easily liquefies at a pressure of 2 atmospheres.

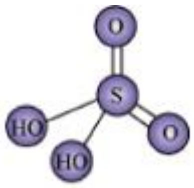
Oxo Acids of Sulphur

Concentrated sulphuric acid is known as oil of vitriol. It is also known as the King of Chemicals due to its vast used in industries.

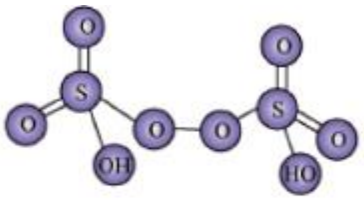
Structures of some important oxoacids of sulphur:



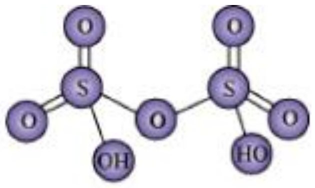
Sulphurous acid
(H_2SO_3)



Sulphuric acid
(H_2SO_4)



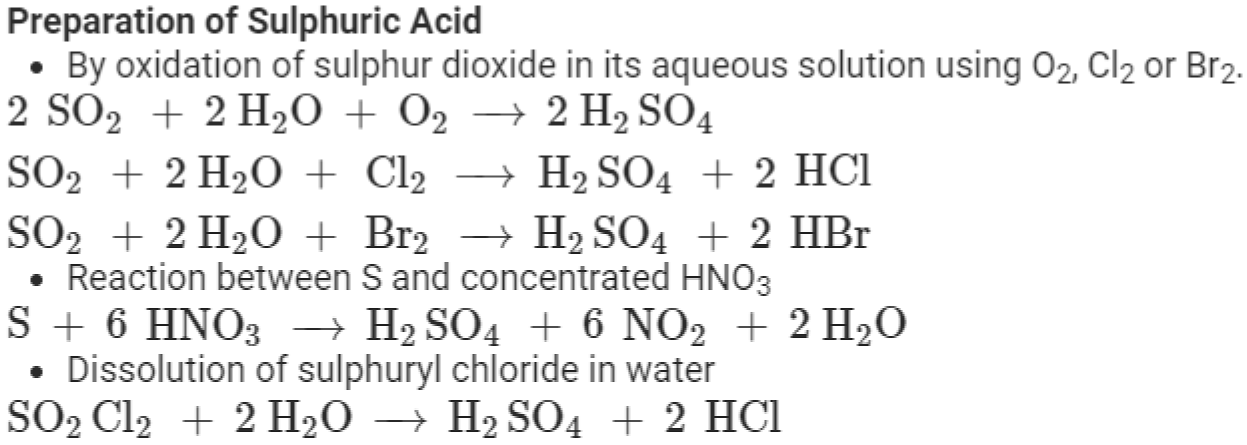
Peroxodisulphuric acid
($H_2S_2O_8$)



Pyrosulphuric acid (Oleum)
($H_2S_2O_7$)

Occurrence of Sulphuric Acid

- In free state:
- Found in hot water sulphur springs
- In combined state:
- Found as :
- Barytes, $BasO_4$
- Gypsum, $CaSO_4.2H_2O$
- Kieserite, $MgSO_4.H_2O$



Preparation of Sulphuric Acid

- By oxidation of sulphur dioxide in its aqueous solution using O_2, Cl_2 or Br_2.

$$2\ SO_2 + 2\,H_2O + O_2 \longrightarrow 2\,H_2SO_4$$

$$SO_2 + 2\,H_2O + Cl_2 \longrightarrow H_2SO_4 + 2\ HCl$$

$$SO_2 + 2\,H_2O + Br_2 \longrightarrow H_2SO_4 + 2\ HBr$$

- Reaction between S and concentrated HNO_3

$$S + 6\ HNO_3 \longrightarrow H_2SO_4 + 6\ NO_2 + 2\,H_2O$$

- Dissolution of sulphuryl chloride in water

$$SO_2Cl_2 + 2\,H_2O \longrightarrow H_2SO_4 + 2\ HCl$$

Manufacture of Sulphuric acid by Contact Process

In contact process, various steps are involved:

- Burning of a pure and dry mixture of two parts of sulphur or sulphide ores and one part of air to produce sulphur dioxide
- Conversion of sulphur dioxide to sulphur trioxide by the reaction with O_2 in presence of vanadium pentoxide or platinised asbestos as catalyst

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{V_2O_5} 2SO_{3(g)}\ ;\ \Delta_r H^\ominus = -196.6\ \text{kJ mol}^{-1}$$

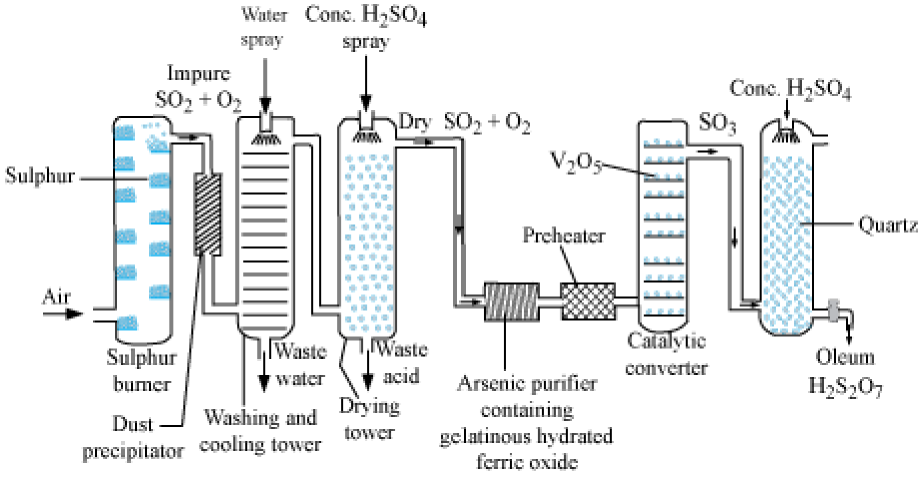
Favourable Conditions for Conversion of SO_2 to SO_3
It is an exothermic reaction; so maintaining a temperature of 410-450°C provides good yield. A pressure of 1-2 atm is used. An excess of oxygen increases the yield of SO_3. V_2O_5 is used as a suitable catalyst to speed up the conversion.

- Absorption of sulphur trioxide in H_2SO_4 to produce pyrosulphuric acid or $H_2S_2O_7$ (oleum)

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

- Dilution of oleum ($H_2S_2O_7$) with water gives sulphuric acid (H_2SO_4) of the desired concentration.

- Flow diagram for the manufacture of H_2SO_4 is given in the figure below.



- The plant is operated at a pressure of 2 bar and a temperature of 720 K.

- H_2SO_4 obtained by this process is 96 – 98% pure.

Physical properties of sulphuric acid

- It is a colourless, odourless, and dense liquid.

- It is an oily liquid with specific gravity of 1.84 at 298 K.

- It freezes at 283 K and boils at 611 K.

- It dissolves in water with the evolution of large quantity of heat.

- Hence, the concentrated acid must be added slowly in water with constant stirring.

Chemical properties of sulphuric acid

- Chemical reactions of H_2SO_4 are because of its
- low volatility
- strong acidic character
- strong affinity for water
- ability to act as an oxidising agent

- In aqueous solution, H_2SO_4 ionises as:

$$H_2SO_{4(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + HSO_4^-{}_{(aq)};\ Ka_1 = \text{Very large } (> 10)$$

$$HSO^-_{4(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + SO_4^{2-}{}_{(aq)};\ Ka_2 = 1.2 \times 10^{-2}$$

- Since $K_{a1} > 10$, H_2SO_4 is largely dissociated into H^+ and HSO_4^-.

- Greater the value of dissociation constant, stronger is the acid. Therefore, it is a strong acid.

- Forms two series of salts:
- Normal sulphates (Example: Na_2SO_4, $CuSO_4$)
- Acid sulphate (Example: $NaHSO_4$)

- Dilute sulphuric acid reacts with active metals, metal oxides, metal hydroxides, metal carbonates, metal bicarbonates, metal sulphites, metal bisulphites and metal sulphides to form their respective metal sulphates and acid sulphates.

$$Mg + H_2SO_4(dil) \rightarrow MgSO_4 + H_2$$
$$K_2O + H_2SO_4(dil) \rightarrow K_2SO_4 + H_2O$$
$$NaOH + H_2SO_4(dil) \rightarrow NaHSO_4 + H_2O$$
$$Na_2CO_3 + H_2SO_4(dil) \rightarrow Na_2SO_4 + H_2O + CO_2$$
$$Na_2SO_3 + H_2SO_4(dil) \rightarrow Na_2SO_4 + H_2O + SO_2$$
$$2\ NaHCO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2\ H_2O + 2\ CO_2$$
$$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + SO_2$$
$$2\ NaHSO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2\ H_2O + 2\ SO_2$$
$$Na_2S + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S$$

Because of low volatility, it can be used for the manufacture of more volatile acids from their corresponding salts.

$2MX + H_2SO_4 \rightarrow 2HX + M_2SO_4$ (X = F, Cl, NO_3) (M = metal)

- Concentrated sulphuric acid is a non-volatile acid. It reacts with salts of volatile acids (HCl, HNO_3, CH_3COOH) to form volatile acids.
-

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$
$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$
$$CH_3COONa + H_2SO_4 \longrightarrow NaHSO_4 + CH_3COOH$$

- Concentrated sulphuric acid is a strong oxidising agent as it produces nascent oxygen on thermal decomposition. This nascent oxygen is capable of oxidising metals, non-metals and inorganic compounds to evolve sulphur dioxide gas.

$$Cu + 2\,H_2SO_4 \longrightarrow CusO_4 + 2\,H_2O + SO_2$$
$$Zn + 2\,H_2SO_4 \longrightarrow ZnSO_4 + 2\,H_2O + SO_2$$
$$C + 2\,H_2SO_4 \longrightarrow CO_2 + 2\,H_2O + 2\,SO_2$$
$$S + 2\,H_2SO_4 \longrightarrow 3\,SO_2 + 2\,H_2O$$
$$2\,P + 5\,H_2SO_4 \longrightarrow 2\,H_3PO_4 + 2\,H_2O + 5\,SO_2$$
$$2\,HBr + H_2SO_4 \longrightarrow Br_2 + 2\,H_2O + SO_2$$
$$H_2S + H_2SO_4 \longrightarrow S + 2\,H_2O + SO_2$$

- It is a strong dehydrating agent because of its great affinity towards water. It extracts water from organic acids, carbohydrates and crystallised salts.

  Do you know what a dehydrating agent is?

  A substance which removes atoms of hydrogen and oxygen in the form of water from the chemical composition of a substance is called dehydrating agent.

- Because of its strong affinity for water, sulphuric acid removes water from hydrated salts and organic compounds (it is evident by charring action on carbohydrates).
- Dehydration of glucose and sugar occurs with formation of a black porous mass of carbon.

  $C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11\,H_2O$

  $C_6H_{12}O_6 \xrightarrow{H_2SO_4} 6C + 6\,H_2O$

- Concentrated sulphuric acid is a moderately strong oxidising agent and can oxidise both metals and non-metals.

  You know that oxidation takes place either on the addition of oxygen or removal of hydrogen. Sulphuric acid undergoes thermal decomposition and liberates nascent oxygen, which oxidises metals and non-metals.

  $Cu + 2H_2SO_4$ (conc.) → $CuSO_4 + SO_2 + 2H_2O$

  $3S + 2H_2SO_4$ (conc.) → $SO_2 + 2H_2O$

  $C + 2H_2SO_4$ (conc.) → $CO_2 + 2SO_2 + 2H_2O$

- Concentrated sulphuric acid has the ability to precipitate out the siluble sulphates of lead, barium, calcium from the aqueous solution of their salts.

$$Pb(NO_3)_2 + H_2SO_4 \longrightarrow PbSO_4 + 2\ HNO_3$$
$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2\ HCl$$

Difference Between Dilute and Concentrated Sulphuric Acid

Dilute H_2SO_4	Concentrated H_2SO_4
Ionises almost completely hence behaves as a strong acid	Does not ionise completely hence behaves as a weak acid
Strong electrolyte	Weak electrolyte
Not an oxidising agent	Good oxidising agent
Not a dehydrating agent	Good dehydrating agent

Uses of sulphuric acid

- As an important industrial chemical
- In the manufacture of fertilisers (e.g., ammonium sulphate, superphosphate)
- In petroleum refining
- In detergent industry
- In the manufacture of pigments, paints, and dyestuff intermediates
- In metallurgical applications (such as in cleansing, electroplating, galvanising)
- In the manufacture of nitrocellulose products
- As a laboratory reagent
- In storage batteries

General Trends of Group 17 Elements

Group 17 Elements

- Fluorine (F), Chlorine (Cl), Bromine (Br), Iodine (I) and Astatine (At)

- Collectively known as halogens

Occurrence

- Fluorine is present as insoluble fluorides – fluorspar (CaF_2), cryolite, and fluoroapatite.
- Fluorine is also present in soils, rivers, bones and teeth of animals.
- Sea water contains chlorides, bromides and iodides of Na, K, Mg and Ca.
- Chlorine is also present in sodium chloride, carnallite, $KCl.MgCl_2.6H_2O$
- Seaweeds contain up to 0.5% of iodine and chile saltpetre contains up to 0.2% of sodium iodate.

Atomic Properties

- General outermost shell electronic configuration is $ns^2 np^5$.
- Atomic and ionic radii increase from F to I due to increasing number of quantum shells.
- Ionisation enthalpy decreases down the group due to increase in atomic size.
- Halogens have the maximum electron gain enthalpy in the corresponding periods.
- Very high electronegativity; electronegativity decreases down the group

Physical Properties

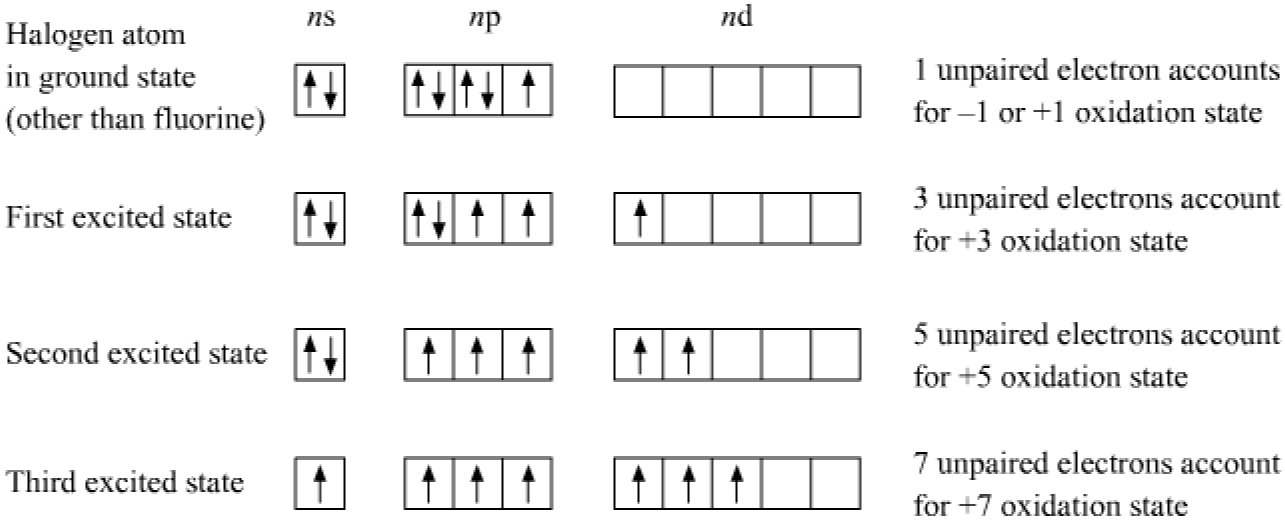
- F and Cl are gases, Br is liquid and I is solid.
- Melting and boiling points steadily increase with atomic numbers.
- Halogens are coloured.
- F and Cl react with water.
- Br and I are only sparingly soluble in water, but soluble in various organic solvents such as $CHCl_3$, CCl_4, CS_2 and hydrocarbons.
- Bond dissociation enthalpy follows the trend

$$Cl-Cl > Br-Br > I-I$$

Chemical Properties

- Exhibit −1 oxidation state

- Cl, Br, I exhibit +1, +3, +5, and +7 oxidation states also.



- Halogens are highly reactive.
- They react with metals and non-metals to form halides.
- Reactivity decreases down the group.
- F_2 is the strongest oxidising agent.
- A halogen oxidises halide ions of higher atomic number.

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

- Fluorine oxides water to oxygen.

$$2F_{2(g)} + 2H_2O_{(l)} \longrightarrow 4H^+_{(aq)} + 4F^-_{(aq)} + O_{2(g)}$$

- Cl_2 and Br_2 react with water to form corresponding hydrohalic and hypohalous acids.

$$X_{2(g)} + H_2O_{(l)} \longrightarrow HX_{(aq)} + HOX_{(aq)} \quad (X = Cl \text{ or } Br)$$

- Reaction of iodine with water is non-spontaneous.
- I^- can be oxidised by oxygen in acidic medium.

$$4I^-_{(aq)} + 4H^+_{(aq)} + O_{2(g)} \longrightarrow 2I_{2(s)} + 2H_2O_{(l)}$$

- All react with hydrogen to form hydrogen halides (HX).
- Acidic strength order: HF < HCl < HBr < HI
- Bond (H−X) dissociation enthalpy order: H−F > H−Cl > H−Br > H−I
- They form many oxides with oxygen, but most of them are unstable.
- Fluorine forms two oxides: OF_2 and O_2F_2
- OF_2 is thermally stable at 298 K.
- They react with metals to form metal halides.
- Order of ionic character of the halides: MF > MCl > MBr > MI

  Where, M is a monovalent metal
- Halogens combine among themselves to form interhalogen compounds.

Anomalous Behaviour of Fluorine

- Ionisation enthalpy, electronegativity, enthalpy of dissociation and electrode potentials − All are higher for fluorine than what is expected from the trends shown by other halogens.
- Ionic and covalent radii, m.p and b.p and electron gain enthalpy are quite lower than expected.
- Low F−F dissociation enthalpy
- Most of the reactions of fluorine are exothermic.
- Reason: Small and strong bonds formed by it with other elements
- HF is a liquid (b.p. = 293 K) while all other hydrogen halides are gases
- Reason: Undergoes strong H-bonding
- Forms only one oxoacid while other halogens form a number of oxoacids
- Reasons for its anomalous behaviour −
- Its small size
- Highest electronegativity

- Low F–F bond dissociation enthalpy
- Non-availability of *d*-orbitals in valence shell

Chlorine

Discovery: Chlorine was first prepared in 1774 by a Swedish chemist, Carl Wilhelm Scheele. He boiled concentrated hydrochloric acid with manganese dioxide, resulting in the formation of a greenish-yellow gas called chlorine.

Position of chlorine in the periodic table

Chlorine has an atomic number of 17 and an atomic mass of 35.5 u. It contains 2, 8, and 7 electrons in K, L, and M shells respectively.

Therefore, it has a valency of 1. It belongs to the group VIIA of the periodic table. This group is also known as halogen group. The name halogen is derived from the Greek word meaning salt producer.

Occurrence: Chlorine does not occur in free state as it is highly reactive in nature.

In combined state,it occurs as rock salt or sodium chloride (NaCl), in mineral carnallite [$KCl.MgCl_2.6H_2O$], etc.

Methods of preparation:

- Deacon's process –

$$4HCl + O_2 \xrightarrow[723\ K]{CuCl_2} 2Cl_2 + 2H_2O$$

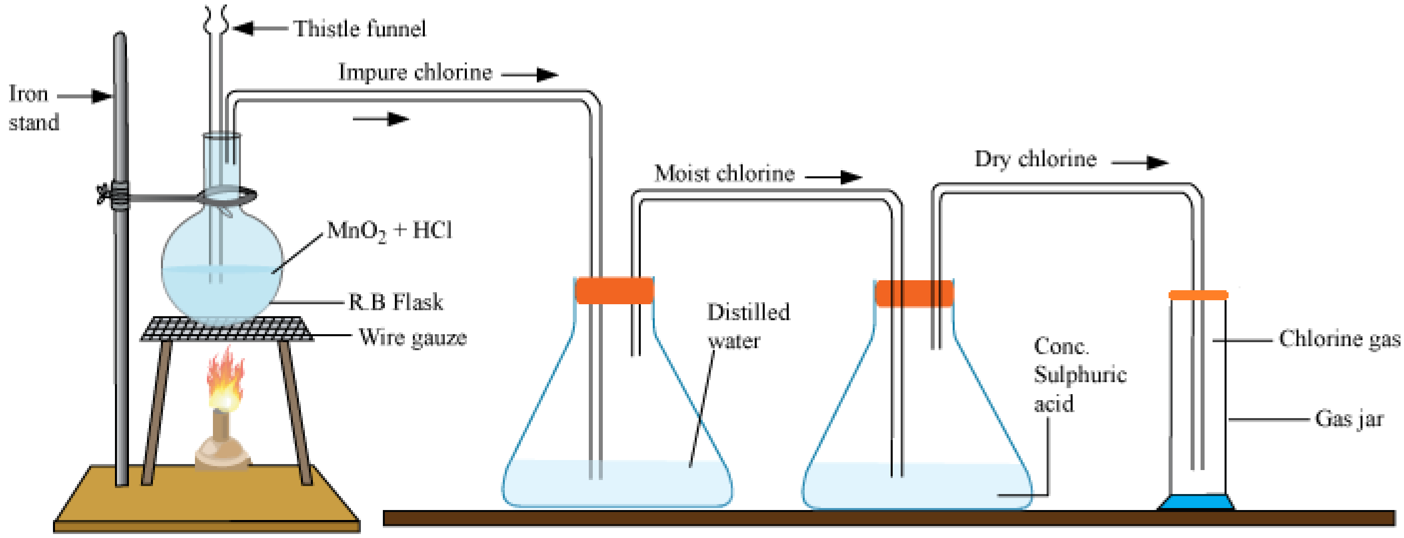
- Electrolytic process –

In the electrolysis of brine (conc. NaCl solution), chlorine is liberated at the anode. The overall reaction of the electrolysis of brine can be written as:

$$2H_2O(l) + 2NaCl(aq) \rightarrow H_2(g) + Cl_2(g) + 2NaOH(aq)$$

- **Laboratory methods -**
- By the oxidation of conc. HCl and manganese dioxide (MnO_2): One mole of manganese dioxide reacts with four moles of hydrochloric acid to form one mole of chlorine gas.

$$MnO_2\ (s) + 4HCl\ (aq) \xrightarrow{\Delta} MnCl_2\ (aq) + 2H_2O\ (l) + Cl_2\ (g)$$



The moist chlorine coming from the flask, containing water is made to bubble through conc. sulphuric acid contained in another conical flask. The conc. H_2SO_4 acts as a dehydrating agent and hence, absorbs water vapour.

- By the action of HCl on $KMnO_4$: Action of concentrated hydrochloric acid on solid potassium premanganate leads to liberation of chlorine gas, as shown in the given chemical reaction:

$2KMnO_4(s) + 16\ HCl(aq) \rightarrow 2KCl(aq) + 2MnCl_2(aq) + 8H_2O(l) + 5Cl_2(g)$

Physical properties of chlorine:

- It is a greenish yellow gas.
- It has a pungent smell.
- It has a slight sour taste.
- It is fairly soluble in water.
- It is 2.5 times heavier than air.
- It is poisonous in nature. When inhaled, it causes severe headache accompanied by cough and breathlessness.

Chemical properties of chlorine:

- Chlorine gas is non-combustible.

- Chlorine reacts with water to form hypochlorous acid.

$$H_2O\,(l) + Cl_2\,(g) \rightarrow HClO\,(aq) + HCl\,(aq)$$

- Reaction with metals and non-metals

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

- When white phosphorus comes in contact with chlorine, it melts and spontaneously catches fire to form dense white fumes.

- Chlorine has strong affinity for hydrogen.

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

- Reaction of chlorine with ammonia

$$\underset{\text{(excess)}}{8NH_3} + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$$

$$NH_3 + \underset{\text{(excess)}}{3Cl_2} \longrightarrow \underset{\substack{\text{Nitrogen}\\ \text{trichloride}\\ \text{(Explosive)}}}{NCl_3} + 3HCl$$

- Reaction of chlorine with alkali

$$\underset{\text{(cold and dilute)}}{2NaOH} + Cl_2 \longrightarrow NaCl + \underset{\substack{\text{Sodium}\\ \text{hypochlorite}}}{NaOCl} + H_2O$$

$$\underset{\text{(hot and conc.)}}{6NaOH} + 3Cl_2 \longrightarrow 5NaCl + \underset{\text{Sodium chlorate}}{NaClO_3} + 3H_2O$$

- Chlorine reacts with slaked lime to give bleaching powder.

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

Composition of bleaching powder: $Ca(OCl)_2.CaCl_2.Ca(OH)_2.2H_2O$

- Reaction of chlorine with hydrocarbons

$$\underset{\substack{\text{Methane}\\ \text{(Saturated)}}}{CH_4} + Cl_2 \xrightarrow{UV} \underset{\substack{\text{Methyl chloride}\\ \text{(Substitution product)}}}{CH_3Cl} + HCl$$

$$\underset{\substack{\text{Ethene}\\ \text{(Unsturated)}}}{C_2H_4} + Cl_2 \xrightarrow{\text{Room temperture}} \underset{\substack{\text{1, 2 – Dichloroethane}\\ \text{(Addition product)}}}{C_2H_4Cl_2}$$

- Oxidising and bleaching properties of Cl_2

$$\underset{\text{(Yellow colour)}}{Cl_2\,\text{Water}} \xrightarrow{\text{on standing}} \underset{\text{(Colourless)}}{HCl + HOCl}$$

HOCl releases nascent oxygen, which is responsible for oxidising and bleaching action.

- Oxidation

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

- Bleaching action

$$Cl_2 + H_2O \longrightarrow 2HCl + O$$
$$\text{Coloured substance} + O \longrightarrow \text{Colourless substance}$$

- Bleaching effect of Cl_2 is permanent. It bleaches vegetable or organic matter in the presence of moisture.

Uses of chlorine

- For bleaching wood pulp, cotton, and textiles
- In the extraction of Au and Pt
- In the manufacture of dyes, drugs and bleaching powder.
- In the manufacture of hydrochloric acid and organic compounds such as CCl_4, DDT, refrigerants, polyvinyl chlorides, chlorofluorocarbons etc.
- In sterilising drinking water
- In the preparation of phosgene ($COCl_2$), tear gas (CCl_3NO_2), and mustard gas ($ClCH_2CH_2SCH_2 CH_2 Cl$)
- In medicines:
- Intravenous solutions have common salt as their major component
- Chloroform ($CHCl_3$) is used as an anaesthetic

Hydrogen chloride (HCl)

Hydrogen chloride (HCl)

Hydrogen chloride was first prepared by Glauber in 1648 by heating rock salt with concentrated sulphuric acid.

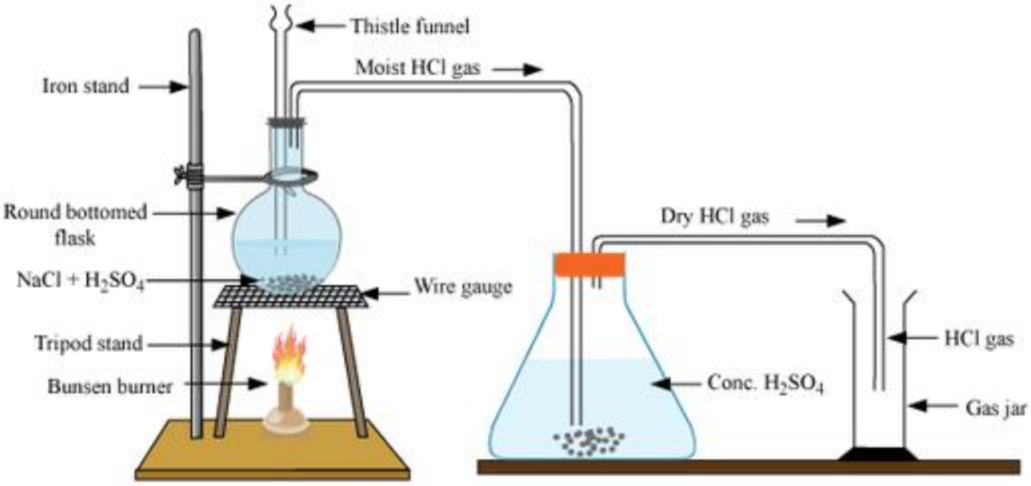
Occurrence

A small quantity of hydrogen chloride gas is found in free state in gases given out by erupting volcanoes. It is also present in the form of gastric juice in the stomach of mammals.

Preparation

- **In laboratory,** hydrogen chloride gas is prepared by heating sodium chloride with concentrated sulphuric acid.

  This is done by taking sodium chloride (i.e., rock salt) in dry round bottomed flask. The apparatus can be set as shown below. Concentrated H_2SO_4 is poured from thistle funnel till its lower end is completely immersed in sulphuric acid. Heat the mixture gently.



$$NaCl + H_2SO_4 \xrightarrow{420K} NaHSO_4 + HCl$$
$$NaHSO_4 + NaCl \xrightarrow{823\ K} Na_2SO_4 + HCl$$

Evolved gas (i.e., hydrogen chloride gas) can be dried by passing though concentrated H_2SO_4. The dry hydrogen chloride gas is collected by upward displacement of water since it is lighter than air.

- Hydrogen chloride gas is also prepared by burning hydrogen gas in the atmosphere of chlorine gas or by exposing hydrogen gas and chlorine gas to diffused sunlight.

$$H_2 + Cl_2 \xrightarrow[\text{Sunlight}]{\text{Diffused}} HCl$$

Do You Know?

Chlorine is a greenish-yellow gas.

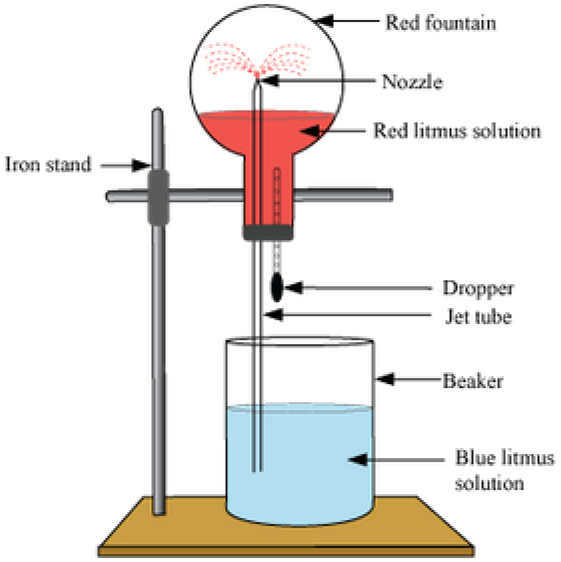
Physical Properties of hydrogen chloride are given below.

- Hydrogen chloride gas is colourless and pungent-smelling with sour taste.
- It has a very irritating odour.
- It is easily liquefied to a colourless liquid. (Boiling point = 189 K)
- It freezes to a white crystalline solid. (Freezing point = 159 K)
- It is extremely soluble in water and ionises as:

$$HCl_{(g)} + H_2O_{(l)} \longrightarrow H_3O^+{}_{(aq)} + Cl^-{}_{(aq)}$$

- High value of K_a indicates that it is a strong acid in water.
- Aqueous solution of HCl is called hydrochloric acid.
- Hydrogen chloride gas is extremely soluble in water. It is described using fountain experiment.

Take hydrogen chloride gas in a round bottomed flask and fix a two-holed stopper in its mouth. Through one hole, pass a long jet tube such that the jet is close to the base of flask. Through the other hole, pass a dropper half filled with water. Clamp the flask with iron stand. Place a beaker containing blue litmus solution under the jet tube.



Press the bulb of dropper. You will notice that blue litmus solution rises up in the jet tube and comes out of the nozzle with a great force and forms a red-coloured fountain.

The fountain is formed because when the water is introduced from dropper, it completely absorbs hydrogen chloride gas, thus creating a pressure within the flask. To make up for this, blue litmus solution rises up. The colour change is due to its acidic character.

- The vapour density of hydrogen chloride gas is 18.25. Therefore, it is heavier than air.

Chemical Properties of hydrogen chloride are given below.

- Hydrogen chloride is neither combustible nor does it support combustion.
- On heating at above 500°C, it dissociates into hydrogen and chlorine.

  $2HCl \xleftrightarrow{500^\circ c} H_2 + Cl_2$

- Action with ammonia

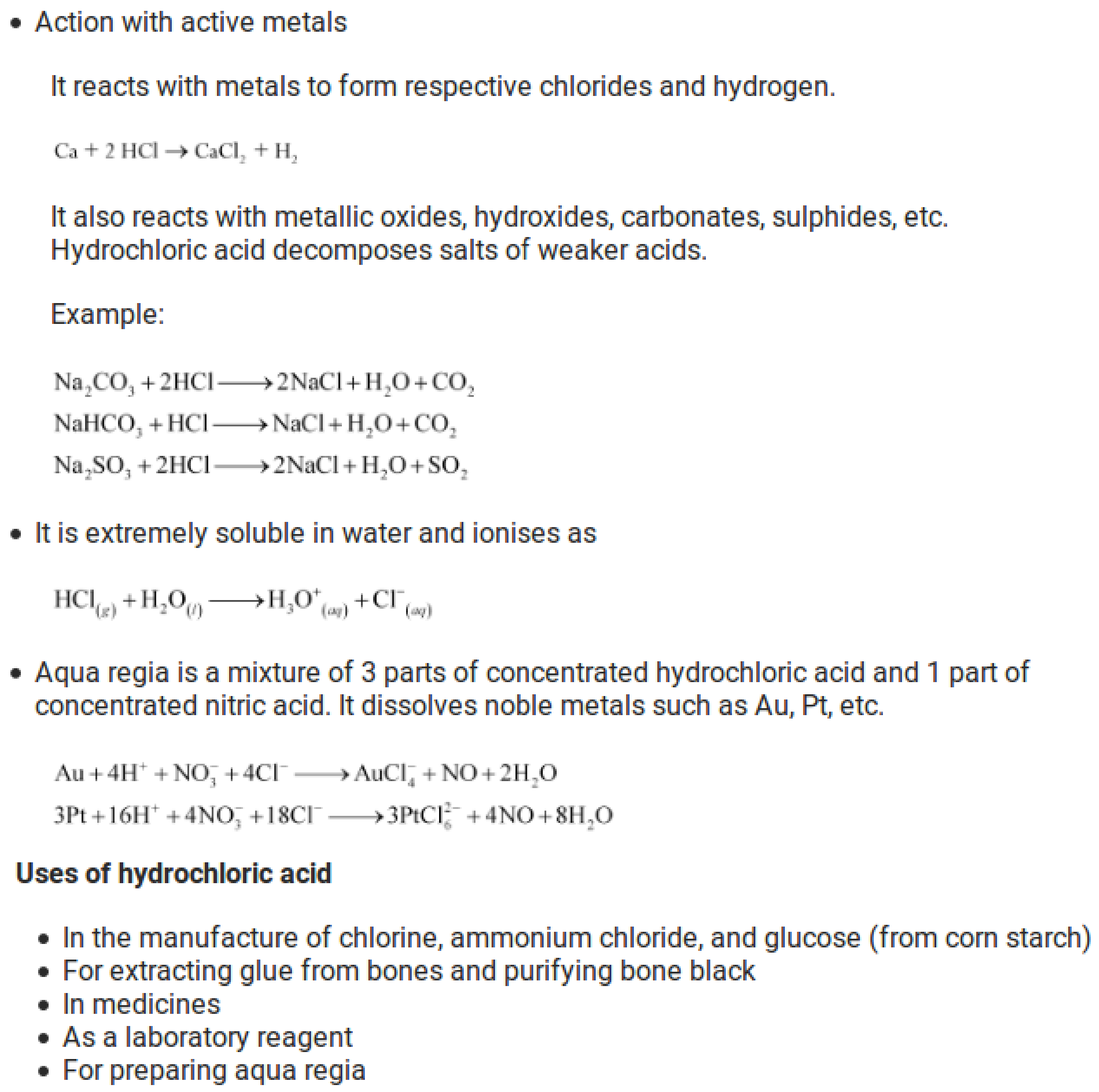
  On mixing with ammonia gas, it forms dense white fumes due to formation of ammonium chloride.

  $NH_3 + HCl \rightarrow NH_4Cl$

- Action with indicators

  Hydrogen chloride turns

- blue litmus solution red
- orange coloured methyl solution pink
- pink coloured alkaline phenolphthalein solution colourless



- Action with active metals

  It reacts with metals to form respective chlorides and hydrogen.

  $Ca + 2\,HCl \rightarrow CaCl_2 + H_2$

  It also reacts with metallic oxides, hydroxides, carbonates, sulphides, etc. Hydrochloric acid decomposes salts of weaker acids.

  Example:

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

- It is extremely soluble in water and ionises as

  $$HCl_{(g)} + H_2O_{(l)} \longrightarrow H_3O^+{}_{(aq)} + Cl^-{}_{(aq)}$$

- Aqua regia is a mixture of 3 parts of concentrated hydrochloric acid and 1 part of concentrated nitric acid. It dissolves noble metals such as Au, Pt, etc.

  $$Au + 4H^+ + NO_3^- + 4Cl^- \longrightarrow AuCl_4^- + NO + 2H_2O$$
  $$3Pt + 16H^+ + 4NO_3^- + 18Cl^- \longrightarrow 3PtCl_6^{2-} + 4NO + 8H_2O$$

Uses of hydrochloric acid

- In the manufacture of chlorine, ammonium chloride, and glucose (from corn starch)
- For extracting glue from bones and purifying bone black
- In medicines
- As a laboratory reagent
- For preparing aqua regia

Oxoacids of Halogens & Inter-halogen Compounds

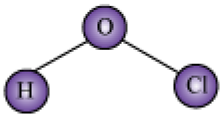
Oxides and Oxoacids of halogen

- Fluorine does not form oxides as it is more electronegative than oxygen. Chlorine, bromine and iodine form many oxides but they decomposed easily on heating such as ClO_2. The only oxoacid, fluorine forms is HOF, which is unstable at room temperature but other halogen atoms form variety of oxoacids.

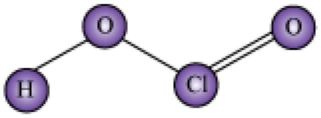
- The oxoacids of halogens are listed in the given table.

Halic (I) acid (Hypohalous acid)	**HOF** (Hypofluorous acid)	**HOCl** (Hypochlorous acid)	**HOBr** (Hypobromous acid)	**HOI** (Hypoiodous acid)
Halic (III) acid (Halous acid)	– –	HOClO (Chlorous acid)	– –	– –
Halic (V) acid (Halic acid)	– –	$HOClO_2$ (Chloric acid)	$HOBrO_2$ (Bromic acid)	$HOIO_2$ (Iodic acid)
Halic (VII) acid (Perhalic acid)	– –	$HOClO_3$ (Perchloric acid)	$HOBrO_3$ (Perbromic acid)	$HOIO_3$ (Periodic acid)

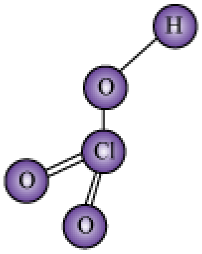
- The structures of oxoacids of chlorine are as follows:



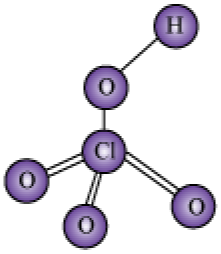
Hypochlorous acid



Chlorous acid



Chloric acid



Perchloric acid

- Since fluorine has high electronegativity and small size, it forms only one oxoacid − HOF (hypofluorous acid).

- Most of the oxoacids are not stable in pure state. They are stable only in aqueous solutions or in the form of their salts.

Interhalogen Compounds

- Two different halogens react with each other to form interhalogen compounds.
- General composition – $XX', XX'_3, XX'_5, \text{and } XX'_7$
- X = Halogen of larger size
- X' = Halogen of smaller size
- X is more electropositive than X'.
- As the ratio between radii of X and X' increases, the number of atoms per molecule also increases.
- **Preparation**
- By the direct combination of halogens or by the action of halogen on lower interhalogen compounds

  Example:

$$\underset{\text{(equal volume)}}{Cl_2 + F_2} \xrightarrow{437\text{ K}} 2ClF$$

$$Cl_2 + \underset{\text{(excess)}}{3F_2} \xrightarrow{573\text{ K}} 2ClF_3$$

$$\underset{\text{(equimolar)}}{I_2 + Cl_2} \longrightarrow 2ICl$$

$$I_2 + \underset{\text{(excess)}}{3Cl_2} \longrightarrow 2ICl_3$$

$$\underset{\text{(diluted with water)}}{Br_2 + 3F_2} \longrightarrow 2BrF_3$$

$$Br_2 + \underset{\text{(excess)}}{5F_2} \longrightarrow 2BrF_5$$

- **Physical Properties**

  Some properties of interhalogen compounds are listed in the given table.

Type	Formula	Physical state and colour

XX'_1	ClF	Colourless gas
	BrF	Pale brown gas
	IF	Very unstable, detected spectroscopically
	BrCl	Gas; at room temperature existence as solid is known
	ICl	Ruby red solid (α-form) Brown red solid (β-form)
	IBr	Black solid
XX'_3	ClF_3	Colourless gas
	BrF_3	Yellow green liquid
	IF_3	Yellow powder
	ICl_3	Orange solid
XX'_5	IF_5	Colourless gas, but solid below 77 K

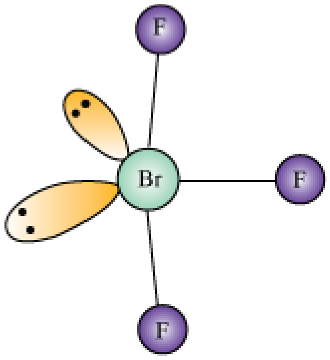
	BrF_5	Colourless liquid
	ClF_5	Colourless liquid
XX'_7	IF_7	Colourless gas

- All are covalent in nature.
- All are diamagnetic in nature.
- Volatile solids or liquids at 298 K (Exception: ClF is a gas)
- Physical properties are intermediate between those of constituent halogens. (Exception: m.p and b.p are a little higher than expected)
- **Chemical Properties**
- More reactive than halogens (except F)

  Reason – $X - X'$ bond in interhalogens is weaker than X – X bond in halogens. (Except F – F bond)
- Undergo hydrolysis
- Give halide ion derived from smaller halogen; and a hypohalite (when XX'), halite (when XX'_3), halate (when XX'_5), and perhalate (when XX'_7) anion derived from the larger halogen

  Example: $XX' + H_2O \longrightarrow XX' + HOX$
- **Structures**
- Can be explained on the basis of VSEPR theory

Example: BrF_3 It has bent T-shape.



The central Br atom has seven electrons in the valence shell.

Three of these will form electron pair bonds with three F atoms, leaving behind four electrons.

Thus, there are three bond pairs and two lone pairs.

According to VSEPR theory, lone pair-lone pair and lone pair-bond pair repulsions are greater than bond pair-bond pair repulsions.

Hence, to minimise these lone pair-lone pair and lone pair-bond pair repulsions, the BrF_3 molecule acquires the shape of slightly bent 'T'.

- The given table lists the inter-halogen compounds with their structures.

Type	Formula	Structure
XX'_3	ClF_3	Bent T-shaped
	BrF_3	Bent T-shaped
	IF_3	Bent T-shaped
	ICl_3	Bent T-shaped

XX'_5	IF_5	Square pyramidal
	BrF_5	Square pyramidal
	ClF_5	Square pyramidal
XX'_7	IF_7	Pentagonal bipyramidal

General Trends of Group 18 Elements

Group 18 Elements

- Helium (He), Neon (Ne), Argon (Ar), Krypton (Kr), Xenon (Xe), and Radon (Rn)
- All are gases.
- Chemically uncreative – Hence, they are termed as noble gases.

Occurrence

- Occur in atmosphere (except Rn)
- Atmospheric abundance in dry air is ~ 1%. (Argon is the major constituent)
- Xe and Rn are the rarest elements of the group.
- Rn is the decay product of ^{226}Ra.

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

- He and Ne are found in minerals of radioactive origin such as pitchblende, monazite, cleveite, etc.

  Atomic Properties

- General outer electronic configuration is $ns^2\ np^6$.

  Exception – He ($1s^2$)

- High ionisation enthalpy
- Reason – Stable electronic configuration
- However, ionisation enthalpy decreases down the group (that is, with the increase in atomic size).
- Atomic radii increase down the group.
- Large positive values of electron gain enthalpy

  Reason – Stable electronic configurations

  Physical Properties

- Monoatomic
- Colourless, odourless, and tasteless
- Sparingly soluble in water
- Low melting and boiling points.

  He has the lowest boiling point of 4.2 K.

- Unusual property of diffusing through most commonly used laboratory materials such as rubber, glass, or plastics

Question

Why do noble gases have very low boiling points?

Answer

Being monoatomic, they have no interatomic forces except weak dispersion force.

Hence, they are liquefied at very low temperature and they have low boiling points.

Chemical Properties

- Less reactive

Reason:

- Completely filled $ns^2\ 2p^6$ valence shell electronic configuration (Except He − $1s^2$)
- High ionisation enthalpy and more positive electron gain enthalpy
- First noble gas compound − $Xe^+PtF_6^-$
- Obtained by mixing PtF_6 and Xe

Xenon-Fluorine Compounds

- XeF_2, XeF_4, and XeF_6
- Obtained by the direct reaction of elements

$$Xe_{(g)} + F_{2(g)} \xrightarrow{673\ K, 1 bar} XeF_{2(s)}$$

(Xe in excess)

$$Xe_{(g)} + 2F_{2(g)} \xrightarrow{873\ K, 7 bar} XeF_{4(s)}$$

(1:5 ratio)

$$Xe_{(g)} + 3F_{2(g)} \xrightarrow{573\ K, 6-70 bar} XeF_{6(s)}$$

(1:20 ratio)

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

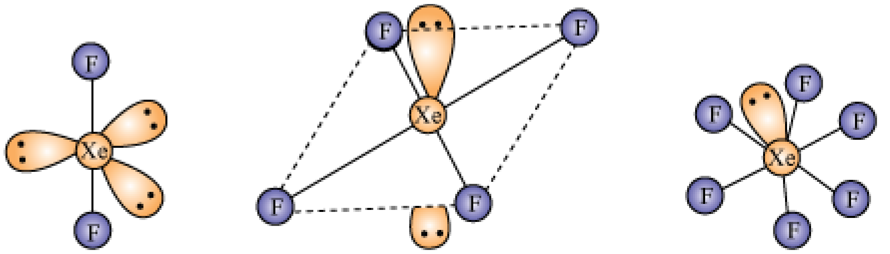
$XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$

- **Properties**
- Colourless crystalline solids
- Sublime at 298 K
- Powerful fluorinating agents
- Readily hydrolysed even by traces of water

Example:

$$2XeF_{2(s)} + 2H_2O_{(l)} \longrightarrow 2Xe_{(g)} + 4HF_{(aq)} + O_{2(g)}$$

- **Structure**
- $XeF_2 \longrightarrow$ Linear
- $XeF_4 \longrightarrow$ Square planar
- $XeF_6 \longrightarrow$ Distorted octahedral



Linear Square planar Distorted octahedral

- **Chemical Properties**

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

Xenon-Oxygen Compounds

- Hydrolysis of XeF_4 and XeF_6 with water gives XeO_3.

$$6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$$

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

- Partial hydrolysis of XeF_6 gives $XeOF_4$ and XeO_2F_2 (oxyfluorides).

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

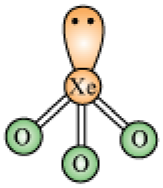
Properties

- XeO_3 is a colourless explosive solid.

- $XeOF_4$ is a colourless volatile liquid.

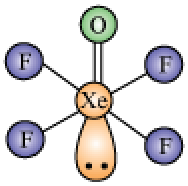
Structure

- XeO_3 has a pyramidal molecular structure.



Pyramidal

- $XeOF_4$ has a square pyramidal molecular structure.



Square pyramidal

Uses of Noble Gases

- **Helium**
- In filling balloons for meteorological observations as it is a non-inflammable and light gas
- In gas-cooled nuclear reactors
- **Liquid Helium**
- As a cryogenic agent
- As a diluent for oxygen in modern diving apparatus

  Reason – Very low solubility in blood
- To produce and sustain powerful superconducting magnets, which are essential parts of modern NMR spectrometers and MRI instruments
- **Neon**
- In discharge tubes and fluorescent bulbs
- Neon bulbs – Used in botanical gardens and in green houses

- **Argon**
- To provide an inert atmosphere in high temperature metallurgical processes
- For filling electric bulbs
- In the laboratory for handling substances that are air-sensitive
- **Xenon and Krypton**
- In light bulbs designed for special purposes