# The p-Block Elements

## The Boron Family & Its Physical and Chemical Properties

- Elements of six groups, from 13 to 18 in the periodic table, represent the *p*-block elements.

- Valence shell electronic configuration is $ns^2np^{1-6}$.

- The given table lists the important oxidation states of the *p*-block elements.

**Table: General Electronic Configuration and Oxidation States of *p*-Block Elements**

| **Group** | **13** | **14** | **15** | **16** | **17** | **18** |
|---|---|---|---|---|---|---|
| General electronic configuration | $ns^2np^1$ | $ns^2np^2$ | $ns^2np^3$ | $ns^2np^4$ | $ns^2np^5$ | $ns^2np^6$ ($1s^2$ for He) |
| First member of the group | B | C | N | O | F | He |
| Group oxidation state | +3 | +4 | +5 | +6 | +7 | +8 |
| Other oxidation states | +1 | +2, −4 | +3, −3 | +4, +2, −2 | +5, +3, +1, −1 | +6, +4, +2 |

- Non-metals and metalloids exist only in the *p*-block of the periodic table.

- Non-metallic character of the elements decreases down the group.

- Non-metals have higher ionisation enthalpies and higher electronegativities than the metals.

- Non-metals readily form ions.

### Group 13 Elements − The Boron Family

- Boron (B) is a non-metal; aluminium (Al) is a metal (but shows many chemical similarities to boron). Gallium (Ga), indium (In) and thallium (Tl) are metallic in character.

- B occurs as $H_3BO_3$, $Na_2B_4O_7.10H_2O$ (borax) and $Na_2B_4O_7 \cdot 4H_2O$ (kernite)

- Two isotopic forms of boron − $^{10}B$ (19%) and $^{11}B$ (81%)

- Aluminium is the most abundant metal. Bauxite $(Al_2O_3 \cdot 2H_2O)$ and cryolite ($Na_3AlF_6$) are the important minerals of aluminium.

### Atomic Properties of the Elements of Group 13

- Outer electronic configuration of these elements is $ns^2np^1$.

- On moving down the group, atomic radius is expected to increase. However, the atomic radius of gallium (135 pm) is less than that of aluminium (143 pm).

- The order of ionisation enthalpies for these elements is $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$. The sum of these ionisation enthalpies for each of the elements is very high.

- Down the group, electronegativity first decreases from B to Al, and then increases marginally.

### Physical Properties of Group 13 Elements

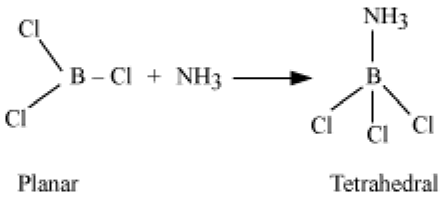
- Boron is a non-metal and is an extremely hard, black-coloured solid. It has a high melting point due to a very strong crystalline lattice.

- Other members are soft metals, with low melting points and high electrical conductivities.

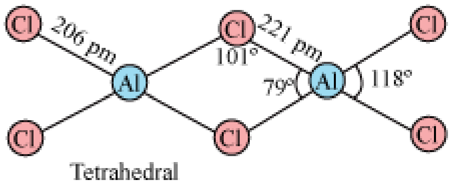
- Density of these elements increases down the group.

## Chemical Properties of Group 13 Elements

- **Oxidation State and Trends in Chemical Reactivity:**
- For aluminium, the sum of the first three ionisation enthalpies is less than that of B. Hence, it forms $Al^{+3}$ ions.
- In Ga, In and Tl, both +1 and +3 oxidation states are observed.
- The relative stability of the +1 oxidation state increases for heavier elements and follows the order- $Al < Ga < In < Tl$
- In thallium, +1 oxidation state is predominant and +3 oxidation state has a high oxidising character.
- In $BF_3$, B is in +3 oxidation state and it contains only six electrons. Hence, it is an electron-deficient molecule.
- $BF_3$ can accept a pair of electrons to attain a stable electronic configuration. Thus, it behaves as a Lewis acid.
- The sum of the first three ionisation enthalpies of boron is very high. Hence, it does not form +3 ions, and forms only covalent compounds.



- $AlCl_3$ achieves stability by forming a dimer.



- Being covalent in trivalent state, most of the compounds are hydrolysed in water.
- Trichlorides on hydrolysis in water form tetrahedral species, $[M(OH)_4]^-$ (M is $sp^3$ hybridised).
- $AlCl_3$ in acidified aqueous solution forms octahedral $[Al(H_2O)_6]^{3+}$ ion, Al is in $sp^3d^2$ hybridised state.

- **Reactivity Towards Air:**
- Boron is un-reactive in crystalline form.
- Aluminium metal and amorphous boron give $Al_2O_3$ and $B_2O_3$ respectively (on heating in air)

$$4E(s)+3O_2(g)\xrightarrow{\Delta}2E_2O_3(s)$$
$$2E(s)+N_2(g)\xrightarrow{\Delta}2EN(s)$$

(E = Element)

- $B_2O_3$ is acidic in nature; aluminium and gallium oxides are amphoteric; and the oxides of indium and thallium are basic in nature.
- **Reactivity towards Acids and Alkalies:**
- Boron does not react with acids and alkalies, even at moderate temperature.
- Aluminium dissolves in mineral acids (HCl) to form hydrogen gas.

$$2Al(s)+6HCl(aq)\longrightarrow 2Al^{3+}(aq)+6Cl^{-}(aq)+3H_2(g)$$

- Aluminium also dissolves in aqueous alkalies to liberate hydrogen gas.

$$\begin{array}{l} 2Al(s)+2NaOH(aq)+6H_2O(l) \\ \qquad\qquad\downarrow \\ 2Na^{+}\left[Al(OH)_4\right]^{-}(aq)+3H_2(g) \\ \qquad\text{Sodium} \\ \text{tetrahydroxoaluminate(III)} \end{array}$$

- Concentrated $HNO_3$ forms a protective oxide layer on the surface of aluminum.
- **Reactivity towards Halogens:**

They react with halogens to form trihalides (Exception − $TlI_3$)

$$2E(s)+3X_2(g)\longrightarrow 2EX_3(s)$$
$$(X = F, Cl, Br, I)$$

**Anomalous Properties of Boron and Some Important Compounds of Boron**

**Important trends and anomalous properties of boron:**

- Tri-chlorides, bromides, and iodides of group 13 elements being covalent in nature are hydrolysed in water.
- Species such as $\left[M(OH)_4\right]^-$ (tetrahedral) and $\left[M(H_2O)_6\right]^{3+}$ (octahedral) exist in aqueous medium. [Exception − Boron]
- Monomeric trihalides are strong Lewis acids (as they are electron deficient).

  $BF_3$ reacts with $NH_3$ (Lewis base) to complete octet around boron.

  $F_3B\ + :NH_3 \longrightarrow F_3B \leftarrow NH_3$

- The maximum covalence of B is 4. This is due to the absence of *d*-orbitals. On the other hand, for aluminium and other elements, the maximum covalence can be expected beyond 4 (since *d*-orbitals are available).
- Most of the other metal halides (such as $AlCl_3$) are dimerised (example, $Al_2Cl_6$) through halogen bridging. Aluminium completes its octet by accepting electrons from halogen in the formation of $Al_2Cl_6$.

Question: Why is boron unable to form $BF_6^{3-}$ ion?

Answer: Boron is unable to expand its octet due to non-availability of *d*-orbitals. The maximum covalence of boron cannot exceed 4.

**Some Important Compounds of Boron**

- **Borax**
- White crystalline solid of formula $Na_2B_4O_7 \cdot 10H_2O$
- It contains tetra-nuclear units of $\left[B_4O_5(OH)_4\right]^{2-}$ and therefore, its correct formula is $Na_2\left[B_4O_5(OH)_4\right] \cdot 8H_2O$.
- It dissolves in water to form an alkaline solution.

$$Na_2B_4O_7 + 7H_2O \longrightarrow 2NaOH + \underset{\text{Orthoboric acid}}{4H_3BO_3}$$

- It loses water molecules and swells up on heating.

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\Delta} \underset{\substack{\text{Sodium}\\ \text{metaborate}}}{Na_2B_4O_7}$$

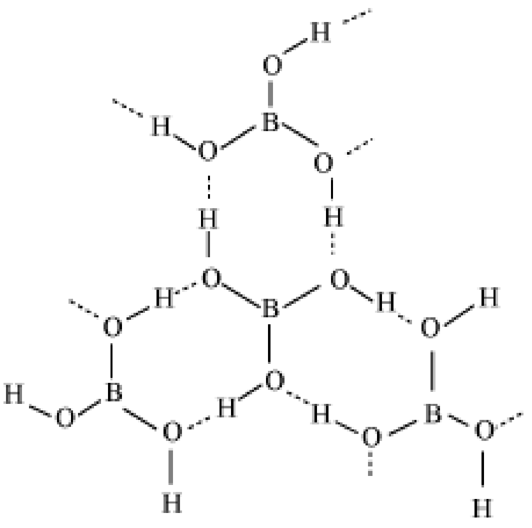
- On further heating, it turns into transparent liquid which solidifies into glass-like material (known as borax bead).

$$Na_2B_4O_7 \xrightarrow{\Delta} \underset{\substack{\text{Sodium}\\ \text{metaborate}}}{2NaBO_2} + \underset{\substack{\text{Boric}\\ \text{anhydride}}}{B_2O_3}$$

- Meta-borates of many transition elements have characteristic colours. The test that can be used to identify these metals in laboratory is called borax bead test.
- **Orthoboric Acid**
- A white crystalline solid with soapy touch
- Sparingly soluble in water and highly soluble in hot water
- Can be prepared by acidifying an aqueous solution of borax

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4B(OH)_3$$

- Also formed by the acidic hydrolysis of most boron compounds such as halides, hydrides, etc.
- Structure − Layered structure with planar $BO_3$ units which are joined by hydrogen bonds (shown in figure)



- A weak monobasic acid (not a protonic acid, but acts as a Lewis acid)

$$B(OH)_3 + 2HOH \longrightarrow [B(OH)_4]^- + H_3O^+$$

- On heating above 370 K, it gives metaboric acid ($HBO_2$), which on further heating yields boric oxide ($B_2O_3$).

$$H_3BO_3 \xrightarrow{\Delta} HBO_2 \xrightarrow{\Delta} B_2O_3$$

- **Diborane**
- Prepared by treating boron trifluoride ($BF_3$) with $LiAlH_4$ in diethyl ether

$$4BF_3 + 3LiAlH_4 \longrightarrow 2B_2H_6 + 3LiF + 3AlF_3$$

- Laboratory preparation − Oxidation of sodium borohydride with iodine gives diborane.

$$2NaBH_4 + I_2 \longrightarrow B_2H_6 + 2NaI + H_2$$

- On industrial scale, it can be produced by the reaction of $BF_3$ and NaH.

$$2BF_3 + 6NaH \xrightarrow{450\ K} B_2H_6 + 6NaF$$

- **Properties**
- Colourless and highly toxic gas with a b. p of 180 K

- Catches fire spontaneously upon exposure to air
- Burns in oxygen to give large amount of energy

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O; \Delta_c H = -1976\ \text{kJ mol}^{-1}$$

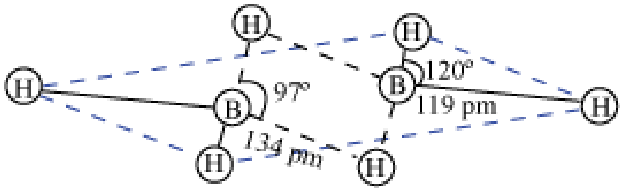
- Readily hydrolysed by water to give boric acid

$$B_2H_6(g) + 6H_2O(l) \longrightarrow 2B(OH)_3(aq) + 6H_2(g)$$

- With Lewis bases (L*)*, they give borane adducts ($BH_3.L$).

$$B_2H_6 + 2NMe_3 \longrightarrow 2BH_3 \cdot NMe_3$$
$$B_2H_6 + 2CO \longrightarrow 2BH_3 \cdot CO$$

- Ammonia reacts with diborane to form $[BH_2(NH_3)_2]^+[BH_4]^-$ , which on further heating gives borazine ($B_3N_3H_6$). Borazine is also called inorganic benzene.
- **Structure**



- Four terminal B-H bonds are two centre - two electron bonds. Two bridge B − H − B bonds are three centre - two electron bonds (shown in figure).
- **Hydridoborates**
- Boron also forms a series of hydridoborates. [Example − $BH_4^-$ ion]
- Lithium and sodium tetrahydridoborates are known as borohydrides.
- They can be prepared by the reaction of metal hydrides with $B_2H_6$ in diethyl ether.

$$2MH + B_2H_6 \longrightarrow 2M^+[BH_4]^-$$

[M = Li or Na]

- $LiBH_4$ and $NaBH_4$ are used as reducing agents in organic synthesis and as starting material for the preparation of other metal borohydrides.

## Boron Halides

- **Backbonding in Boron halides**

As boron halides have 6 electrons in their outermost orbit therefore they are electron deficient and serve as Lewis acid. They can accept electron pair from donor atoms like N, O, P etc to complete their octet.

$$ROR + BF_3 \rightarrow R_2O \rightarrow BF_3$$

The relative strength of Lewis acidity of boron trihalides is found to follow the following trend.

$$BI_3 > BBr_3 > BCl_3 > BF_3$$

While the expected order of Lewis acidity is just reverse of the given trend. The expected order is

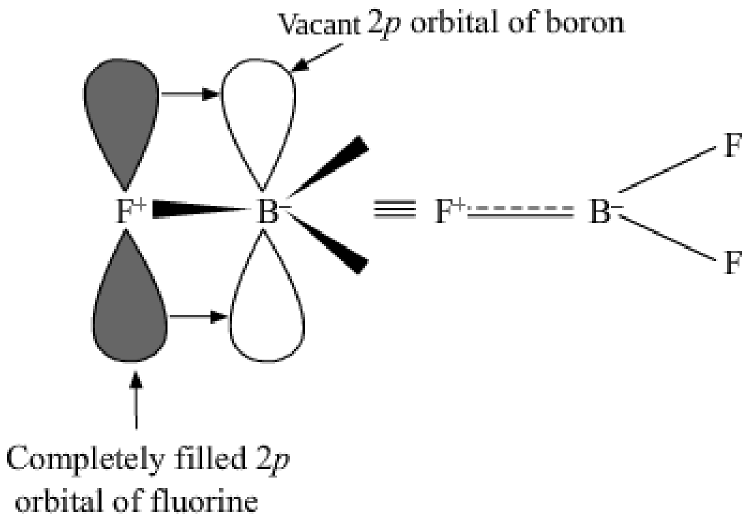
$$BF_3 > BCl_3 > BBr_3 > BI_3$$

As fluorine being the most electronegative, should create the maximum electron deficiency on boron, thus making $BF_3$ the most acidic among the other boron halides. In actual, $BF_3$ is found to be the least acidic.

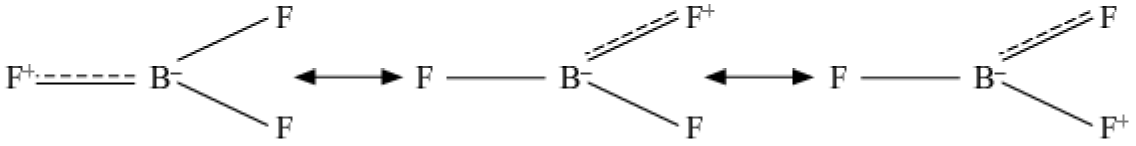
This anomaly can be explained on the basis of back bonding which takes place between completely filled np-orbital of X and empty 2*p*-orbital of B. Let us understand this concept with the help of $BF_3$.

In $BF_3$, each F-atom has completely filled 2p orbitals while B- atom has empty 2p orbital. Since both these orbitals are of same energy level thus they can overlap effectively as a result of which electrons of fluorine get transferred to empty 2p orbital of boron.

This results in the formation of additional p-p bond. This type of bond formation is known as dative or back bonding.

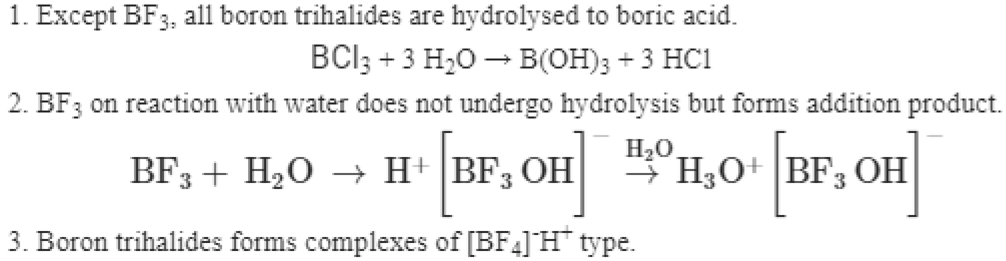


Thus B-F bond has partial double bond character because of back donation. Since back donation can take place between boron and any of the three fluorine atoms, so its structure is best regarded as the resonance hybrid of three structures.



As a result of back bonding the electron deficiency of $BF_3$ is reduced and hence, Lewis acidity is also decreased. The tendency of back bonding is maximum in case of $BF_3$ and it decreases from $BCl_3$ to $BI_3$. This is due to the fact that overlapping of 2p orbitals of boron with 3p, 4p and 5p orbitals cannot takes place easily due to this Lewis acidity increases from $BI_3$ to $BF_3$.

Properties of boron trihalides



1. Except $BF_3$, all boron trihalides are hydrolysed to boric acid.

$$BCl_3 + 3\,H_2O \rightarrow B(OH)_3 + 3\,HCl$$

2. $BF_3$ on reaction with water does not undergo hydrolysis but forms addition product.

$$BF_3 + H_2O \rightarrow H^+\left[BF_3\,OH\right]^- \xrightarrow{H_2O} H_3O^+\left[BF_3\,OH\right]^-$$

3. Boron trihalides forms complexes of $[BF_4]^-H^+$ type.

Use of boron trihalides

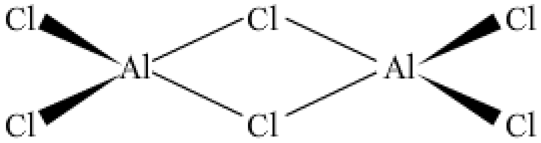
1. $BCl_3$ is a starting material in the preparation of elemental boron.
2. $BF_3$ is used in the preparation of diborane.

3. $BCl_3$ is used as a reagent in the synthesis of organic compounds and also used in the refining of aluminium, magnesium etc.

**Aluminium Halides**

- **Structure of $AlCl_3$**

$AlCl_3$ is an electron deficient molecule which completes its octet by forming dimer. It exist as dimer in both vapour state as well as non polar solvent.
In bridged structure, the chlorine atoms are tetrahedrally arranged around aluminium atom.



The bridged structure of $Al_2Cl_6$ is evidenced by the following facts:

(i) Vapour density of aluminium chloride measured at 400°C shows that it exists as $Al_2Cl_6$.

(ii) Bond distance between bridged Al-Cl $(2.21\overset{o}{A})$ is greater than that of terminal Al-Cl( $(2.06\ \overset{o}{A})$ bond.

(iii) The dimeric structure gets destroyed on dissolution in water as high heat of hydration split the dimeric structure into $[Al(H_2O)_6]^{3+}$ and 2 $Cl^-$ ions. So the solution becomes a good conductor of electricity.

- **Properties of $AlCl_3$**

(i) In pure form, $AlCl_3$ is a white crystalline compound, soluble in water and organic solvents.

(ii) It is extremely hygroscpic and on hydrolysis it forms $Al(OH)_3$ and HCl.

(iii) Dimeric form of aluminium chloride is ionic in nature as on dissolution in water it forms ions and conducts electricity.

- **Uses of $AlCl_3$**

(i) It is used as a catalyst in the synthesis of organic compounds.
(ii) It is used in the polymerisation and isomerisation reactions of hydrocarbons.
(iii) It is the most commonly used Lewis acid and finds many industrial applications.

**Alums**

Generally double sulphates of the type $M_2SO_4$. $M_2'(SO_4)_3.24\ H_2O$, where M is unipositive ion and M' are known as alums. Most important alum is potash alum, $K_2SO_4.Al_2(SO_4)_3.24\ H_2O$.

- **Properties**

1. Potash alum is white crystalline compound and is soluble in water.

2. Its solution is acidic as aluminium sulphate on hydrolysis forms sulphuric acid.

3. On heating it loses water of crystallisation.

4. Since it is a double salt so it gives reactions of all the constituents ions i.e. $K^+$, $Al^{3+}$ and $SO_4^{2-}$.

- **Uses**

1. It is used for the purification of water
2. It is used for stop bleeding.
3. It is used in tanning of leather and as a mordent in dyeing.

**Uses of Boron and Aluminium and their Compounds**

- **Boron and Its Compounds**

- Boron fibres are used in making bullet-proof vest and light composite material for aircrafts.

- $^{10}B$ isotope has high ability to absorb neutrons. Hence, it is used in nuclear industry as protective shields and control rods.

- Borax and boric acid are used in the manufacture of heat resistant glasses, glass wool, and fibre glass.

- Borax is used as flux for soldering metals and is used as a constituent of medicinal soaps.

- An aqueouss solution of orthoboric acid is used as mild antiseptic.

- **Aluminium and its Compounds**

Used in making pipe, tubes, rods, utensils, foils used in packing, in construction, in aeroplane, and in transport industry

# The Carbon Family & Its Physical and Chemical Properties

- Group 14 elements (carbon family): C, Si, Ge, Sn, Pb
- Carbon is the 17th most abundant element in the earth's crust (by mass).
- In elemental state, carbon is available as coal, graphite and diamond.
- In combined state, it exists as carbonates, hydrogen carbonates and carbon dioxide in air (0.03%)
- Two stable, naturally occurring isotopes: $^{12}C$ and $^{13}C$
- $^{14}C$ is a radioactive isotope $(t_{1/2} = 5770 \text{ years})$ used for radiocarbon dating.
- Silicon is the second most abundant element in the earth's crust (27.7% by mass).
- Silicon is the important component of ceramics, glass and cement.
- Germanium is present only in traces.
- Tin exists as cassiterite ($SnO_2$) and lead as galena (PbS).
- Germanium and silicon (in ultra pure form) are used for making transistors and semiconductor devices.

## Atomic Properties of the Elements of Carbon Family

- Valence shell electronic configuration is $ns^2\ np^2$.
- Covalent radius increases from C to Si; after that there is a small increase from Si to Pb.
- First ionisation enthalpy of group 14 members is higher than that of group 13 elements.
- Electronegativity: The elements of this group are slightly more electronegative than the elements of group 13.

## Physical Properties of the Elements of Carbon Family

- All the elements are solids.
- C is non-metal; Si and Ge are metalloids; Sn and Pb are soft metals.

- Melting and boiling points of these elements are higher than those of group 13 elements.

**Chemical Properties**

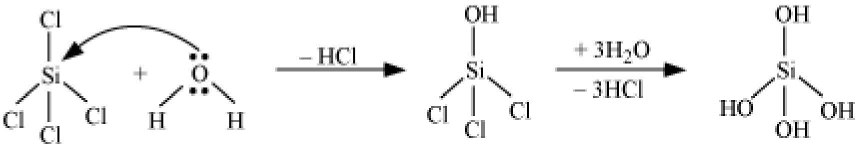
- **Oxidation States:**
- Common oxidation states are +4 and +2.
- Compounds in +4 state are generally covalent. (Since sum of the first four ionisation enthalpies is very high)
- C and Si mostly show +4 oxidation state.
- Ge in +4 state, forms stable compounds, and in +2 state, forms only a few compounds.
- Sn forms compounds in both +2 and +4 oxidation states.
- Compounds of lead in +2 state are stable and in +4 state are strong oxidising agents.
- Due to the presence of *d*-orbitals in Si, Ge, Sn and Pb, these elements can exceed covalence more than 4. Thus, the halides of these elements undergo hydrolysis and have tendency to form complexes by accepting electron pairs from donor species.

  Examples − $SiF_6^{2-}, [GeCl_6]^{2-}, [Sn(OH)_6]^{2-}$ (central atom is $sp^3d^2$)

- Carbon cannot exceed its covalence by more than 4 (due to the absence of *d*-orbitals)
- **Reactivity towards Oxygen:**
- All members form two types of oxides, MO (monoxide) and $MO_2$ (dioxide).
- Oxides with higher oxidation states of elements ($CO_2$, $SiO_2$ and $GeO_2$) are more acidic than those in lower oxidation states. $SnO_2$ and $PbO_2$ are amphoteric.
- Among monoxides, CO is neutral; GeO is acidic; SnO and PbO are amphoteric.
- **Reactivity towards Water:**
- C, Si and Ge are not affected by water.
- Sn reacts with steam to form dioxide and dihydrogen gas.

$Sn + 2H_2O \xrightarrow{\Delta} SnO_2 + 2H_2$

- Due to the formation of a protective oxide film, lead is unaffected by water.
- **Reactivity towards Halogens:**
- Form halides of formula $MX_2$ and $MX_4$ (X = F, Cl, Br, I)
- Most of the $MX_4$ are covalent in nature. (Exceptions − $SnF_4$ and $PbF_4$ are ionic in nature)
- The central metal atom in the covalent halides of the form $MX_4$ undergoes $sp^3$ hybridisation, and the molecule is tetrahedral in shape.
- Most tetrachlorides are easily hydrolysed by water because of the presence of *d*-orbital in the central metal atom. *d*-orbital can accommodate the lone pair of electrons from the oxygen atom of a water molecule.
- For example −



Silicic acid

**Question:** Why does $PbI_4$ not exist?

**Answer:** It does not exist because the Pb-I bond formed initially during the reaction does not release enough energy to un-pair $6s^2$ electrons, to have four un-paired electrons around the lead atom.

**Question:** Why does $[SiF_6]^{2-}$ exist while $[SiCl_6]^{2-}$ does not?

**Answer:** Six large chloride ions cannot be accommodated around $Si^{4+}$ due to its small size. Also, the interaction between the lone pair of chloride ion and $Si^{4+}$ is not very strong. This is why $[SiF_6]^{2-}$ exists while $[SiCl_6]^{2-}$ does not.

## Anomalous Behaviour of Carbon & Allotropes of Carbon

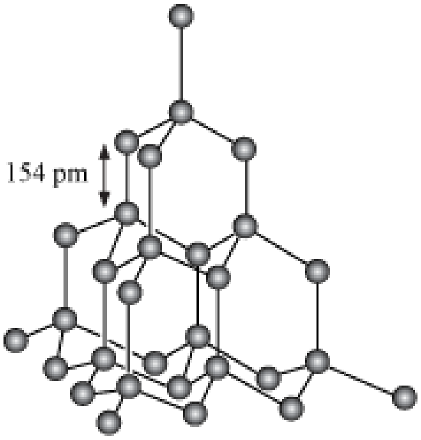
- Due to its smaller size, higher electronegativity, higher ionisation enthalpy and unavailability of *d*-orbitals, a carbon atom differs from the rest of the members of its group.
- The maximum covalence of carbon is four because it contains only *s* and *p* orbitals. On the other hand, other members of the carbon family can expand their covalence due to the presence of *d*-orbitals.
- Ability to form $p\pi - p\pi$ multiple bonds with itself and other atoms of small size and high electronegativity; e.g., C=C, C≡C, C=O, C=S and C≡N. Other members do not form $p\pi - p\pi$ bonds as their atomic orbitals are too large and diffuse to allow effective overlap.
- Tendency to link with one another through covalent bonds to form chains and rings; this property is called catenation
- The order of catenation is C >> Si > Ge ≈ Sn. Pb does not show catenation.
- Ability to show allotropic forms is due to the property of catenation and $p\pi - p\pi$ bonding

**Allotropes of Carbon**

- Diamond
- Graphite
- Fullerenes

**Diamond**

- Each carbon atom undergoes $sp^3$ hybridisation.
- Each carbon is linked to four other carbon atoms in a tetrahedral fashion.
- C−C bond length = 154 pm
- Rigid three-dimensional network of carbon atoms (shown in the figure)



- In this structure, directional covalent bonds are present throughout the lattice.

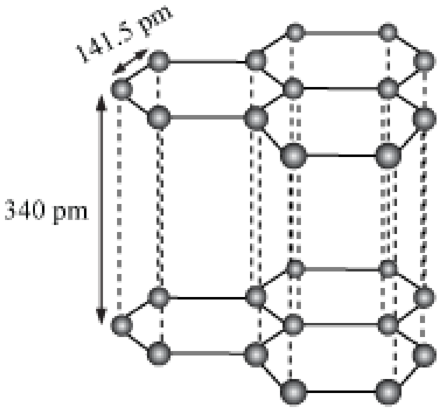
- It is the hardest substance on earth (as it is difficult to break extended covalent bonding).

- It has a very high melting point.

- It is used as an abrasive for sharpening hard tools; also used for making dyes and manufacturing tungsten filaments for electric light bulbs.

**Graphite**

- Layered structure (shown in the figure)



- Layers are held by van der Waals forces

- C−C bond length within the layer = 141.5 pm

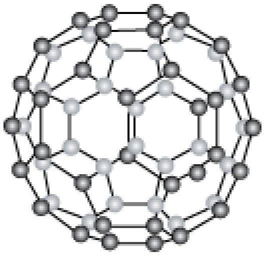
- Each carbon atom is $sp^2$ hybridised.

- Each layer is composed of hexagonal rings of C-atoms.

- Electrons are delocalised over the entire sheet.
- It conducts electricity (as electrons are mobile along the sheets).
- It is used as a dry lubricant in machines running at high temperature as it very soft and slippery (this is because graphite cleaves easily between the layers).

### Fullerenes

- Made by heating graphite in an electric arc, in the presence of inert gases (He or Ar)
- $C_{60}$, with smaller quantity of $C_{70}$, and traces of fullerenes consisting of an even number of carbon atoms up to 350 or above are formed
- They are cage-like structures.
- $C_{60}$ molecule is called *Buckminsterfullerene*.
- $C_{60}$ has a shape like a soccer ball (shown in the figure).



- $C_{60}$ contains 20 six-membered rings and 12 five-membered rings.
- All the carbon atoms are $sp^2$ hybridised.
- Both single and double bonds are present.

C−C bond length = 143.5 pm

C=C bond length = 138.3 pm

- Spherical fullerenes are also called *bucky balls*.

### Other Forms of Carbon

Carbon black, Coke, Charcoal (amorphous form)

- Carbon black is obtained by burning hydrocarbons in a limited supply of air.

- By heating wood or coal at high temperatures in the absence of air, charcoal and coke are obtained respectively.

### Uses of Carbon

- **Graphite** is used for making the electrodes present in batteries and in industrial electrolysis.
- Graphite fibres embedded in plastic material form high strength, lightweight composites. These composites are used in tennis rackets, fishing rods, aircrafts and canoes.
- **Activated charcoal** is used:
- For absorbing poisonous gas
- As water filters to remove organic contaminators
- In air condition systems to control odour
- **Coke** is used as:
- Fuel
- Reducing agent in metallurgy
- **Diamond** is used for making jewellery.
- **Carbon black** is used as:
- A black pigment ink
- A filler in automobile tyres

## Some Important Compounds of Carbon and Silicon

### Compounds of Carbon

### Carbon Monoxide

- **Preparation**
- Carbon in limited supply of air or oxygen yields carbon monoxide.

$$2\mathrm{C}(s)+\mathrm{O}_2(g)\xrightarrow{\Delta}2\mathrm{CO}(g)$$

- Dehydration of formic acid with concentrated $H_2SO_4$ at 373 K gives pure CO.

$$\mathrm{HCOOH}\xrightarrow[\text{conc. }H_2SO_4]{373\mathrm{K}}\mathrm{H_2O}+\mathrm{CO}$$

- The passage of steam over hot coke gives carbon monoxide.

$$\mathrm{C}(s)+\mathrm{H_2O}(g)\xrightarrow{473-1273\mathrm{K}}\mathrm{CO}(g)+\mathrm{H_2}(g)$$

Mixture of CO(*g*) and $H_2$(*g*) → Water gas

- A mixture of CO and $N_2$ (called producer gas) is produced when air is used instead of steam.

$$2\mathrm{C}(s)+\mathrm{O_2}(g)+4\mathrm{N_2}(g)\xrightarrow{1273\mathrm{K}}\underbrace{2\mathrm{CO}(g)+4\mathrm{N_2}(g)}_{\text{(Producer gas)}}$$

- **Properties and Structure**

- Colourless, odourless, and almost water insoluble gas

- Powerful reducing agent − Can reduce almost all metal oxides (exceptions − alkali and alkaline earth metals, aluminium, a few transition metals)

- That is why it is used in the extraction of many metals from their oxide ores.

$$\mathrm{Fe_2O_3}(s)+3\mathrm{CO}(g)\xrightarrow{\Delta}2\mathrm{Fe}(s)+3\mathrm{CO_2}(g)$$
$$\mathrm{ZnO}(s)+\mathrm{CO}(g)\xrightarrow{\Delta}\mathrm{Zn}(s)+\mathrm{CO_2}(g)$$

- The structure of CO can be represented as $:C\equiv O:$ (contains one sigma, and two π bonds; two lone pairs of electrons).

- CO can donate lone pair to certain metal to form metal carbonyls.

- CO is a poisonous gas. It forms stable complex with haemoglobin (which is 300 times more stable than oxygen-haemoglobin complex).

  It prevents haemoglobin from carrying blood and ultimately results in death.

**Carbon Dioxide**

- **Preparation**

- Complete combustion of carbon and carbon containing fuels

$$C(s) + O_2(g) \xrightarrow{\Delta} CO_2(g)$$
$$CH_4(s) + O_2(g) \xrightarrow{\Delta} CO_2(g) + 2H_2O(g)$$

- Action of dilute hydrochloric acid on calcium carbonate (Laboratory preparation):

$$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

- **Properties, Structure, and Uses**
- Colourless and odourless gas
- Low solubility in water
- With water, $CO_2$ forms carbonic acid ($H_2CO_3$).
- $H_2CO_3$ is a weak dibasic acid. It dissociates as

$$H_2CO_3(aq) + H_2O(l) \longleftrightarrow HCO_3^-(aq) + H_3O^+(aq)$$
$$HCO_3^-(aq) + H_2O(l) \longleftrightarrow CO_3^{2-}(aq) + H_3O^+(aq)$$

- $H_2CO_3/HCO_3^-$ buffer system maintains the pH of blood between 7.26 to 7.42.
- $CO_2$ is acidic in nature. It combines with alkali to form metal carbonates.
- In the atmosphere, $CO_2$ is present to the extent of ~0.03% by volume.
- $CO_2$ is used in the process of photosynthesis.

$$6CO_2 + 12H_2O \xrightarrow[\text{Chlorophyll}]{h\nu} C_6H_{12}O_6 + 6O_2 + 6H_2O$$

- Increase in $CO_2$ content of the atmosphere leads to **greenhouse effect** because of which there is rise in the temperature of atmosphere.
- Carbon atom undergoes *sp* hybridisation in the $CO_2$ molecule. It contains two sigma and two pi bonds.
- It has linear shape (with equal C − O bond lengths).

$$:\ddot{O} \overset{115\text{pm}}{=\!=} C \overset{115\text{pm}}{=\!=} \ddot{O}:$$

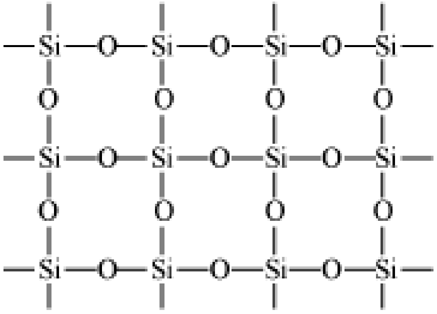
- $CO_2$ has zero dipole moment.
- Resonance structures of $CO_2$ are

- Dry ice is the solid form of $CO_2$. It is used as refrigerant for ice-cream and frozen food.
- Gaseous $CO_2$ is used in carbonated soft drinks.
- It can be used as fire extinguisher.

**Compounds of Silicon**

**Silicon Dioxide ($SiO_2$)**

- Commonly known as silica
- Quartz, cristobalite, and tridymite are the crystalline forms of silica.
- **Structure**
- It is a covalent and three-dimensional network solid.
- Each silicon atom is covalently bonded to four oxygen atoms in tetrahedral manner. (Shown in figure)



- **Reactivity**
- Si − O bond has very high enthalpy. Hence, silica in normal form is almost non-reactive.
- Resists the attack by halogens, most acids, and metals even at elevated temperature
- Reacts with HF and NaOH as

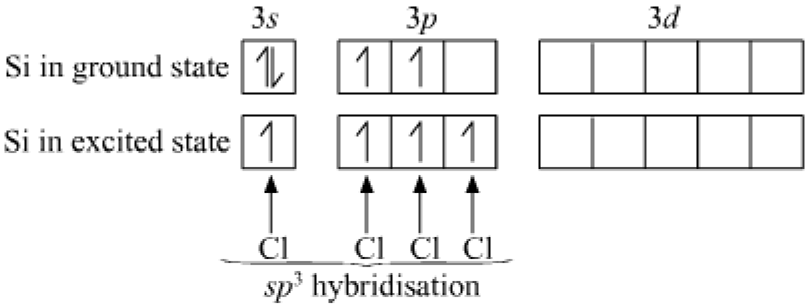
$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$

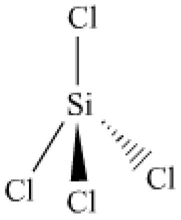
$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

- **Uses**
- Quartz is used as piezoelectric material.
- Silica gel is used as drying agent.
- Silica gel is also used as support for chromatographic materials and catalyst.
- Amorphous form of silica (kieselguhr) is used in filtration plants.

**Silicon tetrachloride**

$SiCl_4$ is covalent and formed by $sp^3$ hybridisation. In $SiCl_4$, 4 $sp^3$ hybrid orbitals of silicon overlap with one 3p orbital of four chlorine atoms giving rise to the tetrahedral structure.





Properties
1. It is volatile and colourless liquid which in moist air gives silicon dioxide and HCl.

$$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4\ HCl$$

2. As silicon has empty d-orbitals thus it gets hydrolysed by water easily forming silicic acid.

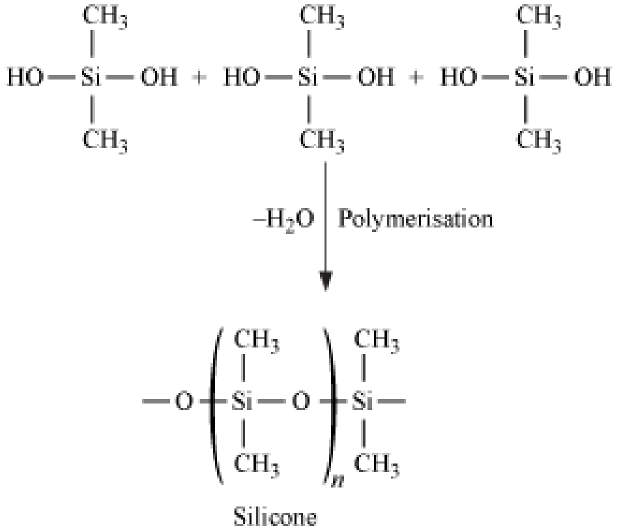
$$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4\ HCl$$

Uses
1. It is used to produce pure silicon and silica for industrial purposes.
2. In its pure form $SiCl_4$ is used in the manufacturing of optical fibres.

## Silicones

- Group of organosilicon polymers
- Repeating units is $-\!\!\left(R_2SiO\right)\!\!-$.
- **Preparation**
- Alkyl or aryl substituted silicon chlorides, $R_nSiCl_{(4-n)}$, are the starting materials for the manufacture of silicones. [R is alkyl or aryl group]

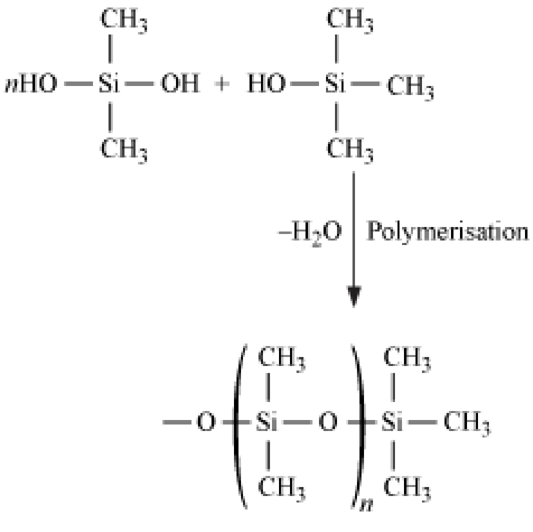
$$2CH_3Cl + Si \xrightarrow[570\ K]{Cu\ powder} (CH_3)_2SiCl_2 \xrightarrow[-2HCl]{+2H_2O} (CH_3)_2Si(OH)_2$$



Silicone

- The chain length of the polymer can be controlled by adding $(CH_3)_3SiCl$.

$$(CH_3)_3SiCl \xrightarrow[-HCl]{+H_2O} (CH_3)_3Si(OH)$$

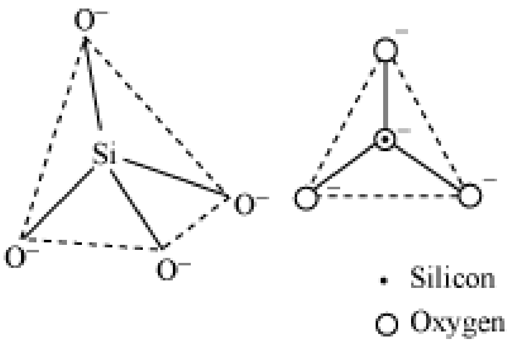


Silicone

- **Properties**
- Silicones are water repelling in nature.
- Have high thermal stability and dielectric strength
- Resistant to oxidation and chemicals
- **Applications**
- Used as sealant, greases, electrical insulator, and for water proofing of fabrics
- Also used in surgical and cosmetic plants

**Silicates**

- Examples − Feldspar, zeolites, mica, asbestos
- Structure
- $SiO_4^{4-}$ is the basic structural unit of silicates.
- In $SiO_4^{4-}$, Si atom is bonded to oxygen atoms in tetrahedral fashion.



- Silicate units are linked together to form chain, ring, sheet, or three-dimensional structures.

- Negative charge on silicate structure is neutralized by positively charged metal ions.

- Glass and cement are two man-made silicates.

### Zeolites

- In the three-dimensional network of silicon dioxide, a few silicon atoms are replaced by aluminium atoms, then the overall structure is called aluminosilicate.

- Aluminosilicate acquires a negative charge.

- The negative charge can be balanced by cations such as $Na^+$, $K^+$, or $Ca^{2+}$.

- Examples − Feldspar and zeolites

### Uses of Zeolites

- Used as catalyst in petrochemical industries for cracking of hydrocarbons and isomerisation

- ZSM−5 (a zeolite) is used to convert alcohols to gasoline.

- Hydrated zeolites are used in softening of hard water as ion exchangers.

## 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: $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$
- 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.

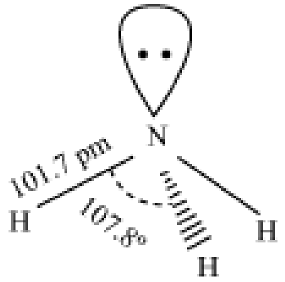
### Occurrence

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:

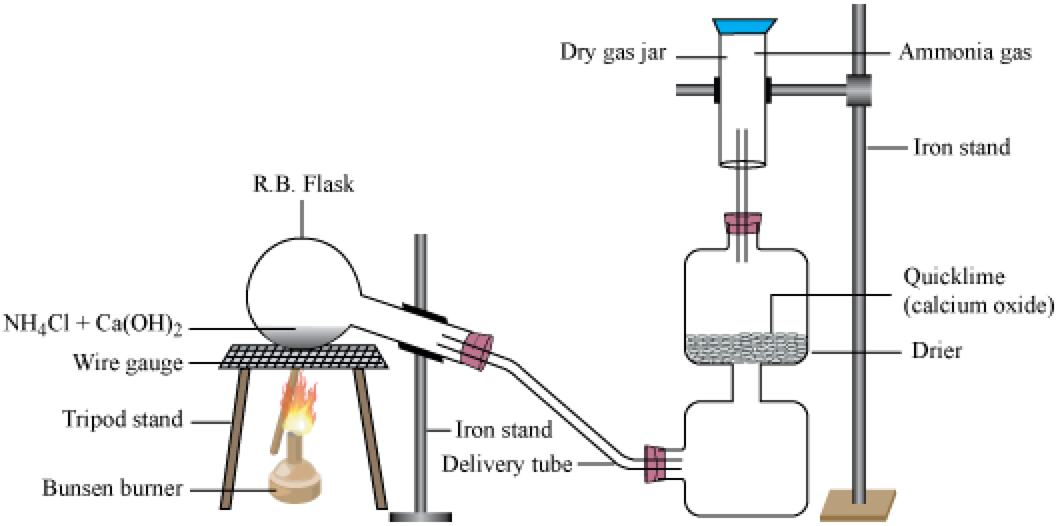
$$2\ NH_4Cl + Ca(OH)_2 \xrightarrow{\Delta} CaCl_2 + 2\,H_2O + 2\ NH_3$$

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

- 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.



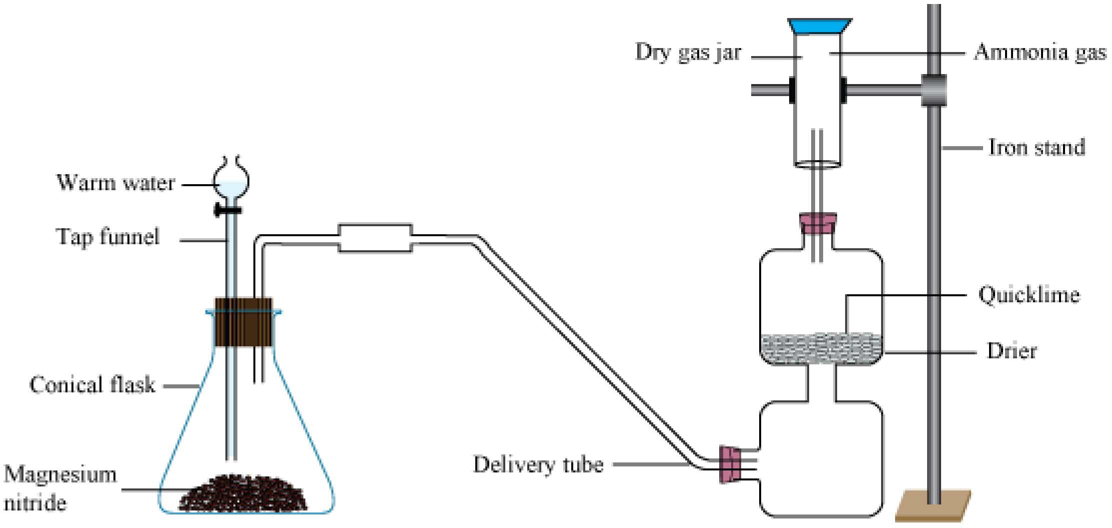
In this method, the mixture of ammonium chloride and dry calcium hydroxide is placed in a round-bottomed flask. It is clamped to an iron stand so that its neck is tilting downwards. This stops water vapours formed by condensation to trickle back into the hot flask.

$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + 2H_2O + CaCl_2$$
$$(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3 + 2H_2O + Na_2SO_4$$

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.

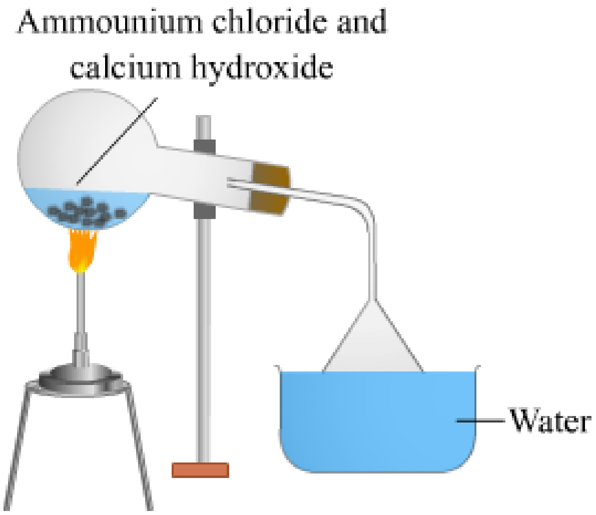
The following reactions take place when water reacts with sodium and magnesium nitride.

$$Na_3N + 3H_2O \rightarrow 3NaOH + NH_3$$

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

- **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.**

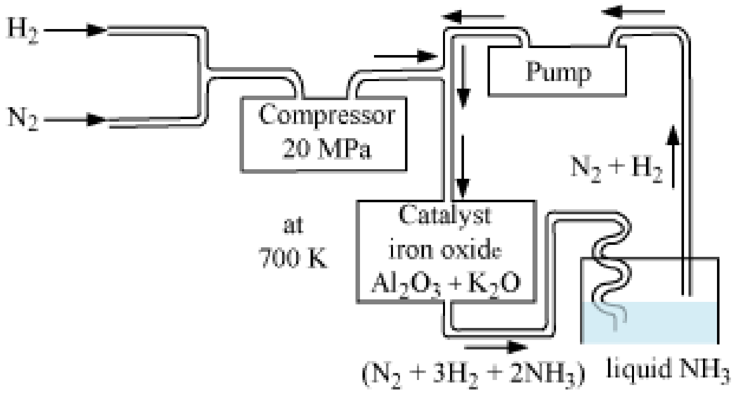
A mixture of hydrogen and nitrogen gases in the ratio 3:1 is taken in the compressor. It is then compressed from 200 atm to 900 atm pressure and passed over the heated catalyst in catalyst chamber.

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 = $200 \times 10^5$ 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

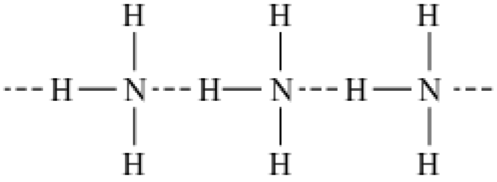
The produced ammonia gas is collected by either **liquefaction** as ammonia has higher boiling point than nitrogen and hydrogen hence, it condenses easily, or **absorption** in water as ammonia is highly soluble in water. The unused mixture of hydrogen and nitrogen gases are recompressed and then recycled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

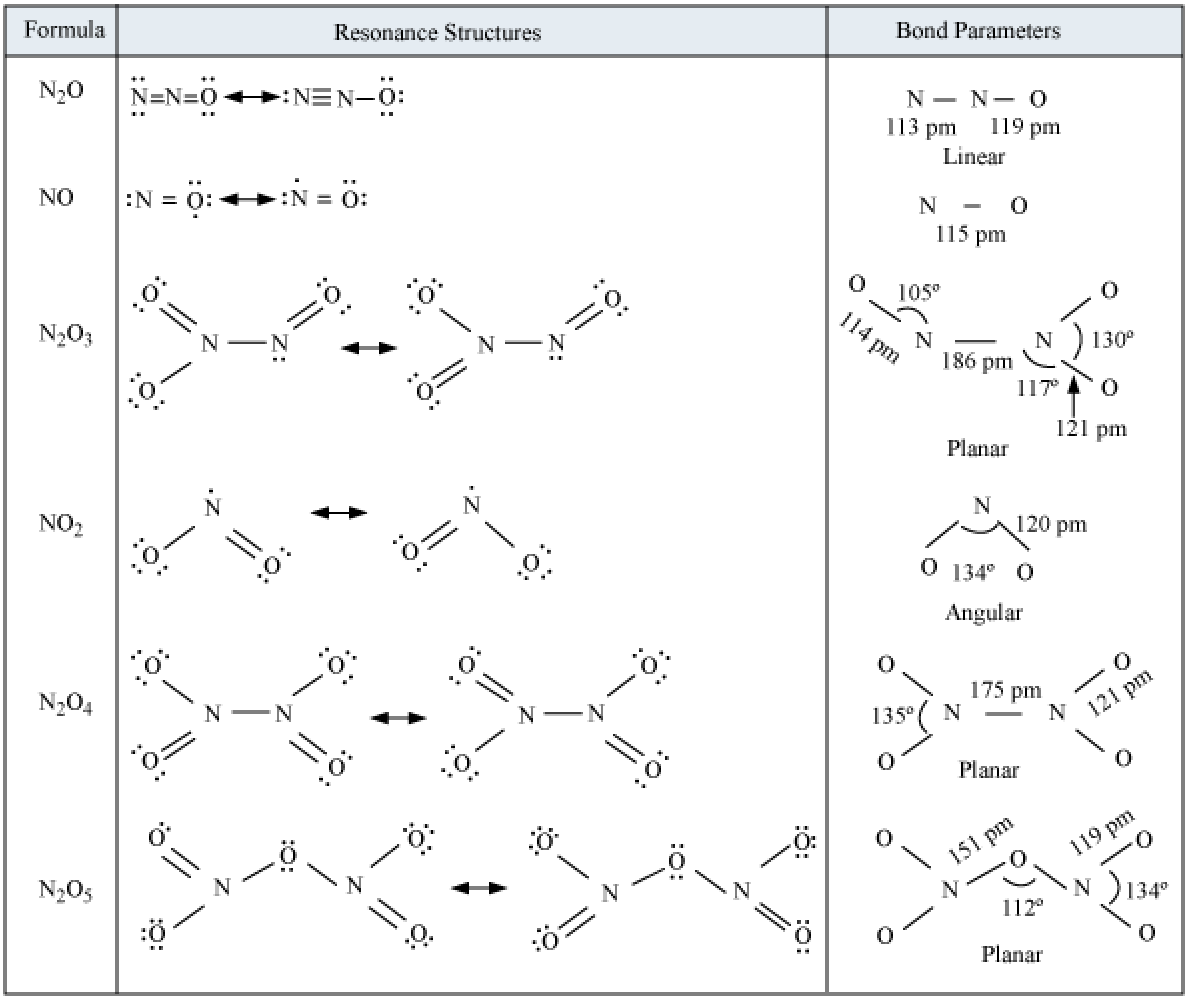
- Forms a number of oxides in different oxidation states

- 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 | NO | + 2 | $2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$ | Colourless gas, neutral |

|  |  |  |  |  |
|---|---|---|---|---|
| [Nitrogen (II) oxide |  |  |  |  |
| Dinitrogen trioxide [Nitrogen (III) oxide] | $N_2O_3$ | + 3 | $2NO + N_2O_4 \xrightarrow{250\ K} 2N_2O_3$ | 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 |
|---|---|---|
| $N_2O$ | $N{=}N{=}O \leftrightarrow N{\equiv}N{-}O$ | N — N — O<br>113 pm 119 pm<br>Linear |
| NO | $N = O \leftrightarrow N = O$ | N — O<br>115 pm |
| $N_2O_3$ | | 105°<br>114 pm<br>186 pm<br>130°<br>117°<br>121 pm<br>Planar |
| $NO_2$ | | 120 pm<br>134°<br>Angular |
| $N_2O_4$ | | 135°<br>175 pm<br>121 pm<br>Planar |
| $N_2O_5$ | | 151 pm<br>119 pm<br>112°<br>134°<br>Planar |

**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 $NH_3$

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

- $2NO_{(g)} + O_{2(g)} \longleftrightarrow 2NO_{2(g)}$

- $3NO_{2(g)} + H_2O_{(l)} \longrightarrow 2HNO_{3(aq)} + NO_{(g)}$

- 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.

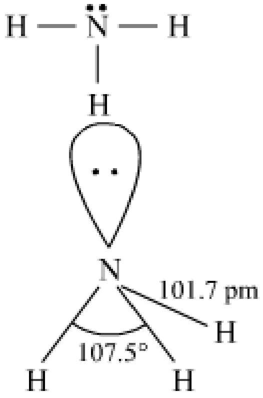
After that, concentrated $H_2SO_4$ is added along the sides of the test tube.

**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

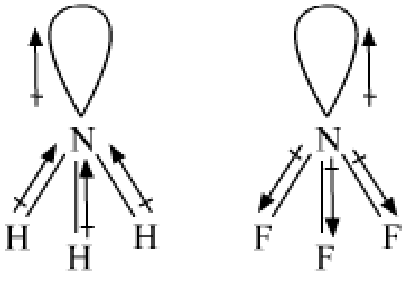
Nitrogen in ammonia molecule is *sp*$^3$ hybridised but due to the presence of lone pair of electron, its structure is distorted and it acquires the pyramidal structure. The bond angle N-H is about 107°.



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 $PH_3$

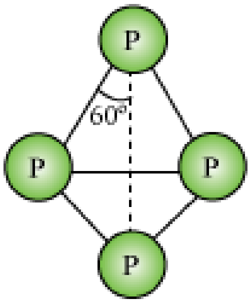
$$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + \underset{\text{Sodium hypophoshite}}{3NaH_2PO_2}$$

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

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

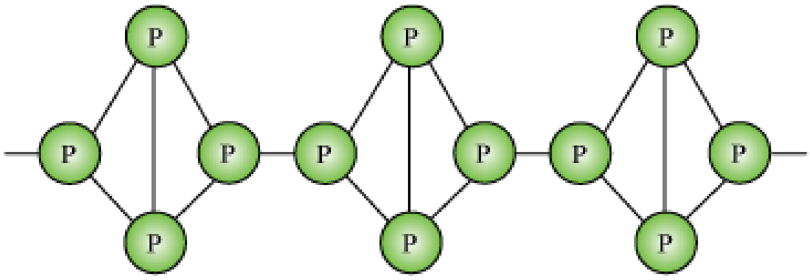
Less stable and is therefore more reactive than the other solid phases. Reason: Angular strain in the $P_4$ molecule where the angles are only 60°

  - 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**

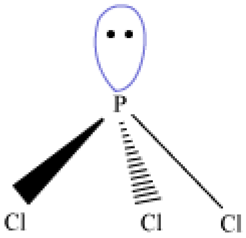
- Colourless oily liquid
- Hydrolyses in the presence of moisture

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

- 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

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

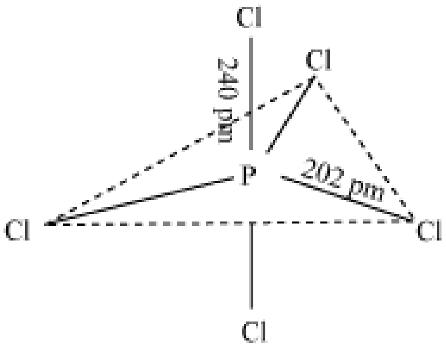
- Converts the organic compounds containing −OH group to chloro derivation

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

- 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.

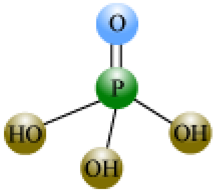
| Name | Formula | Oxidation state of phosphorus | Characteristic bonds and their number | Preparation |
|---|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| Hypophosphorous | $H_3PO_2$ | +1 | One $P-OH$<br>Two $P-H$<br>One $P=O$ | white $P_4$ + alkali |
| Orthophosphorous | $H_3PO_3$ | +3 | Two $P-OH$<br>One $P-H$<br>One $P=O$ | $P_2O_3 + H_2O$ |
| Pyrophosphorous | $H_4P_2O_5$ | +3 | Two $P-OH$<br>Two $P-H$<br>Two $P=O$ | $PCl_3 + H_3PO_3$ |
| Hypophosphoric | $H_4P_2O_6$ | +4 | Four $P-OH$<br>Two $P=O$<br>One $P-P$ | red $P_4$ + alkali |
| Orthophosphoric | $H_3PO_4$ | +5 | Three $P-OH$<br>One $P=O$ | $P_4O_{10} + H_2O$ |
| Pyrophosphoric | $H_4P_2O_7$ | +5 | Four $P-OH$<br>Two $P=O$<br>One $P-O-P$ | heat phosphoric acid |

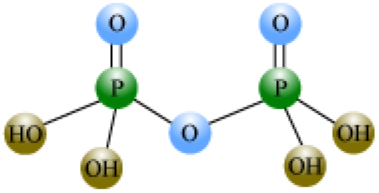
| | | | | |
|---|---|---|---|---|
| Metaphosphoric | $(HPO_3)_n$ | +5 | Three P − OH<br>Three P = O<br>Three P − O − P | phosphorus acid + $Br_2$, heat in a sealed tube |

- **Structures**

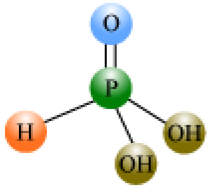
Structures of some important oxoacids of phosphorus are as follows:



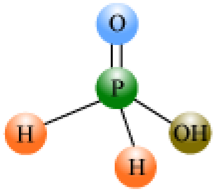
$H_3PO_4$
Orthophosphoric acid



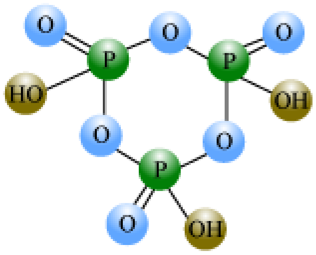
$H_4P_2O_7$
Pyrophosphoric acid



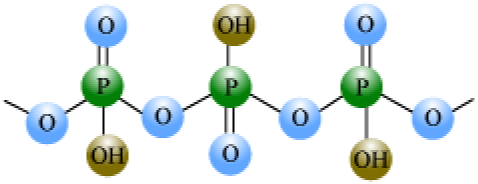
$H_3PO_3$
Orthophosphorous acid



$H_3PO_2$
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 − $SO_2$, $Cl_2O_7$, $CO_2$, $N_2O_5$

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

- 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 ($\Delta H$ = − ve) and an increase in entropy ($\Delta S$ = + ve), leading to large negative value of ΔG.

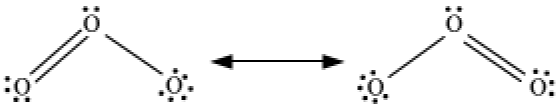
- **Chemical properties**
- Powerful oxidising agent because it liberates nascent oxygen atoms ($O_3 \rightarrow O_2 + O$)

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

- 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:



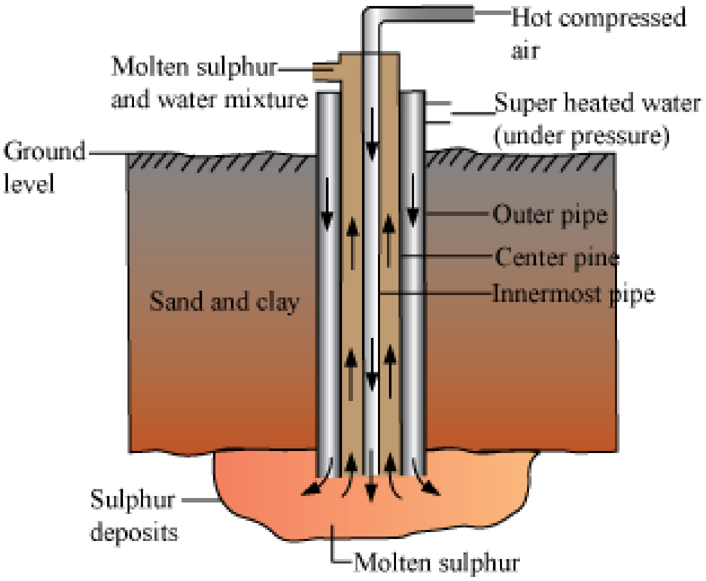
- In resonance hybrid of these two forms, the two O−O bond lengths are identical (128 pm) with a bond angle of about 117°.
- **Uses**
- As a germicide and disinfectant
- For sterilising water
- For bleaching oils, ivory, flour, starch, etc.
- As an oxidising agent in the manufacture of $KMnO_4$

## 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.

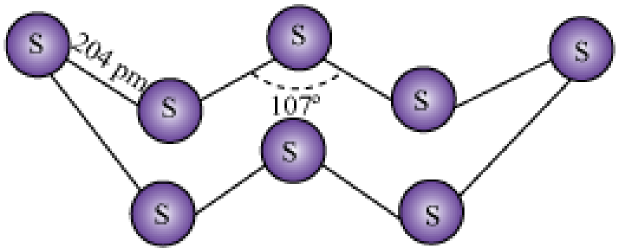
On removing the crust, colourless needle-shaped crystals of β-sulphur are obtained.

**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.

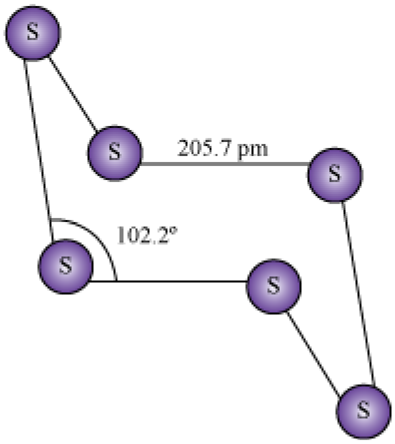
**Structures of Allotropes of Sulphur**

- 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 444ºC, it catches fire and burns with a pale blue flame forming sulphur dioxide gas.

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

- **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 $O_2$

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

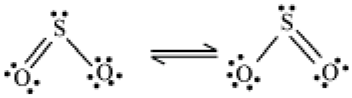
- Moist sulphur dioxide behaves as a reducing agent.

- 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.

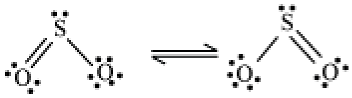
## Sulphur Dioxide

### 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.

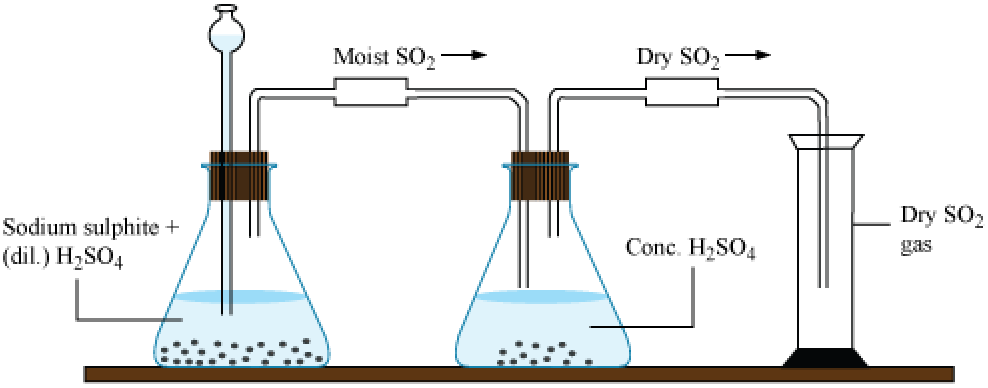
$$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$$

- 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

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

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**

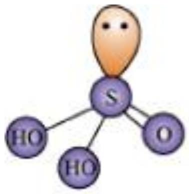
- It is used in refining petroleum and sugar.

- 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.

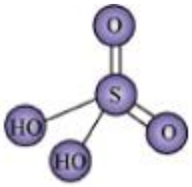
## Oxo Acids of Sulphur

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.

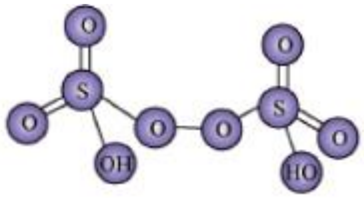
Structures of some important oxoacids of sulphur:



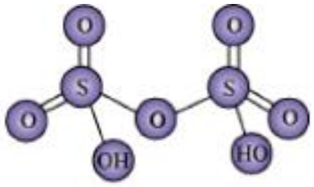
Sulphurous acid ($H_2SO_3$)



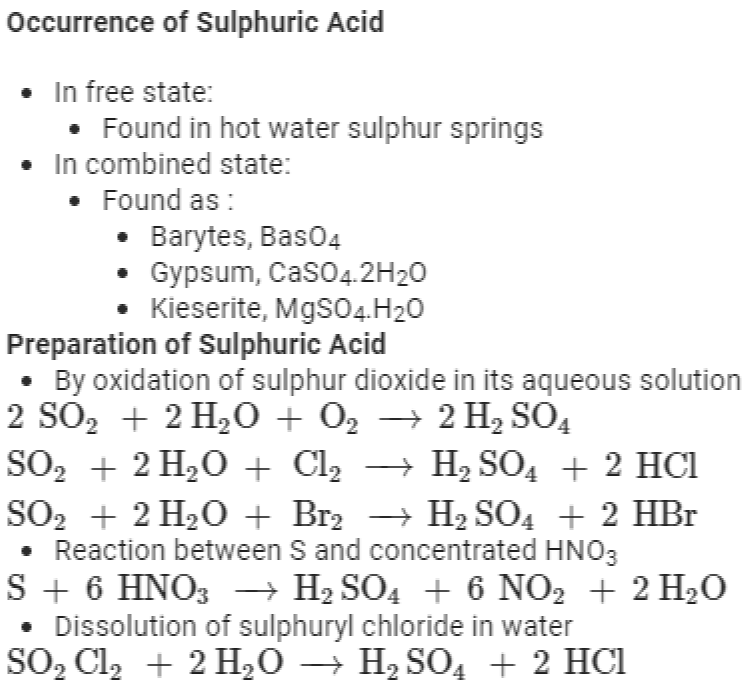
Sulphuric acid ($H_2SO_4$)



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 $Br_2$.

$$2\ SO_2\ +\ 2\,H_2O\ +\ O_2\ \longrightarrow\ 2\,H_2\,SO_4$$

$$SO_2\ +\ 2\,H_2O\ +\ Cl_2\ \longrightarrow\ H_2\,SO_4\ +\ 2\ HCl$$

$$SO_2\ +\ 2\,H_2O\ +\ Br_2\ \longrightarrow\ H_2\,SO_4\ +\ 2\ HBr$$

- Reaction between S and concentrated $HNO_3$

$$S\ +\ 6\ HNO_3\ \longrightarrow\ H_2\,SO_4\ +\ 6\ NO_2\ +\ 2\,H_2O$$

- Dissolution of sulphuryl chloride in water

$$SO_2\,Cl_2\ +\ 2\,H_2O\ \longrightarrow\ H_2\,SO_4\ +\ 2\ HCl$$

**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

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

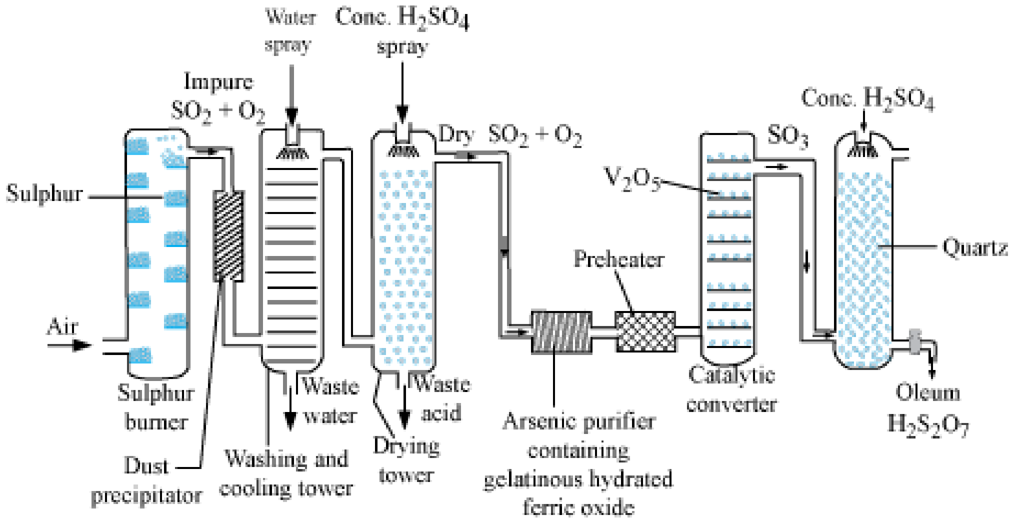
| Favourable Conditions for Conversion of $SO_2$ to $SO_3$ |
|---|
| It is an exothermic reaction; so maintaining a temperature of 410-450$^o$C provides good yield.<br>A pressure of 1-2 atm is used.<br>An excess of oxygen increases the yield of $SO_3$.<br>$V_2O_5$ is used as a suitable catalyst to speed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

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

$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$

Oleum

- 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 $Ka_1 > 10$, $H_2SO_4$ 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.

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

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

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

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

$$
\begin{aligned}
&NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl \\
&NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3 \\
&CH_3COONa + H_2SO_4 \longrightarrow NaHSO_4 + CH_3COOH
\end{aligned}
$$

- 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.

$$
\begin{aligned}
&Cu + 2\,H_2SO_4 \longrightarrow CusO_4 + 2\,H_2O + SO_2 \\
&Zn + 2\,H_2SO_4 \longrightarrow ZnSO_4 + 2\,H_2O + SO_2 \\
&C + 2\,H_2SO_4 \longrightarrow CO_2 + 2\,H_2O + 2\,SO_2 \\
&S + 2\,H_2SO_4 \longrightarrow 3\,SO_2 + 2\,H_2O \\
&2\,P + 5\,H_2SO_4 \longrightarrow 2\,H_3PO_4 + 2\,H_2O + 5\,SO_2 \\
&2\,HBr + H_2SO_4 \longrightarrow Br_2 + 2\,H_2O + SO_2 \\
&H_2S + H_2SO_4 \longrightarrow S + 2\,H_2O + SO_2
\end{aligned}
$$

- 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.

$Cu + 2H_2SO_4 \text{ (conc.)} \rightarrow CuSO_4 + SO_2 + 2H_2O$

$3S + 2H_2SO_4 \text{ (conc.)} \rightarrow SO_2 + 2H_2O$

$C + 2H_2SO_4 \text{ (conc.)} \rightarrow CO_2 + 2SO_2 + 2H_2O$

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

$$\begin{aligned} &Pb(NO_3)_2 \; + \; H_2SO_4 \; \longrightarrow \; PbSO_4 \; + \; 2\ HNO_3 \\ &BaCl_2 \; + \; H_2SO_4 \; \longrightarrow \; BaSO_4 \; + \; 2\ HCl \end{aligned}$$

### 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