7. p-Block Elements

Group 15 elements:

Nitrogen, Phosphorus → Non-metals

Arsenic, Antimony → Metalloids

Bismuth → Metal

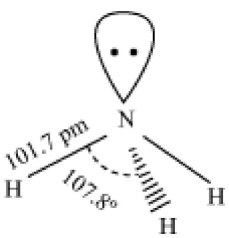
- The valence shell electronic configuration is $ns^2\ np^3$.
- Nitrogen differs in chemical properties from other elements of the group due to its small size, high electronegativity, high ionisation enthalpy and non-availability of *d*-orbitals.
- They exhibit two oxidation states, +3 and +5. Heavier elements exhibit mainly +3 oxidation state due to inert pair effect.

The main use of nitrogen is in the manufacture of ammonia

Ammonia

- On a small scale, ammonia is obtained from ammonium salts, which decompose when treated with caustic soda or lime. It forms metal salt, water, and ammonia gas.
- Ammonia can also be prepared by treating metal nitrides with warm water.

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

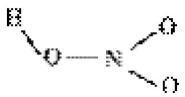


- **Forms**
  - Dry ammonia gas (gaseous ammonia)
  - Liquid ammonia (liquified ammonia)
  - Liquor ammonia fortis (saturated solution of ammonia in water)
  - Laboratory bench reagent (dilute solution of liquor ammonia)
- On large scale, ammonia is obtained by **Haber's process**.
  - Raw material: Mixture of hydrogen and nitrogen gases in the ratio 3:1
  - Pressure: 200 atm to 900 atm pressure
  - Temperature: 450 – 500°C
  - Catalyst: Finely divided iron
  - Promoter: molybdenum or Al_2O_3
- **Properties**:
  - 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.

- It can be liquefied when cooled to 10 ^{o} C under pressure of 6 atm. It forms white crystals on cooling.
- It has basic nature because of the presence of lone pair of electrons.
- It acts as a reducing agent.
- Inhaling this gas causes irritation to the eyes and respiratory system.

- **Uses**:
  - Due to high dielectric constant, ammonia is a good solvent for ionic compounds.
  - It is used as a cleaning agent for removing grease in dry cleaning.
  - It is used in the manufacturing of artificial silk.
  - It is used as laboratory reagent.

- Nitric acid (HNO_3)



1. **Preparation:** Ostwald's process

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

(from air)

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

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

- **Detection of the presence of nitrate:**
  (Brown ring test)

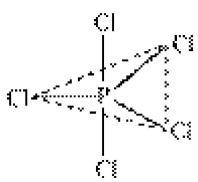
$$NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow NO + 3Fe^{3+} + 2H_2O$$

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

(brown)

- Phosphorus exists as P_4 in elemental form.
- **Allotropic forms of phosphorus:**
  1. White phosphorus
  2. Red phosphorus
  3. Black phosphorus (α-block phosphorus and β-block phosphorus

- Phosphorus forms two types of halides, PX_3(X = F, Cl, Br, I) and PX_5(X = F, Cl, Br).
- The structure of PCl_5 is trigonal bipyramidal



- Phosphorus forms a number of oxoacids such as ortho-phosphoric acid (H_3PO_4), ortho-phosphorus acid (H_3PO_3), hypo-phosphorus acid (H_3PO_2).
- The oxoacids containing P – H bond are strong reducing agents.

Group 16 elements: (known as chalcogens)

Oxygen
Sulphur
Selenium
Tellurium
Polonium

- The valence shell electronic configuration is $ns^2\ np^4$.

Like nitrogen, oxygen differs from other elements of the group due to its small size and high electronegativity

1. Preparation:

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

1. Three stable isotopes – ^{16}O, ^{17}O, ^{18}O

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.

1.

Acidic oxides – Combine with water to give an acid

Example – SO_2, Cl_2O_7, CO_2, N_2O_5

Basic oxides – Combine with water to give bases

Examples – Na^2O, CaO, BaO

Amphoteric oxides – Show the characteristics of both acidic as well as basic oxides

React with both acids and alkalies

Example – Al_2O_3

Neutral oxides – Neither acidic nor basic

Examples – CO, NO, N^{2O}

Ozone (O_3) is an allotropic form of oxygen. It is a powerful oxidising agent.

- **Sulphur –**

Allotropic forms of sulphur:

1. Rhombic sulphur (α – sulphur)
2. Monoclinic sulphur (β – sulphur)

Both rhombic and monoclinic sulphur exist as S_8 molecules.

Oxides of sulphur – SO_2, SO_3

Sulphuric Acid

- Concentrated sulphuric acid is known as oil of vitriol. It occurs in free state in hot water of sulphur springs. In combined state, it occurs as mineral sulphates.
- Sulphuric acid is prepared by contact process. It involves burning of a pure and dry mixture of two parts of sulphur or sulphide ores and one part of air in the presence of vanadium pentoxide or platinised asbestos as catalyst.
- Chemical reactions of H_2SO_4 are because of its

1. low volatility
2. strong acidic character
3. strong affinity for water
4. ability to act as an oxidising agent

- Dilute sulphuric acid reacts with active metals, metal oxides, metal hydroxides, metal carbonates, metal sulphites to form their respective metal sulphates and acid sulphates.
- Because of low volatility, it can be used for the manufacture of more volatile acids from their corresponding salts.
- It is a strong dehydrating agent. Because of its strong affinity for water, sulphuric acid removes water from hydrated salts and organic compounds.
- Concentrated sulphuric acid is a moderately strong oxidising agent and can oxidise both metals and non-metals.

Fluorine
Chlorine
Bromine
Iodine
Astatine

- The valence shell electronic configuration is $ns^2\ np^5$.
- They have very high electronegativity.
- The common oxidation state is –1. However, +1, +3, +5 and +7 oxidation states are also exhibited.
- Fluorine show anomalous properties in the group due to its very small size.

- Chlorine has an atomic number 17 and an atomic mass of 35.5 u.
- It does not occur in free state as it is highly reactive in nature.

Manufacture of chlorine:

- **Laboratory methods of preparation of chlorine**

1. By the oxidation of conc. HCl and manganese dioxide (MnO_2)

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

2. By the action of HCl on $KMnO_4$

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

- **Deacon's process:**

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

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.
- It reacts with burning sodium to form sodium chloride.
- When white phosphorus comes in contact with chlorine, it melts and spontaneously catches fire to form dense white fumes.
- It has strong affinity for hydrogen.

- It reacts with slaked lime to give bleaching powder.
- HOCl releases nascent oxygen, which is responsible for oxidising and bleaching action.
- Bleaching effect of Cl_2 is permanent. It bleaches vegetable or organic matter in the presence of moisture.

Hydrogen Chloride

- In laboratory, hydrogen chloride gas is prepared by heating sodium chloride with concentrated sulphuric acid.
- It is also prepared by burning hydrogen gas in the atmosphere of chlorine gas or by exposing hydrogen gas and chlorine gas to diffused sunlight.
- It is colourless and pungent-smelling with sour taste and a very irritating odour.
- It is extremely soluble in water.
- Hydrogen chloride is neither combustible nor does it support combustion.
- On heating at above 500°C, it dissociates into hydrogen and chlorine.
- On mixing with ammonia gas, it forms dense white fumes due to formation of ammonium chloride.
- Aqueous solution of hydrogen chloride is called **hydrochloric acid**.
- It is prepared by dissolving hydrogen chloride in water.
- It reacts with metals to form respective chlorides and hydrogen gas.
- **Aqua regia** is a mixture of 3 parts of concentrated hydrochloric acid and 1 part of concentrated nitric acid. It is a very corrosive acid and is the only known acid that can dissolve gold.
- Halogens form a number of oxoacids.

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)

- Halogens form a number of inter-halogen compounds (compounds formed by two different halogens).

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

Helium
Neon
Argon
Krypton
Xenon
Radon

- The valence shell electronic configuration is $ns^2\ np^6$. (Exception: Helium $\rightarrow 1s^2$)
- **Physical Properties**
  - Monoatomic
  - Colourless, odourless, and tasteless
  - Sparingly soluble in water
  - Low melting and boiling points.
- **Xenon-Fluorine Compounds**

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

(Xe in excess)

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

(1:5 ratio)

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

(1:20 ratio)

Structure

- XeF_2 ⟶ Linear
- XeF_4 ⟶ Square planar
- XeF_6 ⟶ Distorted octahedral

Xenon-Oxygen Compounds

XeO_3 has a pyramidal

$XeOF_4$ has a square pyramidal