The p-Block Elements

Group 15 elements:

Nitrogen, Phosphorus → Non-metals

Arsenic, Antimony → Metalloids

Bismuth → Metal

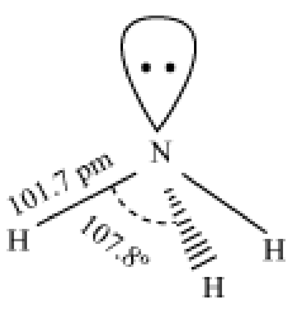
- The valence shell electronic configuration is ns^2 np^3.
- Nitrogen differs in chemical properties from other elements of the group due to its small size, high electronegativity, high ionisation enthalpy and non-availability of *d*-orbitals.
- They exhibit two oxidation states, +3 and +5. Heavier elements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

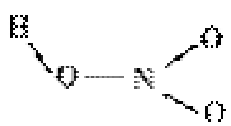


- **Forms**

- 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

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

(from air)

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

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

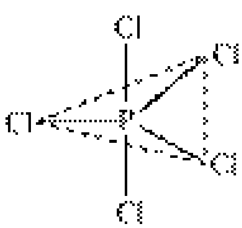
- **Detection of the presence of nitrate:**
  (Brown ring test)

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

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

- 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

Sulphur Dioxide

- In laboratory, sulphur dioxide is prepared by treating sulphites of active metal with dilute sulphuric acid.
- It causes headache when inhaled in small amount while it might prove fatal in large amounts.
- It is a pungent smelling gas, which is soluble in water.
- It is heavier than air and its boiling point si 263 K.
- It is neither combustible nor does it support combustion. Also, it has both acidic and bleaching properties.
- 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 amount, it forms their respective metal hydrogen sulphites.
- It reduces chlorine water to hydrochloric acid and forms sulphuryl chloride with dry chlorine gas.
- Moist sulphur dioxide behaves as a reducing agent.

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)	**HOF**	**HOCl**	**HOBr**	**HOI**

acid (Hypohalous acid)	(Hypofluorous acid)	(Hypochlorous acid)	(Hypobromous acid)	(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)

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- 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**

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

(Xe in excess)

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

(1:5 ratio)

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

(1:20 ratio)

Structure

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

Xenon-Oxygen Compounds

XeO_3 has a pyramidal

$XeOF_4$ has a square pyramidal