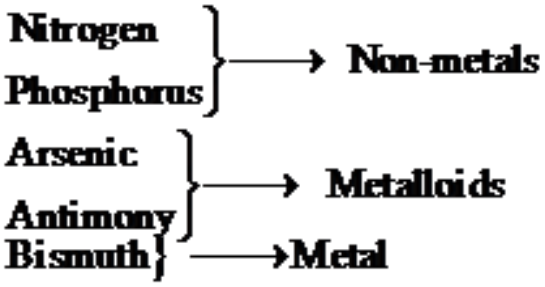
The p-Block Elements

Group 15 elements:



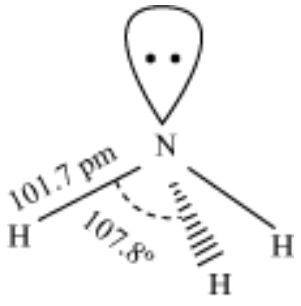
- The valence shell electronic configuration is $ns^2\ np^3$.
- Nitrogen differs in chemical properties from other elements of the group due to its small size, high electronegativity, high ionisation enthalpy and non-availability of *d*-orbitals.
- They exhibit two oxidation states, +3 and +5. Heavier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

The main use of nitrogen is in the manufacture of ammonia

Ammonia

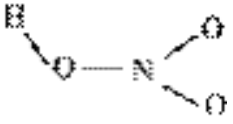
- On a small scale, ammonia is obtained from ammonium salts, which decompose when treated with caustic soda or lime. It forms metal salt, water, and ammonia gas.
- Ammonia can also be prepared by treating metal nitrides with warm water.

- 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

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

(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)

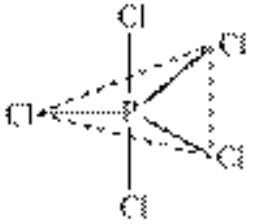
$$NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow NO + 3Fe^{3+} + 2H_2O$$

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

(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

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.