CHAPTER – 7

THE P-BLOCK ELEMENTS

SYNOPSIS :

- The **p-block elements** are placed in **groups 13 to 18** of the periodic table. Their valence shell electronic configuration is **ns2np1–6**

- The **properties of p-block elements** are greatly influenced by atomic sizes, ionisation enthalpy, electron gain enthalpy and electronegativity.

- **Group 15** includes nitrogen, phosphorus, arsenic, antimony and bismuth.

- **Molecular nitrogen** comprises 78% by volume of the atmosphere. In the earth's crust, it occurs as sodium nitrate, $NaNO_3$ (called Chile saltpetre) and potassium nitrate (Indian saltpetre). It is 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) (e.g. fluorapatite $Ca_9(PO_4)_6$. CaF_2) which are the main components of phosphate rocks. Phosphorus is an essential constituent of animal and plant matter, present in bones as well as in living cells.

- **Phosphoproteins** are present in milk and eggs. Arsenic, antimony and bismuth are found mainly as sulphide minerals.

- The **valence shell electronic configuration of group 15** elements is **ns^2np^3**. The s orbital in these elements is completely filled and p orbitals are half-filled, making their electronic configuration extra stable.

- **Covalent** and **ionic radii** increase in size due to the presence of completely filled d and/or f orbitals in heavier members.

- **Ionisation enthalpy** decreases down the group due to gradual increase in atomic size. Because of the extra stable half-filled p orbitals electronic configuration and smaller size, the ionisation enthalpy of the group 15 elements is much **greater than that of group 14** elements in the corresponding periods.

- The **electronegativity value**, decreases down the group with increasing atomic size.

- **Physical Properties:** All the elements of this group are **polyatomic**. **Dinitrogen** is a diatomic gas while all others are solids. Metallic character increases down the group. Nitrogen and phosphorus are non-metals, arsenic and antimony metalloids and bismuth is a metal.

- **Chemical Properties:** The common oxidation states of these elements are –3, +3 and +5.

- **Nitrogen** has unique ability to form $p\pi$ -$p\pi$ multiple bonds with itself and with other elements having small size and high electronegativity e.g. C, O. It forms oxoacids such as $H_2N_2O_2$ (hyponitrous acid), HNO_2 (nitrous acid) and HNO_3 (nitric acid).

- **Anomalous properties of nitrogen:** Nitrogen differs from the rest of the members of this group due to its smaller size, high electronegativity, high ionisation enthalpy and non-availability of d orbitals.

- **Dinitrogen:** It is produced commercially by the liquefaction and fractional distillation of air. Liquid dinitrogen (b.p. 77.2 K) distils out first leaving behind liquid oxygen (b.p. 90 K). In the laboratory, dinitrogen is **prepared by treating** an aqueous solution of ammonium chloride with sodium nitrite.

$$NH_4CI(aq) + NaNO_2(aq) \longrightarrow N_2(g) + 2H_2O(1) + NaCI(aq)$$

- **Properties of Dinitrogen:** It is a colourless, odourless, tasteless and non-toxic gas. It has **two stable isotopes**: ^{14}N and ^{15}N. It has a very low solubility in water (23.2 cm^3 per litre of water at 273 K and 1 bar pressure) and low freezing and boiling points.

- **Uses of dinitrogen:**
  - In the manufacture of ammonia and other industrial chemicals containing nitrogen, e.g. calcium cyanamide.
  - Where an inert atmosphere is required e.g. in iron and steel industry, inert diluent for reactive chemicals.
  - Liquid dinitrogen is used as a refrigerant to preserve biological materials, food items and in cryosurgery.

- **Ammonia:** It is present in small quantities in air and soil where it is formed by the decay of nitrogenous organic matter e.g., urea.

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

On a small scale ammonia is obtained from ammonium salts, which decompose when treated with caustic soda or lime.

- **Properties of Ammonia:** It is a colourless gas with a pungent odour. Its freezing point is 198.4 and boiling point is 239.7 K.

- **Uses of Ammonia:**
  - To produce various nitrogenous fertilisers (ammonium nitrate, urea, ammonium phosphate and ammonium sulphate).
  - In the manufacture of some inorganic nitrogen compounds, the most important one being nitric acid.
  - Liquid ammonia is used as a refrigerant.

- The **ammonia molecule** is trigonal pyramidal with the nitrogen atom at the apex. It has **three bond pairs** and **one lone pair** of electrons.

- **Nitric acid** is prepared by heating KNO_3 or $NaNO_3$ and concentrated H_2SO_4 in a glass retort.

  $NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$

  On a large scale it is prepared mainly by Ostwald's process.

- **Properties of N_2:** It is a colourless liquid (f.p. 231.4 K and b.p. 355.6 K). Laboratory grade nitric acid contains ~ 68% of the HNO_3 by mass and has a specific gravity of 1.504.

- In the gaseous state, **HNO_3** exists as a planar molecule with the structure.

- **Concentrated nitric acid** is a strong oxidising agent and attacks most metals except noble metals such as gold and platinum.

- Oxygen, sulphur, selenium, tellurium and polonium constitute **Group 16** of the periodic table. This is also known as **group of chalcogens**.

- **Oxygen** is the most abundant of all the elements on earth. It forms about 46.6% by mass of earth's crust. Dry air contains 20.946% oxygen by volume.

- **The elements of Group16:** They have six electrons in the outermost shell and ns^2np^4 general electronic configuration. The size of oxygen atom is exceptionally small. The elements of this group have lower ionisation enthalpy values compared to those of Group15 in the corresponding periods.

- **Oxygen** has the highest electronegativity value amongst the elements.

- **Oxygen** and **sulphur** are non-metals, selenium and tellurium metalloids, whereas polonium is a metal. Polonium is radioactive and is short lived (Half-life 13.8 days). All these elements exhibit allotropy.

- **Anomalous behaviour of oxygen:** The anomalous behaviour of oxygen, like other members of p-block present in second period is due to its small size and high electronegativity.

- **Dioxygen** can be obtained in the laboratory by four ways:
  (i) By heating oxygen containing salts such as chlorates, nitrates and permanganates.

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

(ii) By the thermal decomposition of the oxides of metals low in the electrochemical series and higher oxides of some metals

$2Ag_2O(s) \longrightarrow 4Ag(s) + O_2(g)$; $2Pb_3O_4(s) \longrightarrow 6PbO(s) + O_2(g)$

$2HgO(s) \longrightarrow 2Hg(1) + O_2(g)$; $2PbO_2(s) \longrightarrow 2PbO(s) + O_2(g)$

(iii) Hydrogen peroxide is readily decomposed into water and dioxygen by catalysts such as finely divided metals and manganese dioxide

$$2H_2O_2(aq) \longrightarrow 2H_2O(1) + O_2(g)$$

(iv) On larger scale it can be prepared from water or air. Electrolysis of water leads to the release of hydrogen at the cathode and oxygen at the anode.

- **Simple Oxides:** The oxides which give a base with water are known as basic oxides (e.g., Na_2O, CaO, BaO). E.g. CaO combines with water to give $Ca(OH)_2$, a base. $CaO + H_2O \longrightarrow Ca(OH)_2$
  In general, metallic oxides are basic.

- **Ozone:** It is an allotropic form of oxygen. It is too reactive to remain for long in the atmosphere at sea level. At a height of about 20 kilometres, it is formed from atmospheric oxygen in the presence of sunlight. This ozone layer protects the earth's surface from an excessive concentration of ultraviolet (UV) radiations.

- **Properties Of Dioxygen:**
  - It is a colourless and odourless gas.
  - Its solubility in water is to the extent of 3.08 cm^3 in 100 cm^3 water at 293 K which is just sufficient for the vital support of marine and aquatic life.
  - It liquefies at 90 K and freezes at 55 K.
  - It has three stable isotopes: ^{16}O, ^{17}O and ^{18}O.
  - Molecular oxygen, O_2 is unique in being paramagnetic inspite of having even number of electrons.
  - A binary compound of oxygen with another element is called **oxide**.

- **Types of Oxides:** (i) Simple (MgO, Al_2O_3)
  (ii) mixed (Pb_3O_4, Fe_3O_4).

- An oxide that combines with water to give an acid is termed as **acidic oxide**. only non-metal oxides are acidic but oxides of some metals in high oxidation state also have acidic character.
  e.g. Mn_2O_7, CrO_3, V_2O_5.

- **Preparation of Ozone:** When a slow dry stream of oxygen is passed through a silent electrical discharge, conversion of oxygen to ozone (10%) occurs.

- **Properties of Ozone:**
  - Pure ozone is a pale blue gas, dark blue liquid and violet-black solid.
  - Ozone has a characteristic smell and in small concentrations it is harmless.
  - If the concentration rises above about 100 parts per million, breathing becomes uncomfortable resulting in headache and nausea.

- When ozone reacts with an excess of potassium iodide solution buffered with a borate buffer (pH 9.2), **iodine** is liberated.

- **Threat to ozone layer** is probably posed by the use of freons which are used in aerosol sprays and as refrigerants.

- **Uses of Ozone:**
  - It is used as a germicide, disinfectant and for sterilising water.
  - It is used for bleaching oils, ivory, flour, starch.
  - It acts as an oxidising agent in the manufacture of potassium permanganate.

- Sulphur forms numerous allotropes of which the **yellow rhombic** (α-sulphur) and **monoclinic** (β -sulphur) forms are the most important. The stable form at room temperature is rhombic sulphur, which transforms to monoclinic sulphur when heated above 369 K.

- **Rhombic sulphur (α-sulphur):** This allotrope is yellow in colour, m.p. 385.8 K and specific gravity 2.06. Its crystals are formed on evaporating the solution of roll sulphur in CS_2. It is insoluble in water but dissolves to some extent in benzene, alcohol and ether. It is readily soluble in CS_2.

- **Monoclinic sulphur (β-sulphur):** Its m.p. is 393 K and specific gravity 1.98. It is soluble in CS_2. This form of sulphur is prepared by melting rhombic sulphur in a dish and cooling, till crust is formed. Two holes are made in the crust and the remaining liquid poured out. On removing the crust, colourless needle shaped crystals of β-sulphur are formed. It is stable above 369 K and transforms into α-sulphur below it.

- Both rhombic and monoclinic sulphur have **S_8 molecules**.

- **Sulphur Dioxide:** It is formed together with a little (6-8%) sulphur trioxide when sulphur is burnt in air or oxygen:

$$S(s) + O_2(g) \longrightarrow SO_2\ (g)$$

- **Properties Of Sulphur Dioxide:**
  - It is a colourless gas with pungent smell and is highly soluble in water.
  - It liquefies at room temperature under a pressure of two atmospheres.
  - It boils at 263 K.
  - It reacts readily with sodium hydroxide solution, forming sodium sulphite, which then reacts with more sulphur dioxide to form sodium hydrogen sulphite.
  - It reacts with chlorine in the presence of charcoal (which acts as a catalyst) to give sulphuryl chloride, SO_2Cl_2.

- **Uses of Sulphur dioxide:**
  - In refining petroleum and sugar
  - In bleaching wool and silk and
  - As an anti-chlor, disinfectant and preservative.
  - Liquid SO_2 is used as a solvent to dissolve a number of organic and inorganic chemicals.

- **Sulphuric Acid:** It is manufactured by the Contact Process which involves three steps:

  (i) Burning of sulphur or sulphide ores in air to generate SO_2.

  (ii) Conversion of SO_2 to SO_3 by the reaction with oxygen in the Presence of a catalyst (V_2O_5), and

  (iii) Absorption of SO_3 in H_2SO_4 to give Oleum ($H_2S_2O_7$).

- The sulphuric acid obtained by **Contact process** is 96-98% pure.

- **Properties Sulphuric acid:**
  - It is a colourless, dense, oily liquid with a specific gravity of 1.84 at 298 K.
  - The acid freezes at 283 K and boils at 611 K.
  - It dissolves in water with the evolution of a large quantity of heat.

- **Group 17 Elements:**

  Fluorine, chlorine, bromine, iodine and astatine are members of Group 17.

  These are collectively known as the **halogens** (Greek halo means salt and genes means born i.e., salt producers).

- All **group 17** elements have **seven electrons** in their outermost shell (ns^2np^5) which is one electron short of the next noble gas.

- **Uses of Sulphuric acid:**
  - In Petroleum refining
  - For the Manufacture of pigments, paints and dyestuff intermediates
  - In Detergent industry
  - For Metallurgical applications e.g. cleansing metals before enameling, electroplating and galvanising
  - For Storage batteries
  - In the manufacture of nitrocellulose products
  - As a laboratory reagent.
  - Because of its low volatility, It can be used to manufacture more volatile acids from their corresponding salts.
  - The bulk of sulphuric acid produced is used in the manufacture of fertilisers e.g., ammonium sulphate, superphosphate.

- The **halogens** have the smallest atomic radii in their respective periods due to maximum effective nuclear charge.

- **Properties of Halogens:**
  - They have little tendency to lose electron.
  - They have very high ionisation enthalpy.
  - They have maximum negative electron gain enthalpy in the corresponding periods.
  - Due to increase in atomic size, ionisation enthalpy decreases down the group.
  - They have very high electronegativity. The electronegativity decreases down the group. Fluorine is the most electronegative element.

- **Physical Properties of Halogens:**
  - All halogens are coloured.
  - **Bromine** and **iodine** are only sparingly soluble in water but are soluble in various organic solvents such as chloroform.
  - **Fluorine** and **chlorine** are gases, **bromine** is a liquid and **iodine** is a solid. Their melting and boiling points steadily increase with atomic number.

- **Chemical Properties of Halogens:**
  - All the halogens exhibit –1 oxidation state.
  - However, chlorine, bromine and iodine exhibit + 1, + 3, + 5 and + 7 oxidation states.
  - The higher oxidation states of chlorine, bromine and iodine are realised mainly when the halogens are in combination with the small and highly electronegative fluorine and oxygen atoms. e.g. in interhalogens, oxides and oxoacids.

- **Chlorine:** Chlorine was discovered in 1774 by Scheele by the action of HCl on MnO_2. In 1810 Davy established its elementary nature and suggested the name 'chlorine' on account of its colour (Greek, chloros = greenish yellow).

- **Preparation of Chlorine:** It can be prepared by two methods:

(i) By heating manganese dioxide with concentrated hydrochloric acid.

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

Sometimes a mixture of common salt and concentrated H_2SO_4 is used in place of HCl.

$$4NaCl + MnO_2 + 4H_2SO_4 \longrightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$$

(ii) By the action of HCl on potassium permanganate.

$$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

- **Properties of Chlorine:**
  - It is a greenish yellow gas with pungent and suffocating odour.
  - It is about 2-5 times heavier than air.
  - It can be liquefied easily into greenish yellow liquid which boils at 239 K.
  - It is soluble in water.
  - Chlorine reacts with a number of metals and non-metals to form chlorides.
  - It has great affinity for hydrogen.

- Chlorine reacts with hydrocarbons and gives substitution products with saturated hydrocarbons and addition products with Unsaturated hydrocarbons. It reacts with compounds containing hydrogen to form HCl.

- **Uses of Chlorine:**
  - For bleaching woodpulp (required for the manufacture of paper and rayon), bleaching cotton and textiles,
  - In the extraction of gold and platinum
  - In the manufacture of dyes, drugs and organic compounds such as CCl_4, $CHCl_3$, DDT, refrigerants, etc.
  - In sterilising drinking water and
  - Preparation of poisonous gases such as phosgene ($COCl_2$), tear gas (CCl_3NO_2), mustard gas ($ClCH_2CH_2SCH_2CH_2Cl$).

- **Hydrogen Chloride:** By heating common salt with concentrated sulphuric acid, we get it. Davy in 1810 showed that it is a compound of hydrogen and chlorine.

- **Preparation of Hydrogen Chloride:** It is prepared by heating sodium chloride with concentrated sulphuric acid.

- **Properties of Hydrogen Chloride:**
  - It is a colourless and pungent smelling gas.
  - It is easily liquefied to a colourless liquid (b.p.189 K) and freezes to a white crystalline solid (f.p. 159 K).
  - It is extremely soluble in water.
  - Its aqueous solution is called 'hydrochloric acid'.

- When three parts of concentrated HCl and one part of concentrated HNO_3 are mixed, aqua regia is formed which is used for dissolving noble metals, e.g. gold, platinum.

- **Uses of Hydrogen Chloride:**
  - In the manufacture of chlorine, NH4Cl and glucose (from corn starch)
  - For extracting glue from bones and purifying bone black
  - In medicine and as a laboratory reagent.

- **Oxoacids of Halogens:** Due to high electronegativity and small size, fluorine forms only one oxoacid, HOF known as 'fluoric (I) acid' or 'hypofluorous acid'. The other halogens form several oxoacids.

- **Properties of Oxoacids:**
  - Most of them cannot be isolated in pure state.
  - They are stable only in aqueous solutions or in the form of their salts.

- **Interhalogen Compounds:** When two different halogens react with each other, interhalogen compounds are formed. They can be assigned general compositions as XX' , XX_3 ', XX_5' and XX_7', where X is halogen of larger size and X' of smaller size. X is more electropositive than X'.

- **Preparation of Interhalogen Compounds:** It can be prepared by the direct combination or by the action of halogen on lower interhalogen compounds.

- **Properties of Interhalogen Compounds:**
  - These are all covalent molecules.
  - They are diamagnetic in nature.
  - They are volatile solids or liquids except CIF which is a gas at 298 K.

- **Physical properties of Interhalogen Compounds:**
  - They are intermediate between those of constituent halogens.
  - Their m.p. and b.p. are a little higher than expected.
  - Their chemical reactions can be compared with the individual halogens.
  - They are more reactive than halogens except fluorine.
  - Their molecular structures are very interesting which can be explained on the basis of VSEPR theory.

- **Uses of Interhalogen Compounds:**
  - These compounds can be used as non aqueous solvents.
  - Interhalogen compounds are very useful fluorinating agents.
  - ClF_3 and BrF_3 are used for the production of UF_6 in the enrichment of ^{235}U.

- **Group 18 Elements:** It consists of six elements:
  - Helium
  - Neon
  - Argon
  - Krypton
  - Xenon
  - Radon

  All these are gases and chemically unreactive. They form very few compounds, so they are termed **noble gases**.

- **Noble gases:**
  - All noble gases except radon occur in the atmosphere.
  - Their atmospheric abundance in dry air is ~ 1% by volume of which argon is the major constituent.
  - Helium and sometimes neon are found in minerals of radioactive origin.
  - All noble gases have general electronic configuration ns^2np^6 except helium which has $1s^2$.
  - Due to stable electronic configuration, they exhibit very high ionisation enthalpy.
  - Atomic radii increase down the group with increase in atomic number.
  - Since noble gases have stable electronic configurations, they have no tendency to accept the electron, so they have large positive values of electron gain enthalpy.

- **Physical Properties of Noble gases:**
  - All the noble gases are monoatomic
  - They are colourless, odourless and tasteless
  - They are sparingly soluble in water
  - They have very low melting and boiling points
  - Helium has the lowest boiling point (4.2 K) of any known substance.
  - It has an unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.

- **Chemical Properties Noble gases:** In general, noble gases are least reactive. Their inertness to chemical reactivity is attributed to the following reasons:
  - The noble gases except helium ($1s^2$) have completely filled ns^2np^6 electronic configuration in their valence shell.
  - They have high ionisation enthalpy and more positive electron gain enthalpy
  - Noble gases being monoatomic have no interatomic forces except weak dispersion forces
  - They are liquefied at very low temperatures
  - They have low boiling points.

- **Uses of Helium:** It is a non-inflammable and light gas.
  - It is used in filling balloons for meteorological observations.
  - It is used in gas-cooled nuclear reactors.
  - **Liquid helium** is used to produce and sustain powerful superconducting magnets which form an essential part of modern NMR spectrometers and Magnetic Resonance Imaging (MRI) systems for clinical diagnosis.
  - It is used as a diluent for oxygen in modern diving apparatus because of its very low solubility in blood.

- **Uses of Neon:**
  - It is used in discharge tubes and fluorescent bulbs for advertisement display purposes.
  - Neon bulbs are used in botanical gardens and in green houses.

- **Uses of Argon:**
  - It is used mainly to provide an inert atmosphere in high temperature metallurgical processes (arc welding of metals or alloys).
  - It is used for filling electric bulbs.

- **Uses of Xenon and Krypton:**
  - They are used in light bulbs designed for special purposes.
  - As such there are no other significant uses of **Xenon** and **Krypton**.