

CLASS 11 Chemistry Chapter 11 p- Block Elements

Group 13 to 18 of the periodic table of elements constitute the p-block. The p-block contains metals, metalloids as well as non-metals. The p-block elements have general valence shell electronic configuration $ns^2 np^{1-6}$. The first member of each group from 13–17 of the p-block elements differ in many respects from the other members of their respective groups because of small size, high electronegativity and absence of d-orbitals.

The highest oxidation of p-block element is equal to the group number minus 10. Moving down the group, the oxidation state two less than the highest group oxidation state becomes more stable in groups 13 to 16 due to inert pair effect (reluctance of s-subshell electrons to participate in chemical bonding)

Inert Pair Effect:

- Reluctance of ns^2 electrons of valence shell to participate in bond formation is termed as inert pair effect.
- It arises due to poor or insufficient shielding of ns^2 electrons by intervening d- or f-electrons & hence increases down the group.

Causes of Anomalous Behavior of First Element in groups of p-Block:

- (i) Very small size
- (ii) Unavailability of vacant d-orbital
- (iii) Tendency to form $p\pi - p\pi$ multiple bonds.

Group No-13 Elements: THE BORON FAMILY (B, Al, Ga, In, Tl, Nh)

- **General Electronic Configuration:** $ns^2 np^1$
- **Atomic radius:** On moving down the group, for each successive member one extra shell of electrons is added and therefore, atomic radius is expected to increase. Atomic radius of Ga is less than of Al. The presence of additional 10 d-electrons offer only poor screening effect for the outer electrons from the increased nuclear charge in gallium. Consequently, the atomic radius of

gallium (135 pm) is less than that of aluminium (143 pm).

- **Ionization Enthalpies:** The ionization enthalpy values as expected from the general trends do not decrease smoothly down the group. The decrease from B to Al is associated with increases in size. The observed discontinuity in the ionization enthalpy values between Al and Ga, and between In and Tl are due to inability of d- and f electrons, which have low screening effect, to compensate the increase in nuclear charge.
- **Electronegativity:** Down the group, electronegativity first decreases from B to Al and then increases marginally. This is because of the discrepancies in atomic size of the elements. $B > Tl > In > Ga > Al$.
- **Oxidation States:** B (+3), Al (+3), Ga (+3, +1), In (+3, +1), Tl (+1, +3)
Tl (+1) is more stable than Tl (+3) due to inert pair effect.

USES OF BORON: Boron is used in the construction of high impact-resistant steel and, since it absorbs neutrons, in reactor rods for controlling atomic reactions.

- **Nature of Compounds:** Compounds of group 13 elements are electron deficient i.e. Lewis Acid and hence used as industrial catalyst *e.g.* BF_3 , $AlCl_3$.

● Oxides:	B_2O_3	Al_2O_3 , Ga_2O_3	In_2O_3	Tl_2O
	Acidic	Amphoteric	Basic	Strongly Basic

- **Halides:** MX_3 type, Electron deficient (Lewis acid), $AlCl_3$ exist as dimer.
- **Borax:** $Na_2B_4O_7 \cdot 10H_2O$. On heating it forms transparent glassy bead consisting of $NaBO_2 + B_2O_3$.

- **Boric acid:** H_3BO_3 , It acts as a Lewis acid by accepting electron pair from OH^- ions of water.
- **Diborane:** B_2H_6 , Colourless & toxic gas, acts as Lewis acid due to having electron deficient $3c-2e^-$ bonds. Obtained by treating BF_3 with LiAlH_4 or NaH , Also, obtained by treating NaBH_4 with I_2 .
- **Borazine:** $\text{B}_3\text{N}_3\text{H}_6$, It is isostructural with benzene and hence known as inorganic benzene. Prepared by heating B_2H_6 with NH_3 .

Group -14 Elements: THE CARBON FAMILY (C, Si, Ge, Sn, Pb, Fl)

Carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb) are the members of group 14. Naturally occurring carbon contains two stable isotopes: ^{12}C and ^{13}C . In addition to these third isotopes, ^{14}C is also presents, it is a radioactive isotope with half-life 5770 years and used for radiocarbon dating. Silicon is a very important component of ceramics, glass and cement.

Germanium exists only in traces. Tin occurs mainly as cassiterite, SnO_2 and lead as galena, PbS . Ultrapure form of germanium and silicon are used to make transistors and semiconductor devices.

- **General Electronic Configuration:** $ns^2 np^2$
- **Atomic radius:** $\text{C} < \text{Si} < \text{Ge} < \text{Sn} < \text{Pb}$
- **Ionisation Enthalpy:** The first ionization enthalpy of group 14 members is higher than the corresponding members of group 13. The influence of inner core electron is visible here also. In general the ionisation enthalpy decreases down the group.

Small decreases in ΔiH from Si to Ge to Sn and slight increase in ΔiH from Sn to Pb is the consequence of poor shielding effects of intervening d and f-orbitals

and increases in size of the atom. LiH_x : $C > Si > Ge > Sn < Pb$

- **Oxidation States:** The group 14 elements have four electrons in outermost shell. The common oxidation states exhibited by these elements are +4 and +2. Carbon also exhibits negative oxidation states. Since, the sum of the first four ionization enthalpies is very high, compound in +4 oxidation state are generally covalent in nature.

In heavier members the tendency to show +2 oxidation state increases in the sequence $Ge < Sn < Pb$. It is due to the inability of ns^2 electrons of valence shell to participate in bonding.

The relative stabilities of these two oxidation states vary down the group. Carbon cannot exceed its covalence more than 4. Other elements of the group can do so. It is because of the presence of d orbital in them. Due to this, their halides undergo hydrolysis and have tendency to form complexes by accepting electron pairs from donor species. For example, the species like $[SiF_6]^{2-}$, $[GeCl_6]^{2-}$, $[Sn(OH)_6]^{2-}$ exist.

- **Electronegativity:** Due to small size, the elements of this group are slightly more electronegative than group 13 elements. The electronegativity value for elements from Si to Pb are almost the same.
- **Oxides:** Form di oxides (MO_2) & mono oxides (MO).
 PbO_2 is powerful oxidizing agent because Pb stabilizes in +2 oxidation state due to inert pair effect. CO_2 is gas while SiO_2 is network solid because C has ability to form $p\pi - p\pi$ multiple bonds.
- **Halides:** Form tetra halides (MX_4) & dihalides (MX_2).
Tetra halides are more covalent due to greater polarizing power of cation. CCl_4 is not hydrolyzed with water as C has no vacant d-orbital to accept electron pair from water.

- **Catenation:** $C \gg Si > Ge \approx Sn \gg Pb$
- **Allotropes of carbon:** Carbon exhibits many allotropic forms; both crystalline as well as amorphous. Diamond and graphite are two well-known crystalline forms of carbon. In 1985 third form of carbon known as fullerenes was discovered by H.W. Kroto, E Smalley and R.F.Curl.

Diamond: It has a crystalline lattice. In diamond each carbon atom undergoes sp^3 hybridization and linked to four other carbon atoms by using hybridised orbitals in tetrahedral fashion. The C–C bond length is 154 pm. The structure extends in space and produces a rigid three dimensional network of carbon atoms. In this structure directional covalent bonds are presents throughout the lattice.

It is very difficult to break extended covalent bonding and therefore, diamond is a hardest substance on the earth. It is used as an abrasive for sharpening hard tools in making dyes and in the manufacture of tungsten filament for electric light bulbs.

Graphite: Graphite has layered structure. Layers are held by van der Waal's forces and distance between two layers is 340 pm. Each layer is composed of planar hexagonal rings of carbon atoms. C – C bond length within the layer is 141.5 pm.

Each carbon atom in hexagonal ring undergoes sp^2 hybridization and make three sigma bonds with three neighboring carbon atoms. Fourth electron forms a π bond. The electrons are delocalized over the whole sheet. Electrons are mobile and, therefore graphite conducts electricity along the sheet. Graphite cleaves easily between the layers and therefore, it is very soft and slippery. For this reason, graphite is used as a dry lubricant in machines running at high temperature, where oil cannot be used as a lubricant.

Fullerenes: Fullerenes are made by the heating of graphite in an electrical arc in the presence of inert gases such as helium or argon. Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds.

Fullerene are cage like molecules. C₆₀ molecule has a shape like soccer ball and called Buckminsterfullerene. It contains twenty-six six-membered rings and twelve five membered rings. A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings. All the carbon atoms are equal and they undergo sp² hybridization.

- **Silicones:** Silicones are synthetic organosilicon compounds containing R₂SiO repeating units. Silicones are water repellent, heat resistant, chemically inert, electrical insulators, resistant to oxidation.
- **Silicates:** Silicates are compounds in which anions are derived from Si–O–Si– tetrahedral units.
- **Zeolites:** Zeolites are 3D silicates in which some of the Si atoms are replaced by Al³⁺ ions and negative charge is balanced by cations such as Na⁺, K⁺, Ca²⁺ etc.
- ZSM-5 is used in petrochemical industries to convert methanol into petrol.

Uses of Carbon

- Graphite fibers embedded in plastic material form high strength, lightweight composites. The composites are used in products such as tennis rackets, fishing rods, aircrafts and canoes. Being good conductor, graphite is used for electrodes in batteries and industrial electrolysis. Crucibles made from graphite are inert to dilute acids and alkalies. Being highly porous, activated charcoal is used in adsorbing poisonous gases; also used in water filters to remove organic contaminants and in air conditioning system to control odour. Carbon black is used as black pigment in black ink and as filler in automobile tyres. Coke is used as a fuel and largely as a reducing agent in metallurgy.

