Unit 11 The *p*-Block Elements (Group 13 and 14)

General Introduction to *p*-Block Elements

- Elements having outer electronic configuration of the type $ns^2\ np^1$ to $ns^2\ np^6$, with all other inner orbitals completely filled, are termed *p*-block elements. In other words, the elements in which the last electron enters into any of the outermost *p*-orbitals are called *p*-block elements. Thus, the general outer electronic configuration of the *p*-block elements is $ns^2\ np^{1-6}$.
- The elements belonging to the group 13 to 18 of the long form of periodic table are *p*-block elements. The *p*-block elements include metals, non-metals and metalloids.
- The *p*-block elements enter into chemical combination by losing, gaining or sharing the valence electrons.
- **Nature of compounds :** The *p*-block elements mostly form covalent compounds. The halogens, however, form ionic compounds with alkali and alkaline earth metals.
- **Oxidation states :** The highest oxidation state shown by a *p*-block element is equal to the total number of valence electrons.
- The first element of a group differs from the heavier elements in their ability to form $p\pi$-$p\pi$ bonds.

GROUP 13 ELEMENTS

- Group 13 of the periodic table contains five elements, boron (B), aluminium (Al), gallium (Ga), indium (In) and thallium (Tl). Aluminium is the most abundant of these elements. Boron occurs rather sparsely and gallium, indium, thallium are not found in concentrated deposits.
- **Electronic configuration :**

Element	Symbol	Electronic configuration [noble gas] ns^2np^1
Boron	$_5B$	$[He]2s^22p^1$
Aluminium	$_{13}Al$	$[Ne]3s^23p^1$
Gallium	$_{31}Ga$	$[Ar]3d^{10}4s^24p^1$
Indium	$_{49}In$	$[Kr]4d^{10}5s^25p^1$
Thallium	$_{81}Tl$	$[Xe]4f^{14}5d^{10}6s^26p^1$

- **Occurrence :** Aluminium is most abundant metal and third most abundant element (after oxygen and silicon).

Element by wt.	Abundance (ppm)	Ore
B	9	Borax : $Na_2[B_4O_5(OH)_4]\cdot 8H_2O$ Boracite : $2Mg_3B_8O_{15}\cdot MgCl_2$ Boric acid : H_3BO_3
Al	83,000	Bauxite : $Al_2O_3\cdot 2H_2O$ Cryolite : Na_3AlF_6 Felspar : $K_2O\cdot Al_2O_3\cdot 6SiO_2$ Corundum : Al_2O_3
Ga	19	Found in germinite : sulphides of Zn, Cu, Ge, As
In	0.24	Found in traces in PbS and ZnS
Tl	0.5	–

Variation in Properties of Group 13 Elements

- **Atomic radii and ionic radii**
  - Group 13 elements and their ions have smaller size than the corresponding group 2 element because of the increase in nuclear charge.
  - Their atomic and ionic radii increase on going down the group with an exception at gallium.

Element	Metallic radius (Å)	Ionic radius	
		M^{3+} (Å)	M^{+} (Å)
B	0.885	–	–
Al	1.43	0.535	–
Ga	1.225	0.620	1.20
In	1.67	0.800	1.40
Tl	1.70	0.885	1.50

- **Melting and boiling points**
  - Melting points of group 13 elements do not vary regularly due to structural changes in the elements. The melting point decreases from B to Ga and then increases.

Element	Melting point (°C)	Boiling point (°C)
B	2300	2550
Al	660	2467
Ga	30	2240
In	157	2050
Tl	303	1470

- Boron shows a very high melting point because it exists as a giant covalent polymer crystal structure consisting of icosahedral units.

- **Ionisation energy**
  - The first ionization energies of these element are less than the corresponding value of *s*-block elements. This is because of less penetrating and shielding effect of *p*-electrons than *s*-electrons,
    $$IE_1 < IE_2 < IE_3$$
  - Sum of the first three ionization energies to produce M^{3+} ions are very high.
  - The ionization energy values do not decrease smoothly down the group. The irregularity is observed in case of gallium and thallium. This is due to the poor shielding by intervening *d* and *f* electrons respectively.

- **Oxidation states**
  - Valence electronic configuration ns^2np^1, suggests that these elements are expected to show +1 and +3 oxidation states.

Element	Oxidation state
B	+3
Al	+1, +3
Ga	+1, +3
In	+1, +3
Tl	+1, +3

  - As we move down in the group, stability of +1 oxidation state increases due to the fact that the two *s*-electron in the other shell tend to remain paired and do not participate in bonding (inert pair effect).
    Thus, $B^{3+} > Al^{3+} > Ga^{3+} > In^{3+} > Tl^{3+}$
    $Tl^+ > In^+ > Ga^+ > Al^+ > B^+$
    $B^{3+} > B^+$ while $Tl^+ > Tl^{3+}$

- **Electronegativity**
  - Group 13 elements are more electronegative than group 1 (alkali metals) and group 2 (alkaline earth metals).
  - Electronegativity first decreases from B to Al and then increases due to poor shielding by *d*-electrons.

Element	B	Al	Ga	In	Tl
Pauling's electronegativity	2.0	1.5	1.6	1.7	1.8

- Elements of this group form ionic compounds because of bigger size and smaller ionization energy as compared to B and Al. Al can form both covalent and ionic compounds while B forms only covalent compounds.
- **Complex formation :** Owing to smaller size and greater charge, these elements have a greater tendency to form complexes than the *s*-block elements.
- **Reducing property**
  - The reducing power of the elements of group 13 decreases down the group *i.e.*, Al > Ga > In > Tl, since electrode potential increases down the group.
  - Aluminium is stronger reducing agent than carbon because aluminium can reduce even those oxides which are not reduced by carbon. This is due to low ionization energy of aluminium than carbon.
    $$4Al + \underset{\text{(Impure air)}}{3O_2} \xrightarrow{\Delta} 2Al_2O_3$$

Trends in Chemical Reactivity

- Groups 13 elements are less reactive than group 1 and group 2 elements.
- The first three ionisation enthalpies of boron (B) are much higher than the corresponding values for the other elements of group 13. Therefore boron does not form ionic compounds. Boron, however, forms covalent compounds by electron-sharing mechanism.
- Other elements of group 13 form ionic compounds containing tripositive (M^{3+}) ions in solutions.
- Al, Ga, In and Tl exhibit a well-defined aqueous chemistry in their +3 states. Species such as $[M(H_2O)_2(OH)_4]^-$, $[M(OH)_4]^-$ and $[M(H_2O)_6]^{3+}$ for Al, Ga and In exist in aqueous solutions.
- **Reaction with air :** Boron in amorphous form is very reactive. When heated at 700°C in air or oxygen it burns with a reddish flame forming a mixture of oxides and nitride.
  $$B + \underbrace{O_2 + N_2}_{\text{Air}} \xrightarrow{700°C} B_2O_3 + BN$$
  Aluminium is not affected by any air. However, a thin oxide layer is formed on the surface of aluminium metal in moist air.
  $$4Al + 3O_2 \xrightarrow{\Delta} 2Al_2O_3$$
  Gallium and indium are not affected by air. Thallium forms an oxide layer on its surface.
- **Reaction with water :** Boron does not decompose water or steam. However, aluminium and other elements decompose boiling water to give hydrogen gas.
  $$2Al + 3H_2O \text{ (boiling)} \rightarrow Al_2O_3 + H_{2(g)}$$
- **Formation of halides :** Group 13 elements form trihalides(MX_3). Monohalides are also given by thallium TlF, TlCl, TlBr and TlI.
  - Due to small size and high electronegativity, all boron halides are covalent and are produced by sp^2 hybridisation. They exist as monomeric molecules.
  - In case of Al, Ga, In and Tl, the trifluorides are ionic and have high melting point.
  - Boron halides BX_3 are electron deficient compounds having six electrons in the outermost orbit thus function as Lewis acid by accepting a pair of electron.
    $BX_3 + NH_3 \longrightarrow \{H_3N \rightarrow BX_3\}$
    The Lewis acid strength follows the order :
    $BF_3 < BCl_3 < BBr_3 < BI_3$
  - Lewis acid character of halides of group 13 elements decreases in the order :
    $BX_3 > AlX_3 > GaX_3 > InX_3$
    Anhydrous $AlCl_3$ is deliquescent in nature and it fumes in moist air due to hydrolysis and is acidic in nature again due to hydrolysis and is used as catalyst in Friedel–Crafts reaction.
  - In addition to trihalides, these elements form di as well as monohalides. Boron forms dihalides B_2X_4.
  - Gallium and indium also form dihalides. Gallium dihalide is more properly represented as $Ga^+[GaCl_4]^-$ showing gallium in +1 and +3 oxidation state.