

CHAPTER-5

BORON FAMILY

5.1 Introduction

The group 13 of the periodic table consists of the elements boron (B), aluminium (Al), gallium (Ga), indium (In) and thallium (Tl). Except boron which is a non-metal all other elements of this group show typical metallic properties. The nonmetallic character of B is possibly due to its small size, high ionization energy and comparatively high electronegativity.

5.2 Electronic Configuration:

The elements of group 13 belong to p -block elements since the last electron in them enters the p -orbital. They have in all three electrons in the valence shell, two of these are present in the s -orbital and one in the p -orbital. Therefore, their general valence shell electronic configuration is represented as $ns^2 np^1$ where $n = 2$ to 6. The complete electronic configuration of these elements are given in the following table.

Element	Atomic Number	Electronic Configuration
Boron (B)	5	[He] $2s^2 2p^1$
Aluminium (Al)	13	[Ne] $3s^2 3p^1$
Gallium (Ga)	31	[Ar] $3d^{10} 4s^2 4p^1$
Indium (In)	49	[Kr] $4d^{10} 5s^2 5p^1$
Thallium (Tl)	81	[Xe] $4f^{14} 5d^{10} 6s^2 6p^1$

5.3 General Characteristics

Some of these properties are discussed below:

- (i) **Atomic and Ionic radii:** The atomic and ionic radii of group 13 elements are smaller than the corresponding elements of group 2.

Explanation: This is because on moving from left to right, *i.e.*, from group 2 to group 13 in a given period the nuclear charge increases while the new electron enters the same shell. Further the electrons in the same shell do not screen each other. Therefore the effective nuclear charge increases and the electrons are pulled more towards the nucleus. This results in decrease in atomic size. Same is true of ionic radius.

On moving down the group, both atomic and ionic radii are expected to increase primarily due to addition of a new electron shell with each succeeding element. However there are some deviations as we move from Al to Ga. For example the atomic radius of Ga (135 pm) is slightly lower than that of Al (143pm).

Explanation: This is due to the filling of electrons in d -orbitals. In-between Al ($Z = 13$) and Ga ($Z = 31$), there are ten elements of the first transition series ($Z = 21$ to 30) which have electrons in the inner d -orbitals. As the d -orbitals are large in size, these intervening electrons do not screen the nucleus effectively. Consequently, effective nuclear charge of Ga is greater in magnitude than that of Al. As a result, the electrons in Ga experience greater force of attraction by the nucleus than in Al and hence atomic radius of Ga is slightly less than that of Al.

The ionic radii however, follow a regular trend.

- (ii) **Ionisation enthalpy :** The first ionization enthalpies or ionization energies (IE_1) of the elements of group 13 are lower than the corresponding elements of group 2 i.e., alkaline earth metals.

Explanation: This is due to the reason that elements of group 13 have three electrons in the valence shell two of these are present in the s -orbital and one in the p -orbital. For the first ionization enthalpy (IE_1) the electron has to be removed from the p -orbital in case of group 13 elements, whereas in alkaline earth metals (group 2 elements) the s -electron of the same principal shell has to be removed. Since an s -electron is nearer the nucleus (more penetrating towards the nucleus), it is more strongly attracted than the p -electron of the same principal shell. Hence the removal of the p -electron is much easier than the s -electron and therefore the first ionization enthalpies (IE_1) of the elements of group 13 are lower as compared to the corresponding values of the alkaline earth metals of group 2.

On moving down the group 13 from B to Al the ionization enthalpies (IE_1) decrease as expected due to an increase in atomic size and screening effect (due to addition of a new shell in every succeeding element), which outweigh the effect of increased nuclear charge. However the **IE_1 of Ga is only slightly higher (1 kJ mol^{-1}) than that of Al** while that of Tl is much higher than those of Al, Ga and In.

Explanation: This is due to the reason that Al follows immediately after s -block element while Ga and In follow after d -block elements and Tl after d - and f -block elements. These extra d - and f -electrons do not shield (or screen) the outer shell electrons from the nucleus very effectively. As a result the valence electrons remain more tightly held by the nucleus and hence larger amount of energy is needed for their removal. This explains why Ga has higher ionization energy than Al. Further on moving down the group from Ga to In the increased shielding effect (due to the presence of additional $4d$ -electrons) outweighs the effect of increased nuclear charge ($49 - 31 = 18$ units) and hence the IE_1 of In is lower than that of Ga. There after the effect of increased nuclear charge ($81 - 49 = 32$ units) outweighs the shielding effect due to the presence of additional $4f$ and $5d$ electrons and hence the IE_1 of Tl is higher than that of In.

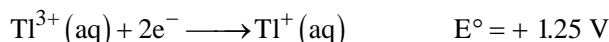
Further as expected, the second and third ionization enthalpies (IE_2 and IE_3) of these elements (of group 13) are quite higher than their respective first ionization energies.

Explanation: This is mainly due to the following reason:

- (i) After the loss of first electron (p -electron), the effective nuclear charge increases with the decrease in ionic size and thus the removal of second and third electrons becomes difficult.
 - (ii) Second and third electrons have to be lost from the more strongly held ns -orbital (more penetrating) and hence large amount of energy is required.
- (iii) **Oxidation states.** The elements of group 13 have two electrons in the s -orbital and one electron in the p -orbital of the valence shell. So these elements are expected to show a uniform oxidation state of +3. This is true of boron and aluminium, which show an oxidation state of +3 only but gallium, indium and thallium show oxidation states of both +1 and +3.

Further, as we move down the group, the stability of the +3 oxidation state decreases while that of +1 oxidation state increases. For example +1 oxidation state of thallium is more stable than +3. i.e. $TlOH$ and $TlClO_4$, are more stable than their corresponding thallic salts.

Thus the order of stability of +1 oxidation state increases in the sequence : Al < Ga < In < Tl. This is supported by the observation that in aqueous solution, Tl^+ is more stable than Tl^{3+} as shown by the redox potential-data.



Explanation: This is because as we move down the group, the tendency of s-electrons of the valence shell to participate in bond formation decreases. This reluctance of the s-electrons to participate in bond formation is called *Inert pair effect*. In other words, the ns^2 electron pair in Ga, In and Tl tends to remain paired. This is due to poor or ineffective shielding of the ns^2 electrons of the valence shell by intervening d- and f-electrons.

Another reason for the inert pair effect is that as the size of atom increases from Al to Tl, the energy required to unpair the ns^2 electrons is not compensated by the energy released in forming the two additional bonds.

The inert pair effect becomes more predominant as we go down the group because of increased nuclear charge which outweighs the effect of the corresponding increase in atomic size. The s-electrons thus become more tightly held (more penetrating) and, therefore, become more reluctant to participate in bond formation. Thus down the group, +1 oxidation state becomes more and more stable as compared to +3 oxidation state.

(+III) oxidation state

The elements all have three outer electrons. Apart from Tl they normally use these to form three bonds, giving an oxidation state of (+III). Are the bonds ionic or covalent. Covalency is suggested by the following:

1. Fajan's rules-small size of the ions and their high charge of 3+ favours the formation of covalent bonds.
2. The sum of the first three ionization energies is very large, and this also suggests that bonds will be largely covalent.
3. The electronegativity values are higher than for Groups 1 and 2, and when reacting with other elements the difference is not likely to be large.

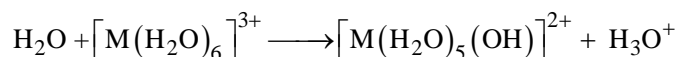
Boron is considerably smaller than the other elements and thus has a higher ionization energy than the others. The ionization energy is so high that B is always covalent.

Many simple compounds of the remaining elements such as $AlCl_3$ and $GaCl_3$, are covalent when anhydrous. However, Al, Ga, In and Tl all form metal ions in solution. The type of bonds formed depends on which is most favourable in terms of energy. This change from covalent to ionic happens because the ions are hydrated and the amount of hydration energy evolved exceeds the ionization energy. Consider $AlCl_3$, 5137 kJ mol^{-1} are required to convert Al to Al^{3+} , $\Delta H_{\text{hydration}}$ for Al^{3+} is $-4665 \text{ kJ mol}^{-1}$ and $\Delta H_{\text{hydration}}$ for Cl^- is -381 kJ mol^{-1} . Thus the total hydration energy is:

$$-4665 + (3 \times -381) = -5808 \text{ kJ mol}^{-1}$$

This exceeds the ionization energy, so $AlCl_3$ ionizes in solution.

The hydrated metal ions have six molecules of water which are held very strongly in an octahedral structure $[M(H_2O)_6]^{3+}$. The metal-oxygen bonds are very strong. This weakens the O—H bonds and protons are released to neighbouring water molecules, forming H_3O^+ (hydrolysis).



(+I) oxidation state – the ‘inert pair effect’

In the *s*-block, Group 1 elements are univalent, and Group 2 elements are divalent. In Group 13 we would expect the elements to be trivalent. In most of their compounds this is the case, but some of the elements show lower valency states as well. There is an increasing tendency to form univalent compounds on descending the group. Compounds with Ga(I), In(I) and Tl(I) are known. With Ga and In the (+I) oxidation state is more stable than the (+III) state. However, the stability of the lower oxidation state increases on descending the group. Tl(I) thallos compounds are more stable than Tl(III) thallic compounds.

How and why does monovalency occur? The atoms in this group have an outer electronic configuration of s^2p^1 . Monovalency is explained by the *s* electrons in the outer shell remaining paired, and not participating in bonding. This is called the *inert pair effect*. If the energy required to unpair them exceeds the energy evolved when they form bonds, then the *s* electrons will remain paired. The strength of the bonds in MX_3 compounds decreases down the group. The mean bond energy for chlorides are $GaCl_3 = 242$, $InCl_3 = 206$ and $TlCl_3 = 153 \text{ kJ mol}^{-1}$. Thus the *s* electrons are most likely to be inert in thallium.

The inert pair effect is not the explanation of why monovalency occurs in Group 13. It merely describes what happens, i.e. two electrons do not participate in bonding. The reason that they do not take part in bonding is energy. The univalent ions are much larger than the trivalent ions, and (+I) compounds are ionic, and are similar in many ways to Group I elements.

The inert pair effect is not restricted to Group 13, but also occurs among the heavier elements in other groups in the *p*-block. Examples from Group 14 are Sn^{2+} and Pb^{2+} and examples from Group 15 are Sb^{3+} and Bi^{3+} . The lower oxidation state becomes more stable on descending the group. Thus Sn^{2+} is a reducing agent but Pb^{2+} is stable and Sb^{3+} is a reducing agent but Bi^{3+} is stable. When the *s* electrons remain paired, the oxidation state is always two lower than the usual oxidation state for the group.

Thus in the *s*-block, Groups 1 and 2 show only the group valency. Groups in the *p*-block show variable valency, differing in steps of two. Variable valency also occurs with elements in the *d*-block. This arises from using different numbers of *d* electrons for bonding, so in this case the valency can change in steps of one (e.g. Cu^+ and Cu^{2+} , Fe^{2+} and Fe^{3+}).

(+II) oxidation state

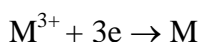
Gallium is apparently divalent in a few compounds, such as $GaCl_2$. However, Ga is not really divalent, as the structure of $GaCl_2$ has been shown to be $Ga^+[GaCl_4]^-$ which contains Ga(I) and Ga(III).

- (iv) **Electropositive character-Metallic character** : The elements of group 13 are less electropositive or metallic as compared to alkali metals (group 1) and alkaline earth metals (group 2). On moving down the group the electropositive character of the elements first increases from boron to aluminium and then decreases from aluminium to thallium.

Explanation: Amongst the elements of group-13 B has the highest sum of first three ionization enthalpies i.e. $IE_1 + IE_2 + IE_3$. As a result it has little tendency to lose electrons and hence is least electropositive amongst group 13 elements. In other words as expected it is a non-metal and a poor conductor of electricity. However as we move from B to Al, the sum of $IE_1 + IE_2 + IE_3$ decreases substantially (6857 kJ mol^{-1} to 5137 kJ mol^{-1}) due to increase in the atomic size and hence Al has a high tendency to lose electrons. In other words, Al is highly electropositive. Therefore, Al is a metal and a good conductor of electricity.

The electropositive character of the remaining elements can be more easily explained on the basis of their respective electrode potentials. Since the electrode potentials for the reaction $M^{3+}(\text{aq}) + 3e^- \rightarrow M(\text{s})$ increases from Al to Tl, therefore their electropositive character decreases accordingly.

The electropositive or metallic nature of the elements increases from B to Al, but then decreases from Al to Tl. This is shown by the standard electrode potentials for the reaction.



The increase in metallic character from B to Al is the usual trend on descending a group associated with increasing size. However Ga, In and Tl do not continue the trend. The elements are less likely to lose electrons (and are thus less electropositive), because of the poor shielding by d electrons.

Table: Standard electrode potentials E_0

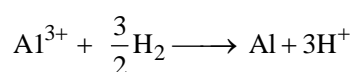
Group-13 Elements	$M^{3+} M$ (volts)	$M^+ M$ (volts)
B	(-0.87*)	
Al	-1.66	+0.55
Ga	-0.56	-0.79**
In	-0.34	-0.18
Tl	+1.26	-0.34

*For $H_3BO_3 + 3H^+ + 3e^- \longrightarrow B + 3H_2O$

**Value in acidic solution.

The standard electrode potentials E° for $M^{3+} | M$ become less negative from Al to Ga to In and the potential becomes positive for Tl. Since $\Delta G = -nFE^\circ$ it follows that ΔG , the free energy of formation of the metal, e.g. $Al^{3+} + 3e \rightarrow Al$, is positive. Thus it is difficult to make this reaction work. (The reverse reaction $Al \rightarrow Al^{3+} + 3e$ occurs spontaneously). The standard potential becomes less negative on descending the group so it becomes less difficult for the reaction $M^{3+} \rightarrow M$ to occur. Thus the (+III) oxidation state becomes less stable in aqueous solution on descending the group. In a similar way, the E° values for $M^+ | M$ show that the (+I) state increases in stability. With Tl, the (+I) state is more stable than the (+III) state.

It should be remembered that in this type of argument E° and ΔG refer to the reaction with H_2 .



- (v) **Electronegativity** : The elements of boron family (group 13) are more electronegative than the elements of alkali metals (group 1) and alkaline earth metals (group 2). The electronegativity first decreases from B to Al and then increases marginally.

Explanation : This is because of the increase in the atomic size and consequently decrease in the attraction of the nucleus for electrons.

- (vi) **Melting points and boiling points** : The melting points of group 13 elements do not show a regular trend as shown by elements of groups 1 and 2. This is probably due to the unusual crystal structures of B and Ga. Actually the melting point decreases sharply on moving down the group upto Ga and then increase from In to Tl. So much so Ga is a liquid with an incredible low melting point of 303K.

Boron has a high melting point (2453 K) because its crystal structure consists of icosahedral (it is a solid of 20 faces) units with B atoms at all the 12 corners and each boron atom is bonded to five equidistant neighbours. In contrast, the crystal structure of Ga is quite different from that of B. Each