ST. LAWRENCE HIGH SCHOOL

A JESUIT CHRISTIAN MINORITY INSTITUTION
STUDY MATERIAL FOR CHEMISTRY (CLASS-11)
TOPIC- GROUP-13 ELEMENTS (P-BLOCK)
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What are Group 13 Elements?

The group 13 elements are the first group in the p-block of the periodic table. All the elements of group 13 are also called the boron family. The periodic table is segregated into s, p, d and f-blocks. This segregation is done based on the valence electron, if the valence electron falls on the p subshell, it comes in p-block and so on.

The members of Group 13 elements are:

- **Boron**
- **Aluminium**
- **Gallium**
- **Indium**
- **Thallium**

The general electronic configuration for the group 13 elements is ns^2 np^1.

- Oxidation States
- Covalent Character
- Anomalous Behaviour of Boron
- Chemical Properties
- Physical Properties
- Compounds of Group 13 Elements

Oxidation States and Inert Pair Effect

The general oxidation state exhibited by the group 13 elements in the group are +3, and +1. As we go down the group of Boron family, the tendency to form +1 ion increases. This is due to inert pair effect.

To elucidate, consider B^{3+} and B^{+}. It is shown experimentally that B^{3+} is more stable than B^{+}. Now consider, Tl^{3+} and Tl^{+}. It was seen that Tl^{+} is more stable than $Tl^{3+.}$

This can be explained using the inert pair effect. It is the non-participation of the s-orbital during chemical bonding due to the poor shielding of the intervening electrons.

Simply put, for elements like Indium and Thallium, d and f orbitals are filled with electrons. Since the shielding ability of d and f orbitals are very poor, the nuclear charge that seeps through attracts the s orbital closer to the nucleus. This makes the s orbital reluctant to bond, thereby only the p electrons are involved in bonding.

Covalent Character of Group 13 Elements

There are three reasons for the formation of covalent compounds by group 13 elements.

- Fajan’s rule may be applied. Smaller the cation more is the covalence.
- They have very high ionisation enthalpies (IE1+IE2+IE3) which makes the formation of ionic compounds hard.
- They have relatively higher electronegativities and hence the formation of compounds would not result in a higher electronegativity difference.

Reason Behind the Anomalous Behaviour of Boron

Boron behaves differently from the rest of the elements present in group 13 because of the following reasons.

- It has a very small size
- It has very high ionisation enthalpy
- It has high electronegativity owing to its small size
- The absence of d-orbital in the valence shell

Chemical Properties of Group 13 Elements

Reactivity of Group 13 towards Oxygen

All of the elements of group 13 react at high temperature forming trioxides, M_2O_3.

$4M_{(s)} + O_{2\,(g)} \rightarrow 2M_2O_{3(s)}$

Tl besides forming Tl_2O_3 also forms Tl_2O.

The reactivity of group 13 elements towards oxygen increases down the group.

Boron is unreactive towards oxygen in its crystalline form. Finely divided amorphous boron reacts with oxygen on heating to form B_2O_3.

Thermodynamically, Aluminium should react with air, but it is stable. This is because Al_2O_3 forms as a protective layer on the surface of the metal, thereby making it inert.

Reactivity of Group 13 towards Acids and Alkalis

Boron does not react with non-oxidising acids like HCl, but at higher temperatures, it reacts with strong oxidizing acids like a mixture of hot concentrated H2SO4 and HNO3 to give boric acid.

$B_{(s)} + 3HNO_{3\,(aq)} \rightarrow H_3BO_{3\,(aq)} + 3NO_{2\,(g)}$

Boron resists the action of alkalis (NaOH and KOH) up to 773 K, above which they form borates.

$2B_{(s)} + 6KOH_{(s)} \rightarrow 2K_3BO_{3(s)} + 3H_{2(g)}$

All the other elements of group 13 react both with non-oxidising and oxidising acids liberating hydrogen gas.

Note: The action of concentrated HNO3 renders Aluminium and Gallium passive by forming a protective layer of oxide.

Aluminium and Gallium can also react with alkalis liberating hydrogen gas.

$2Al_{(s)} + 2NaOH_{(aq)} + 6H_2O_{(l)} \rightarrow 2Na[Al(OH)_4]_{(aq)} + H_{2\,(g)}$

Reactivity of Group 13 towards Halogens

They react with halogens at high temperatures to form trihalides MX_3.

$2M_{(s)} + 3X_{2\,(g)} \rightarrow 2MX_3$ (where X=F,Cl,Br,I)

Tl however, only forms TlF_3 and $TlCl_3$.

Note: Tl also forms mono-halides.

Reactivity of Group 13 towards Water and Metals

Reactivity towards Water :

Boron does not react with water or steam, however, at very high temperatures it reacts with steam.

$2B + 3H_2O \rightarrow B_2O_3 + 3H_2$

If the oxide layer is absent, Aluminium decomposes cold water to yield hydrogen gas. Gallium and Indium do not react with water unless oxygen gas is present. Thallium forms **TlOH** in moist air.

$4Tl + 2H_2O + O_2 \rightarrow 4TlOH$

Reactivity towards Metals:

Only boron combines with metals to form borides. The rest of the elements of group 13 are reluctant to combine with metals. This portrays the non-metallic character of Boron.

$3Mg + 2B \rightarrow Mg_3B_2$

Complex Forming Tendency

Group 13 elements have more tendency to form complexes than s-block elements due to their smaller size and more polarising power.

Boron can form many complexes like $[BF_4]^-$. It has an sp^3 hybridized orbitals and tetrahedral geometry. Other elements also form complex compounds like $Li[AlH_4]$, $[GaCl_6]^{3-}$.

Physical Properties of Group 13 Elements

Atomic and Ionic Radii

The atomic radii of group 13 elements are lesser than their corresponding group 2 elements. This is because the effective nuclear charge increases which make the size of the atom smaller.

The atomic and ionic radii down the group increases due to the addition of a new shell. There is a deviation, however, on moving from Aluminium (143 pm) to Gallium (135 pm). This arises due to the poor shielding of the intervening d-orbitals in Gallium, making the size smaller than Aluminium.

Boron<Aluminium> Gallium < Indium< Thallium

Ionization Energy

Down the group, the values of Ionization Enthalpy do not decrease smoothly. From Boron to Aluminium, the Ionization Enthalpy increase as expected. But from Aluminium to Gallium, the Ionization Enthalpy increase slightly. The first Ionization Enthalpy of Thallium is greater than Aluminium.

Reason: This trend is observed due to the poor shielding of d and f orbitals. Gallium is smaller than Aluminium due to poor d shielding, therefore, IE1 of Aluminium< IE1 of Gallium. Similarly, Thallium has intervening f orbitals which are very poor at shielding, thereby increasing the IE1 of Thallium.

Element	**IE1 (KJmol^{-1})**
B	801
Al	577
Gallium	579
In	558
Tl	589

Electronegativity

The electronegativity first decreases from B to Al, then it increases slightly from Aluminium to Tl. This can be attributed to the poor shielding of the intervening d and f orbitals.

Electropositivity

The trend expected should be the exact opposite of electronegativity. The metallic character first increases from B to Al, then it decreases slightly from Aluminium to Tl.

This is due to the fact that the group 13 has a very high Ionization Enthalpy. Also, larger the size of the ion, lesser is its Ionization Enthalpy. Therefore Aluminium is the most metallic. This can further be explained using the standard reduction potentials.

Element	B	Al	Ga	In	Tl
$M^{3+}_{(aq)}/M_{(s)}$	-0.87	-1.66	-0.56	-0.34	+1.26

This shows that Aluminium is the most metallic and that Tl^{3+} isn't that stable, as the potential is positive, making Gibb's free energy positive. ($\Delta G = -nFE$)

Density

The elements of group 13 have higher densities than group 2 elements. This is because they have smaller sizes, and hence small volumes. The density increases from B to Tl.

Acid-Base Characteristics

The acidic character of oxides of group 13 elements decreases down the group and the basic character increases.

Note: Both Al and Gallium are amphoteric in nature.

H_3BO_3 is a monobasic acid in water. This is because water acts as a Lewis base and H_3BO_3 acts as a Lewis acid. This results in the release of a proton,

$B(OH)_3 + H_2O \leftrightarrow [B(OH)_4]^- + H^+$

Compounds of Group 13 Elements

Oxides

All the elements of group 13 form sesquioxides (sesqui means one and a half). The formula of the oxide formed is $MO_{3/2}$ or M_2O_3.

B_2O_3 is formed by heating amorphous boron in air,

$4B + 3O_2 \rightarrow 2B_2O_3$

Boron suboxide $(BO)_2$ is formed by heating B_2O_3 with boron at 1050°C.

$B + B_2O_3 \rightarrow (BO)_2$

The oxides of the other elements can be prepared by the thermal decomposition of their nitrates or their hydroxides.

$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$

Halides

Boron forms trihalides with Fluorine, Chlorine, and Iodine. All of the trihalides formed are planar molecules and sp^2 hybridized.

Since all the elements of group 13 possess only 6 electrons in their valance shell, they act as Lewis acids.

The order of the Lewis acid character exhibited by the trihalides is,

$BBr_3 > BCl_3 > BF_3$

Reason: This is not in accordance with the normal trend observed, surely, we can claim that BF_3 to be the most acidic as F is the most electronegative.

The reason for the above trend is back bonding, specifically, pπ-pπ back bonding. The lone pair on F is given to the empty p-orbital of B making it less electropositive, and thereby, reducing the acidic character.

The overlap of B and F is maximum as their sizes are compatible. Boron cannot form effective back bonding with Cl or Br as they are bigger than B. The halides of Al, Gallium, In and Tl are largely covalent.

Borates

Borates are compounds of group 13 containing discrete $[BO_3]^{3-}$ units. Each unit is sp^2 hybridized. They are classified according to the way the individual units are linked.

- **Orthoborates:** They contain discrete BO_3^{3-} units. For example, $Mg_3(BO_3)_2$.
- **Pyroborates:** Two units of BO_3^{3-} are linked via a common oxygen atom. The formula is $B_2O_5^{4-}$. For example, $Mg_2B_2O_5$.
- **Metaborates:** They have a structure where each unit shares two oxygen atoms. Therefore they are either in the form of chains or cyclic. The general formula is $(BO_2)_n^{n-}$.
- **Sheet borate:** The two-dimensional network of borates where all the three oxygen atoms are shared.

Boron Hydrides

The binary compounds formed by boron and hydrogen are called boranes. The simplest borane known is B_2H_6. They are classified into three major types,

- Closo-boranes (B_nH_{2n+2})
- Nido-boranes (B_nH_{2n+4})
- Arachno-boranes (B_nH_{2n+6})

Diborane (B_2H_6)

It can be prepared by reacting BCl3 with hydrogen gas over a Cu-Al catalyst at 450°C.

2BCl3 + 6H2 → B2H6 + 6HCl

Diborane on heating alone or in the presence of hydrogen, higher boranes are obtained.

Structure of Diborane

The total number of valence electrons present in diborane = 3 × 2 + 1 × 6 = 12 electrons.

The number of valence electrons in ethane (C_2H_6) = 4 × 2 + 1 × 6 = 14 electrons.

Therefore, we can see that diborane is electron deficient and hence should be unstable.

From the data obtained from electron diffraction studies, we were able to elucidate the structure of diborane.

It has two types of hydrogen atoms, terminal and bridged. The four terminal B-H bonds have the same bond length, and they are normal covalent bonds.

The two bridged hydrogen atoms, however, the H-B-H bond are much longer than the terminal B-H bond. The H-B-H bond is unusual as the two bridges involve only one electron from each hydrogen atom giving a total of four electrons. That is, each H-B-H bond has two electrons delocalized over three centres, giving rise to a three-centred two-electron bond.

Borazine

Boron-Nitrogen species that carry only one substituent on each atom, and exist as trimers are called Borazine ($B_3N_3H_6$).

It is prepared by heating diborane and ammonia in 1:2 molar ratio at -120°C, which gives ionic species which on heating gives borazine.

$B_2H_6 + 2NH_3 \rightarrow [H_2B(NH_3)_2]^+[BH_4]^- \rightarrow B_3N_3H_6 + 6H_2$

Similarities of Borazine with Benzene

1. Borazine is isoelectric with benzene. i.e. the total number of electrons in benzene = 6 × 6 + 1 × 6 = 42 electrons and the total number of electrons in borazine = 3 × 5 + 3 × 7 + 6 × 1 = 42 electrons.
2. Borazine is isosteric with benzene. That is, the total number of atoms are same.
3. Borazine possesses a cyclic structure of alternating boron and nitrogen atoms.
4. Both the N and B are sp^2 hybridized.

Properties of Borazine

1. It readily undergoes addition reaction. This is because the B-N bond is polar unlike the covalent C-C bond, and hence addition reactions happen easily.

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