

p-Block Elements
 a way that the double bond no longer involved protons, rather it involved two such a 'three centre bonds'.

***sp*³-Hybridization And Structure Of B₂H₆:**

It is supposed that boron atoms undergo *sp*³ hybridisation. Each boron then utilizes *sp*³ such orbitals containing one electron each for bonding with terminal hydrogens. There are now two *sp*³ hybrid orbitals and one electron left with each boron atom. Also there are two *1s* orbitals containing one electron each belonging to two hydrogen atoms not yet bonded. Thus, in all, there are six atomic orbitals and four electrons available which can form two three centre bonds known as the hydrogen bridges between the boron atoms as shown in Fig. (6.3)

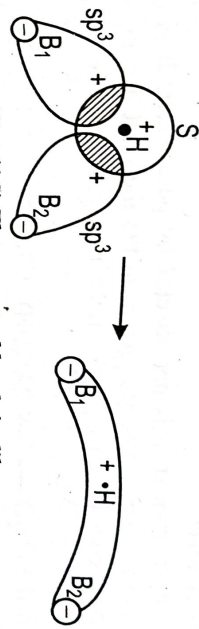


Fig. (6.3) Three-centred bonds in diborane.

The molecule of diborane contains two such bonds. Due to repulsion between the two hydrogen nuclei, the delocalised orbitals or bridges are bent away from each other in the middle (∠H-B-H = 120°). This is why the hydrogen bridge orbitals is shifted upwards in the middle. The other bridge orbital will be shifted downwards. This is the reason that these three atom orbitals are frequently referred to as **banana bonds**. The molecule in a more simple form may be represented as in Fig. (6.4).

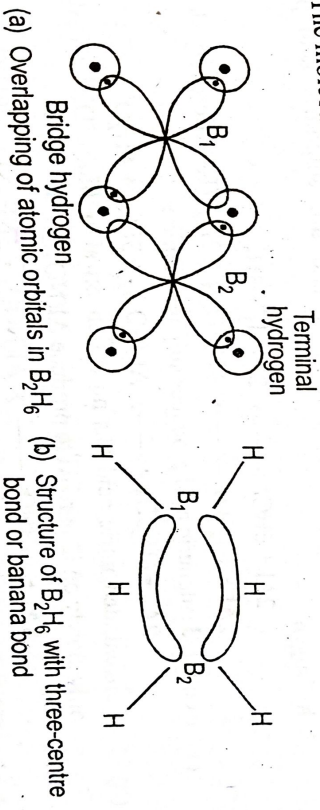


Fig. (6.4) Representation of structure of diborane.

6.5 Aluminium:

Occurrence Of Aluminium:

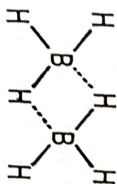
Aluminium does not occur free in nature. It is a constituent (2%) of clay, slate and many types of silicate rocks. It forms 7.28% of the earth crust. It occurs: as oxides, fluorides, silicates and sulphates. Its metallurgy is discussed in the chapter of industries.

6.5.1 Physical Properties Of Aluminium:

- (i) It is a light metal (density 2.7 g cm⁻³).
- (ii) Aluminium shows a bluish white lustre (∠) which is destroyed on long exposure to air due to the formation of a layer of oxide on it.

(i) Normal Hydrogen Bond Concept:

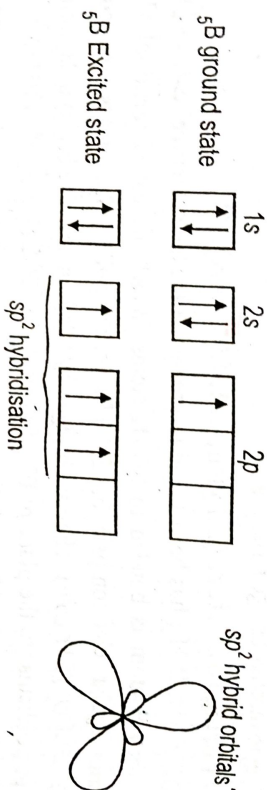
This concept was proposed by Buraway that the bridge between the boron atoms involves normal hydrogen bonds as shown below:



However, this concept is not acceptable due to a very small difference in the electronegativity values of B (1.00) and H (2.1) atoms.

(ii) Protonated Double Bond Concept:

R. S. Pitzer (1945) suggested the concept of a double bond between the two boron atoms. Each boron atom undergoes sp^2 hybridization as follows:



Now, we are bond to think that one of the sp^2 hybrid orbitals of each boron atom overlaps to form one B-B σ bond. There is one unhybridized empty p orbital associated with each boron atom which lies in a plane perpendicular to the sp^2 hybrid orbitals. Sideways overlapping of these p orbitals gives a π bond between the two boron atoms. Hence there is a π bond between the two boron atoms. The two, so called different hydrogen atoms, provide electrons to this π bond. They are, consequently, converted into protons which lie in the electron charge cloud of the π bond. In this way, the four hydrogen atoms will be coplanar with the two boron atoms, while the other two will lie above and below this plane.

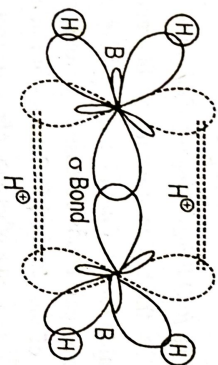


Fig. (6.2) Structure of diborane.

This structure is consistent with the results of infrared and electron diffraction studies and also explains hindered rotation around B-B axis.

Draw Back Of This Structure:

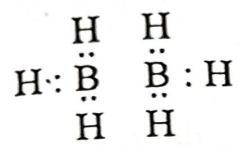
This structure envisages ($U^{\text{H}}C^{\text{H}}J^{\text{H}}$) acidic properties which are, however, not given by the compound.

(iii) Three-centre Bond Concept:

This concept, was proposed by Longuet-Higgins and Professor William N. Lipscomb. It is a sort of molecular orbital concept. These people modified Pitzer's concept in

Structure Of Diborane (B_2H_6): (Electron Deficient Molecule)

6.4.1 This is an electron deficient compound. Its structure presents an interesting case since there are not enough valence electrons to form the expected number of covalent bonds. Boron atom has three electrons in the outermost orbit in the excited state. Therefore, it can link itself with three hydrogen atoms. Each of the boron atoms in diborane can link itself to three hydrogen atoms, there are no electrons left to form a bond between the two boron atoms.



This is a sort of anomaly. Various structures for diborane have been proposed. But we are going to discuss bridge structure.

Hydrogen Bridge Structure (Ethylene-type Structure):

Diborane, B_2H_6 , has been found to possess a bridge structure (پل نما ساخت). In this structure each B atom is bonded to two H atoms. Which are called **terminal H atoms**. They form regular electron-pair bonds. The resulting BH_2 fragments are **co-planar** (دونوں BH_2 یونٹس ایک پلین میں ہوتے ہیں). They are bridged by two H atoms. The bridging H atoms are in a plane perpendicular to the plane of BH_2 fragments (پل پر موجود H ایٹمز کا پلین باقی مائیگیول کے عموداً ہے). One H-atom lies above and other H-atom below the plane to the rest of the molecule. It prevents rotation between the two boron atoms (دونوں B ایٹمز کی باہمی روٹیشن ممکن نہیں ہے). The various bond distances and angles are shown in Fig. (6.1).

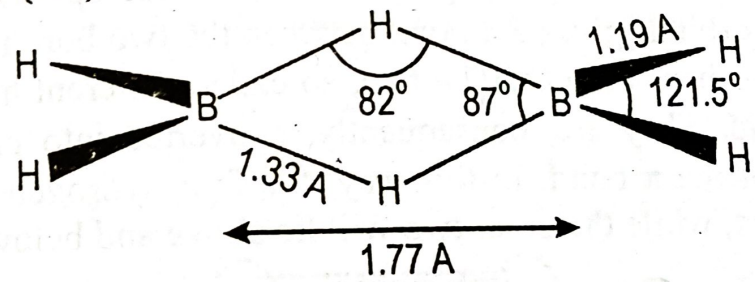


Fig. (6.1) Bridge structure of diborane.

When we keep in view the bridge structure of diborane. It has 8 bonds. Actually there are 12 electrons available for bonding (3 per B and 1 per H), hence, all the bonds in the molecule cannot be electron-pair bonds because they would required 16 electrons for the structure of Fig. (6.1) Four of the terminal H-B bonds are normal single bonds. This gets support as evidenced (گواہی دینا) by bond angles and infrared stretching frequencies. The other two hydrogen atoms and four electrons are in a different environment.

The bond lengths between boron and hydrogen at the bridges is 133 pm while that of terminal positions is 119 pm. The terminal B-H distances are the same as the bond lengths measured in non-electron deficient compounds. It means that the electron deficiency is associated with the bridge groups.

Theories Of Bridging H-atoms:

A number of bonding theories have been proposed to account for the nature of the bridge in...

250 **Properties Of Diborane (B₂H₆):**

- (i) **Combustion:**
It burns in air or oxygen producing large amount of heat.

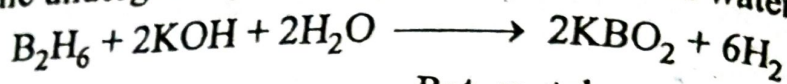


For this reason, it is used as a fuel in internal combustion engines. $\Delta H = -201.7 \text{ kJ mol}^{-1}$

(- طور پر استعمال کیا جاتا ہے۔)

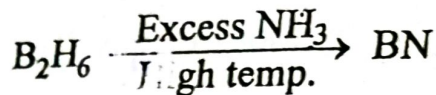
- (ii) **Action Of Alkalies:**

Diborane undergoes hydrolysis in the presence of water or alkalies.

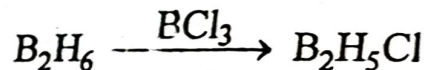
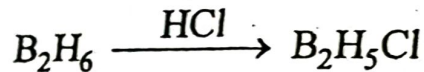


Pot. metaborate

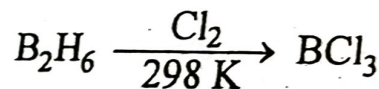
- (iii) With excess NH₃, it gives BN, boron nitride.



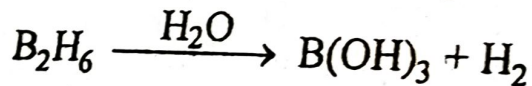
- (iv) One of H can be replaced by Cl atom.



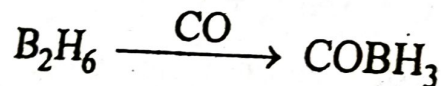
- (v) BCl₃ can be obtained by treatment with Cl₂ at 25°C.



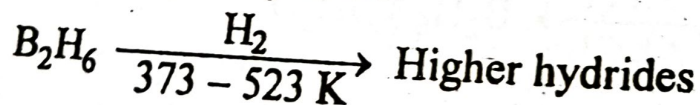
- (vi) Hydrolysis with H₂O gives H₃BO₃. (Boric acid)



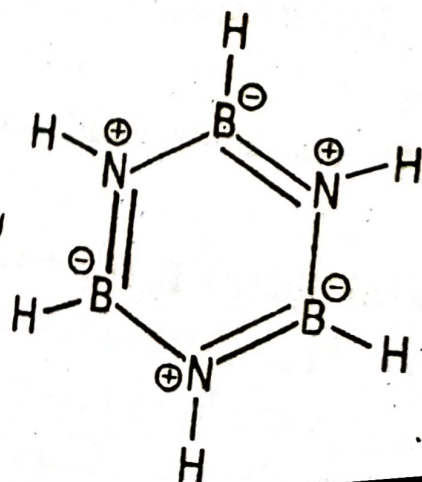
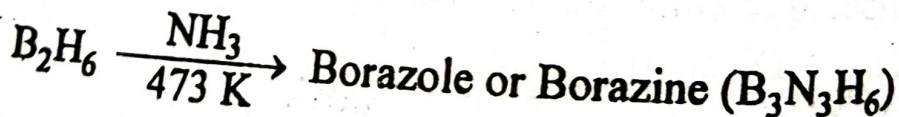
- (vii) With CO, we get COBH₃.



- (viii) Preparation of higher hydrides.



- (ix) With NH₃ it gives borazole.



اس کی ساخت بنزین کی طرح ہے۔

Inorganic benzene/Borazole بھی کہتے ہیں۔

(viii) For the preparation of metaborates like NaBO_2 , $\text{Ba}(\text{BO}_2)_2$, $\text{Cu}(\text{BO}_2)_2$, $\text{Co}(\text{BO}_2)_2$ etc.

Hydrides Of Boron, (Boranes) Electron Deficient Molecules

Hydrides of boron are electron deficient molecules like AlCl_3 etc.

Preparation:

Some common methods of preparation of hydride are given as under.

By Pyrolysis Of Diborane:

Normally diborane required for the purpose is made by treating sodium borohydride, with concentrated H_2SO_4 .



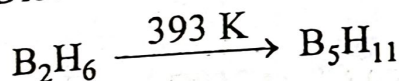
Sodium borohydride

Diborane

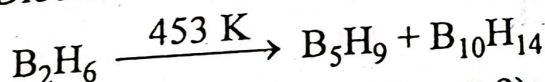
Diborane is a source for obtaining the higher hydrides mainly B_4H_{10} , B_5H_{11} , B_5H_9



Diborane Tetraborane



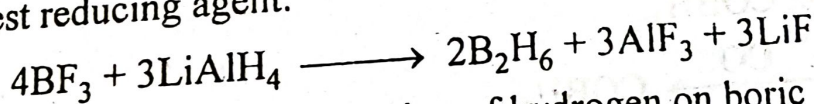
Diborane (Pentaborane-11)



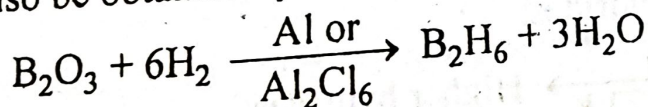
(Pentaborane-9)

By Reduction Of Boron Halide:

LiAlH_4 is best reducing agent.

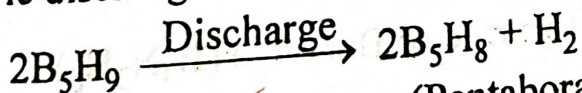


Diborane can also be obtained by action of hydrogen on boric oxide.



Boron oxide

By passing electric discharge either on lower boranes.

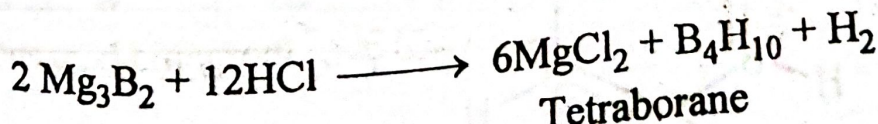


(Pentaborane-9)

(Pentaborane-8)

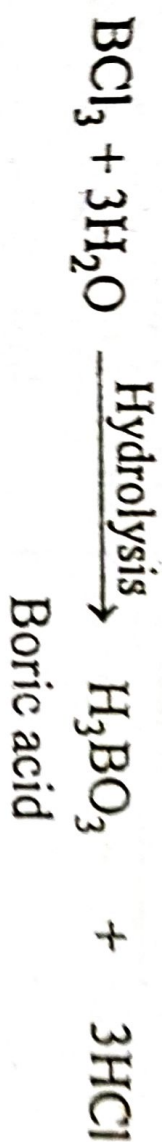
By Hydrolysis Of Magnesium Boride:

Magnesium boride on dissolving in aqueous acids yields mainly B_4H_{10} , B_5H_9 and

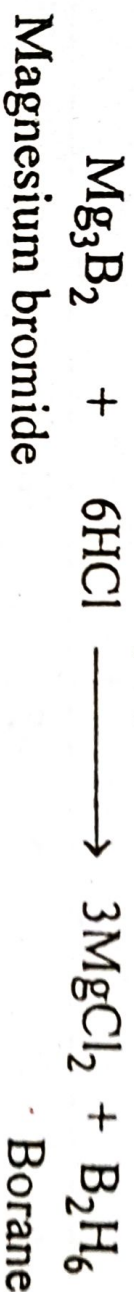


Tetraborane

Magnesium boride

**(v) Nature Of Hydrides:**

Hydrides of boron and silicon known as boranes and silanes, respectively are covalent in nature and have similar methods of preparation.

**(vi) Reaction Of Nitrides With Water:**

The nitrides of both boron and silicon decompose steam and liberate ammonia.



Boron nitride
Steam



Silicon nitride
Steam

p-Block Elements Group III-A [13] Boron And Aluminium Family

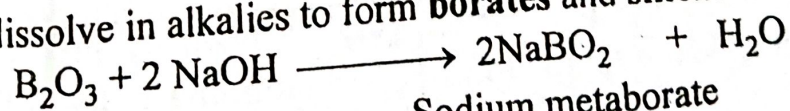
(vii) Boron does not decompose water or steam.	(vii) Al decomposes steam to form hydrogen. $2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2$
(viii) Boron forms covalent compounds only.	(viii) Al forms both covalent and electrovalent compounds.
(ix) Boron reacts with hydrogen to form a number of hydrides like B_2H_6 , B_5H_9 etc.	(ix) Al does not form any stable hydride.
(x) $B(OH)_3$, i.e., H_3BO_3 is weakly acidic.	(x) $Al(OH)_3$ is amphoteric.
(xi) BCl_3 is a fuming liquid.	(xi) $AlCl_3$ is amphoteric.
(xii) Boron combines with metals to form borides. $3Mg + 2B \rightarrow Mg_3B_2$	(xii) Al combines with metals to form alloys.
(xiii) Boron has maximum covalency as four.	(xiii) Al has maximum covalency as six.
(xiv) Boron is oxidised by conc. HNO_3 to form boric acid. $B + 3HNO_3 \rightarrow H_3BO_3 + 2NO_2$	(xiv) Al becomes passive with conc. HNO_3 .
(xv) Boron dissolves in fused alkalis to form hydrogen. $2B + 6NaOH \rightarrow 2Na_3BO_3 + 3H_2$	(xv) Al dissolves in hot alkalis to form hydrogen. $2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$
(xvi) Borates are very stable.	(xvi) Aluminates are less stable.

6.2.1 Diagonal Relationship (قطری تعلق) Between Boron ($_5B$) And Silicon ($_{14}Si$):
Boron, the first member of group III-A (13), differs from other members in certain respects and resembles silicon, the second member of group IV A (14), to which it is diagonally related.

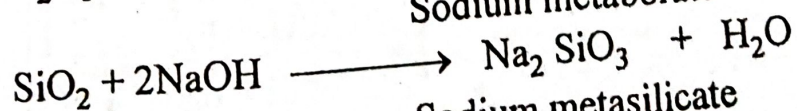
Similarities In Boron (B) And Silicon (Si)

(i) **Conductivity:**
Both boron and silicon are **semiconductors** in their crystalline form and possess high melting points.

(ii) **Nature Of Oxides:**
Both boron and silicon form oxides such as B_2O_3 and SiO_2 respectively which are acidic in nature. They dissolve in alkalis to form **borates** and **silicates**.



Sodium metaborate



Sodium metasilicate

(iii) **Nature Of Hydroxide:**
Boron and silicon form hydroxides which are **weak acids** with no basic properties.

(iv) **Hydrolysis Of Halides:**
Boron and silicon halides (except BF_3) readily hydrolyse to give their corresponding acids.

Tl are ionic. However, the other halide of these elements are covalent when anhydrous. For example, anhydrous AlCl_3 is covalent but in water it get hydrolyzed to give $\text{Al}^{3+}(\text{aq})$ ions. This change is mainly due to high hydration energy of Al^{3+} ions. Some members of the group also form complex halides e.g., $[\text{AlF}_6]^{3-}$ $[\text{GaCl}_6]^{3-}$ etc.

(xiii) Formation Of Oxides And Hydroxides:

All the elements of this group form oxides and hydroxides. As we move from boron to thallium, the oxides and hydroxides of these elements change from acidic through amphoteric to basic. Thus oxides and hydroxides of boron are acidic, those of Al and Ga are amphoteric while those of In and Tl are basic.

(xiv) Flame Test:

Boron gives a green-edged flame. Aluminium does not give any colour. Gallium gives violet (بنفشى) colour, indium a dark blue (گہرا نیلا), and thallium a green coloured flame on heating.

Anomalous (خلاف معمول) Properties Of Boron In Group III-A:

Boron differs in many properties from the other elements of its own subgroup. The main points of difference are.

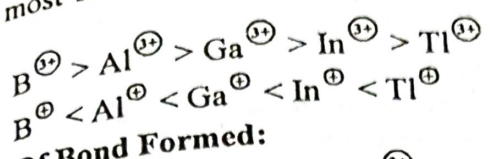
- (i) B has a very small atomic radius.
- (ii) The hypothetical (تھائی) B^{3+} ion has very small size, high charge and hence high charge density. This value is so high that B^{3+} ion does not-exist.
- (iii) All the compounds of boron are covalent.
- (iv) Boron has less than four valence-electrons and this gives it a great electron accepting power. Its compounds behave as strong Lewis acids and hence forms a large number of complex compounds.
- (v) Boron shows a maximum covalency of four and does not exhibit inert pair effect.

2 Comparison Of Boron And Silicon

Points Of Dissimilarity Between Boron (B) And Aluminium (Al)

Boron (${}_5\text{B}$)	Aluminium (${}_{13}\text{Al}$)
Boron is a non-metal and is a bad conductor of heat and electricity.	(i) Aluminium is a metal and is a good conductor of heat and electricity.
It has high melting point (2300°C).	(ii) It has low melting point (660°C).
There are two electrons in the penultimate shell (2, 3).	(iii) There are eight electrons in the penultimate shell (2, 8, 3).
Its crystalline form is very hard.	(iv) It is sufficiently soft.
Boron shows allotropy and is found in two forms viz. crystalline and amorphous.	(v) It does not show allotropy.
Boron does not react with dil. acids.	(vi) Al reacts with dil. acids to form hydrogen. $2\text{Al} + 3\text{H}_2\text{SO}_4 \rightarrow \text{Al}_2(\text{SO}_4)_3 + 3\text{H}_2 \uparrow$

do not form M^{\oplus} cations. Since the inert pair effect increases from Ga to Tl, the stability of +3 oxidation state decreases while that of +1 state increases down the group. Thus (+1) compounds are unstable, In(+1) compounds are moderately stable whereas those of (+1) are the most stable. The relative stability order of $M^{3\oplus}$ and M^{\oplus} cations is shown below.



Nature Of Bond Formed:

(vii) The nature of the compounds of $M^{3\oplus}$ ions is decided by Fajan's rule. It states that the smaller the cation, the greater is its tendency to form covalent compounds. Thus with the increase of the size of $M^{3\oplus}$ ions from $B^{3\oplus}$ to $Tl^{3\oplus}$, their tendency to form covalent compounds decreases.

Ionization Energies:

(viii) First ionization energies of these elements correspond to the removal of np^1 electron from ns^2p^1 configuration. The second and third ionization energies correspond to the removal of ns^2 electrons in succession. Because of the increase in size of Al, the ionization energy decreases from B to Al.

But in going from Al to Ga the value of ionization energy increases. The increase in the case of gallium is due to the fact that the intervening d-electrons in Ga are not able to shield the nuclear charge effectively and hence the valence electrons in Ga are more firmly held to the nucleus and its ionization energy increases.

Electropositive Or Metallic Character:

(ix) Electropositive character of the elements increases as we move from B to Tl. Thus B is a semi-metal i.e., it is closer to non-metals than to metals in its properties, while other members are metallic in nature. Al, Ga, In and Tl have almost equal electropositive character as is evident from their almost equal ionization energy values.

Reactivity Of Elements:

(x) Pure boron is almost unreactive at ordinary temperature. It reacts with air only when heated. Boron does not react with water. It is attacked only by hot concentrated acids and alkalis.

Aluminium decomposes water and reacts readily in air at ordinary temperature to form a protective layer (ایسی تہہ جو حفاظت کرے) of its oxide. This layer protects it from further action. Gallium and indium are not affected by air even when heated. However, thallium is a little more reactive and forms an oxide on its surface.

Formation Of Hydrides:

(xi) Boron forms a large number of polymeric hydrides which are called boranes, e.g., B_2H_6 , B_4H_{10} , B_5H_9 , B_5H_{11} etc. These hydrides are covalent in nature. Aluminium forms only one high molecular weight polymeric hydride, $(AlH_3)_x$. Gallium gives GaH_4 which is called gallane. It is an unstable and volatile liquid. Indium gives polymerised solid hydride, $(InH_3)_x$. The hydrides given by Tl are extremely unstable. The element of this group also form the complex anionic hydrides like $Li^{\oplus} [BH_4]^{\ominus}$, $Li^{\oplus} [AlH_4]^{\ominus}$ etc.

Formation Of Trihalides:

(xii) The elements of this group react with halogens to form trihalides (MX_3). The trihalides of boron (BX_3) are covalent and act as Lewis acids. The fluorides of Al, Ga, In and

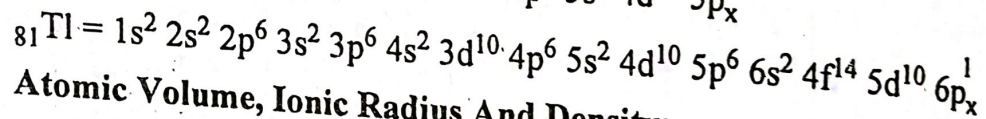
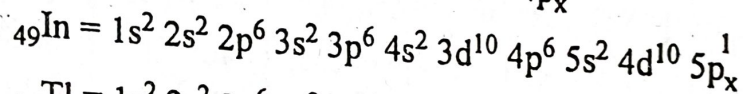
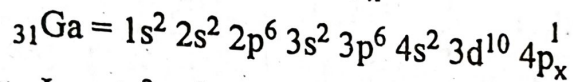
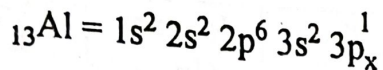
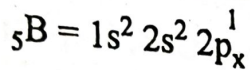
13	Electronegativity	2.0	1.5	1.6	1.7	1.8
14	Electron affinity (kJ mol ⁻¹)	26.8	42.6	29.0	29.0	29.0
15	Standard reduction potential for $M^{3+}(aq) + 3e^{-} \rightleftharpoons M(s)$ reaction (volts)	-0.87	-1.68	-0.52	-0.34	+0.72
16	Metallic character	Metalloid	← Almost same metallic character →			

6.1.1 Gradation Of The Characteristic Properties Of Group IIIA (B)

Elements:

The gradation (کسی سلسلہ کا مرتبہ) in the physical and chemical properties of the elements with the rise of atomic number is as follows:

(i) Electronic Configuration:



(ii) Atomic Volume, Ionic Radius And Density:

Atomic volume and ionic radius of M^{3+} ions go on increasing down the group. The reason is additional shells.

(iii) Density:

The values of densities in $g\ cm^{-3}$ go on increasing down the groups.

(iv) Melting Points And Boiling Points:

In the case of melting points, there is sudden fall down from aluminium to gallium followed by a gradual rise again to thallium. The melting point of boron is extremely high indicating strong bonding between individual atoms. The melting points of other elements especially gallium, indium and thallium, are significantly low indicating that the metallic lattices in them are much more readily ruptured (ٹوٹ جاتا). Boiling points show a continuous decrease with increasing atomic number.

(v) Heat Of Sublimation (عمل تسعید):

The successive (ایک کے بعد دوسرا) decrease in heat of sublimation indicates that the atoms of these elements are held less and less closely, as we move from boron (5) to thallium (81).

(vi) Oxidation States:

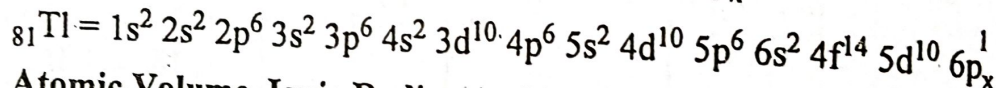
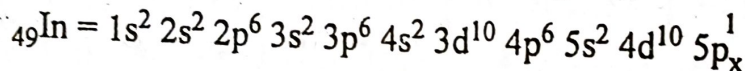
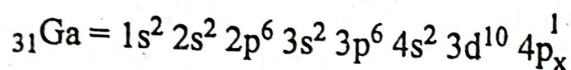
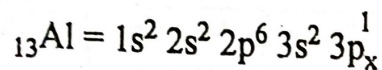
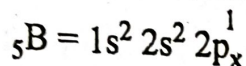
M^{3+} cations are obtained when all the three $ns^2 p^1$ electrons are lost, while M^{+} cations are formed when only one np^1 electron is lost. Boron and aluminium show an oxidation state of +3 while other members show both +1 and +3 oxidation states. In the formation of M^{+} cations the electron pair in ns orbital remains inert. This is called inert pair effect (ایسا اثر جو الیکٹران کے جوڑے کا نہ ٹوٹنے کا رجحان سے ہے). B and Al do not show inert pair effect and

13	Electronegativity	2.0	1.5	1.6	1.7	1.8
14	Electron affinity (kJ mol ⁻¹)	26.8	42.6	29.0	29.0	29.0
15	Standard reduction potential for $M^{3+}(aq) + 3e^{-} \rightleftharpoons M(s)$ reaction (volts)	-0.87	-1.68	-0.52	-0.34	+0.72
16	Metallic character	Metalloid	← Almost same metallic character →			

6.1.1 Gradation Of The Characteristic Properties Of Group IIIA (B) Elements:

The gradation (کسی سلسلہ کا مرتبہ) in the physical and chemical properties of the elements with the rise of atomic number is as follows:

(i) Electronic Configuration:



(ii) Atomic Volume, Ionic Radius And Density:

Atomic volume and ionic radius of M^{3+} ions go on increasing down the group. The reason is additional shells.

(iii) Density:

The values of densities in $g\ cm^{-3}$ go on increasing down the groups.

(iv) Melting Points And Boiling Points:

In the case of melting points, there is sudden fall down from aluminium to gallium followed by a gradual rise again to thallium. The melting point of boron is extremely high indicating strong bonding between individual atoms. The melting points of other elements especially gallium, indium and thallium, are significantly low indicating that the metallic lattices in them are much more readily ruptured (ٹوٹ جاتا). Boiling points show a continuous decrease with increasing atomic number.

(v) Heat Of Sublimation (عمل تسعید):

The successive (ایک کے بعد دوسرا) decrease in heat of sublimation indicates that the atoms of these elements are held less and less closely, as we move from boron (5) to thallium (81).

(vi) Oxidation States:

M^{3+} cations are obtained when all the three $ns^2 p^1$ electrons are lost, while M^{+} cations are formed when only one np^1 electron is lost. Boron and aluminium show an oxidation state of +3 while other members show both +1 and +3 oxidation states. In the formation of M^{3+} cations the electron pair in ns orbital remains inert. This is called inert pair effect (جوڑے کا نہ ٹوٹنے کا رجحان سے ہے).

Introduction

Group III-A (13) consists of five elements. ${}_5\text{B}$ (Boron), ${}_{13}\text{Al}$ (Aluminium), ${}_{31}\text{Ga}$ (Gallium), ${}_{49}\text{In}$ (Indium), ${}_{81}\text{Tl}$ (Thallium). B and Al are typical elements (مثالی نمائندگی کرنے والے عناصر) and we will concentrate on their discussion.

6.1 Physical Properties

Some important physical properties are given in the Table (6.1).

Table (6.1): Some Important Physical Properties Of The Elements Of Group IIIA (13)

S. No.	Property	Boron (B_5)	Aluminium (Al_{13})	Gallium (Ga_{31})	Indium (In_{49})	Thallium (Tl_{81})
1	Electronic configuration	$[\text{He}]_2 2s^2 2p^1$ or 2, 3	$[\text{Ne}]_{10} 3s^2 3p^1$ or 2, 8, 3	$[\text{Ar}]_{18} 4s^2 4p^1$ or 2, 8, 3	$[\text{Kr}]_{36} 5s^2 4d^{10} 5p^1$ or 2, 8, 18, 18, 3	$[\text{Xe}]_{54} 6s^2 4f^{14} 5d^{10} 6p^1$ or 2, 8, 18, 32, 18, 3
2	Atomic mass (amu)	10.81	26.98	69.72	114.82	204.37
3	Abundance in Earth's crust (ppm)	3	81,300	15	0.1	≈ 2
4	Single bond covalent radius (pm)	85	143	135	167	170
5	Radius of M^{3+} ion (pm)	20	50	62	81	95
6	Radius of M^+ ion (pm)	—	—	11.3	132	140
7	Density (g cm^{-3})	2.34	2.70	5.91	7.31	11.85
8	Stable oxidation states	+3	+3	+3, +1	+3, +1	+3, +1
9	Heat of sublimation (kJ/mol)	5.648	324.3	273.2	241.4	179.1
10	Melting point ($^{\circ}\text{C}$)	2030	659	28.8	156.4	303
11	Boiling point ($^{\circ}\text{C}$)	2550	2450	2237	2000	1457
12	1 st ionisation energy (kJ mol ⁻¹)	798	581	577	556	589