# Group 13 (IIIA) elements

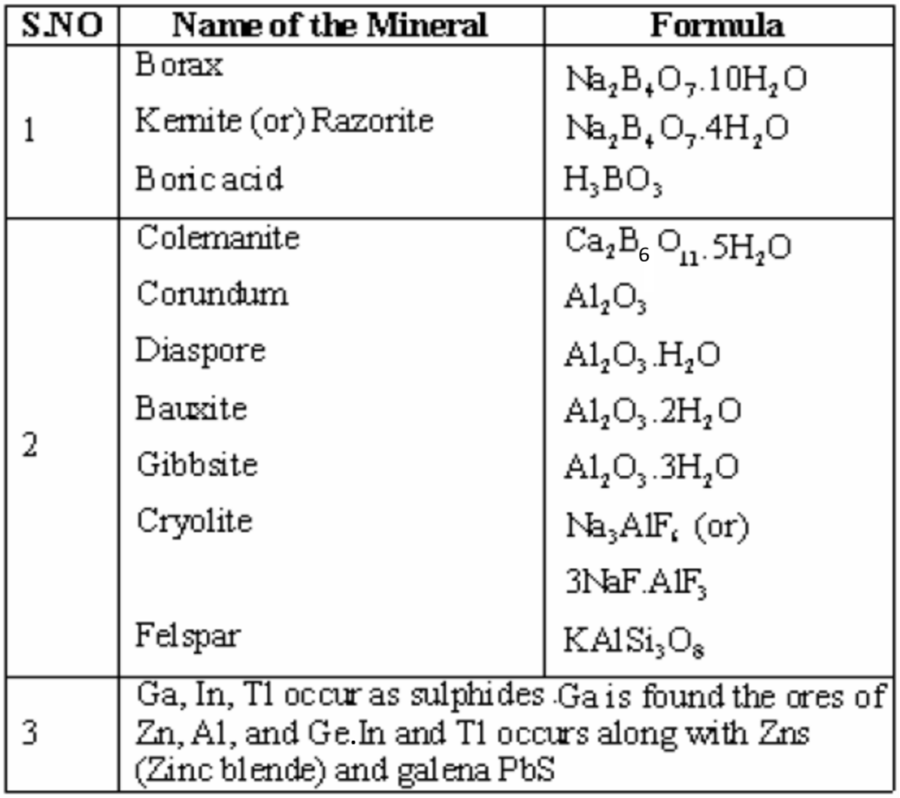
## Module 17.1: General introduction, Electronic configuration, Occurrence, Oxidation states of IIIA group

IIIA or 13th group consists of 5 elements namely Boron, Aluminium, Gallium, Indium and Thallium. This group elements show a wide variation in properties. Boron is a typical non - metal, Aluminium is a metal but shows many chemical similarities to boron. Gallium, Indium and Thallium are almost exclusively metallic in character. Boron differs in many respects from the physical and chemical characters of other elements of the group.

### Occurrence:

Boron is a fairly rare element, mainly occurs as ortho boric acid ($H_3BO_3$), borax ($Na_2B_4O_7.10H_2O$) and Kernite ($Na_2B_4O_7.4H_2O$). Boron occurs in two isotopic forms $^{10}B$ (19%) and $^{11}B$ (81%). The abundance of boron in the earth's crust is less than 0.0001% by mass. Aluminium is the most abundant metal and the third most abundant element in earth's crust (8.3% by mass) after oxygen (45.5%) and silicon (27.7%). Bauxite ($Al_2O_3.2H_2O$) and cryolite $Na_3AlF_6$ are the important minerals of aluminium. Gallium, Indium and Thalium are less abundant elements in nature. Gallium, Indium and Thallium occur in traces along with the sulphide ores of Zinc and lead.

### Minerals of 13th group:



| S.NO | Name of the Mineral | Formula |
|---|---|---|
| 1 | Borax | $Na_2B_4O_7.10H_2O$ |
| | Kemite (or) Razorite | $Na_2B_4O_7.4H_2O$ |
| | Boric acid | $H_3BO_3$ |
| 2 | Colemanite | $Ca_2B_6O_{11}.5H_2O$ |
| | Corundum | $Al_2O_3$ |
| | Diaspore | $Al_2O_3.H_2O$ |
| | Bauxite | $Al_2O_3.2H_2O$ |
| | Gibbsite | $Al_2O_3.3H_2O$ |
| | Cryolite | $Na_3AlF_6$ (or)<br>$3NaF.AlF_3$ |
| | Felspar | $KAlSi_3O_8$ |
| 3 | Ga, In, Tl occur as sulphides .Ga is found the ores of Zn, Al, and Ge.In and Tl occurs along with Zns (Zinc blende) and galena PbS | |

## Electronic configuration:

General electronic configuration of these elements is $ns^2np^1$ as these elements have 3 electrons in the outermost orbit. Because of similarity in electronic configuration of outermost shell they closely resemble in their physical and chemical properties. The penultimate shell of Boron has $s^2$ electrons, aluminium has $s^2p^6$ and other 3 elements have $s^2p^6d^{10}$ electrons. Thus Boron is expected to differ from aluminium and other elements of the group.

| Element | Atomic. No | Electronic configuration |
|---|---|---|
| Boron (B) | 5 | $1s^22s^22p^1$ |
| Aluminium ( Al) | 13 | $1s^22s^22p^63s^23p^1$ |
| Gallium (Ga) | 31 | $1s^22s^22p^63s^23p^63d^{10}4s^24p^1$ |
| Indium (In) | 49 | $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^1$ |

|  |  |  |
|---|---|---|
| Thallium (Tl) | 81 | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14}$<br>$5s^2 5p^6 5d^{10} 6s^2 6p^1$ |

An examination of electronic configuration suggests that while Boron and Aluminium have noble gas core, Gallium and Indium have noble gas plus 10 d-electrons and Thallium has noble gas plus 14 f-electrons plus 10 d-electrons cores.

## Oxidation states:

Due to small size of boron, the sum of its first three ionization enthalpies is very high. This prevents it from +3 ions and forces it to form only covalent compounds. But as we move from B to Al, the sum of the first three ionization enthalpies of Al considerably decreases and is therefore able to form $Al^{3+}$ ions. In fact Al is highly electropositive metal. However, down the group , due to poor shielding effect of intervening ***d*** and ***f*** orbitals, the increased effective nuclear charge holds ***ns*** electrons tightly (responsible for inert pair effect ) and thereby , restricting their participation in bonding. As a result of this only p-orbital electron may be involved in bonding. In fact in Ga , In and Tl , both +1 and +3 oxidation states are observed. The relative stability of +1 oxidation state progressively increases for heavier elements: **Al < Ga < In < Tl**. In thallium +1 oxidation state is predominant whereas the +3 oxidation state is highly oxidizing in character. Tl (+1) compounds are more stable than that of Tl (+3). This is due to the fact that the 2s electrons in the outer shell tend to remain paired and do not participate in compound formation (Inert pair effect). The compounds in +1 oxidation state, as expected from energy considerations, are more ionic than those in +3 oxidation state.

Ga, In and Tl show inert pair effect in their compounds.
In fact Tl (+1) salts resemble alkali metals because it has large size and low oxidation state.

## Assignment Questions:

1. What are the elements present in the group 13 of the periodic table. Write their names in the order.

2. Write the atomic numbers and the electronic configurations of all the elements in 13th group in the periodic table.
3. How do the elements of group 13 occur in nature? Write the minerals of B and Al.
4. Explain the oxidation states of group 13 elements. Discuss the stability of +3 oxidation state in the group.
5. Write a brief note on the oxidation states of boron family of elements.

**SAQs:**

1. The general electronic configuration of the 13th group elements is ______
   a. $ns^2 np^1$
   b. $ns^2 (n-1) d^9 np^2$
   c. $ns^2np^2$
   d. $ns^1 (n-1) d^{10} np^2$

**Solution:** a)

2. the chemical formula of borax is
   a. $Na_2B_4O_7.10H_2O$
   b. $Na_2B_4O_7$
   c. $Ca_2B_6O_{11}$
   d. $Na_2B_4O_7.4\ H_2O$

**Solution:** a)

3. The most abundant metal in the earth's crust is ______
   a. In
   b. Al
   c. Ga
   d. B

**Solution:** b)

4. The common oxidation state of Tl is ______
   a. + 3
   b. + 2
   c. + 1
   d. + 5

**Solution:** c)

**LAQs:**

1. Write a note on the electronic configuration of elements of 13th group.

**Solution:**

| **Element** | **Atomic. No** | **Electronic configuration** |
|---|---|---|
| Boron (B) | 5 | $1s^2 2s^2 2p^1$ |
| Aluminium ( Al) | 13 | $1s^2 2s^2 2p^6 3s^2 3p^1$ |
| Gallium (Ga) | 31 | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$ |
| Indium (In) | 49 | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^1$ |
| Thallium (Tl) | 81 | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^1$ |

2. Which of the Boron family elements is the most abundant? Mention the minerals of boron and aluminium.

**Solution:**

Aluminium is the most abundant metal. It is the 3rd most abundant element (1st is oxygen, 2nd is silicon) by weight

Boron is a fairly rare element, mainly occurs as ortho boric acid ($H_3BO_3$), borax ($Na_2B_4O_7.10H_2O$) and Kernite ($Na_2B_4O_7.4H_2O$). Bauxite ($Al_2O_3.2H_2O$) and cryolite $Na_3AlF_6$ are the important minerals of aluminium.

3. Discuss the 13th group elements with reference to their oxidation states.

**Solution:**

**Oxidation states:**

Due to small size of boron, the sum of its first three ionization enthalpies is very high. This prevents it from +3 ions and forces it to form only covalent compounds. But as we move from B to Al, the sum of the first three ionization enthalpies of Al considerably decreases and is therefore able to form $Al^{3+}$ ions. In fact Al is highly electropositive metal. However, down the group , due to poor shielding effect of intervening ***d*** and ***f*** orbitals, the increased effective nuclear charge holds ***ns*** electrons tightly (responsible for inert pair effect ) and thereby , restricting their participation in bonding. As a result of this only p-orbital electron may be involved in bonding. In fact in Ga , In and Tl , both +1 and +3 oxidation states are observed. The relative stability of +1 oxidation state progressively increases for heavier elements: **Al < Ga < In < Tl**. In thallium +1 oxidation state is predominant whereas the +3 oxidation state is highly oxidizing in character. Tl (+1) compounds are more stable than that of Tl (+3). This is due to the fact that the 2s electrons in the outer shell tend to remain paired and do not participate in compound formation (Inert pair effect). The compounds in +1 oxidation state, as expected from energy considerations, are more ionic than those in +3 oxidation state.

Ga, In and Tl show inert pair effect in their compounds.
In fact Tl (I) salts resemble alkali metals because it has large size and low oxidation state.

**Problem set:**

1. An element of 13th group with no d–electrons in it is _____
    a. Tl
    b. In
    c. Al
    d. Both a) and b)

**Solution:** c)

2. Cryolite is represented by
   a. $Na_2B_4O_7.10\ H_2O$
   b. $Na_3\ AlF_6$
   c. $3\ NaF.AlF_3$
   d. Both b) and c)

**Solution:** d)

3. Razorite has the same molecular formula as that of
   a. Borax
   b. Kernite
   c. Bauxite
   d. Cryolite

**Solution:** b) $Na_2B_4O_7.4\ H_2O$

4. Justify the inclusion of B, Al, Ga, In and Tl in the same group of the periodic table with reference to
   a. Electronic configurations
   b. Oxidation states.

**Solution:**

**a. Electronic configurations:**

| **Element** | **Atomic. No** | **Electronic configuration** |
|---|---|---|
| Boron (B) | 5 | $1s^22s^22p^1$ |
| Aluminium ( Al) | 13 | $1s^22s^22p^63s^23p^1$ |
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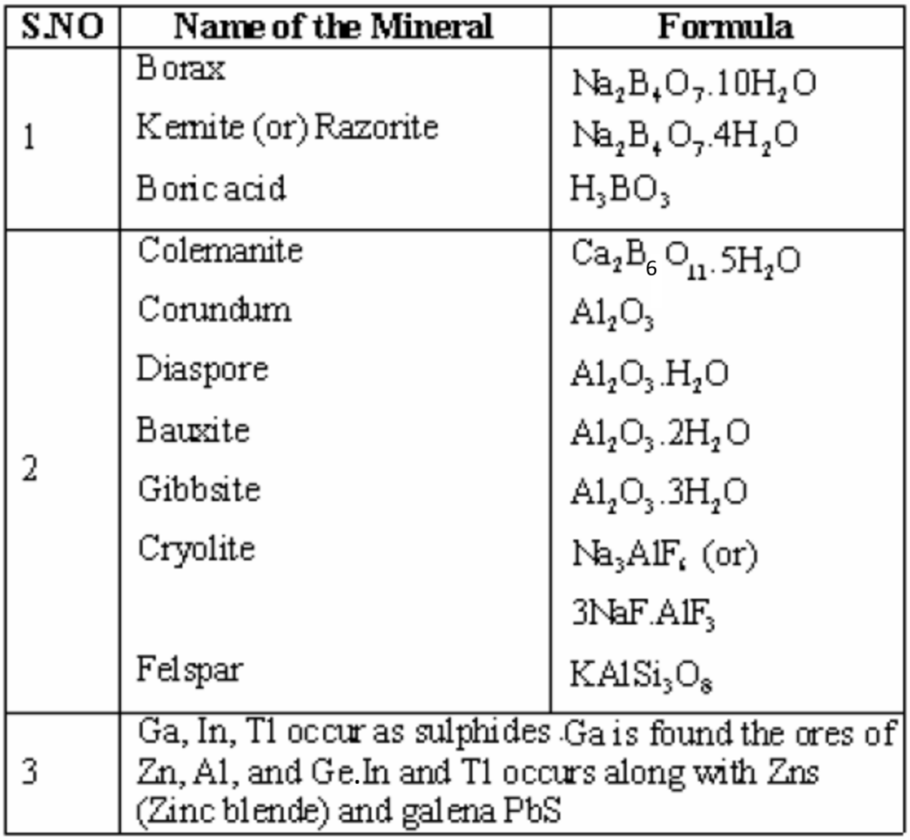
| Indium (In) | 49 | $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^1$ |
| Thallium (Tl) | 81 | $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4f^{14}$ $5s^25p^65d^{10}6s^26p^1$ |

**b. Oxidation states:**

These elements have +3 oxidation state due to the presence of 3 electrons in the valency shell, except Boron and Aluminium. These elements also show stable +1 oxidation state as one move down the group, due to inert pair effect. +1 oxidation state becomes more stable down the group thus Tl (+1) compounds are more stable than that of Tl (+3). This is due to the fact that the 2s electrons in the outer shell tend to remain paired and do not participate in compound formation (Inert pair effect). Ga, In, Tl can show inert pair effect in their compounds. In fact Tl (I) salts resemble alkali metals because it has large size and low oxidation state.

4. The elements of the Boron family occur in the combined state only. Give the names and the formulas of the minerals of boron family.

**Solution:**



| S.NO | Name of the Mineral | Formula |
|---|---|---|
| 1 | Borax<br>Kernite (or) Razorite<br>Boric acid | $Na_2B_4O_7.10H_2O$<br>$Na_2B_4O_7.4H_2O$<br>$H_3BO_3$ |
| 2 | Colemanite<br>Corundum<br>Diaspore<br>Bauxite<br>Gibbsite<br>Cryolite<br>Felspar | $Ca_2B_6O_{11}.5H_2O$<br>$Al_2O_3$<br>$Al_2O_3.H_2O$<br>$Al_2O_3.2H_2O$<br>$Al_2O_3.3H_2O$<br>$Na_3AlF_6$ (or) $3NaF.AlF_3$<br>$KAlSi_3O_8$ |
| 3 | Ga, In, Tl occur as sulphides .Ga is found the ores of Zn, Al, and Ge.In and Tl occurs along with Zns (Zinc blende) and galena PbS | |

## Exercise questions:

1. Why are the elements B, Al, Ga, In and Tl included in the same group of the periodic table? Justify their inclusion with reference to their hydrides, and oxides
2. How Boron does differ from other elements of the group? Discuss.

## Solutions:

# Group 13 (IIIA) elements

## Module 17.4: Boron hydrides

Boranes are the hydrides of boron. It is important to note that Boron does not form simple monomeric hydride i.e., $BH_3$ although boron hydrides are well known and quite stable compounds. Actually when $BH_3$ molecules come in contact with each other, they combine to form diborane, $B_2H_6$. Thus $BH_3$ can exist only as complex compounds like $BH_3Z$ with donors (Z) like CO, $(CH_3)_3N$, $PF_3$. The hydrides of boron can be compared with hydrocarbons. These are all electron deficient compounds.

Based on their molecular formula Boron hydrides are classified in to 2 types.

i. Those with general formula $B_nH_{n+4}$. These are quite stable and hence are more important. These are commonly known as boranes.

**Example:**

$B_2H_6$ (diborane)
$B_6H_{10}$ (hexaborane -10)
$B_{10}H_{14}$ (decaborane – 14)
$B_5H_9$ (pentaborane – 9)
$B_8H_{12}$ (octaborane – 12)

ii. Those with general formula $B_nH_{n+6}$

These are unstable and have low melting points. These are known as hydroboranes.

**Example:**

$B_4H_{10}$ (Tetraborane – 10), $B_5H_{11}$ (Pentaborane – 11), $B_6H_{12}$ (Hexaborane – 12)

The numbers suffixed with the names indicate the number of hydrogen atoms present in a molecule of the hydride. By this the confusion that might arise in the nomenclature of these compounds can be overcome.

For example $B_6H_{10}$ and $B_6H_{12}$ are both hexaboranes only. To differentiate them the number of hydrogen atoms in them is indicated.

Of the hydrides of boron, diborane is the most common are Diborane

## Preparation:

It is prepared by treating boron triflouride with $LiAlH_4$ in diethyl ether.

$$4BF_3 + 3LiAlH_4 \longrightarrow 2B_2H_6 + 3LiF + 3AlF_3$$

A convenient laboratory method for the preparation of diborane involves the oxidation of sodium borohydride with iodine

$$2NaBH_4 + I_2 \longrightarrow B_2H_6 + 2NaI + H_2$$

Diborane is produced on an industrial scale by the reaction of $BF_3$ with sodium hydride.

$$2BF_3 + 6NaH \xrightarrow{450K} B_2H_6 + 6NaF$$

A mixture of Boron Trichloride and hydrogen is subjected to silent electric discharge. Diborane is produced.

$$2BCl_3 + 6H_2 \xrightarrow[\text{Or cu – Al catalyst at } 450^0\text{C}]{\text{Electric discharge}} B_2H_6 + 6HCl$$

Diborane can also be prepared by the action of dilute $H_2SO_4$ on sodium-borohydride

$$2NaBH_4 + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2 + B_2H_6$$

## Physical properties:

Diborane is a colorless gas with a foul smell and is extremely toxic. Boiling point of Diborane is 180K. At low temperatures in the absence of moisture and grease, it is stable. At ordinary temperatures it undergoes dissolution and gives other hydrides of Boron

## Chemical properties:

Diborane catches fire spontaneously upon exposure to air. It burns in oxygen releasing an enormous amount of energy. Hence these are used as rocket fuels.

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$$

### Action of heat:

All boron hydrides decompose at red heat to boron and hydrogen

$$B_2H_6 \xrightarrow{>100^0C} 2B + 3H_2$$

### Hydrolysis:

Boranes are readily hydrolised by water to give boric acid. Therefore these are used as reducing agents.

$$B_2H_6(g) + 6H_2O(l) \longrightarrow 2B(OH)_3(aq) + 6H_2(g)$$

### Action of alkalies:

When treated with alkali, it forms hypoborates, metaborates

$$B_2H_6 + 2KOH + 2H_2O \longrightarrow 2KBO_2 + 6H_2$$

## Action with Ammonia:

Reaction of Ammonia with diborane gives initially $B_2H_6.2NH_3$ which is formulated as

$$[BH_2(NH_3)_2]^+[BH_4]^-$$

Further heating gives borazine (or) borazole $B_3N_3H_6$, known as inorganic benzene. In view of its ring structure with alternate BH and NH groups, that is similar to benzene it is known as inorganic benzene.

$$\begin{array}{l} 3B_2H_6 + 6NH_3 \longrightarrow 3[BH_2(NH_3)_3]^+[BH_4]^- \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad 2B_3N_3H_6 + 12H_2 \end{array}$$

## Action of halogens:

Diborane reacts with halogens (except $I_2$) and gives different products.

$$B_2H_6 + 6Cl_2 \xrightarrow{\text{at } 25^0\text{c}} 2BCl_3 + 6HCl$$

$$B_2H_6 + Br_2 \xrightarrow{\text{at } 100^0\text{c}} B_2H_5Br + 4Br$$

Carbon monoxide reacts with diborane at $1000^0$c at 2 atm pressure to give borane carbonyl.

$$B_2H_6 + 2CO \longrightarrow 2[BH_3.CO]$$

## Reducing agent:

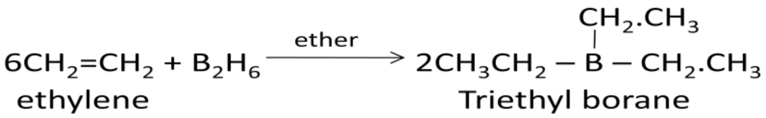
Diborane also acts as a powerful reducing agent for some functional groups

$$RCHO \xrightarrow{(B_2H_6)} RCH_2OH$$

$$RCN \xrightarrow{(B_2H_6)} RCH_2NH_2$$

## Reaction with Olefins:

Diborane readily adds at O$^0$c to 25$^0$c to the olefinic or acetylenic compound to form trialkyl boranes. The reaction is known as hydroboration.



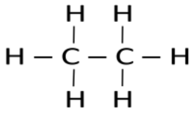
$$\underset{\text{ethylene}}{6CH_2{=}CH_2} + B_2H_6 \xrightarrow{\text{ether}} \underset{\text{Triethyl borane}}{2CH_3CH_2-\overset{\overset{\displaystyle CH_2.CH_3}{|}}{B}-CH_2.CH_3}$$

Diborane undergoes cleavage reactions with Lewis bases (L) to give borane adducts, $BH_3.L$

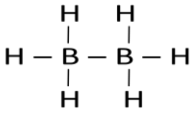
$$B_2H_6 + 2NMe_3 \longrightarrow 2BH_3.NMe_3$$

## Structure of Diborane:

Diborane is an example of electron deficient molecules. In these molecules the no. of electrons sufficient for formation of all covalent bonds is not available. Therefore a peculiar situation arises. Each Boron atom is $B_2H_6$ contributes three electrons and each hydrogen atom contributes one electron for the bond formation. That means 12 electrons are available. They can form 6 covalent bonds only. If diborane has to have ethane like structure 14 electrons are necessary.

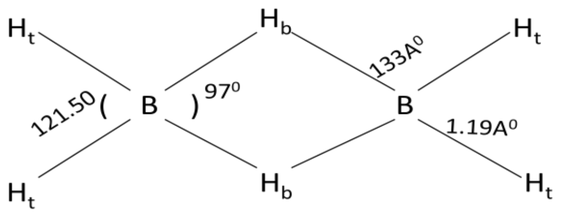


Ethane



Diborane

Electron diffraction studies have shown that diborane contains two coplanar $BH_2$ groups. From this the structure of diborane can be represented as follows.

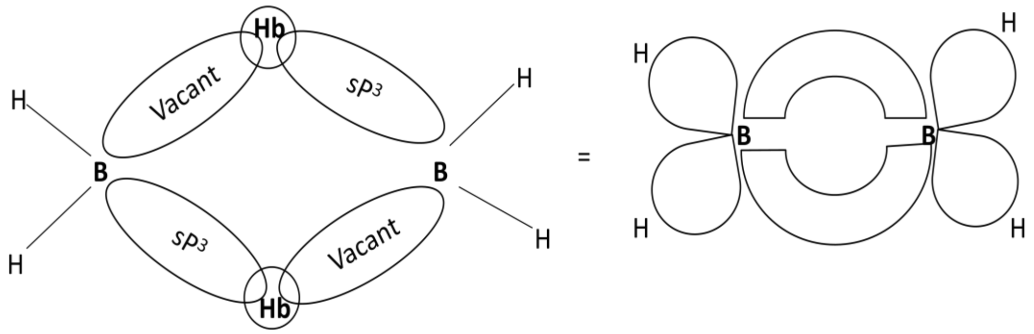


| | |
|---|---|
| B – B bond length | 1.77A$^0$ |
| B – H bridge bond length | 1.33A$^0$ |
| B – H terminal bond length | 1.19A$^0$ |
| H terminal BH term Bond angle | 121.5$^0$ |
| H bridge BH Bridge Bond angle | 97$^0$ |

The 4 hydrogen atoms (represented by $H_t$) present in $BH_2$ groups are known as terminal hydrogen atoms. The remaining two hydrogen (represented by $H_b$) atoms are called as bridge hydrogens because they link the two $BH_2$ groups in the molecule. One of the bridge hydrogens lies above the plane and the other one lies below the plane.

## Nature of Bonds in Hydrogen Bridge:

Boron atom undergoes $sp^3$ hybridization resulting in 4 equivalent orbitals, three of these orbitals have one electron each and 4th hybrid orbital is vacant. In forming the B – H – B bridge $sp^3$ hybrid orbital with one electron each and 4th hybrid orbital is vacant. In forming the B – H – B bridge $sp^3$ hybrid orbital with one electron from one Boron atom, is orbital of one bridge hydrogen and the vacant $sp^3$ hybrid orbital of the 2nd boron atom overlap as shown in the figure.



Overlap of orbitals is $B_2H_6$ – Banana bond. The 2 B – H – B bridges present in diborane are abnormal bonds. They are considered as 3 centered 2 electron bonds.

Due to repulsion between the two hydrogen nuclei the delocalized orbitals of bridges are bent away from each other in the middle giving the shape of banana. Thus the 3 centre – 2 electron bonds are also known as banana bonds. In this type of bond a pair of electrons holds 3 atoms together.

In diborane there are two such bridges. Thus diborane molecule has four 2 – centre – 2 electron bonds and two 3 – centre 2 – electron bonds.

## Evidences for the structure of diborane:

The 1st experimental evidence in favour of the structure of diborane came in 1951 from the electron diffraction measurement, further supported by measurement of the Raman and infra – Red spectra. The physical devices revealed the following points. All of these favour the bridge type structure for diborane.

1. The 2 boron atoms and 4 terminal hydrogen atoms lie in the same plane, the 2 bridging hydrogen atoms are in a plane perpendicular to the rest of the molecule and prevent rotation about the 2 boron atoms. The presence of 2 types of boron hydrogen bonds is confirmed by the chemical evidence that only four of the hydrogen atoms of the diborane molecule are replaceable by methyl groups. Any attempt to effect further substitution results in cleavage of the molecule in to two fragments. Each containing one boron atom.
2. The bond distances and bond angles are consistent with the two types of hydrogen atoms
3. Tetramethyl diborane is not found to possess any terminal hydrogen atom.

## Assignment questions:

1. Discuss the physical properties of diborane.
2. Write all the chemical reactions of $B_2H_6$
3. Discuss the structure of diborane.

## SAQs:

1. The hydrides of boron are called as ________
    a. Boranes
    b. Boron hydrides
    c. Borazine
    d. Both a) and b)

**Solution:** d)

2. The general formula for boron hydrides is,
    a. $B_nH_{n+4}$
    b. $B_nH_{n+6}$
    c. $B_nH_{n+5}$
    d. Both a) and b)

**Solution:** d)

3. Predict the product for the following reaction:

$$2BF_3 + 6NaH \xrightarrow{450K} ? + NaF$$

    a. $NaBH_4$
    b. $BH_3$
    c. $B_2H_6$
    d. $NaBF_4$

**Solution:** c)

4. Inorganic benzene is
    a. Borazole

   b. Borazine
   c. $B_3N_3H_6$
   d. All the above

**Solution:** d)

5. diborane molecule has
   a. four 2 – centre 2 electron bonds and two 3 – centre 2 electron bonds.
   b. three 2 – centre 2 electron bonds and two 3 – centre 2 electron bonds.
   c. four 2 – centre 2 electron bonds and one 3 – centre 2 electron bonds.
   d. two 2 – centre 2 electron bonds and two 3 – centre 2 electron bonds.

**Solution:** a)

**Example set:**

1. from $B_2H_6$ , the following can be prepared:
   a. $B_2O_3$
   b. $H_3BO_3$
   c. $NaBH_4$
   d. All of these

**Solution:** d)

2. The hybridization of boron in diborane is:
   a. sp
   b. $sp^2$
   c. $sp^3$
   d. $dsp^2$

**Solution:** c)

3. Which of the following is an electron deficient compound?
   a. $C_2H_6$
   b. $SiH_4$
   c. $PH_3$

d. $B_4H_{10}$

**Solution:** d)

4. Which of the following is correct?
    a. the members of $B_nH_{n+6}$ are less stable than $B_nH_{n+4}$ series
    b. diborane is an unstable coloured compound at room temperature
    c. the reaction of diborane with oxygen is endothermic
    d. all of these

**Solution:** a)

**LAQs:**

1. Write a note on classification of boranes.

**Solution:**

Boranes are the hydrides of boron.

Based on their molecular formula Boron hydrides are classified in to 2 types.

i. Those with general formula $B_nH_{n+4}$. These are quite stable and hence more important. These are commonly known as boranes.

**Example:**

$B_2H_6$ (diborane) $B_5H_9$ (pentaborane – 9)
$B_6H_{10}$ (hexaborane -10) $B_8H_{12}$ (octaborane – 12)
$B_{10}H_{14}$ (decaborane – 14)

ii. Those with general formula $B_nH_{n+6}$

These are unstable and have low M.Ps. These are called hydroboranes.

**Example:**

$B_4H_{10}$ (Tetraborane – 10), $B_5H_{11}$ (Pentaborane – 11), $B_6H_{12}$ (Hexaborane – 12)

2. How do you prepare $B_2H_6$ using the following reactions?
   a. $LiAlH_4$
   b. $NaBH_4$
   c. $BCl_3$

**Solution:**

a. $B_2H_6$ is prepared by treating boron triflouride with $LiAlH_4$ is diethyl ether.

$$4BF_3 + 3LiAlH_4 \longrightarrow 2B_2H_6 + 3LiF + 3AlF_3$$

b. Diborane can also be prepared by the action f dilute $H_2SO_4$ on sodium-borohydride

$$2NaBH_4 + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2 + B_2H_6$$

c. A mixture of Boron Trichloride and hydrogen is subjected to silent electric discharge. Diborane is produced.

$$2BCl_3 + 6H_2 \xrightarrow[\text{Or cu – Al catalyst at } 450^0\text{C}]{\text{Electric discharge}} B_2H_6 + 6HCl$$

**Problem set:**

1. In $B_2H_6$:
   a. There is direct boron-boron bond
   b. The boron atoms are linked through hydrogen bridges
   c. All the B - H bond distances are equal
   d. All the atoms are coplanar.

**Solution:** b)

2. Which hydride does not exist in nature?
   a. $BH_3$
   b. $(AlH_3)_n$
   c. $B_2H_6$

   d. $B_4H_{10}$

**Solution:** a)

3. Which one of the following is not a borane Formula?
   a. $B_5H_9$
   b. $B_5H_{10}$
   c. $B_5H_{11}$
   d. $B_6H_{10}$

**Solution:** b)

4. In which of the following a salt of the type $KMO_2$ is obtained
   (Where H = Boron atom)
   a. $B_2H_6 + KOH\ (aq) \rightarrow$
   b. $B_2O_3 + NH_3 \rightarrow$
   c. $B_2H_6 + KCl\ (aq) \rightarrow$
   d. All of these

**Solution:** a)

5. Write down the chemical properties of $B_2H_6$ with the following
   a. Action of alkali
   b. Reaction with $NH_3$
   c. Action of heat
   d. Action with olefines

**Solution:**

   a. **Action of alkalies:**

   When treated with an alkali it forms hypoborates, metaborates

$$B_2H_6 + 2KOH + 2H_2O \longrightarrow 2KBO_2 + 6H_2$$

   b. **Action with Ammonia:**

Reaction of Ammonia with diborane gives initially $B_2H_6.2NH_3$ which is formulated as

$$[BH_2(NH_3)_2]^+[BH_4]^-$$

Further heating gives borazine (or) borozole $B_3N_3H_6$, known as inorganic benzene. In view of its ring structure with alternate BH and NH groups that is similar to benzene it is known as inorganic benzene.

$$\begin{tikzcd}
3B_2H_6 + 6NH_3 \arrow[r] & 3[BH_2(NH_3)_3]^+[BH_4]^- \arrow[d] \\
& 2B_3N_3H_6 + 12H_2
\end{tikzcd}$$

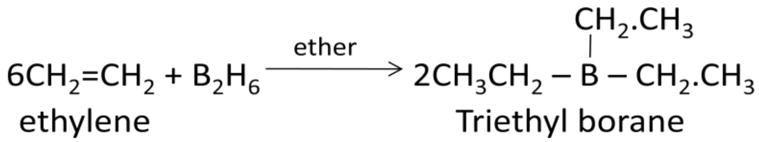
c. **Action of heat:**

All boron hydrides decompose at red heat to boron and hydrogen

$$B_2H_6 \xrightarrow{>100^0C} 2B + 3H_2$$

d. **Reaction with Olefins:**

Diborane readily adds at $O^0$c to $25^0$c to the olefinic or acetylenic compound to form trialkyl boranes. The reaction is known as hydroboration.



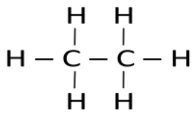
$$\underset{\text{ethylene}}{6CH_2{=}CH_2} + B_2H_6 \xrightarrow{\text{ether}} \underset{\text{Triethyl borane}}{2CH_3CH_2 - \overset{\displaystyle CH_2.CH_3}{\overset{|}{B}} - CH_2.CH_3}$$

6. Discuss the structure of diborane.

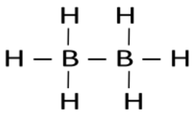
**Solution:**

**Structure of Diborane:**

Diborane is an example of electron deficient molecules. In these molecules the no. of electrons sufficient for formation of all covalent bonds is not available. Therefore a peculiar situation arises. Each Boron atom is $B_2H_6$ contributes three electrons and each hydrogen atom contributes one electron for the bond formation. That means 12 electrons are available. They can form 6 covalent bonds only. If diborane has to have ethane like structure 14 electrons are necessary.

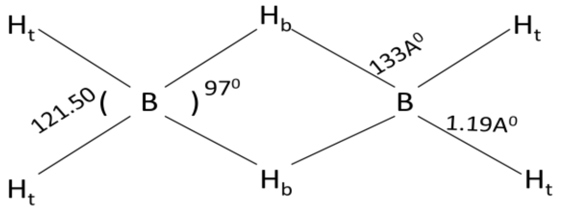


Ethane



Diborane

Electron diffraction studies have shown that diborane contains two coplanar $BH_2$ groups. From this the structure of diborane can be represented as follows.



B – B bond length 1.77A$^0$
B – H bridge bond length 1.33A$^0$
B – H terminal bond length 1.19A$^0$
H terminal BH term Bond angle 121.5$^0$
H bridge BH Bridge Bond angle 97$^0$

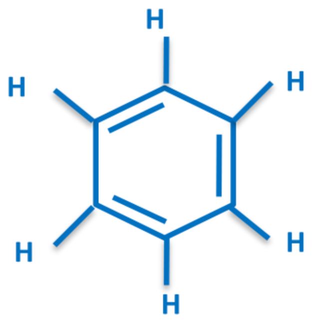
The 4 hydrogen atoms (represented by $H_A$) present. $BH_2$ groups are known as terminal hydrogen atoms. The remaining two hydrogen (represented by $H_b$) atoms are called as bridge hydrogens because they link the two $BH_2$ groups in the molecule. One of the bridge hydrogens lies above the plane and the other one lies below the plane.

**Exercise questions:**

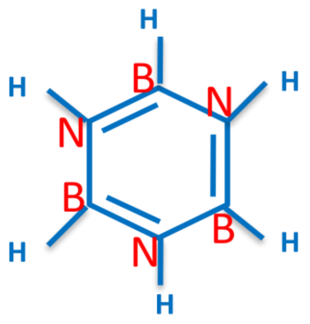
1. What is inorganic benzene? Why is it so called? How will you get it from diborane?
2. Write a reason for diborane for being used as a rocket fuel.
3. Write a note on banana bond.
4. Explain the nature of bonds in diborane.

**Solutions:**

1. Borazine (or) borozole ($B_3N_3H_6$ ) is known as inorganic benzene, in view of its ring structure with alternate BH and NH groups. It is so called because its structure is similar to that of benzene.



Benzene



Borozine or borozole

At lower temperature, diborane reacts with ammonia to form an addition compound

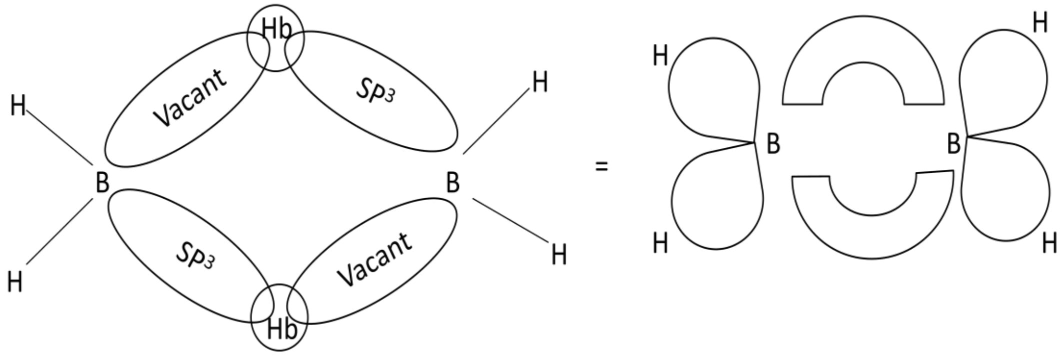
$$3B_2H_6 + 6NH_3 \longrightarrow 3[BH_2(NH_3)_3]^+[BH_4]^-$$
$$\downarrow$$
$$2B_3N_3H_6 + 12H_2$$

2. Diborane catches fire spontaneously upon exposure to air. It burns in oxygen releasing an enormous amount of energy. Hence these are used as rocket fuels.

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$$

3. Overlap of orbitals in $B_2H_6$ is – Banana bond. The 2 B – H – B bridges present in diborane are abnormal bonds. They are considered as 3 centered 2 electron bonds.
4. Due to repulsion between the two hydrogen nuclei the delocalized orbitals of bridges are bent away from each other in the middle giving the shape of banana. Thus the 3 centre – 2 electron bonds are also known as **banana bonds**. In this type of bond a pair of electrons holds 3 atoms together.
5. **Nature of Bonds in hydrogen bridge:**

   Boron atom undergoes $sp^3$ hybridization resulting in 4 equivalent orbitals. 3 of these orbitals have one electron each and 4th hybrid orbital is vacant. In forming the B – H – B bridge $sp^3$ hybrid orbital with one electron each and 4th hybrid orbital is vacant. In forming the B – H – B bridge $sp^3$ hybrid orbital with one electron from one Boron atom, is orbital of one bridge hydrogen and the vacant $sp^3$ hybrid orbital of the 2nd boron atom overlap as shown in the figure.



# Group 14 elements

## Module 18.1: Introduction to group 14 elements (Carbon family)

### Introduction:

Carbon (C), Silicon (Si), Germanium (Ge), Tin [ latin name: Stannum] (Sn) and Lead [latin name: Plumbum] (Pb) and ununquadrium (recently named as Flerovium)(Fl) are the members of group 14. The six elements constitute a family known as carbon family.

Carbon is the seventeenth most abundant element by mass in the earth's crust. It is widely distributed in nature in Free State as well as in the combined state. In elemental state it is available as coal, graphite and diamond. In combined state it is present as carbonates of metals, as hydrocarbons and as carbon dioxide gas in air etc. It is an essential constituent of all living matter. It is present in them as proteins, carbohydrates and fats. $CO_2$ is essential for photosynthesis. There is no organic chemistry without carbon containing compounds. The fields of organo-metallic compounds, carbides and π-complexes are fast developing. We can emphatically say that carbon is the most versatile element in the world.

Silicon is the second most abundant element on earth's crust (27.7% by mass) and is present in the nature in the form of silica or silicates.

It is a very important component of ceramics, glass, cement and silicones. In microelectronic industries (***Ex:*** transistors, computer chips) very pure silicon is required.

Germanium occurs only in traces, but tin and lead are very common elements. Tin occurs mainly as cassiterite ($SnO_2$) and lead as galena (PbS). They have easy extraction methods and many uses.

## Electronic configuration:

The group 14 elements are called carbon family. These are the elements of p-block. The electronic configurations of these elements are represented by the general formula $ns^2$ $np^2$. The configurations are represented in the table given below.

### Electronic configurations of group 14 elements:

| S.No | Name of the element | Symbol | Atomic number | Electronic configuration |
|---|---|---|---|---|
| 1 | Carbon | C | 6 | $1s^2 2s^2 2p^2$ |
| 2 | Silicon | Si | 14 | $1s^2 2s^2 2p^6 3s^2 3p^2$ |
| 3 | Germanium | Ge | 32 | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$ |
| 4 | Tin | Sn | 50 | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^2$ |
| 5 | Lead | Pb | 82 | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 5d^{10} 6s^2 6p^2$ |
| 6 | Flerovium | Fl | 114 | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 5d^{10} 5f^{14} 6s^2 6p^6 6d^{10} 7s^2 7p^2$ |

The inner core of each of the electronic configurations of elements in this group differs. C has only‘s’ electrons. Silicon has‘s’ and ‘p’ electrons in their penultimate shells. But in Ge, Sn, Pb d-electrons are also present in their respective penultimate shells. Because of this difference in electronic configurations, **C** and **Si** are different from other elements of this group**.**

## Occurrence:

All the elements are present abundantly in nature except germanium. Carbon and silicon are widely distributed compared to tin and lead. They occur in the earth’s crust to the extent of C = 0.032%, Si = 27.12 %, Ge = $7.0X10^{-4}$ %, Sn = $4X10^{-3}$ % and Pb = $1.6x10^{-3}$ %. The last member, Flerovium (Fl) is recently discovered element. It is synthetic, radioactive and unstable element. Not much is known about its properties.

## The natural sources of group 14 elements are:

| Elements | Source | Formula of the substance available |
|---|---|---|
| C | Graphite, diamond, $CO_2$,CO,Coal, Crude oil, Carbonates in rocks | —— |
| Si | Silica, sand, quartz, Silicate minerals, clays, kaolin, Feldspar | $SiO_2$, $[Al_2(OH)_4\ Si_2O_5]$, $[NaAl_2(SiO_3)_4.H_2O]$ |
| Ge | Some silver and zinc ores, some types of coal. | —— |
| Sn | Casitterite (or) Tinstone | $SnO_2$ |
| Pb | Galena, Cerussite, anglesite | PbS, $PbCO_3$, $PbSO_4$. |

## Assignment questions:

1. Write the electronic configurations of all the elements of 14th group.
2. What are the different sources of 14th group elements?

## SAQs:

1. Carbon is ________ most abundant element by mass in the earth’s crust.
   a. 5th
   b. 10th
   c. 17th
   d. 8th

**Solution:** c)

2. Silicon is the important component of,
   a. Ceramics
   b. Glass
   c. Silicones
   d. All of these

**Solution:** d)

3. 14th group elements are ----------- block elements
   a. s

   b. p
   c. d
   d. f

**Solution:** b)

4. The general electronic configuration of carbon family of elements is,
   a. $ns^2np^5$
   b. $ns^2$
   c. $ns^2np^1$
   d. $ns^2np^2$

**Solution:** d)

5. occurrence of carbon in the earth’s crust is
   a. 0.3 %
   b. 0.032 %
   c. 0.5 %
   d. 0.2 %

**Solution:** b)

6. The Latin name of Tin is,
   a. Plumbum
   b. Stibium
   c. Stannum
   d. Scandium

**Solution:** c)

7. In elemental state, carbon is available as,
   a. Graphite
   b. Diamond
   c. Coal
   d. All the above

**Solution:** d)

8. Pure silicon is used in

a. Transistors
b. Computer chips
c. Paper industry
d. Both a) and b)

**Solution:** d)

9. Write down electronic configurations of 14th group elements

**Solution:**

| S.No | Name of the element | Symbol | Atomic number | Electronic configuration |
|---|---|---|---|---|
| 1 | Carbon | C | 6 | $1s^2 2s^2 2p^2$ |
| 2 | Silicon | Si | 14 | $1s^2 2s^2 2p^6 3s^2 3p^2$ |
| 3 | Germanium | Ge | 32 | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$ |
| 4 | Tin | Sn | 50 | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^2$ |
| 5 | Lead | Pb | 82 | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 5d^{10} 6s^2 6p^2$ |

10. Give a brief note on occurrence of 14th group elements.

**Solution:**

All the elements are present abundantly in the nature except germanium. Carbon and silicon are widely distributed compared to tin and lead. They occur in the earth's crust to the extent of C = 0.032%, Si = 27.12 %, Ge = $7.0\text{X}10^{-4}$ %, Sn = $4\text{X}10^{-3}$ % and Pb = $1.6\text{x}10^{-3}$ %

**Problem set:**

1. Cassiterite is an ore of _______
   a. Si
   b. Sn
   c. Pb

    d. Ge

**Solution:** b)

2. The atomic number of lead is,
    a. 50
    b. 80
    c. 82
    d. 52

**Solution:** c)

3. Cerussite is chemically
    a. PbS
    b. $SnO_2$
    c. $SiO_2$
    d. $PbCO_3$

**Solution:** d)

4. Give the natural sources of 14th group elements.

**Solution:**

| **Elements** | **Source** | **Formula of the substance available** |
|---|---|---|
| C | Graphite, diamond, $CO_2$,CO,Coal, Crude oil, Carbonates in rocks | ___ |
| Si | Silica, sand, quartz, Silicate minerals, clays, kaolin, Feldspar | $SiO_2$, $[Al_2(OH)_4\ Si_2O_5]$, $[NaAl_2(SiO_3)_4.H_2O]$ |
| Ge | Some silver and zinc ores, some types of coal. | ____ |
| Sn | Casitterite (or) Tinstone | $SnO_2$ |
| Pb | Galena, Cerussite anglesite | PbS, $PbCO_3$,$PbSO_4$. |

5. Carbon and silicon show differences from other elements of 14th group. Why?

**Solution:**

The inner core of each of the electronic configurations of elements in this group differs. C has only‘s’ electrons. Silicon has‘s’ and ‘p’ electrons in their respective penultimate shells. But in Ge, Sn, and Pb d-electrons are also present in their penultimate shells. Because of this difference in electronic configurations, **C and Si are different from other elements of this group.**

## Exercise questions:

1. Write the formulae of the following.
    a. Butter of tin
    b. White lead
    c. Red lead
    d. Sugar of lead
    e. Litharge
    f. Carborundum
    g. Phosgene
    h. Chrome yellow
    i. Water glass
    j. Dry cold (or) dry ice

## Solutions:

1.

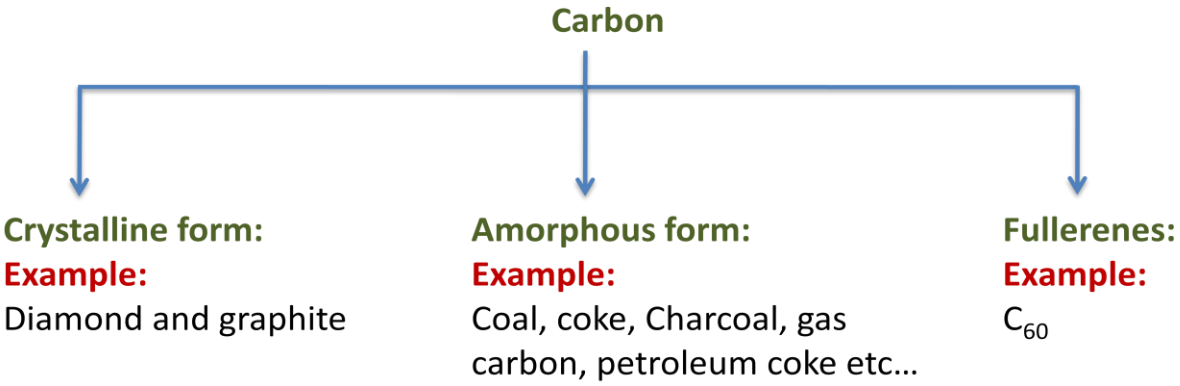
| | | |
|---|---|---|
| a. | $SnCl_4.5H_2O$ | (Stannic chloride) |
| b. | $2\ PbCO_3.Pb(OH)_2$ | (Basic lead carbonate) |
| c. | $Pb_3O_4$ | (Tri lead tetra oxide) |
| d. | $Pb(CH_3COO)_2$ | (Lead acetate) |
| e. | $PbO$ | (Lead monoxide) |
| f. | $SiC$ | (Silicon carbide) |
| g. | $COCl_2$ | (Carbonyl chloride) |
| h. | $PbCrO_4$ | (Lead chromate) |
| i. | $Na_2SiO_3$ | (Sodium silicate) |
| j. | $CO_2$ | (Carbon dioxide in solid sate) |

# Group 14 elements

## Module – 18.4: Allotropic forms of carbon

### Allotropes of carbon:

**“The phenomenon of the existence of an element in different physical forms but possessing similar chemical characteristics”** is known as allotropy. The different forms of the elements are known as **allotropes** or **allotropic modifications**. These allotropes result from the different arrangements of atoms of the elements. Carbon exists in many allotropic forms.

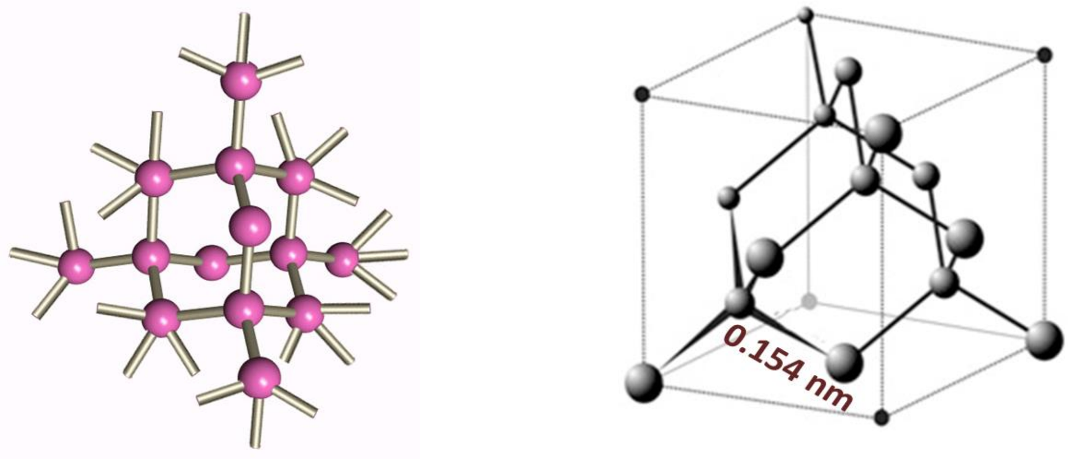


### Crystalline carbon:

Diamond and graphite are the two most important crystalline forms of carbon. Because of the difference in the arrangement of atoms and the bonding nature, these two allotropes differ in their physical and chemical properties. A third form of carbon was discovered by H. W. Kroto, E .Smalley and R. F. Curl were awarded the Nobel Prize in 1996.

### Diamond:

Each carbon undergoes $sp^3$ hybridization. A carbon atom is bonded to four other carbon atoms arranged in tetrahedral symmetry with single bonds. Its polymeric structure extends in space and produces a rigid three - dimensional network of carbon atoms. In this structure directed covalent bonds are present throughout the lattice.



Structure of Diamond

**Properties:**

1. Very hard substance, difficult to break due to extended covalent bonds
2. High melting point 3927 $^{0}$C
3. C – C bond energy is very high (348 kJ mol$^{-1}$ )
4. Non conductors due to the lack of lone electrons or electron pairs
5. C – C bond length is 1.54 A$^{0}$ or 0.154 nm.
6. $\angle$CCC bond angle $109^{0}\,28^{1}$
7. Transparent to x- rays
8. High refractive index
9. The value of diamond is measured in carats. (1 carat = 200 mg) Kohinoor diamond is 186 carats and Pitt diamond is 136 carats
10. It is insoluble in any solvent

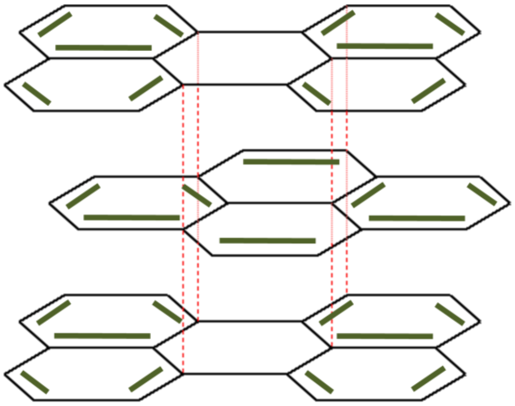
11. It is stable in vacuum up to1500 $^{0}$C but at 1800 $^{0}$C – 2000 $^{0}$C it changes in to graphite.

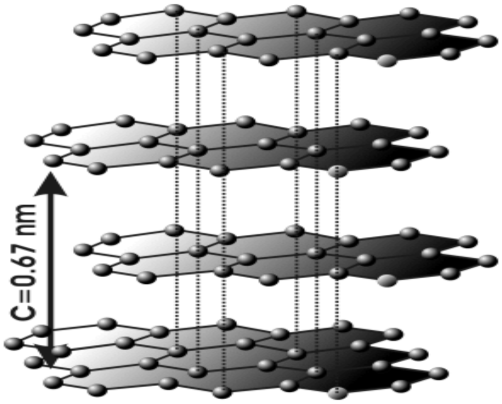
## Uses:

1. Diamonds reflect and refract the incident radiations and so are used in jewellery
2. Dies are made up of diamond. Dies are used to draw fine wires
3. Diamonds are hard enough to be used in cutting glass and for sharpening of instruments

## Graphite:

Graphite has a two dimensional, layered structure. Layers are held by van der Waals forces and the bond distance between two layers is 3.35 A$^{0}$. Carbon atoms, in graphite, form hexagonal rings. Each carbon undergoes sp$^{2}$ hybridization. A carbon atom forms three covalent bonds with three separate carbons. The fourth unhybridized orbital is a pure p-orbital having an unpaired electron. This electron participates in π bond formation. So graphite has a collection of π - electrons, because of these π electrons graphite is good conductor. The C – C bond length in graphite (in hexagonal ring) is 1.42 A$^{0}$. Because of these covalent bonds in the ring, graphite has a high m.p. (3500 $^{0}$C). The electrons are delocalized over the whole sheet. It cleaves easily between the layers, so soft and slippery.





## Structure of graphite

### Uses:

1. Used as a lubricant due to its soft and slippery nature and can be cleaved between the layers.
2. Used as a electrode in electric furnaces
3. Used in electrotyping and electro printing
4. Used as a pencil lead
5. Used in the preparation of refractory crucibles.

### Preparation:

It is prepared by **Acheson's method**. The carbon electrodes in an electric furnace or joined by carbon chains. In the furnace, a mixture of coke and sand is taken and heated to 3450 $^0$C. Silicon carbide is formed which decomposes to give silicon and graphite. Silicon vaporizes and graphite is left in the furnace.

$$3\text{ C} + \text{SiO}_2 \xrightarrow{3450\ ^0\text{C}} \text{SiC} + 2\text{ CO} \uparrow$$

$$\text{SiC} \longrightarrow \text{Si} + \text{C (Graphite)}$$

### Properties:

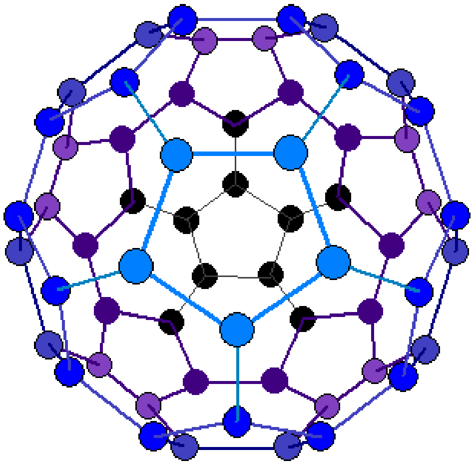
It is soft, greasy, dark grayish coloured crystalline solid. Its density is 2.5 g mL$^{-1}$. It is good conductor of electricity and its conductivity increases with temperature. It leaves a black mark on paper. It is called **black lead** or **pumbago**.

Graphite is thermodynamically more stable than diamond and its free energy of formation is 1.9 kJ less than that of diamond.

$$\text{Graphite} \xrightarrow[50{,}000 - 60{,}000\ \text{atm}]{1600\ ^{0}\text{C}} \text{Diamond}$$

## Fullerenes:

Fullerenes are the third kind carbon allotrope. Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gas such as helium or argon. They are cage like molecules. Fullerenes are the only pure form of carbon because they have smooth structure without having free bonds. The sooty material formed by condensation of vaporized $C_n$ molecules consists of mainly $C_{60}$ with smaller quantity of $C_{70}$ and traces of fullerenes consisting of even number of carbon atoms up to 350 or above. $C_{60}$ molecule has a shape like soccer ball and called **Buckminsterfullerene.**



**Structure of fullerene**

It consists of 20 six member rings and 12 five member 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 $sp^2$ hybridization. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon is delocalized in molecular orbitals. This, in turn gives aromatic character to the molecule. It contains both single and double bonds with C – C distances of 143.5 pm and 138.3 pm. Spherical fullerenes are also called **Bucky balls**.

It is very important to know that graphite is thermodynamically most stable allotrope of carbon and, therefore, $\Delta_f H^{-}$ of graphite is taken as zero. $\Delta_f H^{-}$ values of diamond and fullerene ($C_{60}$) are 1.90 and 38.1 kJ $mol^{-1}$ respectively.

### Uses of carbon:

1. Mainly C is used as a reducing agent
2. In the manufacturing of $CS_2$

### Amorphous forms of carbon: coal, charcoal, soot (or) lamp black:

### Coal:

It is the crude form of carbon. It is formed in nature as a result of slow decomposition of vegetable matter under the influence of heat, pressure and limited supply of air. The common variety of coal is bituminoucoal. It is hard like stone and burns with smoky flame. The superior quality is anthracite which burns with non-smoky flame. This is formed by the carbonization of wood in stages.

### Uses:

1. Coal is mainly used as a fuel,
2. Coal is mainly used for the manufacture of coal gas, coal tar and coke.
3. Coal is mainly used in the manufacture of synthetic petrol.

### Charcoal:

This form of carbon is obtained by burning wood. Cellulose or any other carbonaceous matter in a limited supply of air. Charcoal is of various forms such as wood charcoal, sugar charcoal, coconut charcoal etc. Wood charcoal is used as an adsorbent. When charcoal is given a special treatment in order to increase its adsorption capacity, it results in activated charcoal and the process of treatment is called as activation.

### Uses:

1. It is used in removing offensive odour from air in the air conditioning process.
2. In making filters in cigarettes to remove vapours of nicotine.
3. In removing fusel oil from crude oil from crude spirit.
4. In decolorizing sugar syrup and refining process.

### Lamp black or carbon black or soot:

It is obtained by burning substances rich in carbon content such as kerosene, petroleum, turpentine oil, acetylene etc., in a limited supply of air. These substances yield a large amount of smoke (soot) which is passed into chambers having wet blankets. The soot collected on these blankets is called lampblack.

### Uses:

1. It is used for making printing inks, black paints, boot polishes and ribbons of type writers.
2. It used as a filler in making rubber tyres.

## Assignment questions:

1. Define an allotrope? Sketch the structures of any two crystalline allotropes of carbon.
2. What is the impact of structure on physical properties of two allotropes?
3. What are the allotropes of amorphous carbon? Give a brief account of each of them.
4. Give reasons for the following:
    a. Graphite is used as lubricant

b. Diamond is used as an abrasive

**Self check questions:**

1. A crystalline form of carbon ________
   a. Coal
   b. Graphite
   c. Diamond
   d. Both b) and c)

**Solution:** d)

2. In diamond, carbon undergoes ________ hybridization.
   a. $sp^2$
   b. sp
   c. $sp^3$
   d. $sp^3d$

**Solution:** c)

3. Dies are made up of _______
   a. Graphite
   b. Coal
   c. Diamond
   d. Fullerene

**Solution:** c)

4. _______ has a two dimensional layer structure
   a. Graphite
   b. Diamond
   c. Fullerene
   d. Charcoal

**Solution:** a)

5. Free energy of formation of graphite is ________ than diamond
    a. 1.9 kJ greater than that of diamond
    b. 1.9 kJ lesser than that of diamond
    c. equal to that of diamond
    d. either more or less than that of diamond.

**Solution:** b)

6. Spherical fullerenes are also called as ________
    a. Buckminsterfullerene
    b. Anthracite
    c. Bucky balls
    d. Both a) and c)

**Solution:** d)

7. ________ is used for making ribbons of type writers.
    a. Coal
    b. Coke
    c. Char coal
    d. Lamp black

**Solution:** d)

**Example set:**

1. A rigid three-dimensional network of carbon atoms is present in _______
    a. Graphite
    b. Diamond
    c. Fullerene
    d. All

**Solution:** b)

2. Graphite is _______
    a. A good conductor of heat
    b. Softer than diamond
    c. An amorphous variety of carbon
    d. Both a) and b)

**Solution:** d)

3. Which of the following is a chemically inactive allotrope of carbon?
    a. Diamond
    b. Coal
    c. Charcoal
    d. Animal charcoal

**Solution:** a)

4. Bucky ball is ________
    a. an allotrope of carbon
    b. referred as $C_{60}$
    c. having $sp^2$ hybridized carbon
    d. All

**Solution:** d)

5. Write the properties of diamond.

**Solution:**

a. Very hard substance, difficult to break due to extended covalent bonds

b. High melting point 3927 $^0C$

c. C – C bond energy is very high. 348 kJ $mol^{-1}$

d. Non conductors due to the lack of lone electrons or electron pairs

e. C – C bond length is 1.54 $A^0$ or 0.154 nm.

f. $\angle$CCC bond angle $109^0\ 28^1$

g. Transparent to x- rays

h. High refractive index
i. The value of diamond is measured in carats. (1 carat = 200 mg) Kohinoor diamond is 186 carats and Pitt diamond is 136 carats
j. It is insoluble in any solvent
k. It is stable in vacuum up to1500 $^0$C but at 1800 $^0$C – 2000 $^0$C it changes in to graphite.

6. Give a brief account of the uses of coal, charcoal, lamp black

**Solution:**

**Coal:**

It is the crude form of carbon. It has been formed in nature as a result of slow decomposition of vegetable matter under the influence of heat, pressure and limited supply of air.

**Uses:**

a. Coal is mainly used as a fuel,
b. Coal is mainly used for the manufacture of coal gas, coal tar and coke.
c. Coal is mainly used in the manufacture of synthetic petrol.

**Charcoal:**

This form of carbon is obtained by burning wood, cellulose or any other carbon form occur matter in a limited supply of air.

**Uses:**

a. It is used in removing offensive odour from air in the air conditioning process.
b. In making filters in cigarettes to remove vapours of nicotine.
c. In removing fusel oil from crude oil from crude spirit.

d. In decolorizing sugar syrup and refining process.

### Lamp black or carbon black or soot:

It is obtained by burning substances rich in carbon content such as kerosene, petroleum, turpentine oil, acetylene etc., in a limited supply of air.

### Uses:

a. It is used for making printing inks, black paints, boot polishes and ribbons of type writers.
b. It used as a filler in making rubber tyres.

## Problem set:

1. Diamond is hard, because ________
   a. All the four valence electrons of C are bonded to other carbon atoms by covalent bonds.
   b. It is giant molecule
   c. It can not be burnt
   d. C – C bond length is maximum

**Solution:** a)

2. Graphite is a good conductor of electricity because it contains
   a. Mobile electrons
   b. Strong C – C bonds
   c. $sp^2$ hybridized C
   d. All the above

**Solution:** a)

3. Buckminsterfullerene contains _______ six membered rings and _______ five membered rings.
   a. 12 & 12

   b. 20 & 20
   c. 20 & 12
   d. 12 & 20

**Solution:** c)

4. $\Delta_f H^-$ of graphite is taken as _______
   a. 1.98 kJ
   b. 38.1 kJ
   c. 3.81 kJ
   d. Zero

**Solution:** d)

5. Diamond is covalent, yet it has high melting point. Why?

**Solution:**

Diamond has three-dimensional network involving strong C – C bonds. These are very difficult to break and, therefore has high melting point.

6. Diamond is very hard, while graphite is soft. Explain.

**Solution:**

Diamond has giant three-dimensional polymeric structure in which each carbon is $sp^3$ hybridized and linked to four other carbon atoms. This structure makes diamond hardest. Graphite possesses layer structure in which each carbon atom is $sp^2$ hybridized. There is wide separation between various layers. One layer can slide over easily on the other. This makes graphite soft in nature.

**Exercise questions:**

1. Which allotropic form of ‘C’ has the lowest energy?
2. Explain the difference in density between diamond and graphite
3. Explain the difference in the electrical conductivities of diamond and graphite
4. How do you convert graphite into diamond?

## Solutions:

1. Graphite has the lowest energy. Graphite has three σ – bonds and one π – bond. Where as in diamond there are four σ – bonds.
2. Graphite is composed of flat two – dimensional sheets of carbon atoms, it possesses layer structure. The distance between layers is 3.35 $A^0$. The bonding between layers is weak and cleaves easily. The wide spacing of sheets in graphite also means that the atoms do not pack together to fill space very effectively. Thus the density of graphite (2.22 g $cm^{-3}$) is lower than that of diamond. (3.51 g $cm^{-3}$)

3. Graphite has electrical conductivity, while diamond is an insulator. Because in diamond each ‘C’ atom is tetrahedrally surrounded by four other ‘C’ atoms. i.e. 4 valence electrons are involved in forming four σ – bonds. In graphite only three of the valence electrons of each carbon atom are involved in forming three σ – bonds. The fourth electron forms a π – bond. The π – electrons are delocalized over the whole sheet. They are mobile. Hence graphite conducts electricity.

4. Graphite is thermodynamically more stable than diamond and its free energy of formation s 1.9 kJ less than diamond.

$$\text{Graphite} \xrightarrow[\text{50,000 – 60,000 atm}]{1600\ ^{0}\text{C}} \text{Diamond}$$