

CHAPTER - 00

P-BLOCK ELEMENTS- I

Prepared by Anoop S (CAN)

In p-block elements, the last electron enters the outermost p orbital. The number of p orbital is three and, therefore the maximum number of electrons that can be accommodated in a set of p-orbital is six. Consequently, there are six groups of p-block elements in the periodic table numbering from 13 to 18. Their valence shell electronic configuration is $ns^2 np^{1-6}$ (except for He). The inner core electronic configuration may however differ. The difference in inner core of elements greatly influences their physical properties (such as atomic and ionic radii, ionisation enthalpy etc) as well as chemical properties.

The maximum oxidation state shown by a p-block elements is equal to the total number of valence electrons. In addition to group oxidation state, p-block elements may show other oxidation states which normally, but not necessarily, differ from the total number of valence electrons by unit of two. The occurrence of oxidation states two unit less than the group oxidation states are sometime attributed to the inert pair effect.

General characteristics of p-block elements

1. Non-metals, and metalloids exist only in the p-block of the periodic table.
2. The non-metallic character of elements decreases down the group. The heaviest element in each p-block group is the most metallic in nature.
3. Non-metals have higher ionisation enthalpies and higher electronegativities than the metals. The compound formed by highly reactive non-metals with highly reactive metals all generally ionic because of large differences in their electronegativities.
4. Compounds formed between non-metals themselves are largely covalent in character because of small differences in their electronegativities.
5. The change of non-metallic to metallic character can be best illustrated by the nature of oxides they form. The non-metal oxides are acidic or neutral whereas metal oxides are basic in nature.

Anomalous properties of second period elements

The first member of p-block differs from the remaining members of their corresponding group in two major respects.

- a. Size - The first element has small size. The smaller size can affect other periodic properties.
- b. Absence of d orbitals

Eg : The first element in B forms $[BF_4]^-$ that Al can form $[AlF_6]^{3-}$. ie the covalency of first element is limited to four.

The combined effect of small size and absence of d-orbital influences the ability of these elements to form π -bonds.

Eg : $C = C$, $C \equiv C$, $N = O$, $C \equiv N$, $N \equiv N$. The heavier elements do form $p\pi - p\pi$ -bonds but this involves d-orbitals ($d\pi - d\pi$ or $p\pi - d\pi$).

The co-ordination number of heavier element is higher than the first element in the same oxidation state. For example, in +5 oxidation state both N and P form oxoanions like NO_3^- and PO_4^{3-} . Here the first element N is coordinated to 3 oxygen but heavier element P is co-ordinated to 4 oxygen atoms.

Occurrence of group 13 elements

Boron is a fairly rare element, mainly occur as orthoboric acid (H_3BO_3), borax ($Na_2B_4O_7 \cdot 10H_2O$), Kernite ($Na_2B_4O_7 \cdot 4H_2O$) and colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$). In India, borax occurs in Puga Valley (Ladakh) and Sambhar lake (Rajasthan). The abundance of boron in earth crust is 0.0001 % by mass.

There are two isotopic forms of boron $^{10}_5B$ (19%) and $^{11}_5B$ (81%). Aluminium is the most abundant metal and the third most abundant element in the earth's crust (8.3% by mass) after oxygen (45.5%) and silicon (27.7%). Bauxite ($Al_2O_3 \cdot 2H_2O$), Cryolite (Na_3AlF_6) are the important minerals of Al - In India, Al is found as mica $KAl_2(AlSi_3O_{10})(OH, F, Cl)_2$.

Anhydrous alumina (Al_2O_3) is also called corundum.

Al also present in Beryl ($Be_3Al_2Si_6O_{18}$). Highest concentration of Ga found in the rare mineral Germanite having the formula $Cu_{26}Fe_4Ge_4S_{32}$. It contain Ga, Zn, Mo, As and V as impurities.

Traces of In are found in the sulphide ore of zinc called sphalerite. All natural sphalerite contains concentration of various impurities. The most common cation impurities are In, Ge, Mn, Cd, Hg.

Thallium (Tl) are found in the sulphide ore of lead $[(Tl, Pb)_2 As_5S_9]$

1. Atomic properties

The outer electronic configuration of these elements is $ns^2 np^1$.

$_5B$ - $[He] 2s^2 2p^1$

$_{13}Al$ - $[Ne] 3s^2 3p^1$

$_{31}Ga$ - $[Ar] 3d^{10} 4s^2 4p^1$

$_{49}In$ - $[Kr] 4d^{10} 5s^2 5p^1$

$_{81}Tl$ - $[Xe] 4f^{14} 5d^{10} 6s^2 6p^1$

$_{113}Nh$ - $[Rn] 5f^{14} 6d^{10} 7s^2 7p^1$

The electronic configuration suggests that boron and aluminium have noble gas core, gallium and indium have noble gas plus 10 d-electrons. Thallium has noble gas plus 14f electrons plus 10-d electrons core.

Nihonium has atomic number 113 and atomic mass 286 g/mol. Nihonium is a synthetically

prepared radioactive element.

2. Atomic Radii

Property	Boron (B)	Aluminium (Al)	Gallium (Ga)	Indium (In)	Thallium (Tl)
Atomic radius/Pm	88	143	135	167	178

On moving from Al to Ga, atomic radius decreases. This is due to the poor shielding effect of d-orbitals in gallium. In the case of elements from Ga to Tl, atomic radius increases. This is due to the extent of inter electronic repulsions which is higher than the increased effective nuclear charge.

Order of atomic radii - $B < Ga < Al < In < Tl$

Ionic radii

Property	Boron (B)	Aluminium (Al)	Gallium (Ga)	Indium (In)	Thallium (Tl)
Ionic radius M^{3+} /Pm	27	53.5	62	80	88.5

On moving down the group, ionic radius in +3 state increases.

Property	Boron (B)	Aluminium (Al)	Gallium (Ga)	Indium (In)	Thallium (Tl)
Ionic radius M^{3+} /Pm	-	-	120	140	150

On moving down the group, ionic radius in +1 state increases. B and Al exhibit +3 state only.

3. Ionisation enthalpy

The first ionisation enthalpies of the elements of group 13 are lower than the corresponding elements of group 2. In group 2 the last electron present in s subshell but in group 13, the last electron present in p-orbital. On comparing s and p subshell, s subshell is more closer to the nucleus than p orbital. Hence more energy is required for the removal of s electron in group 2 element than that in the case of p-electron in group 13.

Property	Boron (B)	Aluminium (Al)	Gallium (Ga)	Indium (In)	Thallium (Tl)
Ionisation $\Delta_i H_1$	801	577	579	558	589
Enthalpy $\Delta_i H_2$	2427	1816	1979	1820	1971
(kJ / mol) $\Delta_i H_3$	3659	2744	2962	2704	2877

We are focussing only the first ionisation enthalpy values of group 13 elements. B has higher ionisation enthalpy because of its smaller size. The second highest ionisation enthalpy is observed in Tl because Tl involves maximum effective nuclear change due to the poor shielding effect of f-orbitals. The third highest value for Ga due to the poor shielding effect of 3d-orbitals. On comparing Al & In, Al has

smaller size than In. Therefore order of first ionisation enthalpy - $B > Tl > Ga > Al > In$.

4. Electronegativity

In the case of second period elements, the order of EN is

Li	Be	B	C	N	O	F
1	1.5	2	2.5	3	3.5	4

Property	B	Al	Ga	In	Tl
EN	2	1.5	1.6	1.7	1.8

On moving from B to Al, EN decreases because boron is a typical non-metal but aluminium is a metal. On moving from Al to Tl, EN increases due to the increase in effective nuclear charge.

5. Electropositivity

It is the ability of an element to donate more electrons.

Property	Boron (B)	Aluminium (Al)	Gallium (Ga)	Indium (In)	Thallium (Tl)
Ionisation $\Delta_i H_1$	801	577	579	558	589
Enthalpy $\Delta_i H_2$	2427	1816	1979	1820	1971
(kJ / mol) $\Delta_i H_3$	3659	2744	2962	2704	2877

The sum of first three ionisation enthalpy values of boron are equal to 6887 kJ/mol and that of aluminium is 5137 kJ/mol. Electropositivity is measured in terms of their reduction potential values.

Property	Boron (B)	Aluminium (Al)	Gallium (Ga)	Indium (In)	Thallium (Tl)
$E_{M^{3+}/M}^0$ in V		-1.66	-0.56	-0.34	1.26

B has reduction potential value in acidic and basic medium.

In acidic $B(OH)_3 \longrightarrow B$; $E_{M^{3+}/M}^0 = -0.89$

In basic $B(OH)_4^- \longrightarrow B$; $E_{M^{3+}/M}^0 = -1.61$

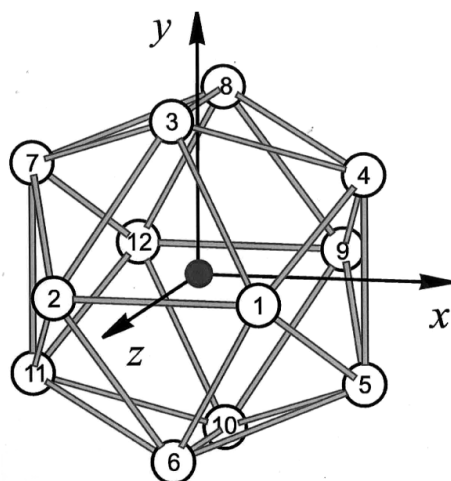
Order of electropositivity - $Tl < In < Ga < B < Al$

Physical properties**Melting point**

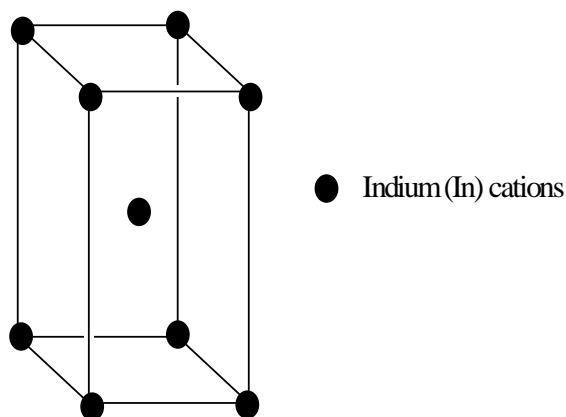
Property	Boron (B)	Aluminium (Al)	Gallium (Ga)	Indium (In)	Thallium (Tl)
Melting point in K	2453	933	303	430	576

The melting point decreases sharply on moving from B to Ga and then increases from Ga to Tl. Among the elements, Ga has the lowest melting point (303 K) and could exist as a liquid at room temperature in summer.

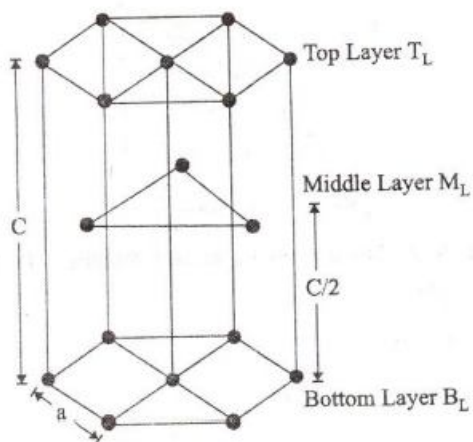
Boron has high melting point because its crystal structure consist of icosahedral units B atoms at all the 12 corners and it has 20 faces.

B₁₂ crystal structure

In has body centred tetragonal crystal system.



Tl has hexagonal close packed structure.



Order of melting point - B > Al > Tl > In > Ga

Boiling point

Property	Boron (B)	Aluminium (Al)	Gallium (Ga)	Indium (In)	Thallium (Tl)
Boiling point K	3923	2740	2676	2353	1730

On moving down the group, bp decreases. Gas has high boiling point due to greater cohesive forces. (Cohesive force is the attractive force operating between the same molecules). Due to these force, the molecules of Ga are sticking together and the metallic bonding become stronger.

Ga has lower melting point and high boiling point so that it is used in high temperature thermometer

Order of boiling point - B > Al > Ga > In > Tl

Density

Due to smaller atomic and ionic radii, the elements of group 13 have higher densities as compared to elements of group 2.

Property	Boron (B)	Aluminium (Al)	Gallium (Ga)	Indium (In)	Thallium (Tl)
Density/g/cm ³ at 298 K	2.35	2.7	5.9	7.31	11.85

On moving down the group, the densities increase. On moving down the group, atomic mass of element increases which outweighs the effect of increased atomic size.

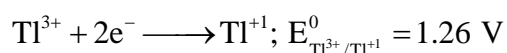
Order of density - B < Al < Ga < In < Tl

Chemical properties of group 13 elements

1. Oxidation state

Boron and Aluminium show an oxidation state of +3 only but Ga, In and Tl shows +3 and +1 due to inert pair effect. The relative stability of +1 state, increases in the order Ga < In < Tl

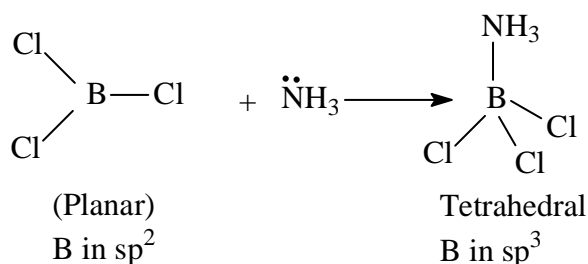
If Tl in +3 state, it can easily converted into +1 state.



Because of higher reduction potential, Tl can act as oxidant and it has high oxidising character and itself reduced.

In trivalent state, the no. of electrons around the central atom in a molecule of these elements will be only six and thus behave as electron deficient molecules.

In other words, they behave as Lewis acids (e^- pair acceptors)

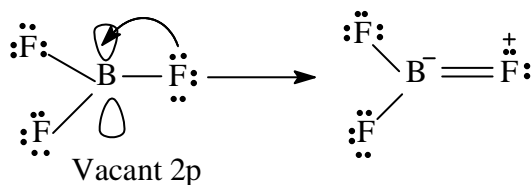


On moving down the group, Lewis acid behaviour decreases with increase in atomic size,



In boron halides, order of Lewis acid behaviour is $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3 < \text{BI}_3$

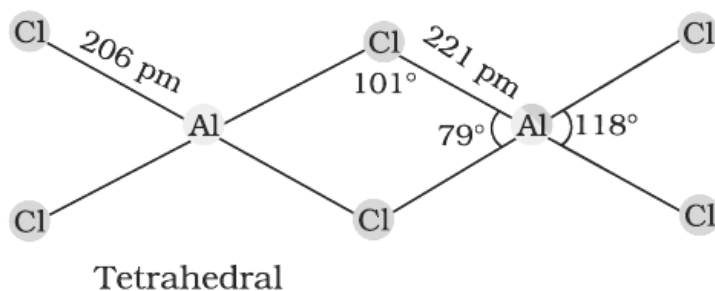
Reason : In BF_3 , F can donate a lone pair from its 2p orbital to the vacant 2p orbital of B, the energies of these two 2p orbitals are almost similar.



Due to this back bonding electron deficiency of B atoms gets compensated. In BCl_3 , BBr_3 and BI_3 , 3p of Cl, 4p of Br and 5p of I cannot overlap effectively with vacant 2p orbital of B.

The back bonding in BF_3 molecule also gets support from the fact that the observed B-F bond length in BF_3 is shorter than the normal B-F bondlength ($\text{B} = 0.80 \text{ \AA}$, $\text{F} = 0.72 \text{ \AA}$)

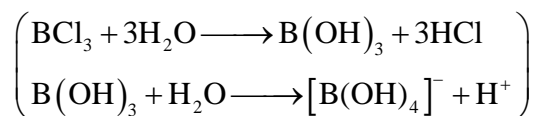
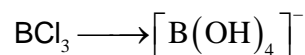
In trivalent state, AlCl_3 is also electron deficient but it exists as a dimer in the vapour state as well as in inert organic solvent such as benzene.



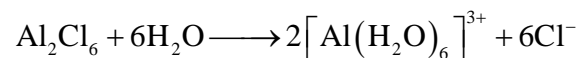
(Dimer structure of AlCl_3 exists in vapour state and at low temperature 473 K. At higher temperature it dissociates to trigonal planar AlCl_3 .)

In trivalent state, most of the compounds being covalent are hydrolysed by water to form either tetrahedral species or octahedral.

Due to small size and absence of d-orbital, B can form only tetrahedral complex during hydrolysis.



Al_2Cl_6 on hydrolysis gives octahedral $[\text{Al}_2(\text{H}_2\text{O})_6]^{3+}$



Hence Al_2Cl_6 is converted into $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$.

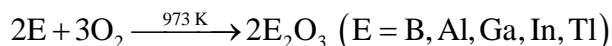
In $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, oxidation state of Al is +3.

During the addition of H_2O to Al_2Cl_6 , large amount of hydration enthalpy is released which overcomes the ionisation enthalpy of Al.

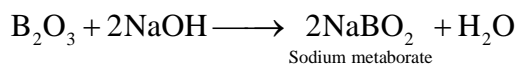
2. Reactivity towards air

Boron is unreactive in crystalline form. Al forms a very thin oxide layer on the surface which protects the metal from further attack.

Amorphous B and Al on heating in air forming B_2O_3 and Al_2O_3 respectively



Borontrioxide is acidic and it react with basic oxide forming metal borates.

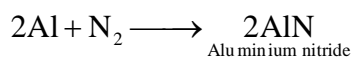
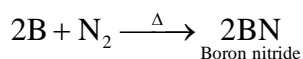


Al_2O_3 and Ga_2O_3 are amphoteric but In_2O_3 and Tl_2O_3 are basic oxide.

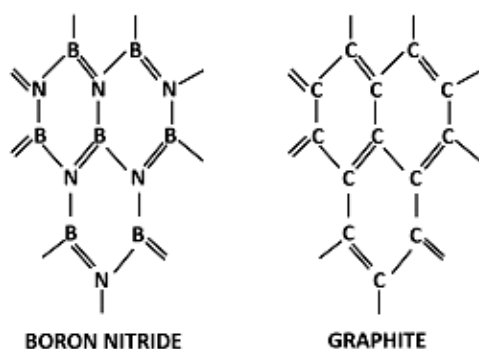
Along Tl_2O_3 , Tl can also form Tl_2O because of stable +1 state due to inert pair effect.

Reaction with N_2

In group 13, only B and Al react with N_2 at very high T.



Boron nitride has almost same structure as graphite consisting of sheets made up of hexagonal rings of alternate B and N atoms joined together. Because of the similarity, boron nitride is called inorganic graphite (white graphite or Borazon)

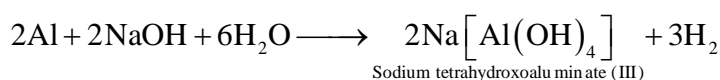
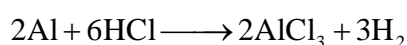


Reactivity towards acids and alkalies

Boron does not react with acids and alkalies even at moderate temperature. Boron does not react with non-oxidising acids such as HCl, but it is attacked at high temperature by strong oxidising agents.

(Mixture of conc. H_2SO_4 and conc. HNO_3 in 2 : 1) forming boric acids. $B + 3HNO_3 \longrightarrow H_3BO_3 + 3NO_2$.

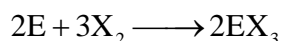
Aluminium dissolves in mineral acids and aqueous alkalies and thus show amphoteric character.



With conc.HNO₃, Al become passive due to the formation of a thin protective layer of its oxide (Al₂O₃) on the surface of metal which prevents it from further action

Reactivity towards halogens

Group 13 element react with halogens at high T forming trihalides of the general formula MX₃.



TII₃ exist as TI⁺¹ and I₃⁻

$\left(\overset{+1}{\text{TII}} + \text{I}_2^0 \longrightarrow \text{TII}_3 \right)$. Due to small size and high ionisation enthalpy, boron forms covalent trihalides.

BF₃ - gas, BCl₃ and BBr₃ - liquid, BI₃ - solid

Among boron halides, order of Lewis acid character - BI₃ > BBr₃ > BCl₃ > BF₃

Anomalous properties of B

Boron shows anomalous behaviour due to three reasons.

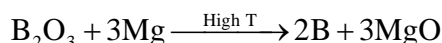
- Exceptionally small atomic and ionic radii
- High I.E.
- Absence of d-orbitals

The most important anomalous properties of boron are

1. Boron being small and it is harder than other elements of its group
2. It has higher melting and boiling point
3. Boron forms only covalent compounds while all other members form both ionic and covalent compounds.
4. Boron trihalides are covalent and they are hydrolysed by water. The hydrolysis product is always a tetrahedral species $\left[\text{B}(\text{OH})_4 \right]^-$.
5. The trihalides of B are monomeric being electron deficient and act as Lewis acids.

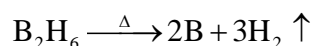
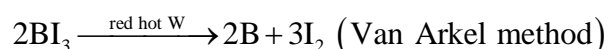
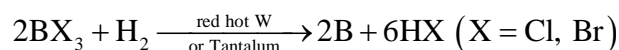
BORON

It is prepared by reduction of B₂O₃ with Mg, Na or K in the absence of air



The product is boiled with HCl and filtered when MgO dissolves leaving behind elemental boron. (95 – 98%). It contain impurities of metal borides.

Boron of highest purity (99.9%) is obtained by the following reactions.



Boron exist in 5 forms. Among them, four of which are crystalline and one is amorphous. Crystalline form are α – rhombohedral, β – rhombohedral, γ – orthorhombic, α – Tetragonal

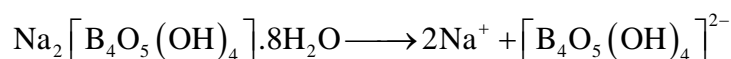
Amorphous form is finely divided powder. All crystalline forms are black in colour and chemically inert. But amorphous form is brown and chemically active.

Some important compounds of B

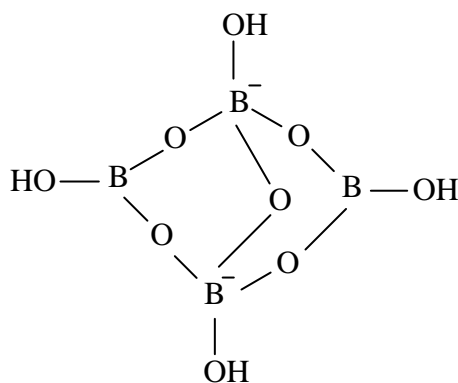
Borax

The chemical name is sodium tetraborate decahydrate having the formula $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$.

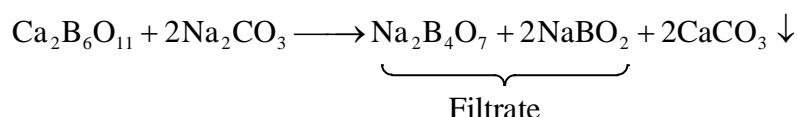
It can also be written as $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$.



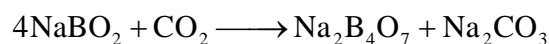
Borax consist of tetranuclear units.



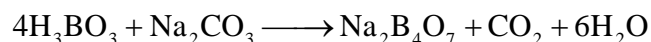
It is prepared from either colemanite or orthoboric acid.



The ppt CaCO_3 is removed by filtration and the filtrate is concentrated by heating and then cooling $\text{Na}_2\text{B}_4\text{O}_7$ crystals separate out. The filtrate contain NaBO_2 only.

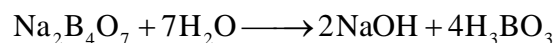


Orthoboric acid is treated with Na_2CO_3 , $\text{Na}_2\text{B}_4\text{O}_7$ is formed with brisk effervescence of CO_2 gas.

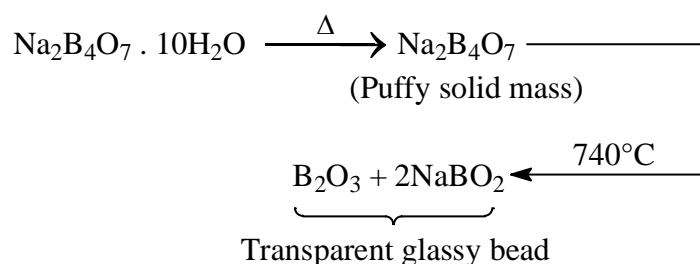


Properties of borax

1. Borax dissolves in water to give an alkaline solution.



2. Action of heat

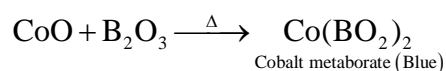
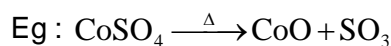


Transparent glassy bead is commonly called borax bead.

Application of borax bead

Borax bead is employed in qualitative analysis for the detection of certain coloured basic radicals such as Ni^{2+} , CO^{2+} , Cr^{3+} , Cu^{2+} etc.

When a metal salt contain certain metal ion is heated with borax bead on a Pt wire, the salt decomposes to form the corresponding metal oxide which then combine with B_2O_3 present in the glassy bead to form coloured metaborates. This test is called borax bead test.



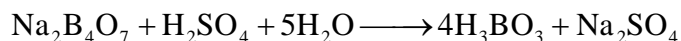
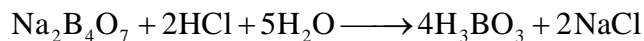
Metal	Co	Ni	Cr	Mn	Cu
Formula of metaborate	$\text{Co}(\text{BO}_2)_2$	$\text{Ni}(\text{BO}_2)_2$	$\text{Cr}(\text{BO}_2)_3$	$\text{Mn}(\text{BO}_2)_2$	$\text{Cu}(\text{BO}_2)_2$
Colour of metaborate	Blue	Brown	Green	Pink	Dark blue

Uses of Borax

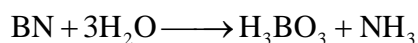
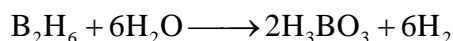
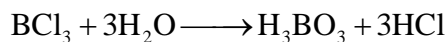
1. It is used in the manufacture of glazed tiles. The glazed surface is resistant to heat, stains and scratches.
2. It is used in the preparation of medicinal soap due to its antiseptic properties
3. It is used in the manufacture of heat resistant borosilicate glass (pyrex)

Ortho boric acid (H_3BO_3 or $\text{B}(\text{OH})_3$)

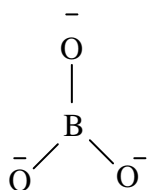
It is white crystalline solid with soapy touch. It is sparingly soluble in water but highly soluble in hot water. It is prepared by acidifying an aqueous solution of borax.



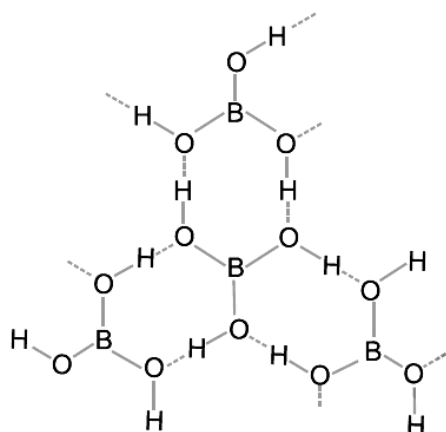
Boric acid is also prepared by the hydrolysis of halides, hydrides and nitrides of boron.

**Structure of boric acid**

In H_3BO_3 , B atom is sp^2 hybridised. The three sp^2 hybrid orbitals of B overlap with 3p orbital of O^- ion to form BO_3^{3-} units. BO_3^{3-} (borate ion) has trigonal planar structure.



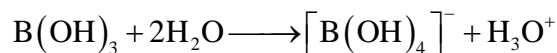
In boric acid, BO_3^{3-} units are associated through unbalanced hydrogen bond to give layered structure.



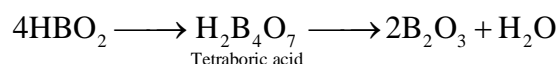
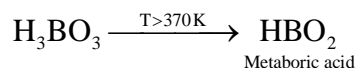
The adjacent layers in the crystal of boric acid are held together by weak forces of attraction. Because of weak forces of attraction, one layer can slide over the other. This makes boric acid soft and soapy to touch.

Properties of orthoboric acid

1. Boric acid act as weak monobasic acid.
2. It cannot act as protonic acid heat it act as Lewis acid by accepting pair of electrons from a hydroxyl ion in water.



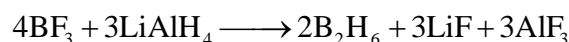
3. Action of heat

**Uses of boric acid**

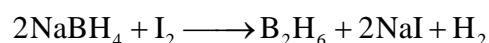
1. It is used in the manufacture of heat resistant borosilicate glass.
2. It is used as preservative for milk and food stuffs.
3. The aqueous solution of boric acid is used as mild antiseptic as eye wash under the name boric lotion.

Diborane

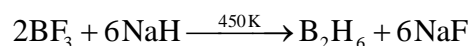
The simplest boron hydride known, is diborane. It is prepared by treating boron trifluoride with LiAlH_4 in diethyl ether.



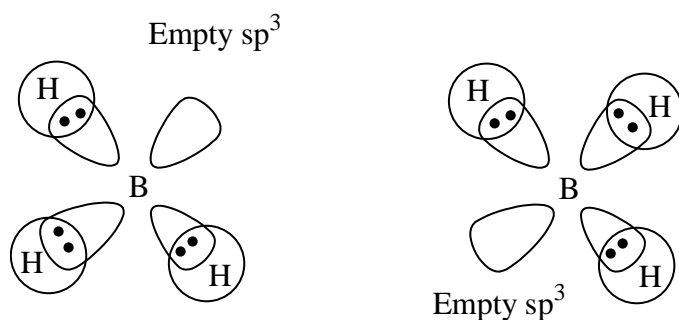
A convenient laboratory method for the preparation of diborane involves the oxidation of sodium borohydride with iodine.



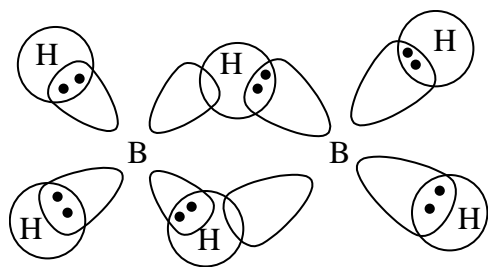
Diborane is produced on an industrial scale by the reaction of BF_3 with sodium hydride.

**Structure of diborane**

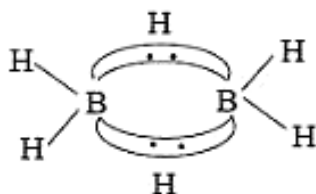
In B_2H_6 , the hybridisation of B is sp^3 . B_2H_6 can be written as $(\text{BH}_3)_2$. Boron in each BH_3 unit can form sp^3 hybrid orbitals. The three sp^3 hybrid orbital of each B overlap with 1s orbital of H atom to form 6 B–H bonds. The remaining one sp^3 hybrid orbital in each B have no electron (empty sp^3 hybrid orbital).



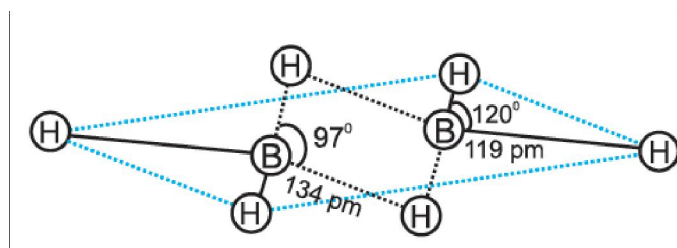
The empty sp^3 hybrid orbital in each B overlap again with the bridged H to form B–H–B 3 centre -2 electron bond.



In the two B–H–B bonds, the e pair is dispersed. As a result the bond pair acquire banana shape. Hence 2 B–H–B bonds are called banana bonds.



The entire structure with bond parameters can be represented as



B_2H_6 contain 12 electrons (6 electrons from 2 B atoms and the remaining 6 electrons from 6H atoms).

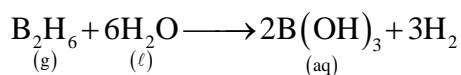
The two B atoms and the 4 terminal H atoms are lie in one plane. The two bridged H atoms lie above and below the plane of two B atoms. The four terminal B–H bonds are regular and they are 2 centre-2-electron bond. The two B–H–B bonds are irregular and they are 3-centre-2-electron bond. The two B–H–B bonds are also called banana bonds.

Properties of Diborane

1. It is colourless, highly toxic gas with boiling point of 180 K
2. Diborane burns in oxygen releasing enormous amount of energy



3. B_2H_6 readily hydrolysed by water to give boric acid



4. Diborane undergo symmetrical cleavage reactions with Lewis bases like $(\text{CH}_3)_3\text{N}$, CO to give borane adducts.

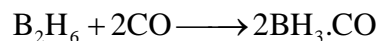
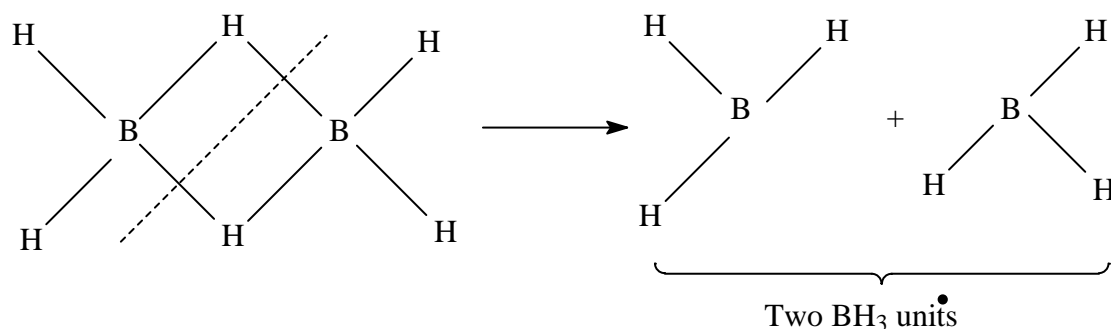
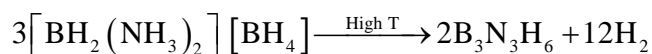
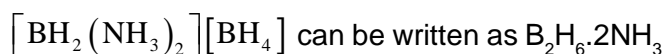
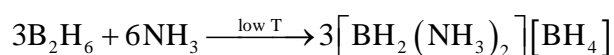
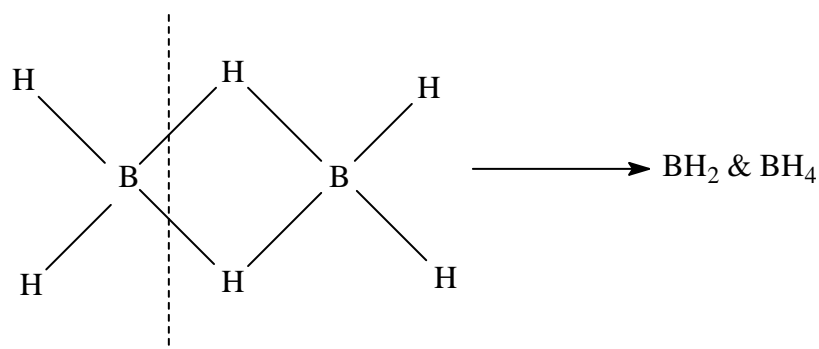


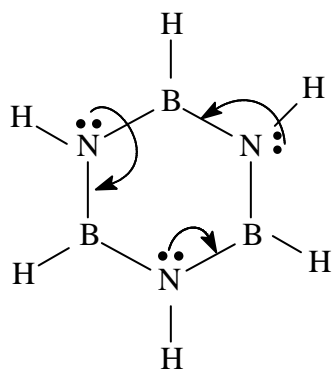
Figure of symmetrical cleavage



Diborane undergo unsymmetrical cleavage with NH_3 . The unsymmetrical cleavage represented as

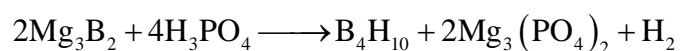


$\text{B}_3\text{N}_3\text{H}_6$ is called borazine or borazole. Borazine is isoelectronic (same no. of electrons) and isosteric (same no. of atoms) with benzene and its structure is similar to that of benzene except that in benzene, the π -electrons are completely delocalised but in borazine, they are only partially delocalised.

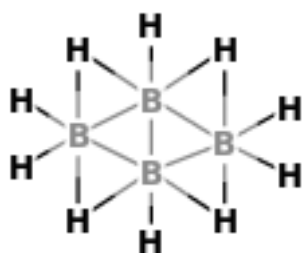


In both benzene and borazine, 30 electrons are present. Hence they are isoelectronic. Both benzene and borazine contain 12 atoms. Hence they are isosteric.

Tetraborane (B_4H_{10})



Structure of B_4H_{10}



In B_4O_{10} , there are 4 B–H–B 3 centre-2-electron bond, two BH_2 units, one B–B bond and two B–H bonds are present. Hence 22 electrons are present.

$$4 \text{ B–H–B bonds} \longrightarrow 4 \times 2 = 8$$

$$2 \text{ BH}_2 \text{ units} \longrightarrow 2 \times 4 = 8$$

$$1 \text{ B–B bond} \longrightarrow 1 \times 2 = 2$$

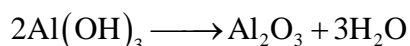
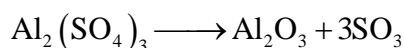
$$2 \text{ B–H bond} \longrightarrow 2 \times 2 = 4$$

22 electrons

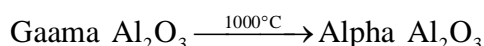
Some important compounds of Al**Aluminium oxide (Al₂O₃)**

1. It is the most stable compound of Al
2. It occurs in nature as colourless corundum and in the form of several coloured oxides like Ruby (red), Topaz (yellow), Sapphire (blue), Emerald (green).

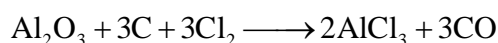
Pure Al₂O₃ is obtained by igniting Al₂(SO₄)₃, Al(OH)₃

**Properties**

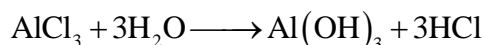
It is insoluble in water but soluble in acids as well as alkalies thus amphoteric in nature. It is a polar covalent compound exists in two forms - Alpha Al₂O₃ and gamma Al₂O₃.

**Aluminium chloride (AlCl₃)**

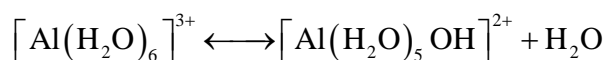
It is prepared by heating a mixture of Al₂O₃ and coke and passing chlorine over it.

**Properties**

1. When exposed to air, anhydrous AlCl₃ produces white fumes of HCl



2. When AlCl₃ is dissolved in water, it undergoes hydrolysis rapidly to produce Al(OH)₃ which is a weak base and HCl which is a strong acid. Hence the solution is acidic.

**Uses of boron, aluminium and their compounds**

1. Boron fibres have enormous tensile strength and hence it is used to make bullet-proof vests and light composite material for aircrafts.
2. The boron-10 isotope has ability to absorb neutrons and metal borides are used in nuclear industry as protective shields and control rods.
3. Borax and boric acid are used in the manufacture of heat resistant glass (pyrex) and fibre glass.
4. Borax is also used as flux in soldering of metals and used as a constituent of medicinal soap due to its antiseptic properties.
5. Borax is also used to manufacture glazed tiles, the glazed surface is resistant to heat, stains and scratches.
6. Borax is used to make peroxoborate an important cleansing and bleaching agent present in washing powders. They also act as brighteners since they absorb uv light and emit visible light.

7. Aluminium is used for making transmission cables for winding the moving coils of dynamo and motors.
8. It is used for making aluminium paint for protection of iron and zinc.
9. Aluminium resist corrosion so that it is used for making house hold utensils.
10. Aluminium forms alloy with Cu, Mn, Mg, Si and Zn

Eg : Al bronze (Al, Cu), Magnalium (Al, Mg), Duralumine (Al, Cu, Mg, Mn)

Group 14 elements - Carbon family

It includes carbon (C), Silicon (Si), Germanium (Ge), Tin (Sn), Lead (Pb) and Flerovium (Fl)

Carbon and silicon are non-metals, Germanium is metalloid. Sn and Pb are soft metals.

Occurrence of group 14 elements

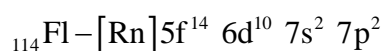
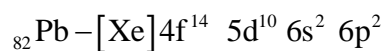
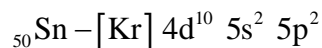
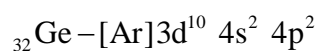
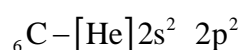
Carbon is the seventeenth most abundant element by mass in the earth's crust. It is widely distributed in nature in free as well as in the combined state. In elemental state it is available as coal, graphite and diamond, however, in combined state it is present as metal carbonates, hydrocarbons and carbon dioxide gas (0.03%) in air. Carbon is the most versatile element in the world. Its combination with other elements such as dihydrogen, dioxygen, chlorine and sulphur provides an astonishing array of materials ranging from living tissues to drugs and plastics. Organic chemistry is devoted to carbon containing compounds. It is an essential constituent of all living organisms. Naturally occurring carbon contains two stable isotopes. ^{12}C and ^{13}C . In addition to these, third isotope, ^{14}C is also present. It is a radioactive isotope with half-life 5770 years and used for radiocarbon dating. Silicon is the second (27.7% by mass) most abundant element on the earth's crust and is present in nature in the form of silica and silicates. Silicon is a very important component of ceramics, glass and cement. Germanium exists only in traces. Tin occurs mainly as cassiterite, SnO_2 and lead as galena, PbS .

Ultrapure form of germanium and silicon are used to make transistors and semiconductor devices.

Atomic and physical properties of group 14 elements

1. Electronic configuration

The valence shell electronic configuration is $ns^2 np^2$



The electronic configuration suggest that C and Si have noble gas core, Germanium and tin have noble gas plus 10-d electrons. Pb has noble gas plus 14 f electrons plus 10 d electron core.

Flerovium has atomic number 114 and atomic mass 289 g/mol.

2. Covalent radius

Property	C	Si	Ge	Sn	Pb
Covalent radius/pm	77	118	122	140	146

The covalent radii of group 14 elements are smaller than the corresponding elements of group 13 due to increase in effective nuclear charge.

On moving down the group, covalent radii increases due to the poor shielding effect of d and f orbitals.

Order of covalent radii - C < Si < Ge < Sn < Pb

3. Ionisation enthalpy

The first ionisation enthalpies of group 14 elements are higher than those of the corresponding group 13 elements.

Property		C	Si	Ge	Sn	Pb
Ionisation enthalpy in kJ/mol	$\Delta_i H_1$	1086	786	761	708	715
	$\Delta_i H_2$	2352	1577	1537	1411	1450
	$\Delta_i H_3$	4620	3228	3300	2942	3081
	$\Delta_i H_4$	6220	4354	4409	3929	4082

The first ionisation enthalpy decreases steadily on moving down the group from carbon to tin. The decrease is very sharp from carbon to silicon while there is a slight increase in lead as compared to that of tin.

The decrease in ionisation enthalpy from C to Sn is due to increase in atomic size and screening effect of inner electrons which outweigh the effect of increased nuclear charge. A small increase in ionisation enthalpy from Sn to Pb is due to the increased nuclear charge which outweighs the shielding effect due to the presence of additional 4f and 5d electrons.

Order of first ionisation enthalpy - C > Si > Ge > Pb > Sn

4. Electronegativity

The elements of group 14 are more electronegative than group 13 elements because of smaller size.

Property	C	Si	Ge	Sn	Pb
EN	2.5	1.8	1.8	1.8	1.9

Due to small size, group 14 elements are slightly more electronegative than group 13 elements. The electronegativity values for elements from Si to Pb are almost the same.

Physical properties

All the elements of group 14 are solids.

Melting point

Property	C	Si	Ge	Sn	Pb
Melting point K	4373	1693	1218	505	600

Among the elements, Tin has low mp because tin forming distorted 12 co-ordinated structure. Lead has face centred cubic structure. Order of mp - C > Si > Ge > Pb > Sn

Boiling point

Property	C	Si	Ge	Sn	Pb
Boiling point/ K	-	3550	3123	2896	2024

On moving down the group, boiling point decreases.

Order of b.p. - Si > Ge > Sn > Pb

The melting and boiling point of group 14 elements are much higher than those of the corresponding elements of group 13

Density

Property	C	Si	Ge	Sn	Pb
Density g/cm ³	* 3.51	2.34	5.32	7.26	11.34

* represents the density of diamond (allotropic form of carbon)

If graphite, its density is 2.22 g/cm³

On moving down the group, atomic mass increases which outweigh increase in atomic size.

Order of density - Si < C_{diamond} < Ge < Sn < Pb

Order of density - C_{graphite} < Si < Ge < Sn < Pb

Chemical properties of group 14 elements**Oxidation state**

The group 14 elements have 4 electrons in their outermost shell. The common oxidation state exhibited by these elements are +4 and +2. Carbon also exhibits negative oxidation states.

Eg-1 : In Be_2C , oxidation state of C is -4 (C^{4-})

Eg-2 : In CaC_2 , oxidation state of C is -1 (C_2^{2-})

The C^{4+} ion does not exist because the sum of first four ionisation enthalpy values are very high. So that it is not usually available in chemical reactions. Therefore carbon can form covalent compounds.

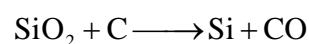
Carbon and silicon show +4 oxidation state. Germanium forms stable compound in +4 state and only few compounds in +2 state. Tin forms compounds in both +2 and +4 state. Tin in +2 state act as reducing agent. Lead compounds in +2 state are more stable and in +4 state it act as oxidising agent.

Reactivity towards oxygen

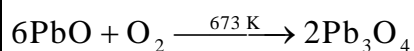
All the elements of group 14 when heated in oxygen form oxides. Two types of oxides are formed - monoxide and dioxide.

Monoxide	Dioxide
CO	CO_2
SiO	SiO_2
GeO	GeO_2
SnO	SnO_2
PbO	PbO_2

SiO exist only at high temperature



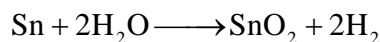
Besides monoxide and dioxide, lead also form another oxide called trilead tetroxide or red lead or sindhur (Pb_3O_4). It is obtained by heating PbO (litharge) with excess of air or O_2 at 673 K.



CO \longrightarrow neutral	CO_2	} Acidic
SiO	SiO_2	
GeO \longrightarrow acidic	GeO_2	
SnO \longrightarrow amphoteric	SnO_2	} Amphoteric
PbO \longrightarrow amphoteric	PbO_2	

Reactivity towards water

C, Si and Ge are not affected by water at all. Tin decomposes steam to form tin dioxide and dihydrogen gas.



Lead is unaffected by water, probably because of a protective oxide film formation.

Reactivity towards halogens

Group 14 elements form two types of halides of the formula MX_4 and MX_2 .

Except carbon, all the other members react directly with halogen to form their halides.

Tetrahalides

All the elements of group 14 form tetrahalides of the formula MX_4

Most of the tetrahalides are covalent in nature. The central atom is sp^3 hybridised and the molecule is tetrahedral in shape. SnF_4 and PbF_4 are ionic in nature.

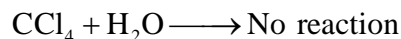
The thermal stability and ionic character of these halides decrease with the increasing atomic number or size of the halogen atom. PbCl_4 is stable, PbBr_4 is unstable while PbI_4 is unknown.

PbBr_4 is unstable due to the strong oxidising power of Pb^{4+} ion and weak reducing power of Br^- ion. The non-existence of PbI_4 related to the following reason.

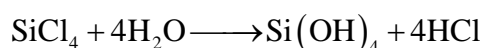
The Pb–I bond initially formed during the reaction does not release enough energy to unpair $6s^2$ electrons are unable to excite one of them to 6p orbital to have four unpaired electrons around lead atom.

Qn. CCl_4 is not hydrolysed by water but SiCl_4 can easily hydrolysed?

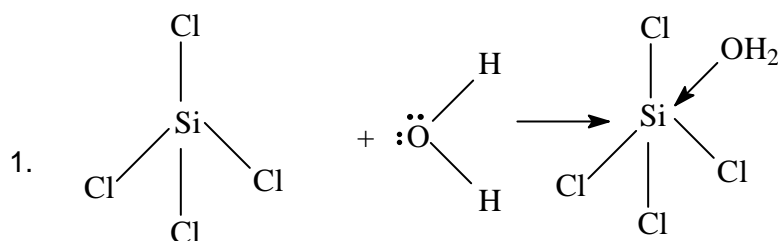
In CCl_4 , central atom is C, it has no d-orbital in the valence shell so that its covalency is limited to four. Hence it cannot expand its covalency for the accommodation of water molecules.

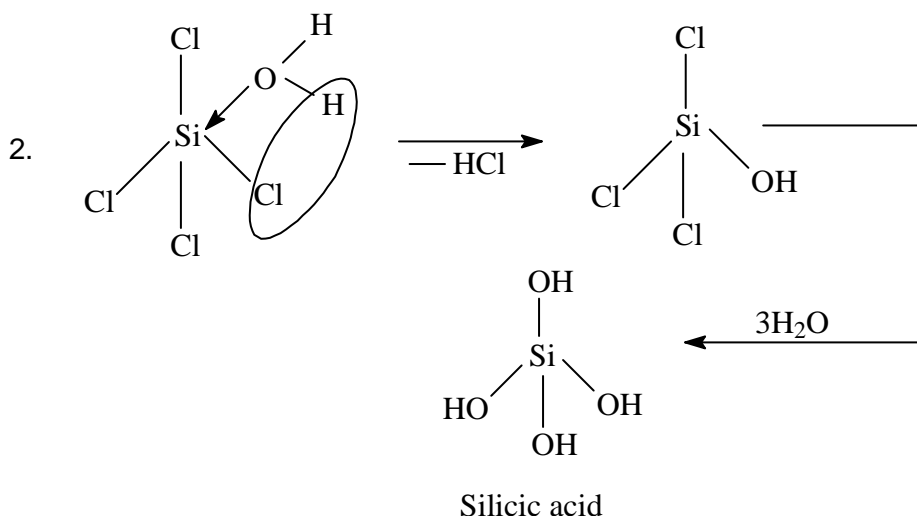


Silicon can expand its octet due to the availability of energetically suitable vacant d orbitals in its atom.

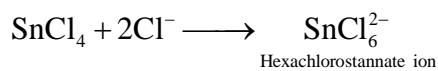
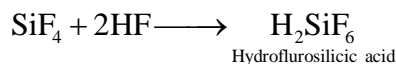


The mechanism of hydrolysis of SiCl_4 involves the following steps.



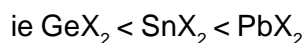


The tetrahalides of carbon do not form complexes due to the absence of d-orbitals in the valence shell. Tetrahalides of Ge, Sn, Pb behave as Lewis acids.



Dihalides

Except carbon and silicon, Ge, Sn, Pb form dihalides. The stability of dihalides increases steadily due to inert pair effect on moving down the group from Ge to Pb.



GeX_4 is more stable than GeX_2 but PbX_2 is more stable than PbX_4 .

Anomalous behaviour of carbon

Anomalous behaviour of carbon arises due to the following reasons.

- Exceptionally small atomic and ionic size
- Higher EN
- Higher I.E,
- Absence of d-orbitals in the valence shell

Carbon also has unique ability to form $p\pi - p\pi$ multiple bonds with itself and with other atoms of small size and high electronegativity. Few examples of multiple bonding are: $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$, $\text{C}=\text{O}$, $\text{C}=\text{S}$ and $\text{C}\equiv\text{N}$. Heavier elements do not form $p\pi - p\pi$ bonds because their atomic orbitals are too large and diffuse to have effective overlapping.

Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called catenation. This is because C—C bonds are very strong. Down the group the size increases and electronegativity decreases, and thereby, tendency to show catenation decreases. This can be clearly seen from bond enthalpies values. The order of catenation is $C \gg Si > Ge \approx Sn$. Lead does not show catenation.

Bond	Bond enthalpy / kJ mol^{-1}
C—C	348
Si—Si	297
Ge—Ge	260
Sn—Sn	240

Due to property of catenation and $p\pi - p\pi$ bond formation, carbon is able to show allotropic forms.

Allotropes of carbon

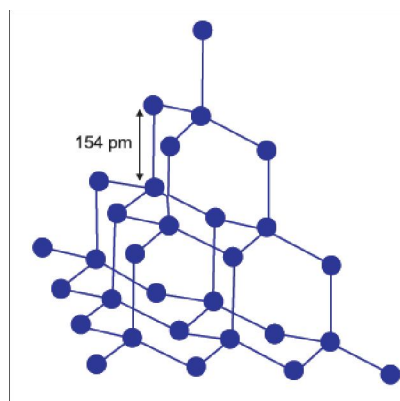
The phenomenon of existence of an element in two or more forms which have different physical properties but identical chemical properties is called allotropy and the different forms are called allotropes.

Carbon exists in two allotropic forms

1. Crystalline
2. Amorphous

The crystalline allotropic forms of carbon are graphite, diamond and fullerenes.

Diamond



In diamond, each carbon is tetrahedrally linked to four neighbouring carbon atoms through four strong C—C, sp^3-sp^3 sigma bonds. This network extends in three dimension and it is very rigid.

Properties of diamond

1. Diamond is the purest form of carbon
2. Because of sp^3 hybridisation, C—C bond length in diamond is 154 pm (1.54 \AA)
3. Diamond exist as three dimensional networks solid, it is the hardest substance known with high density and melting point.

4. All the electrons are firmly held in C–C sigma bonds, there are no free electrons in diamond crystal. Therefore diamond is a bad conductor of electricity.
5. Diamond can reflect and refract light therefore it is a transparent substance.
6. Diamond has the highest thermal conductivity (five times that of Cu) so that diamond tipped tools do not over heat and hence are extensively used for drilling and cutting purposes.

Diamond is a precious stone and it is measured in carat. Carat is the unit of measurement for the physical weight of diamond.

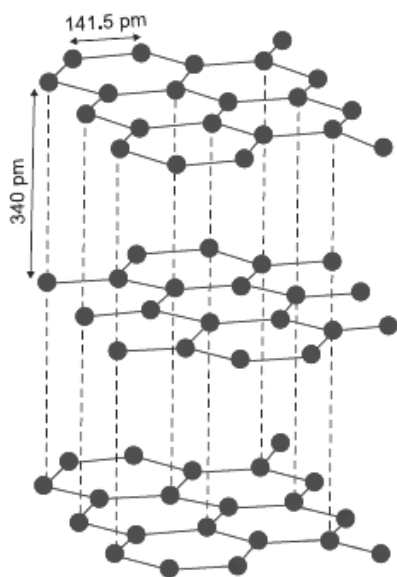
1 Carat diamond = 0.0002 kg = 0.2 g = 200 mg

Uses of diamond

1. Because of its hardness, diamond is used for cutting glass.
2. It is used as abrasive for sharpening hard tools.
3. It is used in the manufacture of W filament for electric light bulbs.

Graphite

It has 2D layered structure and layers are held together by Vander Waals forces with a layer distance of 340 pm. Each layer is composed of planar hexagonal ring with C–C bond length 141.5 pm.

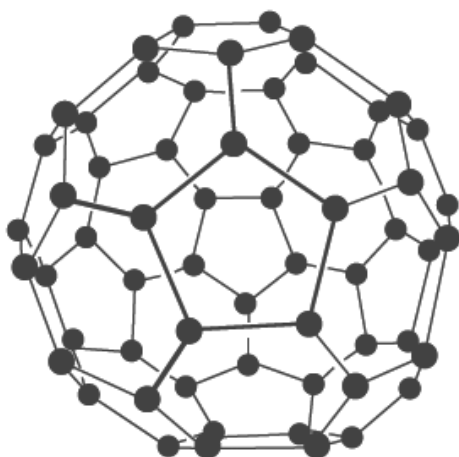


Each carbon is sp^2 hybridised and makes three sigma bonds with three neighbouring carbon atoms. Fourth electron form a pi bond which are delocalised over the whole sheet and are mobile. Hence graphite conduct electricity along the sheet. It cleaves easily between the layers, hence soft and slippery. For this reason, graphite is used as dry lubricant in machines running at high T.

Fullerenes

Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gases such as helium or argon. The sooty material formed by condensation of vapourised C^n small 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. Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds. Fullerenes are cage like molecules. C_{60} molecule has a shape like soccer ball and called Buckminsterfullerene.

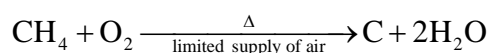
It contains twenty six-membered rings and twelve five-membered rings. A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings. All the carbon atoms are equal and they undergo sp^2 hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon is delocalised in molecular orbitals, which in turn give aromatic character to molecule. This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C–C distances are 143.5 pm and 138.3 pm respectively. Spherical fullerenes are also called bucky balls in short.



The structure of C_{60} , Buckminster-fullerene :
Note that molecule has the shape of a soccer ball (football)

Amorphous allotropic forms of carbon are coke, carbon black and charcoal.

Carbon black is obtained by burning hydrocarbons in a limited supply of air. Charcoal and coke are obtained by heating wood or coal respectively at high T in the absence of air. Carbon black is also called lamp black and prepared by the following method.



Uses of carbon

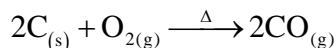
Graphite fibres embedded in plastic material form high strength, lightweight composites. The composites are used in products such as tennis rackets, fishing rods, aircrafts and canoes. Being good conductor, graphite is used for electrodes in batteries and industrial electrolysis. Crucibles made from graphite are inert to dilute acids and alkalis. Being highly porous, activated charcoal is used in adsorbing poisonous gases; also used in water filters to remove organic contamination and in airconditioning system to control odour. Carbon black is used as black pigment in black ink and as filler in automobile tyres. Coke is used as a fuel and largely as a reducing agent in metallurgy.

Some important compounds of carbon

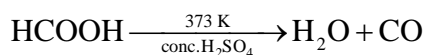
The important stable oxides of carbon are carbon monoxide and carbon dioxide. The less stable oxides are carbon suboxide (C_3O_2) and graphite oxides C_2O and C_2O_3 .

Carbon monoxide

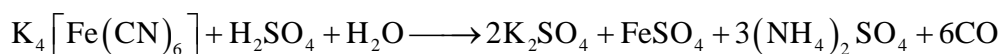
Direct oxidation of C in limited supply of oxygen or air yields carbon monoxide.



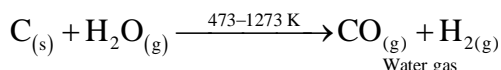
On small scale, pure CO is prepared by dehydration of formic acid with concentrated H_2SO_4 at 373 K.



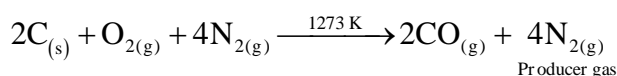
In the laboratory, CO is also prepared from potassium ferrocyanide on reacting with conc. H_2SO_4 .



On commercial scale it is prepared by the passage of steam over hot coke. The mixture of CO and H_2 thus produced is known as water gas or synthesis gas.



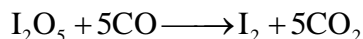
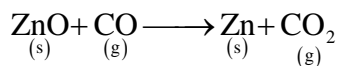
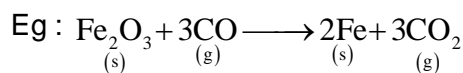
When air is used instead of steam, a mixture of CO and N_2 is produced, which is called producer gas.



Water gas and producer gas are very important industrial fuels. Carbon monoxide in water gas or producer gas can undergo further combustion forming carbon dioxide with the liberation of heat.

Properties

1. It is a colourless, odourless and almost insoluble in water.
2. It is a powerful reducing agent and reduces almost all metal oxides other than those of the alkali and alkaline earth metals, aluminium and a few transition metals.



In CO molecule, there are one sigma and two π bonds between carbon and oxygen :C = O: . Because of the presence of a lone pair on carbon, CO molecule acts as a donor and react with certain metals when heated to form metal carbonyls. The highly poisonous nature of CO arises because of its ability to form a complex with haemoglobin. Which is about 300 times more stable than the oxygen-haemoglobin complex. This prevents haemoglobin in the red blood corpuscles from carrying oxygen round the body and ultimately resulting in death.

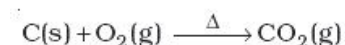
In CO both C and O are sp hybridised. The molecule is resonance stabilised.



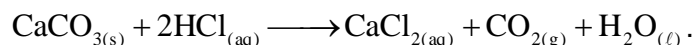
The carbon-oxygen bond length is 113 pm.

Carbon dioxide

It is prepared by complete combustion of carbon and carbon containing fuels in excess of air.

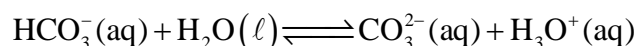
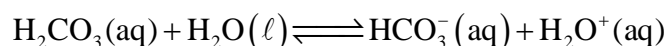


In the laboratory it is conveniently prepared by the action of dilute HCl on calcium carbonate.



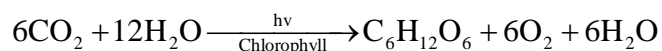
On commercial scale it is obtained by heating limestone.

It is a colourless and odourless gas. Its low solubility in water makes it of immense biochemical and geo-chemical importance. With water, it forms carbonic acid, H_2CO_3 which is a weak dibasic acid and dissociates in two steps:



$\text{H}_2\text{CO}_3 / \text{HCO}_3^-$ buffer system helps to maintain pH of blood between 7.26 to 7.42. Being acidic in nature, it combines with alkalis to form metal carbonates.

Carbon dioxide, which is normally present to the extent of –0.03% by volume in the atmosphere, is removed from it by the process known as photosynthesis. It is the process by which green plants convert atmospheric CO_2 into carbohydrates such as glucose. The overall chemical change can be expressed as:

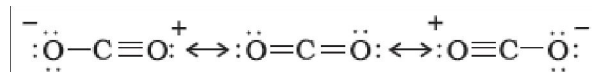


By this process plants make food for themselves as well as for animals and human beings. Unlike CO, it is not poisonous. But the increase in combustion of fossil fuels and decomposition of limestone for cement manufacture in recent years seem to increase the CO_2 content of the atmosphere. This may lead to increase in green house effect and thus, raise the temperature of the atmosphere which might have serious consequences.

Carbon dioxide can be obtained as a solid in the form of dry ice by allowing the liquefied CO_2 expand rapidly. Dry ice is used as a refrigerant for ice-cream and frozen food. Gaseous CO_2 is extensively used to carbonate soft drinks. Being heavy and non-supporter of combustion it is used as fire extinguisher. A substantial amount of CO_2 is used to manufacture urea.

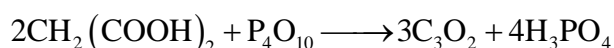


In CO_2 molecule carbon atom undergoes sp hybridisation. Two sp hybridised orbitals of carbon atom overlap with two p -orbitals of oxygen atoms to make two sigma bonds while other two electrons of carbon atom are involved in $p\pi - p\pi$ bonding with oxygen atom. This results in its linear shape [with both $\text{C}-\text{O}$ bonds of equal length (115 pm) with no dipole moment. The resonance structures are shown below.

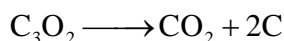


Carbon suboxide (C_3O_2)

It is an evil smelling gas and can be made by dehydrating propanedioic acid (malonic acid) with P_4O_{10} .



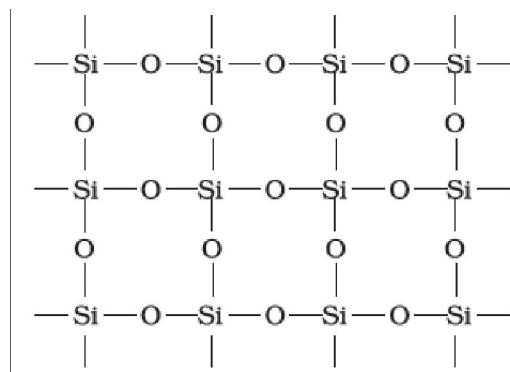
At 200°C it decomposes into CO_2 and C



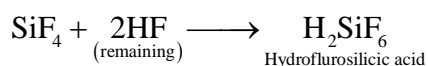
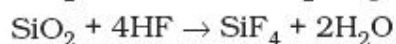
Some important compounds of silicon

Silicone dioxide, SiO_2

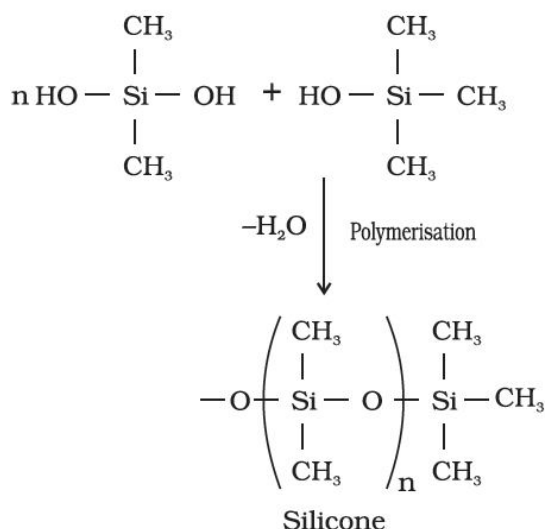
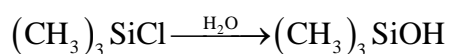
95% of the earth's crust is made up of silica and silicates. Silicon dioxide, commonly known as silica, occurs in several crystallographic forms. Quartz, cristobalite and tridymite are some of the crystalline forms of silica, and they are interconvertible at suitable temperature. Silicon dioxide is a covalent, three-dimensional network solid in which each silicon atom is covalently bonded to another silicon in a tetrahedral manner to four oxygen atoms. Each corner is shared with another tetrahedron. The entire crystal may be considered as giant molecule in which eight membered rings are formed with alternate silicon and oxygen atoms.



Silica in its normal form is almost non-reactive because of very high $\text{Si}-\text{O}$ bond enthalpy. It resists the attack by halogens, dihydrogen and most of the acids and metals even at elevated temperatures. However, it is attacked by HF and NaOH .



The chain length of the polymer can be controlled by adding $(\text{CH}_3)_3\text{SiCl}$ which blocks the ends as shown below.



Uses of silicones

1. For making water proof papers, wool, textiles, wool etc by coating them with a thin film of silicone
2. Being biocompatible, they are used in surgical and cosmetic implants. Eg : Plastic surgery.
3. It is used as sealants (material used for sealing something so as to make it airtight or watertight) and electrical insulators.

Silicates

Binary compound of silicon with oxygen are called silicates but they contain different metals in their structure. Since the EN difference between Si and O is about 1.7 so Si–O bond can be considered as 50% ionic and 50% covalent.

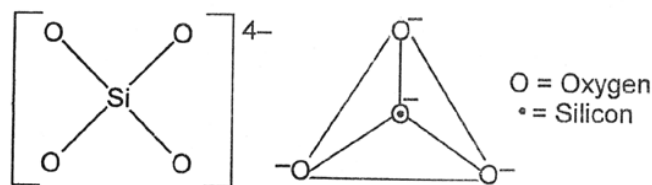
The basic structural unit of silicate is SiO_4^{4-} tetrahedral unit in which each Si is bonded to four oxygen atoms in tetrahedral fashion. SiO_4^{4-} units may exist as discrete units or may polymerise into larger units by sharing 1, 2, 3 or 4 oxygen atoms per silicate units. When silicate units are linked together they form chain, ring, sheet or three dimensional structures. Negative charge on silicate structure is neutralised by positively charged metal ions..

Two important non made silicates are glass and cement.

CLASSIFICATION OF SILICATES:

A. Orthosilicates:

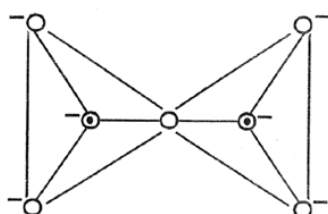
These contain discrete $[\text{SiO}_4]^{4-}$ units i.e., there is no sharing of corners with one another as shown is figure.



Eg: Zircon (ZrSiO_4), Forsterite of Olivine (Mg_2SiO_4), Willemite (Zn_2SiO_4), Phenacite Be_2SiO_4

B. Pyrosilicate:

In these silicates two tetrahedral units are joined by sharing oxygen at one corner thereby giving $[\text{Si}_2\text{O}_7]^{6-}$ units. There is no charge on shared oxygen atom.



e.g. Thortveitite ($\text{Sc}_2\text{Si}_2\text{O}_7$), Hemimorphite ($\text{Zn}_3(\text{Si}_2\text{O}_7)\text{Zn}(\text{OH})_2\text{H}_2\text{O}$)

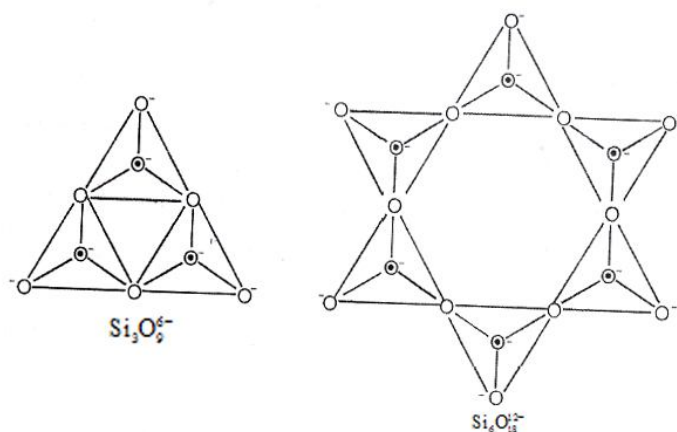
(-) charge will be present on the oxygen atoms which is bonded with one Si atom.

C. Cyclic silicates:

If two oxygen atoms per tetrahedron are shared to form closed rings such that the structure with general formula $(\text{SiO}_3)^{2-}$ or $(\text{SiO}_3)_n^{2n-}$ is obtained, the silicates containing these anions are called cyclic silicates. $\text{Si}_3\text{O}_9^{6-}$ and $\text{Si}_6\text{O}_{18}^{12-}$ anions are the typical examples of cyclic silicates.

Benitoite $\text{BaTi}(\text{Si}_3\text{O}_9)$

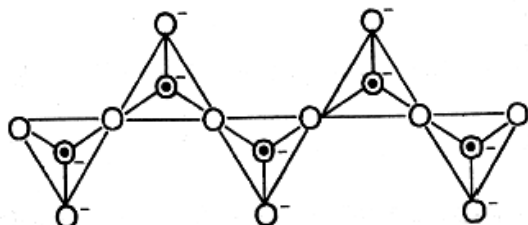
Beryl : $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$



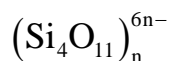
D. Chain silicates:

Chain silicates may be further classified into simple chain and double chain compounds. In case of simple chains two corners of each tetrahedron are shared and they form a long chain of tetrahedron.

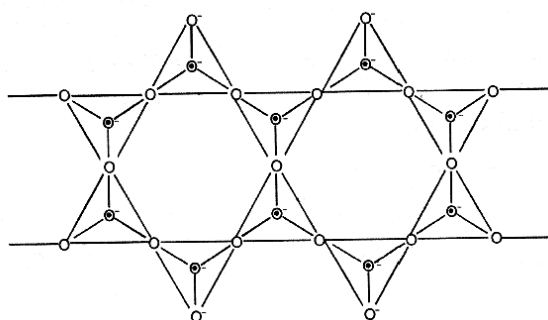
Their general formula is also same as the cyclic silicates i.e. $(\text{SiO}_3)_n^{2n-}$



Similarly, double chain silicates can be drawn in which two simple chains are joined together by shared oxygen. Such compounds are also known as amphiboles. The asbestos mineral is a well known example of double chain silicates. The anions of double chain silicates have general formula



Tremolite $\text{Ca}_2\text{Mg}_5[(\text{Si}_4\text{O}_{11})_2](\text{OH})_2$



Eg: Synthetic silicates (Li_2SiO_3 , Na_2SiO_3), Tremolite ($\text{Ca}_2\text{Mg}_5(\text{Si}_4\text{O}_{11})_2(\text{OH})_2$), etc.

E. Two dimensional sheet silicates:

In such silicates, three oxygen atoms of each tetrahedral are shared with adjacent SiO_4^{4-} tetrahedrals.

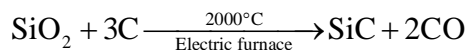
Such sharing forms two dimension sheet structure with general formula $(\text{Si}_2\text{O}_5)_n^{2n-}$

Eg: Talc ($\text{Mg}(\text{Si}_2\text{O}_5)_2\text{Mg}(\text{OH})_2$), Kaolin $\text{Al}_2(\text{OH})_4(\text{Si}_2\text{O}_5)$

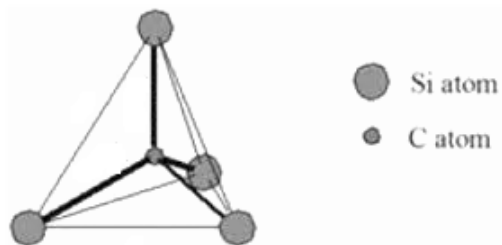
F. Three dimensional sheet silicates:

These silicates involve all four oxygen atom in sharing with adjacent SiO_4^{4-} , tetrahedral units.

Eg: Quartz, Tridymite, Cristobalite, Feldspar, Zeolite and Ultramarines.

Silicone carbide (SiC)

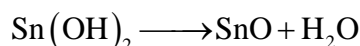
It is commonly called carborundum. It has diamond like structure in which each atom is sp^3 hybridised.

**Zeolites**

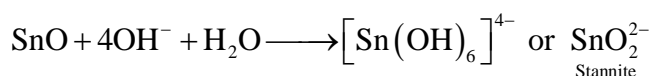
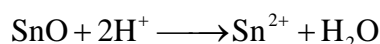
Zeolites are hydrated three dimensional aluminosilicates having Al–O–Si frame work. Here some Si^{4+} ions are replaced by Al^{3+} in AlO_4^{5-} to produce an extra negative charge. This is balanced by the presence of Na^+ , K^+ , Ca^{2+} cations. Zeolites are widely used as catalyst in petrochemical industries for cracking of hydrocarbons and isomerisation. Eg : ZSM-5 used to convert alcohols directly into gasoline. Hydrated zeolites are used as ion exchangers in softening of hard water.

Compounds of Tin**Stannous oxide (SnO)**

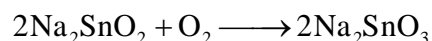
It is prepared by heating $\text{Sn}(\text{OH})_2$ in absence of air.



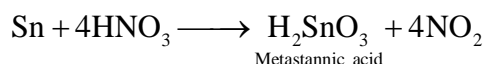
SnO is amphoteric dark grey or black solid oxide insoluble in water. It dissolves in acids to form stannous salt.

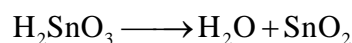


Stannites are only known in aqueous solution. Stannite absorbs oxygen from air and they are oxidised to stannate which are stable in nature.

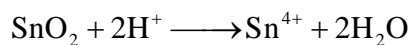
**Stannic oxide (SnO₂)**

It is prepared by heating tin with concentrated HNO_3

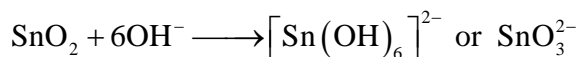




SnO_2 is amphoteric in nature. It dissolve in concentrated H_2SO_4 to form stannic sulphate

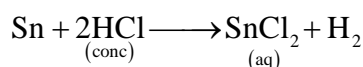


It dissolves in concentrated alkalies to form alkali metal stannate solution.



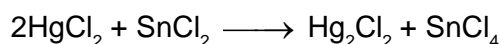
Stannous chloride

Preparation

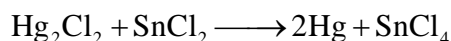


SnCl_2 is a stronger reducing agent

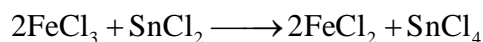
Eg-1 : It reduces HgCl_2 to Hg_2Cl_2



Eg-2 : It reduces Hg_2Cl_2 to Hg



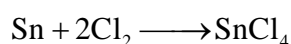
Eg-3 : It reduces FeCl_3 to FeCl_2



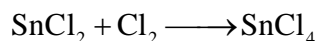
Stannic chloride (SnCl_4)

Preparation

1. By the action of Cl_2 gas on heated Sn

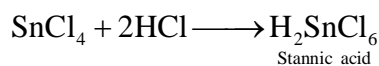
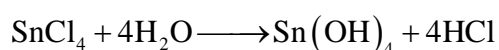


2. By the action of Cl_2 on stannous chloride



Properties

It absorbs moisture and becomes converted into hydrated stannic chlorides, $\text{SnCl}_4 \cdot 3\text{H}_2\text{O}$, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, $\text{SnCl}_4 \cdot 6\text{H}_2\text{O}$ and $\text{SnCl}_4 \cdot 8\text{H}_2\text{O}$, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ is known as buffer of tin. It can also be represented as $[\text{Sn}(\text{H}_2\text{O})_2\text{Cl}_4] \cdot 3\text{H}_2\text{O}$. SnCl_4 hydrolyses in dilute solution but it is incomplete and can be repressed in presence of halogen acid.

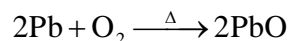


Compounds of Lead (PbO)

It exist in two forms

1. A yellow powder commonly known as massicot
2. A buff coloured crystalline form known as litharge

PbO is prepared by heating Pb in O₂ at 180°C. It is a yellow organic solid



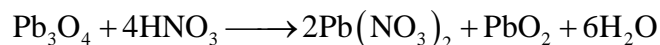
It is an amphoteric oxide and dissolves in acids as well as alkalies.

Litharge is alpha lead monoxide, a toxic solid formed from the oxidation of lead in air and used as a pigment. Litharge has tetragonal crystal structure and it has red or reddish orange colour. Massicot is beta lead monoxide has an yellow colour and it has orthorhombic crystal structure. Litharge is stable below 448°C but massicot is stable above 448°C

Red lead (Pb₃O₄) (minium or sindhur)

It is prepared by heating litharge of 450°C for a long time $6\text{PbO} + \text{O}_2 \longrightarrow 2\text{Pb}_3\text{O}_4$

It is red powder insoluble in water but when heated with concentrated HNO₃, it gives a red precipitate of PbO₂.

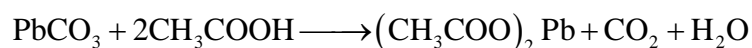
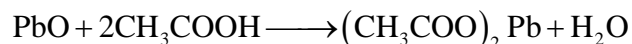


This indicate that Pb₃O₄ is a mixture of PbO and PbO₂

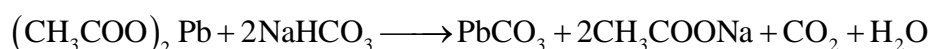
It is used for making protecting paints like red oxide paint for making special lead cement

Lead acetate (Sugar of lead)

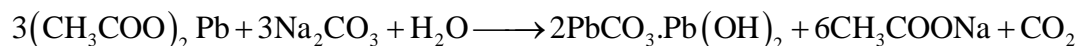
It is obtained by dissolving lead oxide or lead carbonate in acetic acid.

**Properties**

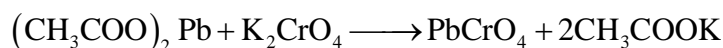
1. It is a white crystalline solid, soluble in water. Its solution has sweet taste and known as sugar of lead but it is poisonous in nature.
2. It gives white ppt. of lead carbonate on reaction with sodium bicarbonate.



3. It gives a white ppt: of basic lead carbonate with a solution of sodium carbonate



4. It gives a yellow precipitate of lead chromate with potassium chromate solution.



Chrome yellow (PbCrO_4)

It is obtained by adding potassium chromate to lead acetate. It is used as yellow pigment under the name chrome yellow. On treatment with NaOH, it gives basic lead chromate PbCrO_4 . PbO known as chrome red.

Hydrides of group 14 elements

All the elements form tetravalent, covalent hydrides of the molecular formula MH_4 .

Carbon forms a large number of hydrides cyclic and acyclic ie $\text{C}_n\text{H}_{2n+2}$, $\text{C}_n\text{H}_{2n-2}$ and aromatic hydrocarbons.

Silicon forms volatile hydrides called silanes.

Eg: SiH_{2n+2} where n is less than 8

If $n = 1$ it is SiH_4 (Silane)

If $n = 2$ it is Si_2H_6 (Disilane)

Germanium forms hydrides called germanes GeH_{2n+2} where $n < 5$

Eg: If $n = 1$ it is GeH_4 (Germane)

If $n = 2$ it is Ge_2H_6 (Digermane)

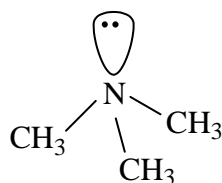
If $n = 3$ it is Ge_3H_8 (Trigermane)

Tin forms only two hydrides, stannane, SnH_4 and distannane Sn_2H_6 . Lead form only one hydride known as plumbane PbH_4 .

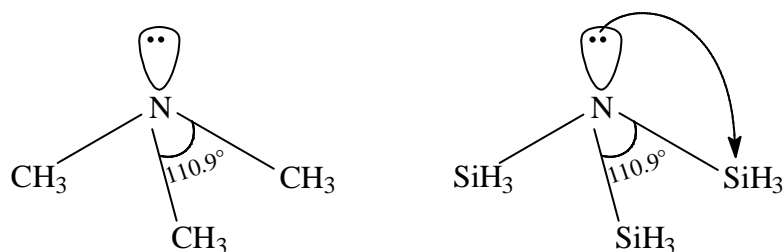
The thermal stability of hydrides decreases in the order : $\text{CH}_4 > \text{SiH}_4 > \text{GeH}_4 > \text{SnH}_4 > \text{PbH}_4$

Additional information

- Carbon does not have d orbitals and hence it does not form $d\pi - p\pi$ multiple bond. Silicon and other heavier elements of this group can form $d\pi - p\pi$ bond due to the presence of vacant d orbitals. For example, in trimethyl amine $(\text{CH}_3)_3\ddot{\text{N}}$ both C and N are sp^3 hybridised and one of the hybrid orbital accommodate lone pair of nitrogen and the geometry is pyramidal.

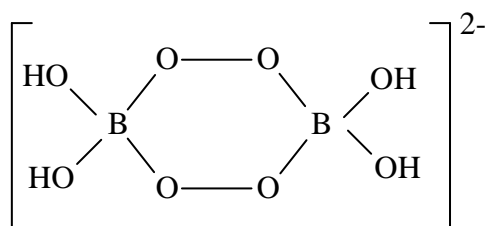
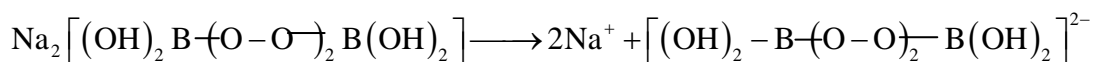
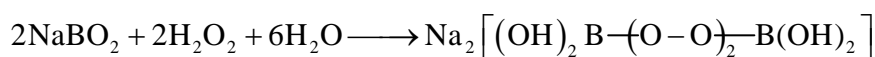


In trisilylamine $\text{N}(\text{CH}_3)_3$, N is sp^2 hybridised. Here, the lone pair of electron in 2p orbital of N overlap with an empty d orbital of Si to form $d\pi - p\pi$ bonds. As a result the hybridisation of N changes from sp^3 to sp^2 .

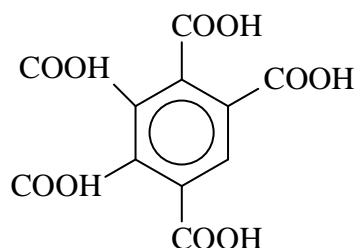


Due to the presence of $d\pi - p\pi$ bonding, the lone pair electron is transferred from nitrogen to silicon. As a result, $(\text{SiH}_3)_3\text{N}$ is a weaker base than $(\text{CH}_3)_3\text{N}$.

2. Sodiumperoxoborate is a brightner in washing powder (absorb uv and emit visible light). It can be prepared by the oxidation of sodium metaborate with H_2O_2 .



3. Diamond is unaffected by concentrated acid but graphite changes to mellitic acid having the formula $\text{C}_6(\text{COOH})_6$ (Benzene hexacarboxylic acid)



4. Reaction of diborane with ammonia at different conditions

