

The p-Block Elements : Boron and carbon family

- In p-block elements the last electron enters the outermost p-orbital.
- As we know that the number of p orbitals is three and, therefore, the maximum number of electrons that can be accommodated in a set of p orbitals is six. Consequently there are six groups of p-block elements in the periodic table numbering from 13 to 18.

General Electronic configuration and Oxidation states of p-Block Elements

Group	13	14	15	16	17	18
General Electronic configuration	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6 ($1s^2$ for He)
First number of group	B	C	N	O	F	He
Group oxidation state	+3	+4	+5	+6	+7	+8
Other oxidation states	+1	+2, -4	+3, -3	+4, +2, -2	+5, +3, +1, -1	+6, +4, +2

First member of p-block :

- The first member of p-block differs from the remaining members of their corresponding group in two major respects. First is the size and all other properties which depend on size.
- The presence of d-orbital influences the chemistry of the heavier elements in a number of other ways. The combined effect of size and availability of d orbitals considerably influences the ability of these elements to form π bonds. The first member of a group differs from the heavier members in its ability to form $p\pi - p\pi$ multiple bonds to itself (e.g., $C = C$, $C \equiv C$, $N \equiv N$) and to other second row elements (e.g., $C = O$, $C = N$, $C \equiv N$, $N = O$). This type of π – bonding is not particularly strong for the heavier p-block elements.
- The heavier elements do form π bonds but this involves d orbitals ($d\pi - p\pi$ or $d\pi - d\pi$). As the d orbitals are of higher energy than the p orbitals, they contribute less to the overall stability of molecules than does $p\pi - p\pi$ bonding of the second row elements. However, the coordination number in species of heavier elements may be higher than for the first element in the same oxidation state.

Inert Pair effect

In boron, carbon and nitrogen families the group oxidation state is the most stable state for the lighter elements in the group. However, the oxidation state two unit less than the group oxidation state becomes progressively more stable for the heavier elements in each group.

The occurrence of oxidation states two unit less than the group oxidation states are sometime attributed to the ‘inert pair effect’.

Stability of oxidation state : $\text{Bi}^{3+} > \text{Bi}^{+5}$
 $\text{Pb}^{+2} > \text{Pb}^{+4}$
 $\text{Tl}^{+1} > \text{Tl}^{+3}$

Relative stability of oxidation states in boron family : $\text{Al}^{+1} < \text{Ga}^{+1} < \text{In}^{+1} < \text{Tl}^{+1}$
 $\text{Al}^{+3} > \text{Ga}^{+3} > \text{In}^{+3} > \text{Tl}^{+3}$

Relative stability of oxidation states in Carbon family : $\text{C}^{+4} > \text{Si}^{+4} > \text{Ge}^{+4} > \text{Sn}^{+4} > \text{Pb}^{+4}$
 $\text{C}^{+2} < \text{Si}^{+2} < \text{Ge}^{+2} < \text{Sn}^{+2} < \text{Pb}^{+2}$

Q. How can you explain higher stability of BCl_3 as compared to TlCl_3 ? (NCERT Exercise)

Sol. BCl_3 is quite stable. Because there is absence of d- and f-electrons in boron three valence electrons ($2s^2 2p_x^1$) are there for bonding with chlorine atom. In Tl the valence s-electron ($6s^2$) are experiencing maximum inert pair effect. Thus, only $6p^1$ electron is available for bonding. Therefore, BCl_3 is stable but TlCl_3 is comparatively unstable.

Q. In some of the reactions thallium resembles aluminium, whereas in others it resembles with group 1 metals. Support this statement by giving some evidences. (NCERT Exercise)

Sol. Tl shows both the oxidation state +1 and +3 due to inert pair effect. Tl forms basic oxide like group- 1 elements. Tl_2O is basic as Na_2O .

Atomic Radii

- Generally as we move down in the group atomic size increases but here a deviation can be seen.
- Atomic radius of Ga is less than that of Al. This can be understood from the variation in the inner core of the electronic configuration. The presence of additional 10 d-electrons offer only poor screening effect (Unit 2) for the outer electrons from the increased nuclear charge in gallium. Consequently, the atomic radius of gallium (135 pm) is less than that of aluminium (143 pm).

Size : $\text{B} < \text{Al} > \text{Ga} < \text{In} < \text{Tl}$

Size : $\text{C} < \text{Si} < \text{Ge} < \text{Sn} < \text{Pb}$

Ionization Enthalpy :

$\text{B} > \text{Al} < \text{Ga} > \text{In} < \text{Tl}$

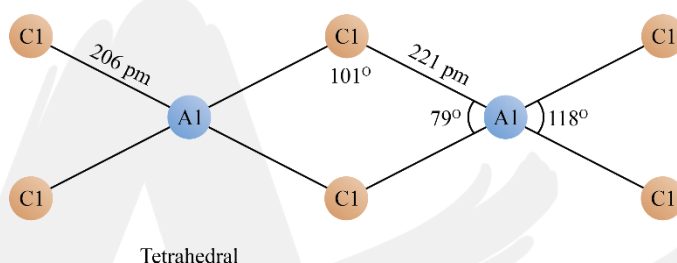
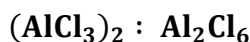
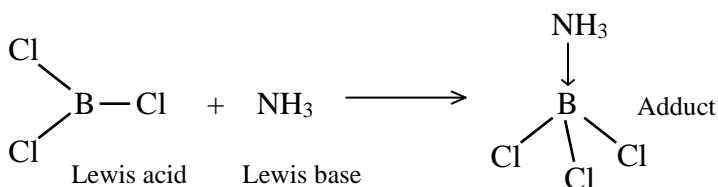
$\text{C} > \text{Si} > \text{Ge} > \text{Sn} < \text{Pb}$

Physical Properties :

- Boron is non-metallic in nature. It is extremely hard and black coloured solid. It exists in many allotropic forms. Due to very strong crystalline lattice, boron has unusually high melting point.
- Gallium with unusually low melting point (303K), could exist in liquid state during summer. Its high boiling point (2676 K) makes it a useful material for measuring high temperatures.

Electron deficient molecules

These molecules have tendency to accept a pair of electrons to achieve stable electronic configuration and thus, behave as Lewis acids.



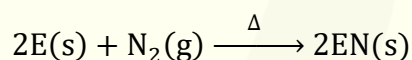
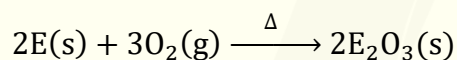
Q. Boron is unable to form BF_6^{3-} ion. Explain.

(NCERT Example)

Sol. Due to non-availability of d orbitals, boron is unable to expand its octet. Therefore, the maximum covalence of boron cannot exceed 4.

Reactivity towards air

Amorphous boron and aluminium metal on heating in air form B_2O_3 and Al_2O_3 respectively. With dinitrogen at high temperature they form nitrides.



(E = B, Al)

Q. White fumes appear around the bottle of anhydrous aluminium chloride. Give reason.

(NCERT Example)

Sol. Anhydrous aluminium chloride is partially hydrolysed with atmospheric moisture to liberate HCl gas. Moist HCl appears white in colour.

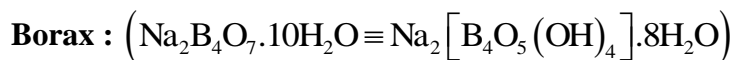
Aluminium

- Aluminium dissolves in dilute HCl and liberates dihydrogen.

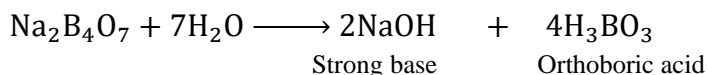
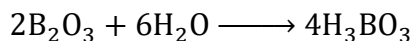
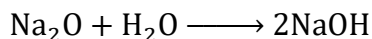
$$2\text{Al}(\text{s}) + 6\text{HCl}(\text{aq}) \longrightarrow 2\text{Al}^{3+}(\text{aq}) + 6\text{Cl}^{-}(\text{aq}) + 3\text{H}_2(\text{g})$$
- Concentrated nitric acid renders aluminium passive by forming a protective oxide layer on the surface.
- Aluminium also reacts with aqueous alkali and liberates dihydrogen.

$$2\text{Al}(\text{s}) + 2\text{NaOH}(\text{aq}) + 6\text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{Na}^{+}[\text{Al}(\text{OH})_4]^{-}(\text{aq}) + 3\text{H}_2(\text{g})$$

Sodium
tetrahydroxoaluminate (III)

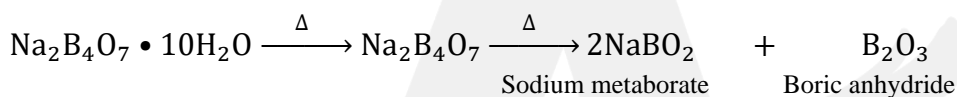


- Borax dissolve in water to give an alkaline solution. $(\text{Na}_2\text{B}_4\text{O}_7 \equiv \text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3)$

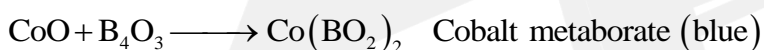
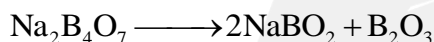


Borax Bead Test

- On heating, borax first loses water molecules and swells up. On further heating it turns into a transparent liquid, which solidifies into glass like material known as borax bead.

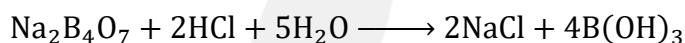


- The metaborates of many transition metals have characteristic colours and, therefore, borax bead test can be used to identify them in the laboratory. For example, when borax is heated in a Bunsen burner flame with CoO on a loop of platinum wire, a blue coloured $\text{Co}(\text{BO}_2)_2$ bead is formed.



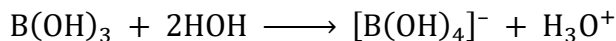
Orthoboric Acid

- Orthoboric acid, H_3BO_3 is a white crystalline solid, with soapy touch. It is sparingly soluble in water but highly soluble in hot water. It can be prepared by acidifying an aqueous solution of borax.

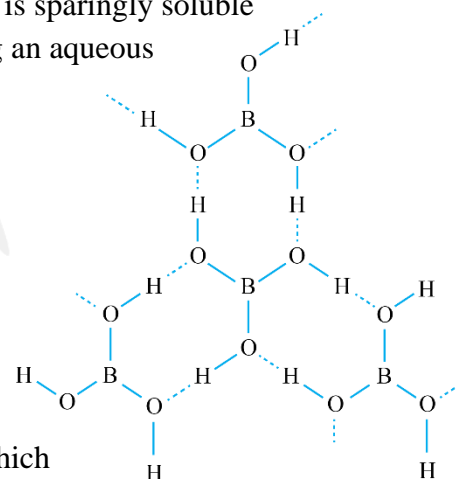


It has a layer structure in which planar BO_3 units are joined by hydrogen bonds.

- Boric acid is a weak monobasic acid. It is not a protonic acid but acts as a Lewis acid by accepting electrons from a hydroxyl ion:



- On heating, orthoboric acid above 370K forms metaboric acid, HBO_2 which on further heating yields boric oxide, B_2O_3 .



Structure of boric acid; the dotted lines represent hydrogen bonds

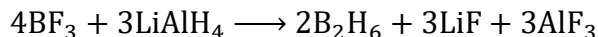
Q. Why is boric acid considered as a weak acid?

(NCERT Example)

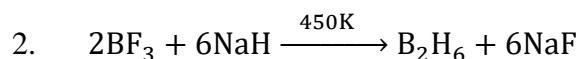
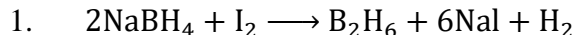
Sol. Because it is not able to release H^+ ions on its own. It receives OH^- ions from water molecule to complete its octet and in turn releases H^+ ions

Diborane, B₂H₆

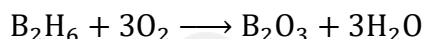
The simplest boron hydride known, is diborane. It is prepared by treating boron trifluoride with LiAlH₄ in diethyl ether.



Other methods :

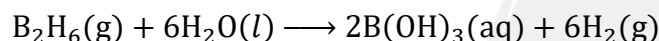


- It burns in oxygen releasing an enormous amount of energy.

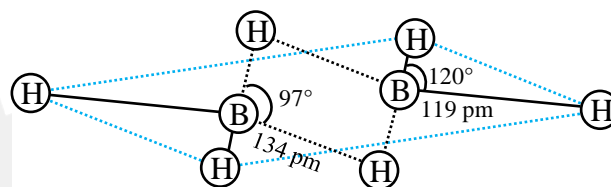


$$\Delta_c H^\ominus = -1976 \text{ kJ mol}^{-1}$$

- Boranes are readily hydrolysed by water to give boric acid.



Structure : The four terminal hydrogen atoms and the two boron atoms lie in one plane. Above and below this plane, there are two bridging hydrogen atoms. The four terminal B-H bonds are regular two centre-two electron bonds while the two bridge (B-H-B) bonds are different and can be described in terms of three centre two electron bonds.



- Boron also forms a series of hydridoborates; the most important one is the tetrahedral [BH₄]⁻ ion.



Q. Aluminium trifluoride is insoluble in anhydrous HF but dissolves on addition of NaF.

Aluminium trifluoride precipitates out of the resulting solution when gaseous BF₃ is bubbled through. Give reason. (NCERT Exercise)

Sol. Anhydrous HF is covalent compound and weak acid due to high bond dissociation energy. AlF₃ does not dissolve in HF.

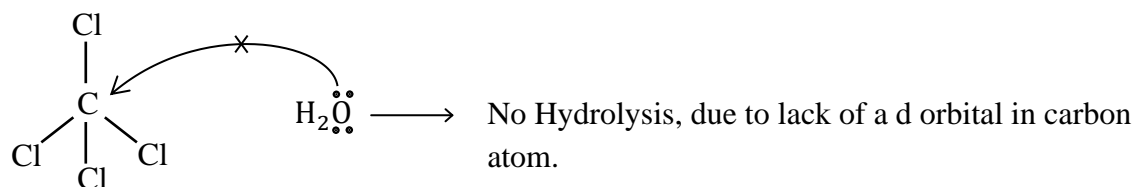
- Whereas NaF is ionic compound. $3\text{NaF} + \text{AlF}_3 \longrightarrow \text{Na}_3[\text{AlF}_6]$
- $\text{Na}_3[\text{AlF}_6] + 3\text{BF}_3(\text{g}) \longrightarrow \text{AlF}_3 + 3\text{Na}^+ [\text{BF}_4]^-$

Carbon Family

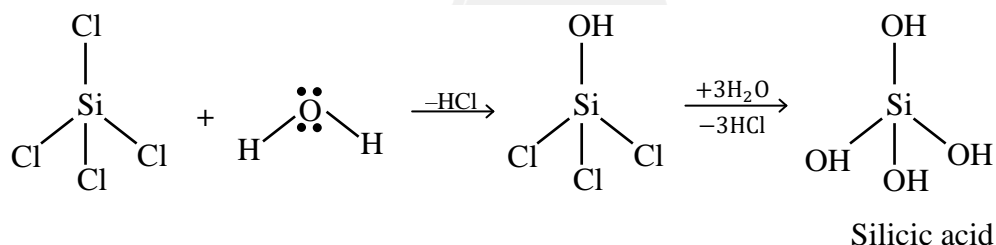
- Naturally occurring carbon contains two stable isotopes: ¹²C and ¹³C. In addition to these, third isotope, ¹⁴C is also present. It is a radioactive isotope.
- Silicon is the second (27.7 % by mass) most abundant element on the earth's crust and is present in nature in the form of silica and silicates.
- Ultrapure form of germanium and silicon are used to make transistors and semiconductor devices.
- All members of group 14 are solids.

Hydrolysis :

- Except CCl_4 , other tetrachlorides are easily hydrolysed by water because the central atom can accommodate the lone pair of electrons from oxygen atom of water molecule in d orbital.



- Hydrolysis can be understood by taking the example of SiCl_4 . It undergoes hydrolysis by initially accepting lone pair of electrons from water molecule in d orbitals of Si, finally leading to the formation of Si(OH)_4 as shown below :

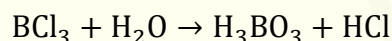


- Thermal & chemical stability : $\text{GeX}_4 > \text{GeX}_2$
: $\text{PbX}_2 > \text{PbX}_4$ (due to inert pair effect)

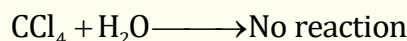
Q. Consider the compounds, BCl_3 , and CCl_4 . How will they behave with water justify?

(NCERT Exercise)

Sol. In BCl_3 , there is only six electrons in the valence shell of B atom. Thus, the octet is incomplete and it can accept a pair of electrons from water and hence BCl_3 undergoes hydrolysis.



Whereas, in CCl_4 , C atom has 8 electrons and its octet is complete. That's why it has no tendency to react with water.



Q. $[\text{SiF}_6]^{2-}$ is known whereas $[\text{SiCl}_6]^{2-}$ not. Give possible reasons.

(NCERT Example)

Sol. The main reasons are :

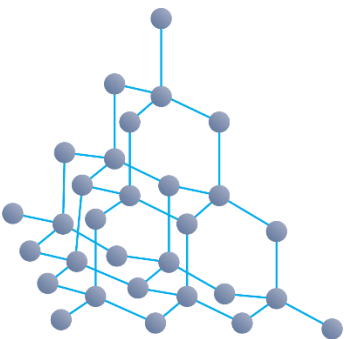
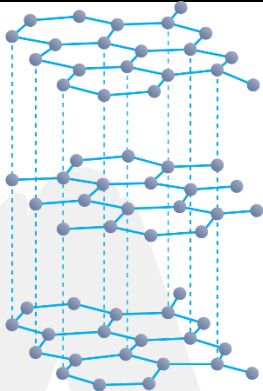
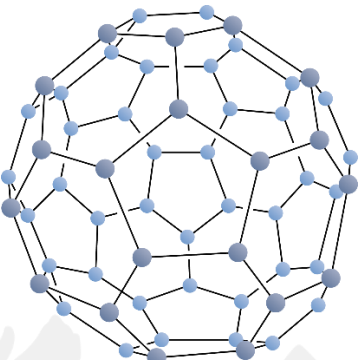
- Six large chloride ions cannot be accommodated around Si^{4+} due to limitation of its size.
- Interaction between lone pair of chloride ion and SiCl_4 is not very stable.

Catenation

Elements having the tendency to link with one another through covalent bonds to form chains and rings is called catenation. This is because C — C bonds are very strong.

- The order of catenation is $C \gg Si > Ge \approx Sn$. Lead does not show catenation.

Allotropes of carbon

Diamond	Graphite	Fullerene
		
Hybridisation : sp^3	sp^2	sp^2
Density : 3.51	2.22	1.65
One type of C — C bond	One type of C — C bond	Two types of C — C bond
<ul style="list-style-type: none"> Crystalline lattice. 3-D network : each C-atoms is linked to four other C-atoms in tetrahedral manner. One of the hardest Uses : sharpening hard tools, cutter tools; as a gem. 	<ul style="list-style-type: none"> Layered structure Interlayer force-Vanderwaal's forces Each carbon atom is linked to three other carbon atoms, fourth electron forms a π bond. Good conductor along the sheet and semi-conductor perpendicular to the sheet. Inter layer distance 340 pm so cleavage between layers is easy. Soft and slippery-lubricant at high temperature. Natural graphite is found as a mixture with mica, quartz & silicates. $3C + SiO_2 \xrightarrow{\Delta} SiC + 2CO \xrightarrow{2500^\circ C} C(\text{graphite}) + Si \text{ gas}$ <ul style="list-style-type: none"> Thermodynamically most stable among allotropes. $\text{Graphite} \xrightarrow[50000-6000 \text{ atm}]{1600^\circ C} \text{synthetic diamond}$	<ul style="list-style-type: none"> Cage like molecules. C_{60} – Soccer ball shape-Buckminsterfullerene 20-six membered rings and 12-five membered rings. Six membered ring is fused with six or five membered ring Five membered ring is fused only with six membered ring. Heating of graphite in an electrical arc in the presence of inert gases such as helium or argon can result into fullerene

Q. What is the state of hybridisation of carbon in

(NCERT Exercise)

(a) CO_3^{2-}

(b) diamond

(c) graphite?

Sol. (a) CO_3^{2-} (sp^2)

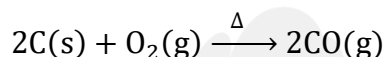
(b) Diamond (sp^3)

(c) Graphite (sp^2)

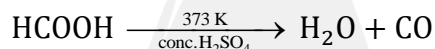
Important Compounds of Carbon and Silicon

Carbon Monoxide (CO)

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



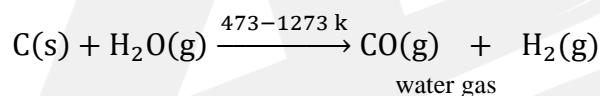
On small scale



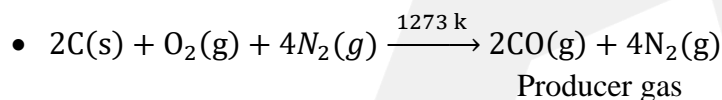
On commercial scale

Water gas : $\text{CO} + \text{H}_2$

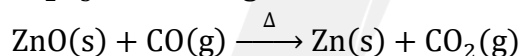
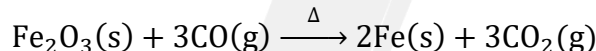
Producer gas : $\text{CO} + \text{N}_2$



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



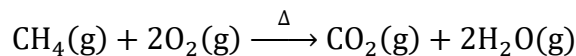
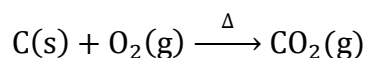
- CO : As Reducing Agent



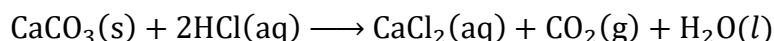
- The highly poisonous nature of CO arises because of its ability to form a **complex with haemoglobin**, which is about 300 times more stable than the oxygen-haemoglobin complex. This prevents haemoglobin in the red blood corpuscles from carrying oxygen round the body and ultimately resulting in death.

Carbon Dioxide

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



Laboratory Method



- Carbon dioxide can be obtained as a solid in the form of **dry ice** by allowing the liquified CO_2 to 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.

Q. How is excessive content of CO₂ responsible for global warming?

(NCERT Exercise)

Sol. Excess of CO₂ absorbs heat radiated by the earth. Some of it is dissipated into the atmosphere while the remaining part is radiated back to the earth. As a result, temperature of the earth increases. This is the cause of global warming.

Q. (a) Classify the following oxides as neutral, acidic, basic or amphoteric

CO, B₂O₃, SiO₂, CO₂, Al₂O₃, PbO₂, Tl₂O₃

(b) Write suitable equations to show their nature.

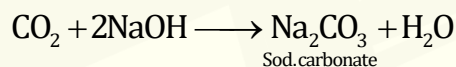
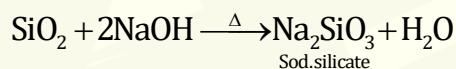
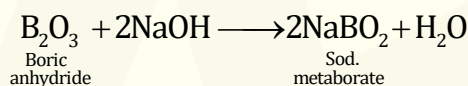
(NCERT Exercise)

Sol. (a) Neutral — CO

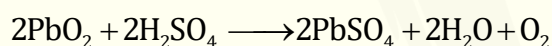
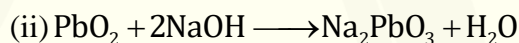
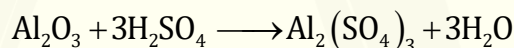
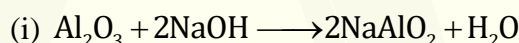
Acidic — B₂O₃, SiO₂, CO₂ Basic — Tl₂O₃ Amphoteric — Al₂O₃, PbO₂

(b) (1) CO does not react with acid as well as base at room temperature.

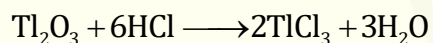
(2) Being acidic B₂O₃, SiO₂ and CO₂ reacts with alkalis to form salts.



(3) Being amphoteric, Al₂O₃ and PbO₂ react with acids and bases.

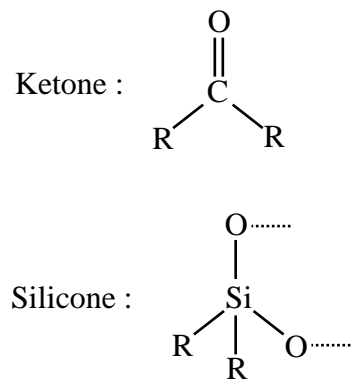
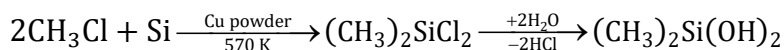


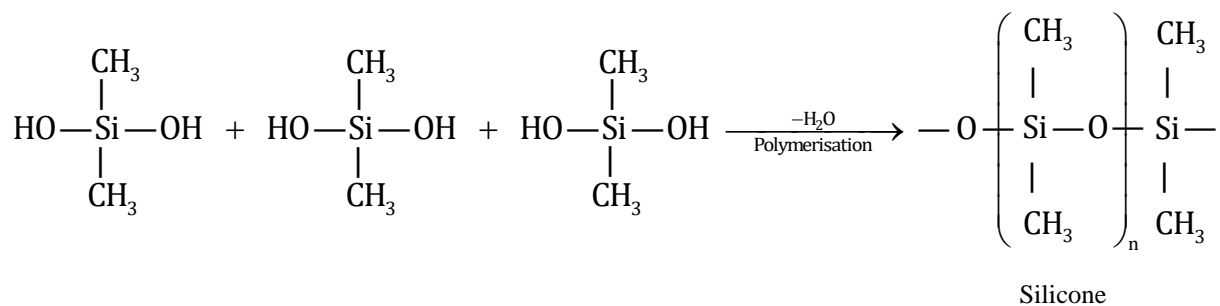
(4) Being Basic Tl₂O₃ dissolves in acids.



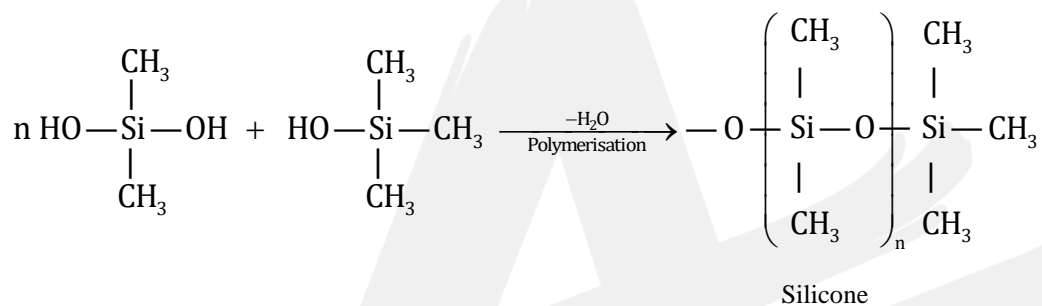
Silicones

- A group of organosilicon polymers, which have (R₂SiO) as a repeating unit.
- The starting materials for the manufacture of silicones are alkyl or aryl substituted silicon chlorides(R₂SiCl₂).
- Hydrolysis of dimethyl-dichlorosilane, (CH₃)₂SiCl₂ followed by condensation polymerisation yields straight chain polymers.





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

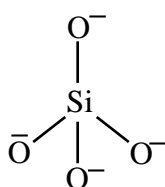


- Silicones being surrounded by non-polar alkyl groups are water repelling in nature. They have in general high thermal stability, high dielectric strength and resistance to oxidation and chemicals.

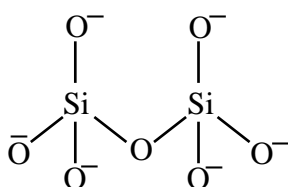
Uses : They are used as sealant, greases, electrical insulators and for water proofing of fabrics. Being biocompatible they are also used in surgical and cosmetic plants.

Silicates

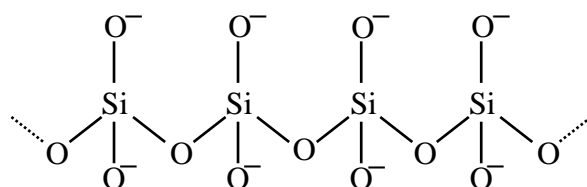
- The basic structural unit of silicates is SiO_4^{4-} in which silicon atom is bonded to four oxygen atoms in tetrahedron fashion.
- In silicates either the discrete unit is present or a number of such units are joined together via corners by sharing 1,2,3 or 4 oxygen atoms per silicate units. When 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.
- If all the four corners are shared with other tetrahedral units, three-dimensional network is formed.



Ortho silicate

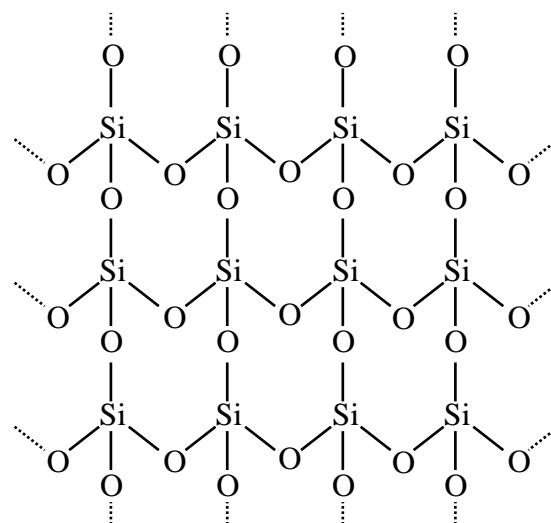


Para silicate



Chain silicate

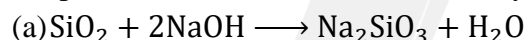
- Negative charge on silicate structure is neutralised by positively charged metal ions.
- If all the four corners are shared with other tetrahedral units, three-dimensional network is formed.
- Two important man-made silicates are glass and cement.



3-D silicate (SiO_2)

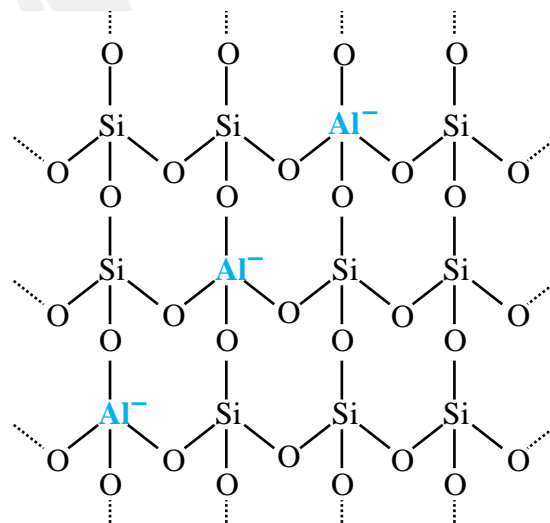
Silica Dioxide, SiO_2 (Silica)

- Silicon dioxide is a covalent, three-dimensional network solid in which each silicon atom is covalently bonded in a tetrahedral manner to four oxygen atoms. Each oxygen atom in turn covalently bonded to another silicon 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 Si — 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.



Zeolites

- If aluminium atoms replace few silicon atoms in three-dimensional network of silicon dioxide,
- overall structure known as aluminosilicate, acquires a negative charge.
- Cations such as Na^+ , K^+ or Ca^{2+} balance the negative charge.
- Examples are feldspar and zeolites.
- Zeolites are widely used as a catalyst in petrochemical industries for cracking of hydrocarbons and isomerisation, e.g., ZSM-5 (A type of zeolite) used to convert alcohols directly into gasoline.
- Hydrated zeolites are used as ion exchangers in softening of “hard” water.



3-D Aluminosilicate

Important NCERT Questions

Q. Rationalise the given statements and give chemical reactions: (NCERT Exercise)

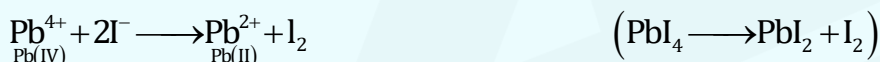
- (a) Lead (II) chloride reacts with Cl_2 to give PbCl_4 .
- (b) Lead (IV) chloride is highly unstable towards heat.
- (c) Lead is known not to form an iodide PbI_4 .

Sol. (a) $\text{PbCl}_2 + \text{Cl}_2 \longrightarrow \text{PbCl}_4$

This is because Pb can show +2 oxidation state more easily than +4 due to inert pair effect. Heat

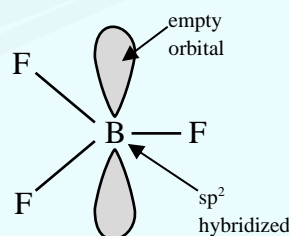
(b) $\text{PbCl}_4 \xrightarrow{\text{Heat}} \text{PbCl}_2 + \text{Cl}_2$ Stability : $\text{Pb}^{2+} > \text{Pb}^{4+}$ (Due to Inert pair effect)

(c) PbI_4 does not exist because I^- ion being a powerful reducing agent reduces Pb^{4+} ion to Pb^{2+} ion in solution.



3. Why does borontrifluoride behave as a Lewis acid?

Sol. In BF_3 , central atom has only six electrons after sharing with the electrons of the F atoms. It is an electron-deficient compound and thus behaves as a Lewis acid.



7. Describe the shapes of BF_3 and BH_4^- . Assign the hybridisation of boron in these species.

Sol.	BF_3	BH_4^-
	Boron is sp^2 hybridized. \therefore shape of BF_3 = planar.	Boron is sp^3 hybridized, thus the shape is tetrahedral.

9. What are electron deficient compounds? Are BCl_3 and SiCl_4 electron deficient species?

Sol. Electron deficient species are those in which the central atom in their molecule has the tendency to accept one or more electron pairs.

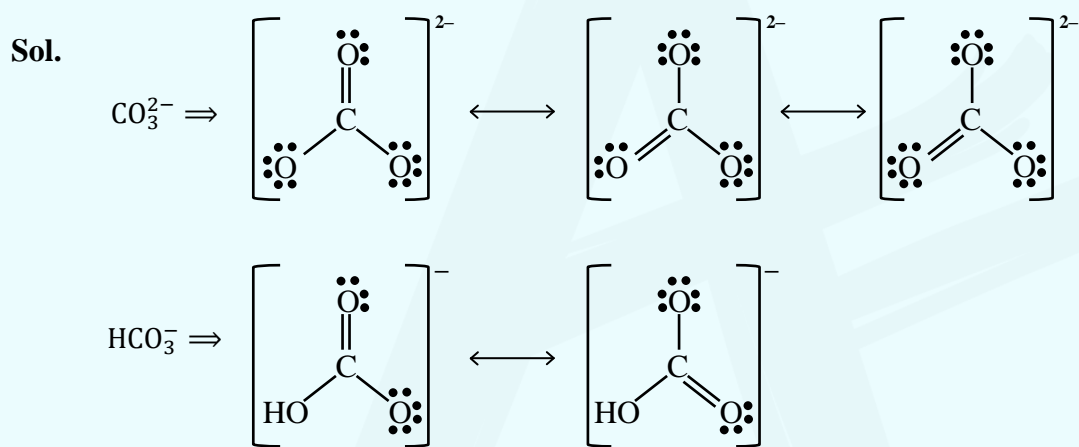
They are also known as Lewis acid. BCl_3 and SiCl_4 both are electron deficient species.

Since, in BCl_3 , B atom has only six electrons. Therefore, it is an electron deficient compound.

In SiCl_4 the central atom has 8 electrons but it can expand its covalency beyond 4 due to the presence of d-orbitals.

Thus, SiCl_4 should also be considered as electron-deficient species.

10. Write the resonance structure of CO_3^{2-} and HCO_3^- .



“Kuch bada karne ke sapne dekho, par usmei se thoda bahut bhi karlo to khushi manao, be grateful, jisse jeevan mai aur adhik karne ki taakat mille”

Ab Phod Do!

