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# **p-Block Elements (Part-1)**





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# p-Block Elements (Part-1)

## GROUP 13 ELEMENTS

### Ionisation Energy

The first ionisation energies ( $IE_1$ ) of group 13 elements (Boron family) are lower than the corresponding elements of group 2 (AEM). This is due to the electronic configuration of group 13 elements  $ns^2 np^1$  and the electron thus has to be removed from the p-orbital which is much easier than removing an s-electron of AEM elements, which is more strongly attracted by the nucleus. Boron has higher ionisation energy than its group members because its is considerable smaller. The ionization energy is so high that boron is always covalent.

### Oxidation State

Due to  $ns^2, np^1$  configuration of the valence shell, group 13 elements are expected to be trivalent but there is increase in ability to form univalent compounds on moving down the group. The oxidation state of B and Al is +3 while Ga, In, Tl show oxidation state of both +3 and +1. It is due to **Inert Pair Effect**.

### Metallic Character/Reducing Power

The order is :  $B < Al > Ga > In > Tl$

The increase in metallic character from Boron to Aluminium due to increase in atomic size but Ga, In, Tl do not follow the trend. They follow immediately after a row of ten transition elements and thus have 10 d-electrons which are less efficient for shielding the nuclear charge than s,p electrons. Thus outer most electrons being more firmly held by the nucleus are more difficult to remove than expected. This leads to decrease in size as well as decreases in metallic character than would be expected. This phenomenon is know as d-block Contraction.

### Concept Ladder



Stability of +3 oxidation state :  $B > Al > Ga > In > Tl$   
Stability of +1 oxidation state :  $Ga < In < Tl$   
Ionisation energy :  $B > Al < Ga > In < Tl$

### Rack your Brain



Why boron has high melting and boiling point?

### Previous Year's Questions



The correct order of atomic radii in group 13 elements is

[NEET 2018]

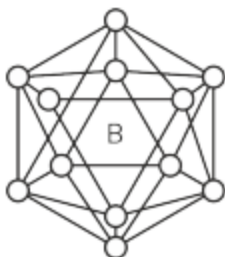
- (1)  $B < Al < In < Ga < Tl$
- (2)  $B < Al < Ga < In < Tl$
- (3)  $B < Ga < Al < Tl < In$
- (4)  $B < Ga < Al < In < Tl$



Similarly for Tl which is followed immediately after 14-f-block elements, there is much change in the size and metallic character of it. It is due to the Lanthanide Contraction which is due to the f-block elements. Note that in general the size increases down the group but is less than as expected.

### Acidic Character

From B to Tl acidic character decreases and basic character increases because ionization energy increases. Thus we find that  $B(OH)_3$ , and  $B_2O_3$  are acidic;  $Al(OH)_3$  and  $Al_2O_3$  are amphoteric;  $Ga(OH)_3$  and  $Ga_2O_3$  are amphoteric; and  $In(OH)_3$ ,  $Tl(OH)_3$  are basic.



### Boron & Its Compound

#### Physical Properties and Occurrence

Boron occurs in two allotropic form :

- Crystalline – It is chemically inert, very hard and black in color.
- Amorphous – It is chemically active, a non-conductor, difficult to fuse and brown in color.

All allotropic forms contain icosahedral unit with atoms at all 12 corners. The important minerals of boron are :

Borax (Tincal)	$Na_2B_4O_7 \cdot 10H_2O$	Boric acid	$H_3BO_3$
Kernite (Resorite)	$Na_2B_4O_7 \cdot 4H_2O$	Boronatro calcite	$CaB_4O_7 \cdot NaBO_2 \cdot 8H_2O$
Colemanite	$Ca_2B_6O_{11} \cdot 5H_2O$	Boracite	$2Mg_3B_8O_{15} \cdot MgCl_2$
Pandertie	$Ca_2B_6O_{11} \cdot 3H_2O$		

### Concept Ladder



The electropositive or metallic character of group 13 elements increases from B to Tl. B being a non metal and thus forms an acidic hydroxide. Al forms amphoteric hydroxide and Tl, the most metallic from basic hydroxides.

### Rack your Brain



Which elements of group 13 will form most ionic and covalent compounds respectively?

# BORON FAMILY

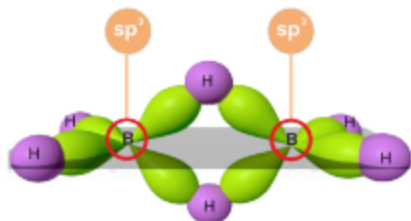


## ELECTRONIC CONFIGURATION



$ns^2 np^1$   
Valence electrons = 3

## Diborane (B<sub>2</sub>H<sub>6</sub>)



BH<sub>3</sub> is an electron deficient molecule. It has six electrons and a vacant orbital. So, it is used as an electrophile in organic reactions.



Borax (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) is used for cleaning and washing purposes.



Aluminium was classified as precious metal during 19<sup>th</sup> century. Napoleon III gave aluminium cutlery to his most valuable guests, all other guests had to eat with gold cutlery.

## PHYSICAL STATE

Boron is a non metal  
Aluminium, Indium,  
Gallium are metalloids.

Gallium has the second lowest melting point after mercury. it remains in liquid phase even at high temperatures.



## AMPHOTERIC

Al(OH)<sub>3</sub> is amphoteric



strength between Al—O  
and O—H is same

Bond strength Al—O = Bond strength O—H

Aluminium is used in tins, aeroplanes and even in iPhone



Indium is used in display screens of television and mobiles

Thallium is used as rat poison.

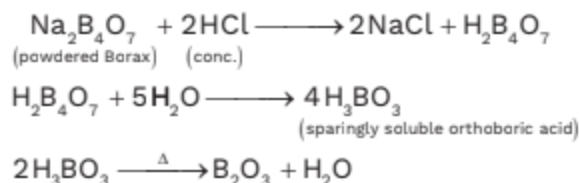




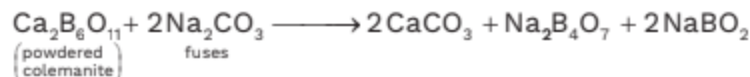
**Extraction of Boron :** It includes 2 steps :

**1. Preparation of Boric anhydride ( $B_2O_3$ ) :**

**[Method-I]**



**[Method-II]**



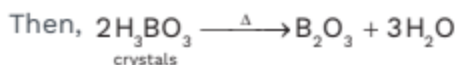
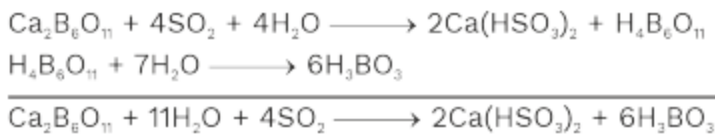
The fused mass is extracted with  $\text{CaCO}_3$  remains filtrate and insoluble containing sodium metaborate. By obtained borax crystals, borax is put to crystallisation. The remaining solution is treated with  $\text{CO}_2$ .



Then Method I is followed.

**[Method III]**

Suspension of colemanite mineral in  $\text{H}_2\text{O}$  is formed and  $\text{SO}_2$  gas is passed to obtain crystal of boric acid on cooling.



**Rack your Brain**



If Borax can be formulated as  $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$  then how would you formulate Colemanite?

**Concept Ladder**



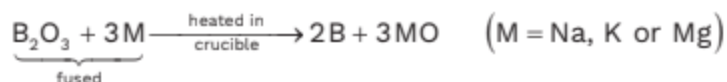
On a large scale, boron is extracted from its minerals, borax  $\text{Na}_2\text{B}_4\text{O}_7$  and colemanite  $\text{Ca}_2\text{B}_6\text{O}_{11}$ . The latter is first converted to borax by boiling with a solution of sodium carbonate in the requisite proportion and then the same method is followed.





## 2. Reduction $B_2O_3$

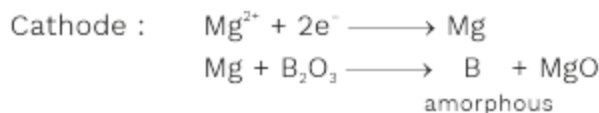
### [Method-I]



To oxidise unreacted metal M, the fused mass is stirred with iron rod. The mass is then boiled with dil. HCl to obtain insoluble amorphous boron powder which is 95% pure.

### [Method-II] : Modern Method

A fused mixture containing magnesium fluoride, boric anhydride and magnesium oxide at  $1100^\circ\text{C}$  is electrolysed in a carbon crucible (anode). Iron rod is used as cathode.



### [Method-III]

To obtain crystalline boron in small amounts,  $B_2O_3$  is reduced with aluminium powder.



Removal of Aluminium is made by heating the fused mass with NaOH solution.

### Chemical Properties of Boron

1. B is unaffected by  $H_2O$  under ordinary conditions but :



### Rack your Brain



What acts as a reducing agent during the reduction of boron?

### Concept Ladder



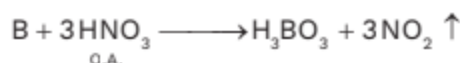
Boron generally forms covalent bonds rather than  $+3$  ions. This is due to the small size of boron which makes the sum of its first three ionization enthalpies very high. Boron is generally unreactive when comes in contact with acids and alkalis at moderate temperatures.



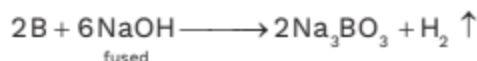
2. Amorphous boron burns in air at 700°C with a reddish flame forming oxide and nitride.



3. Boron is unaffected by reducing acids. With oxidising acids it gives boric acid.



4. Boron dissolves in fused alkalis liberating hydrogen.



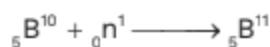
5. Generally, boron forms Non-Stoichiometric compounds with metals (not of Group 1)



6. Action of non-metals :



**Uses :** Boron carbide rods are used to control nuclear reactions. Boron has a very high cross-section for capturing the neutrons. Also to make boron of having an even number of neutrons B absorbs neutrons.



### [a] Diborane $\text{B}_2\text{H}_6$ :

#### Structure and Physical Properties :

In diborane the bridge hydrogens form abnormal 3 centre 2 electron 'banana-shaped' bonds with two B atoms.

For having delocalized molecular orbital covering all three nuclei, an  $\text{sp}^3$  hybrid orbital from each boron atom overlaps with 1s orbital of hydrogen.

### Concept Ladder



Boron is added to glass to increase its resistance to heat shock. Most chemistry glassware is made from borosilicate glass.



### Previous Year's Questions

Which one of the following elements is unable to form  $\text{MF}_6^{3-}$  ion?

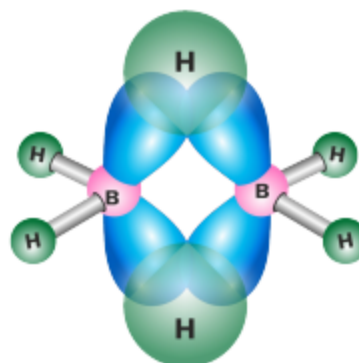
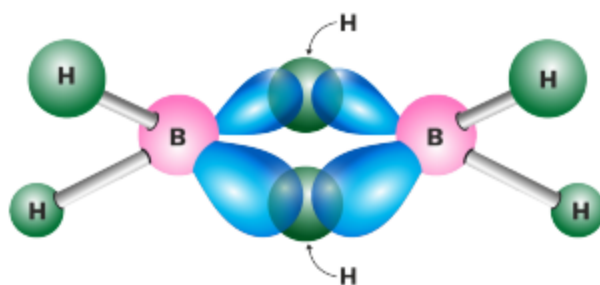
[NEET 2018]

- (1) Ga                      (2) Al  
(3) B                        (4) In

### Concept Ladder

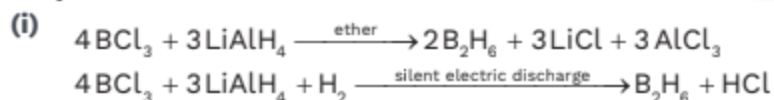


Boron forms hydrides of the type  $\text{B}_n\text{H}_{n+4}$  and  $\text{B}_n\text{H}_{n+6}$  which are called Boranes.



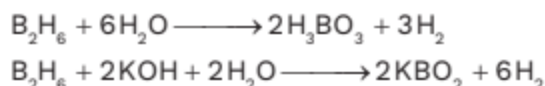
Diborane is a highly reactive and colorless gas with disagreeable odour. It is used as a catalyst in polymerization reactions and a reducing agent in organic reactions.

**Preparation :**



**Chemical Properties :**

1. It is instantly hydrolysed by aqueous alkali or water.



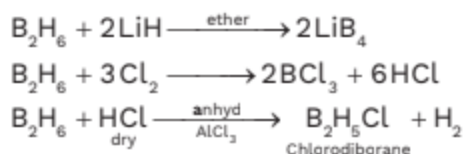
2. It catches fire spontaneously in air and explodes with dioxygen.



Thus in the laboratory, diborane is handled in a vacuum frame.



4. Other reactions :



**Rack your Brain**



Why boranes are electron deficient compounds?

**Previous Year's Questions**



The tendency of  $\text{BF}_3$ ,  $\text{BCl}_3$  and  $\text{BBr}_3$  to behave as Lewis acid decreases in the sequence

[AIPMT 2010]

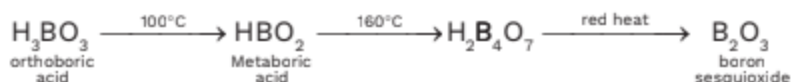
- (1)  $\text{BCl}_3 > \text{BF}_3 > \text{BBr}_3$
- (2)  $\text{BBr}_3 > \text{BCl}_3 > \text{BF}_3$
- (3)  $\text{BBr}_3 > \text{BF}_3 > \text{BCl}_3$
- (4)  $\text{BF}_3 > \text{BCl}_3 > \text{BBr}_3$





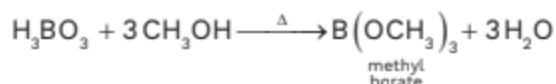
## Chemical Properties :

### 1. Effect of heat



Thus,  $\text{B}_2\text{O}_3$  is also called boric anhydride as it is the anhydride of boric acid.

### 2.



$\text{H}_2\text{O}$  is removed by conc.  $\text{H}_2\text{SO}_4$  and the mixture boruns with green flame. This is used as a test for boron compounds.

3. Boric acid dissolves in  $\text{HF}(\text{aq})$  to give fluoroboric acid  $\text{HBF}_4$  which is a strong acid. In dry  $\text{HF}$  borates give  $\text{BF}_3$  which burns with a green colour.

### Uses:

Boric acid is used as an antiseptic and in glass industry and eyewash under the name 'Boric Lotion'.

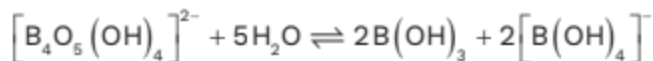
## [c] Borax :

### Structure :

Borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) is better written as  $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$  having 8 water molecules and the ion  $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$  associated with  $\text{Na}^+$ .

### Chemical Properties :

1. When borax dissolves in  $\text{H}_2\text{O}$  equal amounts of weak acid and its salt are formed. Thus it is used as a buffer.



### Rack your Brain



What is the hybridisation of B in boric acid?

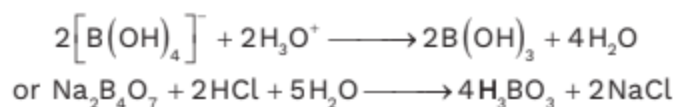
### Concept Ladder



Boric acid loses water in three different stages ultimately giving boron trioxide.



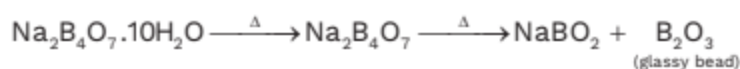
2. Borax will react with 2 moles of acid because only  $[\text{B}(\text{OH})_4]^-$  formed will react with  $\text{H}^+$ .



Methyl oranges are used as the indicator, it is unaffected by the  $\text{H}_3\text{BO}_3$  formed.

**3. Borax Bead Test :**

Metaborates  $[\text{M}(\text{BO}_2)]$  of many transition elements have characteristic colours and this provides a means of identifying the metal through this test.



**Uses :**

- In analytical chemistry it is used in Borax Bead Test.
- Used as flame retardant for wood and fabric.
- Used in glass industry.
- Used as a flux in silver soldering and brazing/

**Aluminium :**

- Thermodynamically Al should react with  $\text{H}_2\text{O}$  and air, but in fact it is stable in both. As very thin oxide film of  $\text{Al}_2\text{O}_3$  is formed on surface and protects it. Due to this resistance to high thermal conductivity and corrosion it is used in making domestic utensils.
- Reduction of some metal oxides like  $\text{Mn}_3\text{O}_4$  and  $\text{Cr}_2\text{O}_3$  require temperature high enough for carbon to be used as a reducing agent. Thus Al, a highly electropositive metal which

**Rack your Brain**



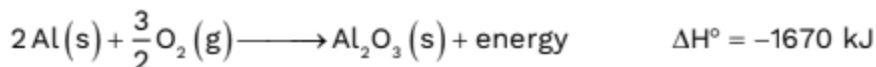
What property of Borax makes it suitable for behaving like water softener and cleaning agent?

**Concept Ladder**



When borax is heated above its melting point until all the water of crystallization is expelled, it forms a colourless glassy substance known as borax glass. It then decomposes to give sodium meta borate and boron (III) oxide. When this mixture is fused with metallic oxide it forms characteristic coloured beads. With the help of the colour, the metal ions can be identified.

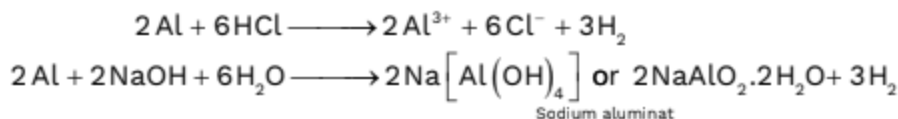
on oxidation liberates a large amount of energy to  $\text{Al}_2\text{O}_3$ , which is used as the reducing agent. This is known as the thermite process. The thermite reaction is :



3. Aluminium metal is moderately soft but lighter and much stronger when alloyed with metals. Some alloys of Aluminium are :

Alloys	Composition	Uses
Magnalium	Al – 95%, Mg – 5%	In construction of airships, balances.
Duralumin	Al – 95%, Cu – 4%, Mg – 0.5%, Mn – 0.5%	In aeroplanes and automobile parts
Aluminium bronze	Cu – 90%, Al – 9.5%, Sn – 0.5%	To make utensils, cheap artificial jewellery.
Alnico	Steel – 77%, Al – 20%, Ni – 2%, Co – 1%	To make permanent magnet.

4. Al is amphoteric hence dissolves in both acid and bases.



However, conc.  $\text{HNO}_3$  renders it passive due to the formation of a protective oxide layer.

**[a] Aluminium Oxide  $\text{Al}_2\text{O}_3$  (Alumina) :**

Alumina is a white crystalline powder, insoluble in water. It is quite unreactive, stable and amphoteric in nature. The  $\alpha$ -form of  $\text{Al}_2\text{O}_3$  called corundum and found as mineral in nature.

**Previous Year's Questions**



$\text{AlF}_3$  is soluble in HF only in presence of KF. It is due to the formation of

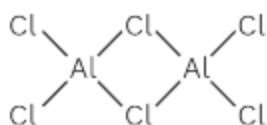
**[NEET (II) 2016]**

- (1)  $\text{K}_3[\text{AlF}_3\text{H}_3]$       (2)  $\text{K}_3[\text{AlF}_6]$   
 (3)  $\text{AlH}_3$               (4)  $\text{K}[\text{AlF}_3\text{H}]$



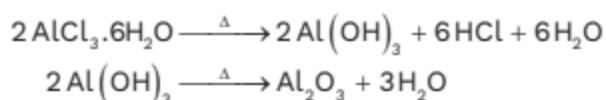
### [b] Aluminium Trichloride $\text{AlCl}_3$ :

$\text{AlCl}_3$  exists as a dimer, thus attaining an octet of electrons. It is largely covalent when reacts with a non-polar solvent such as  $\text{C}_6\text{H}_6$ .

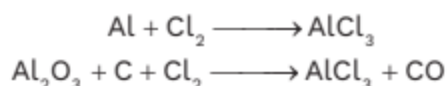


However, when dissolved in  $\text{H}_2\text{O}$ , the high enthalpy of hydration is sufficient to break the covalent dimer into  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  and  $3\text{Cl}^-$  ions. At low temperature,  $\text{AlCl}_3$  exists as a close packed lattice of  $\text{Cl}^-$  with  $\text{Al}^{3+}$  occupying octahedral holes.

Crystalline  $\text{AlCl}_3$  exist as  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ . On heating it cannot give anhydrous salt just like  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  (diagnol relationship). Instead it undergoes hydrolysis on heating :



The anhydrous compound is prepared by action of dry chlorine gas on aluminium or alumina :



### Concept Ladder



Aluminium chloride is mainly produced using an exothermic reaction of two elements namely aluminium and chlorine.

### Rack your Brain



$\text{AlCl}_3$  — Lewis acid or base?

### Concept Ladder



$\text{AlCl}_3$  in solid-state features as a cubic close-packed layered structure. In this case, it will be octahedral. When aluminium chloride is in a liquid or molten state it exists as a dimer. Here its coordination geometry will be tetrahedral. At higher temperatures, the dimers dissociate into trigonal planar.





## GROUP 14 ELEMENTS

### Metallic Character

On moving down the group metallic character decreases. C and Si are non metals, Ge is a metalloid and Sn and Pb are metals.

### Oxidation State

Oxidation state of C and Si is +4 while for Ge, Sn, Pb it has value of both +4 and +2 by Inert Pair Effect.

### Catenation

C has the property of linking to other carbon atoms forming long chains due to its smaller size and higher electron negativity. However on moving down the group the tendency for catenation decreases in the order :



### Carbon and its Compounds

#### Allotropy

Carbon exists in a large number of allotropic forms. Two main form are diamond and graphite.

Diamond	Graphite
Extremely unreactive, colourless, non conductor and shows brilliant shine due to total internal reflection.	Quite reactive and soft.
The structure comprises of $sp^3$ hybrid C atoms forming $\sigma$ -bonds and arranged tetrahedrally.	It has a structure with layers held together by weak van der waal's forces. Each sheet consists of hybridised carbon atoms that are covalently bonded to three carbon atoms by $\sigma$ -bonds. The fourth $e^-$ is in unhybridised 'p' orbital and forms a partial $\pi$ -bond.

### Concept Ladder



Reactivity :  $C < Si < Ge < Sn < Pb$

Metallic character :  $C < Si < Ge < Sn < Pb$

### Previous Year's Questions

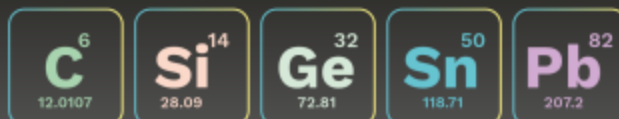


Which of the following does not show electrical conduction?

[AIPMT]

- (1) Diamond      (2) Graphite  
(3) Potassium    (4) Sodium

# CARBON FAMILY



## Electronic configuration



## REACTIVITY

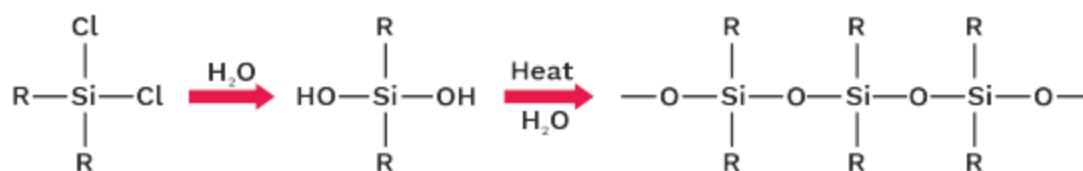
The carbon family elements tend to be fairly unreactive. The elements tend to form covalent compounds, though tin and lead also form ionic compounds.

## CARBIDES

Carbon combines with other elements and forms carbides  $Al_4C_3$ ,  $Be_2C$ ,  $SiC$  and  $B_4C$  are considered as the hardest compounds.

## SILICONES

Silicones are organo-silicon polymers and are formed by hydrolysis of  $R_2SiCl_2$



## Linear silicones

### CARBON-GODLY ELEMENT

Every human being and everything around us consists of carbon.



### NON STICK PAN

Nonstick pan has a Teflon layer on its surface. Teflon  $(CF_2-CF_2)_n$ .



### LEAD PENCILS

Lead Pencils which we use do not contain Lead. It contains Graphite (an allotrope of carbon).



### SILICON

Silicon is used in semiconductor devices, which are used in modern day computers.



### TIN-CANS

Initially we used Tin for making cans, later it was replaced by Aluminium.



### Chemical Properties :

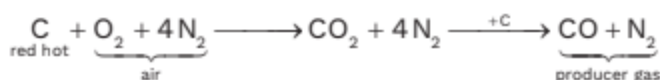
1. Water gas is made by blow of air through white or red hot coke :



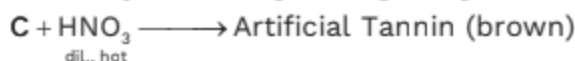
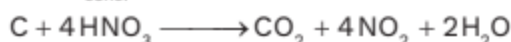
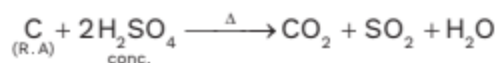
2. All allotropes burn in oxygen to form  $\text{CO}_2$ .



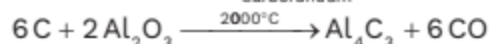
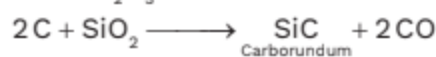
Producer gas is made by blow of air through red hot coke.



3. Carbon as reducing agent :

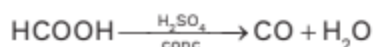


4. Carbon as Oxygen acceptor :

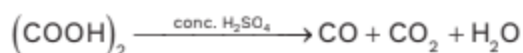


### Preparation of CO :

- (i) In laboratory it is prepared by dehydrating formic acid with concentrated  $\text{H}_2\text{SO}_4$



Also,



$\text{CO}_2$  is removed by passing through soda



### Concept Ladder



Diamond has a three dimensional polymeric structure involving very strong covalent bonds by which the atoms are held together. Hence diamond possesses high melting point inspite of its covalent nature.

### Rack your Brain



Carbon monoxide — A good reducing or oxidising agent?

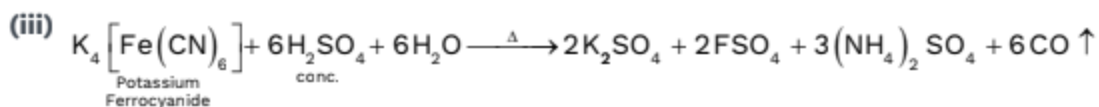
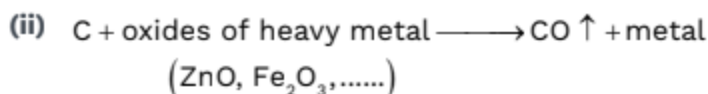
### Previous Year's Questions



It is because of inability of  $ns^2$  electrons of the valence shell to participate in bonding that

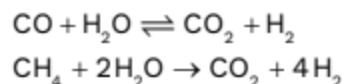
[NEET 2017]

- (1)  $\text{Sn}^{2+}$  is oxidising while  $\text{Pb}^{4+}$  is reducing
- (2)  $\text{Sn}^{2+}$  and  $\text{Pb}^{2+}$  are both oxidising and reducing
- (3)  $\text{Sn}^{4+}$  is reducing while  $\text{Pb}^{4+}$  is oxidising
- (4)  $\text{Sn}^{2+}$  is reducing while  $\text{Pb}^{4+}$  is oxidising

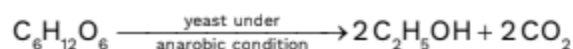


#### Preparation of CO<sub>2</sub> :

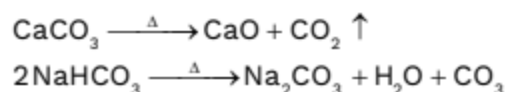
(i) The most important industrial source is as a by product from the manufacture of hydrogen for making ammonia :



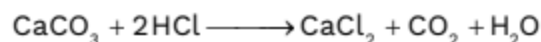
(ii) It is recovered from alcoholic fermentation :



(iii) It is obtained by heating carbonates :



(iv) In laboratory CO<sub>2</sub> is prepared by the action of dilute acids on carbonates :



#### [a] Silicones :

They are groups of organo - silicon polymers containing Si - O - Si linkages.

#### Preparation :

They are formed by the hydrolysis of alkyl or aryl substituted chlorosilanes (formed by reaction Grignard reagents and silicon tetrachloride) and their subsequent polymerization.

#### Rack your Brain



How does CO<sub>2</sub> react with lime water?

#### Previous Year's Questions



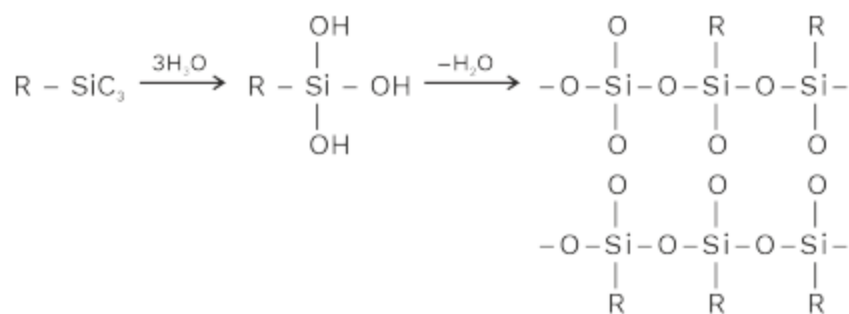
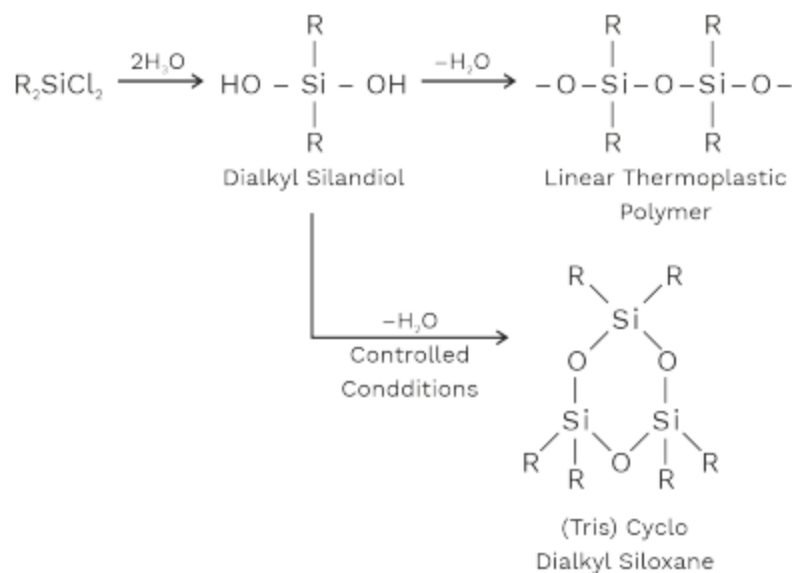
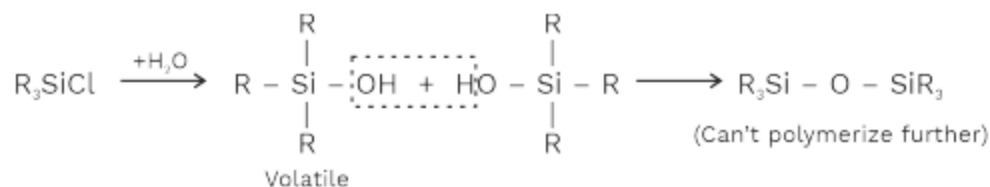
Carbon and silicon belong to (IV) group. The maximum coordination number of carbon in commonly occurring compounds is 4, whereas that of silicon is 6. This is due to

[AIPMT]

- (1) availability of low lying d-orbitals in silicon
- (2) large size of silicon
- (3) more electropositive nature of silicon
- (4) both (2) and (3)

**Rack your Brain**

Why the name silicone resembles with ketone?

**(i) Formation of cross - linked silicones :****(ii) Formation of linear polymers :****(iii) Formation of dimers :**



### Properties :

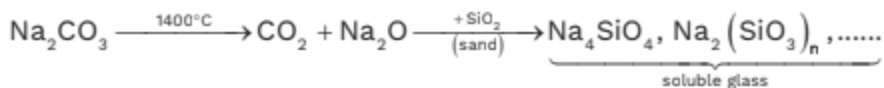
1.  $R_3SiCl$  is a chain stopping unit and reduces polymer size as it blocks the end of chain. While  $R_3SiCl$  is used to produce new cross – links and increase polymerization.
2. Silicones are electrical insulators, water-repellent, strong and inert. Their boiling point and viscosity increases with increase in chain length.
3. Silicones are stable towards heat.  $ph > CH_3 > Et > Pr$  is the order of stability which varies with attaching R in the order.
4. Being water – repellent silicones are used for treating glass ware and fabrics.
5. They are also used as silicone rubbers and hydraulic fluids.

### [b] Silicates :

Silicates are derivatives of silicic and  $Si(OH)_4$  or  $H_2SiO_4$ . They have basic tetrahedral units  $SiO_4^{4-}$  and Si – O bond is considered to be 50% ionic and 50% covalent.

### Preparation :

Silicates can be prepared in an electric furnace at about  $1400^\circ C$  by fusing an alkali metal carbonate with sand.



### Rack your Brain



What makes silicones useful for making sealants and electrical insulator?

### Concept Ladder



The basic structural unit in silicates is the  $SiO_4$  tetrahedron. The  $SiO_4$  tetrahedral can be linked in several different ways. Depending on the number of corners (0, 1, 2, 3 or 4) of the  $SiO_4$  tetrahedral shared, various kinds of silicates, single or double chains, rings, sheet or three-dimensional networks are formed.

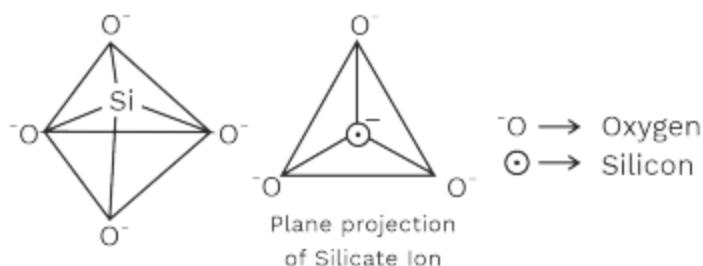


### Classification of Silicate Minerals :

(i) **Orthosilicates** : These contain single discrete unit of  $\text{SiO}_4^{4-}$  tetrahedral.

<b>Ex :</b> Zircon (gemstone)	$\text{ZrSiO}_4$
Forestrite or Olivine	$\text{Mg}_2\text{SiO}_4$
Phenacite	$\text{Be}_2\text{SiO}_4$
Willemite	$\text{Zn}_2\text{SiO}_4$

Number of shared oxygen atom = 0



(ii) **Pyrosilicates** : These silicates contain two units of  $\text{SiO}_4^{4-}$  joined along a corner containing oxygen atom. These are also called as island

silicate.

Pyrosilicate ion  $\text{Si}_2\text{O}_7^{6-}$



### Concept Ladder



The ortho silicate ion is the strong conjugate base of weak orthosilicic acid as well as it will not persist in aqueous solutions. Hence in nature, ortho silicate minerals are rare and only found with cations which form highly insoluble salts.

### Previous Year's Questions



Which of the following anions is present in the chain structure of silicates?

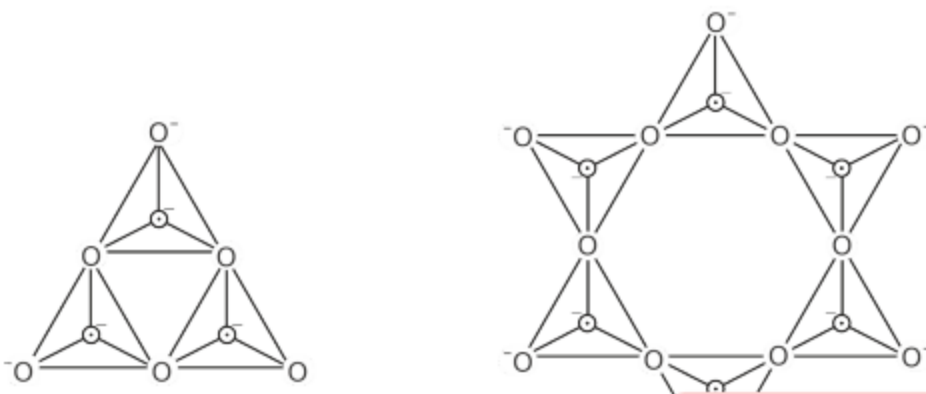
[AIPMT]

- (1)  $(\text{Si}_2\text{O}_5^{2-})_n$       (2)  $(\text{SiO}_3^{2-})_n$   
 (3)  $\text{SiO}_4^{4-}$       (4)  $\text{Si}_2\text{O}_7^{6-}$



**Ex :** Thortveitite  $\text{Sc}_2\text{Si}_2\text{O}_7$   
 Hemimorphite  $\text{Zn}_3(\text{Si}_2\text{O}_7)\cdot\text{Zn}(\text{OH})_2\cdot\text{H}_2\text{O}$   
 Number of shared oxygen atom = 1

**(iii) Cyclic structure :** They are also known as ring silicates having general formula  $(\text{SiO}_3)_n^{2n-}$ . Structure and example of cyclic silicates containing  $\text{Si}_3\text{O}_9^{6-}$  and  $\text{Si}_6\text{O}_{18}^{12-}$  ions are given below :

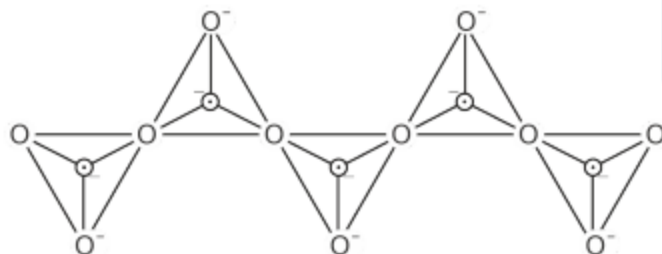


**Ex :** Beryl  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$   
 Wollastonite  $\text{Ca}_3\text{Si}_3\text{O}_9$   
 Number of shared oxygen atoms = 2

**(iv) Chain silicates :** These are formed by sharing two  $\text{O}_2$  atoms of each tetrahedral units. Anions of chain silicates have 2 general formula.

**Ex :** Spodumene  $\text{LiAl}(\text{SiO}_3)_2$   
 Diposide  $\text{CaMg}(\text{SiO}_3)_2$   
 Tremolite  $\text{Ca}_2\text{Mg}_5(\text{Si}_4\text{O}_{11})_2(\text{OH})_2$

(a)  $(\text{SiO}_3)_n^{2n-}$



### Rack your Brain



Cyclic silicates are oligomer of which unit?

### Concept Ladder

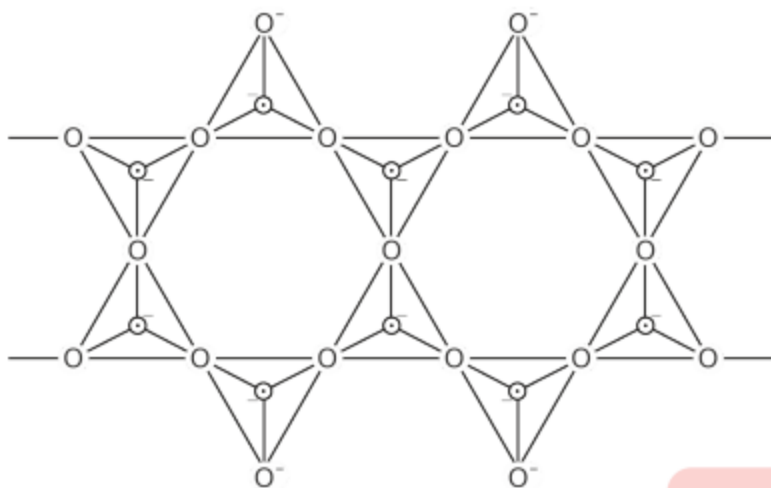


The single and double chain silicates are collectively known as Inosilicates.





Number of shared oxygen atom = 2



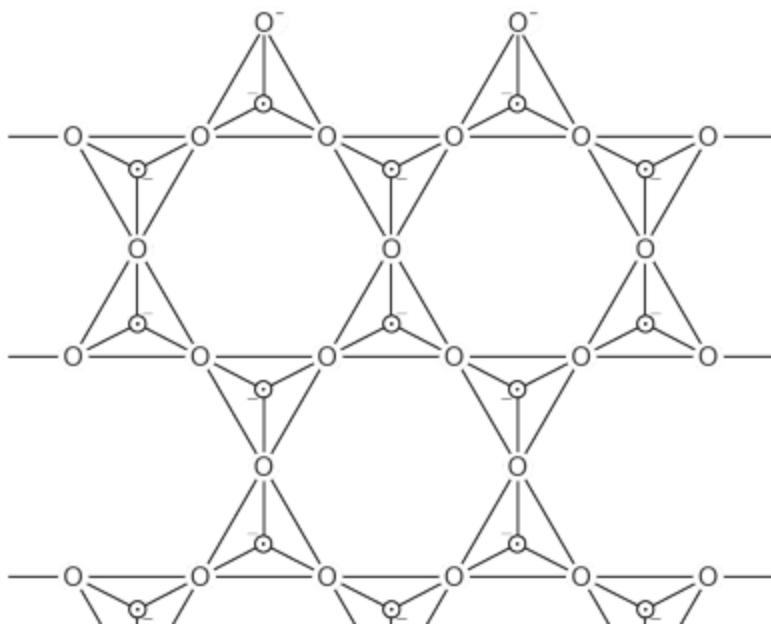
#### Rack your Brain



If  $\text{SiO}_4^{4-}$  units are replaced by  $\text{AlO}_4^{5-}$  units, the structure formed is called?

Number of shared oxygen atom = 2.5

**(v) Two dimensional sheet silicates :** In such silicates, three oxygen atoms of each tetrahedral are shared with adjacent  $\text{SiO}_4^{4-}$  tetrahedral, such sharing forms two dimensional sheet structure with general  $(\text{Si}_2\text{O}_5)_n^{2n-}$ .



**Ex :** Tale  $\text{Mg}(\text{Si}_2\text{O}_5)_2\text{Mg}(\text{OH})_2$   
 Kaolin  $\text{Al}_2(\text{OH})_4(\text{Si}_2\text{O}_5)$   
 Number of shared oxygen atom = 3

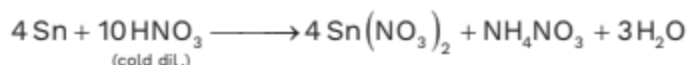
**(vi) 3D Sheet Silicates :** These silicates involve all four oxygen atoms in sharing with adjacent  $\text{SiO}_4^{4-}$  tetrahedral. For example, Quartz, Zeolites, Ultramarines and Feldspars. Here all four oxygen atoms are shared.

### Tin and its compounds :

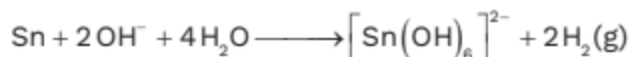
Tin is a soft, white lustrous, malleable metal. It produces a cracking sound called tin cry whenever it is bent.

### Properties :

1. Tin reacts with steam to give  $\text{SnO}_2$  and  $\text{H}_2$ .
2. It dissolves in dilute  $\text{HNO}_3$  forming  $\text{Sn}(\text{NO}_3)_2$ .



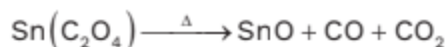
3. It is rapidly attacked by hot alkalies and slowly by cold alkalies. Thus it is amphoteric.



4. Sn is used in tin plating (coating iron or steel sheets with tin) and making alloys like solder (67% + 33% Pb) and bronze (75% Cu + 25% Sn).

### $\text{Sn}^{2+}$ and $\text{Sn}^{4+}$

Tin ion exists in two states +2 and +4 with the +6 state being more stable.  $\text{SnO}_2$  is called as cassiterite and found as a mineral in nature. The other oxide  $\text{SnO}$  is obtained by heating stannous oxalate and is less stable in nature.



### Concept Ladder



The two common forms (allotropes) of tin white tin and gray tin. The sudden degradation of white tin into gray tin is called tin pest.

### Rack your Brain



Why tin is used in electroplating?

# CARBON FAMILY

<b>C</b> <sup>6</sup> 12.0107	<b>Si</b> <sup>14</sup> 28.09	<b>Ge</b> <sup>32</sup> 72.61	<b>Sn</b> <sup>50</sup> 118.71	<b>Pb</b> <sup>82</sup> 207.2
----------------------------------	----------------------------------	----------------------------------	-----------------------------------	----------------------------------

**Carbon** has three main solid state allotropes: **Graphite, Diamond** and **Fullerenes** (the most commonly known of which, **buckminster fullerene**, is also known as a "bucky-ball").

## do you know

- Carbon is a non-metal
- silicon and germanium are metalloids
- Lead and tin are metal

### Germanium



Camera

Germanium is a rare element used in the manufacturing of semi-conductor devices. The physical and chemical properties of germanium are very similar to those of silicon. Germanium is grey-white in color and forms crystal structures.

### Silicon

Silicon is the second most common element in the earth's crust (after oxygen) and it is the backbone of the mineral world. Silicon is used extensively as a semiconductor in solid-state devices in the computer and microelectronics industries



Tablet

### Tin



Tin is malleable, ductile, and crystalline. It is a superconductor at low temperatures. Tin reacts with bases, acid salts and strong acids. Tin chlorides are good reducing agents and often used to reduce iron ores. Tin fluoride is often the anticavity "fluoride" additive in toothpastes.

### Lead

It is a soft, malleable metal with a low melting point. Lead is toxic to humans, especially children. Even low levels of exposure can cause nervous system damage and can prevent proper production of haemoglobin. Its oxides have many industrial uses as oxidizing agents, such as cathodes in lead-acid storage cells.

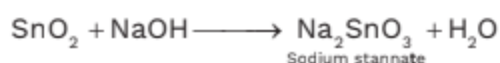


### Point to Remember

Carbon has the highest melting/sublimation point of the elements. The melting point of diamond is 3550°C, with the sublimation point of carbon is around 3800°C.



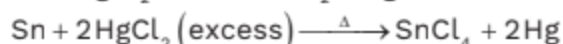
Both SnO and SnO<sub>2</sub> are amphoteric but SnO is slightly more basic than SnO<sub>2</sub> and a good reducing agent too.



Among halides, stannous chloride (SnCl<sub>2</sub>) and stannic chloride (SnCl<sub>4</sub>) are the most important. SnCl<sub>2</sub> exists as a di-hydrate which undergoes hydrolysis on heating.



The anhydrous salt SnCl<sub>2</sub> is obtained by reaction of Sn with a calculated quantity of HgCl<sub>2</sub>. Excess of HgCl<sub>2</sub> result in the formation of stannic chloride.



Most of the reactions of SnCl<sub>2</sub> are due to its reducing character. It reduces MnO<sub>4</sub><sup>-</sup> to Mn<sup>2+</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> to Cr<sup>3+</sup> and itself get oxidized to Sn<sup>4+</sup>.

#### Lead and its compounds

- (i) Pb is a bluish grey soft metal which is extremely poisonous and can be cut with a knife.
- (ii) Lead often appears more unreactive than expected from its standard electrode potential. The unreactiveness of Pb is due to the surface coating of basic carbonate 2PbCO<sub>3</sub>·Pb(OH)<sub>2</sub> which forms over lead when exposed to air and moisture. Thus lead is unaffected by water.
- (iii) Pb is amphoteric hence dissolves in both acids and hot alkalies similar to Sn. In



#### Concept Ladder



Stannic sulphide exists in yellow glistening scales which is used for decorative purposes under and the name mosaic gold.

#### Rack your Brain



What is the Latin word for tin?



#### Previous Year's Questions

Which of the following oxidation states are the most characteristic for lead and tin respectively?

[AIPMT]

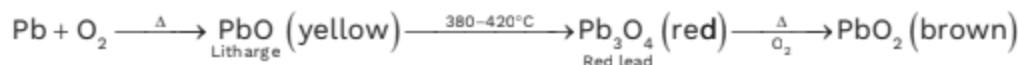
- |            |            |
|------------|------------|
| (1) +2, +4 | (2) +4, +4 |
| (3) +2, +2 | (4) +4, +2 |

alkali it forms plumbates like  $\text{Na}_2[\text{Pb}(\text{OH})_6]$  or  $\text{Na}_2\text{PbO}_3$ . However, due to formation of surface coating of  $\text{PbCl}_2$ , lead does not dissolve in concentrated HCl.

- (iv) Pb is used in making lead chamber for  $\text{H}_2\text{SO}_4$  plant and certain alloys like solder (Sn Pb).

#### [a] Oxides :

Pb exists as  $\text{Pb}^{+2}$  and  $\text{Pb}^{+4}$  with  $\text{Pb}^{+2}$  being more stable, because of inert pair effect which increases the stability of +2 state while going down the group. Oxide formation is shown as :



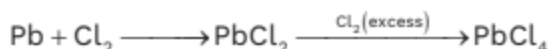
- (i)  $\text{PbO}$  and  $\text{PbO}_2$  are both amphoteric and dissolve in both acids and bases.



- (ii)  $\text{Pb}_3\text{O}_4$  or Red Lead may be represented as  $2\text{PbO} \cdot \text{PbO}_2$  and is used in paint to prevent the rusting of iron and steel.
- (iii) Lead oxide (Litharge) is commercially important and is used in large amounts to make lead glass.  $\text{PbO}_2$  is used as a strong oxidising agent and produced in lead storage batteries.

#### [b] Chlorides :

They are prepared by passing lead through a current of chlorine gas.



#### Rack your Brain



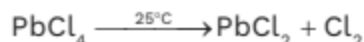
What is the formula of sindhur?

#### Concept Ladder



White lead is a white crystalline solid, which turns black when exposed to  $\text{H}_2\text{S}$  due to  $\text{PbS}$  formation. It is highly poisonous.

Dissolving  $\text{Pb}^{2+}$  salt ( $\text{PbO}$ ,  $\text{PbCO}_3$ ,  $\text{Pb}(\text{NO}_3)_2$ ) in  $\text{HCl}$  produces  $\text{PbCl}_2$ .  $\text{PbCl}_4$  is less stable and decomposes on heating at room temperature and liberates  $\text{Cl}_2$ .



**[c] Tetraethyl Lead  $(\text{CH}_2\text{CH}_2)_4\text{Pb}$  :**

Tetraethyl lead is produced in large amount. It is used as an 'anti-knock' additive for increment in the octane number of petrol. Its commercial preparation is used as a sodium/lead alloy.



For the new cars to run lead-free petrol,  $(\text{CH}_2\text{CH}_2)_4$  is declined rapidly once was produced in very larger tonnages than any other organometallic compound.

**Concept Ladder**



Covalent character follows the order :



**Q.1** Standard electrode potential values,  $E^\ominus$  for  $\text{Al}^{3+}/\text{Al}$  is  $-1.66\text{ V}$  and that of  $\text{Tl}^{3+}/\text{Tl}$  is  $+1.26\text{ V}$ . Predict about the formation of  $\text{M}^{3+}$  ion in solution and compare the electropositive character of the two metals.

**Sol.** Standard electrode potential values for 2 half cell reactions suggest that  $\text{Al}$  has high tendency to make  $\text{Al}^{3+}(\text{aq})$  ions, while  $\text{Tl}^{3+}$  is a powerful oxidising agent but unstable in solution also. Thus  $\text{Tl}^+$  is more stable in solution than  $\text{Tl}^{3+}$ . Aluminium being able to form +3 ions easily, is more electropositive than thallium.

**Q.2** White fumes appear around the bottle of anhydrous aluminium chloride. Give reason.

**Sol.** Anhyd.  $\text{AlCl}_3$  is partially hydrolysed with atmospheric moisture to liberate  $\text{HCl}$  gas. Moist  $\text{HCl}$  appears white in colour.



**Q.3** Boron is unable to form  $\text{BF}_6^{3-}$  ion. Explain.

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

**Q.4** Why is boric acid considered as a weak acid?

**Sol.** As it is not able to release  $\text{H}^+$  ions on its own. From  $\text{H}_2\text{O}$  molecules it receives  $\text{OH}^-$  ions to complete its octet and in turn releases  $\text{H}^+$  ions.

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

**Sol.** Diamond has a 3D network involving strong C—C bonds, which are difficult to break & in turn has high melting point.

**Q.6** What are silicones?

**Sol.** Simple silicones consist of  $\left( \begin{array}{c} | \\ -\text{Si}-\text{O}- \\ | \end{array} \right)_n$  chains in which alkyl or phenyl groups

occupy the remaining bonding positions on each Si atom. They are hydrophobic (water repellent) in nature.

**Q.7** Explain the following :

- (i)  $\text{CO}_2$  is a gas whereas  $\text{SiO}_2$  is solid.
- (ii) Silicon forms  $\text{SiF}_6^{2-}$  ion whereas the corresponding fluoro compound of carbon is not known.



**Sol.** (i) Si has a large size compared to C. It does not form good pi overlapping. It forms 4 single covalent bonds with O<sub>2</sub> atoms. Each O<sub>2</sub> atom is linked with two Si atoms. Thus, a large giant molecule of a 3D structure is formed whereas C form a double bond with O<sub>2</sub> atom due to pi overlapping.

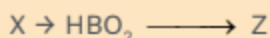
(ii) Si has lower energy 3D orbital so it can expand its octet giving sp<sup>3</sup>d<sup>2</sup> hybridization while d orbitals are not present in the valence shell of C. It can undergo sp<sup>3</sup> hybridisation only. The size of the C atom is very small to accommodate six F-anions.

**Q.8** The +1 oxidation state in group 13 and +2 oxidation state in group 14 becomes more and more stable with increasing atomic number. Explain.

**Sol.** Because of poor shielding of s-orbital electrons by d and f orbitals, the tendency of s-orbital to form the bond and it will decreases down the group in group 13 and 14.

This property is known as inner pair effect. Thus, the +1 O.S. in group 13 and +2 oxidation state in group 14 becomes more stable with increasing atomic number.

**Q.9** Identify the compounds A, X and Z in the following reactions :



**Sol.** A is Borax which reacts with hydrochloric acid in presence of water to give Orthoboric acid (X).

On heating orthoboric acid it gives metaboric acid and further on heating gives the compound Z i.e. Boron trioxide.

**Q.10** Explain the following :

(i) Gallium has a higher ionisation enthalpy than aluminium.  
(ii) Boron does not exist as B<sup>3+</sup> ion.





- Sol.** (i) The effective nuclear charge on gallium is slightly higher than that on aluminium because of ineffective shielding of valence e<sup>-</sup>s by the intervening 3d e<sup>-</sup>.
- (ii) Boron has 3 electrons in the valence shell. Because of its small size and a high sum of the first three IE, it does not form B<sup>3+</sup> ion.

**Q.11** Carbon and silicon both belong to the group 14, but despite the stoichiometric similarity, the dioxides, (i.e., carbon dioxide and silicon dioxide), differ in their structures. Comment.

- Sol.** C can form stable pπ-pπ bonding with itself and other small atoms like O<sub>2</sub> and N<sub>2</sub> due to its small size. In CO<sub>2</sub> each O<sub>2</sub> atom is double-bonded with the C atom with pπ-pπ overlapping. Si cannot form this bonding because of its large size.

**Q.12** Explain the nature of boric acid as a Lewis acid in water.

- Sol.** H<sub>3</sub>BO<sub>3</sub> is a weak monobasic acid and accepts electrons from a hydroxyl ion therefore acts as a Lewis acid.



H<sub>3</sub>BO<sub>3</sub> accepts OH<sup>-</sup> and the formation of hydroxyl ion takes place. Thus, H<sub>2</sub>BO<sub>3</sub> act as a Lewis acid in H<sub>2</sub>O.

**Q.12** Explain the following :

- (i) Carbon shows catenation property but lead does not.  
(ii) BF<sub>3</sub> does not hydrolyse.

- Sol.** (i) The catenation property depends on the size of atom and the M—M bond energy. Atomic radii is inversely proportional to the M—M bond energy, the greater is the tendency to show catenation. On descending down the group the size of atom increases and the M—M bond energy also reduces.
- (ii) BF<sub>3</sub> does not hydrolyze completely. Instead, it hydrolyzes incompletely to form H<sub>3</sub>BO<sub>3</sub> and HBF<sub>4</sub>. As HF first formed reacts with H<sub>3</sub>BO<sub>3</sub>.

## Chapter Summary

1. Al atom is larger in size than Ga atom.
2.  $B_4C_3$  (Boron Carbide) is one of the hardest known artificial substance and is called Norbide.
3. Jewellers borax is  $Na_2B_4O_7 \cdot 5H_2O$ .
4. Al is most abundant element on earth crust.
5. Conc.  $HNO_3$  renders Al passive.
6.  $H_3BO_3$  renders Al passive.
7.  $AlCl_3$  exists as  $Al_2Cl_6$  in solid state. When dissolved in water it dissociates as  $[Al(H_2O)_6]^{3+} + 3Cl^-$ .
8. **Tin disease or tin plague or tin pest** - When white tin changes to grey tin its volume increase, it becomes brittle and crumbles in form of powder. It is called tin disease.
9. **Tin cry** - When bent, tin metal produces cracking sound (due to rubbing of crystals) which is called tin cry.
10.  $PbO_3O_4$  (Red lead or minimum) is mixed oxide of  $PbO_2 \cdot 2PbO$ .
11.  $CO_2$  is anhydride of  $H_2CO_3$ .
12.  $CCl_4$  can't be hydrolysed and  $SiCl_4$  is easily hydrolysed.
13. Solid  $CO_2$  is called dry ice because it cools surface without wetting it. Trade name of dry ice is **drikold**.
14. **Plumbo solvency** is dissolution of lead in  $H_2O$  containing air and  $CO_2$  forming soluble  $Pb(OH)_2$  which gives highly poisonous  $Pb^{2+}$  ions. So lead pipes are not used for carrying water.
15. Thermodynamically graphite is more stable than diamond.
16. Carbogen is (95%  $O_2$  and 5%  $CO_2$ ) and is used in artificial respiration.
17. **Pyrene** is trade name of  $CCl_4$  and is used as fire extinguishes.
18. U.V. rays are checked by Crooke's glass.
19. Lead marks paper just like graphite, therefore graphite pencils are called lead pencils.
20. BN and graphite have similar structure.
21. Lead is used in making radiation shields because it stops harmful radiations.



