

P-block Elements

There are six groups of p-block elements in periodic table → group 13 to 18.

Boron, Carbon, Nitrogen, Oxygen, Fluorine and helium head the groups.

E.C → $ns^2 np^{1-6}$ (except for He)

- * The maximum oxidation state shown by a p-block element is equal to the total no. of valence electrons (i.e sum of s and p electrons)
- * In boron, carbon and Nitrogen families the group oxidation state is the most stable state for lighter element in the group.
- Inert Pair Effect → Occurrence of oxidation state two unit less than the group Oxidation states.
- Non-metals and metalloids exists only in p-block.
- Heaviest element in p-block = most metallic
- In general, non-metals have higher ionisation enthalpies and higher electronegativities than metal
- Metals readily form cations.
- Non-Metals readily form anions.

- * Compounds formed by highly reactive non metals with highly reactive metals are generally ionic.
 - Compounds formed b/w non-metals are largely covalent.
 - Non-metals oxides → acidic, Metal Oxides → Basic.
 - The presence of the d-orbitals influences the chemistry of heavier elements.
 - first member of group differs from heavier members due to its ability to form p π -p π multiple bonds to itself and to other second row elements.
 - * C:N in species of heavier elements may be higher than for the first element in the same oxidation state:
eg → In +5 O-State of both N and P form oxoanions → NO_3^- and PO_4^{3-} .

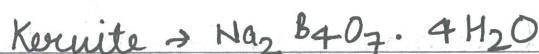
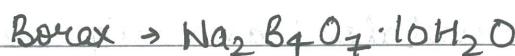
Group 13 Elements → Boron family

B → typical non-metal

Al → metal

Gra In Td] less abundant
 → exclusively metallic in character elements

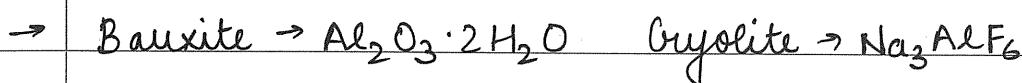
B → fairly rare element occurs as
orthoboric Acid \rightarrow H_3BO_3



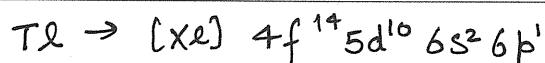
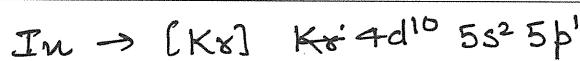
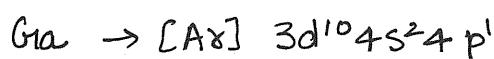
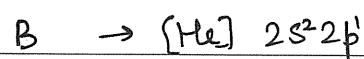
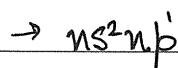
- * abundance of boron \rightarrow less than 0.0001% by mass

Isotopes of B \longleftrightarrow ^{10}B (19%)
 \longleftrightarrow ^{11}B (81%)

Al \rightarrow most abundant metal of 3rd most abundant in earth's crust (8.3% by mass) after Oxygen (45.5%) and Si (27.7%).



Electronic Configuration



Atomic Radii

- \rightarrow On moving down the group, atomic radius is expected to increase.
- \rightarrow atomic radius of Ga is less than of Al due to variation in the inner core of the Electronic Configuration. Due to poor screening effect, atomic radius of Ga (135 pm) is less than that of Aluminium (143 pm).

Ionization Enthalpy

- \rightarrow Decrease from B to Al is associated with ~~size~~ increase.
- \rightarrow This discontinuity is in I.E due to inability of d and f electrons which have low screening effect, to compensate the ~~size~~ in nuclear charge.

$$\Delta iH_1 < \Delta iH_2 < \Delta iH_3$$

- * sum of I.E for each element is very high.

Electronegativity

- first decreases from B to Al and then increases marginally (Refers NCERT Pg - 310) because of discrepancies in atomic size of the elements.

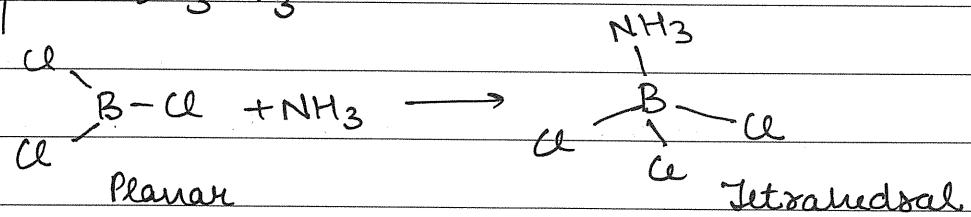
Physical Properties

- Due to very strong crystalline lattice, boron has unusually high M.P., rest of metals are soft metals.
- Ga → low M.P., exists in liquid state during summer.
- Density → ↑s down the group.

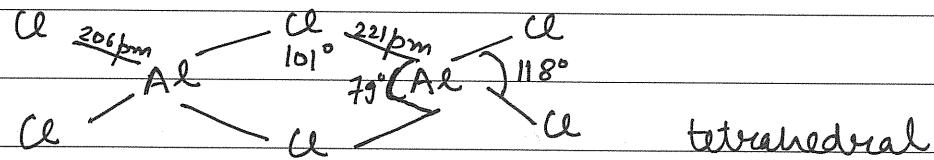
Chemical Properties

- * Oxidation states & Trends in Chemical Reactivity
 - Due to small size of B, sum of its first I.E are high. This prevents it to form +3 ions & forces it to form only covalent bonds.
- But whenever move from B to Al, sum of first 3 I.E considerably ↓s of Al, therefore able to form Al^{3+} ions.
 $\text{Al} \rightarrow$ highly electropositive element
- * Down the group, due to poor shielding effect of intervening d & f orbitals, the increased effective nuclear charge holds ns electrons tightly (responsible for inert pair effect).
- Ga, In & Tl → +1 & +3 Oxidation state.
- Stability of +1 Oxidⁿ state → $\text{Al} < \text{Ga} < \text{In} < \text{Tl}$

- In Ti^{+1} Oxd^m state is predominantly whereas +3 Oxd^m state is highly oxidising in character.
 - Compounds in +1 Oxd^m state are more ionic than those in +3 Oxd^m state.
 - Tendency to behave as Lewis acid decreases with the ↑ se in the size down the group.
 - BCl_3 easily accepts a lone pair of e^- from ammonia to form $\text{BCl}_3 \cdot \text{NH}_3$.

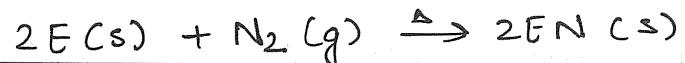
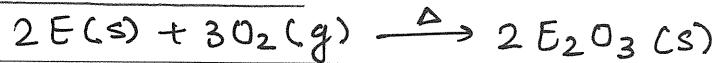


- AlCl₃ by forming dimer achieves stability.



- * Trichlorides on hydrolysis of water form tetrahedral species $[M(OH)_3]^-$ $M = sp^3$ hybridised
 - * Aluminium forms octahedral $[Al(H_2O)_6]^{3+}$ ion.
 $\hookrightarrow Al \rightarrow sp^3 d^2$ hybridised

1. Reactivity towards air



B → unreactive in crystalline form

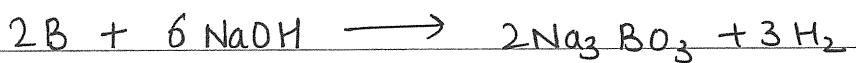
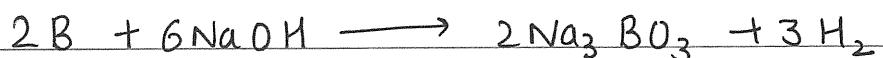
$\text{Al} \rightarrow$ forms a thin layer of Oxide on the surface.

Amorphous B & Al → forms B_2O_3 & Al_2O_3 on heating in air.

B → Boron trioxide is acidic (forms metal borates)
 Al → amphoteric
 Cr → "
 In → basic in
 Te → properties * nature of oxides varies down the group

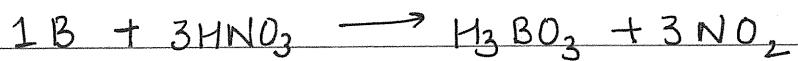
2) Reactivity towards acids & alkalies

Boron dissolves in fused alkalies only to produce corresponding Borates along with liberation of H₂ gas.

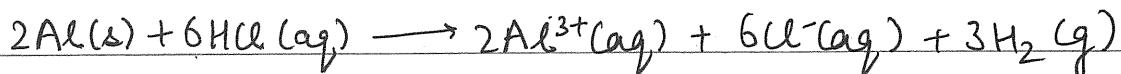


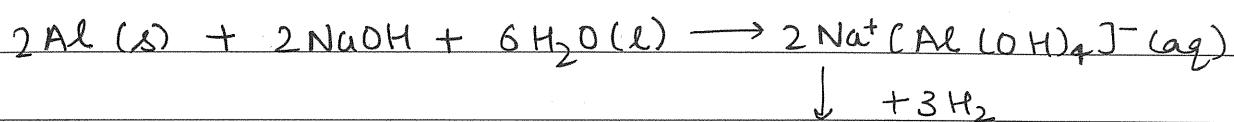
Boron in general is not affected by non-oxidising acids eg → HCl, dil H₂SO₄.

However, strongly Oxidising acids such as conc. H₂SO₄ or conc. HNO₃ do react with Boron.



Aluminium dissolves in mineral acids and aqueous alkalies → shows its amphoteric nature.

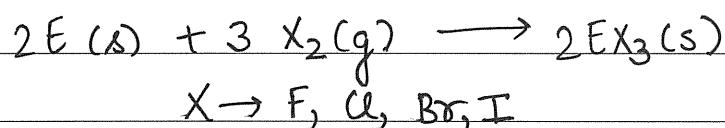




sodium tetrahydroxy
aluminate (II)

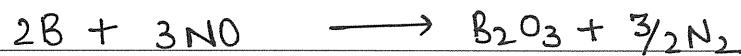
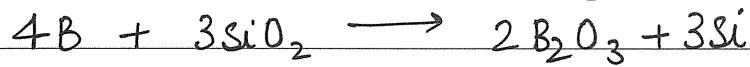
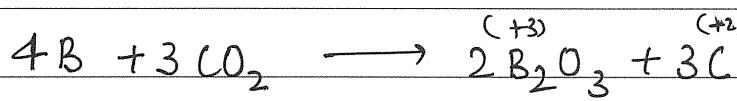
3.) Reactivity towards Halogens

→ formation of Trihalides

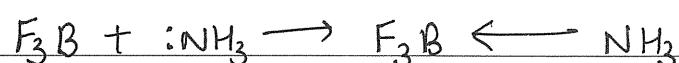


4.) Reaction involving reducing nature of Boron

→ Boron is a powerful reducing agent for reaction with non-metal Oxides like CO_2 , SiO_2 , NO_2 , NO etc.



★ Boron Trifluoride easily reacts with Lewis bases such as NH_3 to complete octet around boron.

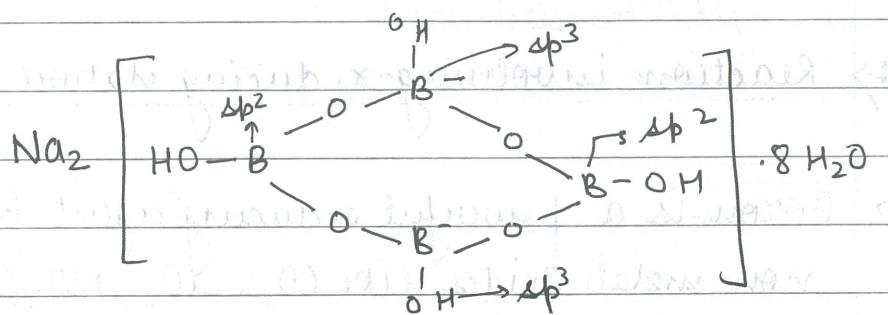


It is due to absence of d-orbitals that the maximum covalence of B is 4.

Compounds Of Boron

1) Borax

- white crystalline solid
- $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
- $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$
- contains tetrานuclear units $\rightarrow [\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$

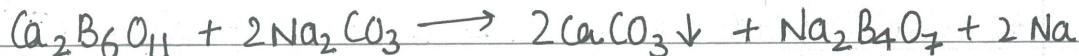


- Borax dissolves in water to give an alkaline medium.



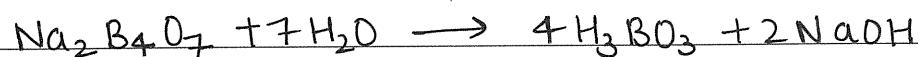
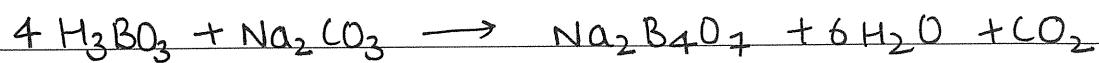
Preparation

i) from colemanite



sodium
metaborate

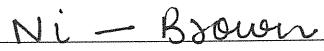
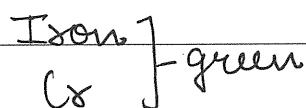
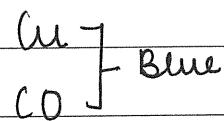
ii) Borax can also be prepared by neutralising H_3BO_3 by Na_2CO_3



Borax Bead Test

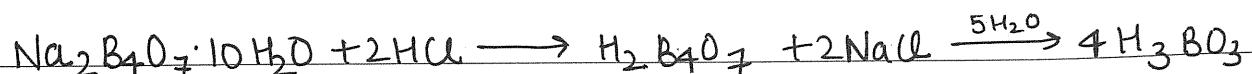
On heating above its melting point Borax first swells and then loses its water of crystallisation to finally give a hot glassy mass of B_2O_3 . When this mass on platinum wire loop is brought in contact with a coloured salt, the B_2O_3 forms characteristic coloured metaborates with basic oxides:

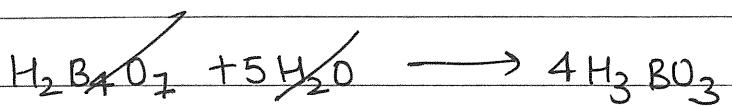
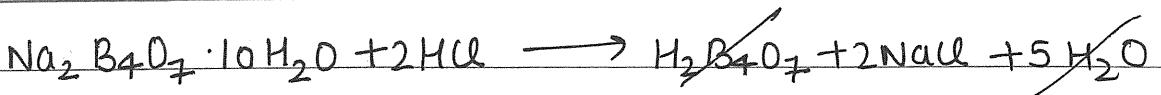
This Test is called as Borax Bead Test.



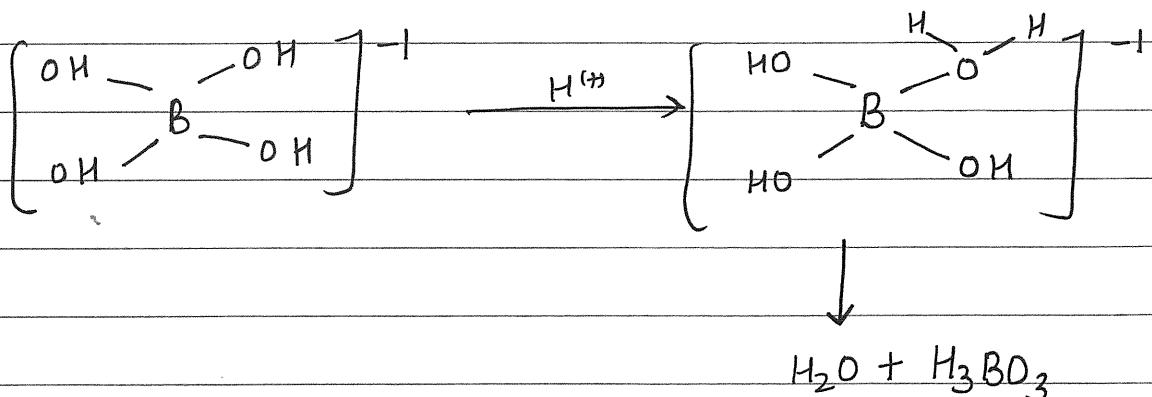
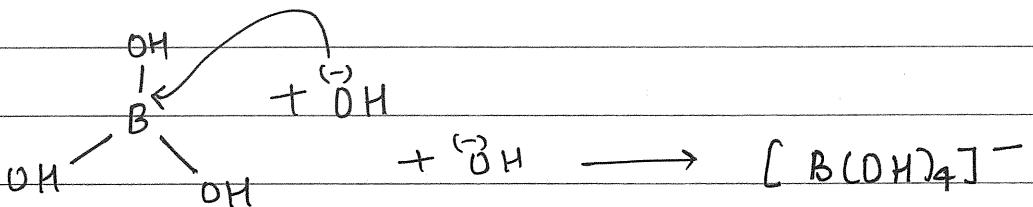
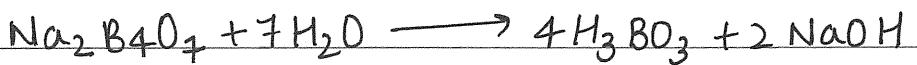
[Blue flame]

Reaction of Borax with acids

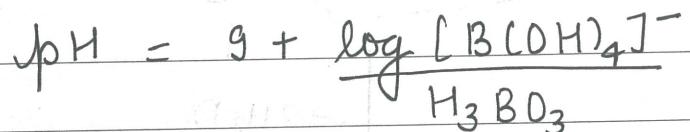
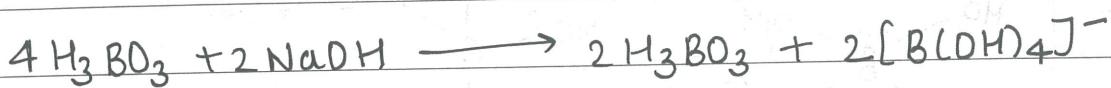




→ One mole of borax reacts with 2 moles of H^+ aqueous. This is because aqueous solution of Borax produces two moles of H_3BO_3 and two moles of its conjugate base $[\text{B}(\text{OH})_4^-]$. Out of these two species only $[\text{B}(\text{OH})_4^-]$ is capable of reacting with H^+ .



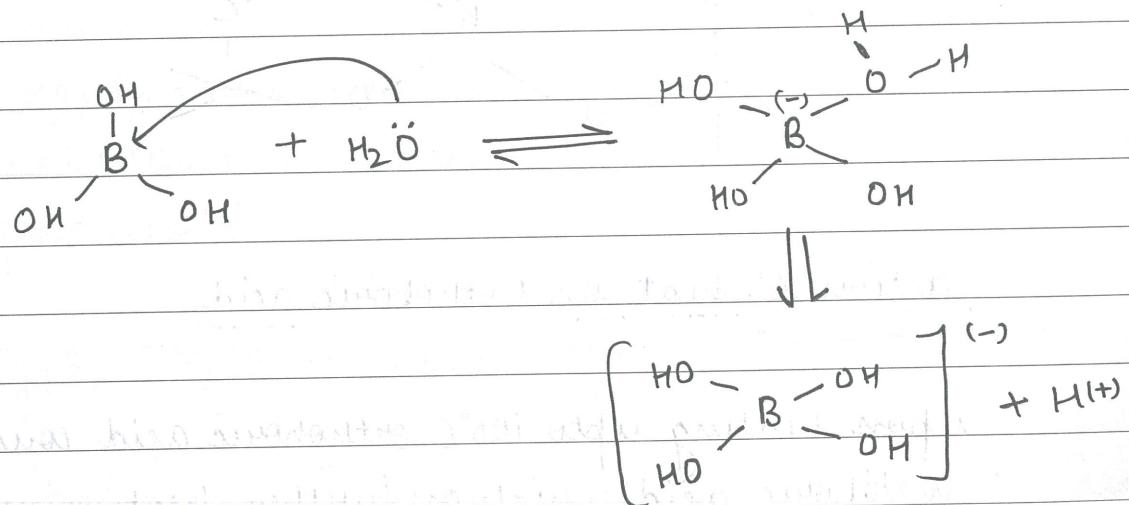
Q An aqueous solution of Borax is prepared by dissolving 0.1 mole of Borax in 2 litres of water. Find out the pH of the system if ionisation constant of boric acid is 10^{-9} .



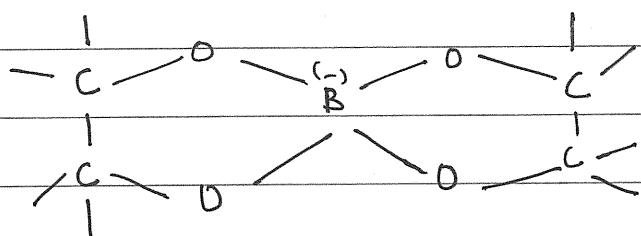
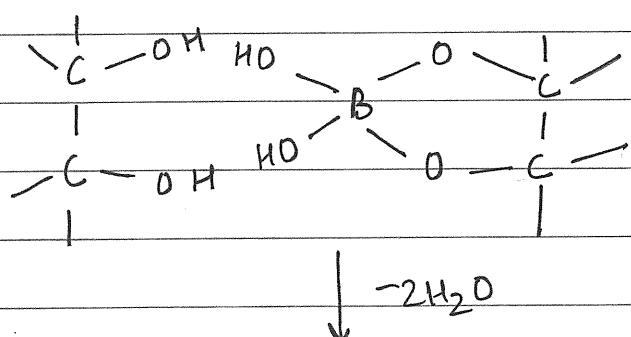
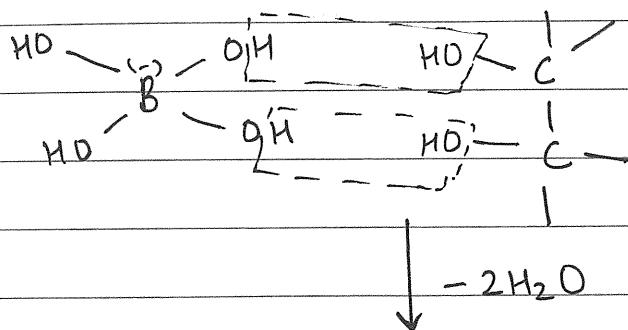
$$= 9$$

Orthoboric Acid

- white crystalline solid with soapy touch.
- orthoboric acid is an e⁻ deficient compound and hence its aqueous solution behaves as a weak monobasic lewis acid.

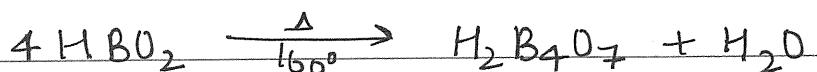
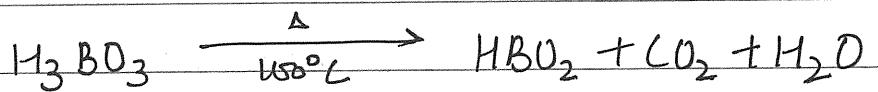


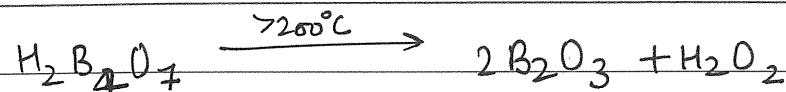
The acidic strength of H_3BO_3 may be increased in presence of polyalcohols in cis-diols configuration such as glycerol, mannitol, some other sugars etc.



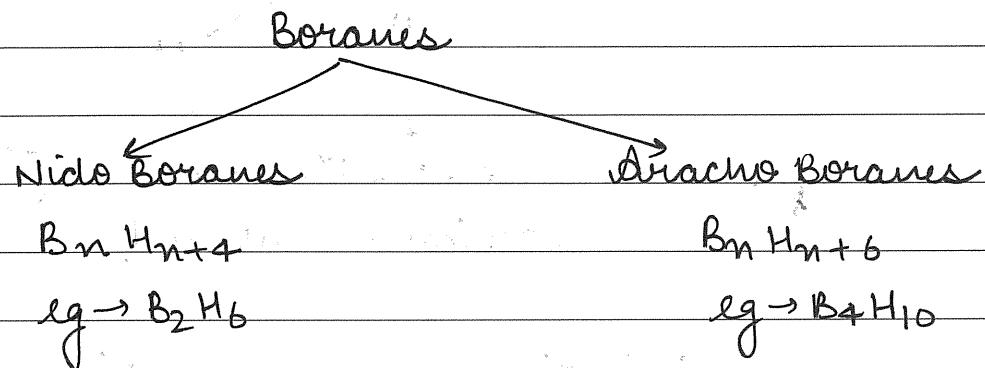
Action of heat on Orthoboric acid

upon heating upto 100°C orthoboric acid converts into metaboric acid which on further heating upto 160°C gives tetraboric acid finally at greater than 200°C the tetraboric acid yields B_2O_3 .



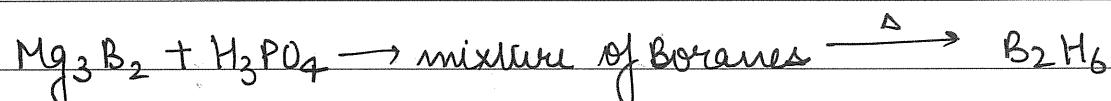


Boranes

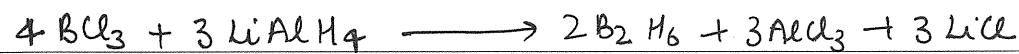
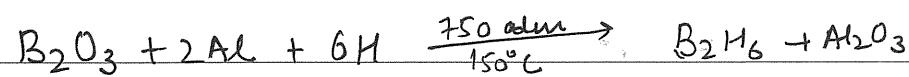


Preparation of Diboranes

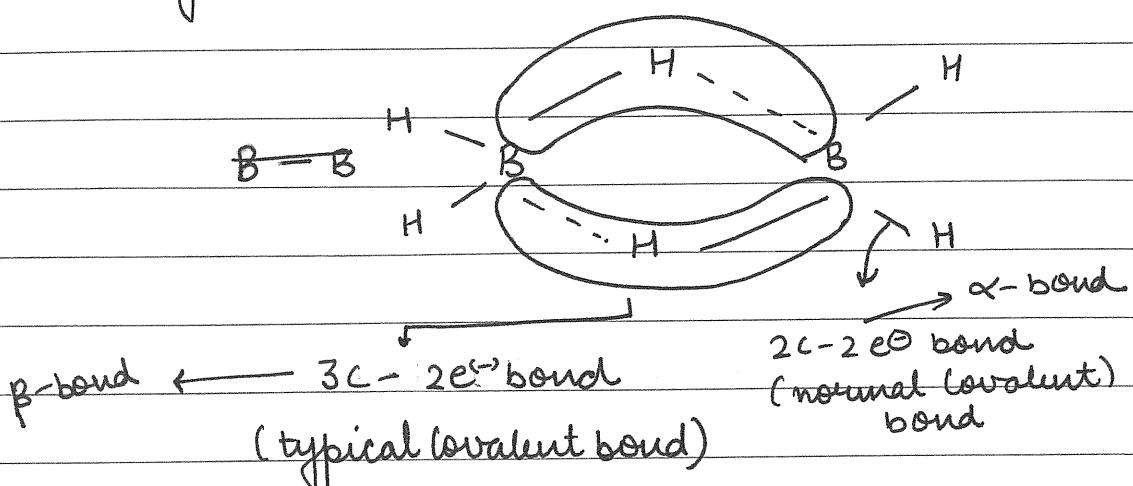
Diborane was first prepared by Alfred Stock by reaction of Mg_3B_2 with H_3PO_4 which resulted into mixture of boranes and upon strong heating the mixture majority produces Diborane.



- (a) Compounds of Boron with highly electronegative atoms.
- (b) a highly electropositive metal
- (c) a source of Hydrogen



Structure of Diborane



sp^3 hybridisation due to formation of 4 sigma bonds.

for all types of boranes the total no. of α -Bonds &
 β -Bonds respectively are $B_b H_h^q$.

$$\alpha = \frac{1}{2} (b + h - 3q)$$

$$\beta = b + q$$

(q is charge on molecule)

for eg $\rightarrow B_4 H_{10}$

$$\alpha = \frac{1}{2} (4 + 10 - 3 \times 0)$$

$$= 7$$

$$\begin{aligned}\beta &= 4 + 0 \\ &= 4\end{aligned}$$

Characteristics Reaction of Diboranes

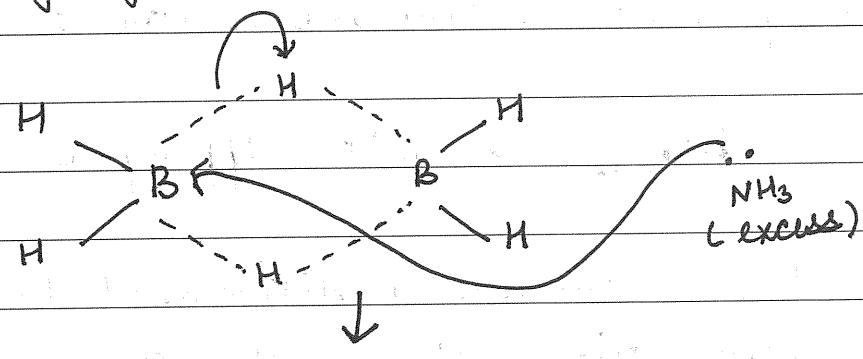
- 1) Diboranes catches fire spontaneously upon exposure to O_2 .

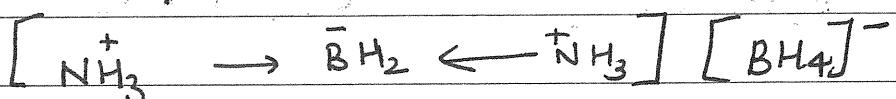
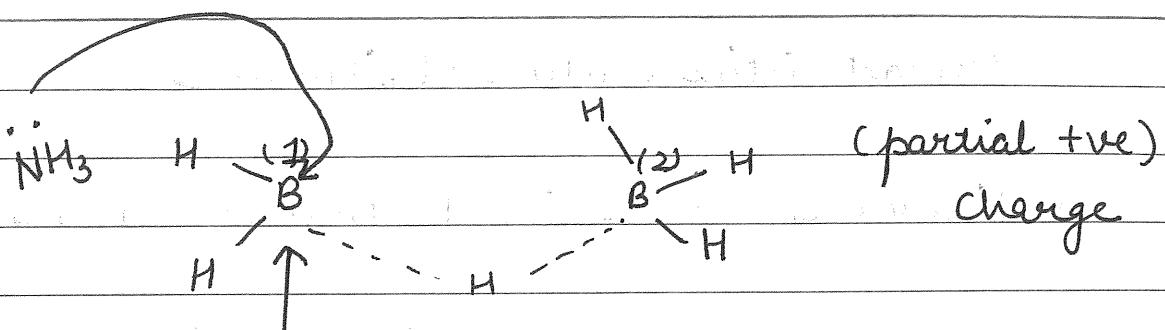


- 2) for reaction with compounds containing acidic Hydrogen B_2H_6 behaves as a source of hydride ion thereby eventually liberating hydrogen gas in the process. Boron atom accepts the nucleophilic portion of the starting compound.



As Boron is electron deficient in diborane hence usually a nucleophile attacks on the Boron atom leading to either symmetric cleavage or non-symmetric cleavage of the $3C-2e^-$ bonds present in system.



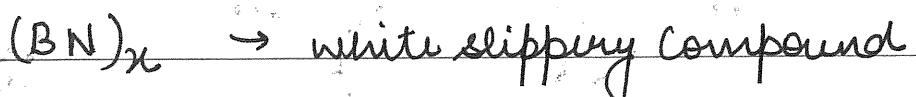


ADDUCT Ionic compound

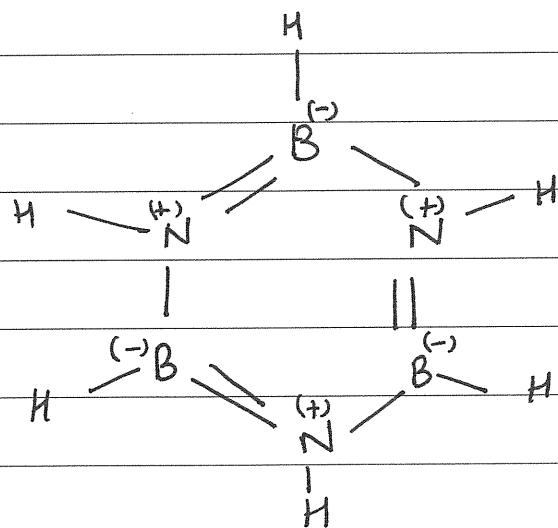
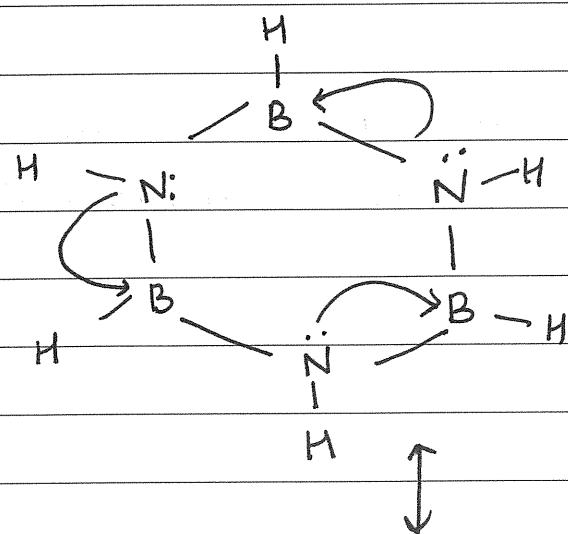
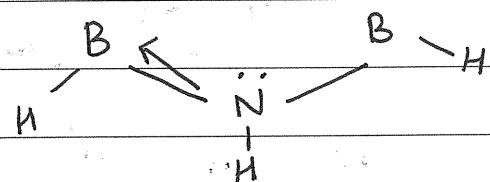
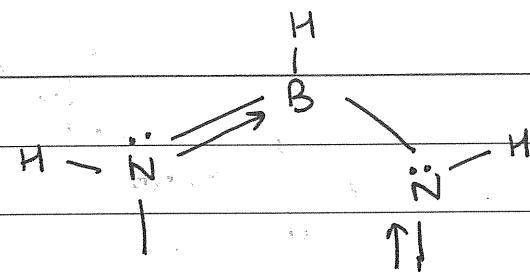
ADDUCT → The product of lewis acid base neutralisation is called an adduct.

- The above ionic adduct is obtained at low temp. However in presence of high temp the product obtained is Boron Nitride $(\text{BN})_x$.

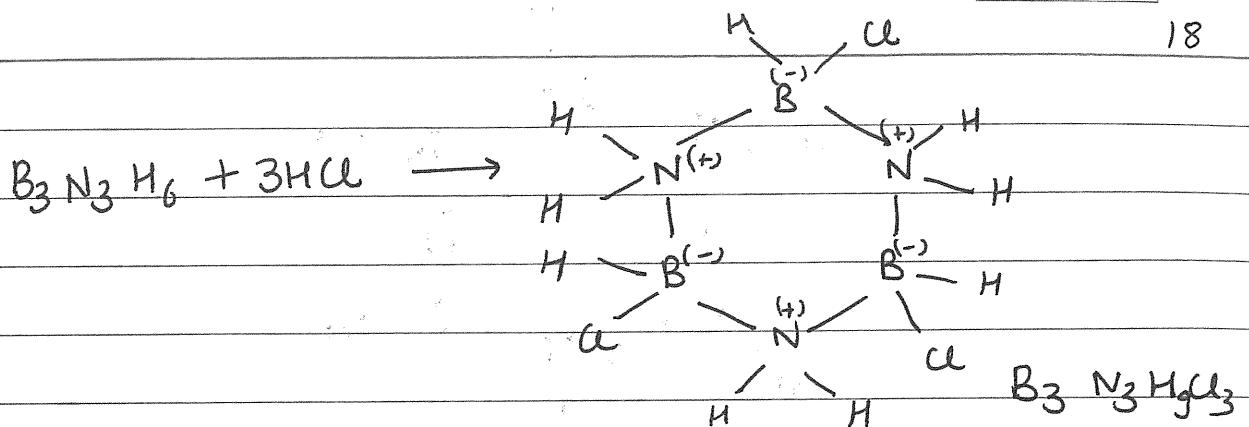
This compound has the same structure as that of graphite i.e parallel layers stacked together with weak Vanderwall forces between the layers. This happens as one boron and one Nitrogen together have the same no. of electrons as present in two carbon atoms.



- Under controlled conditions of Temperature & molar ratio of 1:2 and between Diborane and ammonia the product obtained is $\text{B}_3\text{N}_3\text{H}_6$ (Borazine or Inorganic Benzene)

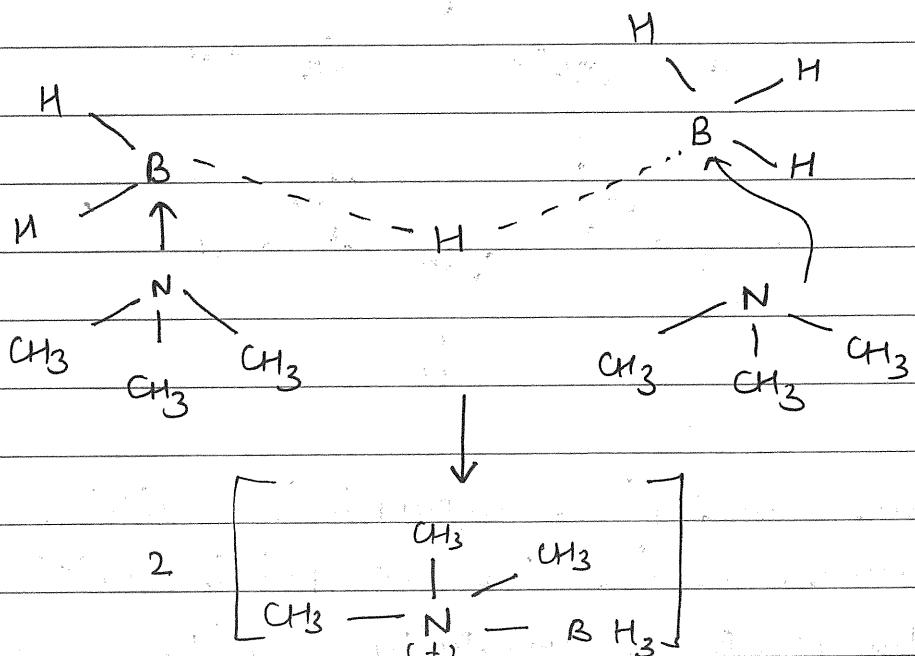
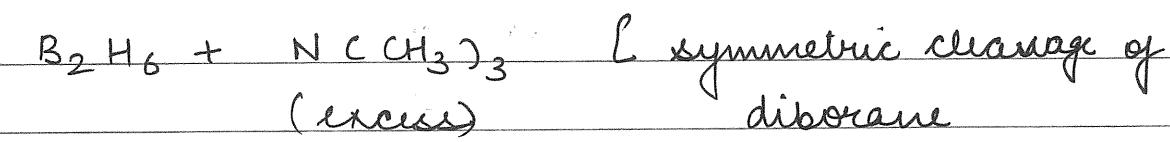
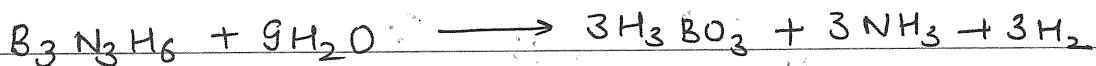


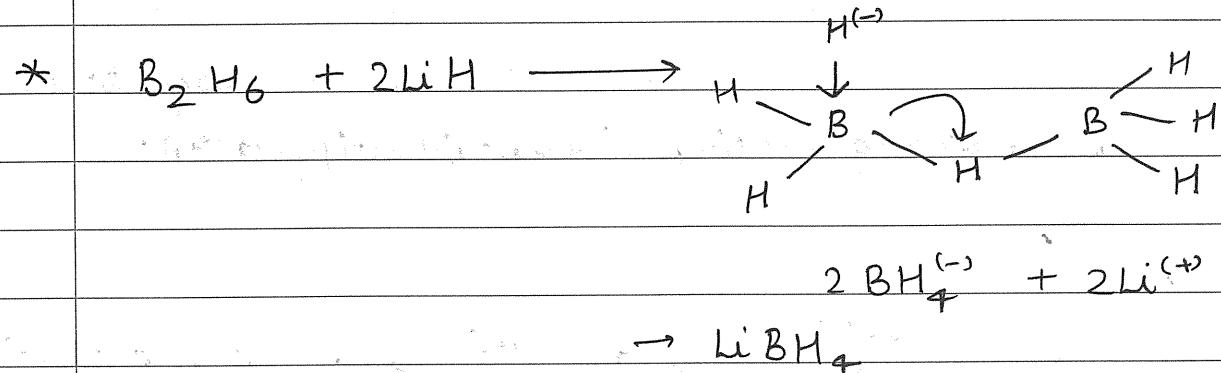
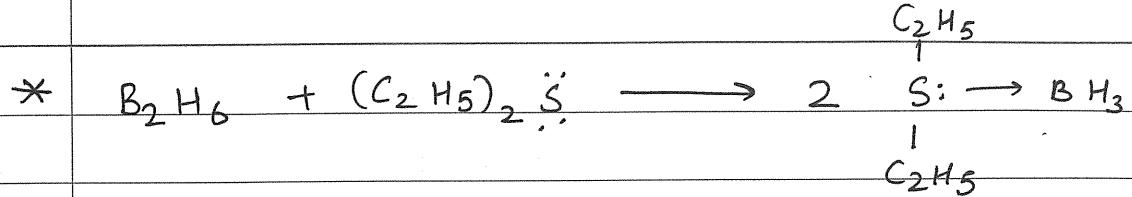
- Benzene never gives electrophilic addition reaction however borazine give electrophilic addition reaction as the extent of aromaticity is quite less as compared to benzene.



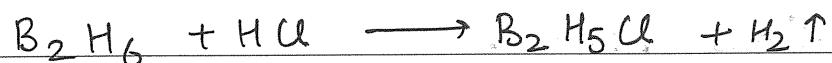
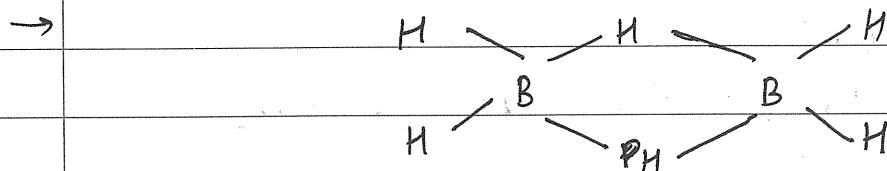
(electromeric effect)

→ If heated with water, Borazine hydrolyses slowly to liberate ammonia, hydrogen and orthoboric acid.

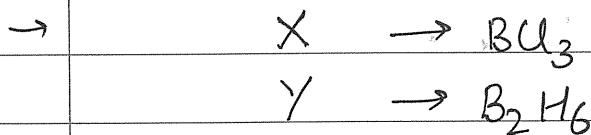




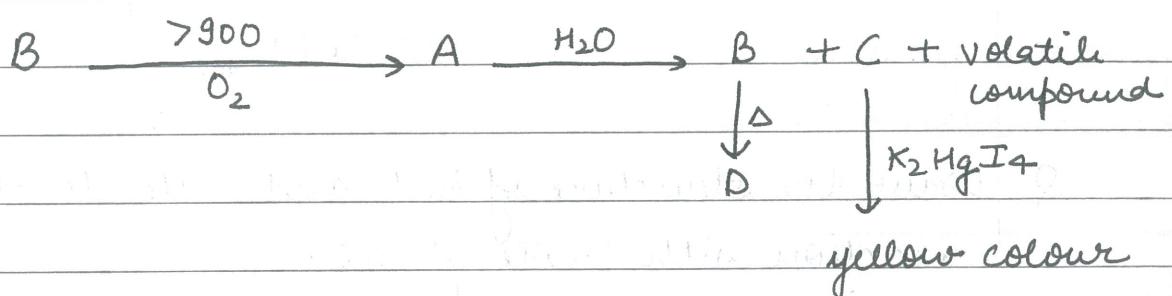
Q Draw the structure of B_2H_6 and write its chemical reaction with 1 mole of HCl.



Q A halide X on reaction with $LiBH_4$, A hydride Y containing 21.72% Hydrogen. The compound X reacts with air explosively resulting in B_2O_3 .



Q Boron on heating at 900°C in air gives a white compound A which is decomposed when heated in a current of steam to give a white powder B and a gas C and some other volatile products. Gas C gives yellow color with Nessler Reagent. Compound B on strong heating gives D. Identify A to D.

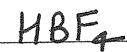
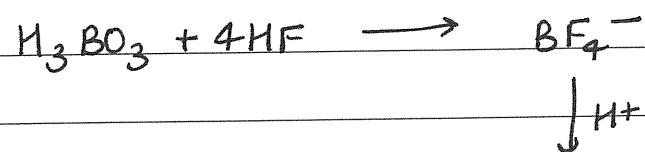
 \rightarrow 

Halides of Boron

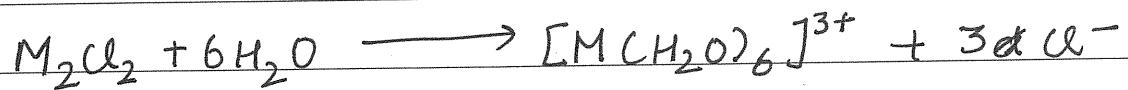
Boron upon direct reaction with halogens produces corresponding boron trihalides. Among these trihalides the strongest lewis acid turns out to be BF_3 and weakest is BCl_3 . Except BF_3 all halides of boron hydrolyse completely giving -



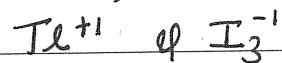
→ However BF_3 hydrolyses incompletely and forms fluoroborates. This happens as HF form in the first step further reacts with H_3BO_3 .



→ AlCl_3 , AlB_3 and GaCl_3 exists as dimer due to large size of central atom. The dimeric form retains in non-polar solvent as well as in gaseous state. However the compound ionised in water due to high enthalpy of hydration.



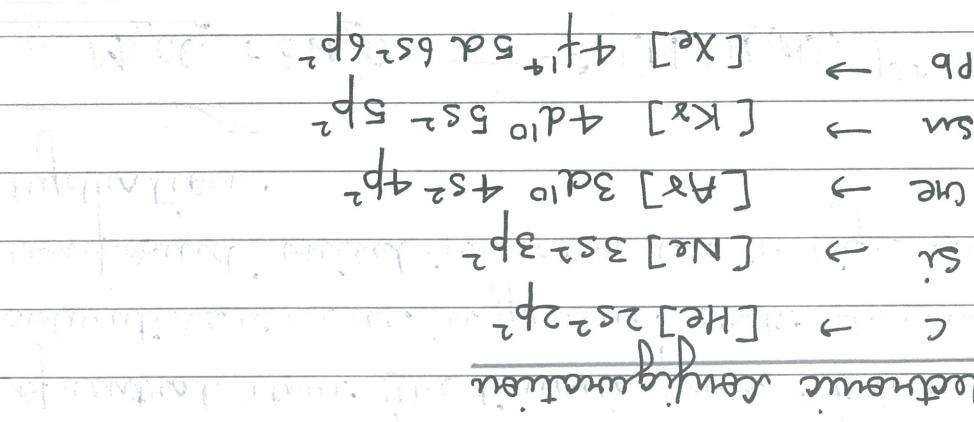
→ TlI_3 is an unusual compound and is isomorphous (same structure) with CsI_3 .



Moving down the group, i.e. down.
Tensile strength is higher than group 13.
Tensile strength

A.R of 14 < A.R of 13 group.

down to ↓ in the case of noble gases.
atomic radii increase on going down the group
Atomic Radii



Non-metals like → SnO₂, PbS, ZnS, PbCO₃ etc.

and others.
Silicon → present in nature as Silica (SiO₂)

Pb
Sn
Ge
Si → second most abundant element

Group 14 elements → halogen family

Melting and Boiling Point

- On moving down the group, M.P and B.P decreases.

Catenation

- ability of like atoms to link with one another through covalent bonds.



- * Carbon primarily exists in 7 allotropic forms out of which graphite and diamond are the most important. Diamond exists in cubic cell with each carbon atom being tetrahedrally surrounded by 4 other carbon atoms.

$$C-C = 1.54 \text{ \AA}$$

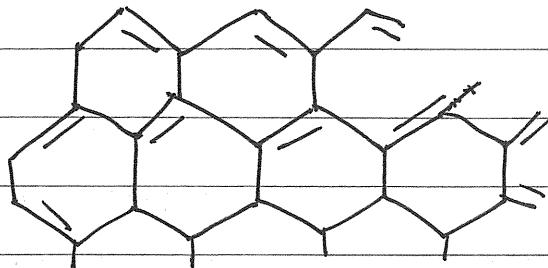
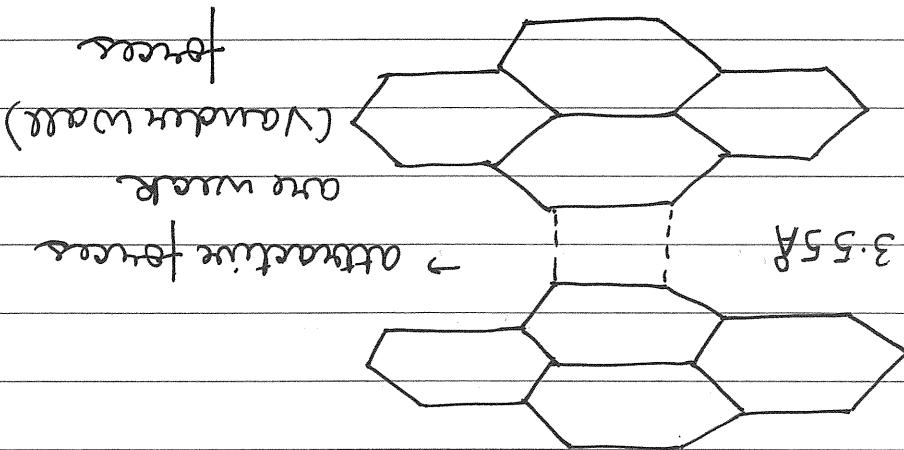
- Q The size of voids usually is smaller than that of lattice points but in case of diamonds the radius of carbon atom occupying the void has the same radius that is of lattice point. Why?

- This is because void is smaller only in case of ionic compounds whereas in case of covalent compounds overlapping takes place due to which same radius atoms can be present at the voids.

* Out of time the azeotropic is determined in relative humidity without azeotrope it is quite accurate in nature. Azeotrope is determined and its free enthalpy as compared to the standard enthalpy of formation.

Ammonium acetate
Same magnitude in diff. direction
outward force
outward force

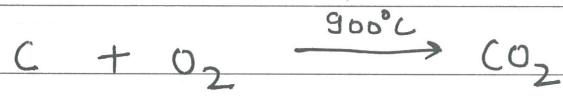
outward force
characteristic of
in diff. direction
diff. magnitude
Ammonium



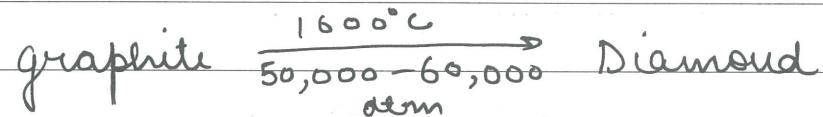
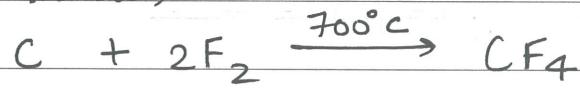
System of fused benzene rings.

Hydrophobic in the actual should have a lower enthalpy which may also be considered as a

energy of formation is 1.9 kJ/mol , lower at room temperature and pressure than diamond. Also, it is favourable for diamond to turn into graphite. The reverse is not possible, as the activation energy required for the process is very high. Synthetic diamonds are however produced at 1600°C and $50,000 - 60,000 \text{ atm P}$ on graphite.



(Diamond)



Compounds of Carbon

In the entire carbon family, carbon forms more no. of oxides than the other elements and these oxides differ from those of other elements on account of $\pi - \pi$ orbitals overlapping.

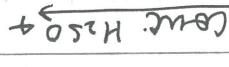
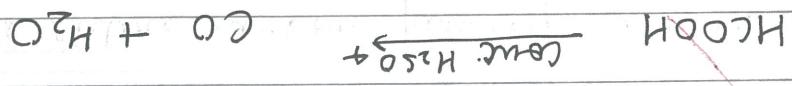
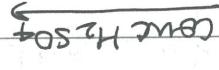
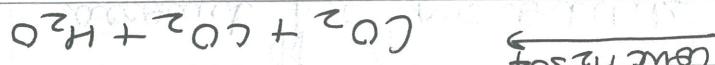


Less stable oxides are C_3O_2 , C_5O_2 and C_{12}O_9 .

Transient oxides of carbon are C_2O & C_2O_3 .

CO is a good reducing agent that converts many

Preparation of CO



2) By dry distillation of ferromagnetic carbide of Oxalic acid



1) Partial Oxidation of carbon

Mechanisms of Preparation

Oxidation state

Lanthanide oxidation state without oxidation in liquid

Note → Metallic oxides may be formed in this

solvating solvent in water and is neutral.

With a blue form.

Colorless, odorous, pungent gas that burns

Golden Mercuric CO

metal Oxides into metals:



Reaction with I₂O₅

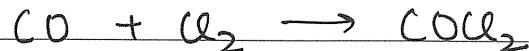


↓ starch paper
used in iodimetry blue

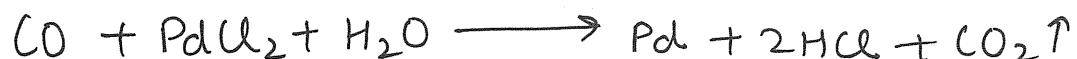
Reaction with sulphur

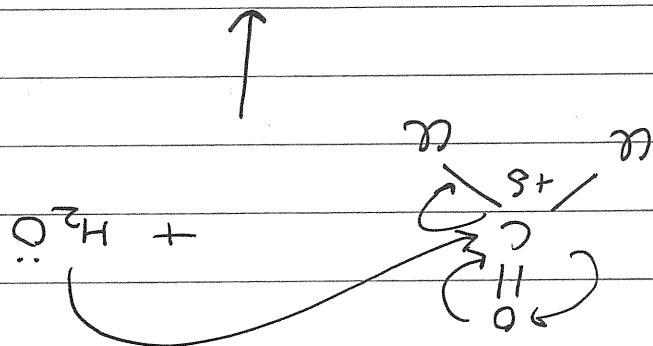
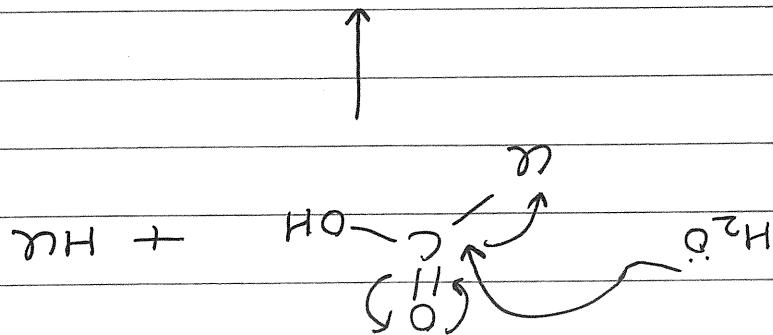
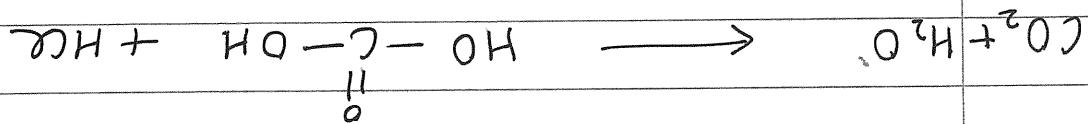
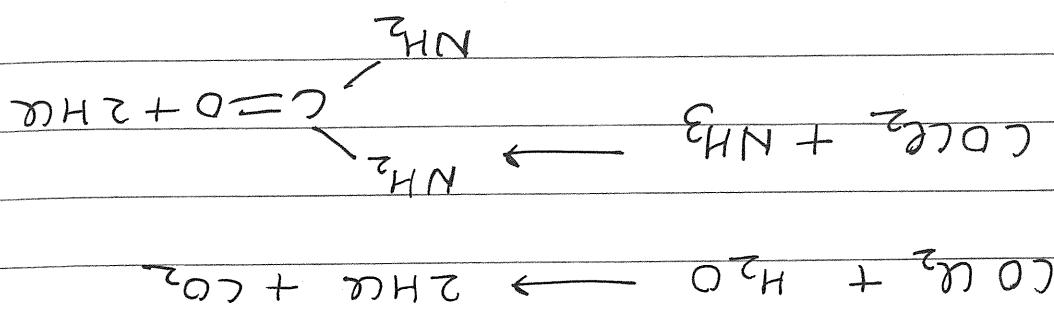


Reaction with chlorine



Carbon monoxide can reduce aqueous solution
of PdCl₂ to Pd.

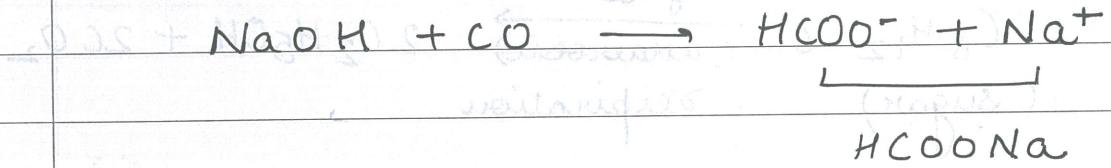




Mechanism :-

The carbonyl doublets formed by the reaction of CO with malonate (mainly CH_3COO^-) are present with anomalous water.

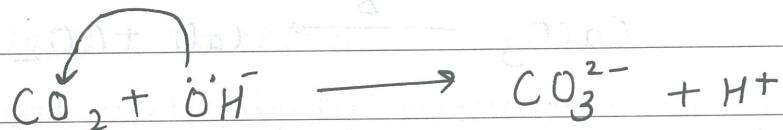
On heating with NaOH (fused) at high temp and pressure it forms.



(sodium formate)

Carbon Dioxide (CO_2)

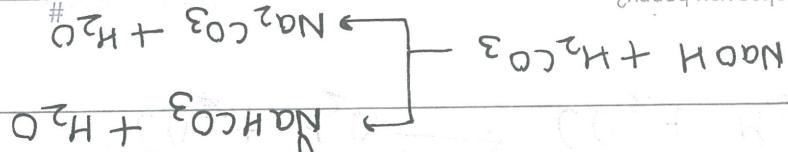
- is a colourless and odourless gas.
- fairly soluble in water.
- acidic in nature.
- turns lime water milky.



Methods of Preparation

- 1.) It is obtained as a byproduct in the manufacture of H_2 .





If aqueous solution of CO_2 reacts with base to form salts.

aqueous solution of CO_2 reacts with base to form salts.



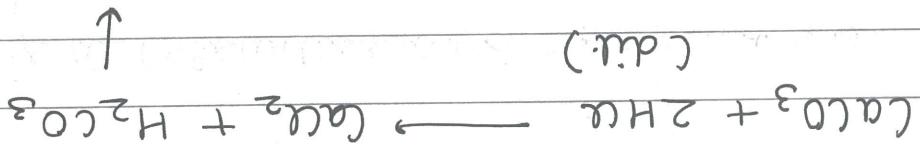
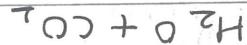
Reaction with water

Reactions of CO_2

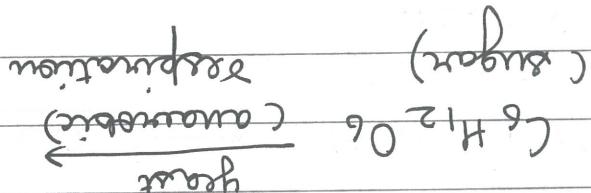


CaCO_3 Group 2 carbonates

It is also obtained by thermal decomposition for



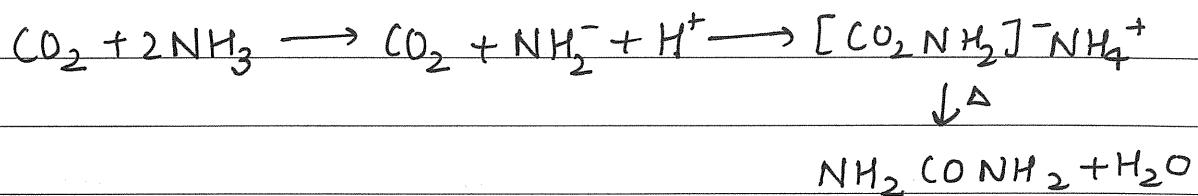
It is also obtained by the action of dilute acids on metal carbonates.



It is also obtained by fermentation process.

In breweries.

Reaction with ammonia

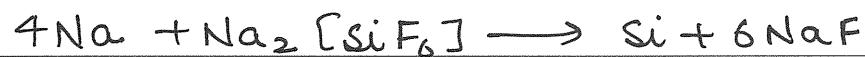


Silicon

is extracted by reducing SiO_2 with high purity coke.



It may also be obtained by sodium reduction of Na_2SiF_6 .



Highly pure silicon is obtained by reacting silicon with chlorine to form SiCl_4 which is purified by distillation.

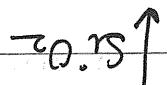
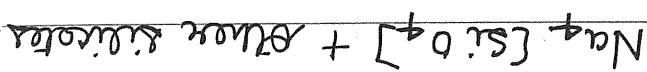
Treatment with highly electropositive element such as Mg or Zn provides pure elemental silicon.



area of contact.

(ii) $\text{Na}_4[\text{SiO}_4] + \text{Alumina} \rightarrow \text{Alumina silicate} \rightarrow \text{Na}_4[\text{SiO}_4] - \text{water}$

In the basic form of the mineral $\text{Na}_4[\text{SiO}_4]$, silicates may be classified as tetravalent silicates are formed together the



silicates now be prepared on a commercial scale by fusing alumina together with sand in electric furnace at about 1400°C .

Structure of Silicate

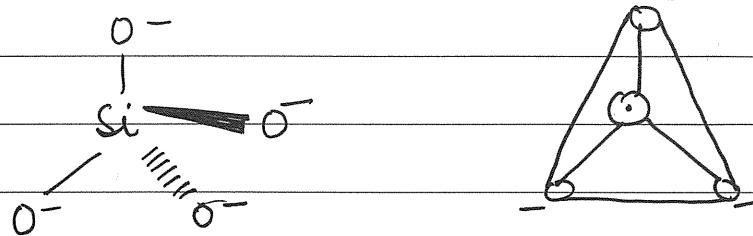
silicate minerals to all the hydrogous silicate minerals with all the hydrogous silicate minerals to form very stable silicate minerals.

It reacts slowly with cold aqueous NaOH solution, it remains unaffected by water and

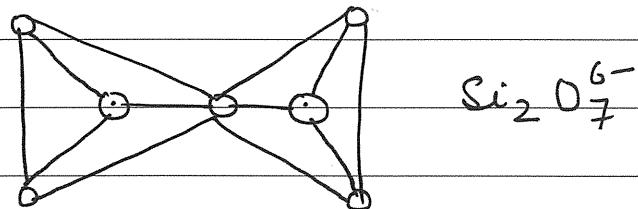
but, it remains unaffected by water and

Properties of Silicate

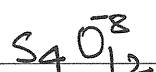
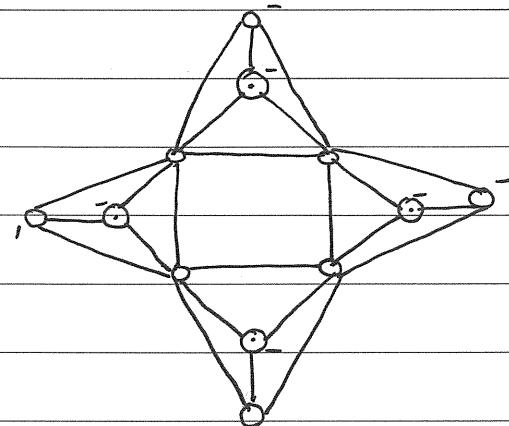
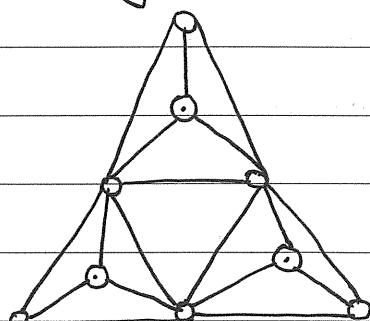
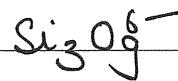
←



(ii) Pyrosilicate \rightarrow also called as disilicates and these silicates are corner O₂ atoms gets shared between 2 units.

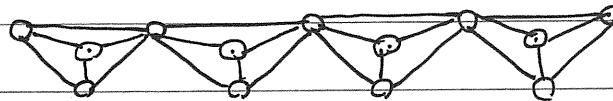


(iii) Cyclic silicates \rightarrow If two Oxygen atoms per tetrahedron are shared then rings containing 3, 4, 6 & 8 tetrahedra units are known to be obtained. This constitutes the cyclic silicates



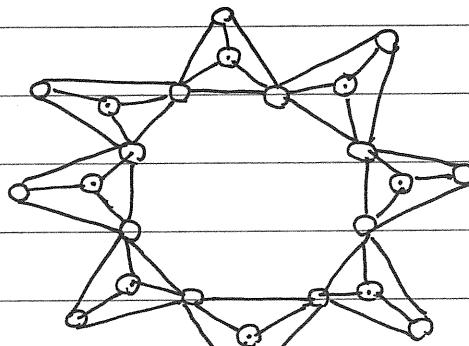
Silicate structures → These are also called polymer.
Silicates and clay have the general formula $(Si_2O_5)_{2n}$

(V)

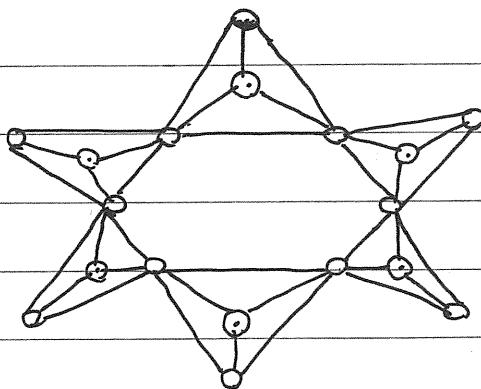


Chain silicates also called polyoxoanions are formed.
tetrahedral units in a straight chain, two tetrahedra gets linked about from the terminal atoms form chain silicates → If two oxygen atoms per

(IV)



Si_8O_{24}



Si_6O_{12}

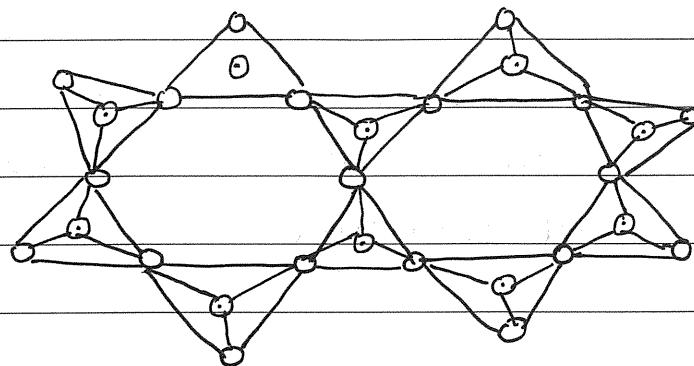
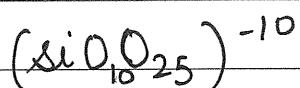
where $n = 3, 4, 6 \text{ or } 8$

No. of silicons = no. of silicones for quaternary silicate
general formula = $(Si_nO_{3n})_{2n}$

34



Date



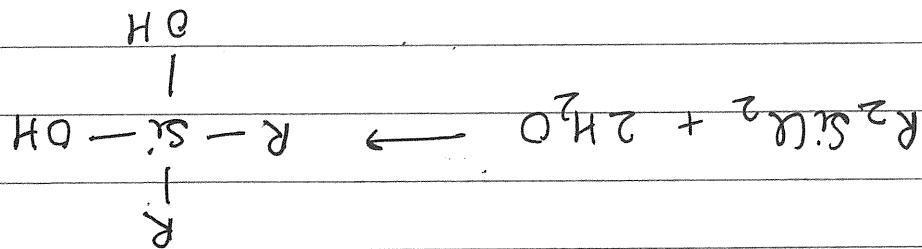
In these silicates, three oxygen atoms per tetrahedron gets shared thereby resulting in a giant sheet of silicate ions.

(vi) 3-D silicates \rightarrow sharing of all 4 oxygen atoms of a tetrahedral unit results in the formation of 3-D silicates

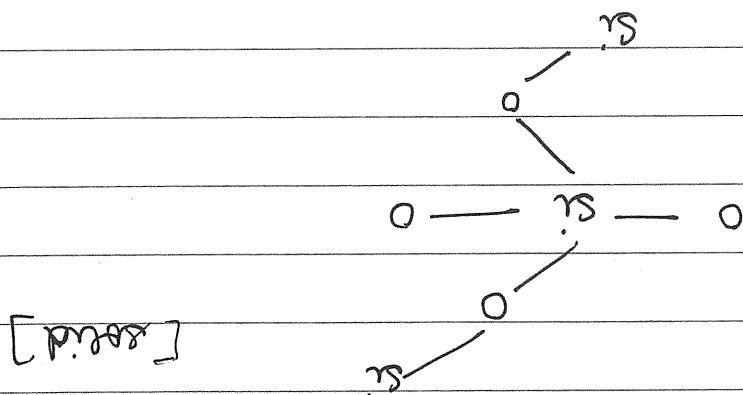
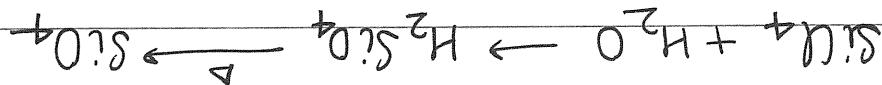
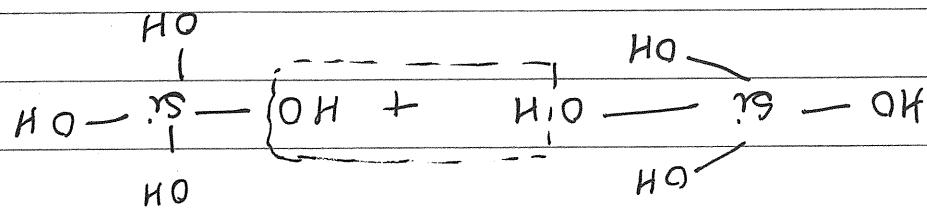
Q. Which of the following silicate is formed when 3 oxygen atoms of $[\text{SiO}_4]^{4-}$ tetrahedral units are shared.

- (a) Pyrosilicate
- (b) Cyclic silicate
- (c) Linear chain silicate
- (d) None

\rightarrow (d)



Hydrolysis of alkyl substituted silanes because
leads to formation of long chain polymers
that are technically useful silanes.



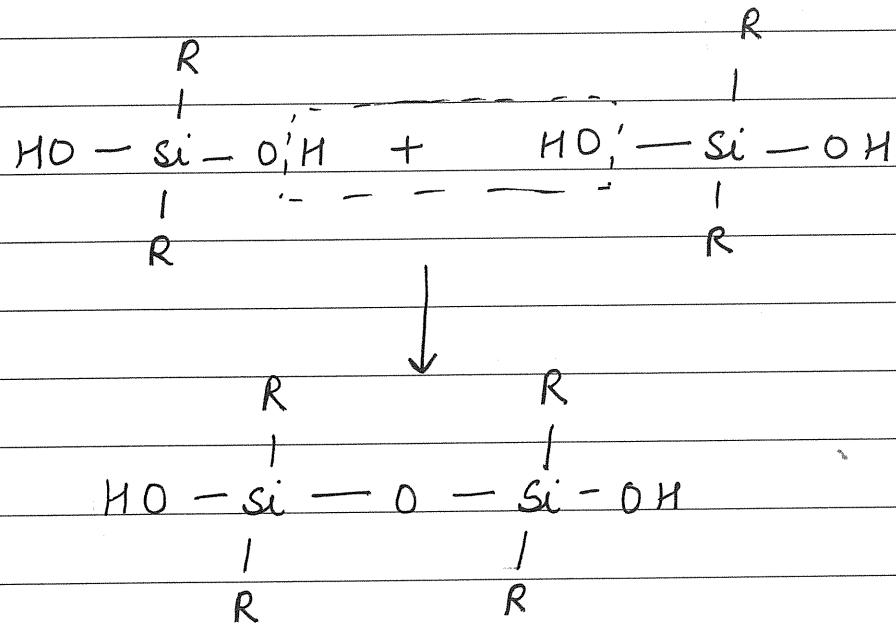
stable 3-D silanol structure
in the formation of SiO_2 without loss a very

mechanism: The compact hydroxyls of $SiCl_4$ react

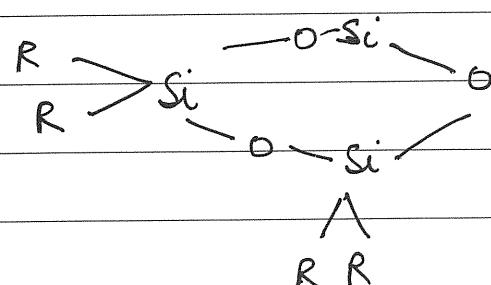
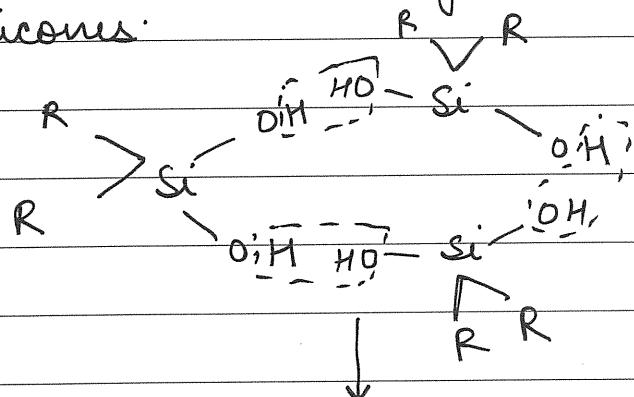
which are formed by hydrolysis of silane

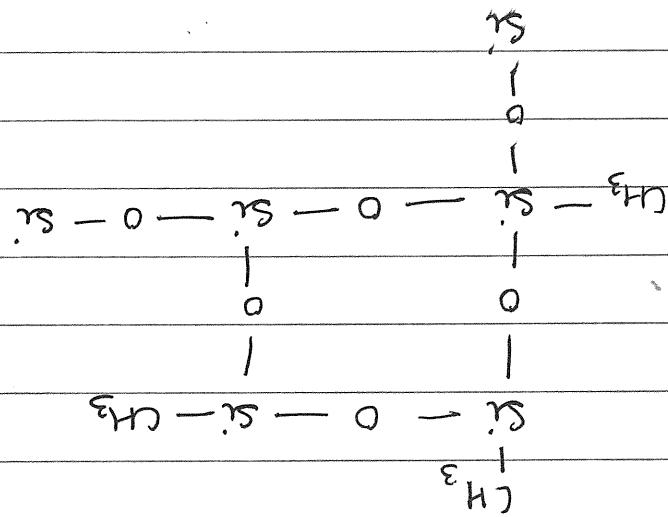
silanes are group of organosilicon polymers

Siloxanes

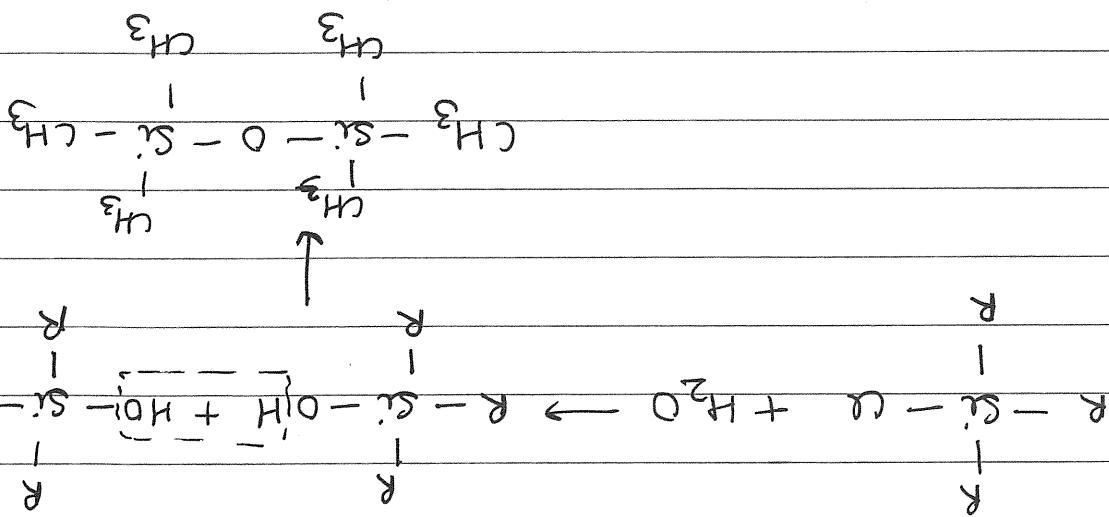


→ The hydrolysis of dialkyl substituted chlorosilanes leads to the formation of the linear polymers however hydrolysis under carefully controlled conditions can produce cyclic structures with rings containing 3, 4, 5 or 6 silicones.





If some titanium carbide is now mixed, the structure becomes the following polymer chain. It forms two ends at which it attacks.



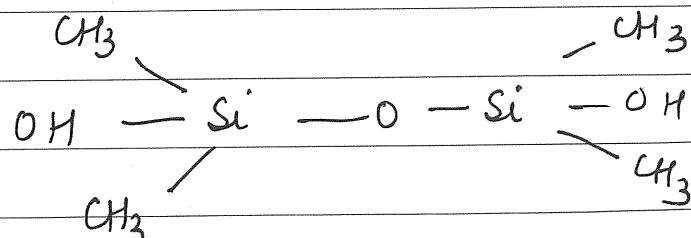
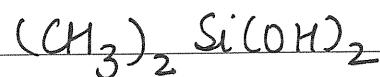
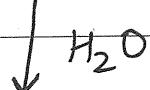
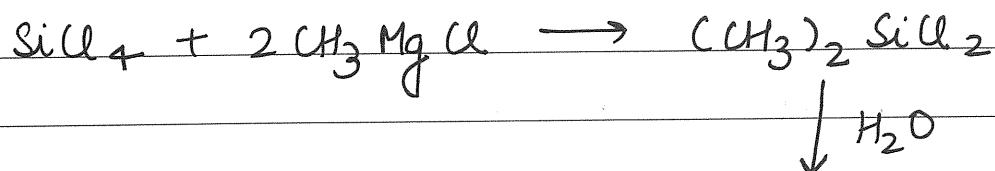
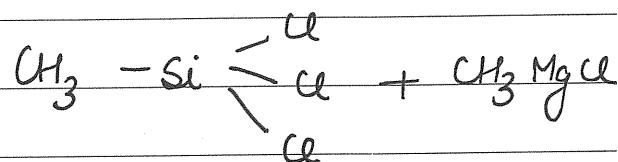
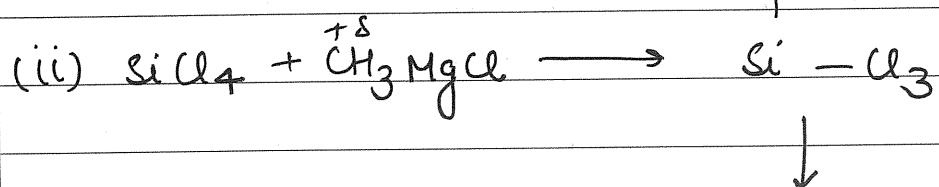
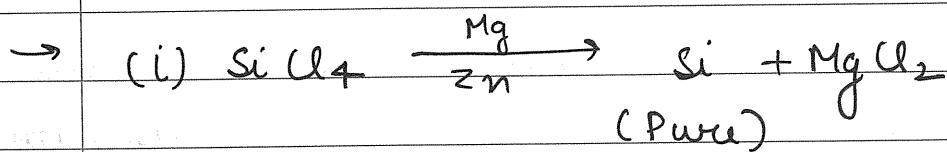
Formation of a dinner. A volatile liquid that condenses in the hydroxyl of mutual ester shows because a volatile liquid that condenses in the

Q Starting from SiCl_4 prepare the following compound in steps not exceeding the no. given in the brackets.

i) silicon (I)

ii) linear silicon containing methyl groups (II)

iii) Na_2SiO_3 (III)



It is because the size of silicon atom is larger than that of carbon due to which bond length

←

as compared to carbon.

Q) Explain why covalent property is less in silicon

←

The bond length between Ca and C₂ is small but the bond length between atoms of C₂ is greater than 2 Å, i.e.

←

Because in calcium carbide (CaC₂)?

Find out the total no. of bonds and its bond

←

charge polar.

Vacant orbitals are absent in the delocalization

stable conjugate base, whereas in case of carbon the presence of vacant orbitals gives following a

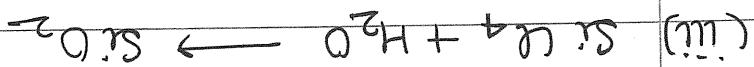
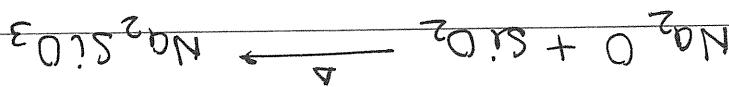
enough of H⁺ ions delocalized to sit down due to

the negative charges that comes on oxygen atom

R₃-SiOH is more acidic than R₃-COH because

←

Q) Compare the acidic strength for R₃-SiOH & R₃-COH



length b/w Silicon atoms increases thus reducing bond strength and in turn formation of more no of bonds i.e less catenation property.

Q. Silicon has diamond like structure only but not an allotropic like graphite. Explain.

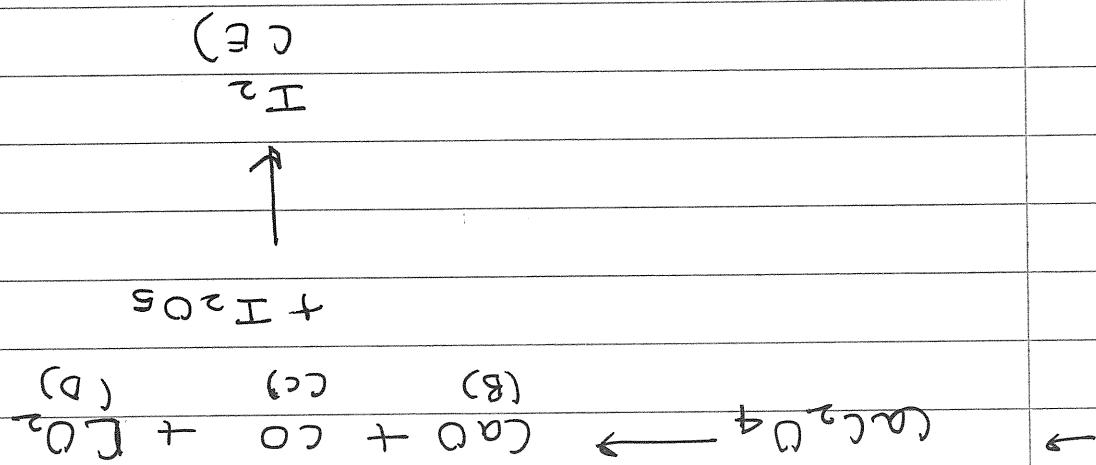
→ Due to its large size silicon cannot undergo effective overlapping thus reducing the chances of formation of σ bond and thus it can only form sigma bonds resulting in a tetrahedral structure like that of diamond and rules out the possibility of having structure like that of graphite.

Q HCN is a weak acid in water but a strong acid in pure state. Explain.

→ HCN in presence of water undergoes the phenomenon of Tautomerism i.e movement of acidic hydrogen from one part of acidic hydrogen from one part of molecule to another.



Thus, its proton releasing tendency decreases in water therefore, it is a weak acid in water whereas in



A white powder A on heating decomposes to
burnt lime with a blue flame and on heating
gives a soluble B and two gases C and D.
C burns with a blue flame and on heating
with H_2O gives D or E. E on heating with
starch solution gives blue colour and D
disappears in water gives our colourless solution.

Now it is strong acid in formic acid.