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for JEE-MAIN

One Shot

By VJ Sir

7:00 PM Tonight 🔥

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GROUP 13 ELEMENTS: THE BORON FAMILY :

Boron is a typical non-metal, aluminium is a metal but gallium, indium and thallium are almost exclusively metallic in character.

OCCURANCE

Boron: Boron is a fairly rare element, mainly occurs as orthoboric acid, (H_3BO_3), borax, $Na_2B_4O_7 \cdot 10H_2O$, and kernite, $Na_2B_4O_7 \cdot 4H_2O$.

There are two isotopic forms of boron $^{10}B(19\%)$ and $^{11}B(81\%)$.

ALUMINIUM :

* Aluminium is the most abundant metal.

B — नान
Al } metal

O > Si > Al > Fe

Third most abundant element in the earth's crust (8.3% by mass) after oxygen (45.5%) and Si (27.7%).

Bauxite, $Al_2O_3 \cdot 2H_2O$ and cryolite, Na_3AlF_6 are the important minerals of aluminium.

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ELECTRONIC CONFIGURATION :



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

ATOMIC RADII :



On moving down the group, for each successive member one extra shell of electrons is added and, therefore, atomic radius is expected to increase.

However, a deviation can be seen.

Atomic and Ionic radii order



$\text{B} < \text{Ga} < \text{Al} < \text{In} < \text{Te}$

Ionization Enthalpy



The ionisation enthalpy values as expected from the general trends do not decrease smoothly down the group.

Ionization Enthalpies order

$\text{B} > \text{Te} > \text{Ga} > \text{Al} > \text{In}$

R

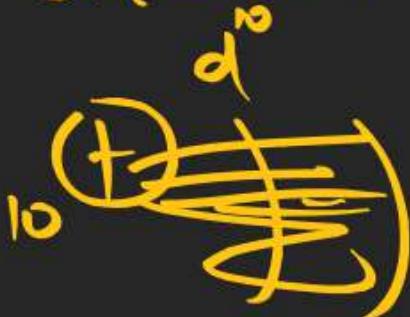
$\text{Al} \quad 143 \text{ pm}$

$\text{Ga} = 135 \text{ pm}$

In

Te

$\text{Gla} = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$



$\text{B} > \text{Te} > \text{Gla} > \text{Al} > \text{In}$

Electronegativity

B > Tl > In > Ga > Al

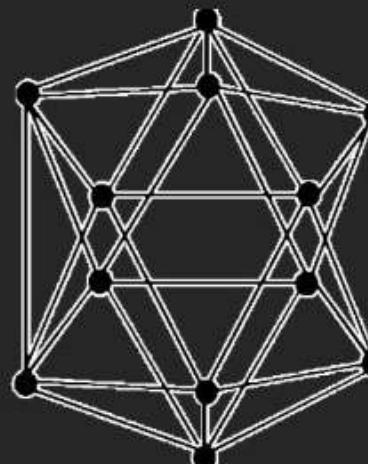
Physical Properties

(i) Boron is non-metallic in nature.

It is extremely hard and black coloured solid.

Boron exists in many allotropic forms. All the allotropes have basic building units made up of polyhedron having 20 faces and 12 corners.

For example one is the simplest form : α -rhombohedral boron.



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But Al, In & Tl all have close packed metal structure.

(ii) Rest of the members are soft metals with low melting point and high electrical conductivity

(iii) Gallium with unusually low melting point (303K), could exist in liquid state during summer.

(iv) Density of the elements increases down the group from boron to thallium.

Melting and Boiling points order

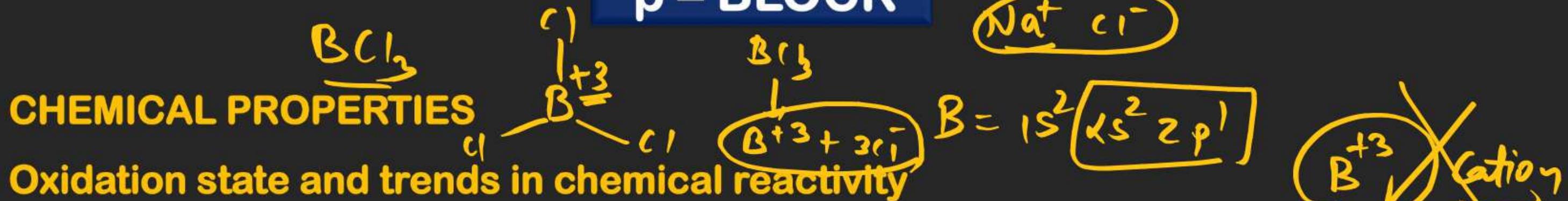
M.P. B > Al > Tl > In > Ga

B.P. B > Al > Ga > In > Tl

Electropositive Character

$B < \frac{Al < Ga < In < Tl}{\text{Non metals}}$

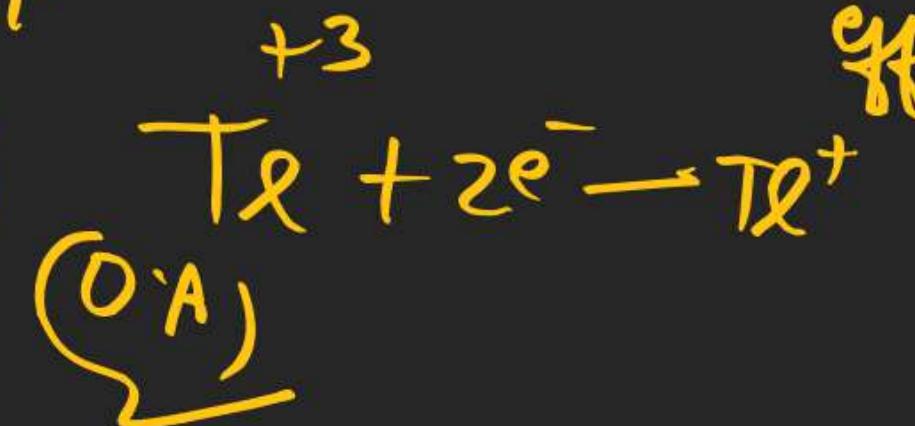
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- (i) Due to small size of boron, the sum of its first three ionization enthalpies is very high. This prevents it to form +3 ions and forces it to form only covalent compounds.
- (ii) The relative stability of +1 oxidation state progressively increases for heavier elements: Al < Ga < In < Tl. In thallium +1 oxidation state is predominant whereas the +3 oxidation state is highly oxidizing in character.
- (iii) The compounds in +1 oxidation state, as expected from energy considerations, are more ionic than those in +3 oxidation state.

$\Sigma > P > d > f$

Stability



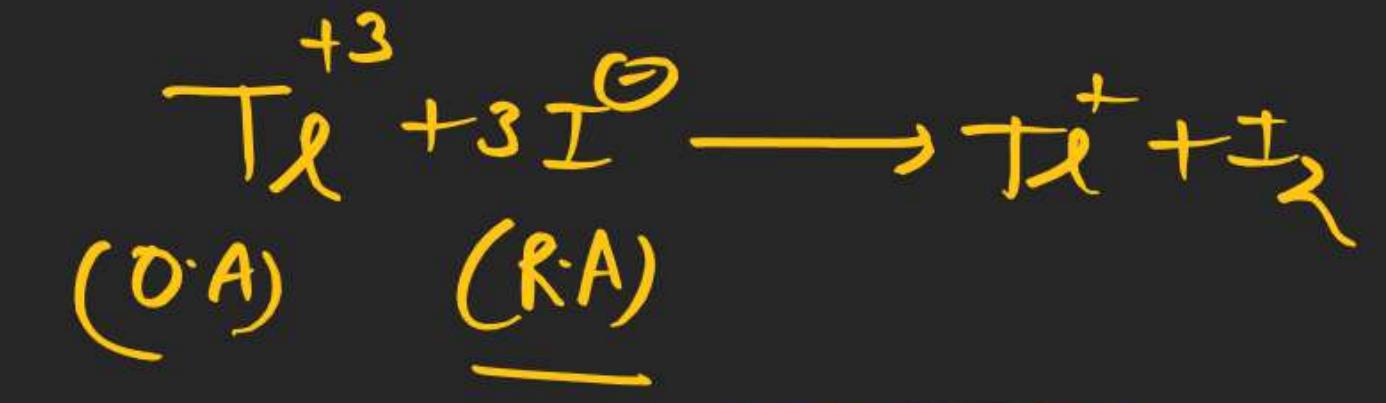
Inert pair effect

the tendency of inertness of $ns e^-$ towards bonding is inert pair effect

lowers O.S. stable
+3 due to inert pair

effect [due to poor S.E. of
4f sub shell]

Ques TlI₃ does not exist why

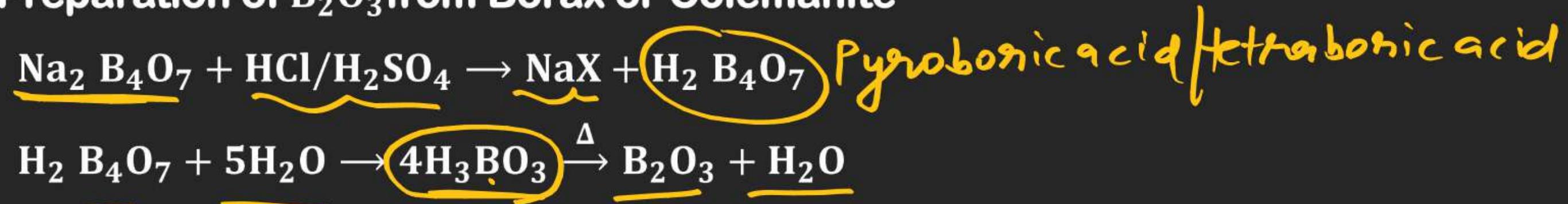


Ans TlI₃ exists with I₃[⊖]

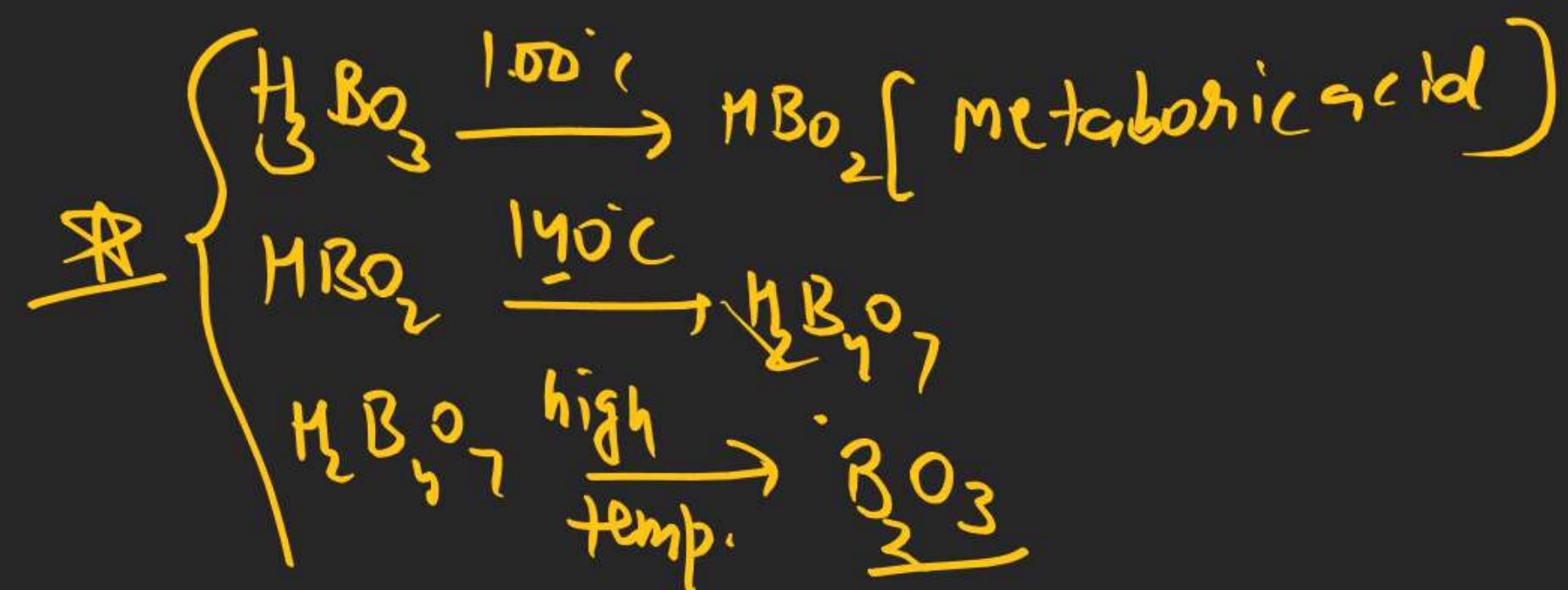
Yes Tl⁺ + I₃[⊖]

Preparation of Boron :

(i) Preparation of B_2O_3 from Borax or Colemanite



(ii) Reduction of B_2O_3

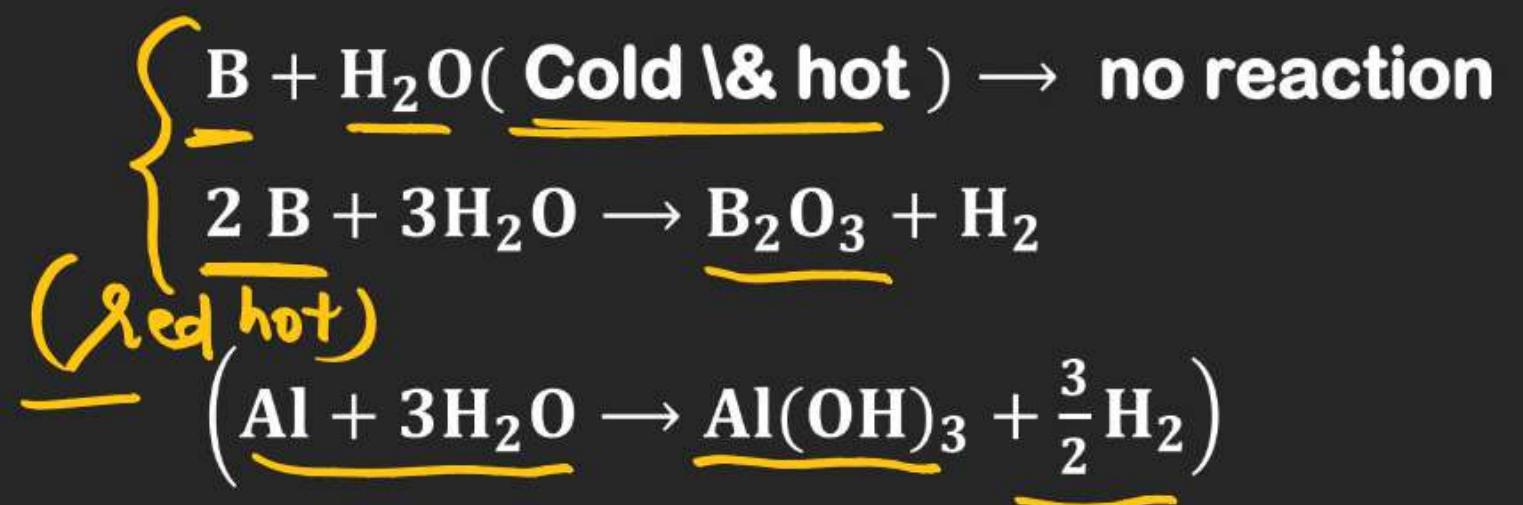


Chemical Properties :

(i) Burning in air : $4 \text{B} + 3\text{O}_2 \rightarrow 2 \text{B}_2\text{O}_3$



(ii) Reaction with water



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(iii) $B + \underline{HCl} \rightarrow \text{no reaction}$

$\{ B + \underline{H_2SO_4} (\text{dil}) \rightarrow \text{no reaction}$



$(Al + HNO_3 (80\%) \rightarrow Al_2O_3 \text{ (passive layer)} \text{ and does not react further.})$

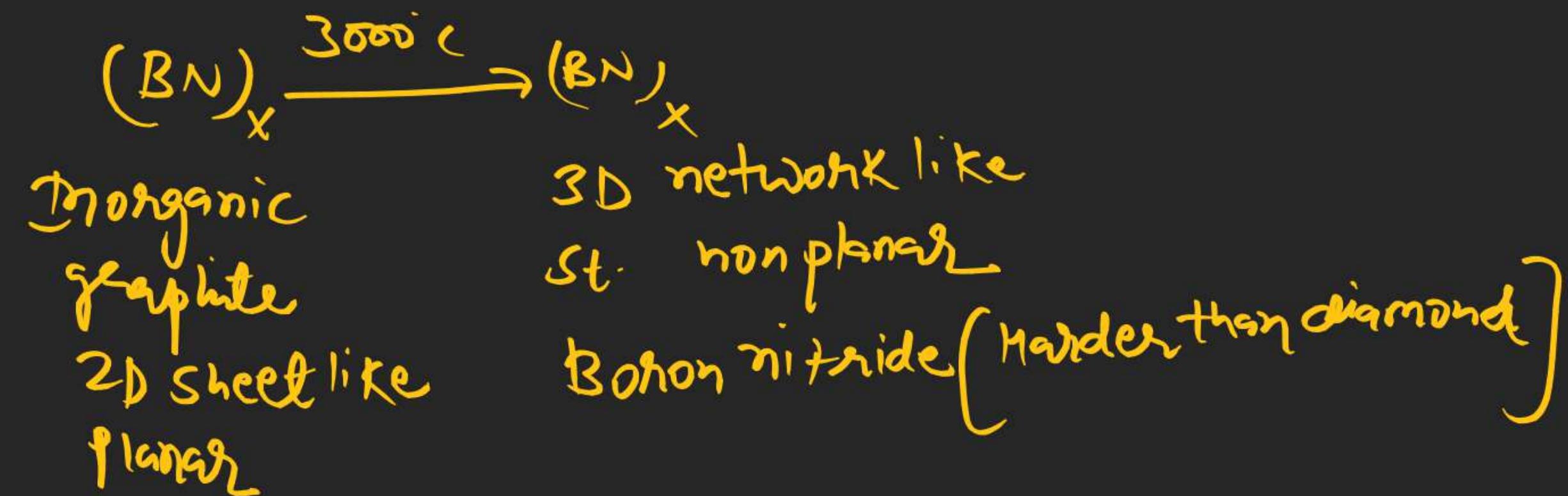
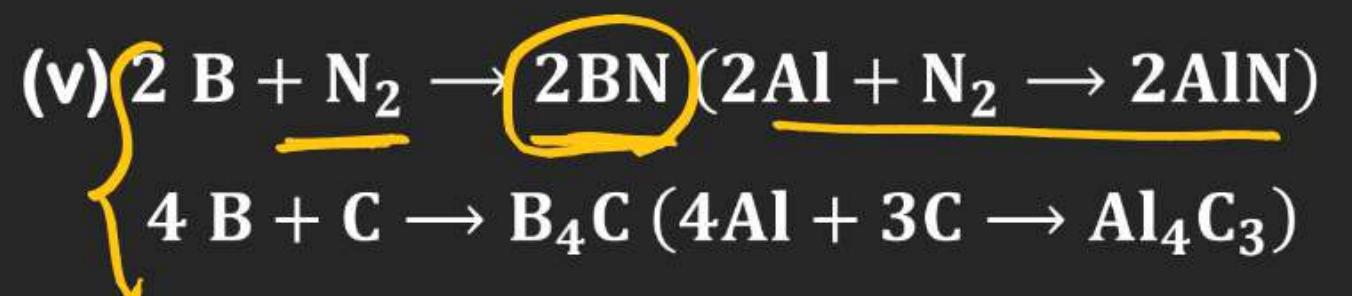
Al and $Cr \rightarrow$ Passive layer
of oxide with
Conc. HNO_3

(vi) Ga, In, Tl dissolve in dilute acids liberating H_2 . Ga is amphoteric like Al and it dissolves in aq.

NaOH liberating H_2 and forming gallates.



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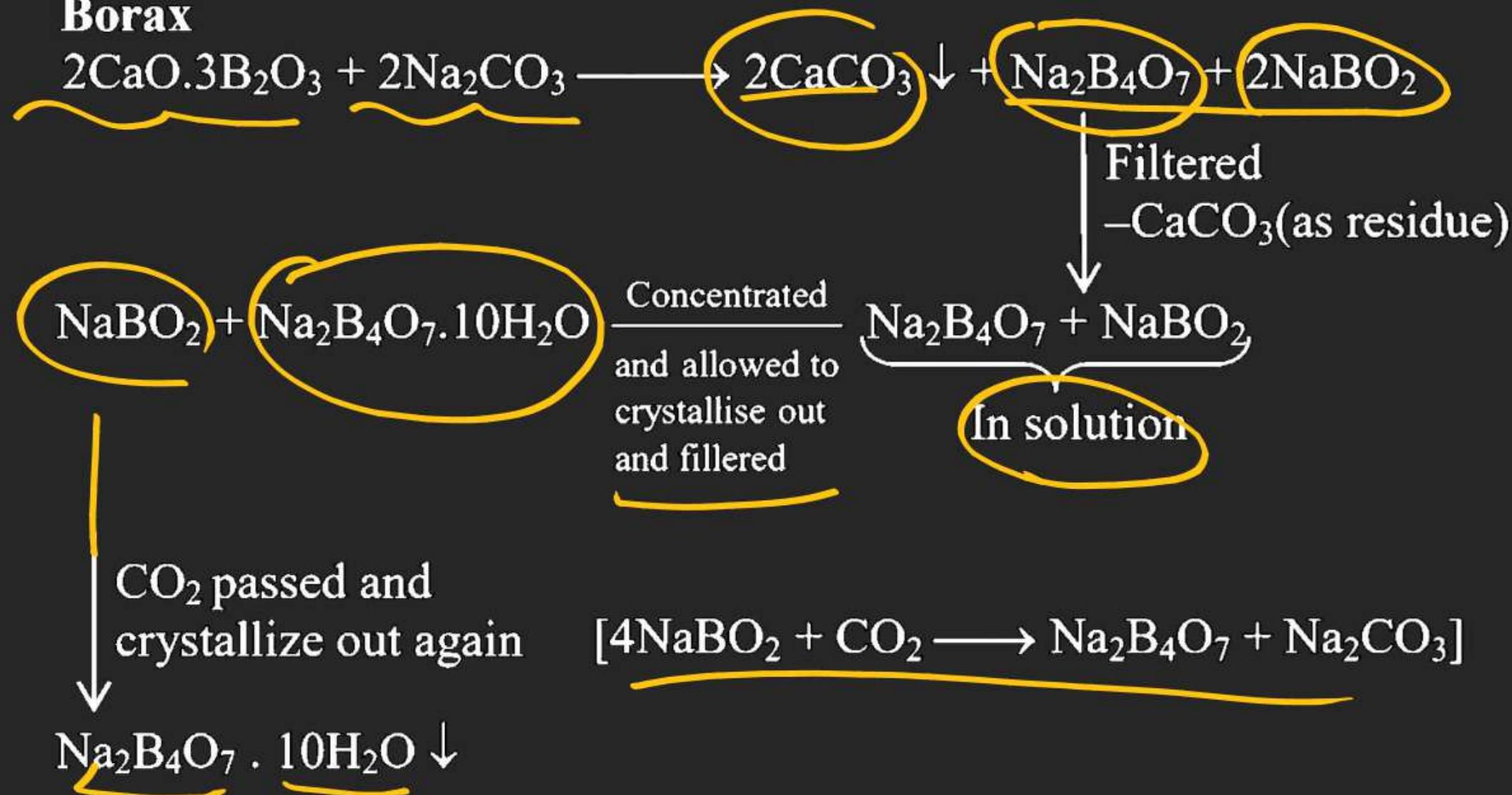


SOME IMPORTANT COMPOUNDS OF BORON

Some useful compounds of boron are borax, orthoboric acid and diborane. We will briefly study their chemistry.

Preparation of Borax :

Borax



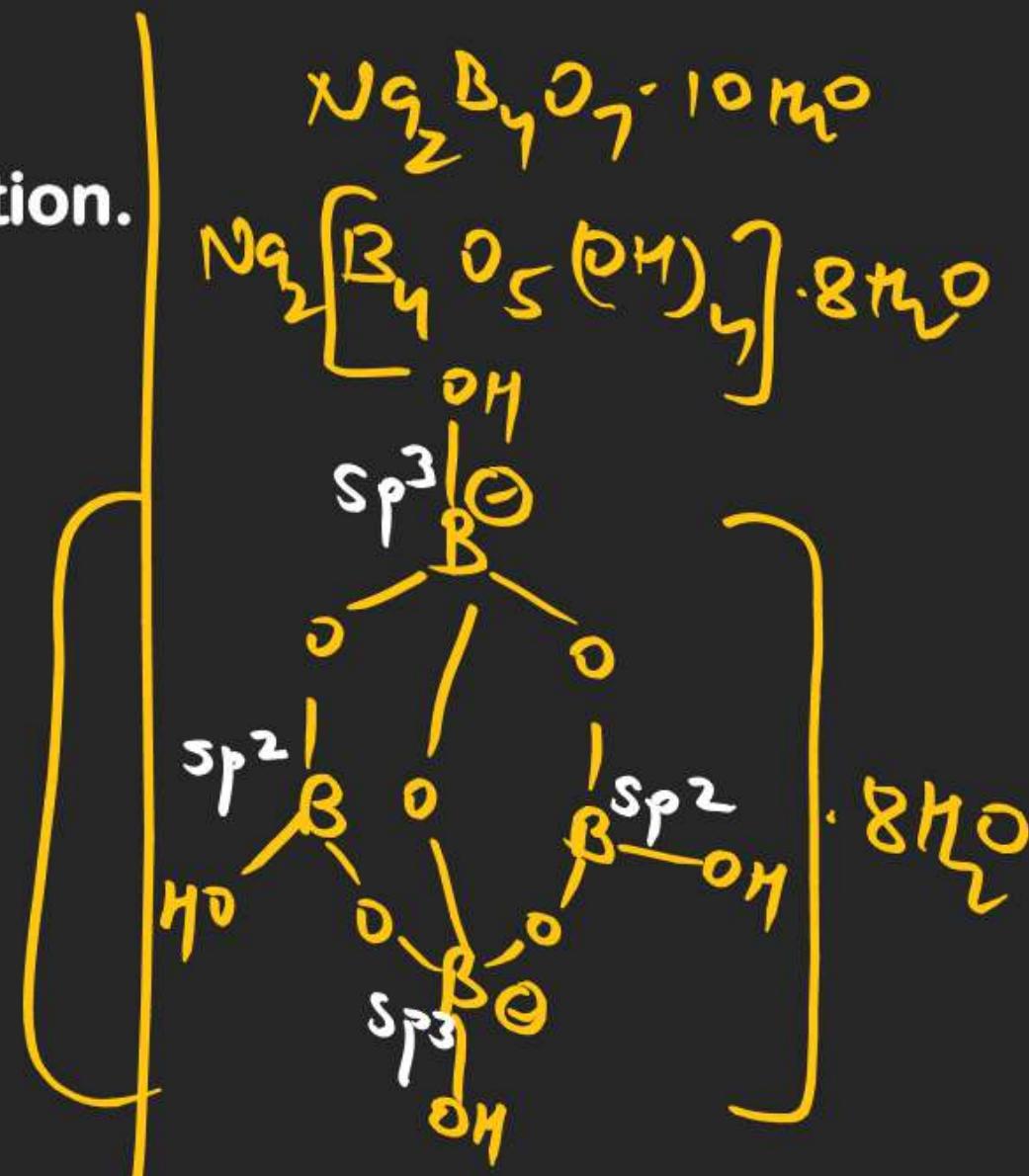
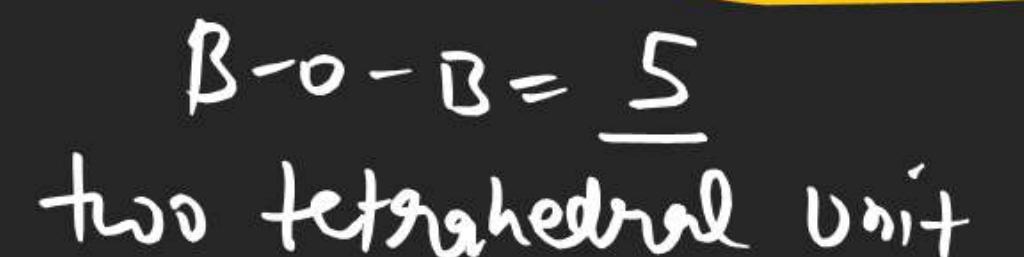
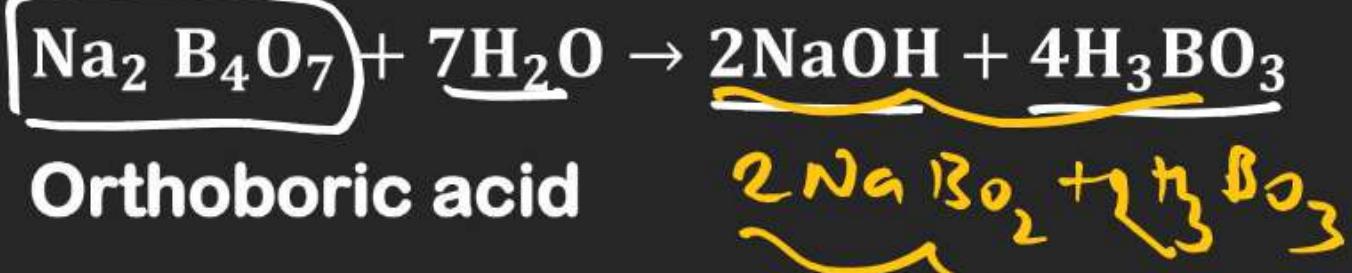
Borax

$$\text{Co}(\text{Bz}_2)_2 \rightarrow \text{blue}$$

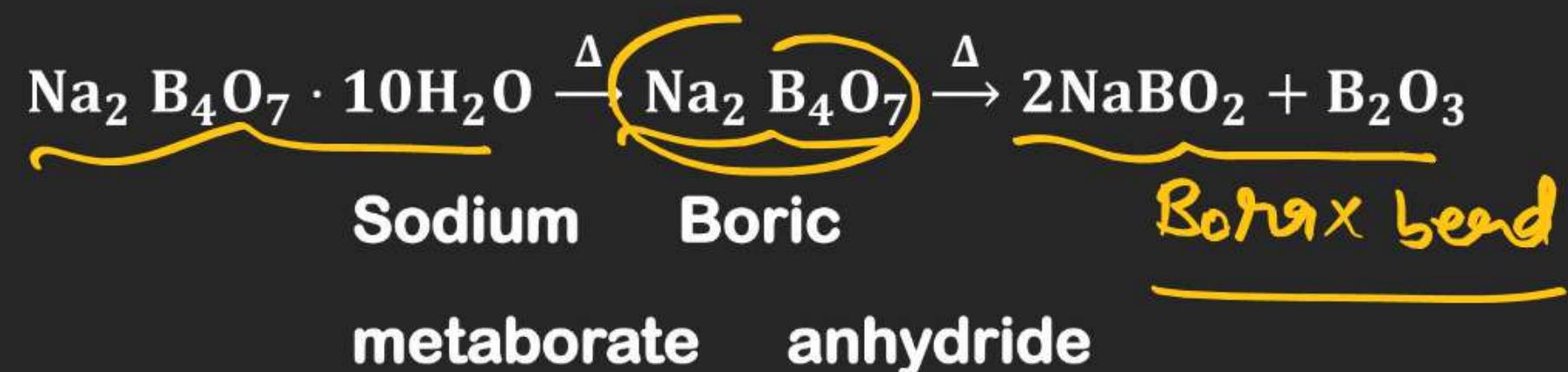
- (i) It is a white crystalline solid of formula $\text{Na}_2 \text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. In fact it contains the tetranuclear units $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ and correct formula; therefore, is



- (ii) Borax dissolves in water to give an alkaline solution.



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



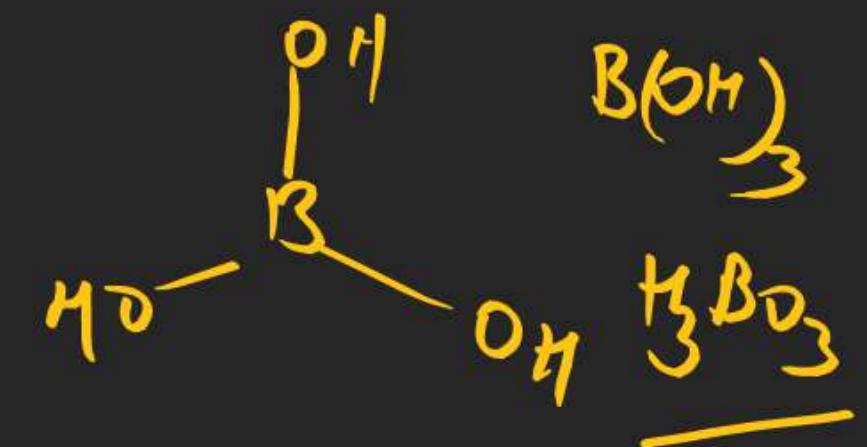
The metaborates of many transition metals have characteristic colours and, therefore, borax bead test can be used to identify them in the laboratory. For example, when borax is heated in a Bunsen burner flame with CoO on a loop of platinum wire, a blue coloured $\text{Co}(\text{BO}_2)_2$ bead is formed.

Orthoboric acid :**Preparation :**

(i) It can be prepared by acidifying an aqueous solution of borax.



(ii) It is also formed by the hydrolysis (reaction with water or dilute acid) of most boron compounds (halides, hydrides, etc.)



Property :

~~(i) Orthoboric acid, H_3BO_3 is a white crystalline solid, with soapy touch.~~

~~(ii) It is sparingly soluble in water but highly soluble in hot water.~~

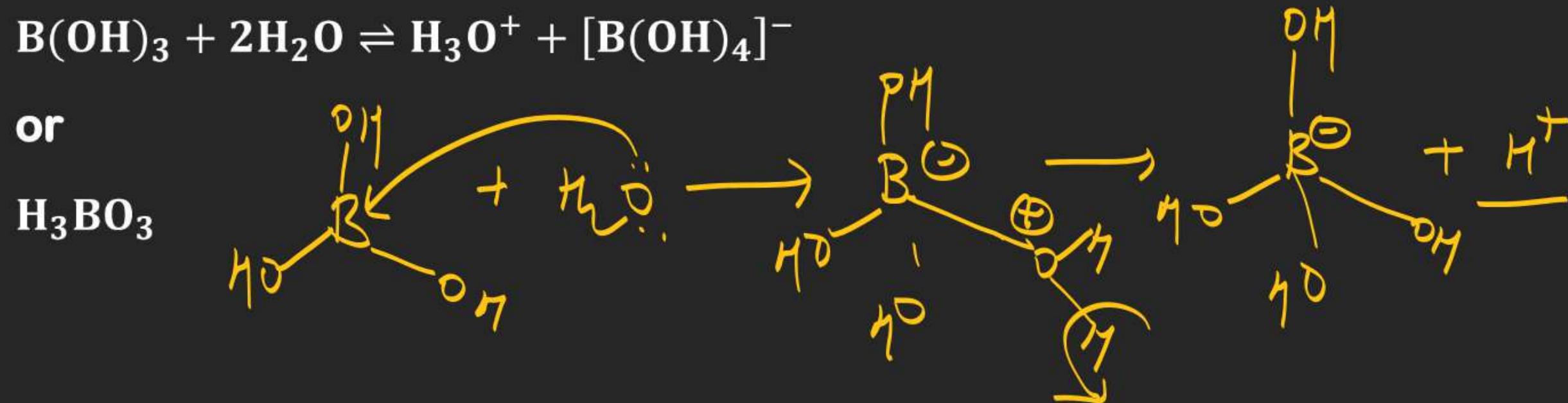
~~(iii) H_3BO_3 is soluble in water and behaves as weak monobasic acid. It does not~~

~~donate protons like most the acids, but rather it accepts OH^- . It is therefore is~~

Lewis acid ($B(OH)_3$)

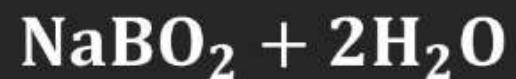


or



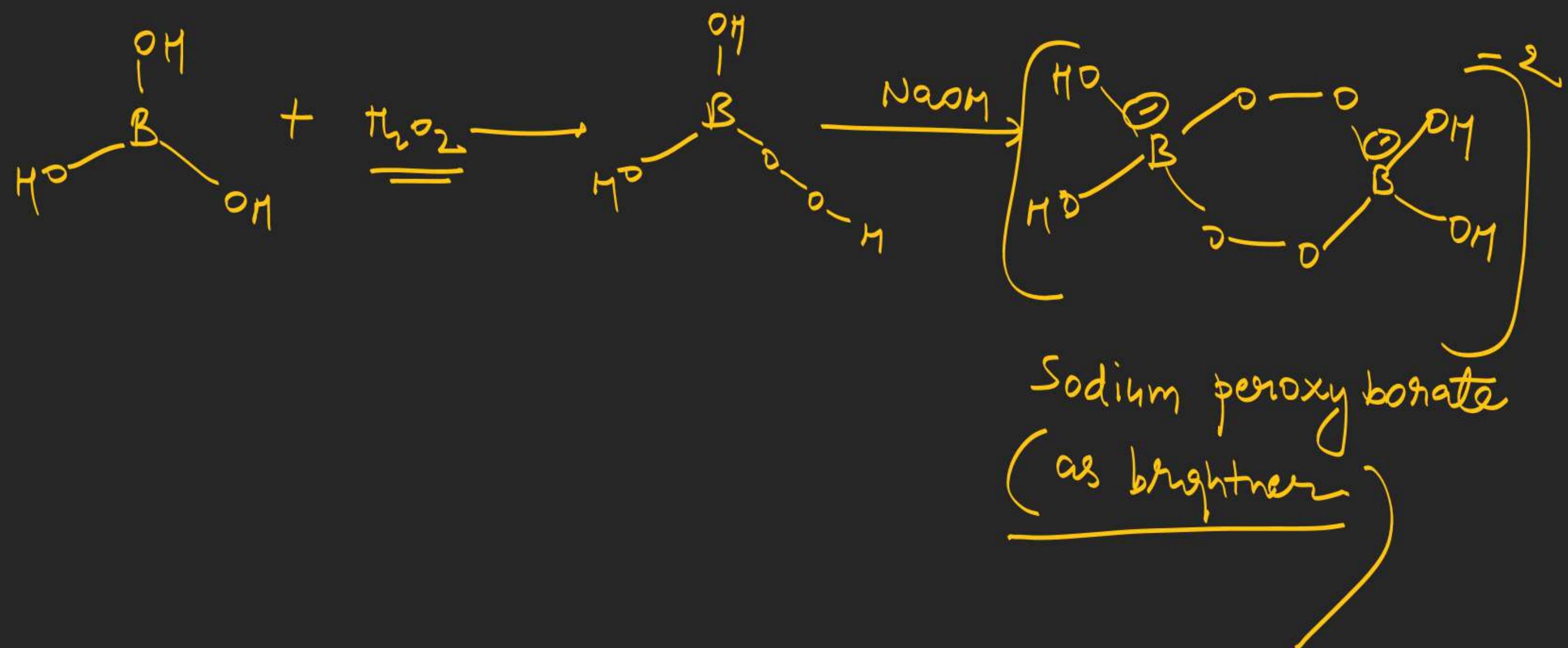
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Since $\text{B}(\text{OH})_3$ only partially reacts with water to form H_3O^+ and $[\text{B}(\text{OH})_4]^-$ it behaves as a weak acid. Thus it cannot be titrated satisfactorily with NaOH as a sharp end point is not obtained. If certain polyhydroxy compounds such as glycerol, mannitol or sugar are added to the titration mixture then $\text{B}(\text{OH})_3$ behaves as a strong monobasic acid. and hence can now be titrated with NaOH and end point is diluted using phenolphthalein as indicator.



The added compound must be a diol to enhance the acidic properties in this way the cisdiol forms very stable complexes with $[\text{B}(\text{OH})_4]^-$ formed in forward direction above, thus effectively removing it from solution. Hence reaction proceeds in forward direction

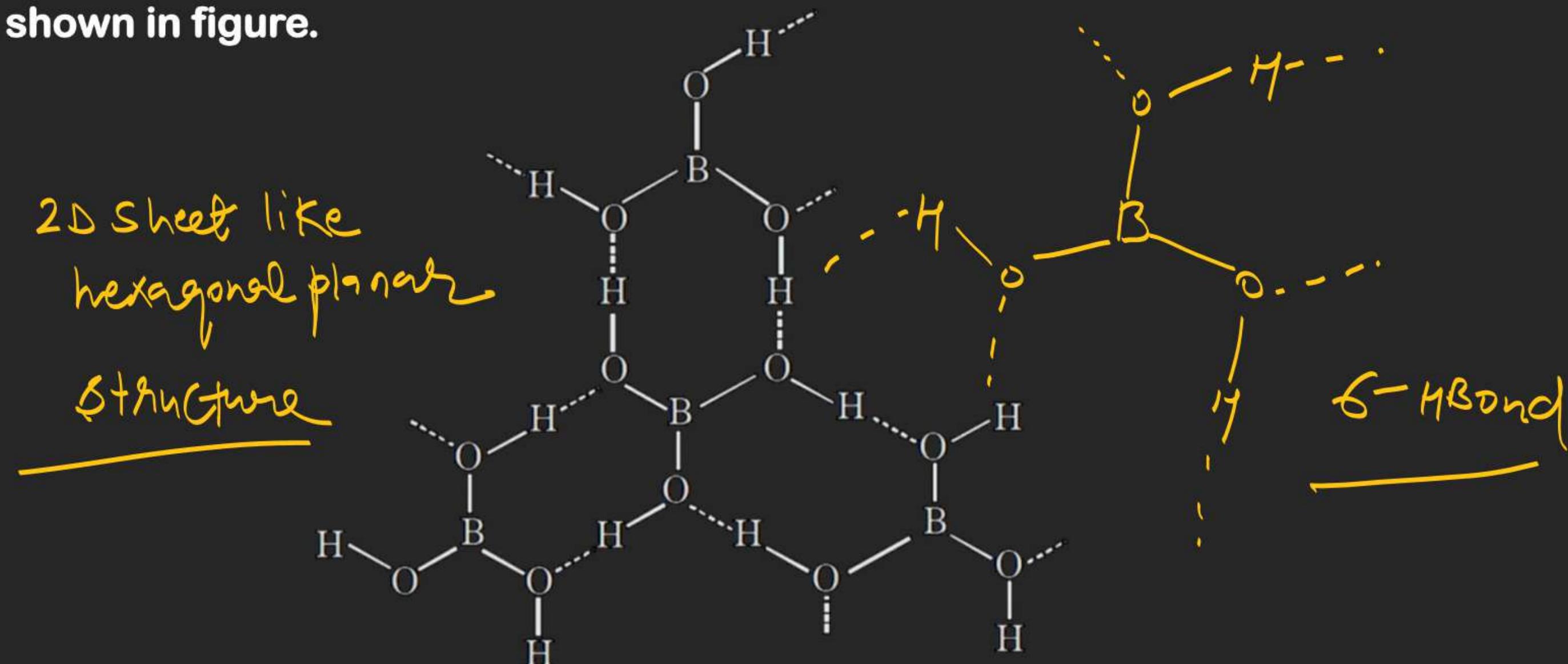
(Le-Chatelier principle.)



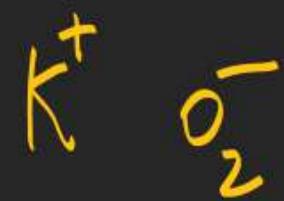
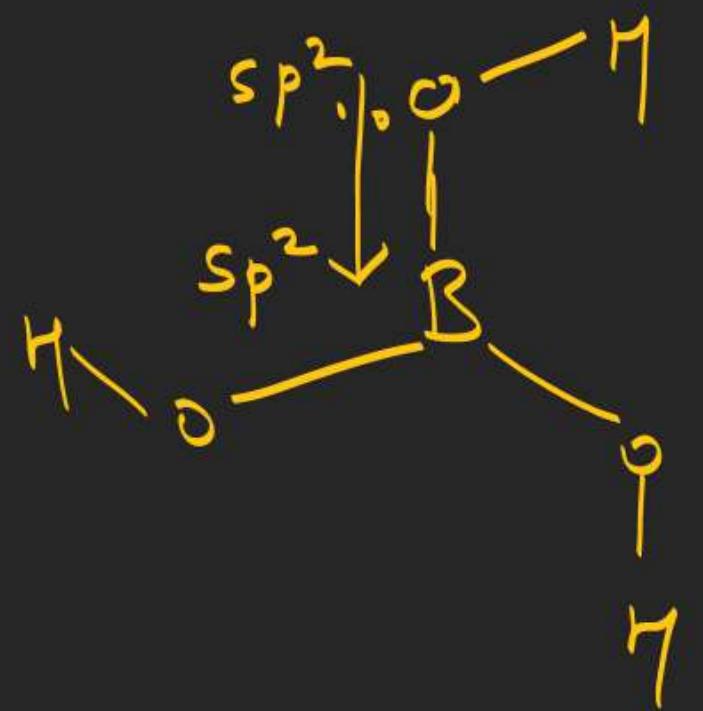
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STRUCTURE

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



Structure of boric acid; the dotted lines represent hydrogen bonds.



Uses of boric acid :

- (i) **Boric acid is used in manufacturing of optical glasses**
- (ii) With borax, it is used in the preparation of a buffer solution.

~~**Diborane, B_2H_6**~~

The simplest boron hydride known, is diborane.

~~**Preparation :**~~

- (i) **It is prepared by treating boron trifluoride with $LiAlH_4$ in diethyl ether.**



- (ii) **Laboratory method:** For the preparation of diborane involves the oxidation of sodium borohydride with iodine.



(iii) Industrial scale : By the reaction of BF_3 with sodium hydride.



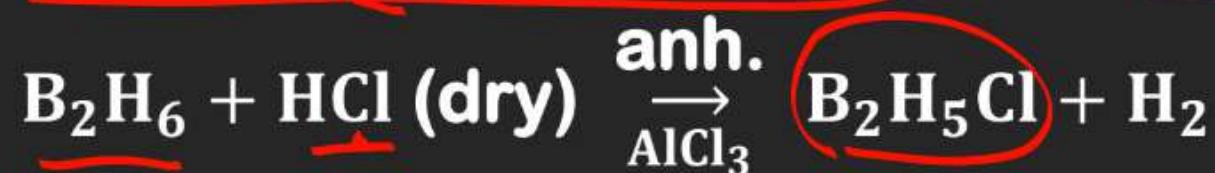
Properties :

- (i) Diborane is a colourless, highly toxic gas with a b.p. of 180 K.
- (ii) Diborane catches fire spontaneously upon exposure to air.
- (iii) It burns in oxygen releasing an enormous amount of energy.



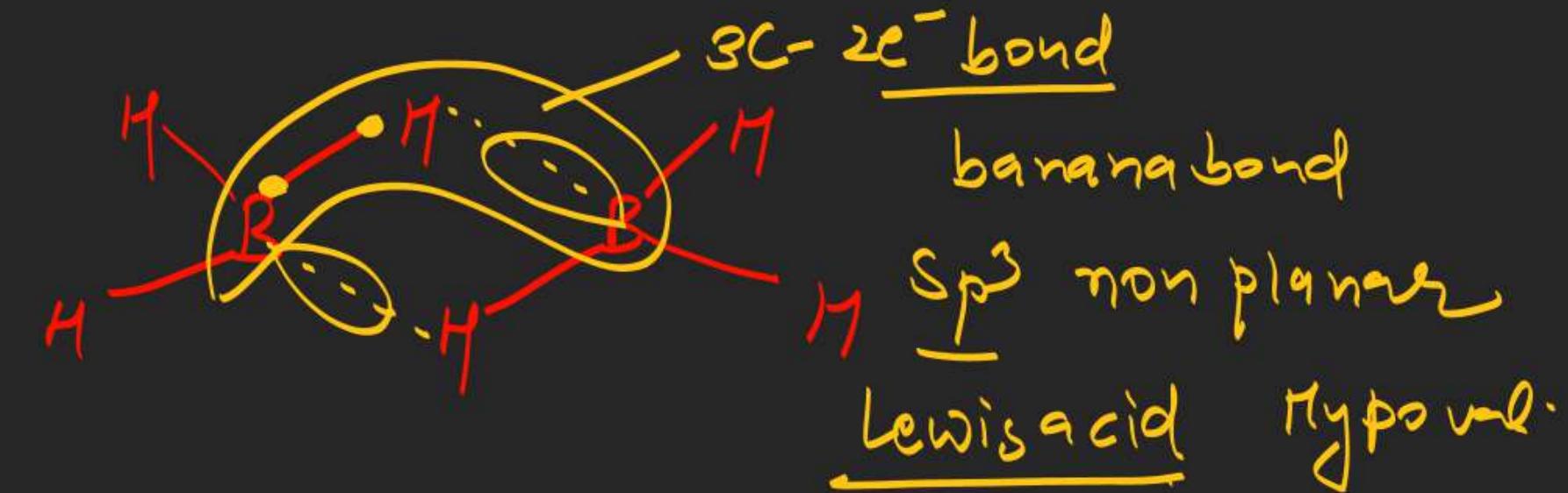
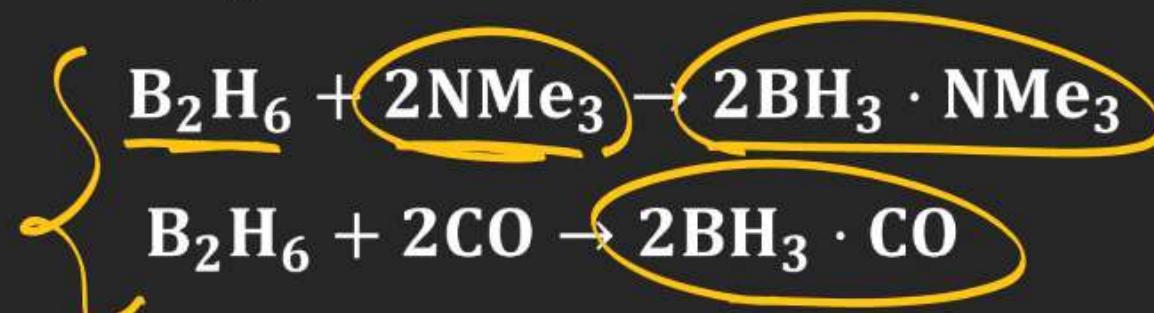
Most of the higher boranes are also spontaneously flammable in air.

(iv) Boranes are readily hydrolysed by water to give boric acid. $\text{B}_2\text{H}_6(\text{g}) +$



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(v) Diborane undergoes cleavage reactions with Lewis bases(L) to give borane adducts,



Reaction of ammonia with diborane gives initially $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$ which is formulated as $[\text{BH}_2(\text{NH}_3)_2]^+ [\text{BH}_4]^-$; further heating gives **borazine, $\text{B}_3\text{N}_3\text{H}_6$ known as "inorganic benzene" in view of its ring structure with alternate BH and NH groups.**

Borazine



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(VI) Metal hydrido borates : Boron also forms a series of hydridoborates; the most important one is the tetrahedral $[\text{BH}_4]^-$ ion. Tetrahydridoborates of several metals are known. Lithium and sodium tetrahydridoborates, also known as borohydrides, are prepared by the reaction of metal hydrides with B_2H_6 in diethyl ether.



Both LiBH_4 and NaBH_4 are used as reducing agents in organic synthesis.

They are useful starting materials for preparing other metal borohydrides.



preparation :



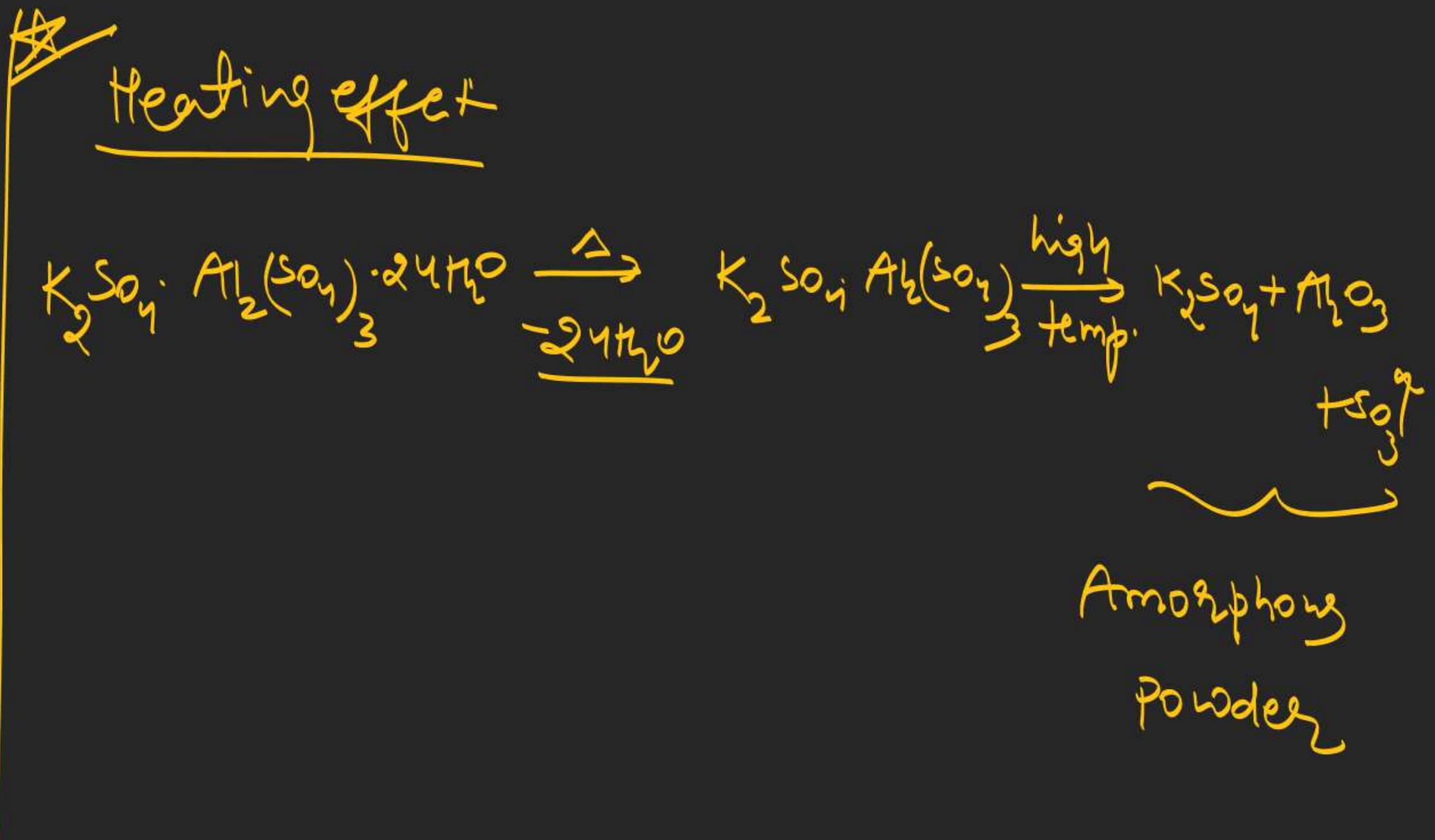
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Props:ALUM**Swelling characteristics**where M = Na⁺, K⁺, Rb⁺, Cs⁺, As⁺, Tl⁺, NH₄⁺M' = Al⁺³, Cr⁺³, Fe⁺³, Mn⁺³, Co⁺³ $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ Potash alum $(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ Ammonium alum $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$ Chrome alum $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$ Ferric alum**Preparation:**

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Uses:

- (i) Act as coagulant
- (ii) Purification of water
- (iii) Tanning of leather
- (iv) Mordant in dying
- (v) Antiseptic



USES OF BORON AND ALUMINIUM AND THEIR COMPOUNDS

Boron :

- (i) Boron being extremely hard refractory solid of high melting point, low density and very low electrical conductivity, finds many applications.
- (ii) Boron fibres are used in making bullet-proof vest and light composite material for aircraft.

- (iii) The boron-10 (^{10}B) isotope has high ability to absorb neutrons and, therefore, metal borides are used in nuclear industry as protective shields and control rods.
- (iv) The main industrial application of borax and boric acid is in the manufacture of heat resistant glasses(e.g., Pyrex), glass-wool and fibreglass.

- (v) Borax is also used as a flux for soldering metals, for heat, scratch and stain resistant glazed coating to earthenwares and as constituent of medicinal soaps.
- (vi) An aqueous solution of orthoboric acid is generally used as a mild antiseptic.

Aluminium :

- (i) Aluminium is a bright silvery-white metal, with high tensile strength.
- (ii) It has a high electrical and thermal conductivity.
- (iii) On a weight-to-weight basis, the electrical conductivity of aluminium is twice that of copper.
- (iv) Aluminium is used extensively in industry and every day life.
- (v) It forms alloys with Cu, Mn, Mg, Si and Zn.
- (vi) Aluminium and its alloys can be given shapes of pipe, tubes, rods, wires, plates or foils and, therefore, find uses in packing, utensil making, construction, aeroplane and transportation industry.
- (vii) The use of aluminium and its compounds for domestic purposes is now reduced considerably because of their toxic nature.

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GROUP 14 ELEMENTS

The carbon family

Carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb) are the members of group 14.

Si } non metal
Ge } metalloide
Sn }
Pb } metal

Occurrence of element

- (i) Carbon : Carbon is the seventeenth most abundant element by mass in the earth's crust. Naturally occurring carbon contains two stable isotopes: ^{12}C and ^{13}C . In addition to these, third isotope, ^{14}C is also present. It is a radioactive isotope with halflife 5770 years and used for radiocarbon dating.
- (ii) Silicon : Silicon is the second (27. 7% by mass) most abundant element on the earth's crust.
- (iii) Germanium : Germanium exists only in traces.

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(iv) Tin : Tin occurs mainly as cassiterite, SnO_2

(v) Lead : Lead as galena, PbS .

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

Electronic Configuration

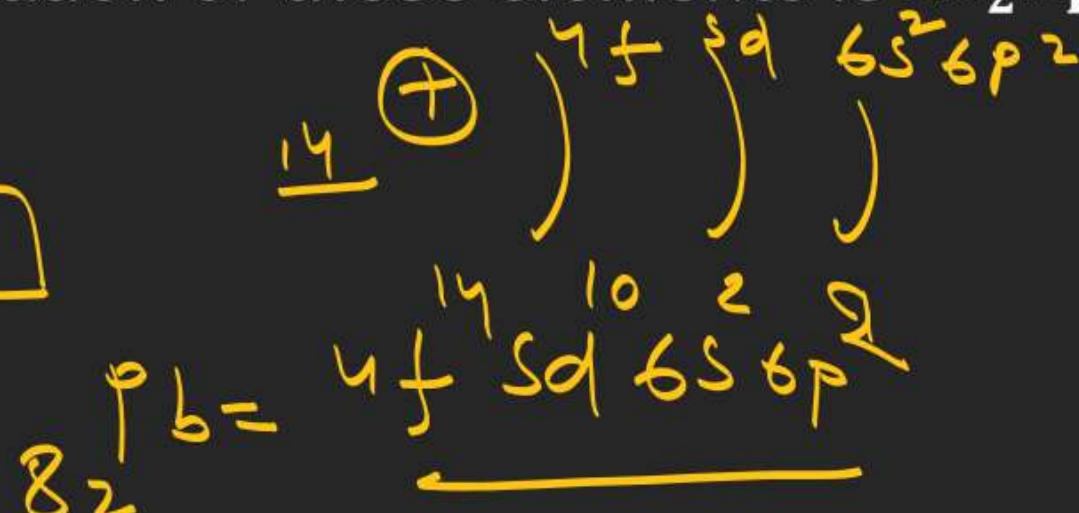
The valence shell electronic configuration of these elements is ns_2np_2 .

Covalent Radius

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

Ionization Enthalpy

$\text{C} > \text{Si} > \text{Ge} > \text{Pb} > \text{Sn}$ (IE_1 values)



Melting and Boiling Points

M.P. : C > Si > Ge > Pb > Sn

B.P. : Si > Ge > Sn > Pb

Electronegativity

C > Si = Ge = Sn = Pb

Due to small size, the elements of this group are slightly more electronegative than group 13 elements.

The electronegativity values for elements from Si to Pb are almost the same.

Physical Properties

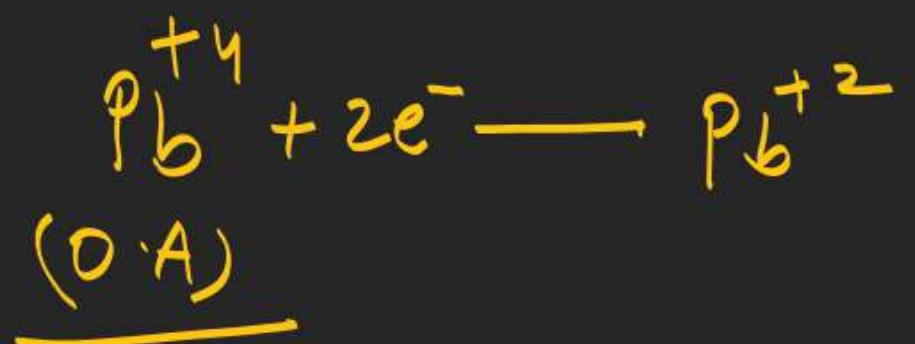
All group 14 members are solids. Carbon and silicon are non-metals, germanium is a metalloid, whereas tin and lead are soft metals with low melting points.

Chemical Properties

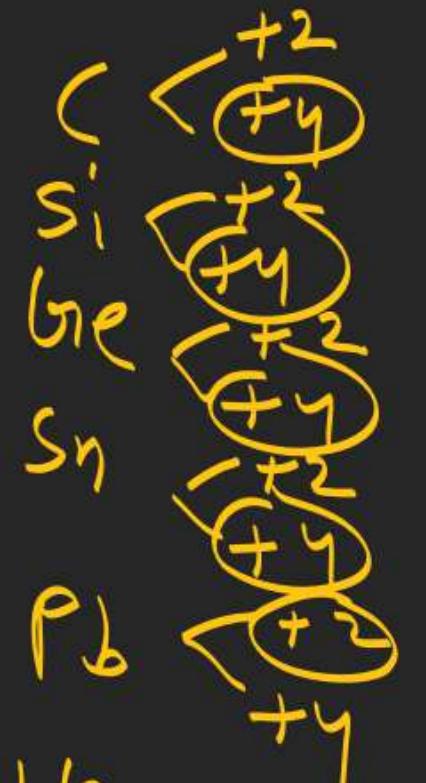
Oxidation states and trends in chemical reactivity

- (i) The group 14 elements have four electrons in outermost shell.
- (ii) The common oxidation states exhibited by these elements are +4 and +2 .
Carbon also exhibits negative oxidation states.
- (iii) In heavier members the tendency to show +2 oxidation state increases in the sequence Ge < Sn < Pb. It is due to the inability of ns₂ electrons of valence shell to participate in bonding. The relative stabilities of these two oxidation states vary down the group.
- (iv) Carbon and silicon mostly show +4 oxidation state.
- (v) Germanium forms stable compounds in +4 state and only few compounds in +2 state.

$$\underline{Pb^{+2} > Pb^{+4}}$$

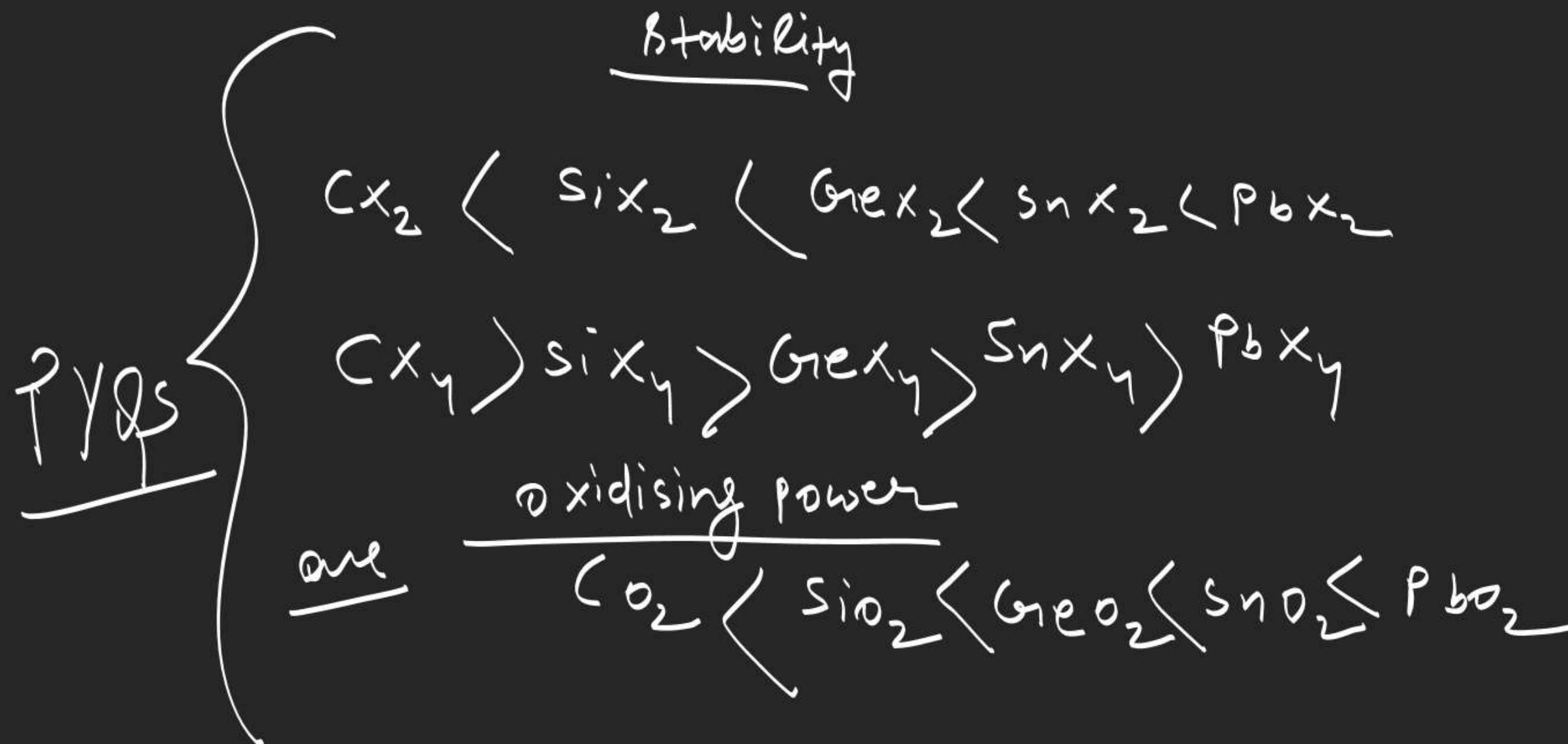


lower O.S. stable
due to inert pair effect



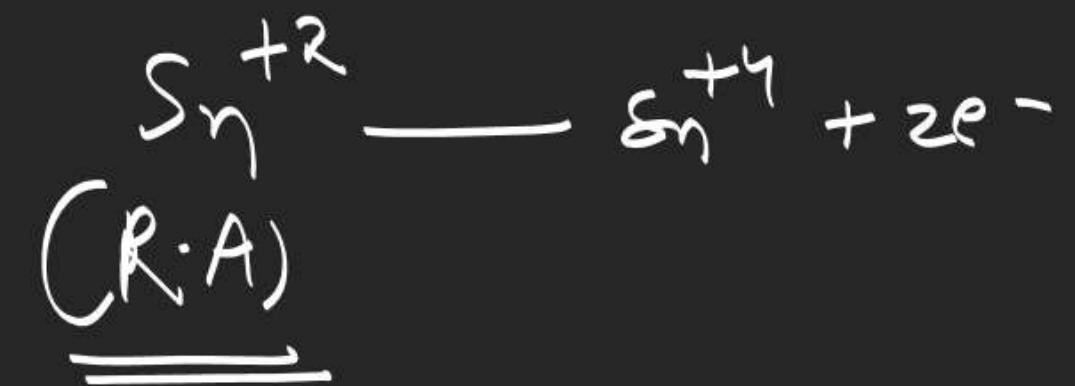
why $Pb I_4$ does not exist due to Redox





(vi) Tin forms compounds in both oxidation states (Sn in +2 state is a reducing agent).

(vii) Lead compounds in +2 state are stable and in +4 state are strong oxidising agents.



Reactivity towards oxygen

There are mainly two types of oxides, i.e., monoxide and dioxide of formula MO and MO₂ respectively. SiO only exists at high temperature.

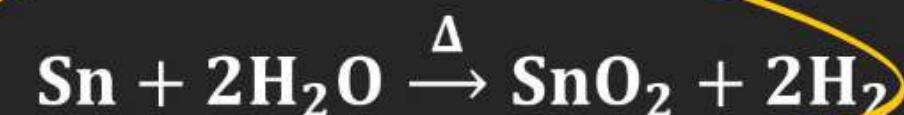
The dioxides –CO₂, SiO₂ and GeO₂ are acidic, whereas SnO₂ and PbO₂ are amphoteric in nature.

CO = neutral

Among monoxides, CO is neutral, GeO is distinctly acidic whereas SnO and PbO are amphoteric.

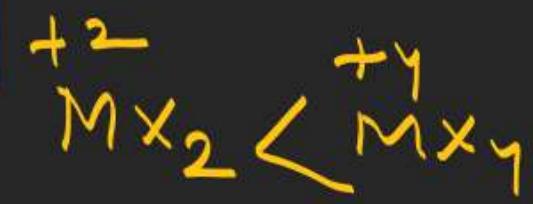
Reactivity towards water

Carbon, silicon and germanium are not affected by water. Tin decomposes steam to form dioxide and dihydrogen gas.



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

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**Reactivity towards halogen**

- (i) These elements can form halides of formula MX_2 and MX_4 (where $X = F, Cl, Br, I$).
 Except carbon, all other members react directly with halogen under suitable condition to make halides.
- tive ↑ Covalent Ch. 1
- (ii) Most of the MX_4 are covalent in nature. The central metal atom in these halides undergoes sp^3 hybridisation and the molecule is tetrahedral in shape.
 Exceptions are SnF_4 and PbF_4 , which are ionic in nature.
- (iii) PbI_4 does not exist.
- (iv) Heavier members Ge to Pb are able to make halides of formula MX_2 .
- (v) Stability of dihalides increases down the group. Considering the thermal and chemical stability, GeX_4 is more stable than GeX_2 , whereas PbX_2 is more than PbX_4 .
- (vi) Except CCl_4 , other tetrachlorides are easily hydrolysed by water.

Catenation Property

Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called catenation. This is because C – C bonds are very strong. The order of catenation is C >> Si > Ge ≈ Sn. Lead does not show catenation.

CC ly → no hydrolysis
due to absence of vac. orbital

Bond	Bond enthalpy/kJ mol ⁻¹
C – C	348
Si – Si	297
Ge – Ge	260
Sn – Sn	240

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

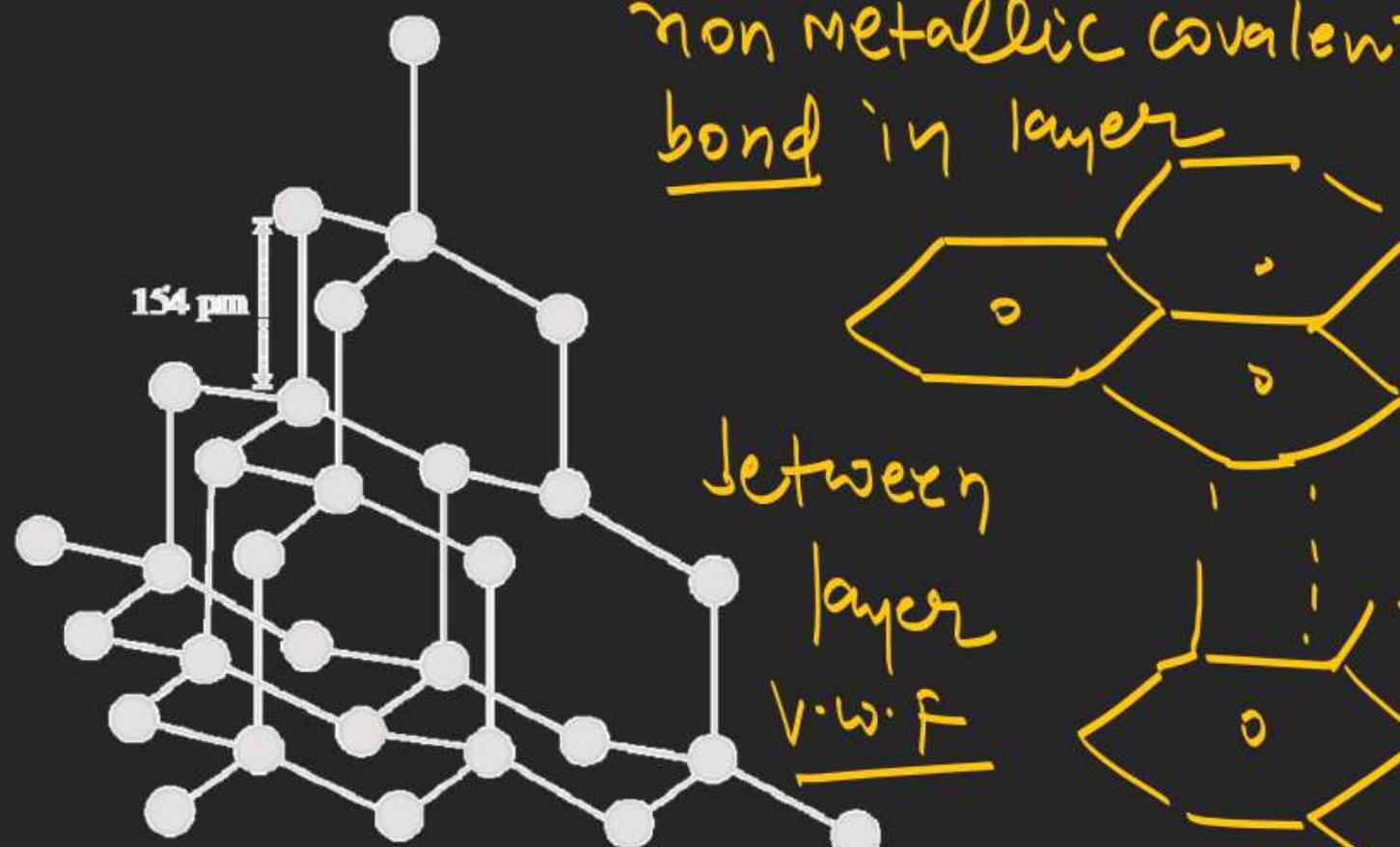
ALLOTROPIES OF CARBON

Diamond

- (i) It has a crystalline lattice.
- (ii) In diamond each carbon atom undergoes sp^3 hybridisation. 3d Network
- (iii) The C – C bond length is 154pm.
- (iv) The structure extends in space and produces a rigid threedimensional network of carbon atoms.



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sp^2
planar
aromatic
Conductor

The structure of diamond

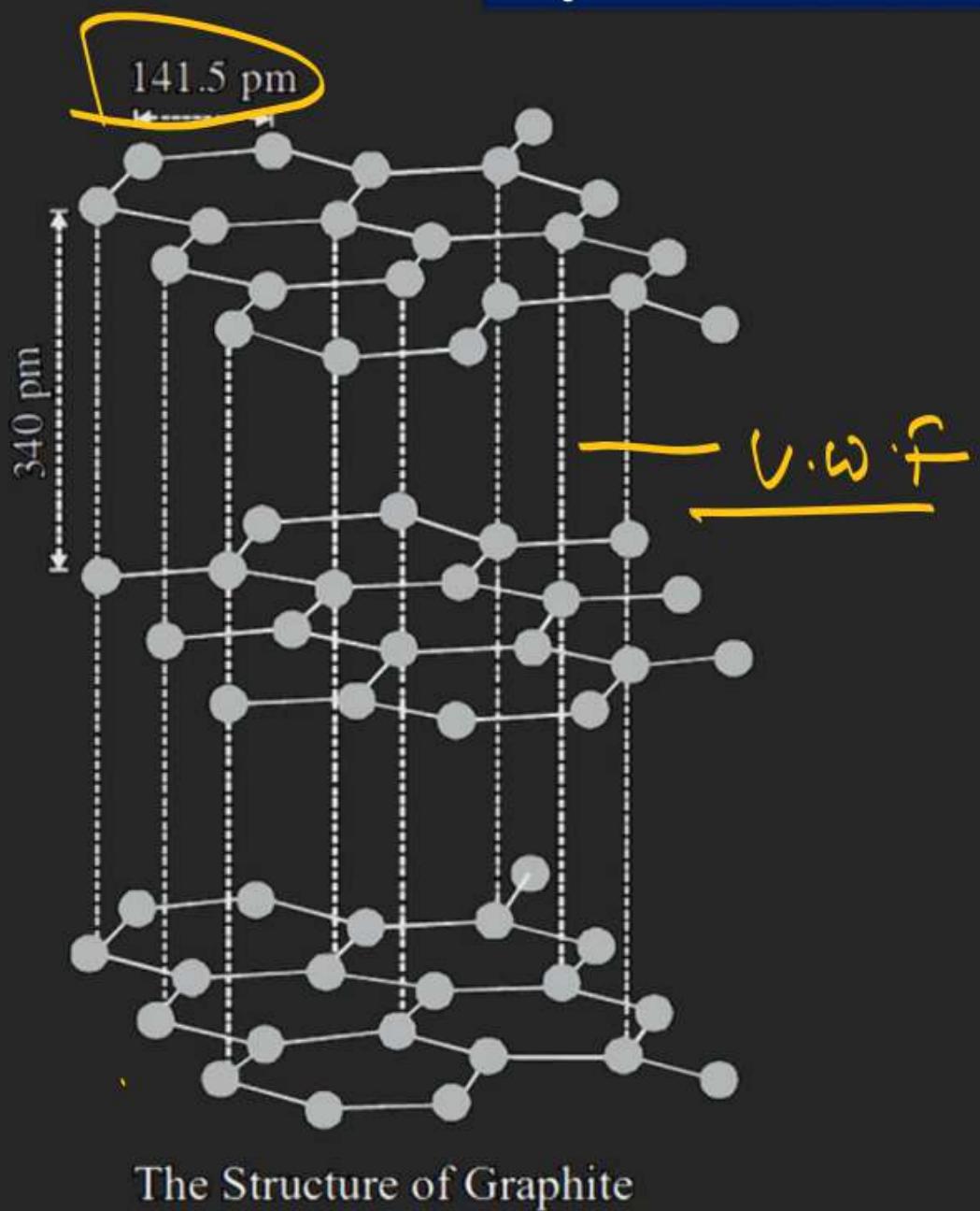
It is very difficult to break extended covalent bonding and, therefore, diamond is a hardest substance on the earth.

Use : It is used as an abrasive for sharpening hard tools, in making dyes and in the manufacture of tungsten filaments for electric light bulbs.

Graphite

- (i) Graphite has layered structure figure.
- (ii) Layers are held by van der Waals forces.
- (iii) Each layer is composed of planar hexagonal rings of carbon atoms. C – C bond length within the layer is 141.5pm.
- (iv) Each carbon atom in hexagonal ring undergoes sp^2 hybridisation and makes three sigma bonds with three neighbouring carbon atoms. Fourth electron forms a p bond. The electrons are delocalized over the whole sheet. Electrons are mobile and, therefore, graphite conducts electricity along the sheet.

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The Structure of Graphite

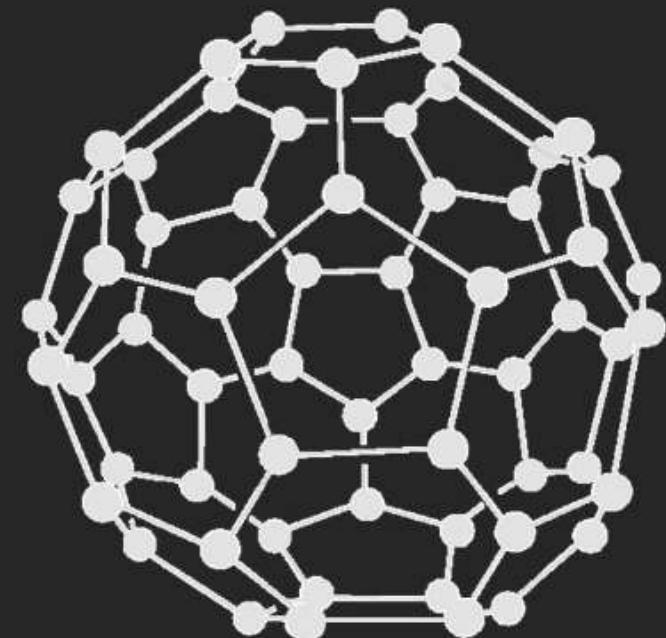
- (v) Graphite cleaves easily between the layers and, therefore, it is very soft and slippery. For this reason graphite is used as a dry lubricant in machines running at high temperature, where oil cannot be used as a lubricant.

p – BLOCK

- (ii) It contains twenty six six-membered rings and twelve five membered rings.
- (iii) All the carbon atoms are equal and they undergo sp^2 hybridisation.
- (iv) This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C – C distances of 143.5pm and 138.3pm respectively. Spherical fullerenes are also called bucky balls in short.

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sp^2
aromatic

each \rightarrow pentagonal
only surrounded by hexagonal

20 hexagonal rings

12 pentagonal rings

each hexagonal \rightarrow surrounded by hexagonal and pentagonal

p – BLOCK

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

Note: It is very important to know that graphite is thermodynamically most stable allotrope of carbon.

Note: Other forms of elemental carbon like carbon black, coke, and charcoal are all impure forms of graphite or fullerenes.

Carbon black is obtained by burning hydrocarbons in a limited supply of air.

Charcoal and coke are obtained by heating wood or coal respectively at high temperatures in the absence of air.

Uses of Carbon

- (i) Used in products such as tennis rackets, fishing rods, aircrafts and canoes.
- (ii) Being good conductor, graphite is used for electrodes in batteries and industrial electrolysis.
- (iii) Crucibles made from graphite are inert to dilute acids and alkalies.
- (iv) Being highly porous, activated charcoal is used in adsorbing poisonous gases; also used in water filters to remove organic contaminators and in airconditioning system to control odour.
- (v) Carbon black is used as black pigment in black ink and as filler in automobile tyres.
- (vi) Coke is used as a fuel and largely as a reducing agent in metallurgy.
- (vii) Diamond is a precious stone and used in jewellery. It is measured in carats
(1 carat = 200mg).

Graphite > D_{ia}n

Conduction

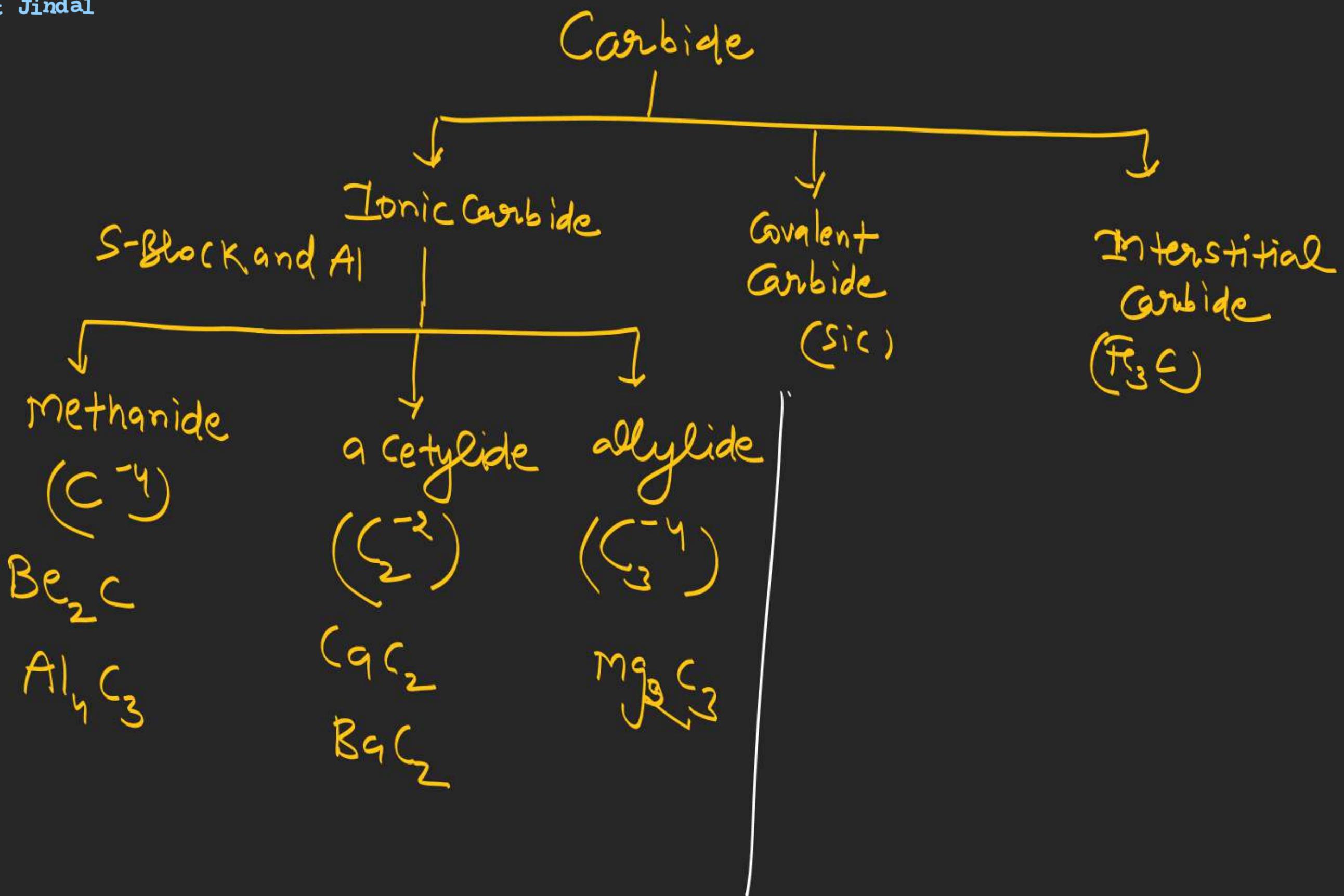
graphite > SiC

Thermal Conductor

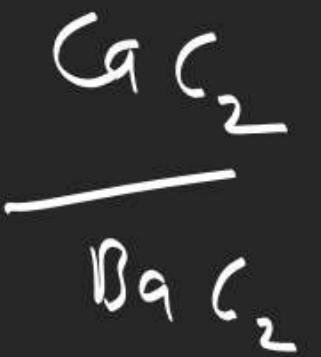
SiC > graphite

Thermodynamic Stability

graphite > SiC



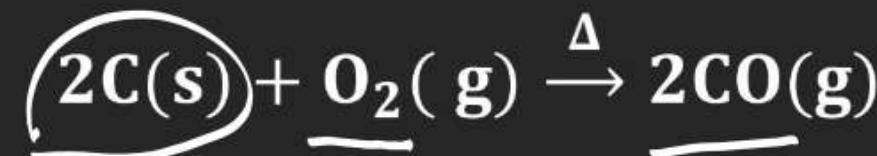




Carbon Monoxide

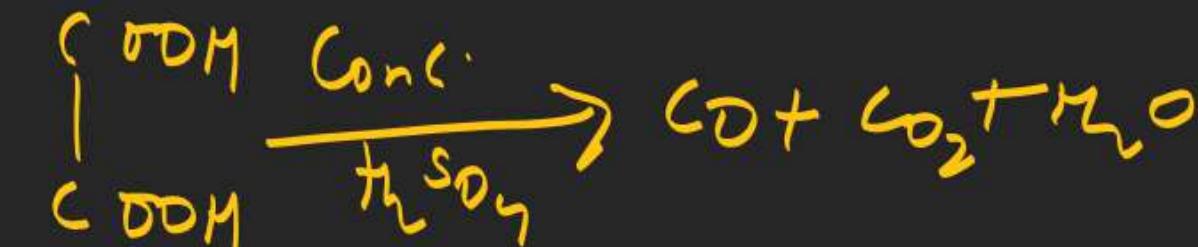
Preparation:

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

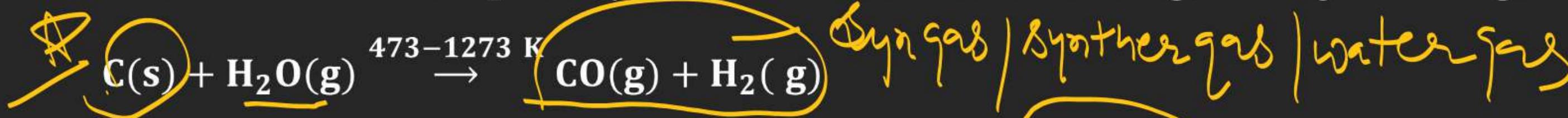


(ii) On small scale pure CO is prepared by dehydration of formic acid with

concentrated H_2SO_4 at 373 K



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

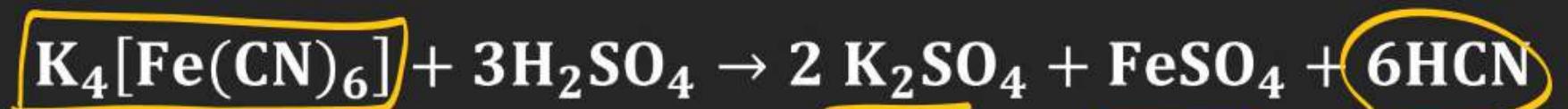


When air is used instead of steam, a mixture of CO and N_2 is produced, which is called producer gas.



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

 (iv) By heating potassium ferrocyanide with conc. H_2SO_4 : When potassium ferrocyanide in powdered state is heated with concentrated H_2SO_4 , CO is evolved. Dilute H_2SO_4 should never be used because it shall evolve highly poisonous gas HCN.



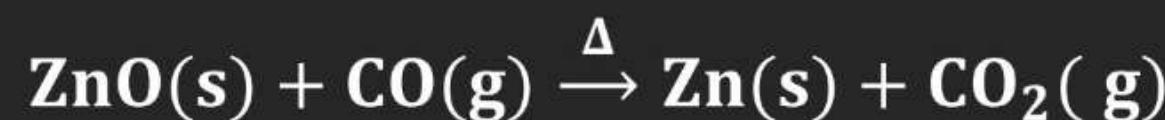
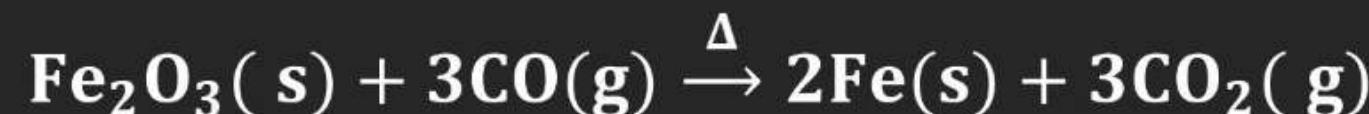
Formic acid



Properties :

- (i) Carbon monoxide is a colourless, odourless and almost water insoluble gas.
- (ii) It is a powerful reducing agent and reduces almost all metal oxides other than those of the alkali and alkaline earth metals, aluminium and a few transition metals.

This property of CO is used in the extraction of many metals from their oxides ores.



DETECTION

(a) burns with **blue flame**

(b) **CO is passed through** PdCl_2 solution giving rise to black ppt.



Black metallic

Deposition

ESTIMATION**ABSORBERS**

(a) **Cu_2Cl_2** : $\text{Cu}_2\text{Cl}_2 + 2\text{CO} + 4\text{H}_2\text{O} \rightarrow [\text{CuCl}(\text{CO})(\text{H}_2\text{O})_2]$

Bonding in CO mole

In CO molecule, there are one sigma and two p bonds between carbon and oxygen.

Because of the presence of a lone pair on carbon, CO molecule acts as a donor and reacts with certain metals when heated to form metal carbonyls.

Poisonous nature of CO

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

Carbon Dioxide

Preparation :

- (i) It is prepared by complete combustion of carbon and carbon containing fuels in excess of air.



- (ii) Laboratory by the action of dilute HCl on calcium carbonate.



- (iii) Commercial scale by heating limestone.

Note :

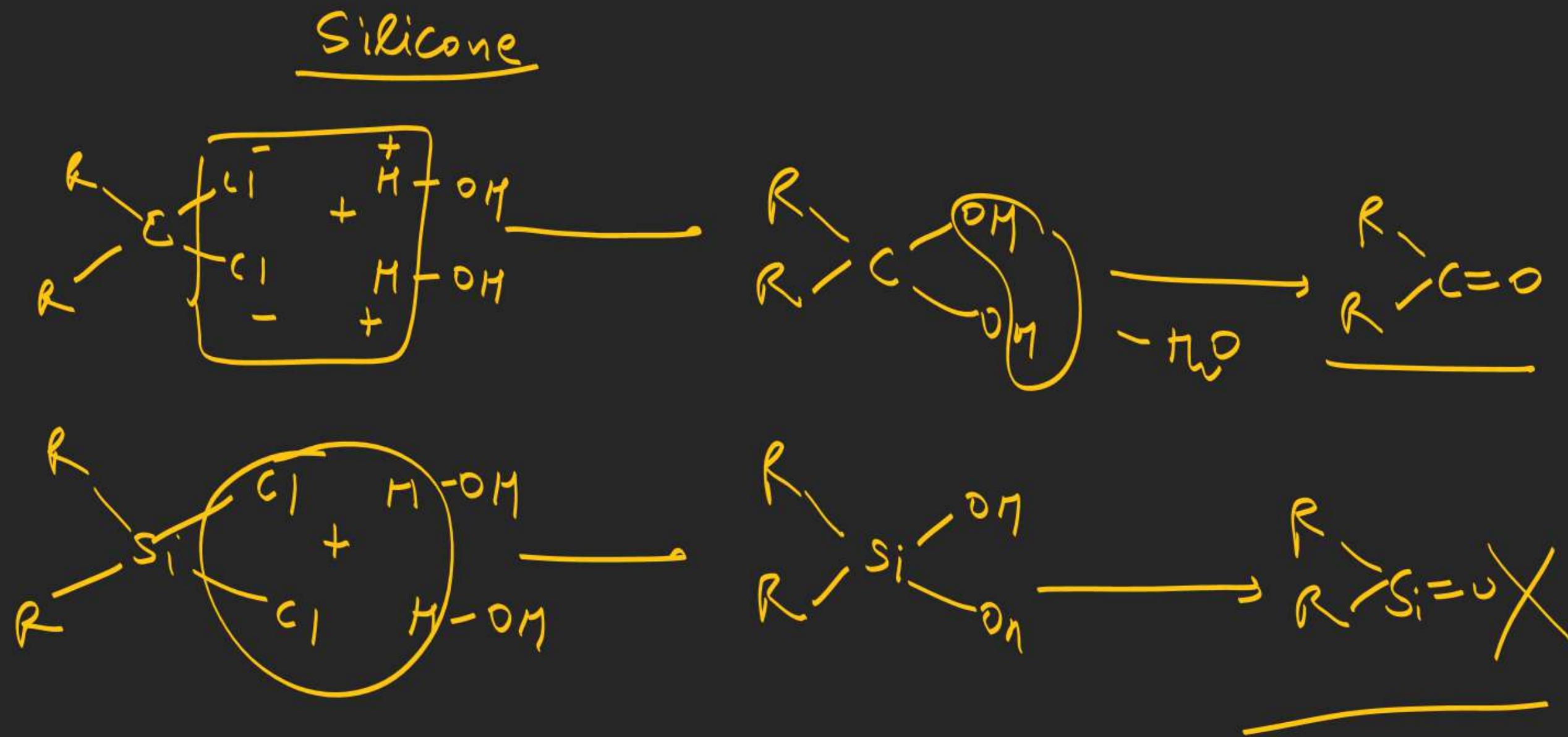
Carbongene has 95% O_2 and 5% CO_2 and is used as an antidote for posining of CO .

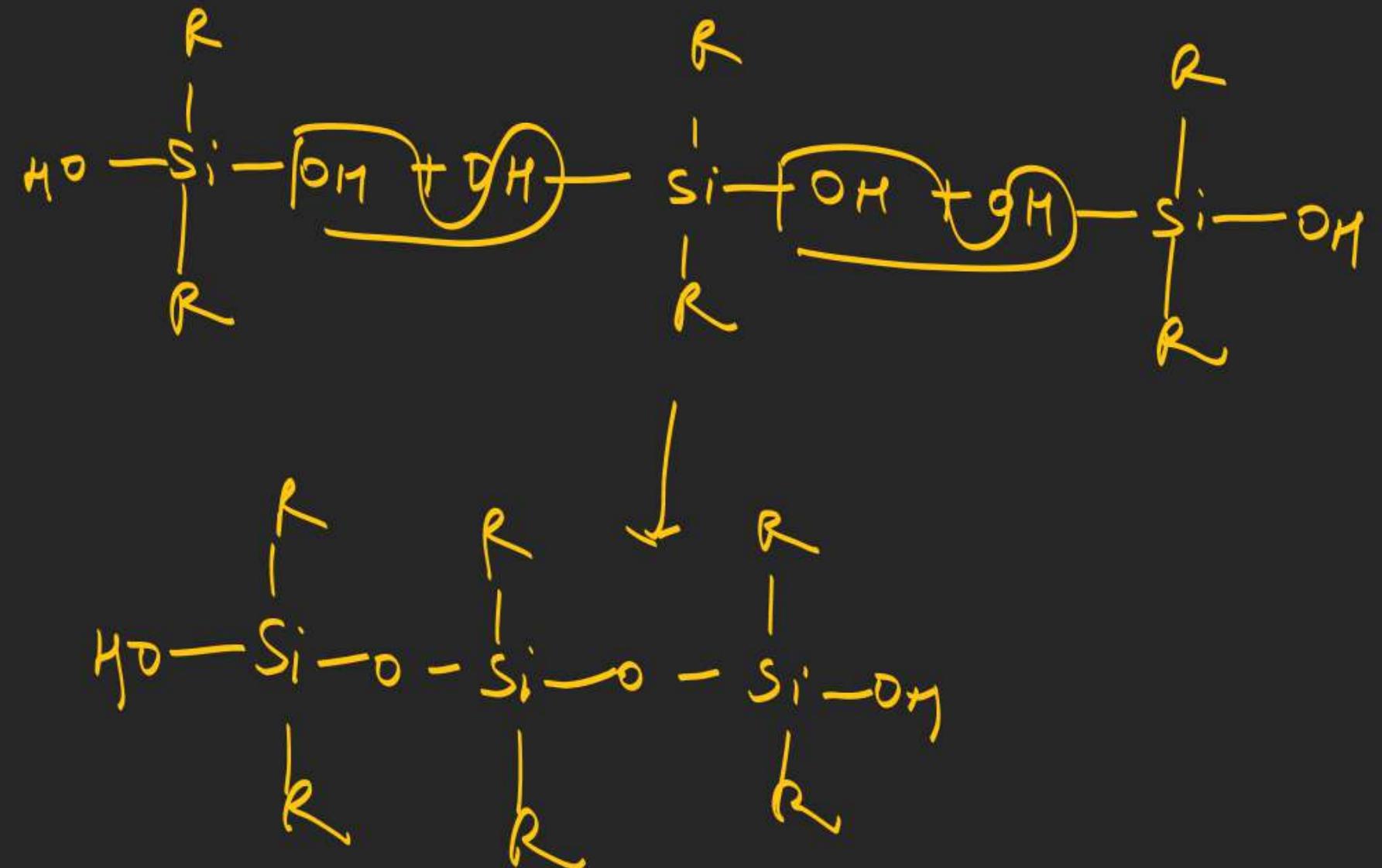
Teflon $-(CF_2 - CF_2)_n -$



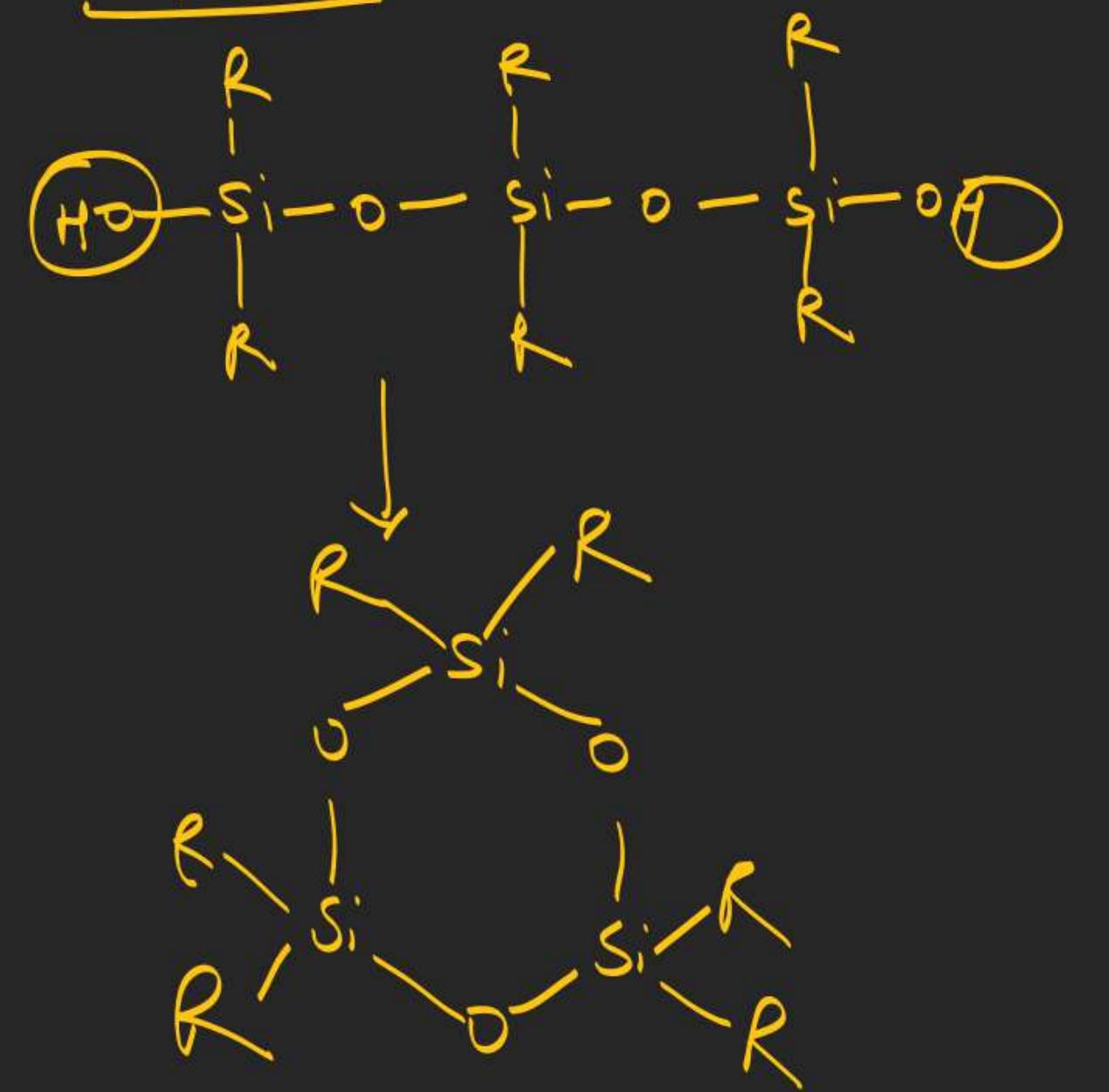
Purpose

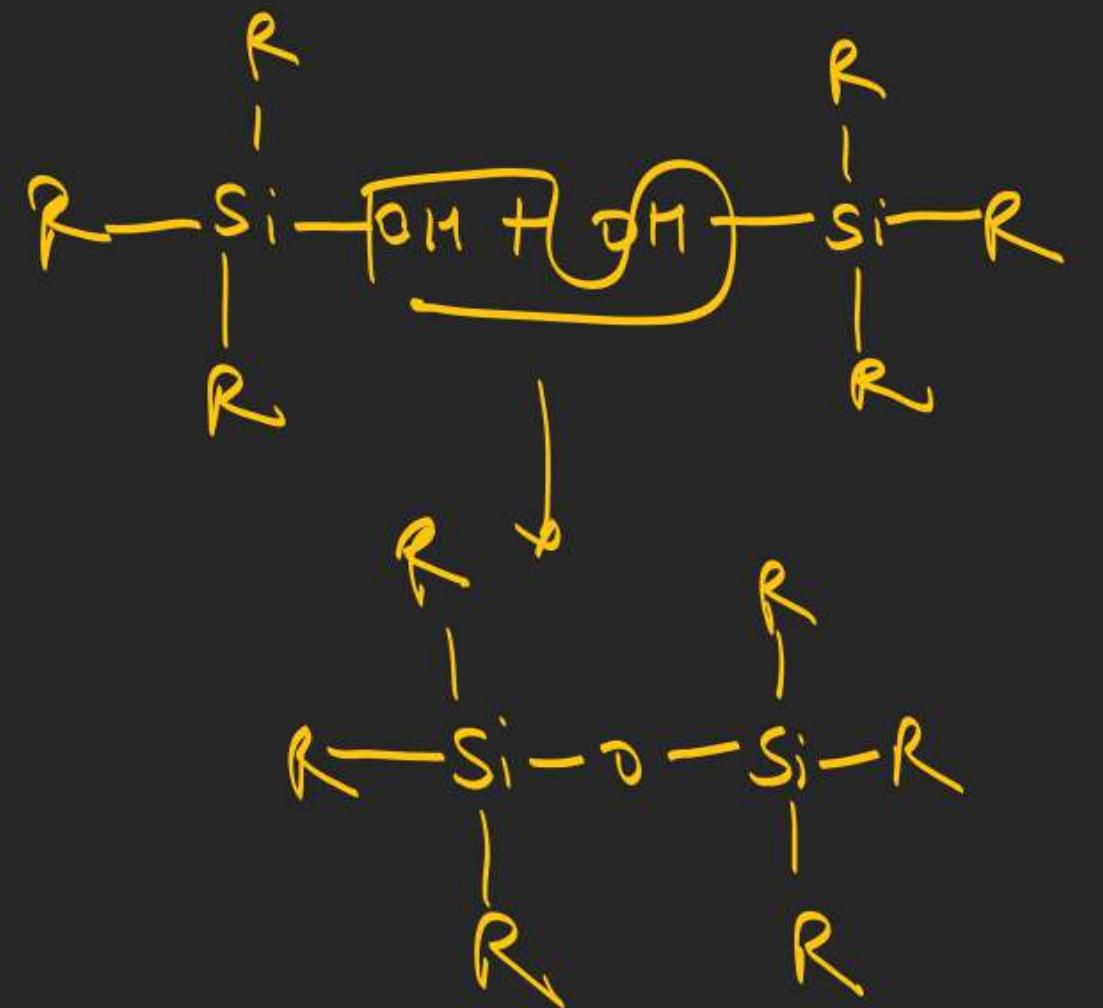
Temperature with standing capacity upto 500 – 550°C (1st organic compound withstand this kind of high temperature)

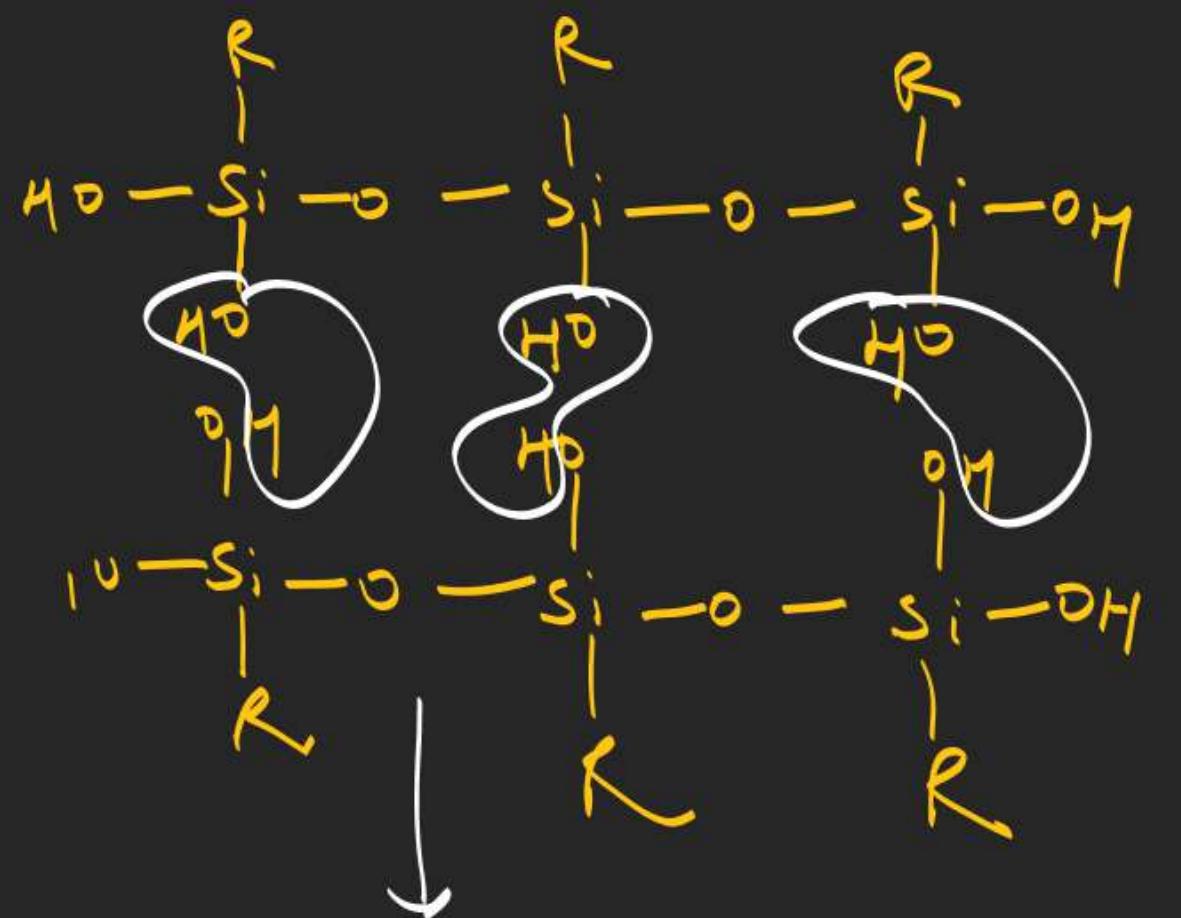


Linear

Cyclic



Dimer

Crosslinked

Ques Which of the following
can form dimer

Silicone

Catalyst



\textcircled{2} none