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SECTION:SR 13_GROUP Prepared by Dr. APR

B Al Ga iN Tl

General electronic configuration ns^2np^1

Oxidation states: +1,+3

The possible oxidation states are +1 (due to involvement of only p electron)

+3 (due to involvement of both s and p electrons. Down the group the stability of +3 oxidation state decreases that of +1 O.S increases due to increasing inertness of the electrons. Thallium(Tl) can exhibit stable +1 cannot exhibit stable +3 due to inert pair effect. Thallium resembles group 1 elements due to its +1 oxidation state.

(electronacceptor, Hence Tl⁺³ is an Oxidising agent)

Compounds of Tl^{+3} are unstable, changes to more stable Tl^{+1} by accepting the electrons ,compounds of Tl^{+3} act as oxidising agents

$$Ga^{+1} \rightarrow Ga^{+3}$$

$$In^{+1}$$

$$(unstable)$$

$$(stable)$$

electron donor (reducing agents)

 Ga^{+1} , In^{+1} changes to more stable Ga^{+3} , In^{+3} by donating electrons and they act as reducing agents.

 Ga^{+1} is more reducing than In^{+1} $(Ga^{+} < In^{+}) \rightarrow$ lesser the stability, greater the reducing

character

 \rightarrow The oxidation state of Ga in GaX_2 appears to be +2. But, it is not +2, it is a compound with Ga^{+1} and Ga^{+3}

$$Ga^+[GaX_4]^-$$

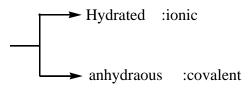
 \rightarrow GaX or Ga⁺ and InX or In⁺ are unstable and undergoes disproportion- ation in aqueous solution.

$$3Ga^{+1}X \xrightarrow{H_2O} 2Ga + GaX_3$$
$$3In^{+1}X \xrightarrow{H_2O} 2In + InX_3$$

Nature of compounds:

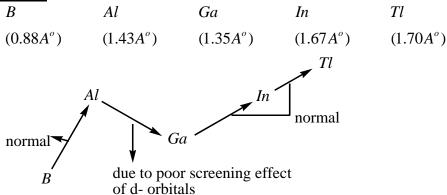
- → boron always forms covalent compounds due to high ionisation energy.
- $\rightarrow B^{+3}$ in aqueous solution cannot exist.

Compounds of Al:



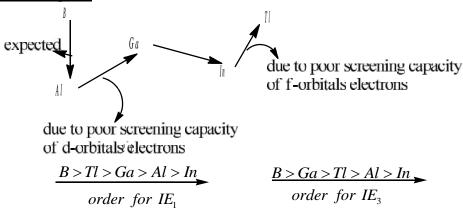
The hydration energy of Al^{+3} is greater than $IE_1 + IE_2 + IE_3$ of Al, therefore hydrated compounds are ionic in nature.

Atomic radii:



Sudden jump in atomic radii from B to Al is due to difference in number of electrons in penultimate shell.

Ionisation energies:



Melting point:

- \rightarrow 'B' is giant covalent polymer with large number of strong covalent bonds. Hence, it has high melting point.
- \rightarrow Gallium exists as Ga_2 molecule. There exists weak attractive forces between molecules.

$$B(2300^{\circ}C)$$

$$Ga$$

$$(30^{\circ}C)$$
 Tl

$$B > Al > Tl > In > Ga$$
 order of M.P

- \rightarrow regular decrease in B.Ps is observed.
- \rightarrow Ga have high liquid range. \therefore used in high temperature thermometers as thermometric liquid.

Density:

 \rightarrow regular increase is observed B = ----- Tl(11.85g/cc)

Chemical reactivity towards air:

- → Crystalline boron is unreactive.
- \rightarrow Aluminium is unreactive towards air due to layer of Al_2O_3 .
- \rightarrow Amorphous boron and Al on heating in air forms corresponding oxides (B_2O_3, Al_2O_3) .
- \rightarrow On heating to high temperature, forms corresponding nitrides. (BN, AlN)

Hydrides:

 \rightarrow Group 3 elements are expected to form MH_3 type of simple hydrides but no element forms simple MH_3 type hydrides but forms complex hydride of the type .

$$type: Li[BH_4], Li[AlH_4]$$

→ Due to availability of vacant P orbital, they form complex hydrides.

$$BX_{3} + LiH \rightarrow \Box BH_{3} + LiX$$

$$\downarrow Li^{+}H^{-}$$

$$Li[BH_{4}]$$

$$Li[BH_{4}] \quad Na[BH_{4}] \quad K[BH_{4}]$$

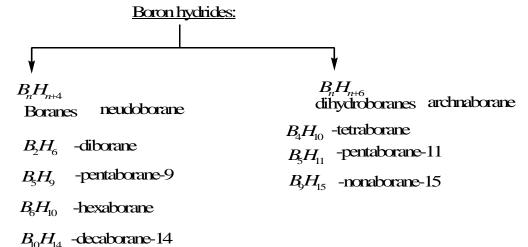
 (\uparrow) order of stability

 BH_4^- is a larger anion, more stabilised by larger cation

- → Complex hydrides are good selective reducing agents
- → lesser the stability of complex hydride, greater the reducing character

$$Li[BH_4]$$
 $NaBH_4$ KBH_4

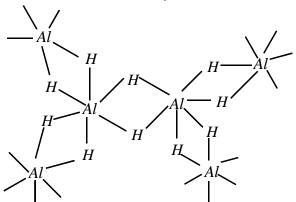
(↓) order of reducing character



Hydrides of other elements are polymeric.

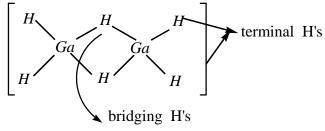
'Al'hydrides are called allanes $(AlH_3)_n$

Each 'Al' is surrounded by 6 'H' atoms



 \rightarrow $(GaH_3)_2$ is dimeric in vapour state

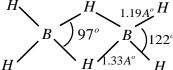
All bridging 'H' bonds are $2e^{-3}C$ bonds



- \rightarrow $(GaH_3)_2$ is polymeric in solid state
- \rightarrow $(InH_3)_n$ exists as polymer in both vapour and solid state.

B_2H_6 (diborane):

Well established structure of diborane



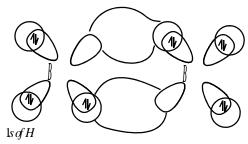
No. Of terminal hydrogens is 4; No of bridging hydrogens is 2

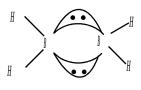
The specific heat data indicates there is no B-B rotation

- \rightarrow The electron diffraction studies indicate BH_2 groups and bridging H's are in different plane.
- → proton nuclear magnetic resonance (NMR) indicates different types of hydrogens in the compound.

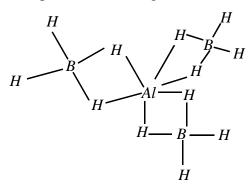
Orbital structure of diborane

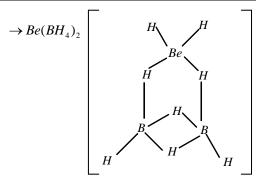
Hybridisation of boron is sp^3





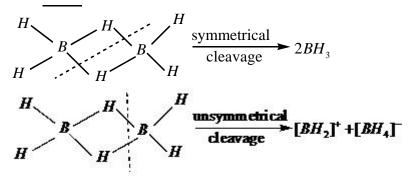
- \rightarrow The no. Of 2e 2c bonds are 4
- $\rightarrow sp^3 s \dagger bonds = 4$
- ightarrow The no.of 2e 3c bonds are 2. These bonds are called banana bonds or tau bonds.
- $\rightarrow sp^3 s sp^3$ bonds are 2
- → terminal B-H bond order :1
- \rightarrow bridging B-H bond order :0.5
- \rightarrow other compounds containing 2e 3c bonds are $Al(BH_4)_3$ (aluminium tetrahydro borate)





 \rightarrow Diborane have less no. of electrons (12) than required for bond formation (16) $\dot{\cdot}$ classified as electron deficient compound (lewis acid).

Cleavage of B_2H_6 :



 \rightarrow symmetrical cleavage takes place in presence of bulky soft bases with S,P donor atoms or $(CH_3)_3N$ or CO or Et_2O , THF each bulky group is attached to each boron.

 \rightarrow unsymmetrical cleavage takes place in presence compact hard bases like $H^-, NH_3, CH_3NH_2, (CH_3)_2NH$.

→ two compact hard bases are attached to one boron atom

$$B_2H_6 + 2CO \rightarrow 2BH_3CO$$

$$B_2H_6 + 2N(CH) \rightarrow 2BH_3[N(CH_3)_3]$$

$$B_2H_6 + 2H^- \rightarrow 2BH_4^-$$

$$B_2H_6 + 2NH_3 \rightarrow [BH_2(NH_3)_2]^+[BH_4]^-$$

Reaction with NH₃:

$$B_2H_6 + NH_3 \xrightarrow[\text{excess}]{\approx 120^{\circ} C} [BH_22NH_3]^+ [BH_4]^- \text{ (or) } B_2H_6.2NH_3 \xrightarrow{\Delta} B_3N_3H_6 \text{ Borazine iso structured}$$

with benze called as inorganic benzene

$$B_{2}H_{6} + NH_{3} \xrightarrow{highT} (BN)_{n}$$
 it is isostructural with graphite

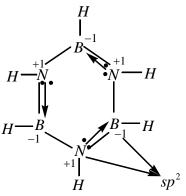
 $3.34A^{\circ}$

B-N(similar to graphite) bond order is 1.33 bond order

$$=1+\frac{no.of\ f\ bonds\ /\ dative\ bonds}{no.of\ elements\ sharing}=1+\frac{2}{6}=1+\frac{1}{3}=1.33A^{\circ}$$

Boron of 2^{nd} layer is placed over nitrogen of the 1^{st} layer . crystalline forms of BN is harder than diamond . $MP = 3000^{\circ} C$

$$B_2H_6 + NH_3 \xrightarrow{ratio 1:2} B_3N_3H_6$$



Compared to benzene it's chemical properties are different .it has delocalisation of f electrons, aramatic Unlike benzene, when heated with water slowly undergoes hydrolysis

$$1)B_{3}N_{3}H_{6} + H_{2}O \xrightarrow{heated} B(OH)_{3} + NH_{3} \uparrow + H_{2} \uparrow$$

$$\underset{H_{3}BO_{3} \text{ orthoboric acid}}{\overset{or}{\underset{H_{3}BO_{3}}{H_{3}BO_{3}}}}$$

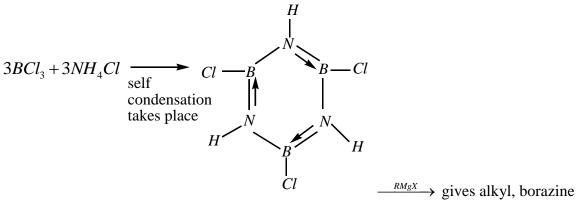
Addition with HCl

$$2)B_3N_3H_6 + 3HCl \rightarrow B_3N_3H_9Cl_3$$
 (chlorine is attached to boron)

Number of isomers in disubstituted borazine :4

Preparation of borazine:

Prepared by condensation of equimolar quantities of BCl₃ and NH₄Cl



B-trichloro borazine reduce with NaBH₄ H N H N H N H borazine

Preparation of N-trialkyl borazine:

Prepared by condensation of equilmolar quantities of BCl_3 and alkylammonium chloride followed by reduction with $NaBH_4$

$$3BCl_3 + 3RNH_3Cl \rightarrow B_3N_3Cl_3R_3$$

$$\begin{pmatrix} N - trialkyl B - chloro borazine \end{pmatrix}$$

$$\begin{pmatrix} NaBH_4 \\ B_3N_3H_3R_3 \\ (N - trialkyl borazine) \end{pmatrix}$$

Properties of B_2H_6 :

- $-B_2H_6$ is a gas at low temperature, high thermal stability
- easily undergoes hydrolysis and alkaline hydrolysis.
- it burns with O which is highly exothermic

1)
$$B_2H_6 + H_2O \to B(OH)_3 + H_2 \uparrow$$

$$2)B_2H_6 + KOH + H_2O \rightarrow KBO_2 + H_2 \uparrow$$
(potassium metaborate)
$$3)B_2H_6 + HCl \xrightarrow{AlCl_3} B_2H_5Cl + HCl$$

$$4)B_2H_6 + 3Cl_2 \rightarrow 2BCl_3 + H_2 \uparrow$$

$$5)B_2H_6 + 6Cl_2 \rightarrow BCl_3 + HCl$$

Preparation of B_2H_6 :

1)Reaction of phosphoric acid with magnesium boride:-

$$Mg_3B_2 + H_3PO_4 \rightarrow Mg_3(PO_4)_2 + mixture \ of \ boranes(mainly \ B_4H_{10})$$

$$\downarrow \Delta$$

$$\downarrow B_2H_6$$

2) **Industrial method**: by reduction of BF_3 with sodiumhydride at 450K:-

$$BF_3 + NaH \rightarrow B_2H_6 + NaF \quad or \ \ Na[BF_4]$$

3)Laboratory method: reduction of BCl₃ with LiAlH₄:

$$BCl_3 + LiAlH_4 \rightarrow B_2H_6 + LiCl + AlCl_3$$

$$B_2O_3 + Al \xrightarrow{H_2} Al_2O_3 + B_2H_6$$

5) oxidation of $NaBH_4$ with iodine:

$$Na[BH_4] + I_2 \rightarrow B_2H_6 + NaI + H_2$$

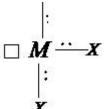
6)Reaction with methyliodide:-

$$B_2H_6 + CH_3I \rightarrow B_2H_2(CH_3)_4$$

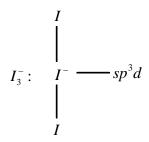
Formation of tetramethyldiborane indicates the presence of four terminal hydrogens.

Halides: (MX_3)

Fluorides of Al, Ga, In are ionic, rest of the trihalides are covalent (Cl^-, Br^-, F^-, I^-)



In all these trihalides, central atom has incomplete octet, and thus are classified as electroon deficient compounds



TlF₃-not exists(cannot exist as 'F' does not contain d- orbitals

 TlI_3 exists (which contains I_3^-

The central atom of trihalides have a tendency to accept pair of electrons to complete the octet . . acts as lewis acids.

Lewis acidic character:

$$\underbrace{BX_3 \quad AlX_3 \quad GaX_3 \quad InX_3}_{\text{decreasing order of Lewis acidic character}}$$

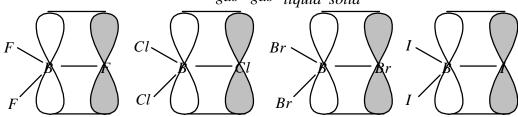
The above order is applicable to compact hard bases

$$\frac{BX_3 \quad AlX_3 \quad GaX_3 \quad InX_3}{\text{order of Lewis acidic character}}$$

Above order is applicable to soft bases.

Lewis acidic character of boron trihalides : $BF_3 < BCl_3 < BBr_3 < BI_3$ the order of acidic character can be

explained by strength of back bonding(BF_3 , BCl_3 , BBr_3 , BI_3) gas gas liquid solid)



Stronger the back bond lesser the lewis acidic character. The strength of the bond (\downarrow) from BF_3 to BI_3 lewis acidic character of trihalides increases

<u>Hydrolysis</u>: BF_3 undergoes incomplete hydrolysis. Where as other halides are completely hydrolyzed.

 $BX_3 + 3H_2O \longrightarrow H_3BO_3 + 3HX$ (X = Cl, Br, I). BF₃ incomplete hydrolysis is due to formation of $BF_4^ BF_3 + 3H_2O \longrightarrow H_3BO_3 + 3HF$, $BF_3 + HF \longrightarrow HBF_4$

Complex Halides:

Maximum coordination number of B is 4 and maximum coordination number Al is 6, satisfied by only 'F' $BF_4^ AlF_6^{-3}$

Halides:

 \rightarrow Broron trihalides are monomers as the e^- deficient character is satisfied by back bonding.

In case of $AlCl_3$, Al cannot form f -bond with the Cl: satisfies its e^- deficient character by formation of dimer.

Alternates:

'B' atom is too small to accommodate with 4 larger halides Cl^- , $Br^- \& I^-$

 \therefore cannot exist as dimer. Fluorine is smaller than other halides . BF_3 is expected to form dimer but actually it is not so.

Reason: In BF_3 , $B-F_f$ bond (P_f-P_f) is stronger, more energy is required to break it. This much energy is not released when it forms a bridged structure. it remains as a monomer.

B-F bond length in BF₃ is shorter than B-F single bond length. B-F B.E greater in BF₃ than B-F than single bond due to back bonding

All B-F bond lengths are equal due to resonance.

$$\begin{array}{c}
\mathbf{F} \\
\mathbf{F}
\end{array}$$

$$\mathbf{B} = \mathbf{F} \leftrightarrow \begin{array}{c}
\mathbf{F} \\
\mathbf{F}
\end{array}$$

$$\mathbf{B} = \mathbf{F} : \mathbf{Bond order is 1.33}$$

Preparation of BF₃ prepared by reaction of Boric acid with Hydrogen floride $H_3BO_3 + 3HF \rightarrow BF_3 + 3H_2O$ AlCl₃.6H₂O:

$$1. Al_2O_3 + C \xrightarrow{Cl_2} AlCl_3 + CO$$

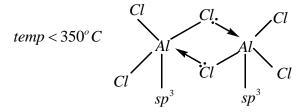
2.
$$Al(OH)_3 + HCl \rightarrow AlCl_3 + H_2O$$

3.
$$Al + Cl_2 \rightarrow AlCl_3$$

1 and 3 are used for preparation of anhydrous and method 2 is used for preparation of hydrated $AlCl_3$

Structure of AlCl₃:

In fused state vapour state dissolved in organic solvents exists as a dimer

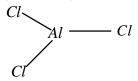


no.of terminal chlorides=4, no. Of bridging chlorides=2 all are $2e^{-}2C$ bonds

 $t < 350^{\circ} C \dim er$, $t > 350^{\circ} C monomer$

in solid state C.No.of Al^{+3} is 6

in vapour state $,>350^{\circ}C$, it exists as a monimer



hydrated $AlCl_3$ cannot be converted to anhydrous by heating but can be converted by(using heating in presence of $SOCl_2$). $SOCl_2 \Rightarrow$ "thionylchloride". $SOCl_2 + H_2O \rightarrow SO_2 + 2HCl$

 \rightarrow AlCl₃ when exposed to moist air gives fumes

$$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl_{(funes)}$$

 \rightarrow AlCl₃ when dissolved in water gives hydrated cation

$$AlCl_3 + H_2O \rightarrow [Al(H_2O)_6]Cl_3$$
 (hydrated cation)

 \Rightarrow Reaction with *NaOH*:

$$\begin{array}{ccc} AlCl_{3} + NaOH & \longrightarrow Al(OH)_{3} \downarrow & \xrightarrow{excess} & \left[Al(OH)_{4}\right]^{-} or \ AlO_{2}2H_{2}O \\ few drops & white \ ppt & (or) \\ & & (or) \\ & \left[Al(OH)_{3}(H_{2}O)_{3}\right] & \left[Al(OH_{4})(H_{2}O)_{2}\right]^{-} \end{array}$$

hydrated allu min ium hydroxide ppt

hydrated tetrahydraxo alu min ate

\Rightarrow Reaction with $NH_{4}OH$:

$$AlCl_3 + NH_4OH \rightarrow Al(OH)_3 \downarrow \frac{NH_4OH}{excess}$$
 Insoluble (remains as it is)

State	AlF_3	$AlCl_3$	$AlBr_3$	AlI_3
Solid state	C.No=6	C.No=6	C.No=4	C.NO=4
			Molecular dimer	Molecular dimer
At M.P/fused state	-	C.No=4	"	"

		Molecular dimer		
Vapour state	monomer	Dimer C.No=4	"	"
		$At < 350^{\circ}C$		
		$> 350^{\circ} C(monomer)$		

$$AlCl_3 + LiH \rightarrow (AlH_3)_n \ polymer + LiCl_{(excess)}$$

$$AlCl_3 + \underset{(excess)}{LiH} \rightarrow LiAlH_4 + LiCl$$

Oxyacids of Boron:

Fluorine is the only non-metallic element which cannot form stable oxy acid due to its more eletronegativity than 'O' and lack of vacant d- orbitals .

- i) H_3BO_3 Orthoboric acid
- ii) HBO₂ metaboric acid
- iii) $H_2B_4O_7$ tetraboric acid
- iv) $H_6B_4O_9$ pyroboric acid
- i) H₃BO₃ (Orthoboric acid): B(OH)₃

White crystalline slippery solid.

Slightly soluble in cold water, plently soluble in hot water

$$\square B(OH)_3 + H^+OH^- \rightleftharpoons [B(OH)_4]^- + H^+$$

It is a weak monobasic Lewis acid. To increase the acidic character of H_3BO_3 or shift the equilibrium towards right hand side Cis di-ol or Cis-poly hydroxy compounds are used

Cis di-ol eliminates $[B(OH)_4]^-$ from equilibrium state in the form of complex [max.coordination number Boron is 4]

$$[B(OH)_4]^- + \bigcirc OH$$

$$OH$$

$$Complex$$

$$Complex$$

To get the exact end point during the titration of H_3BO_3 with standard NaOH, cisdiol are added, phenolphthalein indicator is used.

Preparation of H_3BO_3 :

1)
$$\begin{array}{c|c}
B & N & +H_2O \rightarrow B(OH)_3 + NH_3 \\
3OH^- & 3H^+ & or \\
& H_3BO_3 & Lewis base
\end{array}$$
Lewis acid

2)
$$\begin{array}{c|c} OH^{-} & H^{+} \\ B_{2} & S_{3} \end{array} + H_{2}O \rightarrow B(OH)_{3} + H_{2}S \\ Lewis\ acid & Lewis\ base \\ bron\ sulphide \end{array}$$

3)From calemanite $(Ca_2B_6O_{11})$ by passing SO_2

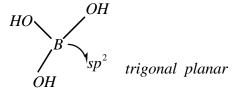
$$Ca_2B_6O_{11} + H_2O + SO_2 \rightarrow Ca(HSO_3)_2 + H_3BO_3$$

Effect of heat:

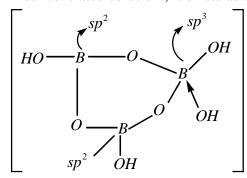
 B_2O_3 is anhydride of H_3BO_3

Structure:

In dilute solution, it exists as a monomer



In concentrated solution, it exists as a trimer



B-O-B bonds:3

; *-OH* groups attached to B=4

In solid state , it has 2 dimensional sheet structure with H- bonding

It dissolves in HF acid

$$H_3BO_3 + HF \rightarrow H[BF_4] + H_2O$$

Hydrogen tetrafluoro borate is stronger acid than H_3BO_3

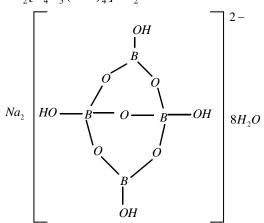
Borax: $(Na_2B_4O_7.10H_2O)$ prismatic borate / common form of borax.

 $Na_2B_4O_7.5H_2O$ octa hedral borax/jewellery

 $Na_2B_4O_7$ Borax glass – glassy transparent material . fairly soluble in cold water , freely soluble in hot water

Structure of Borax:

 $Na_2[B_4O_5(OH)_4]8H_2O$



no of sp^3 or trtrahydral boronatons are 2

 sp^2 or trigonal planar boron atoms are 2

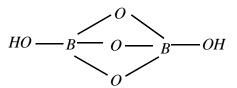
No. Of water molecules attached to the metal ion is 8

No. of B-O-B bonds is 5

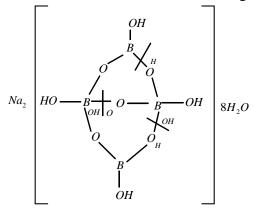
No. of sp^3 boron atoms is equal to the no of -Ve charges

No.of 'O' atoms around boron is equal to the no. of B-O-B bonds

$$[B_3O_3(OH)_5]^{2-}$$
 2 sp³ boronatoms $[B_5O_6(OH)_4]^{-1}$
3 B-O-B bonds



When borax is dissolved in water ring is broken



$$Na_{2}[B_{4}O_{5}(OH)_{4}].8H_{2}O + H_{2}O \rightarrow 2[B(OH)_{4}]^{-} + 2B(OH)_{3}$$
 HCl
 $2NaCl + H_{2}O + B(OH)_{3}$

Aqueous solution of Borax completely reacts with 2 moles of (HCl) acid Borax is a metaborate.

$$Na_2B_4O_7 + H_2O \rightarrow 2B(OH)_3 + 2Na[B(OH)_4] \xrightarrow{\quad 2HCl \quad} 2NaCl + H_2O + 2B(OH)_3$$

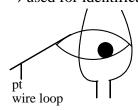
- → Aqueous solution of Borax acts as a buffer
- \rightarrow Acidic hydrolysis of Borax gives $B(OH)_3$
- → Aqueous solution of Borax is (basic) alkaline in nature

$$Na_2 B_4 O_5$$

$$NH_4Cl + Na_2B_2O_7 \xrightarrow{\Delta} (BN)$$
high high temp $B(amorphous)$
 $B_2H_5 + NH_3$

Borax bead test:

→ used for identification of metal salts



- 1) Borax is taken and heated on a platinum wire loop and heated in the flame.
- 2) Glassy transparent bead is formed

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$$
 glassy transparent sodium metaborate glassy transparent

3)Glassy transparent bead is dipped into given metal solution and heated in the flame. Based on the colour of the bead, metal ion is identified.

Eg:
$$CuSO_4 \xrightarrow{\Delta} CuO + SO_2 + O_2$$

 $CuO + B_2O_3 \xrightarrow{\Delta} Cu(BO_2)_2$
 $copper metaborate(blue)$
 $chromium - Cr(BO_2)_3$ (Green)

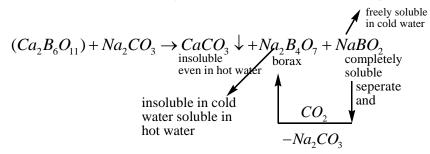
$$Mn - Mn(BO_2)_2$$
 (light pink)

Zn-Zincmetaborate (colourless d^{10} configuration.) $Zn(BO)_2$

- → colour in the boraxbead test is due to the formation of metalmetaborates.
- → Metals which can form coloured metaborates are identified by this test.
- \rightarrow B_2O_3 is the intermediate compound.

Method of preparation of Borax:

1)From colemanite $(Ca_2B_6O_{11})$ from reaction with Na_2CO_3



2)From orthoboric acid by reaction with Na_2CO_3

$$Na_2CO_3 + H_3BO_3 \rightarrow Na_2B_4O_7 + H_2O + CO_2$$

Oxides:-
$$(M_2O_3)$$

$$B_2O_3$$
 Al_2O_3 Ga_2O_3 In_2O_3 Tl_2O

$$B(OH)_3$$
 $Al(OH)_3$ $Ga(OH)_3$ $In(OH)_3$ $TlOH$ acidic amphoteric basic

 B_2O_3 :-

$$H_3BO_3 \xrightarrow{\text{Red hot}} B_2O_3$$

- $\rightarrow B_2O_3$ is anhydride of orthoboric acid
- \rightarrow In presence of strong acidic oxidic oxides like SO_3 , P_4O_{10} , P_2O_3 acts as a base.

$$\begin{array}{c} B_2O_3 + SO_3 \longrightarrow B_2(SO_4)_3 \\ {}_{(base)} \quad {}_{acidic} \quad {}_{boron \, sulphate} \\ \longrightarrow B_2O_3 + P_4O_{10} \longrightarrow BPO_4 \\ {}_{bron \, phosphate} \end{array}$$

Al_2O_3 :-

$$\gamma - Al_2O_3$$

$$2Al(OH)_3 \xrightarrow{450^{\circ}} X - Al_2O_3$$

Soft: used as dehydrating agent & absorbent

$$\Rightarrow BI_3 \xrightarrow{vapours are allowed} B + I_2 (van arkel method)$$
 is

colourless but can be coloured with Fe_2O_3 or Cr_2O_3

 \Rightarrow syntnetic rubies are prepared by heating with Cr_2O_3 which are used in jewellery

$\alpha - Al_2O_2$

$$Al(OH)_3 \xrightarrow{1000^{\circ}} r - Al_2O_3$$

Very hard :known as corundum

 \Rightarrow Al_2O_3 is used as refractory material. The material is chemically inert with high M.P

Mixture of Al_2O_3 with SiO_2 and FeO is called emray which is used in sand paper.

Alums:

Double sulphates of mono positive and tri positive cations with $24H_2O$ molecules

$$M_{2}^{I}SO_{4}.M_{2}^{III}(SO_{4})_{3}.24H_{2}O$$

 $\stackrel{\cdot}{M}\stackrel{\cdot \cdot \cdot}{M}(SO_4)_2.12H_2O$

Each metal is surrounded by $6H_2O$ molecules

 $Na^+,K^+,Rb^+,NH_4^+,Tl^+$ all these mono positive cations can form alums except Lithium

Lithium cannot form Alum as it is too small to accommodate $6H_2O$ molecules

 Al^{+3} , Ga^{+3} , In^{+3} , Fe^{+3} , CO^{+3} , Cr^{+3} , Mn^{+3} , Ti^{+3} , V^{+3} , Rh^{+3} , Ir^{+3} all these tri positive cations can form Alums

Pseudo Alums:

Double sulphates of di positive and tri positive cations with $24H_2O$ are called pseudo Alums.

 $MnSO_4.Al_2(SO_4)_3.24H_2O$

Potash Alum / common Alum:-

$$KSO_4.Al_2(SO_4)_3.24H_2O$$

$$(NH_4)_2 SO_4$$
 .Fe $_2(SO_4)_3.24H_2O$ ferrica comonium alum (or) ferricalum

→ Aqueous solution of potash Alum is acidic in nature.

Preparation of potash Alum:

 $K_2SO_4.Al_2(SO_4)_3.24H_2O$ - potash alum/ common alum

$$1. \ \ K_2SO_4 + Al_2(SO_4)_3 \rightarrow \underset{Sol.}{sol.} \quad \underset{K_2SO_4 \ and \ Al_2(SO_4)_3}{sol.} \xrightarrow{crystalisation} \quad K_2SO_4.Al_2(SO_4)_3.24H_2O$$

2.From Alum stone (alunite):-

$$K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$$

Step-1: Alunite is dissolved in H_2SO_4 . Entire $Al(OH)_3$ is converted into $Al_2(SO_4)_3$

$$Al(OH)_3 + H_2SO_4 \rightarrow Al_2(SO_4)_3 + H_2O$$

Step-2: Calculated quantity K_2SO_4 is added resulting solution and evaporated and crystalised to get common alum

$$Al_2(SO_4)_3.K_2SO_4 + K_2SO_4 \rightarrow sol^n \xrightarrow{crystalisation} K_2SO_4.Al_2(SO_4)_3.24H_2O$$

→ Alums swell on heating due to loss of water

Uses of Alums:

- 1) Used for purification of drinking water
- 2) A antiseptic
- 3) As mordant \rightarrow fixing agent in dye industry
- 4) Alums form Aluminium hydroxide on the cloth. The dye sticks to the $Al(OH)_3$

Extraction of Boron:

Ores: 1)Borax (tincal)- impure /crude borax

- 2) kernite (rasorite) $Na_2B_2O_7.4H_2O$
- 3) colemanite $(Ca_2B_6O_{11}.5H_2O)$
- 4) panderinite $(Ca_2B_6O_{11}.3H_2O)$

Extraction of Boron involves 2 steps:

Step-I: conversion of Ore to B_2O_3

Step-II: Reduction of B_2O_3 -Boron

Step-I: a) B_2O_3 from borax.

$$Na_{2}B_{4}O_{7}.10H_{2}O \xrightarrow{H_{2}O} H_{3}BO_{3} + NaCl + H_{2}O$$

$$H_{3}BO_{3} \xrightarrow{red hot} B_{2}O_{3}$$
b) (i) $B_{2}O_{3}$ from $Ca_{2}B_{6}O_{11}.5H_{2}O$

$$Ca_{2}B_{6}O_{11}.5H_{2}O + H_{2}O + SO_{2} \rightarrow H_{3}BO_{3} + Ca(HSO_{3})_{2}$$

$$H_{3}BO_{3} \xrightarrow{red hot} B_{2}O_{3}$$
b) (ii) $B_{2}O_{3}$ from $Ca_{2}B_{6}O_{11}.5H_{2}O$

$$Ca_{2}B_{6}O_{11} + Na_{2}CO_{3} \rightarrow CaCO_{3} + Na_{2}B_{4}O_{7} + NaBO_{2}$$

$$CO_{2}$$

$$-Na_{2}CO_{3}$$

$$Na_2B_4O_7 + H_2O \xrightarrow{HCl} B(OH)_3 + NaCl + H_2O$$

$$Red hot$$

$$B_2O_3$$

Step-2: Reduction of B_2O_3 to boron. Na/Mg can be used

$$B_2O_3 + Na/Mg \rightarrow B + MgO/Na_2O$$

Boron prepared by the above method is impure called Moissan boron small amount of crystalline boron can be prepared by the following methods:

1)
$$BCl_3 + H_2 \xrightarrow{\text{heated}} B + HCl$$

2)
$$B_2H_6 \xrightarrow{\approx 1400^{\circ} C} B + H_2 \uparrow$$
vapours are allowed

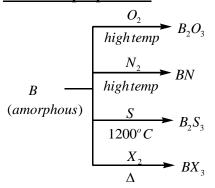
$$_{3)}BI_{3} \xrightarrow{vapours are allowed} B + I_{2} (van arkel method)$$

Properties of Boron:

- 1) Among the 13th group elements, only 'B' is polymorphic (allotropic modifications)
- 2) It has high M.P due to unusual crystal structure.

Reason: Boron exhibits 4 allotropic modifications due to its e^- deficient character. All the allotropic modifications contain icosahedral units. They differ in arrangement of these units. Among the modifications Γ -rbombo hydral is thermodynamically more stable. In icosahedrol units each 'B' is attached to 5 other 'B' atoms on 12 corners.

Chemical properties:



Uses of Boron:

- 1) Used in nuclear reactors as control rods.
- 2) Boron nitride (BN) threads are used in bullet proof cloth.

Comparision between 'B' and 'Al':-

Reagent	В	Al
Air	Crystalline boron is unreactive . $\begin{array}{ccc} B + O_2 & \xrightarrow{high temp} & B_2O_3 \\ & & & & & & \\ & & & & & & \\ & & & & &$	Readily reacts with air and forms oxide layer $Al + O_2 \xrightarrow{\text{room temp}} Al_2O_3$ Prevents the metal to further react . $Al + N_2 \xrightarrow{\text{high temp}} AlN$
Water	No reaction with water at room temp only red hot boron can decompose water $B + H_2O \rightarrow B_2O_3 + H_2 \uparrow$	Stable towards water due to formation of oxide layer (Al_2O_3) however it liberates H_2 with steam after removal of oxide layer $Al + H_2O \rightarrow Al_2O_3 + H_2 \uparrow$ In industry purposefully Al_2O_3 layer is created by electrolysis of $dil.H_2SO_4$ using ' Al ' sheet as anode The process is called anodising $H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$ $H_2O \rightleftharpoons H^+ + OH^-$ (-)cathode: $2H^+ + 2e^- \rightarrow H_2$ (+)anode: $OH^- \rightarrow 2H_2O + O_2 \uparrow$ combines with Al sheet and forms uniform Al_2O_3 layer
Reaction with acids (non-oxidising acids HCl, dil.H ₂ SO ₄ , dil.HNO ₃)	Not attacked by non-oxidising acidslike (HCl , $dil.H_2SO_4$, $dil.HNO_3$) Attacked by oxidising acids like $conc.HNO_3$, $conc.H_2SO_4$ $B+HNO_3 \rightarrow H_3BO_3 + NO_2 + H_2O$ $B+H_2SO_4 \rightarrow H_3BO_3 + SO_2 + H_2O$ Boron dissolves only in fused $NaOH$	conc.HNO ₃ makes Al passive due to formation of Al_2O_3 protective layer. (also with $HClO_4, H_2CrO_4$). Dissolves both in conc. & dil.HCl $Al + conc HCl \rightarrow AlCl_3 + H_2 \uparrow$ No reaction with cold $dil.H_2SO_4$, reacts with hot conc H_2SO_4 $Al + dil.H_2SO_4 \xrightarrow{\Delta} H_2 + Al_2(SO_4)_3$ Dissolves in aq.soln of $NaOH$

Anamalous properties of Boron:

- 1)Boron always form covalent compounds other elements can form ionic and covalent compounds.
- 2)Only Boron exhibits allotropy others cannot exhibit allotropy.
- 3) B_2O_3 is acidic $.Ga_2O_3, Al_2O_3$ -amphoteric.
- 4)Boron is not attacked by non-oxidising acids. Other elements are attacked.
- 5)Maximum coordination no. Of 'B' is 4. Other elements is 6
- (6) B^{+3} is not existing in aqueous solution, other can form their tripositive cations in aqueous solutions.