$B(OEt)_3$ imparts green colour to the bunsen flame.

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Boron Family (Gp 13)

	Oxidation state	
B	+1	+3
Al	+1	+3
Ga	+1	+3
In	+1	+3
Tl	+1	+3

↓ Stability of lower O.S. increases due to inert pair effect.

Radius

$r_{Al} \geq r_{Ga}$ due to shielding effect.

- $Al(OH)_3$ more stable — $Al(OH)$
- ~~$GaCl_2$~~ $Tl(OH)$ More stable — $Tl(OH)_3$
- $GaCl_2$:- $Ga^+[GaCl_4]^-$
- $TlCl_2$:- $Tl^+[TlCl_4]^-$

Boron Halide

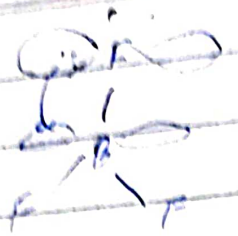
BX_3

BF_3
BCl_3
BBr_3
BI_3

Order of Lewis acid

$BI_3 > BBr_3 > BCl_3 > BF_3$

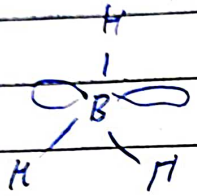
→



Tendency to accept e^- of decreases this weaker Lewis acid

BH_3 does not exist but BF_3 exist

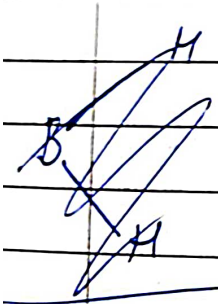
due to back bonding

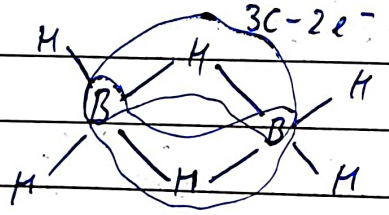


There is no back bonding

$BH_3 \longrightarrow B_2H_6$

↘ Diborane



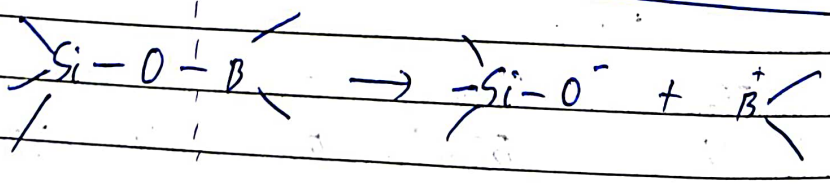


3C-2e⁻ Banana Bond

B has sp^3 hybridisation

$BF_3 + NH_3 \longrightarrow BF_3 \leftarrow NH_3$

sp^2 sp^3 sp^3 sp^3



Boron has

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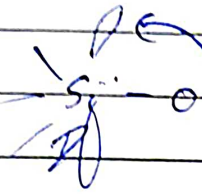
$B^{\oplus}-F$ Resonance, Stability increases
F

∴ Will be easier to break than $B^{+}-CH_3$ do
CH_3



Bond enthalpy

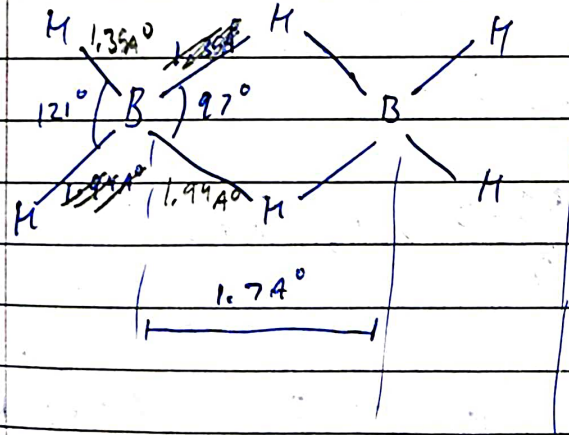
∴ Stability order can be judged by stability of ions.

Boron hydride

Nidoborane

B_nH_{n+4} ⇒ More stable

eg:- B_2H_6



Used in Rocket Fuel

Arachno Borane

B_nH_{n+6} ⇒ Less stable

eg:- B_4H_{10}
B_5H_{11}

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$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O$ + heat

$\Delta H = -2165$ kJ

&

B_2H_6 Properties :-

① Colourless gas
② Highly reactive
③ Spontaneously catches fire in air
④ Most higher ~~boranes~~ Boron hydride are liquid but B_5H_{10}, $B_{10}H_{14}$ are solids
⑤ All boranes act as lewis acid.

Imp.

B_2H_6 :-

① B_2H_6 → Structure

② B_2H_6 + Ammonia :-

B_2H_6 $\xrightarrow[\text{Low Temp.}]{\text{Excess } NH_3}$ $B_2H_6 \cdot 2NH_3$

sp^3

↓

Ionic Compound

$[NH_3 \rightarrow BH_2 \leftarrow NH_3]^+ [BH_4]^-$

sp^3 sp^3

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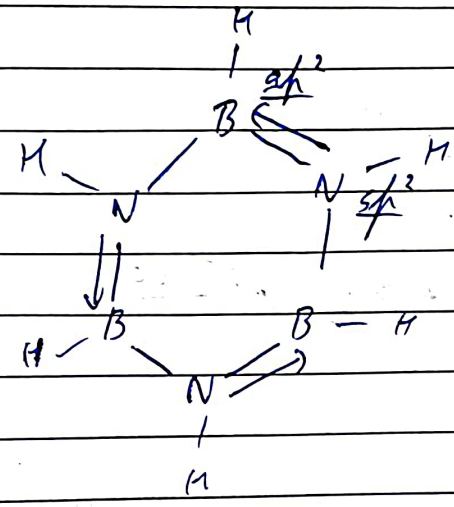
$B_2H_6 \xrightarrow[\text{High Temp.}]{\text{Excess } NH_3} (BN)_x$ Boron Nitride
Same structure as graphite

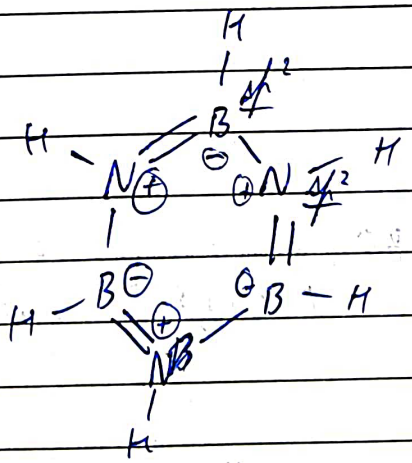
(2:1 ratio of NH_3 & B_2H_6)

③ $B_2H_6 \xrightarrow[\text{High Temp.}]{2NH_3 + B_2H_6} B_3N_3H_6$

Borazine / Borazone / Inorganic Benzene

- Aromatic compound
- More reactive towards electrophilic additions than benzene





- Benzene never gives addition reactions or unsaturation test while inorganic benzene gives addition reac^n & unsaturation tests

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(5) $(BN)_x$

- Consists of planar sheets of atoms like graphite.
- Has hexagonal layer structure.
- Boron-Nitrogen distance within sheet << B-N distance b/w two sheet
- $(BN)_x$ is a slippery material. Used as a lubricant & in cosmetic industry.

(4) $B_3N_3H_6$

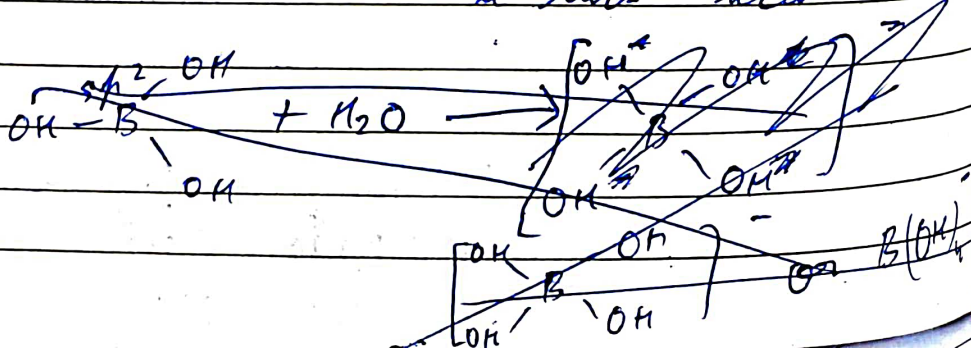
$$3BCl_3 + 3NH_4Cl \xrightarrow{140^\circ C} B_3N_3H_3Cl_3 \xrightarrow{NaBH_4} B_3N_3H_6$$

$B_3N_3H_6 \xrightarrow{3HCl} B_3N_3H_9Cl_3$

$B_3N_3H_6 \xrightarrow{9H_2O} 3NH_3 + 3H_3BO_3 + 3H_2$

H_3BO_3 : Boric acid (Weak acid)

$B(OH)_3$ => Not a protic acid, it is a lewis acid



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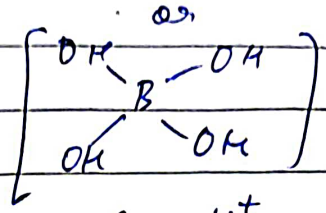
$B(OH)_3 + H_2O \longrightarrow$ $B(OH)_4^-$

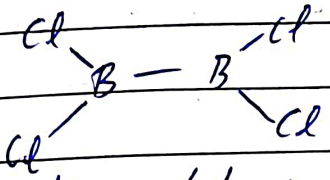
sp^2



$+ H^+$

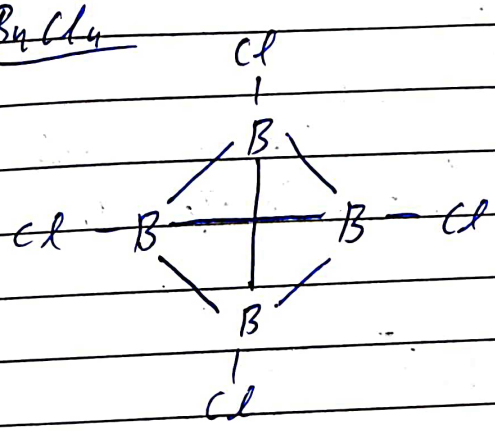
(Comes from water)

B_2Cl_4



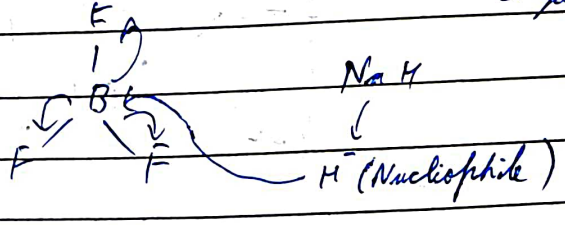
Non-eclipsed

B_4Cl_4



- $2BF_3 + 6NaH \xrightarrow{450K} B_2H_6 + 6NaF$

(Major Product)



$BF_3 + NaBH_4 \longrightarrow B_2H_6 + NaF$

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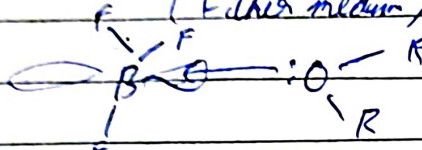
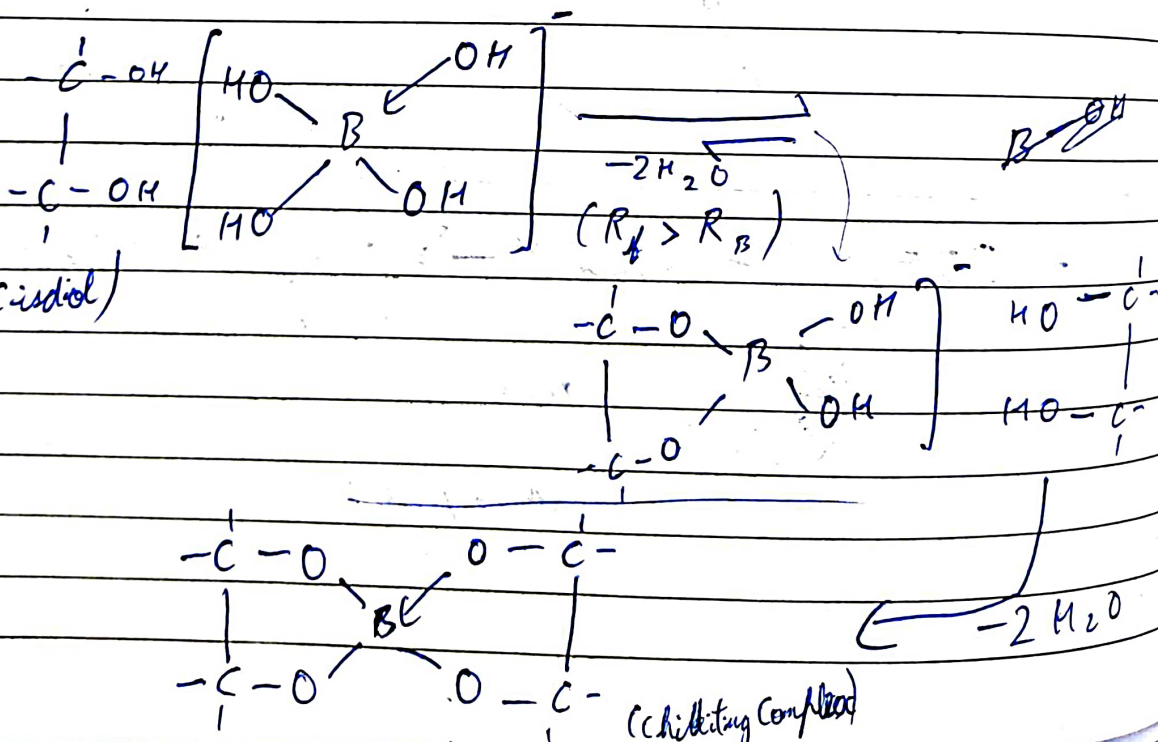
- $4BF_3 + 3LiAlH_4 \longrightarrow 3LiF + 3AlF_3 + 2B_2H_6$ (Major)
- $2NaBH_4 + I_2 \longrightarrow B_2H_6 + 2NaI + H_2$ (Major)
- $3LiBH_4 + 4BF_3 \longrightarrow 3LiBF_4 + 2B_2H_6$ (Major)
- $6LiH + 8Et_2O \cdot BF_3 \longrightarrow 6LiBF_4 + B_2H_6 + 8Et_2O$ (Ether medium) (Major)



- $B_2H_6 + 2KOH \longrightarrow 2KOBH_3 + H_2\uparrow$

Boric Acid (H_3BO_3)

- Behave like a weak acid.
  $pK_a = 9.5$
- Cannot be titrated ~~with NaOH~~ satisfactory with NaOH. Sharp end pt not obtained.



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Boric acid behaves as strong acid in presence of cisdiol. Sharp and fit is obtained when titrated with NaOH

- If organic polyhydroxide like cisdiol (glycerol, manitol, sugar) are added to titrated mixture $B(OH)_3$ behaves like strong monobasic acid, sharp and fit is obtained with NaOH (PHPh indicator)

- $B(OH)_3 + NaOH \rightleftharpoons Na[B(OH)_4]$ Sodium borate
  or $NaBO_2 + 2H_2O$

- Heating effect

$H_3BO_3 \xrightarrow{100^\circ C} HBO_2 \xrightarrow{160^\circ} H_2B_4O_6 \xrightarrow[\text{Heat}]{\text{red}} B_2O_3$

Ortho-Boric Acid — Meta-Boric Acid — Tetra-Boric acid — Boric Anhydride (Sesqui oxide or $MO_{3/2}$)

Used in Borax bead test

(Used in Borax Bead test)

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Borax

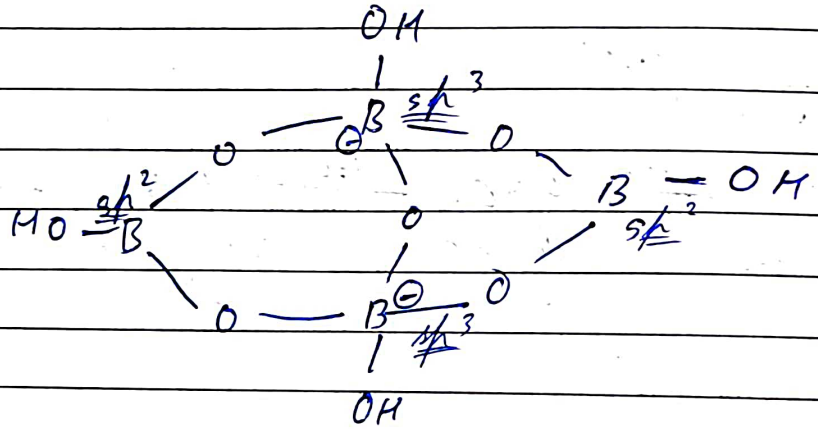
$Na_2B_4O_7 \cdot 10H_2O$ or $Na_2[B_4O_5(OH)_4]\,8H_2O$

Meta Borate

$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$

Borax (Act as a buffer)

2 tetrahedral units &
2 triangular units



- $[B_4O_5(OH)_4]^{2-} + 5H_2O \rightleftharpoons 2B(OH)_3 + 2[B(OH)_4]^-$

Weak acid + Salt

Buffer

- $Na_2[B_4O_5(OH)_4]\cdot 8H_2O + 2HCl \rightleftharpoons 2NaCl + 4H_3BO_3 + 5H_2O$

Indicator :- Methyl Orange

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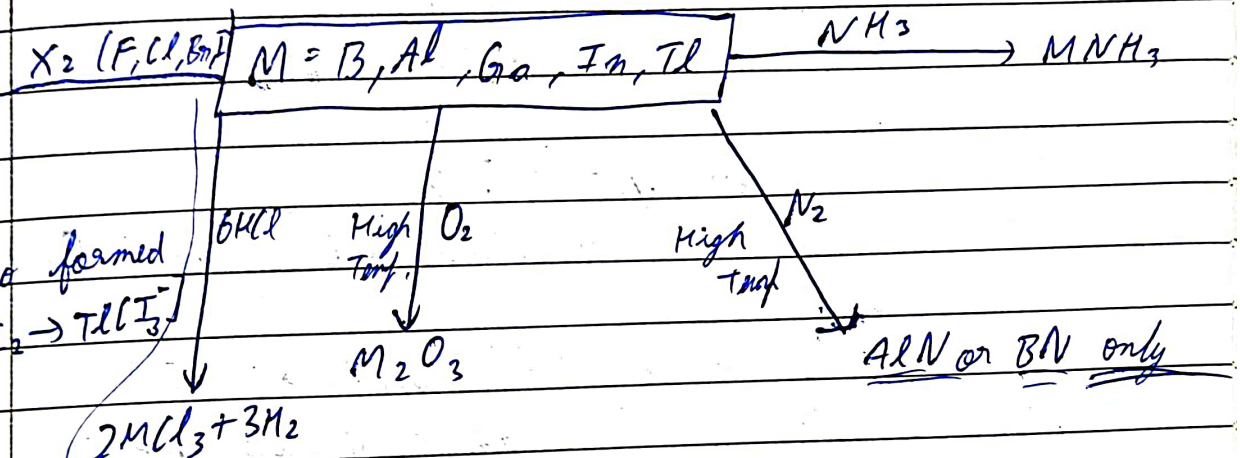
2 moles of HCl because borax is dissolved in water $B(OH)_3 + [B(OH)_4]^-$ are formed but only $B(OH)_4^-$ react with HCl.

$$2[B(OH)_4]^- + 2H_3O^+ \longrightarrow 2B(OH)_3 + 4H_2O$$



Aluminium Oxide

Al_2O_3 → $\alpha - Al_2O_3$ ⇒ Corundum ⇒ Unaffected by acid

Al_2O_3 → $\gamma - Al_2O_3$ ⇒ dissolved in acid (Used in chromatography)

$Al(OH)_3$ & $Ga(OH)_3$ ⇒ Amphoteric

→

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$Al(OH)_3 \xrightarrow{NaOH}$ ($NaAl(OH)_4$ or
$NaAlO_2 \cdot H_2O$ or
$[Al(OH)_4]^-$

) Has diff. structure at diff. pH & conc.

At pH 8 – 12 :
Ions polymerize, using OH bridge & each Al is octahedrally co-ordinated.

At pH > 13 :
dilution, tetrahedral $[Al(OH)_4]^-$

at conc. 1.5M, pH > 13 :
ion exist as dimer
$[(OH)_3 - Al - O - Al - (OH)_3]$

Alums

Double Sulphates having general formula
$X_2SO_4 \cdot M_2(SO_4)_3 \cdot 24H_2O$
X → Monovalent cation (eg :- Na^+, NH_4^+, K
M → Trivalent Cation (eg :- Al^{3+}, Cr^{3+})

- When M is Al^{3+} then, alum is named after monovalent cation.
eg :- $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
Potash Alum
$Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
- Soda Alum

e.g. Chrome Alum:

$K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$

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- When trivalent cation is not Al, then alum is named after both monovalent & trivalent cations.

eg:- $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$
Ferric Ammonium Alum

Preparation of Potash Alum

Alum stone

$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)_3 + 6H_2SO_4 \rightarrow K_2SO_4 + 3Al_2(SO_4)_3 + 12H_2S$

$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \rightarrow 2[KAl(SO_4)_2 \cdot 12H_2O]$

B_{12} exists in icosahedral Form (20 faces:- equilateral Δ ; 12 corners; 30 edges).
5 Boron atoms are equidistant from a given Boron atom. There are 3C-2e- bonds.

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Aluminium has FCC
or CCP
Coordination No. 12

In :- CCP or FCC
Thalium → CCP

At room temp. Ga exists as liquid (m.p :- 30°C)
Boiling pt is very high (more than 2000°C)
∴ Used to measure high temp. (instead of Hg).

Main Sources of Boron

- Borax, also known as Tincal
- Kernite :-
  $Na_2[B_4O_5(OH)_4].2H_2O$
- 9-BBN

Aluminium Ores

- Bauxite ($Al_2O_3.H_2O$ or $Al(OH)_3$ or $Al_2O_3.3H_2O$)
- ~~Feldspar~~ Felspar (
- Cryolite ($Na_3[AlF_6]$)
- Corundum (
- Colemanite (
- Mica (

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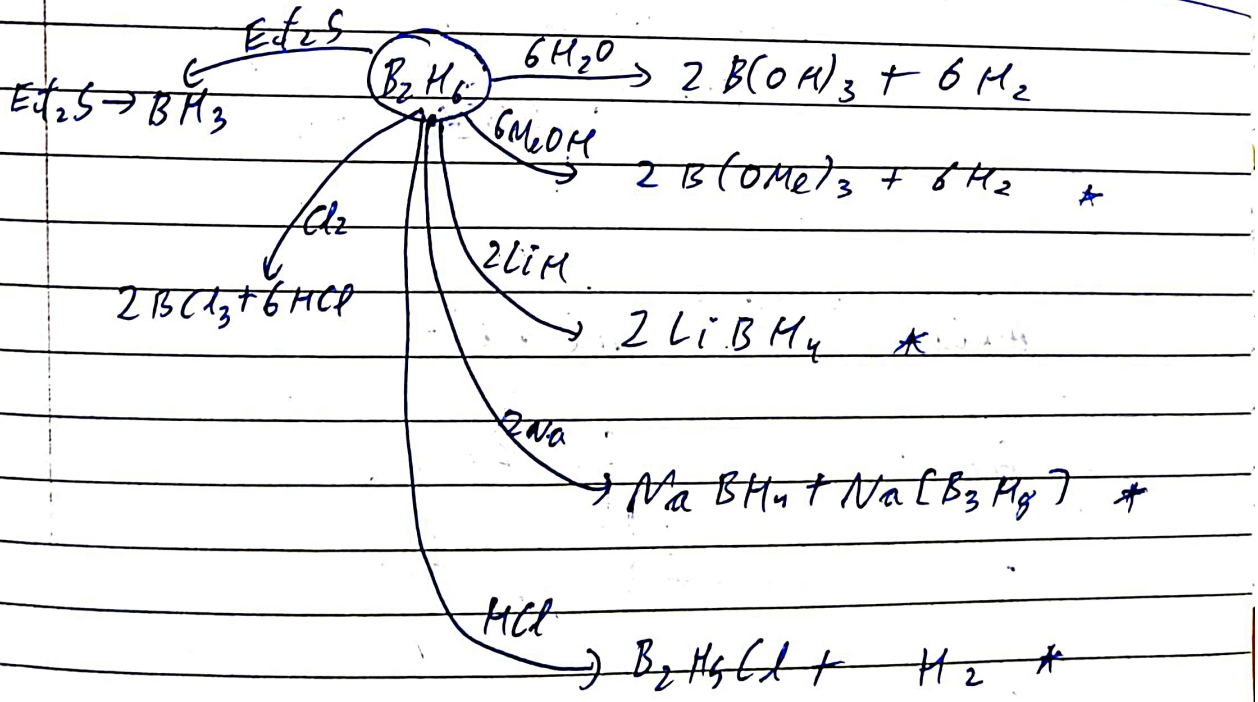
Purification of Al

- Inorganic Stock's Process
- Hall's "
- Serpek's "

Inorganic benzene is more reactive than benzene as benzene is non-polar while Inorganic benzene is polar ($\mu \neq 0$)

Al, Ga are amphoteric & its hydride & oxides are also amphoteric.

$AlCl_3$ exists as dimer in vapour state



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Amphoteric Oxides

ZnO	Al_2O_3	BeO	Cr_2O_3	Ga_2O_3
PbO	SnO	SnO_2		

Song

Alum

$(M^+)\ M = NH_4^+$ (Amina) $\quad Na^+ \quad K^+ \quad Rb^+ \quad Cs^+$

$(M^{3+})\ M = Fe^{+3} \quad Al^{+3} \quad Ga^{+3} \quad Ga^{3+} \quad Cr^{3+} \quad Mn^{3+}$

$BF_3 \xrightarrow{3C_2H_5MgI} B(Et)_3$

$RMgX$ (Grignard Reagent)

R^- → Nucleophile attack

Substitutes Halogens

$AlCl_3 \xrightarrow{3CH_3MgI} Al(Me)_3$

$GaCl_3 \xrightarrow{3EtLi} Ga(Et)_3$

$InBr_3 \xrightarrow{3C_6H_5Li} In(Ph)_3$

$B_3N_3H_3Cl_3 \xrightarrow{CH_3MgBr} B_3N_3H_3(Me)_3$

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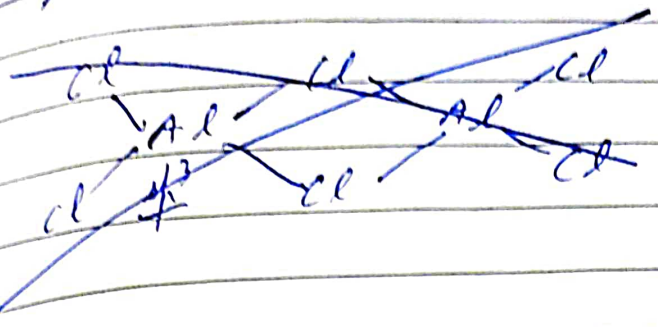
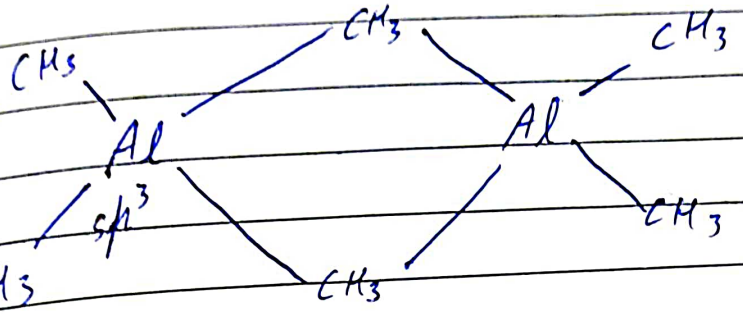
Ziegler Catalyst



Aluminium Trimethyl dimer



($AlCl_3$ is covalent in vapour phase)

$AlCl_3$ is ionic when dissolved in water, gives $[Al.6H_2O]^{3+}3[Cl]^-$

Coordination No. of Al = 6

can exist as $[AlCl_2(H_2O)_4]^+$ or

$[AlCl_4(H_2O)_2]^-$

B_2O_3

(1) Possible to force B_2O_3 to behave as a basic oxide by reacting with strongly acidic compounds. Thus with P_2O_5 or As_2O_5 :-

$$B_2O_3 + P_2O_5 \longrightarrow 2BPO_4$$

→