Group – 13 (Boron Family)

* **Physical State:-** B, Al, Ga, In, Tl

B → Non-metal; Al, Ga, In, Tl → Metals

Ga → exists in liquid state during summers.

* **Oxidation state:-**

(a) Boron can't form '+3' ion; it forms covalent compds.

(b) Al forms '+3' ion.

(c) Ga, In, Tl can both form '+1' and '+3'.

(d) Down the group; the stability of the '+1' O.S. increases due to the inert pair effect.

* **Reactivity towards air:-**

$$2E + 3O_2(g) \xrightarrow{\Delta} 2E_2O_3(s)$$

$$2E + N_2(g) \xrightarrow{\Delta} 2EN(s)$$

Boron trioxides are acidic; Ga_2O_3 and Al_2O_3 are amphoteric; In_2O_3 and Tl_2O_3 are basic in nature.

* **Reactivity with acids and alkalis:-**

(a) Boron doesn't react with acids and alkalis.

(b) Aluminium dissolves in both; showing amphoteric behaviour.

$$2Al(s) + 6HCl(aq.) \longrightarrow 2AlCl_3(aq.) + 3H_2(g)$$

(Acid)

$$2Al(s) + 2NaOH(aq.) + 6H_2O(l) \longrightarrow 2Na[Al(OH)_4](aq.) + 3H_2(g)$$

(Base)

$Al(OH)_3$ primarily acts as a base.

(c) Tl_2O_3 and In_2O_3 are basic and do not form hydrates or hydroxides.

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* Boron (B) :-

(a) Occurrence of boron :- (i) Borax $[Na_2B_4O_7 \cdot 10H_2O]$

(ii) Boric acid $[H_3BO_3]$ (iii) Kernite $[Na_2B_4O_7 \cdot 4H_2O]$

(iv) Colamanite $[Ca_2B_6O_{11} \cdot 5H_2O]$

(b) Extraction of boron:-

(i) $Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 4H_3BO_3 + 2NaCl$

$$2H_3BO_3 \xrightarrow{\Delta} B_2O_3 + 3H_2O$$

$$B_2O_3 + 3Na/Mg \xrightarrow{\Delta} 2B$$

(ii) From KBF_4 :- $KBF_4 + 3K \xrightarrow{\Delta} 4KF + B$

(iii) $2BX_3 + 3H_2 \xrightarrow[W]{\text{Red hot}} 2B + 6HX \quad (X = Cl, Br)$

(iv) Van Arkel method :- $2BI_3 \xrightarrow[W]{\text{Red hot}} 2B + 3I_2\uparrow$

(v) $B_2H_6 \xrightarrow{\Delta} 2B + 3H_2\uparrow$

(c) Properties of boron :-

(i) It exists in five forms :- 4 crystalline + 1 amorphous

(ii) $4B + 3O_2 \longrightarrow 2B_2O_3$; $2B + N_2 \longrightarrow 2BN$

$$BN + 3H_2O \longrightarrow H_3BO_3 + NH_3$$

(iii) $2B + 2NaOH + 2H_2O \longrightarrow NaBO_2 + 3H_2$

(iv) $4B + 3SiO_2 \longrightarrow 2B_2O_3 + 3Si$

* Boron Trioxide (B_2O_3) :-

(a) Preparation :- $H_3BO_3 \xrightarrow{100^\circ C} HBO_2 \xrightarrow{160^\circ C} H_4B_2O_7 \xrightarrow{\text{Red hot}} B_2O_3$

(b) Properties :- * Acidic oxide $\longrightarrow Na_2O + B_2O_3 \longrightarrow Na_3BO_3$

* It forms coloured compounds with transition metal salts.

$$B_2O_3 + Cr_2(SO_4)_3 \xrightarrow{\Delta} 2Cr(BO_3)_3 + SO_3\uparrow$$
(green)

$$B_2O_3 + Cu(NO_3)_2 \xrightarrow{\Delta} 2Cu(BO_2)_2 + NO_2\uparrow + O_2\uparrow$$
(blue)

* $B_2O_3 + 6HF + 3H_2SO_4 \longrightarrow 2BF_3 + 3H_2SO_4 \cdot H_2O$

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* Orthoboric acid (H_3BO_3) :-

(a) Preparation :- (i) $Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + H_3BO_3\downarrow$

(ii) $Ca_2B_6O_{11} + 4SO_2 + 11H_2O \longrightarrow 2Ca(HSO_3)_2 + 6H_3BO_3\downarrow$

(b) Properties :- (i) H_3BO_3 is a weak monobasic acid.

(ii) $B(OH)_3 + 2H_2O \rightleftharpoons [B(OH)_4]^-(aq.) + H_3O^+(aq.)$

(iii) H_3BO_3 is a lewis acid and not a proton donor like others.

(iv) To increase the acidic properties of the boric acid; cis diols are added to its aqueous soln.

eg. → glycerol, catechol, mannitol, salicylic acid etc.

$$[B(OH)_4]^- + 2\begin{pmatrix} CH_2\text{-}OH \\ | \\ CH_2\text{-}OH \end{pmatrix} \rightleftharpoons \left[\begin{array}{c} O \\ \diagdown \\ B \\ \diagup \\ O \end{array}\right]^- + H^+ + 4H_2O$$

(v) When heated; it forms B_2O_3.

$$H_3BO_3 \xrightarrow{100^\circ C} HBO_2 \xrightarrow{160^\circ C} H_2B_4O_7 \xrightarrow[\text{hot}]{\text{Red}} B_2O_3$$

(vi) H_3BO_3 is greasy to touch; less soluble in cold water; but more soluble in hot water. In solid state, the $B(OH)_3$ units are hydrogen bonded in 2-D sheets.

(vii) Test of boric acid is done using ethanol:-

$$H_3BO_3 + 3\,EtOH \longrightarrow (EtO)_3B + 3H_2O$$

(viii) Polymeric metaborates are formed at high conc.

$$3\,B(OH)_3 \rightleftharpoons H_3O^+ + [B_2O_3(OH)_4]^- + H_2O$$

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* Borax ($Na_2B_4O_7 \cdot 10H_2O$):-

(a) Preparation:- (i) $Ca_2B_6O_{11} + Na_2CO_3 \longrightarrow Na_2B_4O_7 + NaBO_2 + CaCO_3$.

(ii) $4H_3BO_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7 + 6H_2O + CO_2\uparrow$

(b) Properties:- (i) It's aqueous solution is alkaline bcoz of hydrolysis to weak acid (H_3BO_3) and strong base (NaOH)

$$Na_2B_4O_7 + 7H_2O \longrightarrow 4H_3BO_3 + 2NaOH$$

(ii) $Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10H_2O\uparrow$

$$Na_2B_4O_7 \xrightarrow{740^\circ C} 2NaBO_2 + B_2O_3 \text{ (Borax-bead)}$$

(iii) oxidation with H_2O_2:-

$$Na_2B_4O_7 \xrightarrow{\Delta} NaBO_2 + 2H_2O_2 + 6H_2O$$

(Used as a brightener in the washing powder).

$Na_2[(OH)_2B(O-O)_2B(OH)_2] \cdot 6H_2O$
Sodium peroxoborate

(iv) One mole of borax reacts with 2 moles acid.

$$[B_4O_5(OH)_4]^{-2} + 5H_2O \rightleftharpoons 2H_3BO_3 + 2[B(OH)_4]^-$$

H_3BO_3 is a weak acid; hence only $[B(OH)_4]^-$ will react with an acid.

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

(v) Borax is also used as a buffer.

(vi) Correct formula of borax is $Na_2[B_4O_5(OH)_4].8H_2O$
It has '5' B–O–B bonds and '8' water of crystallization.

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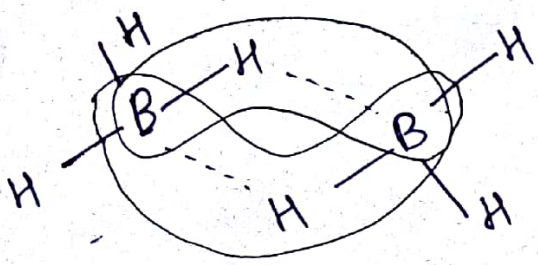
* Diborane (B_2H_6) :- It has 3 centered $2e^-$ bond; banana bonds, the B–H bridge bond is longer and stronger than the terminal B–H bonds.



(a) Preparation:- (i) $BF_3 + LiAlH_4 \xrightarrow{\text{ether}} 2B_2H_6$

(ii) $BCl_3 + 6H_2$ (excess) $\xrightarrow[\text{discharge}]{\text{silent electric}} B_2H_6$

(iii) $2BF_3 + 6NaH \longrightarrow B_2H_6 + 6NaF$

(b) Properties:- (i) B_2H_6 is a colourless and reactive gas.

(ii) It has a high calorific value.

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O \quad \Delta H < 0$$

(iii) $B_2H_6 + 6H_2O \longrightarrow 2B(OH)_3 + 6H_2$

(iv) $B_2H_6 + 6Cl_2 \longrightarrow 2BCl_3 + 6HCl$

(c) Reaction with NH_3 and amines :-

(i) Small amines (NH_3, 1° amine, 2° amine) give the unsymmetrical cleavage. $B_2H_6 + 2NH_3 \longrightarrow [H_2B(NH_3)_2]^+ [BH_4]^-$

(ii) Larger amines (3° amines, pyridine) give the symmetrical cleavage. $2(CH_3)_3N + B_2H_6 \longrightarrow 2H_3B \leftarrow N(CH_3)_3$

Adduct.

(d) Reaction of B_2H_6 with NH_3 in different conditions :-

$B_2H_6 + NH_3$

- (excess NH_3, low temp) → $[BH_2(NH_3)_2]^+ [BH_4]^-$ (Ionic)
- excess NH_3 (high temp) → $(BN)_x$ (Inorganic graphite)
- $NH_3 : B_2H_6 = 2:1$ → $B_3N_3H_6$ (Borazine)

Aluminium (P.T.O.)

* Aluminium (Al) :-

* Al_2O_3 (Aluminium oxide) :- Alumina.

It occurs in the form of bauxite.

(a) Preparation :- (i) $2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O\uparrow$

(ii) By aluminium chloride ($Al_2Cl_3 \cdot 6H_2O$)

* $2Al + 3HCl \longrightarrow 2AlCl_3 + 3H_2\uparrow$
* $Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$
* $Al_2O_3 + 3C + 3Cl_2 \longrightarrow 2AlCl_3(anhyd.) + 3CO\uparrow$

(b) Properties :- (i) Aqueous solution is acidic in nature.

$$[Al(H_2O)_6]^{+3} \rightleftharpoons [Al(H_2O)_5OH]^{+2} + H^+$$

(ii) Alums :- (a) $M_2SO_4 \cdot M'_2(SO_4)_3 \cdot 24H_2O$

where M is any cation (univalent ; except Li^+)

where M' is trivalent cation (eg.- Al^{+3}, Cr^{+3}, Fe^{+3}, Co^{+3} etc.)

(b) Alums are double salts which when dissolved in water produce metal and sulphate ions.

(c) These are used as :-

(i) Mordant in dye industry.

(ii) Germicide for water purification

(iii) Coagulating agent.

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