TDC Part I
Paper I, Group B
Inorganic Chemistry

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TOPIC: - p-block group 13

Oxides, oxoacids and hydroxides

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Trioxides of all elements (M_2O_3) are known Thallium forms the monoxide. On moving down the group, the basicity of the oxide increases along with increase in metallic character of the element. Thus B_2O_3 is acidic, Al_2O_3 and Ga_2O_3 amphoteric while In_2O_3 and Tl_2O_3 are basic. Tl_2O is strongly basic; it dissolves in water forming TlOH, which is as strong a base as KOH. B_2O_3 is obtained by direct combination or by dehydration of boric acid.

$$2B + 3O_2 \longrightarrow B_2O_3$$

$$2H_3BO_3 \xrightarrow{100^0C} 2HBO_2 \xrightarrow{\text{red heat}} B_2O_3$$

Orthoboric acid $-2H_2O$ metaboric acid $-H_2O$

Being the oxide of a non-metal it is acidic in nature. It is the anhydride of boric acid. When fused with metal oxides or salts it forms metaborates. The metaborates of transition metals have characteristic colours and form the basis of borax-bead test of identification of metals.

$$CoO + B_2O_3 \longrightarrow Co(BO_2)_2 \text{ deep blue}$$

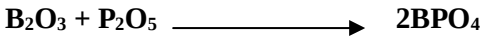
$$CuSO_4 + B_2O_3 \longrightarrow Cu(BO_2)_2 + SO_3$$

Blue

$$Cr_2O_3 + 3B_2O_3 \longrightarrow 2Cr(BO_2)_3$$

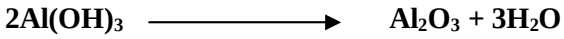
Green

However when B_2O_3 is treated with strongly acidic compounds like phosphorus pentoxide, it is forced to behave as a base.

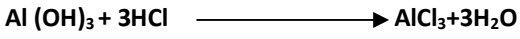


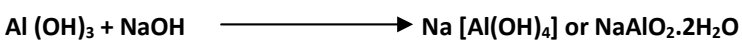
Aluminium oxide occurs in nature as bauxite and corundum and also as gemstones – ruby, emerald, sapphire etc. the colour is due to transition metal ions like iron, chromium, titanium etc. Anhydrous aluminium oxide exists in two forms- α-Al_2O_3 and r-Al_2O_3. r-Al_2O_3 is

obtained by dehydration of Al $(OH)_3$ below 450^0C and unlike α-Al_2O_3 it is soluble in acids, absorbs water and is used in chromatography.

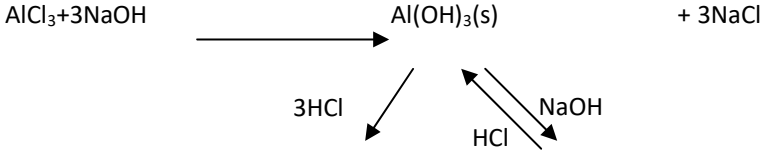


On heating to 1250^0C it changes to the α form which high melting, hard and inert. Aluminium hydroxide is amphoteric and dissolves in both acids and bases.





In sodium hydroxide it forms sodium tetrahyodroxoaluminate (III), commonly referred to as sodium aluminate. If this solution is acidified $Al(OH)_3$ is reprecipitated. The sequence of reactions may be represented as



$AlCl_3 + 3H_2O$ $Na[Al(OH)_4]$

The structure of sodium aluminate is complicated and varies with pH and concentration. Polymeric species with OH bridges are formed between pH 8-12. Above pH13, the tetrahedral $[Al(OH)_4]$-ion exists in dilute solutions white dimeric species are found in concentrated solutions (fig6)

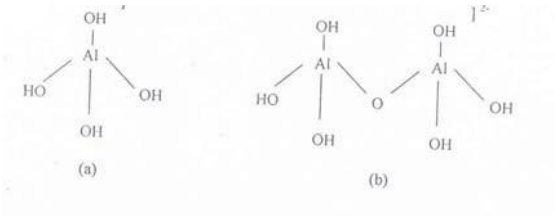


Fig. 6: Hydro complexes of Aluminium at (a) pH8-12 (b) above pH 13

Ga_2O_3 and $Ga(OH)_3$ are amphoteric like Al_2O_3 and $Al(OH)_3$. In_2O_3, Tl_2O_3 and Tl_2O are basic. When a metal exists in two oxidation states, the lower oxidation state is more basic. Thus TlOH is a stronger base than $Tl(OH)_3$.

The most common oxo acid of boron is orthoboric acid which is a flaky solid having a two – dimensional layer structure (fig 7). The BO_3 units are linked by hydrogen bonds and individual layers are held by weak forces, making the substance flaky and waxy.

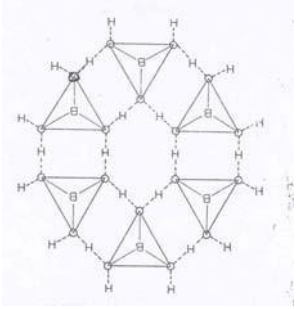
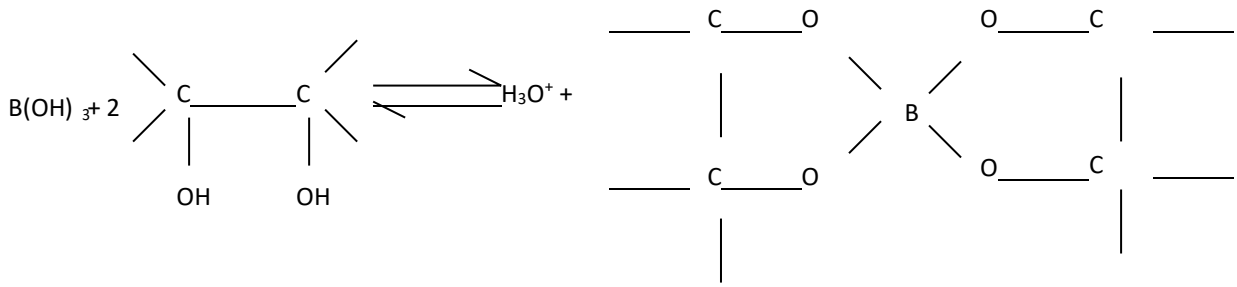


Fig.7: Hydrogen bonded structure of Boric acid

It is a very weak monobasic acid (pKa= 9.25). It is not a proton donor but an OH^- acceptor - thus it acts as a Lewis acid. It is frequently represented as $B(OH)_3$

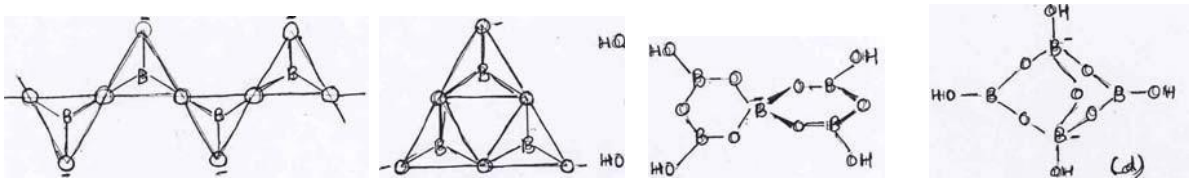
$$B(OH)_3 + 2H_2O \rightleftharpoons H_3O^+ + [B(OH)_4]^-$$

Its acid strength is enhanced in presence of cis-diols like glycerol, mannitol and sorbitol. The cis-diols form stable complexes with the metaborate ion, this shifts the equilibrium to the right making boric acid ionize to its full capacity.



+ $2H_2O$

Salts of boric acid are called the borates. Orthoborates contain discrete BO_3^{3-} units where the boron atom is sp^2 hybridized. In metaborates the simple units join together to give chain and ring structure. The most common borate is borax $Na_2B_4O_7$, $10H_2O$ (Sodium metaborate). The structures of some borates are shown in Fig. 8.



(a) (b) (c) (d)

Fig. 8: Structures of (a) Metaborate chain (b) Metaborate ring (c) Complex metaborate (d) Borax