
Chapter 10
The sp-block elements (III)

CHEM 462
Fri.-Mon. Nov 12,15
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Group 13 Elements

- ◆ Electropositive character of elements still very important
- ◆ Atomic configurations $ns^2 np^1$
- ◆ Bonding in the elements is much stronger and p orbital participation in bonding is important. sp^2 and sp^3 hybridization is common in compounds, except for In and especially Tl in oxidation state I (“inert pair” effect).

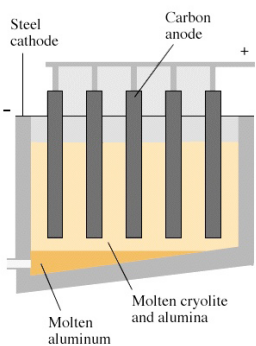
A highly variable group . . .

	melting pts. °C	boiling pts. °C	Density (g•cm ³)	Form, properties
B	2030	3700	2.47	Brown, semicond.
Al	660	2350	2.70	Silvery metal
Ga	30	2070	5.91	Silvery, soft metal
In	157	2050	7.29	Silvery, soft metal
Tl	304	1460	11.87	soft metal

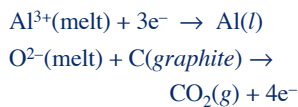
Sources/uses of Group 13 elements

- ◆ Boron from $\text{Na}_2\text{B}_4\text{O}_7 \cdot n\text{H}_2\text{O}$ (*borax*)
- ◆ Al from electrolysis.
- ◆ Ga is a byproduct of Al production; In is a byproduct of Pb/Zn production; Tl must be separated from other “flue-dust” elements (Ni; Zn, Cd, In; Ge, Pb; As; Se, Te).
- ◆ Ga and In have uses in specialized semicond. devices (LEDs, junction metals, dopants in Si & Ge, photoconductors) and low-T solders.

Al production



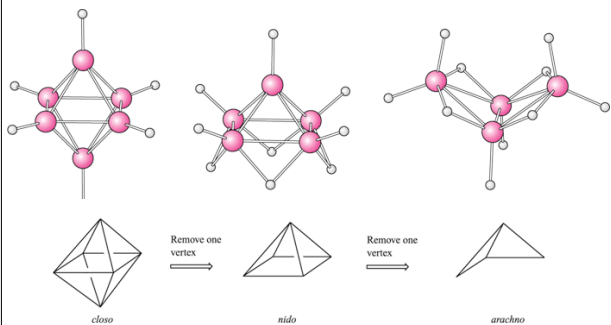
Al is made on a massive scale by electrolytic reduction of Al_2O_3 from bauxite in cryolite (Na_3AlF_6) at $\sim 950^\circ\text{C}$.



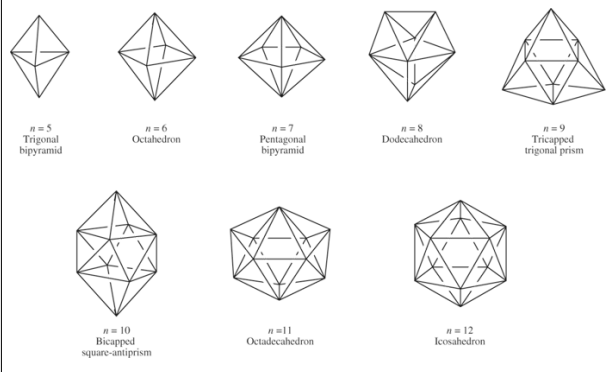
Some general group trends

- ◆ Boron has chemistry that more covalent, with some similarities to silicon in compounds with halogens and oxygen. The chemistry of boron-rich compounds is unique.
- ◆ Al, Ga, and In chemistry is dominated by oxidation state III. Bonds with “ligands” have polar covalent character.
- ◆ Tl has a prominent ox. state I chemistry.

closo: $n+1$ cage bonding e⁻ pairs
 nido: $n+2$ cage bonding e⁻ pairs
 arachno: $n+3$ cage bonding e⁻ pairs

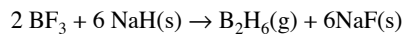


closo deltahedra



Diborane and other boron hydrides

- ◆ B_2H_6 (m.p. $-165^\circ C$; b.p. $-93^\circ C$) Industrial Prep:

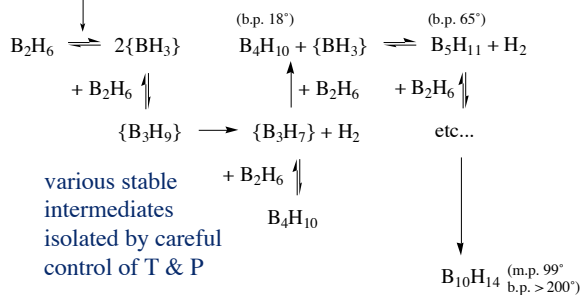


B_2H_6 & many other boranes are spontaneously flammable in air: $B_2H_6 + 3 O_2 \rightarrow B_2O_3(s) + 3 H_2O$ $\Delta H^\circ = -2165 \text{ kJ/mol}$

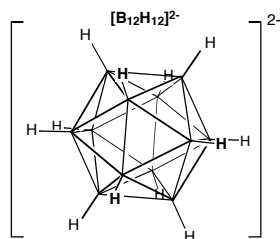
- ◆ Hydroboration w/ B_2H_6 extremely important in organic chemistry (H.C Brown, Nobel, 1979).

Borane Synthesis

$K_p \approx 10^{-5}$ at 25°C (dissociation energy = 155 kJ/mol)

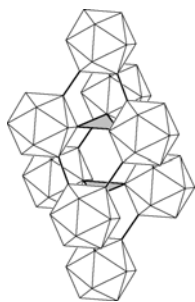


Unique Boron Compounds



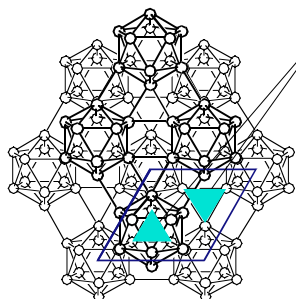
Boron-rich compounds are distinguished by the tendency to form icosahedral and other cages.

Boron-rich solids



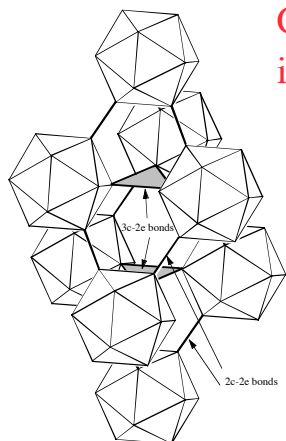
Boron takes on many forms in the solid-state. The icosahedron is the basic building-block of all the forms and of many other boron-rich solids. This shows a cut-away of clusters from 4 layers of the simplest boron form! The network structure makes boron very hard and resistant to chemical attack.

Counting Electrons in α -Rhom-B



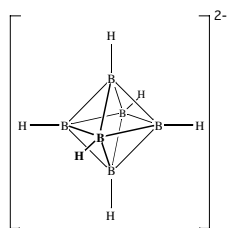
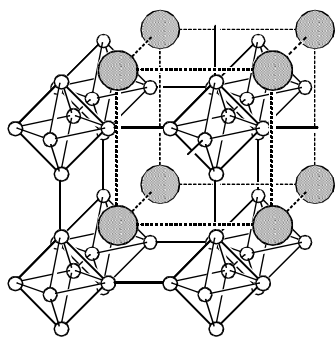
- ◆ There are two 3c-2e bonds ($\sim 2.0 \text{ \AA}$) per B_{12} unit within each layer.
- ◆ Layers stack over each other in an ...ABC... stacking mode.

Counting Electrons in α -Rhom-B



Each of six B-atoms in each B_{12} unit is involved in one 2c-2e bond ($\sim 1.76 \text{ \AA}$).
 Since $10 e^-$ are used in intercluster bonding, $26 e^- (= 2 \cdot 12 + 2)$ remain for cage bonding.

$[B_6H_6]^{2-}$ vs CaB_6



CaB_6 is a semiconductor — Wade's rules satisfied for each B_6 unit. LaB_6 is useful thermionic emitter (metallic).

Boron chemistry - general comments

- ◆ Boron chemistry more like silicon than Al, ...
eg.,
 - B(OH)₃ (*boric acid*) not at all basic. Al(OH)₃ amphoteric, but mostly basic.
 - B₂O₃ and SiO₂ more similar in their network structures - both “acidic” (react with “basic” metallic oxides to form silicates and borates).
 - BX₃ and SiX₄ (X = Cl, Br, I) all readily hydrolyzed. AlX₃ only partially hydrolyzed.
- ◆ Unique boron features: delocalized bonding in boron hydrides and remarkably diverse solid-state elemental and boron-rich chemistry.

Sources, uses of Boron

- ◆ B(OH)₃;
- ◆ Na₂B₄O₇•10H₂O (*borax*);
Na₂[B₄O₅(OH)₄]•2H₂O (*kernite*) — huge deposits in Boron, CA
- ◆ Detergents, soaps, enamels, herbicides, refractory borides. Boron is used to strengthen plastics, it is much stiffer and lighter than Al. Borates used in borosilicate glass (e.g., Pyrex)
— these are lower melting and much more workable than pure SiO₂.

Preparation of Boron

- ◆ Reduction by metals: e.g., by Mg (from electrolysis of MgCl₂)
 - contamination by refractory metal borides a problem
- ◆ Electrolytic reduction of borates or tetrafluoroborates
 - e.g, KBF₄ in KCl/KF (800°C) — cheap, but purity only ~ 95%
- ◆ Reduction of volatile boron compounds by H₂
 - 2 BBr₃ + 3H₂ → 6HBr + B > 99% (Ta filament ~ 1000°C)
- ◆ Thermal decomposition of boron hydrides & halides
 - 2 BI₃ → α-rhombohedral B + 3I₂ > 99% (hot Ta filament)

Boron Trihalides

- ◆ Halides of p-block elements are key intermediates - boron no exception
- ◆ Prep: direct reaction for X = Cl, Br, I;
- ◆ BF_3 :
$$\text{B}_2\text{O}_3 + 3\text{CaF}_2 + 6\text{H}_2\text{SO}_4 \rightarrow 2\text{BF}_3(\text{g}) + 3 \text{“H}_3\text{O}^+[\text{HSO}_4^-]\text{”} + 3\text{CaSO}_4(\text{s})$$
strong B-F bond, insoluble CaF_2 , acid-base rxn
- ◆ BX_3 all good Lewis acids:
acidity: $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$

Boron Trihalides

- ◆ Halides exchange is facile (why so easy?), e.g.:
 - $\text{BF}_3 + \text{BCl}_3 = \text{BF}_2\text{Cl} + \text{BCl}_2\text{F}$, typical $K \sim 0.5 - 2$
- ◆ BF_3 is most versatile reagent in presence of H_2O because others completely hydrolyzed:
$$\text{BX}_3 + \text{H}_2\text{O} \rightarrow \text{B}(\text{OH})_3 + \text{HX} \quad \text{hydrolysis (X = Cl, Br, I)}$$
$$\text{BX}_3 + \text{ROH} \rightarrow \text{B}(\text{OR})_3 + \text{HX} \quad \text{alcoholysis (X = Cl, Br, I)}$$
$$\text{BF}_3 + x\text{s H}_2\text{O} \rightarrow 3\text{H}_3\text{O}^+ + 3 \text{BF}_4^- + \text{B}(\text{OH})_3 \quad (\text{heat})$$
$$\text{BF}_4^- : \text{very stable anion}$$
- ◆ BF_3 especially useful in Friedel-Crafts-like acylations and alkylations.

Oxo compounds of Boron

- ◆ Boric acid,
$$\text{B}(\text{OH})_3 + \text{H}_2\text{O} \rightarrow \text{B}(\text{OH})_3(\text{H}_2\text{O}) = [\text{B}(\text{OH})_4]^- + \text{H}_3\text{O}^+$$
at neutral pH, get condensation (similar to Al chem):
$$3 \text{B}(\text{OH})_3 + \text{H}_2\text{O} = [(\text{B}_3\text{O}_3)(\text{OH})_4]^- + \text{H}_3\text{O}^+ \quad K = 1.4 \times 10^{-7}$$
$$\text{Na}[(\text{B}_3\text{O}_3)(\text{OH})_4] + 2\text{NaOH} (\text{heat}) \rightarrow \text{Na}_3[(\text{B}_3\text{O}_3)\text{O}_3] \quad \text{Pyrex precursor}$$
- ◆ Borate Esters
in acid: $\text{B}(\text{OH})_3 + 3\text{CH}_3\text{OH} \rightarrow \text{B}(\text{OCH}_3)_3 + 3 \text{H}_2\text{O}$
 $\text{B}(\text{OCH}_3)_3$ is a weaker Lewis acid than BF_3 (why?)

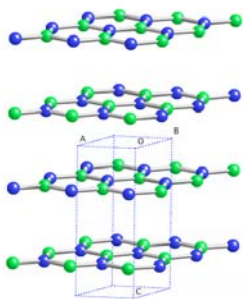
Boron-Nitrogen compounds

- ◆ Other compounds; amine-boranes:
 $(1/2) B_2H_6 + NEt_3 \rightarrow H_3B_3:NEt_3$ solid (adduct)
- ◆ B=N (alkene analogs) very reactive:
“ $H_2B=NH_2$ ” $\rightarrow B_3N_3H_{12}$ “cyclohexane” analog
- ◆ Borazine: 1926 (Stock): $(1/2) B_2H_6 + NH_3 \rightarrow B_3N_3H_6$
not benzene-like, e.g., $B_3N_3H_6 + 3 HCl \rightarrow (NH_2BHCl)_3$
- ◆ borazine derivatives prepared by alternate routes:
reflux C_6H_5Cl : $3NH_4Cl + 3BCl_3 \rightarrow (NHBCl)_3 + 9 HCl(g)$
 $(NHBCl)_3 + 3NaBH_4 \rightarrow (NHBH)_3 + (3/2)B_2H_6(g) + 3NaCl$
 $(NHBCl)_3 + 3RMgCl \rightarrow (NHBR)_3 + MgCl_2(s)$

Boron-Nitrogen compounds

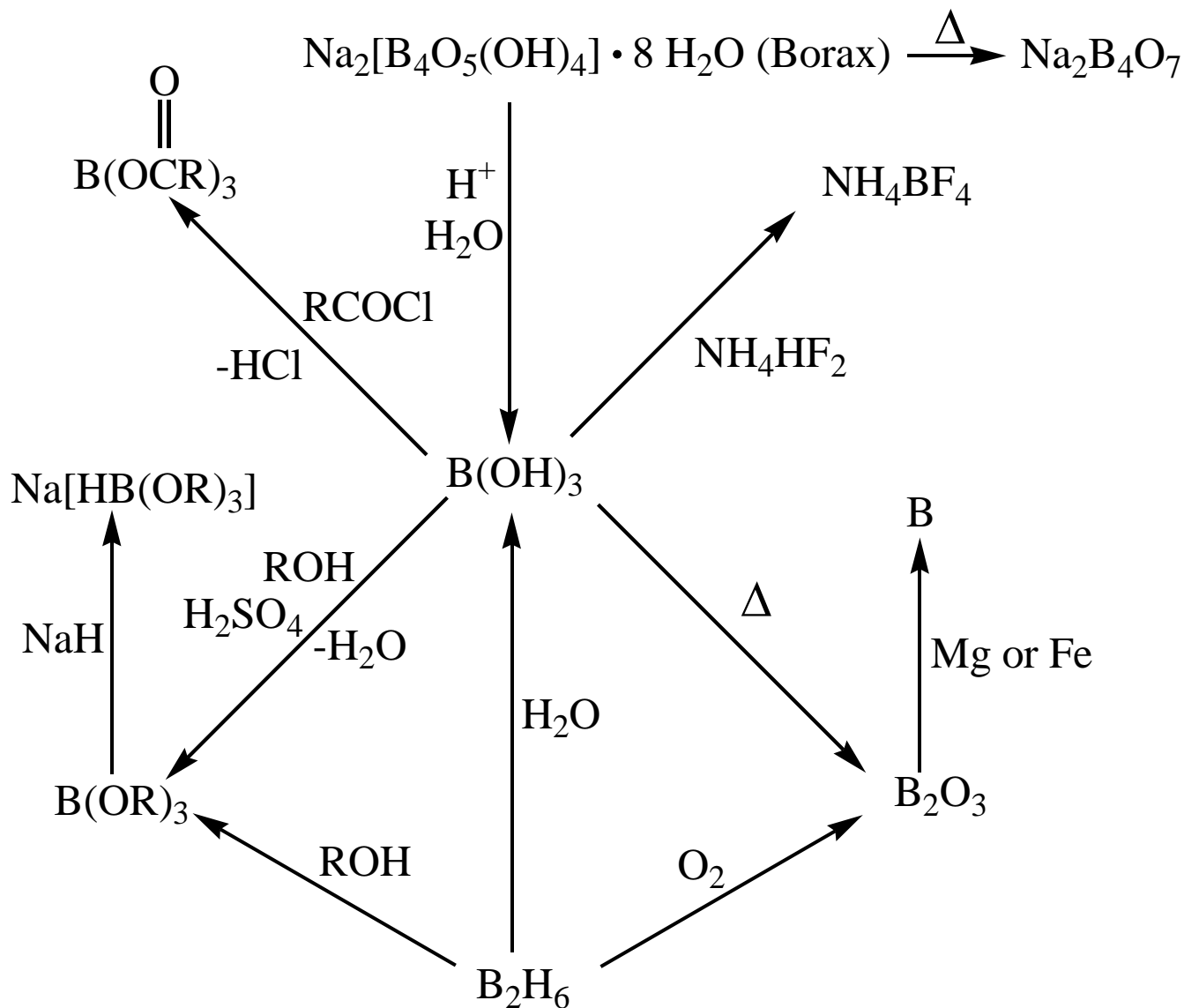
- ◆ Boron Nitride:
 $1200^\circ C: B_2O_3 + 2 NH_3(g) \rightarrow 2 BN(s) + 3 H_2O(g)$
 $1800^\circ C, \text{ high-P: } BN(s, \text{ hex}) \rightarrow BN(s, \text{ cubic})$

Hexagonal Boron Nitride



- ◆ Layers are graphitic, but stacking places N atoms in one layer above and below B atoms in adjacent layers (and vice versa).

Reaction Summary: Boric Acid



adapted from Figure 12-13a, C&W

Reaction Summary: BCl₃

