The sp-block elements (II)

CHEM 102
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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 . . .

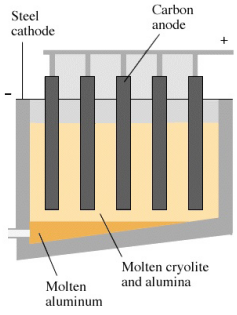
	melting pts. °C	boiling pts. °C	Density (g•cm^3)	Form, properties
B	2030	3700	2.47	Brown, semicond.
Al	660	2350	2.70	Silvery metal
Ga	30	2070	5.91	Silvery, soft metal
In	157	2050	7.29	Silvery, soft metal
Tl	304	1460	11.87	soft metal

Boiling point trend tells us more about bond strengths here!

Sources/uses of Group 13 elements

- Boron from $Na_2B_4O_7{\bullet}nH_2O$ (*borax*)
- Al from electrolysis.
- Ga is 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 ~950 °C.

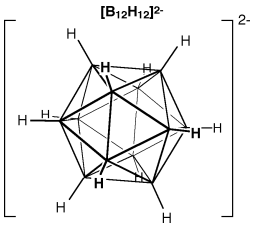
$Al^{3+}(melt) + 3e^- \rightarrow Al(l)$

$O^{2-}(melt) + C(graphite) \rightarrow CO_2(g) + 4e^-$

Some general group trends

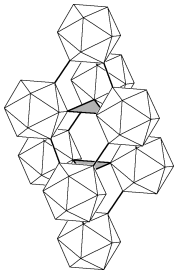
- Boron has chemistry that more covalent, with some similarities to silicon in compounds with halogens and oxygen. The chemistry of boron-rich compounds is unique.
- Al, Ga, and In chemistry is dominated by oxidation state III. Bonds with "ligands" have polar covalent character.
- Tl has a prominent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

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 makes boron very hard and resistant to chemical attack.

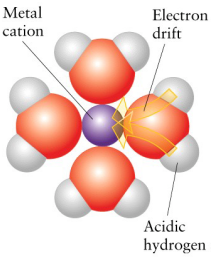
Some key compounds of B and Al

- B_2H_6, $NaBH_4$, BX_3 (X = halides)
- $B(OH)_3$ (*boric acid*).
- Boron is used to strenthen plastics, it is much stiffer and lighter than Al. Borates used in borosilicate glass - which are lower melting and much more workable than pure SiO_2.
- Al_2O_3 (alumina), AlX_3 (X = halides), $Al(OH)_3$ (an insoluble amphoteric hydroxide)

Acidic Behavior

- Boron and aluminum are important as Lewis acids, e.g, $AlCl_3$(*anhyd.*), BCl_3, BF_3, BH_3
- In aqueous solution, $B(OH)_3(aq) + H_2O \rightleftharpoons$
  $H_2O{:}B(OH)_3 \rightleftharpoons [B(OH)_4]^- + H_3O^+$
- BF_3 behaves similarly:
  $H_2O{:}BF_3 \rightleftharpoons [BF_3(OH)]^- + H_3O^+$
- Al^{III} and Ga^{III} in aqueous solution:
  $[Al(H_2O)_6]^{3+} \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H_3O^+$

Hydrolysis of Metal Complexes can give acidic solutions



pK_a's for $[M(H_2O)_6]^{n+}$	
$[Fe(H_2O)_6]^{3+}$	2.46
$[Ga(H_2O)_6]^{3+}$	2.60
$[Cr(H_2O)_6]^{3+}$	3.89
$[Al(H_2O)_6]^{3+}$	4.85
$[Fe(H_2O)_6]^{2+}$	5.89
$[Cu(H_2O)_6]^{2+}$	7.49
$[Ni(H_2O)_6]^{2+}$	9.03

Amphoteric Behavior of Al

- In neutral or moderately basic solutions, Al^{3+} precipitates as an hydroxide, $Al(OH)_3$. But in strongly basic solution, it dissolves again:
  $Al(OH)_3 + OH^- \rightleftharpoons [Al(OH)_4]^-(aq)$

This property is used to separate Al^{3+} from other metal ion impurities in treating raw bauxite before electrolysis. Then a cheap acid, CO_2, is used to precipitate purer $Al(OH)_3$:

$[Al(OH)_4]^-(aq) + CO_2(g) \rightleftharpoons Al(OH)_3(s) + HCO_3^-(aq)$