Chem 241

Lecture 32
Announcement

**Reminder ** Friday, April 23: EXAM 3!!!

Bring calculator
Bring Pencil
- Model Kit -
Recap

Coordination Compounds of Alkaline Earth Metals
Organometallics
Group 13
Boron
Compounds
Homework

Finish Reading Chapter 12
Exercise 1, 2, 5, 6, 7, 8, 10, 12, 15
Aluminum

• 1. Occurrence
  a. Most abundant element in Gp 13, it is the most abundant metal in the Earth’s crust.
  b. Found in clays and aluminosilicates, the commercial source of Al is bauxite, a hydrated aluminum oxide/hydroxide.
  c. Al is extracted by the **Bayer** process as Al(OH)$_3$. The ore is dissolved in hot aqueous NaOH, which dissolves Al$_2$O$_3$ and SiO$_2$, but leaves Fe$_2$O$_3$. The mix is cooled to precipitate Al(OH)$_3$. In the **Hall-Heroult** process, the hydroxide is dissolved in molten cryolite, Na$_3$AlF$_6$, and electrolyzed using a cell with a steel cathode and graphite anode.

\[
2 \text{Al}_2\text{O}_3 + 3\text{C} \rightarrow 4 \text{Al} + 3 \text{CO}_2
\]
Aluminum

• 1. Uses
  a. Most important element commercially in Gp 13
     It is light and corrosion resistant because of a tough oxide layer, and its uses include: cans, foils, aircraft alloys.
  b. Construction
  c. Heat sinks

2. Health Concerns
   a. Competes with Calcium
   b. Alzheimer's disease
Gallium

- Ga chemistry is similar to Al, but with tendencies toward the chemistry of the heavier metals in Gp13.
  - 1. Ga$_2$O$_3$ occurs as an impurity in bauxite, and is recovered in Al manufacture. Like Al, the element is prepared by electrolysis. The element has a low melting point (30 C) but has a normal bp (2070 C), and thus the widest liquid range of any known substance.
Indium

Soft malleable metal

Indium Tin Oxide – clear electrode → solar energy, LCD and touchscreens

Thallium

Thallium compounds are found in flue dusts from roasting sulfide ores (e.g., of Zn and Pb). Great abundance but not commercially extractable.

Poisonous “poisoner’s poison”

Photomultiplier tubes
Hydrides

- AlH$_3$ is a salt with H$^-$ in the lattice.
- Alkyl Al hydrides are molecular compounds that contain Al-H-Al 3c, 2e- bonds. They are used to react with alkenes as in hydroboration, adding Al-H across the double bond.
- LiAlH$_4$ is an important source of H$^-$ in synthesis
  Direct reaction of Li, Al and H$_2$ yields either LiAlH$_4$ or Li$_3$AlH$_6$. The former is more conveniently prepared from AlCl$_3$:
  \[
  4 \text{LiH} + \text{AlCl}_3 \rightarrow \text{LiAlH}_4 + 3 \text{LiCl}
  \]
- Unlike BH$_4^-$, AlH$_4^-$ reacts violently on contact with water (more hydridic).
- Useful in metathesis reactions, where H$^-$ migrates to more electroneg. element:
  \[
  \text{LiAlH}_4 + \text{SiCl}_4 \rightarrow \text{LiAlCl}_4 + \text{SiH}_4
  \]
Halides

-synthesis: Direct reaction with $X_2$ gives $\text{AlX}_3$, but will also react with $\text{HCl}$ or $\text{HBr}$:

$$2 \text{Al} + 6 \text{HCl} \rightarrow 2 \text{AlCl}_3 + 3\text{H}_2$$

- reactions: The fluorides are relatively unreactive and good Lewis acids, although $\text{AlF}_3$ will add $\text{F}^-$ to form $\text{AlF}_6^{3-}$, as in cryolite. The rest are trigonal planar molecules only in the gas phase, and form $\text{Al}_2X_6$ dimers in solution. In the solid, $X = \text{Br, I}$ are dimers, $X = \text{Cl}$- has a layer structure.

- Lewis acids

- Lower valent halides are unstable $\rightarrow$ disproportionation:

$$3 \text{AlX} \rightarrow 2 \text{Al} + \text{AlX}_3$$

-Frield-Craft reaction

- Tl(I) and Gallium(I)/(II) careful
Oxides

- $\text{Al}_2\text{O}_3$ ($\alpha$-alumina) is a very hard refractory material. The structure is hcp in oxide anions with Al(III) in 2/3 of the $O_h$ holes.

- $\text{Al}_2\text{O}_3$ ($\gamma$-alumina) is formed by dehydration of $\text{Al(OH)}_3$ at temperatures below 900 C. → solid phase in chromatography and as a heterogeneous catalyst.

- Gallium oxide, $\text{Ga}_2\text{O}_3$ → vapor deposition

- Indium oxide, $\text{In}_2\text{O}_3$

- Thallium oxide, $\text{Tl}_2\text{O}$ or $\text{Tl}_2\text{O}_3$ → superconductor/ semiconductor
Sulfides

Sulfides

- Only sulfide of Al, Al$_2$S$_3$, is prepared by direct reaction of the elements at elevated T. It is rapidly hydrolyzed in aqueous solution:

\[
2 \text{Al} + 3 \text{S} \rightarrow \text{Al}_2\text{S}_3 \\
\text{Al}_2\text{S}_3 + 6 \text{H}_2\text{O} \rightarrow 2 \text{Al(OH)}_3 + 3 \text{H}_2\text{S}
\]

Group 15

Wide variety of semiconductors with group 13 – isoelectronic with silicon.

Reactive must be kept inert
Organometallics

Boron, electron deficient, Lewis acids

\[ \text{B}_2\text{H}_6 + 6 \text{CH}_2=\text{CH}_2 \rightarrow 2\text{B(\text{CH}_2=\text{CH}_3)}_3 \]

\[ \text{BPh}_3 + \text{NaPh} \rightarrow \text{Na}^+ [\text{BPh}_4]^- \]

Aluminum

\[ 2 \text{Al} + 3 \text{Hg(\text{CH}_3)}_2 \rightarrow \text{Al}_2(\text{CH}_3)_6 + 3 \text{Hg} \]

\[ 2 \text{Al} + 3\text{H}_2 + 6 \text{CH}_2=\text{CH}_2 \rightarrow \text{Al}_2(\text{CH}_2\text{CH}_3)_6 @ \text{ht, hp} \]
Group 13

• b. Higher Boranes and Borohydrides

• Wade’s Rules
  - apply to deltahedra (polyhedra made up of triangular faces)
  - can be used to predict the general shape of molecular and anionic boranes from the formula.

- Step 1. Determine the number of skeletal electrons
  B-H groups contribute 2 skeletal electrons (there are 4 e-, but the 2 e- in the B-H bond are not skeletal electrons.) Additional H atoms contribute 1 e- each.
  (In B$_4$H$_{10}$ there are 4B-H + 6 additional H (8 + 6 = 14 skeletal electrons). Charges count as skeletal e-).

- Step 2. Assign the cluster type. species with the formula B$_n$H$_n^{2-}$ and n+1 pairs of skeletal electrons have a "closo" (cage) structure consisting of a closed deltahedron and no B-H-B 3c, 2e- bonds. (e.g., B$_5$H$_5^{2-}$, B$_6$H$_6^{2-}$ and B$_{12}$H$_{12}^{2-}$).
  Clusters with the B$_n$H$_{n+4}$ and n+2 pairs of e- have the nido (nest) structures. Look like closo structures without one vertex, but have B-H-B and B-B bonds. (e.g. B$_5$H$_9$, 10 + 4 = 14 (7 pairs, nido structure)
Group 13

Clusters with the formula, $B_nH_{n+6}$ and $n+3$ pairs of skeletal electrons have an **arachno** (spider) structure, corresponding to a closo missing two vertices, and must have B-H-B bonds (e.g., $B_5H_{11}$; 5 B-H + 6 = 16 skeletal electrons, 8 pairs).

- Can be used to predict reactivity:
  closo < nido < arachno

- Wade’s rules work because they describe the population of M.O.s
Synthesis

Pyrolysis of diborane to generate BH₃, and condensation, sometimes with quench.

\[ \text{B}_2\text{H}_6 \rightarrow 2 \text{BH}_3 \]
\[ \text{BH}_3 + \text{B}_2\text{H}_6 \rightarrow \text{B}_3\text{H}_7 + \text{H}_2 \]
\[ \text{BH}_3 + \text{B}_3\text{H}_7 \rightarrow \text{B}_4\text{H}_{10} \ldots \]

• Reactions

Reaction with a Lewis base can cleave BHₙ group, abstraction of one or more H⁺, and cluster enlargement.

Deprotonations usually occur at B-H-B groups, 3c, 2e-bonds, and result in B-B bond formation.

The Brønsted acidity of clusters increases approx. with size.

\[ \text{B}_4 10\text{₁₀} < \text{B}_5 10\text{₉} < \text{B}_10 10\text{₁₄} \]
c. Metallaboranes and Carboranes

- One class have M-H bonds (e.g., the intermediates in reductions and hydride formation with BH\(_4^-\)), but more stable clusters have M-B bonds, and take the position of a vertex in the cluster.

- Carboranes are derived by substituting BH- vertices with CH, with which it is isoelectronic and isolobal, but reduces the (-) charge by one for each CH. Thus, B\(_6\)H\(_6\)\(^{2-}\) and B\(_4\)C\(_2\)H\(_6\) are isoelectronic, and isostructural, and obey Wade’s rules.
Synthesis Carboranes

\[
\text{B}_{10}\text{H}_{14}\ +\ 2\ \text{SEt}_2 \rightarrow \text{B}_{10}\text{H}_{12}(\text{SEt}_2)_2\ +\ \text{H}_2...
\]

\[
\text{B}_{10}\text{H}_{12}(\text{SEt}_2)_2\ +\ \text{C}_2\text{H}_2 \rightarrow 1,2-\text{B}_{10}\text{C}_2\text{H}_{12}\ +\ 2\ \text{SEt}_2\ +\ \text{H}_2
\]

The C-H protons are mildly acidic, and so can be lithiated and used in synthesis like LiR reagents, where R is a carborane.

\[
\text{B}_{10}\text{C}_2\text{H}_{12}\ +\ 2\ \text{LiBu} \rightarrow 1,2-\text{B}_{10}\text{C}_2\text{H}_{10}\text{Li}_2\ +\ 2\ \text{C}_4\text{H}_{10}
\]