Chemistry of the Main Group Elements:
Boron through the Pnictogens

Sections 8.5-8.7 and 15.4.1

Friday, November 6, 2015
Group IIA (13): B, Al, Ga, In, and Tl

Diverse group of elements with three valence electrons

- $ns^2p^1$ electron configuration
- boron is a non-metal, all others in group are metals

Group IIA halide complexes

- all members of the group react directly with halogens
  \[
  B_{12} + 18Cl_2 \rightarrow 12BCl_3
  \]
  \[
  2Al^0 + 3Cl_2 \rightarrow 2AlCl_3
  \]
- the metals will also react with hydrohalic acids
  \[
  2Al^0 + 6HCl \rightarrow 2AlCl_3 + 3H_2
  \]
- Group IIA halides are Lewis acids, $BX_3$ is hard, others are soft
- reactivity
  \[
  AlCl_3 + 3MeMgCl \rightarrow AlMe_3 + 3MgCl_2
  \]
  \[
  BCl_3 + 4MeLi \rightarrow Li[BMe_4] + 3LiCl
  \]
  \[
  BCl_3 + 3H_2O \rightarrow B(OH)_3 + 3HCl
  \]
Boranes (Boron Hydride Clusters)

The electron deficient nature of boron favors cluster formation

**Skeletal Electron Counting**

- basic building block is BH unit that contains 4 electrons (3 from B and 1 from H)
- two electrons are used in the B–H bond, leaving two electrons (a pair) for the cluster framework
- each charge adds one electron, so does each extra H

<table>
<thead>
<tr>
<th>Formula</th>
<th>Skeletal e⁻ Pairs</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
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<tr>
<td>([B_nH_n]^{2-})</td>
<td>(n+1)</td>
<td>([B_5H_5]^{2-}) thru ([B_{12}H_{12}]^{2-})</td>
</tr>
<tr>
<td>nido (B_nH_{n+4})</td>
<td>(n+2)</td>
<td>(B_2H_6, B_5H_9, B_6H_{10})</td>
</tr>
<tr>
<td>arachno (B_nH_{n+6})</td>
<td>(n+3)</td>
<td>(B_{4}H_{10}, B_5H_{11})</td>
</tr>
<tr>
<td>hypho (B_nH_{n+8})</td>
<td>(n+4)</td>
<td>(B_8H_{16}, B_{10}H_{18}, B_{14}H_{22})</td>
</tr>
</tbody>
</table>

\[B_6H_6]^{2-} \Rightarrow 6 \text{ BH units}\]
\[6 \times 4 = 24 \text{ BH electrons}\]
\[-6 \text{ B–H} = 12 \text{ B–H bonding electrons}\]
\[+2e^- \text{ for charge} = 2 \text{ extra electrons}\]
\[14 \text{ skeletal electrons}\]

\[B_{12}H_{12}]^{2-}\]
\[4 \times 4 = 16 \text{ BH electrons}\]
\[-4 \text{ B–H} = 8 \text{ B–H bonding electrons}\]
\[+6 \text{ H} = 6 \text{ extra hydrogen electrons}\]
\[14 \text{ skeletal electrons}\]
Boron Hydride Clusters

Closo boron hydride clusters are regular polygon shapes

\[ [B_5H_5]^2− \] trigonal bipyramidal

\[ [B_6H_6]^2− \] octahedral

\[ [B_7H_7]^2− \] pentagonal bipyramidal

Nido and arachno boron hydride clusters are derived from the regular polyhedra with one or two vertices removed, respectively, and bridging hydrogen atoms added.

Also see section 15.4.1
Carbon

Carbon is a remarkable element for its versatility as a building block

- carbon forms double and triple bonds more readily than any other element
- the tetrahedral, trigonal, and linear geometries of carbon provides access to a variety of different structures and allows for lots of structural complexity

Carbon allotropes:

- **diamond** – 3D network of $sp^3$ carbon atoms connected by C–C single bonds
- **graphite** – stacks of 2D sheets of $sp^2$ carbon atoms in fused six-membered rings
- **fullerenes** – geodesic spheres containing $sp^2$ carbons, C$_{60}$, C$_{70}$, C$_{80}$, etc.
- **carbon nanotubes** – a graphene layer rolled up into a cylinder
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Carbon allotropes:

- diamond: 3D network of sp³ carbon atoms connected by C–C single bonds
- fullerenes: geodesic spheres containing sp² carbons, C₆₀, C₇₀, C₈₀, etc.
- carbon nanotubes: a graphene layer rolled up into a cylinder
- graphite: stacks of 2D sheets of sp² carbon atoms in fused six-membered rings
Si, Ge, Sn, & Pb

Heavier congeners of carbon have +2 and +4 oxidation states accessible

\[ Si(s) + 2Cl_2(g) \rightarrow Si^{IV}Cl_4(l) \]

\[ Sn(s) + Cl_2(g) \rightarrow Sn^{II}Cl_2(s) + Cl_2(g) \rightarrow Sn^{IV}Cl_4(l) \]

\[ \text{mp 246 °C} \quad \text{mp –33 °C} \]

\[ Pb(s) + Cl_2(g) \rightarrow Pb^{II}Cl_2(s) + Cl_2(g) \rightarrow \text{no reaction} \]

**Inert pair effect** – heavy p-block metals often ‘hold on’ to their \( ns^2 \) valence electrons better than lighter p-block elements

![PbO Lone Pairs](image)
Notice that germanium has 12 electrons around it. The octet rule can be violated for heavy p-block elements.
Multiple Bonding

While multiple bonding is common for carbon, it is unusual for the heavier elements and often the species are only metastable.

Bulky substituents can prevent polymer formation and allow isolation of molecular compounds.

Mes = Mesitylene (1,3,5-trimethylbenzene)

Si atoms are slightly pyramidalized (i.e., not planar)
Multiple Bonding

There is structural evidence for multiple bonding with heteroatoms

- trisilylamines are planar

- silylethers have large Si–O–Si angles

- silanols form strong hydrogen bonds and are also stronger acids than the analogous alcohols

We can explain this with \( \pi \pi \)–d\( \pi \) bonding

- important to note that the strength of \( \pi \pi \)–d\( \pi \) bonding decreases as you go down the group because of worse orbital overlap
Nitrogen

Virtually all nitrogen compounds are derived from the Haber-Bosch process.
Nitrogen Oxides: NV

Nitrate (NO₃⁻) is an important industrial chemical prepared by a two-step process:

\[ 4NH_3(g) + 7O_2(g) \rightarrow 6H_2O(l) + 4NO_2(aq) \quad \Delta G^\circ = -97 \frac{kcal}{mol} \]

\[ 3NO_2(aq) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g) \quad \Delta G^\circ = -1.2 \frac{kcal}{mol} \]

Compare this to the direct oxidation of N₂ by O₂:

\[ N_2(g) + 2O_2(g) \rightarrow 2NO_2(g) \quad \Delta G^\circ = +12 \frac{kcal}{mol} \]

By first reducing the N₂ with hydrogen, driving force is gained for the oxidation reaction in the formation of water as a byproduct.
Nitrogen Oxides: $N^\text{II}$ and $N^\text{IV}$

Nitrogen dioxide exists as an equilibrium mixture

\[
\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4 \quad K_{eq} = 0.115
\]

- paramagnetic
- brown
- poisonous

NO$_2$ has further reactivity in water

\[
2\cdot\text{NO}_2 + 2\text{OH}^- \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + \text{H}_2\text{O}
\]

\[
\text{NO} (g) + \text{H}_2\text{O} \rightarrow \text{NO}^+ + \text{H}_2\text{O}
\]
Nitrogen Oxides: NO

“Molecule of the Year” in 1992

Nobel Prize in Medicine in 1998 for many biological roles

- neurotransmission
- neuron-to-neuron signaling
- vasodilator (heart disease)
- relaxes smooth muscle tissue (endothelium-derived relaxing factor)
Low-Valent Nitrogen Compounds

\[ \text{N}_2 + 4 \text{H}^+ + 4 \text{e}^- \]

- **Nitrous Oxide**
  - Formal charge: Electrons in bonds are evenly split between atoms (covalent perspective)
  - Oxidation state: Electrons in bonds get assigned to the more electronegative atom (ionic perspective)

- **Azide**
- **Diazene**
- **Hydrazine**

Formal charge – electrons in bonds are evenly split between atoms (covalent perspective)

Oxidation state – electrons in bonds get assigned to the more electronegative atom (ionic perspective)
P, As, Sb, & Bi

Moving down the group, the octet can again be expanded for P, As, and Sb...

\[ P_4(s) + 6Cl_2(g) \rightarrow 4PCl_3(l) \xrightarrow{4Cl_2} 4PCl_5(l) \xrightarrow{4Cl^-} 4PCl_6^- \]

...but the inert pair effect keeps bismuth from going past BiX₃.

The halides are useful starting materials for further chemistry:

- Phosphite
- Phosphineamine
- Phosphine
- Phosphorimide
- Imine