Chemistry 1000 Lecture 24: Group 14 and Boron

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Group 14

- In this group again, we see a full range of nonmetallic to metallic behavior:

C	is a nonmetal.
Si and Ge	are metalloids.
Sn and Pb	are metals.

- Carbon is the central element in most biomolecules.

  Also widely distributed as carbonate minerals (many of biological origin), coal, graphite and diamond.

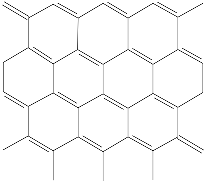
  Also present in atmosphere as CO_2 (seasonally averaged current value of 405 ppm, rising by about 2 ppm/year)
- Si is the second most abundant element in the Earth's crust (after O), mostly present in nature as silicon oxide (sand and related materials), quartz and silicate minerals.
- Sn and Pb are fairly abundant metals.
  Principal ores: SnO_2, PbS, $PbSO_4$ and $PbCO_3$

Allotropes of carbon

- Most stable allotrope: graphite
  - Moderately good electrical conductor, but its conductivity is anisotropic (different in different directions) in single crystals
- Diamond
  - Insulator
  - Hardest naturally occurring substance available in reasonable quantities
    - Lonsdaleite, another allotrope of carbon made during meteorite impacts, and wurtzite boron nitride, synthesized by detonation, may be harder.
  - Metastable at normal pressures
- Fullerenes, carbon nanotubes

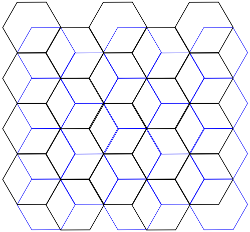
Graphite

- Graphite structure: stacked sheets



+ resonance structures

- Stacking:

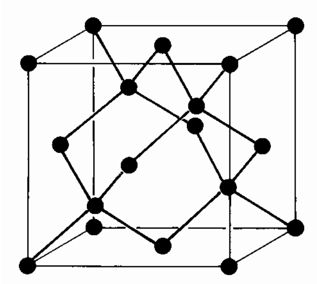


Graphene

- Graphene is a single carbon sheet with the graphite structure.
- Originally made by Geim and Novoselov (Nobel Prize 2010) using very high-tech scientific equipment: adhesive tape!
- Graphene has very strange properties:
  - Although it's only one atom thick, a sheet of graphene absorbs 2.3% of white light impinging on it.
  - Less resistive than silver (best metallic conductor at room temperature)
  - About 200 times stronger than an equivalent weight of steel

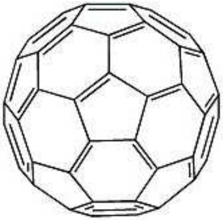
Diamond

- Network solid made of four-coordinate tetrahedral carbons



Fullerenes

- Small carbon "balls" discovered in 1985 by Curl, Kroto and Smalley (Nobel Prize 1996)
- Many different fullerenes, of which the most common is C_{60}



- Made of hexagons and pentagons
- Lots of molecules in this family (C_{70}, C_{76}, C_{78}, ...), including some smaller than C_{60}
- Can put stuff inside the cavity to alter electrical or other material properties

Carbon nanotubes

- Essentially, a rolled-up graphite sheet
  http://upload.wikimedia.org/wikipedia/commons/5/53/Types_of_Carbon_Nanotubes.png
- Incredibly strong material
  - Tensile strength over 50 times larger than that of high-carbon steel
- Can put things inside the nanotubes, including other nanotubes
  http://www.nanotech-now.com/images/multiwall-large.jpg

Oxides of carbon

- There are two oxides of carbon, CO_2 and CO.
- CO_2 is obtained when carbon compounds are burned in an excess of oxygen.
- CO is an incomplete combustion product.
- As seen previously, CO_2 is a Lewis acid.
- CO on the other hand is a Lewis base.

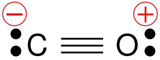
Ocean acidification

- The Lewis acid CO_2 reacts with water:

$$CO_2 + H_2O_{(l)} \rightleftharpoons HCO^-_{3(aq)} + H^+_{(aq)}$$

- As the atmospheric CO_2 concentration increases, Le Chatelier's principle tells us this equilibrium will shift to the right.
- This results in ocean acidification.
- The effects of ocean acidification vary greatly depending on local geography and geology (currents, rock composition, etc.).
- A rough estimate is that acidity of the oceans (i.e. $[H^+]$) is increasing at a rate of about 0.4% per year.
- Dumping large amounts of CO_2 in the atmosphere is a planetary-scaled experiment in altering the chemistry of the biosphere.

CO as a Lewis base

- Lewis diagram: 
- The negative (carbon) end is more strongly Lewis acidic.
- Carboxyhaemoglobin is formed in a Lewis acid-base reaction between CO and the Lewis acidic iron(II) ion in haemoglobin.

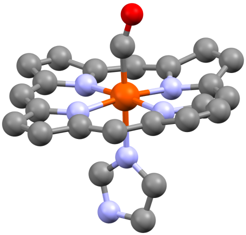
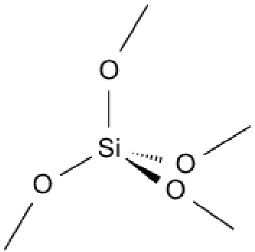


Image source: Wikimedia commons: http://en.wikipedia.org/wiki/File:Carboxyhemoglobin_from_1AJ9.png

Silicon dioxide

- Unlike CO_2, SiO_2 (silicon dioxide, a.k.a. silica) is a network solid.
- There are many different arrangements (including amorphous forms). In each case, the basic building block is an Si coordinated to four oxygen atoms in a tetrahedral shape.



Silicon dioxide: α-quartz

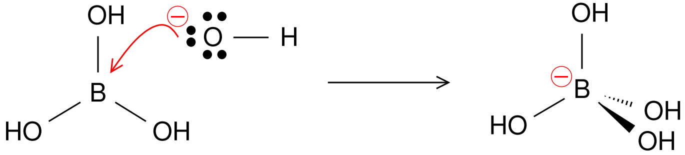
https://homepage.univie.ac.at/michael.leitner/lattice/struk.picts/sio2a.s.png

Boron

- Relatively rare element
- Mostly found in nature as borate minerals (salts of oxoanions of boron)
- Very hard (between Al_2O_3 and diamond)
- Semiconductor
- Similar in chemical properties to Si (diagonal relationship):
  - Under normal conditions, does not react with oxygen, water, acids or bases
- Applications of boron and its compounds:
  - borosilicate glass (e.g. Pyrex)
  - composite materials
  - detergents and bleaches (borax: a mixture of $Na_2B_4O_7$ and related compounds)
  - transistors and microprocessors

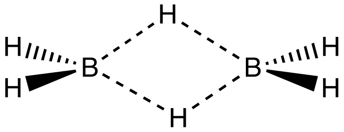
Boron compounds

- Many boron compounds are electron deficient Lewis acids, e.g. BF_3.
- Boric acid, $B(OH)_3$, is a Lewis acid (not a Brønsted oxoacid, and definitely not a Brønsted base):

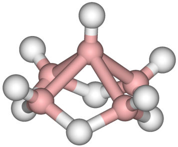


Boranes

- Boranes are boron-hydrogen compounds.
- Simplest borane: diborane, B_2H_6
  (BH_3 only exists in the gas phase at higher temperatures)
- Try to draw a Lewis diagram for diborane.
- Not enough electrons for conventional two-electron bonds
- Three centre-two electron B-H-B bridging bonds



- Lots of other boranes, e.g.
  - Pentaborane, B_5H_9



  - Decaborane, $B_{10}H_{14}$