Chemistry 1000 Lecture 23: Group 15

Marc R. Roussel

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Group 15

- Again, we see a full range of nonmetallic and metallic behavior:

  N and P are nonmetals.
  - Monatomic ions nitride (N^{3-}) and phosphide (P^{3-})

  As and Sb are metalloids.

  Bi is a metal.

- N_2 is 78% of the atmosphere.
- N is also found in nitrate minerals.
- P is mostly found in phosphate minerals.
- ^{209}Bi is an α emitter but has such a long half-life (1.9×10^{19} y) that it can be treated as if it were stable and has many applications since it has unusually low toxicity for a heavy metal.

Chemistry of nitrogen

- Typical simple nitrogen compounds have a lone pair and so can act as Lewis bases.
- N can form single, double and triple bonds.
- N_2 is generally unreactive.
- Ionic nitrides form with lithium, group 2 metals, and Al.

$$3\text{Li}_{(s)} + \frac{1}{2}\text{N}_{2(g)} \rightarrow \text{Li}_3\text{N}_{(s)}$$

- The N^{3-} ion is a powerful base:

$$\text{Li}_3\text{N}_{(s)} + 3\text{H}_2\text{O}_{(l)} \rightarrow 3\text{Li}^+_{(aq)} + 3\text{OH}^-_{(aq)} + \text{NH}_{3(aq)}$$

Group 15 halides

- All the elements in this group form a variety of halides, most of which will not be mentioned here.
- From nitrogen, we can make NX_3 halides.
- The other elements in this group form both MX_3 and MX_5 halides (e.g. PF_3 and PF_5).

Haber-Bosch process

- Original idea due to Haber (Nobel Prize in Chemistry, 1918), with practical refinements by Bosch (Nobel Prize in Chemistry, 1931)
- Ammonia is an important industrial chemical:
  - Fertilizers
    $\sim$ 50% of the nitrogen in the protein you eat comes from the Haber-Bosch process.
  - Household and industrial cleaning solutions
  - Synthesis of other nitrogen compounds

Example of the synthesis of a compound from ammonia

The Ostwald process for producing nitric acid

$$NH_{3(g)} + \frac{5}{4}O_{2(g)} \xrightarrow{\text{Pt,}850^{\circ}\text{C}} NO_{(g)} + \frac{3}{2}H_2O_{(g)}$$

$$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$$

$$3NO_{2(g)} + H_2O_{(l)} \rightarrow 2HNO_{3(aq)} + NO_{(g)}$$

Neutralizing the nitric acid with sodium hydroxide gives sodium nitrate.

Haber-Bosch process (continued)

- By themselves, nitrogen and hydrogen will not react together.
- The reaction does occur at a reasonable rate at high temperatures (above 400°C), high pressures (hundreds of atmospheres) and in the presence of a catalyst (Fe on a support of SiO_2 and Al_2O_3).

$$N_{2(g)} + 3H_{2(g)} \xrightarrow{\text{catalyst}} 2NH_{3(g)}$$

- The reaction is exothermic, so the high temperature decreases the yield, but is necessary to obtain a reasonable rate of formation.
- High pressure increases the yield.
- The result is a mixture of N_2, H_2 and NH_3 in the gas phase.

Haber-Bosch process (continued)

- To separate them, there are two options:
  1. Liquify ammonia by reducing the temperature.
     (Ammonia boiling point: $-33\,^{\circ}\mathrm{C}$)
  2. Bubble the gas mixture through water. Ammonia is highly soluble in water while the other two gases aren't, so we get an aqueous ammonia solution.

- After removing ammonia, the N_2 and H_2 gases are recycled into the reactor to avoid waste.

The Haber-Bosch process in history

- Until 1913, almost all the nitrate used around the world was mined in Chile and Peru.
- In the early twentieth century, it was estimated that nitrate from these mines, the only economically significant deposits known at the time, would run out by 1925.
- Due to the importance of nitrate as a fertilizer, there were concerns that widespread famine would result when the South American deposits ran out.
- These concerns led to a strong focus of the research community on developing methods for fixing nitrogen in the late 19th and early 20th centuries.

The Haber-Bosch process in history (continued)

- The South American nitrate mines were almost all owned by British companies.
- The German company BASF started producing nitrate in 1913 by the combination of the Haber-Bosch and Ostwald processes.
- Nitrate is an essential component of gunpowder, so the availability of synthetic nitrate allowed Germany to prolong the First World War far longer than would have been the case without this material.

The Haber-Bosch process in history (continued)

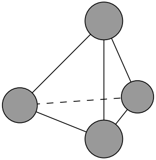
- After the war, the Haber-Bosch process spread quickly.
  Ammonia is cheaper to make than to mine, and of course the mines were likely to run out soon.
- This put Chilean and Peruvian mines out of business almost overnight, which precipitated an economic crisis in those economies.
- On the other hand, the availability of synthetic nitrate prevented the predicted widespread starvation, and in fact was an important factor in the "green revolution".

Phosphorus

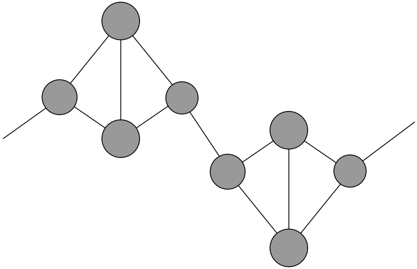
- The main phosphorus-containing mineral is calcium phosphate.
- White phosphorus (P_4) is made by high-temperature reaction of calcium phosphate with sand and coke (a carbon-based material made by heating coal in the absence of air) at high temperature:

$$2Ca_3(PO_4)_{2(s)} + 6SiO_{2(s)} + 10C_{(s)} \rightarrow P_{4(g)} + 6CaSiO_{3(s)} + 10CO_{(g)}$$

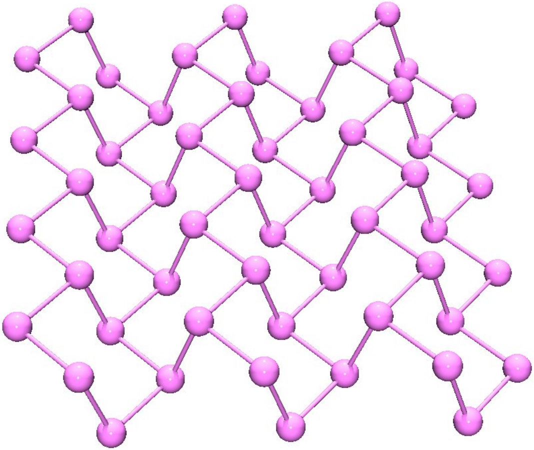
- P_4 is made of tetrahedral molecules of phosphorus:



- Phosphorus has many allotropes.
- Heating white phosphorus under an inert atmosphere produces red phosphorus.
- Red phosphorus is a network solid, i.e. the solid is held together by an extended network of covalent bonds (no discrete molecules).
- Red phosphorus is amorphous, i.e. there is no long-range order as in a crystal lattice.
- Structure consists of P_4 tetrahedra with one bond cut, linked together in random orientations:

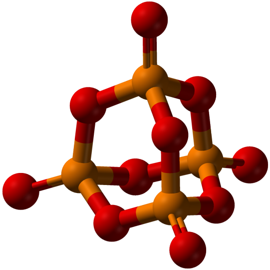


- Heating white phosphorus at high pressure produces black phosphorus.
- Black phosphorus is also a network solid, generally amorphous, best thought of as being made of puckered rings of phosphorus atoms:



Phosphorus(V) oxide

- Complete combustion of phosphorus in air yields phosphorus(V) oxide, P_4O_{10}:

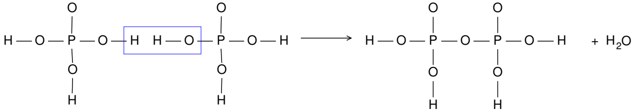


- Reaction of P_4O_{10} with water gives phosphoric acid:

$$P_4O_{10(s)} + 6H_2O_{(l)} \rightarrow 4H_3PO_{4(aq)}$$

Polyphosphoric acids and polyphosphates

- Condensation of phosphoric acid:



- Can be repeated to yield tri- and poly-phosphoric acids
- These can be deprotonated to give polyphosphates.
- Similar chemistry is involved in the biosynthesis of ATP, adenosine triphosphate: