Chemistry 1000 Lecture 14: The group 13 metals

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The group 13 metals

- All the elements in group 13 except boron are metals.
- Common ions: Al^{3+}, Ga^{3+}, In^{+}, Tl^{+}, also sometimes In^{3+} and Tl^{3+}
- Under typical reactions, these metals don't react with water.
- At room temperature, the oxide formed is M_2O_3.
- $Al(OH)_3$, $Ga(OH)_3$ and $In(OH)_3$ are all insoluble in water, but TlOH is very soluble.

Aluminium is a good reducing agent ($E^\circ_{Al^{3+}/Al} = -1.662$).

Thallium

- Thallium has many compounds of its +1 ion.
- Tl^+ and K^+ are very similar in size: 164 and 152 pm, respectively. In the body, Tl^+ can go wherever K^+ can go, which is pretty much everywhere.
- Most thallium compounds are toxic.
  Tl_2SO_4 was once used as a rat and ant poison.
- Thallium(I) sulfate is tasteless, so it was once a popular poison, nicknamed "inheritance powder".
- Unlike K^+, Tl^+ reacts with sulfur ligands, disrupting proteins containing cysteine in particular.

Passivation of aluminium

- Like Be, Al is passivated by an oxide layer which forms extremely rapidly when the metal is exposed to air.

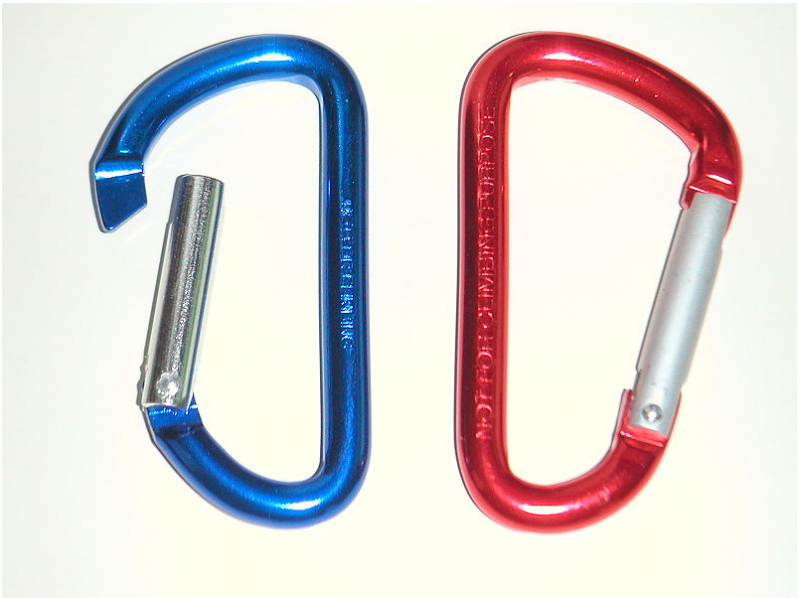
- Aluminium oxide
  - is hard (Mohs hardness 9, just below diamond)
  - has a high melting point (2072 °C)
  - is non-porous

Anodization of aluminium

- Deliberate, electrolytic thickening of the oxide layer:

$$2Al_{(s)} + 3H_2O_{(l)} \rightarrow Al_2O_{3(s)} + 6H^+_{(aq)} + 6e^-$$

- Has the following effects:
  - Makes Al more chemically resistant
  - Makes Al harder
  - May be used to pigment the oxide layer with appropriate additives



Acid-base properties of Al_2O_3

- Al_2O_3 is amphoteric.

Reaction with acid: $Al_2O_{3(s)} + 6H^+_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3H_2O_{(l)}$

Reaction with base: $Al_2O_{3(s)} + 2OH^-(aq) + 3H_2O_{(l)} \rightarrow 2[Al(OH)_4]^-_{(aq)}$

Reactions of Al with acids

- HNO_3 is an oxidizing acid because it typically attacks metals through the reduction of NO_3^-:

$$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$$

- For Al, this reaction, just tends to make the oxide layer thicker, i.e. makes the metal more passive:

$$2Al_{(s)} + 2NO_3^- + 2H^+ \rightarrow Al_2O_{3(s)} + 2NO_{(g)} + H_2O_{(l)}$$

- Al reacts with non-oxidizing acids (e.g. HCl) in the typical way for a metal:

$$Al_{(s)} + 3H^+_{(aq)} \rightarrow Al^{3+}_{(aq)} + \frac{3}{2}H_{2(g)}$$

Why does this work despite the passivation layer?

Reaction of Al with base

- Aluminium metal can be oxidized in aqueous base:

$$\mathrm{Al_{(s)}} + \mathrm{OH^-_{(aq)}} + 3\mathrm{H_2O_{(l)}} \rightarrow \mathrm{[Al(OH)_4]^-_{(aq)}} + \frac{3}{2}\mathrm{H_{2(g)}}$$

- Aluminium can react with acid or base, so it is amphoteric.

Acid-base properties of $Al(OH)_3$

- $Al(OH)_3$ is amphoteric.
- Reaction with acid (typical for metal hydroxides):

$$Al(OH)_{3(s)} + 3H_3O^+_{(aq)} \rightarrow [Al(H_2O)_6]^{3+}_{(aq)}$$

- Reaction with base (unusual for a metal hydroxide):

$$Al(OH)_{3(s)} + OH^-(aq) \rightarrow [Al(OH)_4]^-_{(aq)}$$

Production of aluminium

- Aluminium ore (bauxite) contains Al_2O_3, $AlO(OH)$ and Fe_2O_3 (among other things).
- Al_2O_3 and $AlO(OH)$ dissolve in base, but Fe_2O_3 doesn't:

$$Al_2O_{3(s)} + 2OH^-(aq) + 3H_2O_{(l)} \rightarrow 2[Al(OH)_4]^-_{(aq)}$$

$$AlO(OH)_{(s)} + OH^-(aq) + H_2O_{(l)} \rightarrow [Al(OH)_4]^-_{(aq)}$$

- Filter off solid Fe_2O_3, then precipitate $Al(OH)_3$:

$$[Al(OH)_4]^-_{(aq)} + H_3O^+_{(aq)} \rightarrow Al(OH)_{3(s)} + 2H_2O_{(l)}$$

(There are other ways to precipitate out the hydroxide.)

- Recover aluminium oxide by heating:

$$2Al(OH)_{3(s)} + \text{heat} \rightarrow Al_2O_{3(s)} + 3H_2O_{(g)}$$

Production of aluminium (continued)

- Al_2O_3 has a very high melting point (2072 °C).
- A 15:85 mixture of Al_2O_3 and cryolite (Na_3AlF_6) has a melting point of about 1000 °C.
- This molten mixture is electrolyzed using a graphite anode:

$$\text{Anode: } C_{(s)} + 2O^{2-}_{(l)} \rightarrow CO_{2(g)} + 4e^-$$

$$\text{Cathode: } Al^{3+}_{(l)} + 3e^- \rightarrow Al_{(l)}$$

$$\text{Overall: } 3C_{(s)} + 6O^{2-}_{(l)} + 4Al^{3+}_{(l)} \rightarrow 4Al_{(l)} + 3CO_{2(g)}$$

- Liquid aluminium is denser than the ionic liquid from which it is electrolyzed, so it is collected from the bottom of the electrolysis vat.