Chemistry 1000 Lecture 22: The chalcogens (group 16)

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The chalcogens

- Group 16 (O, S, Se, Te, Po)
- Transition from nonmetallic to metallic behavior from top to bottom of group

O and S	are nonmetals (electrical insulators)
Se and Te	are metalloids (semiconductors)
Po	is a metal

- O, S and Se can form -2 anions.
- O and S are abundant in nature both as elements (O_2, S) and in compounds (CO_2, H_2O, H_2S, metal oxides, metal sulfides).
- Se and Te are rare elements
- Po is a radioactive element whose longest lived isotope has a half-life of just 3 years

Allotropes of oxygen and sulfur

Allotropes: two or more different forms of an element

Allotropes of oxygen: O_2, O_3 (ozone)

- Ozone is made in electrical discharges, and by photochemical reactions

Allotropes of sulfur: rings: S_6, S_7, S_8, S_9, S_{10}, S_{11}, S_{12}, S_{18}, S_{20}; long chains; S_2

- S_8 is the most common solid form (often shown as S in thermodynamic tables or reactions).
- Long chains (i.e. polymers) are also common.
- S_2 is only observed in the gas phase at high temperatures, unlike O_2.

Reactions with metals

- Oxygen reacts readily with almost all metals.
- Metal oxides are consequently very common metal ores.
  Examples:

$$2\mathrm{Fe}_{(s)} + \frac{3}{2}\mathrm{O}_{2(g)} \rightarrow \mathrm{Fe}_2\mathrm{O}_{3(s)} \quad \text{(magnetite or hematite)}$$

$$4\mathrm{Cu}_{(s)} + \mathrm{O}_{2(g)} \rightarrow 2\mathrm{Cu}_2\mathrm{O}_{(s)} \quad \text{(cuprite)}$$

- Similar chemistry is seen with sulfur, resulting in sulfide ores:

$$2\mathrm{Cu}_{(s)} + \mathrm{S}_{(s)} \rightarrow \mathrm{Cu}_2\mathrm{S}_{(s)} \quad \text{(chalcocite)}$$

$$\mathrm{Cu}_{(s)} + \mathrm{S}_{(s)} \rightarrow \mathrm{CuS}_{(s)} \quad \text{(covellite)}$$

$$\mathrm{Pb}_{(s)} + \mathrm{S}_{(s)} \rightarrow \mathrm{PbS}_{(s)} \quad \text{(galena)}$$

Oxygen as an oxidizing agent

- Oxygen is a strong oxidizing agent, although it typically acts slowly.

$$O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)} \quad E^\circ = 1.229\,\text{V}$$
$$O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)} \quad E^\circ = 0.40\,\text{V}$$

  Under what conditions does oxidation by O_2 become fast?
- Liquid oxygen (boiling point 90 K) is much more active as an oxidizing agent than gaseous O_2.
  Why?

Ozone

- Production in the ozone layer (25–35 km above surface):

$$O_2 + h\nu \to O + O$$

$$O_2 + O + M \to O_3 + M$$

(M is a third body, i.e. molecule or particle, that carries away the bond energy from this reaction.)

- Production at ground level due to NO_2 (from internal combustion engines):

$$NO_2 + h\nu \to NO + O$$

$$O_2 + O + M \to O_3 + M$$

  - Formation of NO_2 assisted by volatile organic compounds (often uncombusted fuels)

- Ozone is a powerful oxidizing agent:

$$O_{3(g)} + 2H^+_{(aq)} + 2e^- \rightarrow O_{2(g)} + H_2O_{(l)} \qquad \mathcal{E}^\circ = 2.075\,\text{V}$$

- Ground-level ozone is the main component of photochemical smog.

- Used to purify water (very reactive, very lethal to bacteria)
  - Can react with bromide ions to produce bromate (BrO_3^-), a suspected carcinogen

The ozone layer

- Ozone absorbs UV radiation below 320 nm:

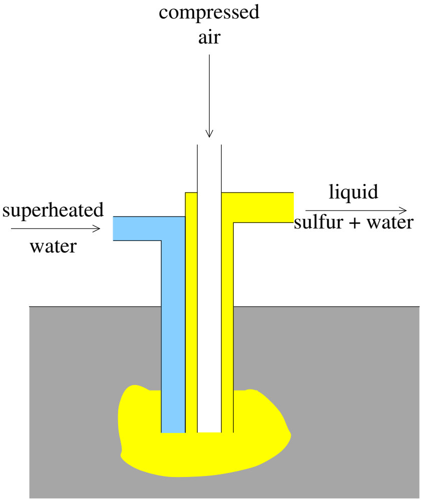
$$O_3 + h\nu \rightarrow O_2 + O$$

$$O_3 + O \rightarrow 2O_2$$

- Balance between photochemical production and destruction
- Highly reactive $\therefore$ balance vulnerable to presence of other compounds in atmosphere

- Chlorofluorocarbons (CFCs) are compounds of carbon, chlorine and fluorine.
    - Very stable $\therefore$ long-lived in atmosphere
    - Can form radicals, releasing Cl.
      Example:
      $$CCl_2F_2 + h\nu \rightarrow CClF_2 + Cl$$
    - Cl degrades ozone:
      $$\begin{array}{ll} & Cl + O_3 \rightarrow ClO + O_2 \\ & O_3 + h\nu \rightarrow O_2 + O \\ & ClO + O \rightarrow Cl + O_2 \\ \hline \textbf{Overall:} & 2O_3 \rightarrow 3O_2 \end{array}$$
    - Note regeneration of chlorine atom
    - Processes that remove chlorine from atmosphere are slow.

Mining sulfur: the Frasch process



Melting point of sulfur: 115 °C

Density: 1.819 g cm^{-3}

Sulfur from the Claus process

- H_2S is a common contaminant in oil and gas.

  $\Longrightarrow$ sour gas
  - Refining/processing separate the H_2S from the hydrocarbon.

- To get S from H_2S:
  - Burn H_2S to obtain SO_2:

$$2H_2S_{(g)} + 3O_{2(g)} \rightarrow 2SO_{2(g)} + 2H_2O_{(g)}$$

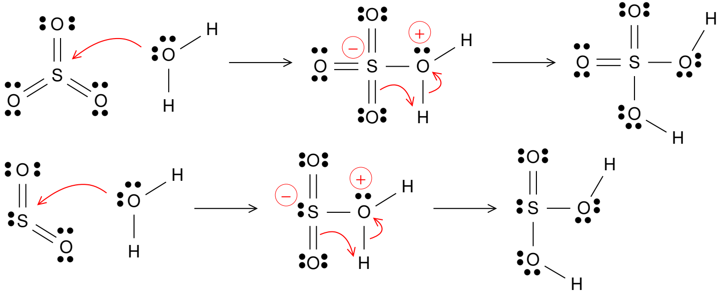
  - React SO_2 with H_2S in the presence of a catalyst:

$$2H_2S_{(g)} + SO_{2(g)} \rightarrow 3S_{(l)} + 2H_2O_{(g)}$$

  (Sulfur melts at 115 °C.)

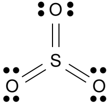
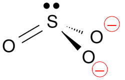
Acid rain

- Burning fuels containing sulfur results in the emission of SO_x gases.
  - Coal is a particular problem.
- SO_x gases are Lewis acids:



- These reactions in the atmosphere result in acid rain.
  pH of acid rain in areas where high-sulfur coal is used may be as low as 2.4 (similar to vinegar or lemon juice).

SO_3 vs SO_3^{2-}

SO_3	SO_3^{2-}
• gas	• exists in solution, or in ionic compounds
• trigonal planar 	• trigonal pyramidal  (and resonance structures)
• bond order 2	• bond order $\frac{4}{3}$
• bond length 142 pm	• bond length 151 pm
• Lewis acid (at S)	• Lewis/Brønsted base (at O)

What a difference an electron pair makes!