Group 16 Elements - Oxygen

- Stable allotropes of oxygen are $O_2(g)$ and $O_3(g)$.

- Standard laboratory preparations for $O_2(g)$ include the following:
  \[
  2\text{KClO}_3 \xrightarrow{\Delta} 2\text{KCl} + 3O_2 \\
  2\text{HgO} \xrightarrow{\Delta} 2\text{Hg} + O_2 \\
  2\text{H}_2\text{O} \xrightarrow{\text{electrolysis}} 2\text{H}_2 + O_2
  \]

- $O_2(g)$ is paramagnetic due to two unpaired electrons in separate $\pi^*$ MOs:
  \[\sigma_{2s}^2(\sigma_{2s}^*)^2(\sigma_{2p}^*)^2(\pi_{2p}^*)^2\]
  - Bond order is 2, and the bond length is 120.75 pm.

- Ozone is produced by passing an electric discharge through $O_2(g)$.
  - It is produced naturally by u.v. (240-300 nm).
    \[
    O_2 \xrightarrow{h\nu} 2O \\
    O + O_2 \rightarrow O_3
    \]

- Ozone is a bent molecule ($\angle O$–O–O $= 116.8^\circ$).
  - Bond order is 1½ for each O–O bond, and the bond length is 127.8 pm.

- Both $O_2$ and $O_3$ are powerful oxidizing agents.
  \[
  O_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \quad E^\circ = +1.23 \text{ V} \\
  O_3 + 2\text{H}^+ + 2e^- \rightarrow O_2 + \text{H}_2\text{O} \quad E^\circ = +2.07 \text{ V}
  \]
Sulfur is found free in nature in vast underground deposits.
- It is recovered by the Frasch process, which uses superheated steam to melt and expel the fluid.

**The Frasch Process**
Sulfur Allotropes

- Three principal allotropes:
  rhombic, $S_8$ (<96 °C, mp = 112.8 °C)
  monoclinic, $S_8$ (>96 °C, mp = 119. °C)
  amorphous, $S_n$ (metastable "plastic" sulfur)
- Rhombic and monoclinic forms contain crown-shaped $S_8$ rings ($D_{4d}$).

- Amorphous sulfur, containing long $S_n$ chains, is formed when molten sulfur is rapidly quenched; conversion to rhombic $S_8$ can take years.
Group 16 Elements - Se, Te, Po

- Se is recovered as an impurity in sulfur deposits.

- Se has several solid allotropes: rhombic (red), monoclinic (red), black, hexagonal (gray).
  - Red forms contain Se$_8$ units.
  - Black form has large polymeric rings.
  - Gray form (thermodynamically most stable) contains infinite helical chains (Se–Se distance = 237 pm).

- Se is a poorly conducting semimetal in the dark, but its conductance increases >20 times in light.

- Te has one form, isostructural with gray Se.

- Polonium, Po, is usually obtained as $^{210}_{84}$Po ($t_{1/2} = 138$ days).
  - Dangerous $\alpha$ emitter.

- Most common group oxidation states are -2, +4, +6.
Ozone is one of the most powerful oxidants known.
- Relative to \( \text{O}_2 \), its oxidations are generally faster and more vigorous.

- \( \text{O}_3 \) is photochemically produced in smog:
  \[
  \text{NO}_2 \overset{h\nu}{\rightarrow} \text{NO} + \text{O} \\
  \text{O} + \text{O}_2 \rightarrow \text{O}_3 \\
  \text{O}_3 + \text{NO} \rightarrow \text{O}_2 + \text{NO}_2
  \]

- \( \text{O}_3 \) reacts with hydrocarbons to produce oxygenated species, which are irritants and potentially carcinogens.
- Inhibits germination of plants, probably by destroying pollen.

- \( \text{O}_3 \) absorbs u.v strongly and is essential in the upper atmosphere.
- \( \text{O}_3 \) is depleted by trace amounts of \( \text{NO}_2 \) or \( \text{Cl}\cdot \) by a complicated series of reactions, including the following.
  \[
  \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \\
  \text{NO}_3 \rightarrow \text{NO} + \text{O}_2 \\
  \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2
  \]

  \[
  2\text{O}_3 \rightarrow 3\text{O}_2
  \]

  \[
  \text{Cl}\cdot + \text{O}_3 \rightarrow \text{ClO}\cdot + \text{O}_2 \\
  \text{ClO}\cdot + \text{O} \rightarrow \text{Cl}\cdot + \text{O}_2
  \]

  \[
  \text{O}_3 + \text{O} \rightarrow 2\text{O}_2
  \]
Oxygen Chemistry - Peroxide

- Hydrogen peroxide is a good oxidant and reductant, which leads to its tendency to decompose by autoredox.

\[
\begin{align*}
\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- & \rightarrow 2\text{H}_2\text{O} \quad E^\circ = 1.77 \text{ V} \\
\text{H}_2\text{O}_2 & \rightarrow \text{O}_2 + 2\text{H}^+ + 2e^- \quad -E^\circ = -0.68 \text{ V}
\end{align*}
\]

\[
2\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}_2\text{O} \quad E^\circ_{\text{cell}} = 1.05 \text{ V}
\]

- The reaction is catalyzed by light, \(\text{Ag}^+\), \(\text{MnO}_2\), \(\text{HBr}\), base, and saliva.

- \(\text{H}_2\text{O}_2\) can be made by acidification of \(\text{BaO}_2\) with \(\text{H}_2\text{SO}_4\):

\[
\text{BaO}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{BaSO}_4 \downarrow + \text{H}_2\text{O}_2
\]

- Today most is made by cold electrolysis of ammonium hydrogen sulfate to make peroxysulfate, \(\text{S}_2\text{O}_8^{2-}\), followed by heating to induce hydrolysis.

\[
\begin{align*}
2\text{NH}_4\text{HSO}_4(aq) \xrightarrow{\text{electrolysis} \sim 0^\circ \text{C}} & (\text{NH}_4)_2\text{S}_2\text{O}_8(aq) + \text{H}_2(g) \\
(\text{NH}_4)_2\text{S}_2\text{O}_8(aq) + 2\text{H}_2\text{O} & \rightarrow 2\text{NH}_4\text{HSO}_4(aq) + \text{H}_2\text{O}_2(l)
\end{align*}
\]

- Reduced pressure fractional distillation gives a 98% pure product.
In the gas phase \( \text{H}_2\text{O}_2 \) has the following \( C_2 \) structure, but the internal dihedral angle is very variable due to a low barrier to rotation.

\[
\begin{array}{c}
\text{H} \\
\text{O} \quad \text{O} \\
\text{H} \\
111^\circ \\
95^\circ \\
147.5 \text{ pm}
\end{array}
\]

- \( \text{H}_2\text{O}_2 \) is appreciably dissociated when pure.

\[
2\text{H}_2\text{O}_2 \rightleftharpoons \text{H}_3\text{O}_2^+ + \text{O}_2\text{H}^- \quad K = 1.5 \times 10^{-12}
\]

- It has a higher dielectric constant (\( \varepsilon = 93 \)) than water (\( \varepsilon = 78 \)), and a 65% solution has an even higher dielectric constant (\( \varepsilon = 120 \)).
- \( \text{H}_2\text{O}_2 \) would be a good ionizing solvent if it were not for its redox activity and tendency to decompose.
Hydrides of S, Se, Te

- All three dihydrides are poisonous and have obnoxious smells.
  - Toxicity of $\text{H}_2\text{S}$ is far greater than HCN.

- $\text{H}_2\text{S}$ dissolves in water at 1 atm to give a solution that is $\sim 0.1\text{M}$.

- All are weak acids.

  \[
  \begin{array}{ccc}
  \text{H}_2\text{A} & K_1 & K_2 \\
  \text{H}_2\text{S} & 1.02 \times 10^{-7} & 1 \times 10^{-19} \\
  \text{H}_2\text{Se} & 2 \times 10^{-4} & - \\
  \text{H}_2\text{Te} & 2.3 \times 10^{-3} & - \\
  \end{array}
  \]

- Sulfide salts of transition metals and other heavy metals are among the most insoluble binary ionic compounds.
  - Their $K_{sp}$ values$^1$ are so small that they precipitate even though the concentration of $\text{S}^{2-}$ ion in a saturated solution of $\text{H}_2\text{S}$ is only $\sim 10^{-19}$ M.

<table>
<thead>
<tr>
<th>Compound</th>
<th>CdS $K_{sp}$</th>
<th>CuS $K_{sp}$</th>
<th>PbS $K_{sp}$</th>
<th>NiS $K_{sp}$</th>
<th>Ag$<em>2$S $K</em>{sp}$</th>
<th>SnS $K_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{sp}$</td>
<td>$8 \times 10^{-28}$</td>
<td>$6 \times 10^{-37}$</td>
<td>$3 \times 10^{-28}$</td>
<td>$3 \times 10^{-20}$</td>
<td>$6 \times 10^{-51}$</td>
<td>$1 \times 10^{-26}$</td>
</tr>
</tbody>
</table>

$^1$For a solubility equilibrium of the type $\text{MS}(s) + \text{H}_2\text{O} \rightleftharpoons \text{M}^{2+}(aq) + \text{HS}^-(aq) + \text{OH}^-(aq)$
Oxides

- Both +4 and +6 oxides, oxoanions, and oxoacids exist.

- Burning the element in air yields the dioxide; e.g.,
  \[ S + O_2 \rightarrow SO_2 \]
  - \( SO_2 \) is a gas, structurally similar to ozone, but its liquid (bp \(-10 \, ^\circ C\)) is a useful nonaqueous solvent despite its low dielectric constant (\( \varepsilon \approx 15 \)).
  - \( SeO_2 \) is a volatile solid with a chain structure.
    \[
    \begin{array}{c}
    O \\
    \text{Se} \\
    O \\
    \text{Se} \\
    O \\
    \text{Se} \\
    \end{array}
    \]
  - \( TeO_2 \) is a nonvolatile solid with a three dimensional structure having four-coordinated Te.
  - \( PoO \) is a nonvolatile solid with the fluorite (CaF\(_2\)) structure.

- Only important trioxide is \( SO_3 \), formed by oxidizing \( SO_2 \) in the contact process.
  \[
  2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3
  \]
  - \( SO_3 \) is planar (\( D_{3h} \)) with \( \pi \) delocalization (bond order 1.6).
  - \( SeO_3 \) is made by dehydrating \( H_2SeO_4 \) with \( P_4O_{10} \) at 160 \( ^\circ C \).
  - \( TeO_3 \), an orange solid, is made by dehydrating \( Te(OH)_6 \).
Sulfur Oxoacids - $\text{H}_2\text{SO}_3$

- SO$_2$ dissolves in water to give an acidic solution generally called "sulfurous acid," but H$_2$SO$_3$ either does not exist or is present in only vanishingly small concentration.

- The equilibria in aqueous solution should be written as follows:
  \[
  \begin{align*}
  \text{SO}_2 + x\text{H}_2\text{O} & \rightleftharpoons \text{SO}_2\cdot x\text{H}_2\text{O} \quad \text{(hydrated } \text{SO}_2) \\
  \text{SO}_2\cdot x\text{H}_2\text{O} & \rightleftharpoons \text{HSO}_3^- + \text{H}_3\text{O}^+ + (x-2)\text{H}_2\text{O} \\
  \text{SO}_2\cdot x\text{H}_2\text{O} & \rightleftharpoons \text{H}_2\text{SO}_3 \\
  \end{align*}
  \]
  \[K << 1\]

- The first acid hydrolysis constant, $K_1$, is
  \[
  K_1 = \frac{[\text{HSO}_3^-][\text{H}_3\text{O}^+]}{[\text{SO}_2]} = 1.3 \times 10^{-2}
  \]
  where $[\text{SO}_2] = \text{C}_{\text{SO}_2} - [\text{HSO}_3^-] - [\text{SO}_3^{2-}]$.

- $K_2$ is the acid hydrolysis constant of the hydrogen sulfite ion:
  \[
  K_2 = \frac{[\text{SO}_3^{2-}][\text{H}_3\text{O}^+]}{[\text{HSO}_3^-]} = 5.6 \times 10^{-8}
  \]
Sulfur Oxoacids - $\text{H}_2\text{SO}_4$

- Sulfuric acid is formed when $\text{SO}_3$ is dissolved in water:
  \[
  \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4
  \]
- Reaction is too exothermic to serve as a commercial process for making sulfuric acid.

- $K_1 \gg 1$, $K_2 = 1.2 \times 10^{-2}$

- Most sulfuric acid is made by the *contact process*:
  1. Oxidation of $\text{SO}_2$
     \[
     2\text{SO}_2 + \text{O}_2 \xrightarrow{\text{V}_2\text{O}_5} 2\text{SO}_3
     \]
  2. Bubbling through concentrated $\text{H}_2\text{SO}_4$ to make "oleum", $\text{H}_2\text{S}_2\text{O}_7$ (*pyrosulfuric acid*).
     \[
     \text{SO}_3(g) + \text{H}_2\text{SO}_4(l) \rightarrow \text{H}_2\text{S}_2\text{O}_7(l)
     \]
  3. Dilution to make sulfuric acid of the desired concentration.
     \[
     \text{H}_2\text{S}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4
     \]

- Concentrated sulfuric acid, as supplied for laboratory use, is 98%.

- Concentrated sulfuric acid has a powerful avidity for water and can be used as a dehydrating agent in desiccators, provided that the substance being dried is not acid sensitive.
Selenium and Tellurium Oxoacids

- SeO_2 dissolves in water to give H_2SeO_3 = (OH)_2SeO (K_1 = 2.3 x 10^{-3}, K_2 = 5.3 x 10^{-9}).

\[ \text{SeO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SeO}_3 \]

- It is a moderately strong oxidizing agent:

\[ \text{H}_2\text{SeO}_3 + 4\text{H}^+ + 4e^- \rightleftharpoons \text{Se} + 3\text{H}_2\text{O} \quad E^0 = 0.74 \text{ V} \]

- H_2TeO_3 (uncertain structure) is best made by hydrolysis of a tetrahalide, because TeO_2 is not soluble in water; e.g.,

\[ \text{TeCl}_4 + 3\text{H}_2\text{O} \rightarrow \text{H}_2\text{TeO}_3 + 4\text{HCl} \]

- SeO_3 is difficult to obtain, but H_2SeO_4 can be synthesized by oxidizing H_2SeO_3 with H_2O_2.

\[ \text{H}_2\text{SeO}_3 + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{SeO}_4 + \text{H}_2\text{O} \]

- Dehydration with P_4O_{10} gives SeO_3.
- Pure H_2SeO_4 is a clear solid (mp 57 °C).
- H_2SeO_4 is somewhat less strong than H_2SO_4 (K_1 >> 1; K_2 = 1.2 x 10^{-2}).

- Te(OH)_6 is the tellurium +6 oxoacid, made by oxidizing TeO_2:

\[ \text{TeO}_2 + \text{H}_2\text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{Te(OH)}_6 \]

- It is a very weak diprotic acid (K_1 \approx 10^{-7}) with an octahedral structure.
**Sulfur Oxo- and Thio- Ions**

- Sulfur forms a number of acids and oxoanions with –O–, O–O, and S–S bonds.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Bond type</th>
</tr>
</thead>
<tbody>
<tr>
<td>thiosulfuric</td>
<td>$\text{H}_2\text{S}_2\text{O}_3$</td>
<td>S–S</td>
</tr>
<tr>
<td>dithionous</td>
<td>$\text{H}_2\text{S}_2\text{O}_4$</td>
<td>S–S</td>
</tr>
<tr>
<td>disulfurous</td>
<td>$\text{H}_2\text{S}_2\text{O}_5$</td>
<td>S–S</td>
</tr>
<tr>
<td>dithionic</td>
<td>$\text{H}_2\text{S}_2\text{O}_6$</td>
<td>S–S</td>
</tr>
<tr>
<td>disulfuric</td>
<td>$\text{H}_2\text{S}_2\text{O}_7$</td>
<td>S–O–S</td>
</tr>
<tr>
<td>polythionic</td>
<td>$\text{H}<em>2\text{S}</em>{n+2}\text{O}_6$</td>
<td>S–S$_n$–S</td>
</tr>
<tr>
<td>peroxomonosulfuric</td>
<td>$\text{H}_2\text{SO}_5$</td>
<td>S–O–OH</td>
</tr>
<tr>
<td>peroxidisulfuric</td>
<td>$\text{H}_2\text{S}_2\text{O}_8$</td>
<td>S–O–O–S</td>
</tr>
</tbody>
</table>

- Peroxydisulfate is formed by cold electrolysis of $\text{H}_2\text{SO}_4$.
  - It is a very strong oxidant.
    \[ \text{S}_2\text{O}_8^{2–} + 4\text{H}^+ + 2e^– \rightarrow 2\text{H}_2\text{SO}_4 \quad E^\circ = +2.01 \text{ V} \]

- Solutions of $\text{SO}_3^{2–}$ in contact with solid sulfur form thiosulfate, $\text{S}_2\text{O}_3^{2–}$, a tetrahedral ion with $C_{3v}$ symmetry.
  \[ \text{SO}_3^{2–}(aq) + \text{S}(s) \rightarrow \text{S}_2\text{O}_3^{2–}(aq) \]
  - It acts as a mild reducing agent, producing tetrathionate ion:
    \[ 2\text{S}_2\text{O}_3^{2–} \rightarrow \text{S}_4\text{O}_6^{2–} + 2e^– \quad –E^\circ = –0.08 \text{ V} \]
Sulfur Catenation

- Sulfur shows limited ability to catenate, as seen in the dithionate ion.

- The S–S bond ($D = 429$ kJ) is competitive with the S-O bond ($D = 522$ kJ).
  - This allows some chain species to form, as in sulfur's allotropes.

- When sulfide solutions are heated with sulfur, solutions containing mostly $S_3^{2-}$ and $S_4^{2-}$ are formed.
  $S^{2-} + xS(s) \rightarrow S_{x+1}^{2-}$
  - Only $S_3^{2-}$ and $S_4^{2-}$ are stable in solution, but a number of crystalline compounds with $S_n^{2-}$ ions with $n = 3–6$ can be prepared, especially with large cations (e.g., Cs$^+$, NH$_4^+$, enH$_2^{2+}$).
Halides and Oxohalides

• A large number of halides are known.

• The only hexahalides are SF$_6$, SeF$_6$ and TeF$_6$.

• The MX$_4$ halides exist for X = F, Cl, Br
  • The only +4 iodide is TeI$_4$.

• A number of dihalides and dimeric monohalides are known; e.g., OF$_2$, O$_2$F$_2$, S$_2$Cl$_2$, SCl$_2$, Se$_2$Cl$_2$, SeCl$_2$, S$_2$F$_2$, S$_2$Cl$_2$, ...

• Sulfur has two important oxohalides, SO$_2$Cl$_2$ (sulfuryl chloride) and SOCl$_2$ (thionyl chloride).
  • Thionyl chloride is an effective dehydrating agent for hydrated metal chlorides that would decompose with heating:
    \[ \text{SOCl}_2 + \text{H}_2\text{O} \rightarrow \text{SO}_2 + 2\text{HCl} \]
    \[ M_m\text{Cl}_n \cdot x\text{H}_2\text{O} + x\text{SOCl}_2 \rightarrow M_m\text{Cl}_n + x\text{SO}_2 + 2x\text{HCl} \]