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:
  
  $$2KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2$$

  $$2HgO \xrightarrow{\Delta} 2Hg + O_2$$

  $$2H_2O \xrightarrow{electrolysis} 2H_2 + O_2$$

- $O_2(g)$ is paramagnetic due to two unpaired electrons in separate $\pi^*$ MOs: $(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^2$.
  - 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.

  $$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad E^o = +1.23 \text{ V}$$

  $$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O \quad E^o = +2.07 \text{ V}$$
Group 16 Elements - Sulfur

- 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.
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 \( \text{Se}_8 \) 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 \(^{210}\text{Po} \) \((t_{1/2} = 138 \text{ days})\).
  - Dangerous \( \alpha \) emitter.

- Most common group oxidation states are -2, +4, +6.
Oxygen Chemistry - Ozone

- Ozone is one of the most powerful oxidants known.
  - Relative to $O_2$, its oxidations are generally faster and more vigorous.

- $O_3$ is photochemically produced in smog:
  
  $$
  \begin{align*}
  NO_2 & \xrightarrow{h\nu} NO + O \\
  O + O_2 & \rightarrow O_3 \\
  O_3 + NO & \rightarrow O_2 + NO_2
  \end{align*}
  $$

- $O_3$ reacts with hydrocarbons to produce oxygenated species, which are irritants and potentially carcinogens.
- Inhibits germination of plants, probably by destroying pollen.

- $O_3$ absorbs u.v strongly and is essential in the upper atmosphere.
  - $O_3$ is depleted by trace amounts of $NO_2$ or $Cl\cdot$ by a complicated series of reactions, including the following.

  $$
  \begin{align*}
  NO_2 + O_3 & \rightarrow NO_3 + O_2 \\
  NO_3 & \rightarrow NO + O_2 \\
  NO + O_3 & \rightarrow NO_2 + O_2
  \end{align*}
  $$

  $$
  2O_3 \rightarrow 3O_2
  $$

  $$
  \begin{align*}
  Cl\cdot + O_3 & \rightarrow ClO\cdot + O_2 \\
  ClO\cdot + O & \rightarrow Cl\cdot + O_2
  \end{align*}
  $$

  $$
  O_3 + O \rightarrow 2O_2
  $$
Oxygen Chemistry - Peroxide

- Hydrogen peroxide is a good oxidant and reductant, which leads to its tendency to decompose by autoredox.
  \[
  \begin{align*}
  \text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- &\rightarrow 2\text{H}_2\text{O} \quad E^o = 1.77 \text{ V} \\
  \text{H}_2\text{O}_2 &\rightarrow \text{O}_2 + 2\text{H}^+ + 2e^- \quad -E^o = -0.68\text{V} \\
  \\
  2\text{H}_2\text{O}_2 &\rightarrow \text{O}_2 + 2\text{H}_2\text{O} \quad E^o_{\text{cell}} = 1.05 \text{ V}
  \end{align*}
  \]
  - 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.
  \[
  2\text{NH}_4\text{HSO}_4(aq) \xrightarrow{\text{electrolysis \ -0^\circ C}} (\text{NH}_4)_2\text{S}_2\text{O}_8(aq) + \text{H}_2(g)
  \]
  \[
  (\text{NH}_4)_2\text{S}_2\text{O}_8(aq) + 2\text{H}_2\text{O} \rightarrow 2\text{NH}_4\text{HSO}_4(aq) + \text{H}_2\text{O}_2(l)
  \]
  - Reduced pressure fractional distillation gives a 98% pure product.
Oxygen Chemistry - Peroxide (cont.)

- 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.

$$\text{H}_2\text{O}_2 \equiv \begin{array}{c} \text{O} \\ \text{H} \\ \text{O} \end{array} \quad 147.5 \text{ pm}$$

- $\text{H}_2\text{O}_2$ 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 \(~0.1\text{M} \).

- All are weak acids.

<table>
<thead>
<tr>
<th>( \text{H}_2\text{A} )</th>
<th>( K_1 )</th>
<th>( K_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{S} )</td>
<td>( 1.02 \times 10^{-7} )</td>
<td>(~1 \times 10^{-19} )</td>
</tr>
<tr>
<td>( \text{H}_2\text{Se} )</td>
<td>( 2 \times 10^{-4} )</td>
<td>—</td>
</tr>
<tr>
<td>( \text{H}_2\text{Te} )</td>
<td>( 2.3 \times 10^{-3} )</td>
<td>—</td>
</tr>
</tbody>
</table>

- 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 presumed concentration of \( \text{S}^{2-} \) ion in a saturated solution of \( \text{H}_2\text{S} \) is only \(~10^{-19} \text{M} \).

<table>
<thead>
<tr>
<th>Compound</th>
<th>( K_{sp} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CdS} )</td>
<td>( 8 \times 10^{-28} )</td>
</tr>
<tr>
<td>( \text{CuS} )</td>
<td>( 6 \times 10^{-37} )</td>
</tr>
<tr>
<td>( \text{PbS} )</td>
<td>( 3 \times 10^{-28} )</td>
</tr>
<tr>
<td>( \text{NiS} )</td>
<td>( 3 \times 10^{-20} )</td>
</tr>
<tr>
<td>( \text{Ag}_2\text{S} )</td>
<td>( 6 \times 10^{-51} )</td>
</tr>
<tr>
<td>( \text{SnS} )</td>
<td>( 1 \times 10^{-26} )</td>
</tr>
</tbody>
</table>

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

For many years, the value of the second dissociation constant of $H_2S$ has been disputed, with most values in the range $pK_{a2} \geq 17$ for the presumed equilibrium

$$\text{HS}^- + H_2O \rightleftharpoons S^{2-} + H_3O^+$$

The OECD Nuclear Energy Agency recommended approximate value$^2$ is $pK_{a2} = 19$.

Most determinations are based on observing the diminishing of the $\text{HS}^-$ ion concentration under hyper-basic conditions (e.g., $C_{\text{NaOH}} = 8.9 - 21\text{M}$) using markers such as the intensity of the $\sim 2600 \text{ cm}^{-1}$ band in the Raman spectrum, owing to the presumed equilibrium

$$\text{HS}^- + \text{OH}^- \rightleftharpoons S^{2-} + H_2O$$

Recently, May et al.$^3$ have shown that the Raman data better fit the production of $\text{NaS}^-$ under such conditions.

$$\text{HS}^- + \text{OH}^- + \text{Na}^+ \rightleftharpoons \text{NaS}^- + H_2O$$

"...$S^{2-}(aq)$ should be expunged from the chemical literature."

---


Oxides

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

• Burning the element in air yields the dioxide; e.g.,
  \[ S + O_2 \rightarrow SO_2 \]
  • SO₂ is a gas, structurally similar to ozone, but its liquid (bp –10 °C) is a useful nonaqueous solvent despite its low dielectric constant (\( \varepsilon \approx 15 \)).
  • SeO₂ is a volatile solid with a chain structure.
    \[ \text{OSeOSeOSe} \]
  • TeO₂ is a nonvolatile solid with a three dimensional structure having four-coordinated Te.
  • PoO is a nonvolatile solid with the fluorite (CaF₂) structure.

• Only important trioxide is SO₃, formed by oxidizing SO₂ in the contact process.
  \[ 2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3 \]
  • SO₃ is planar (\( D_{3h} \)) with \( \pi \) delocalization (bond order 1\( \frac{1}{3} \)).
  • SeO₃ is made by dehydrating H₂SeO₄ with P₄O₁₀ at 160 °C.
  • TeO₃, an orange solid, is made by dehydrating Te(OH)₆.
Sulfur Oxoacids - $\text{H}_2\text{SO}_3$

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

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

- 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 $[\text{SO}_2] = C_{\text{SO}_2} - [\text{HSO}_3^-] - [\text{SO}_3^{2-}]$.

- $K_2$ 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.

- \( K_1 \gg 1, \quad K_2 = 1.2 \times 10^{-2} \)

- 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$_2$SeO$_3$ = (OH)$_2$SeO ($K_1 = 2.3 \times 10^{-3}$, $K_2 = 5.3 \times 10^{-9}$).
  
  $$\text{SeO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SeO}_3$$

  - It is a moderately strong oxidizing agent:
  
  $$\text{H}_2\text{SeO}_3 + 4\text{H}^+ + 4e^- \rightleftharpoons \text{Se} + 3\text{H}_2\text{O} \quad E^\circ = 0.74 \text{ V}$$

- H$_2$TeO$_3$ (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$_2$SeO$_4$ can be synthesized by oxidizing H$_2$SeO$_3$ with H$_2$O$_2$.

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

  - Dehydration with P$_4$O$_{10}$ gives SeO$_3$.
  - Pure H$_2$SeO$_4$ is a clear solid (mp 57 °C).
  - H$_2$SeO$_4$ is somewhat less strong than H$_2$SO$_4$ ($K_1 \gg 1$; $K_2 = 1.2 \times 10^{-2}$).

- 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>H_2S_2O_3</td>
<td>S–S</td>
</tr>
<tr>
<td>dithionous</td>
<td>H_2S_2O_4</td>
<td>S–S</td>
</tr>
<tr>
<td>disulfurous</td>
<td>H_2S_2O_5</td>
<td>S–S</td>
</tr>
<tr>
<td>dithionic</td>
<td>H_2S_2O_6</td>
<td>S–S</td>
</tr>
<tr>
<td>disulfuric</td>
<td>H_2S_2O_7</td>
<td>S–O–S</td>
</tr>
<tr>
<td>polythionic</td>
<td>H_2S_{n+2}O_6</td>
<td>S–S_n–S</td>
</tr>
<tr>
<td>peroxomonosulfur</td>
<td>H_2SO_5</td>
<td>S–O–OH</td>
</tr>
<tr>
<td>peroxidisulfuric</td>
<td>H_2S_2O_8</td>
<td>S–O–O–S</td>
</tr>
</tbody>
</table>

- Peroxydisulfate is formed by cold electrolysis of H_2SO_4.
  - It is a very strong oxidant.
    \[ S_2O_8^{2–} + 4H^+ + 2e^- \rightarrow 2H_2SO_4 \quad E^o = +2.01 \text{ V} \]

- Solutions of SO_3^{2–} in contact with solid sulfur form thiosulfate, S_2O_3^{2–}, a tetrahedral ion with C_3v symmetry.
  \[ \text{SO}_3^{2–}(aq) + S(s) \rightarrow S_2O_3^{2–}(aq) \]
  - It acts as a mild reducing agent, producing tetrathionate ion:
    \[ 2S_2O_3^{2–} \rightarrow S_4O_6^{2–} + 2e^- \quad \text{–}E^o = -0.08 \text{ V} \]
Sulfur Catenation

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

- The S–S bond ($D = 429 \text{ kJ}$) is competitive with the S-O bond ($D = 522 \text{ kJ}$).
  - 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.
  
  \[ S^{2-} + xS(s) \rightarrow S_{x+1}^{2-} \quad x = 2,3,.. \]

  - 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:
    \[
    \text{SOCl}_2 + \text{H}_2\text{O} \rightarrow \text{SO}_2 + 2\text{HCl}
    \]
    \[
    \text{M}_m\text{Cl}_n \cdot x\text{H}_2\text{O} + x\text{SOCl}_2 \rightarrow \text{M}_m\text{Cl}_n + x\text{SO}_2 + 2x\text{HCl}
    \]