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:

$$2KClO_3 \xrightarrow[\Delta]{MnO_2} 2KCl + 3O_2$$

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

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

- $O_2(g)$ is paramagnetic due to two unpaired electrons in separate π^* 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°).
  - Bond order is 1½ for each O–O bond, and the bond length is 127.8 pm.

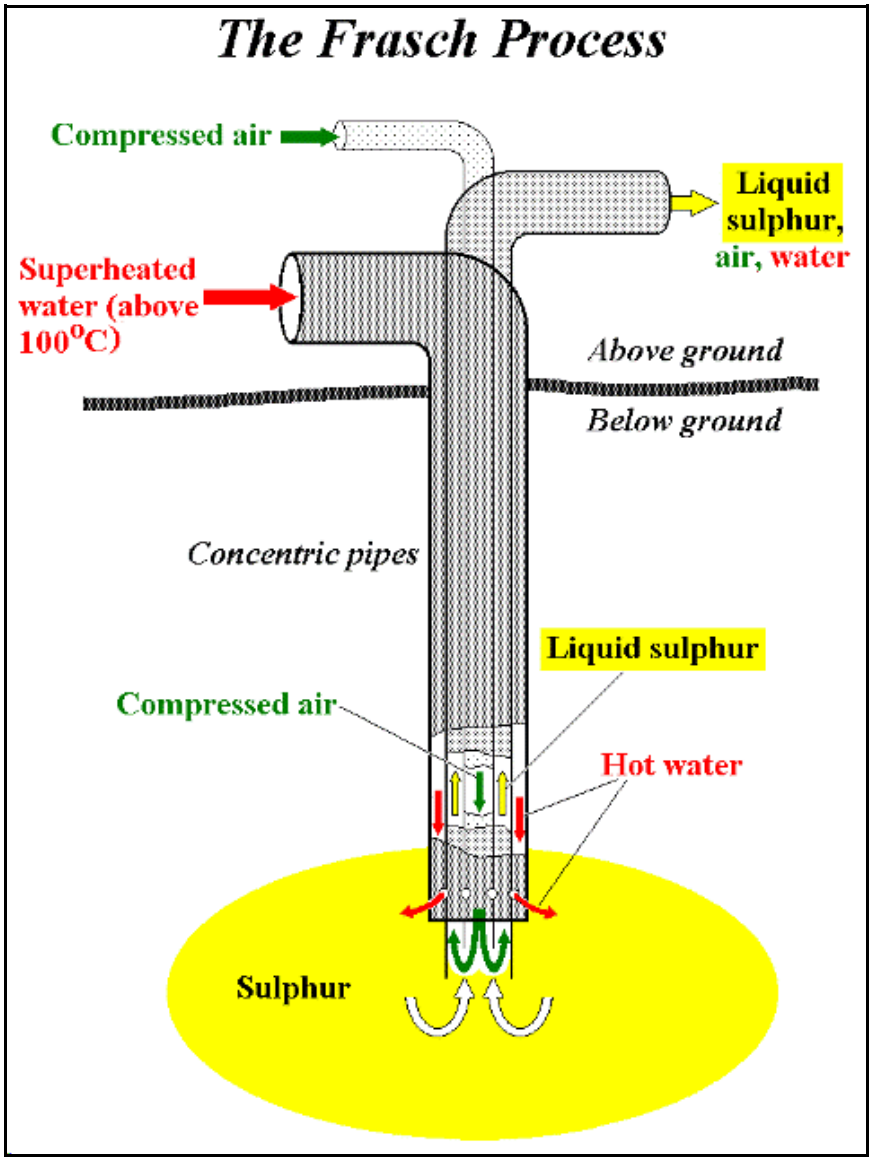
- Both O_2 and O_3 are powerful oxidizing agents.

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

$$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O \qquad E^\circ = +2.07 \text{ V}$$

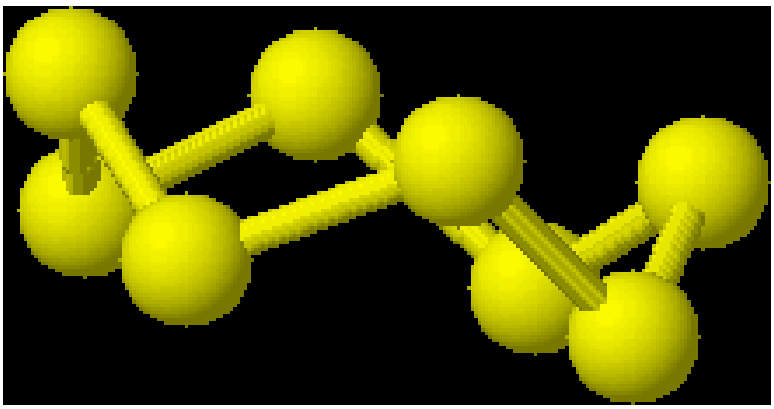
Group 16 Elements - Sulfur

- 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 ºC, mp = 112.8 ºC)
  monoclinic, S_8 (>96 ºC, mp = 119. ºC)
  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 $^{210}_{84}Po$ ($t_{½}$ = 138 days).
  - Dangerous α 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:

$$NO_2 \xrightarrow{h\nu} NO + O$$

$$O + O_2 \rightarrow O_3$$

$$O_3 + NO \rightarrow O_2 + NO_2$$

  - O_3 reacts with hydrocarbons to produced 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.

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

$$2O_3 \rightarrow 3O_2$$

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

$$O_3 + O \rightarrow 2O_2$$

Oxygen Chemistry - Peroxide

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

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad E^o = 1.77\ V$$
$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- \qquad -E^o = -0.68V$$

$$2H_2O_2 \rightarrow O_2 + 2H_2O \qquad E^o_{cell} = 1.05\ V$$

  - The reaction is catalyzed by light, Ag^+, MnO_2, HBr, base, and saliva.

- H_2O_2 can be made by acidification of BaO_2 with H_2SO_4:

$$BaO_2 + H_2SO_4 \rightarrow BaSO_4\downarrow + H_2O_2$$

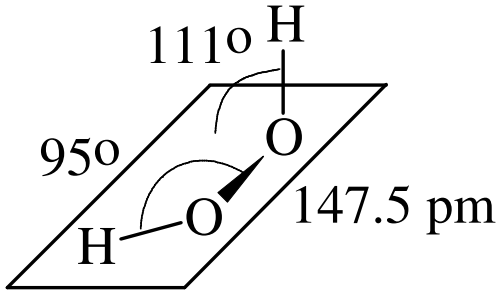
- Today most is made by cold electrolysis of ammonium hydrogen sulfate to make peroxidsulfate, $S_2O_8^{2-}$, followed by heating to induce hydrolysis.

$$2NH_4HSO_4(aq) \xrightarrow[\sim 0\ ^oC]{\text{electrolysis}} (NH_4)_2S_2O_8(aq) + H_2(g)$$
$$(NH_4)_2S_2O_8(aq) + 2H_2O \rightarrow 2NH_4HSO_4(aq) + H_2O_2(l)$$

  - Reduced pressure fractional distillation gives a 98% pure product.

Oxygen Chemistry - Peroxide (cont.)

- In the gas phase H_2O_2 has the following C_2 structure, but the internal dihedral angle is very variable due to a low barrier to rotation.



- H_2O_2 is appreciably dissociated when pure.

$$2H_2O_2 \rightleftharpoons H_3O_2^+ + O_2H^- \qquad K = 1.5 \times 10^{-12}$$

  - It has a higher dielectric constant ($\varepsilon = 93$) than water ($\varepsilon = 78$), and a 65% solution has an even higher dielectric constant ($\varepsilon = 120$).
  - H_2O_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 H_2S is far greater than HCN.

- H_2S dissolves in water at 1 atm to give a solution that is ~0.1M.

- All are weak acids.

H_2A	K_1	K_2
H_2S	1.02×10^{-7}	$\sim 1 \times 10^{-19}$
H_2Se	2×10^{-4}	—
H_2Te	2.3×10^{-3}	—

- 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 S^{2-} ion in a saturated solution of H_2S is only $\sim 10^{-19}$ M.

Compound	CdS	CuS	PbS	NiS	Ag_2S	SnS
K_{sp}	8×10^{-28}	6×10^{-37}	3×10^{-28}	3×10^{-20}	6×10^{-51}	1×10^{-26}

[1]For a solubility equilibrium of the type $MS(s) + H_2O \rightleftharpoons M^{2+}(aq) + HS^-(aq) + OH^-(aq)$

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

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

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

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

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

Recently, May et al.[3] have shown that the Raman data better fit the production of NaS^- under such conditions.

$$HS^- + OH^- + Na^+ \rightleftharpoons NaS^- + H_2O$$

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

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[2]R. J. Lemire, U. Berner, C. Musikas, D. A. Palmer, P. Taylor, and O. Tochiyama, Organization for Economic Cooperation and Development Chemical Thermodynamics Series, *Chemical Thermodynamics of Iron Part 1*, OECS, 2013, vol. 13a.

[3]P. M. May, D. Batka, G. Hefter, E. Königsberger, and D. Rowland, *Chem. Comm.*, 2018, **54**, 1980-1983.

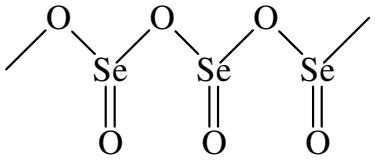
Oxides

- 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 ^{O}C) is a useful nonaqueous solvent dispite its low dielectric constant ($\varepsilon \approx 15$).
  - SeO_2 is a volatile solid with a chain structure.



  - 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 π delocalization (bond order 1⅓).
  - SeO_3 is made by dehydrating H_2SeO_4 with P_4O_{10} at 160 °C.
  - TeO_3, an orange solid, is made by dehydrating $Te(OH)_6$.

Sulfur Oxoacids - H_2SO_3

- SO_2 dissolves in water to give an acidic solution generally called "sulfurous acid," but H_2SO_3 either does not exist or is present in only vanishingly small concentration.

- The equilibria in aqueous solution should be written as follows:

  $SO_2 + xH_2O \rightleftharpoons SO_2 \cdot xH_2O$ (hydrated SO_2)

  $SO_2 \cdot xH_2O \rightleftharpoons HSO_3^- + H_3O^+ + (x-2)H_2O$

  $SO_2 \cdot xH_2O \rightleftharpoons H_2SO_3$ $K \ll 1$

  - The first acid hydrolysis constant, K_1, is

$$K_1 = \frac{[HSO_3^-][H_3O^+]}{[SO_2]} = 1.3 \times 10^{-2}$$

    where $[SO_2] = C_{SO_2} - [HSO_3^-] - [SO_3^{2-}]$.

  - K_2 is the acid hydrolysis constant of the hydrogen sulfite ion:

$$K_2 = \frac{[SO_3^{2-}][H_3O^+]}{[HSO_3^-]} = 5.6 \times 10^{-8}$$

Sulfur Oxoacids - H_2SO_4

- Sulfuric acid is formed when SO_3 is dissolved in water:

  $$SO_3 + H_2O \rightarrow H_2SO_4$$

  - Reaction is too exothermic to serve as a commercial process for making sulfuric acid.

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

- Most sulfuric acid is made by the *contact process*:

  (1) Oxidation of SO_2

  $$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$

  (2) Bubbling through concentrated H_2SO_4 to make "oleum", $H_2S_2O_7$ (*pyrosulfuric acid*).

  $$SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$$

  (3) Dilution to make sulfuric acid of the desired concentration.

  $$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$$

- 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 $H_2SeO_3 = (OH)_2SeO$ ($K_1 = 2.3 \times 10^{-3}$, $K_2 = 5.3 \times 10^{-9}$).

$$SeO_2 + H_2O \rightarrow H_2SeO_3$$

  - It is a moderately strong oxidizing agent:

$$H_2SeO_3 + 4H^+ + 4e^- \rightleftharpoons Se + 3H_2O \qquad E^o = 0.74 \text{ V}$$

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

$$TeCl_4 + 3H_2O \rightarrow H_2TeO_3 + 4HCl$$

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

$$H_2SeO_3 + H_2O_2 \rightarrow H_2SeO_4 + H_2O$$

  - 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 ($K_1 >> 1$; $K_2 = 1.2 \times 10^{-2}$).

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

$$TeO_2 + H_2O_2 + 2H_2O \rightarrow Te(OH)_6$$

  - 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.

Name	Formula	Bond type
thiosulfuric	$H_2S_2O_3$	S–S
dithionous	$H_2S_2O_4$	S–S
disulfurous	$H_2S_2O_5$	S–S
dithionic	$H_2S_2O_6$	S–S
disulfuric	$H_2S_2O_7$	S–O–S
polythionic	$H_2S_{n+2}O_6$	S–S_n–S
peroxomonosulfuric	H_2SO_5	S–O–OH
peroxidisulfuric	$H_2S_2O_8$	S–O–O–S

- Peroxydisulfate is formed by cold electrolysis of H_2SO_4.
  - It is a very strong oxidant.

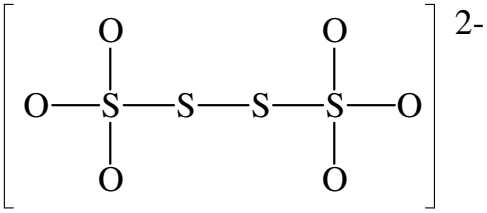
$$S_2O_8^{2-} + 4H^+ + 2e^- \rightarrow 2H_2SO_4 \qquad E^o = +2.01\ V$$

- Solutions of SO_3^{2-} in contact with solid sulfur form thiosulfate, $S_2O_3^{2-}$, a tetrahedral ion with C_{3v} symmetry.

$$SO_3^{2-}(aq) + S(s) \rightarrow S_2O_3^{2-}(aq)$$

  - It acts as a mild reducing agent, producing tetrathionate ion:

$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^- \qquad -E^o = -0.08\ V$$



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.

$$S^{2-} + xS(s) \rightarrow S_{x+1}^{2-} \qquad x = 2,3,..$$

  - 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_2F_2, S_2Cl_2, SCl_2, Se_2Cl_2, $SeCl_2$, S_2F_2, S_2Cl_2, ...

- Sulfur has two important oxohalides, SO_2Cl_2 (sulfuryl chloride) and $SOCl_2$ (thionyl chloride).
  - Thionyl chloride is an effective dehydrating agent for hydrated metal chlorides that would decompose with heating:

    $SOCl_2 + H_2O \rightarrow SO_2 + 2HCl$

    $M_mCl_n \cdot xH_2O + xSOCl_2 \rightarrow M_mCl_n + xSO_2 + 2xHCl$