

# Chapter 9

## Group 16

### 9.1 The Group 16 Elements: The Chalcogens<sup>1</sup>

#### 9.1.1 The elements

The Group 16 elements have a particular name chalcogenes. Table 9.1 lists the derivation of the names of the halogens.

Element	Symbol	Name
Oxygen	O	Greek <i>oxys</i> ( <i>sharp</i> , from the taste of acids) and <i>genēs</i> (producer)
Sulfur (sulphur)	S	From the Latin <i>sulphurium</i>
Selenium	Se	Greek <i>selene</i> meaning <i>Moon</i>
Tellurium	Te	Latin <i>tellus</i> meaning <i>earth</i>
Polonium	Po	Named after Poland, Latin <i>Polonia</i>

**Table 9.1:** Derivation of the names of each of the Group 16(VI) elements.

NOTE: In Latin, the word is variously written *sulpur*, *sulphur*, and *sulfur*. It is an original Latin name and not a classical Greek loan, so the *ph* variant does not denote the Greek letter  $\phi$ . Sulfur in Greek is *thion*, whence comes the prefix *thio-* to denote a sulfur derivative, e.g., a thioketone,  $R_2C=S$ . The simplification of the Latin words *p* or *ph* to an *f* appears to have taken place towards the end of the classical period. The element has traditionally been spelled sulphur in the United Kingdom, India, Malaysia, South Africa, Australia, Ireland, and Canada, but sulfur in the United States. IUPAC adopted the spelling “sulfur” in 1990, as did the Royal Society of Chemistry Nomenclature Committee in 1992.

#### 9.1.1.1 Discovery

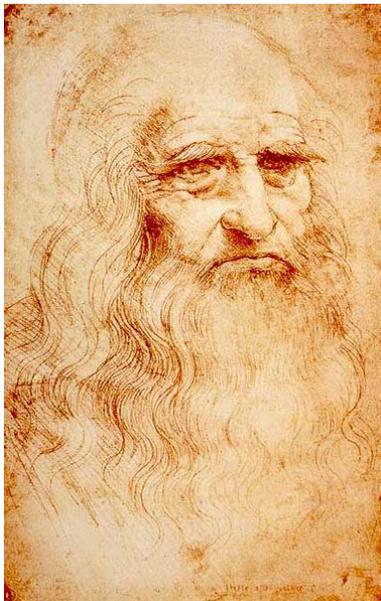
##### 9.1.1.1.1 Oxygen

The 2<sup>nd</sup> century BC Greek writer, Philo of Byzantium, observed that inverting a jar over a burning candle and surrounding the jar’s neck with water resulted in some water rising into the neck. He incorrectly ascribed this to the idea that part of the air in the vessel were converted into the element *fire* and thus were able to

<sup>1</sup>This content is available online at <<http://cnx.org/content/m34993/1.1/>>.

escape through pores in the glass. Much later Leonardo da Vinci (Figure 9.1) suggested that this effect was actually due to a portion of air being consumed during combustion.

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**Figure 9.1:** Italian painter, sculptor, architect, musician, scientist, mathematician, engineer, inventor, anatomist, geologist, cartographer, botanist and writer Leonardo di ser Piero da Vinci (1452 - 1519).

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By the late 17<sup>th</sup> century, Robert Boyle (Figure 9.2) showed that air is necessary for combustion. His work was expanded by English chemist John Mayow (Figure 9.3) by showing that fire requires only a part of air that he called *spiritus nitroaereus* or just *nitroaereus*.



**Figure 9.2:** British natural philosopher, chemist, physicist, and inventor Robert Boyle (1627 - 1691).

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**Figure 9.3:** English chemist, physician, and physiologist John Mayow FRS (1641–1679).

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The reactive nature of nitroaereus was implied by Mayow from his observation that antimony (Sb) increased in weight when heated in air. He also suggested that the lungs separate nitroaereus from air and

pass it into the blood and that animal heat and muscle movement result from the reaction of nitroaereus with certain substances in the body; both concepts that were proven to be correct.

Robert Hooke (Figure 9.4), Ole Borch (Figure 9.5), Mikhail Lomonosov (id1168366758158), and Pierre Bayen (Figure 9.7) all produced oxygen in experiments in the 17<sup>th</sup> and the 18<sup>th</sup> century but none of them recognized it as an element, probably since the prevalence at that time of the phlogiston, and their attempts to fit their experimental observations to that theory.



**Figure 9.4:** Portrait of English natural philosopher, architect Robert Hooke FRS (1635 - 1703).



**Figure 9.5:** Danish scientist, physician, grammarian, and poet Ole Borch (1626 - 1690).

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**Figure 9.6:** Russian scientist and writer Mikhail Vasilyevich Lomonosov (1711 - 1765).

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**Figure 9.7:** French chemist and pharmacist Pierre Bayen (1725 - 1798).

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NOTE: The phlogiston theory was postulated in 1667 by the German alchemist J. J. Becher, and modified in 1731 by the chemist Georg Ernst Stahl. Phlogiston theory stated that all combustible materials were made of two parts. One part, called *phlogiston*, was given off when the substance containing it was burned, while the *dephlogisticated* component was thought to be its true form, or *calx*. Highly combustible materials that leave little residue (e.g., wood) were thought to mostly comprise of phlogiston, while non-combustible substances that corrode (e.g., iron) contained very

little phlogiston. Air did not play a role in phlogiston theory, instead, it was based on observations of what happens when something burns, that most common objects appear to become lighter and seem to lose something in the process. However, one observation that overturned phlogiston theory was that metals, gain weight in rusting when they were supposedly losing phlogiston!

Oxygen was first discovered by Carl Wilhelm Scheele (Figure 9.8) by heating mercuric oxide ( $\text{HgO}$ ). Scheele called the gas *fire air* because it was the only known supporter of combustion. He wrote an account of this discovery in a manuscript (*Treatise on Air and Fire*) submitted in 1775. Unfortunately for Scheele his work was not published until 1777. In August 1774, an experiment conducted by Joseph Priestley (Figure 9.9) sunlight on mercuric oxide ( $\text{HgO}$ ) inside a glass tube, which liberated a gas he named *dephlogisticated air*. Priestley noted that candles burned brighter in this gas. He even went as far as breathing the gas himself, after which he wrote: "The feeling of it to my lungs was not sensibly different from that of common air, but I fancied that my breast felt peculiarly light and easy for some time afterwards." Priestley published his findings in 1775. Because he published his findings first, Priestley is usually given credit for the discovery of what became known as oxygen.



**Figure 9.8:** Swedish chemist Carl Wilhelm Scheele (1742 – 1786). Isaac Asimov called him "hard-luck Scheele" because he made a number of chemical discoveries before others who are generally given the credit.

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**Figure 9.9:** Portrait (by Ellen Sharples) of British clergyman natural philosopher, educator, and political theorist Joseph Priestley (1733 - 1804).

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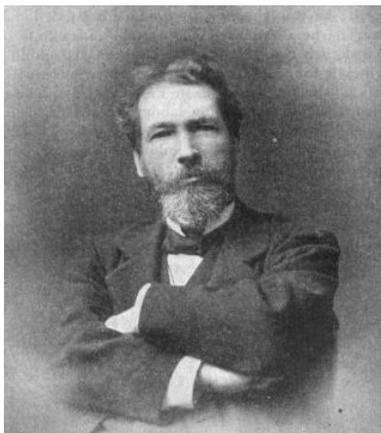
Interestingly, Lavoisier (Figure 9.10) claimed to have discovered this new substance independently. However, Priestley visited Lavoisier in October 1774 and told him about his experiment and how he liberated the new gas. Furthermore, Scheele also posted a letter to Lavoisier on September 30, 1774 that described his own discovery. Lavoisier never acknowledged receiving it, however, a copy of the letter was found in Scheele's belongings after his death.



**Figure 9.10:** Line engraving (by Louis Jean Desire Delaistre) of the French chemist and biologist Antoine-Laurent de Lavoisier (1743 - 1794) often referred to as the *father of modern chemistry* due to his extensive contributions.

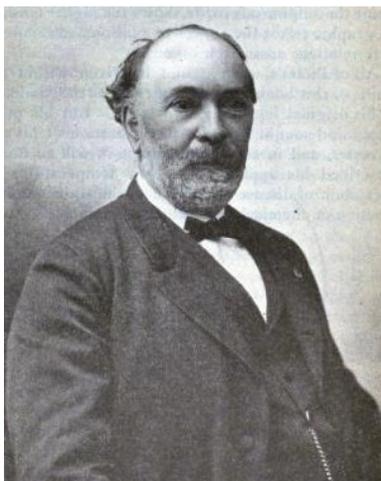
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Raoul Pictet (Figure 9.11) showed that by the evaporation of liquid sulfur dioxide ( $\text{SO}_2$ ), carbon dioxide could be liquefied, which in turn was evaporated to cool oxygen gas enough to liquefy it. Pictet reported his results on December 22, 1877. Two days later, Louis Cailletet (Figure 9.12) announced his own method of liquefying oxygen. In both cases only a few drops could be produced, making analysis difficult. In 1891 James Dewar (Figure 9.13) was able to produce enough liquid oxygen to study. However, it was the process developed independently by Carl von Linde (Figure 9.14) and William Hampson (1854 - 1926).



**Figure 9.11:** Swiss chemist and physicist Raoul Pierre Pictet (1846 - 1929).

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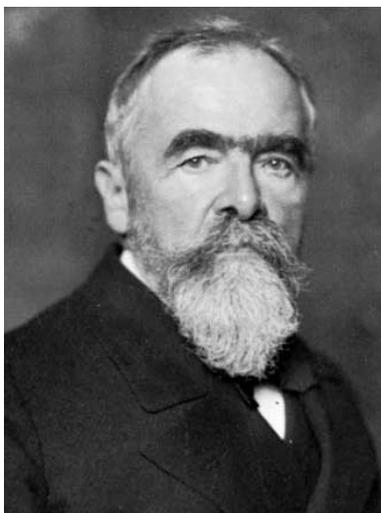
**Figure 9.12:** French physicist Louis Paul Cailletet (1832 - 1913).

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**Figure 9.13:** Scottish chemist and physicist Sir James Dewar FRS (1842 - 1923).

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**Figure 9.14:** German engineer Carl Paul Gottfried von Linde (1842 - 1934).

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#### 9.1.1.1.2 Sulfur

Sulfur was known in ancient times and is referred to in the Bible. English translations of the Bible commonly referred to burning sulfur as *brimstone*, giving rise to the name of *fire-and-brimstone* sermons, in which listeners are reminded of the fate of eternal damnation that await the unbelieving and unrepentant. It is from this part of the Bible that Hell is implied to *smell of sulfur* (likely due to its association with volcanic activity). Sulfur ointments were used in ancient Egypt, while it was used for fumigation in Greece. A natural form of sulfur known as *shiliuhuang* was known in China since the 6<sup>th</sup> century BC. However, it was not until 1777 that Lavoisier (Figure 9.10) convinced the scientific community that sulfur was an element and not a compound.

#### 9.1.1.1.3 Selenium

The element was discovered in 1817 by Berzelius (Figure 9.15), who found the element associated with tellurium. It was discovered as a byproduct of sulfuric acid production.



**Figure 9.15:** Swedish chemist Jöns Jacob Berzelius (1779 - 1848).

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#### 9.1.1.1.4 Tellurium

Tellurium was discovered in the 18<sup>th</sup> century in gold ore from the mines in Zlatna, Transylvania. In 1782 Müller von Reichenstein (Figure 9.16), the Hungarian chief inspector of mines in Transylvania, concluded that the ore was bismuth sulfide. However, the following year, he reported that this was erroneous and that the ore contained mostly gold and an unknown metal very similar to antimony. After three years of work Müller determined the specific gravity of the mineral and noted the radish-like smell of the white smoke evolved when the new metal was heated. Nevertheless, he was not able to identify this metal and gave it the names *aurum paradoxium* and *metallum problematicum*, as it did not show the properties predicted for the expected antimony.



**Figure 9.16:** A stamp showing Hungarian mineralogist Franz-Joseph Müller von Reichenstein (1742 - 1825).

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In 1789 Kitaibel (Figure 9.17) also discovered the element independently in an ore from Deutsch-Pilsen which had been regarded as *argentiferous molybdenite*, but later he gave the credit to Müller. In 1798, the name was chosen by Klaproth (Figure 9.18) who earlier isolated it from the mineral calaverite.

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**Figure 9.17:** Hungarian botanist and chemist Pál Kitaibel (1757 - 1817).

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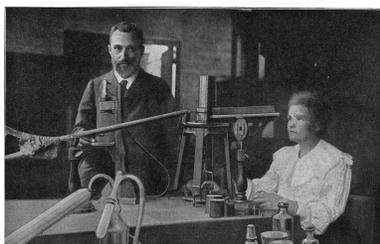


**Figure 9.18:** Figure. German chemist Martin Heinrich Klaproth (1743 –1817).

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#### 9.1.1.1.5 Polonium

Temporarily called *radium F*, polonium was discovered by Marie Curie and her husband Pierre Curie (Figure 9.19) in 1898, but it was later named after Marie Curie's native land of Poland. At the time Poland was not an independent country, but partitioned under Russian, Prussian, and Austrian. It was Curie's hope that naming the element after her native land would publicize its lack of independence. Polonium was the first chemical element named to highlight a political controversy.



**Figure 9.19:** Pierre (1859 - 1906) and Marie Skłodowska-Curie (1867 - 1934) in their Paris laboratory.

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#### 9.1.1.2 Abundance

The abundance of the chalcogenes is given in Table 9.2.

Element	Terrestrial abundance (ppm)
O	$47 \times 10^4$ (Earth's crust), constituent of water, $21 \times 10^4$ (atmosphere)
S	260 (Earth's crust), 870 (sea water), $10^{-3}$ (atmosphere)
Se	0.05 (Earth's crust), 5 (soil), $0.2 \times 10^{-3}$ (sea water)
Te	$5 \times 10^{-3}$ (Earth's crust), 0.03 (soil), $0.15 \times 10^{-6}$ (sea water)
Po	Trace (Earth's crust)

**Table 9.2:** Abundance of Group 16 elements.

### 9.1.1.3 Isotopes

The naturally abundant isotopes of the Group 16 elements are listed in Table 9.3. All of the isotopes of polonium are radioactive.

Isotope	Natural abundance (%)
Oxygen-16	99.76
Oxygen-17	0.039
Oxygen-18	0.201
Sulfur-32	95.02
Sulfur-33	0.75
Sulfur-34	4.21
Sulfur-36	0.02
Selenium-74	0.87
Selenium-76	9.36
Selenium-77	7.63
Selenium-78	23.78
Selenium-80	49.61
Tellurium-120	0.09
Tellurium-122	2.55
Tellurium-123	0.89
Tellurium-124	4.74
Tellurium-125	7.07
Tellurium-126	18.84
Tellurium-128	31.74
Tellurium-130	34.08

**Table 9.3:** Abundance of the non-synthetic isotopes of the Group 16 elements.

There are 38 known nuclear isomers of tellurium with atomic masses that range from 105 to 142. Tellurium is the lightest element known to undergo alpha decay, with isotopes  $^{106}\text{Te}$  to  $^{110}\text{Te}$  being able to undergo this mode of decay.

### 9.1.1.3.1 Cigarettes: it is not only the smoke that kills, but also the radioactivity

Ever since the early 1960s, the presence of polonium-210 in tobacco smoke has been known. The world's biggest tobacco firms spent over 40 years trying to find ways to remove the polonium-210 without success: even to this day. However, they also never published the results, keeping the facts of the radioactive hazards from the consumer.

Radioactive polonium-210 is contained in phosphate fertilizers and is absorbed by the roots of plants (such as tobacco) and stored in its tissues. Tobacco plants fertilized by rock phosphates contain polonium-210, which emits alpha radiation estimated to cause about 11,700 lung cancer deaths annually worldwide.

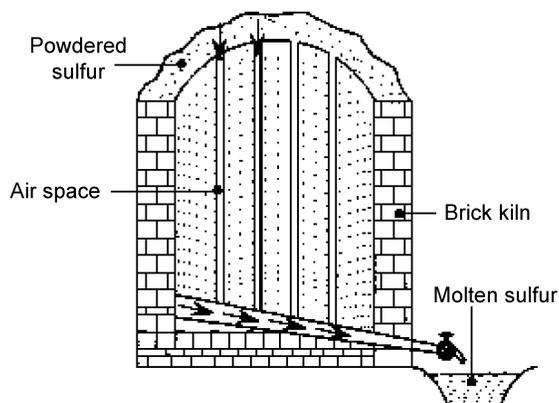
## 9.1.2 Industrial production of the elements

### 9.1.2.1 Sulfur

Elemental sulfur is found near hot springs and volcanic regions in many parts of the world. Volcanic deposits are mined in Indonesia, Chile, and Japan. Significant deposits of sulfur also exist in salt domes along the coast of the Gulf of Mexico, and in eastern Europe and western Asia. The sulfur in these deposits is believed to come from the action of anaerobic bacteria on sulfate minerals. However, fossil-based sulfur deposits from salt domes are the basis for commercial production in the United States, Poland, Russia, Turkmenistan, and Ukraine. Sulfur is mainly extracted from natural sources by two processes: the Sicilian process and the Frasch process.

#### 9.1.2.1.1 Sicilian process

First used in Sicily from where it takes its name, the Sicilian process was used in ancient times to get sulfur from rocks present in volcanic regions. The sulfur deposits are piled and stacked in brick kilns built on sloping hillsides, and with airspaces between them (Figure 9.20). Then powdered sulfur is put on top of the sulfur deposit and ignited. As the sulfur burns, the heat melts the sulfur deposits, causing the molten sulfur to flow down the sloping hillside. The molten sulfur can then be collected in wooden buckets. The sulfur produced by the Sicilian process must be purified by distillation.



**Figure 9.20:** Extraction of sulfur by the Sicilian process.

### 9.1.2.1.2 Frasch process

In 1867, sulfur was discovered in the caprock of a salt dome in Louisiana; however, it was beneath quicksand, which prevented mining. In 1894 Herman Frasch (Figure 9.21), devised a method of sulfur removal using pipes to bypass the quicksand. The process proved successful, but the high cost of fuel needed to heat the water made the process uneconomic until the 1901 discovery of the Spindletop oil field in Texas (Figure 9.22) provided cheap fuel oil to the region.



**Figure 9.21:** German-born American chemist Herman Frasch (1851 - 1914).

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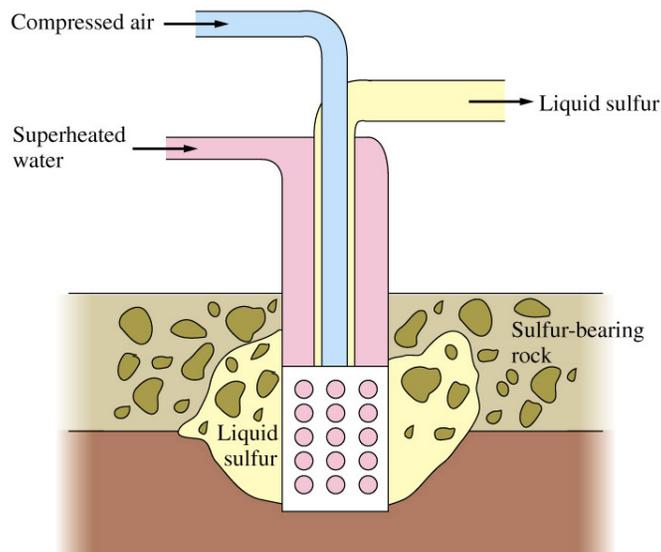


**Figure 9.22:** Spindletop oil field in Beaumont, Texas.

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In the Frasch process three concentric pipes to extract sulfur at high purity directly out of the ground (Figure 9.23). Superheated steam ( $160\text{ }^{\circ}\text{C}$ ) is pumped down the outermost pipe, which melts the sulfur. Hot compressed air is pumped down the innermost pipe, which serves to create foam and pressure. The

resulting molten sulfur foam is then expelled through the middle pipe. The Frasch process produces sulfur with 99.5% purity, which needs no further purification.



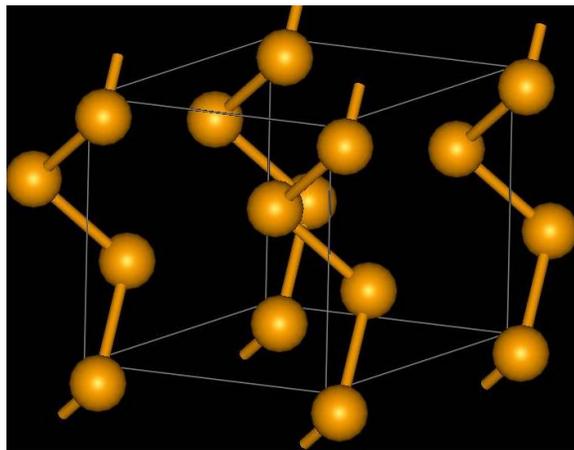
**Figure 9.23:** Schematic diagram of the Frasch process.

Most of the world's sulfur was obtained using the Frasch process until the late 20<sup>th</sup> century, when sulfur recovered from petroleum sources (recovered sulfur) became more commonplace.

### 9.1.2.2 Selenium

Elemental selenium is a rare mineral, and most elemental selenium comes as a byproduct of refining copper or producing sulfuric acid. Isolation of selenium begins by oxidation with sodium carbonate to produce selenium dioxide. The selenium dioxide is then mixed with water and the solution is acidified to form selenous acid (oxidation step). Selenous acid is bubbled with sulfur dioxide (reduction step) to give elemental selenium.

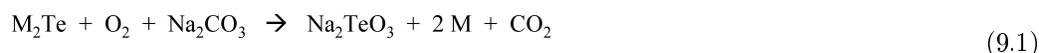
Elemental selenium produced by chemical reactions appears as the amorphous red form. When the red form is rapidly melted, it forms the black, vitreous form. The most thermodynamically stable and dense form of selenium is the electrically conductive gray (trigonal) form, which is composed of long helical chains of selenium atoms (Figure 9.24). The conductivity of this form is notably light sensitive. Selenium also exists in three different deep-red crystalline monoclinic forms, which is composed of  $\text{Se}_8$  molecules, similar to many allotropes of sulfur.



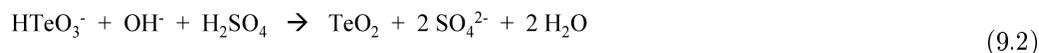
**Figure 9.24:** The structure of trigonal selenium.

### 9.1.2.3 Tellurium

The principal source of tellurium is from anode sludges produced during the electrolytic refining of copper. Treatment of 500 tons of copper ore typically yields 1 lb (0.45 kg) of tellurium. The anode sludges contain the selenides and tellurides of the noble metals in compounds with the formula  $M_2Se$  or  $M_2Te$  ( $M = Cu, Ag, Au$ ). At temperatures of 500 °C the anode sludges are roasted with sodium carbonate ( $Na_2CO_3$ ) under air. The metals are reduced to the metals, while the tellurium is converted to sodium tellurite, (9.1).



Tellurites can be extracted from the mixture with water and are normally present as hydrotellurites  $HTeO_3^-$  in solution. Selenates are also formed during this process, but they can be separated by adding sulfuric acid. The hydrotellurites are converted into the insoluble tellurium dioxide while the selenites stay in solution, (9.2).



The reduction to the metal is done either by electrolysis or by reacting the tellurium dioxide with sulfur dioxide in sulfuric acid, (9.3).



### 9.1.2.4 Physical properties

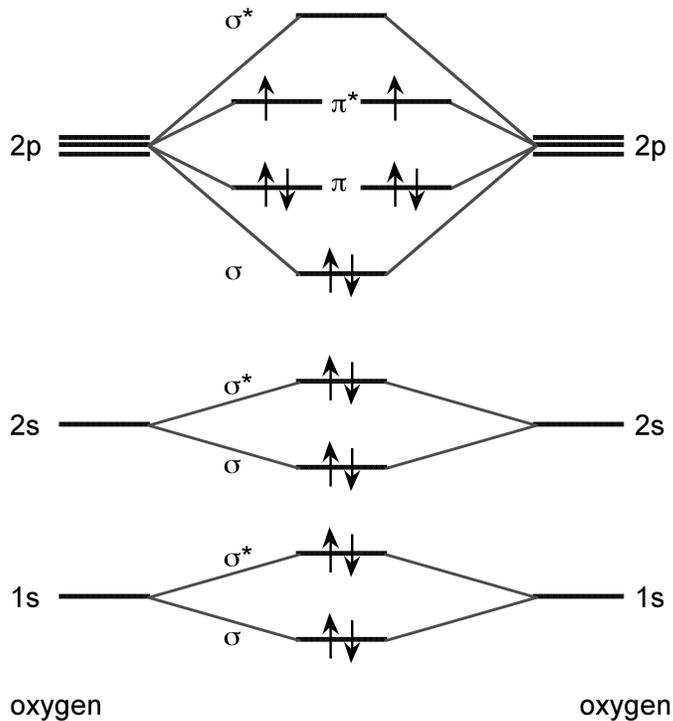
The physical properties of the Group 16 elements encompasses a gas ( $O_2$ ), a non-metallic solid ( $S_2$ ), and metals (Se, Te, Po), Table 9.4.

Element	Mp ( $^{\circ}\text{C}$ )	Bp ( $^{\circ}\text{C}$ )	Density ( $\text{g}/\text{cm}^3$ )
O	-218.79	-182.95	1.429 g/L
S	115.21	444.6	1.819
Se	221	685	4.81 (gray), 4.39 (alpha), 4.28 (vitreous)
Te	449.51	988	6.24 (solid), 5.70 (liquid)
Po	254	962	9.196 (alpha), 9.398 (beta)

**Table 9.4:** Selected physical properties of the Group 16 elements.

### 9.1.2.5 Vapor phase

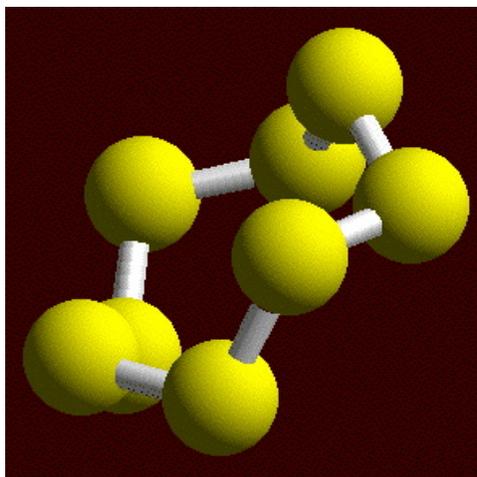
The lighter Group 16 elements form  $\text{X}_2$  dimers in the vapor phase. Sulfur also forms higher allotropes in the vapor phase (e.g.,  $\text{S}_8$  and  $\text{S}_6$ ), while selenium and tellurium forms atomic vapor in addition to the dimmers. Unlike dihydrogen, however, the bonding is associated with the molecular orbital combination of the two  $\pi$ -orbitals (Figure 9.25). All of the dimeric  $\text{X}_2$  molecules are paramagnetic.



**Figure 9.25:** Molecular orbital diagram for the formation of  $\text{O}_2$ .

### 9.1.2.6 Solid state

While sulfur forms over 30 allotropes, the common form of sulfur is cyclooctasulfur ( $S_8$ ) has three main allotropes:  $S_\alpha$ ,  $S_\beta$ , and  $S_\gamma$ . The orthorhombic form ( $S_\alpha$ ) is more stable up to  $95^\circ\text{C}$ , while the  $\beta$ -form is the thermodynamic form. The lone pairs of electrons make the S-S-S bend ( $108^\circ$ ), resulting in  $S_8$  having the shape of a crown (Figure 9.26). When sulfur melts the  $S_8$  molecules break up. When suddenly cooled, long chain molecules are formed in the plastic sulfur that, behave as rubber. Plastic sulfur transform into rhombic sulfur over time.



**Figure 9.26:** The structure of  $S_8$ .

Elemental selenium produced in chemical reactions appears as the amorphous red form. When rapidly melted, it forms the black, vitreous form, which is usually sold industrially as beads. The most thermodynamically stable and dense form of selenium is the electrically conductive gray (trigonal) form, which is composed of long helical chains of selenium atoms (Figure 9.24). The conductivity of gray selenium is light sensitive and is hence used in photocopiers. Selenium also exists in three different deep-red crystalline monoclinic forms, which are composed of  $Se_8$  molecules, similar to many allotropes of sulfur. Unlike sulfur, however, selenium does not undergo the changes in viscosity when heated.

Tellurium is a crystalline metal with a trigonal structure ( $a = 4.4572 \text{ \AA}$ ,  $c = 5.929 \text{ \AA}$ ). Polonium has a simple cubic structure in its  $\alpha$  form ( $a = 3.359 \text{ \AA}$ )

## 9.1.3 Compounds of the Group 16 elements.

The chemistry of the Group 16 elements is dominated by the stability of the -2 oxidation state and the noble gas configuration of the  $X^{2-}$  anion.

### 9.1.3.1 Oxidation state

The electronegativity of oxygen (3.5) results in it having predominantly -2 oxidation state, however, sulfur, selenium and tellurium all form compounds with higher oxidation states, especially with oxygen (Table 9.5).

Element	-2	-1	+4	+6
O	Na <sub>2</sub> O, H <sub>2</sub> O	H <sub>2</sub> O <sub>2</sub>	-	-
S	H <sub>2</sub> S	H <sub>2</sub> S <sub>2</sub>	SO <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub> , SO <sub>3</sub>
Se	H <sub>2</sub> Se	H <sub>2</sub> Se <sub>2</sub>	SeO <sub>2</sub>	SeF <sub>4</sub>
Te	H <sub>2</sub> Te	<sup>t</sup> Bu <sub>2</sub> Te <sub>2</sub>	TeO <sub>2</sub>	Te(OH) <sub>6</sub>

**Table 9.5:** Examples of oxidation states in compounds of the Group 16 elements.

### 9.1.3.2 Catenation

Catenation is the ability of a chemical element to form a long chain-like structure via a series of covalent bonds. Although oxygen shows this property only in the existence of ozone, sulfur is second only to carbon in exhibiting this mode of combination; the chalcogens beyond sulfur show it to diminishing degrees, polonium having no tendency to catenate.

When aqueous metal sulfide salts are heated with elemental sulfur a range of polysulfide ions are formed, (9.4). When alkali polysulfides dissolve in polar solvents (e.g., DMF or DMSO) a deep blue solution is formed. The absorption ( $\lambda_{\text{max}} = 610 \text{ nm}$ ) is associated with the radical anion,  $\text{S}_3^-$ . While, polyselenides and polytellurides are less common, the  $\text{Se}_3^{2-}$  and  $\text{Te}_3^{2-}$  ions are known.



The term *polysulfide* often refers to a class of polymers with alternating chains of several sulfur atoms and hydrocarbon substituents. The general formula is  $\text{R}_2\text{S}_n$ , where  $n$  ranges from 2 – 10. For the selenium and tellurium analogs the extent of catenation is far more limited.

### 9.1.4 Bibliography

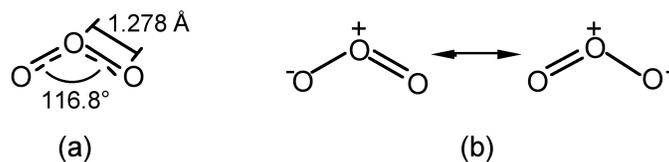
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- M. Davies, *History of Science*, 1989, **22**, 63.
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## 9.2 Ozone<sup>2</sup>

Ozone ( $\text{O}_3$ ) is an allotrope of oxygen that is much less stable than the diatomic molecule ( $\text{O}_2$ ). Ground-level ozone is an air pollutant with harmful effects on the respiratory system, while the ozone layer in the upper atmosphere filters potentially damaging ultraviolet light from reaching the Earth's surface.

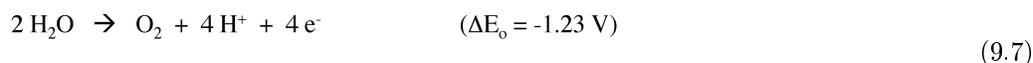
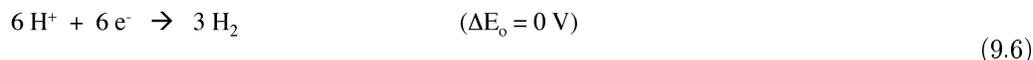
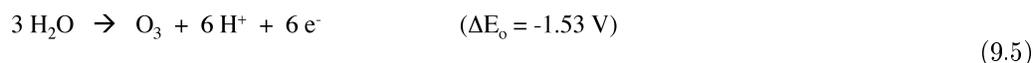
The structure of ozone is bent, with  $\text{C}_{2v}$  symmetry, similar to water (Figure 9.27a). The central oxygen has  $sp^2$  hybridization with one lone pair. As a consequence of the bent structure, and the resonance hybridization (Figure 9.27b) ozone is a polar molecule (dipole moment = 0.5337 D).

<sup>2</sup>This content is available online at <<http://cnx.org/content/m33089/1.2/>>.



**Figure 9.27:** The (a) structural parameters of ozone and (b) its resonance hybridization.

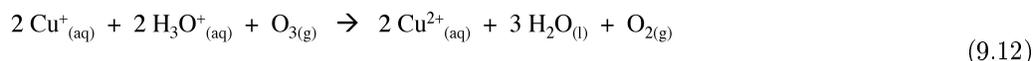
Ozone is made by the exposure of oxygen (O<sub>2</sub>) to an electric discharge. Ozone has a characteristic smell can be commonly smelled after a lightning strike; in fact the name ozone comes from the Greek *ozein* meaning *to smell*. In the laboratory, ozone can also be produced by electrolysis using graphite rod cathode, a platinum wire anode, and sulfuric acid (3 M) electrolyte. The half cell reactions are as follows:



Ozone is also produced through photolysis of oxygen, (9.8) and (9.9), both in the laboratory and the atmosphere.



Ozone is a very strong oxidizing agent, and will readily oxidize a range of materials, e.g., (9.10) and (9.11). It will also oxidize metals (except gold, platinum, and iridium) to their highest oxidation state, e.g., (9.12).



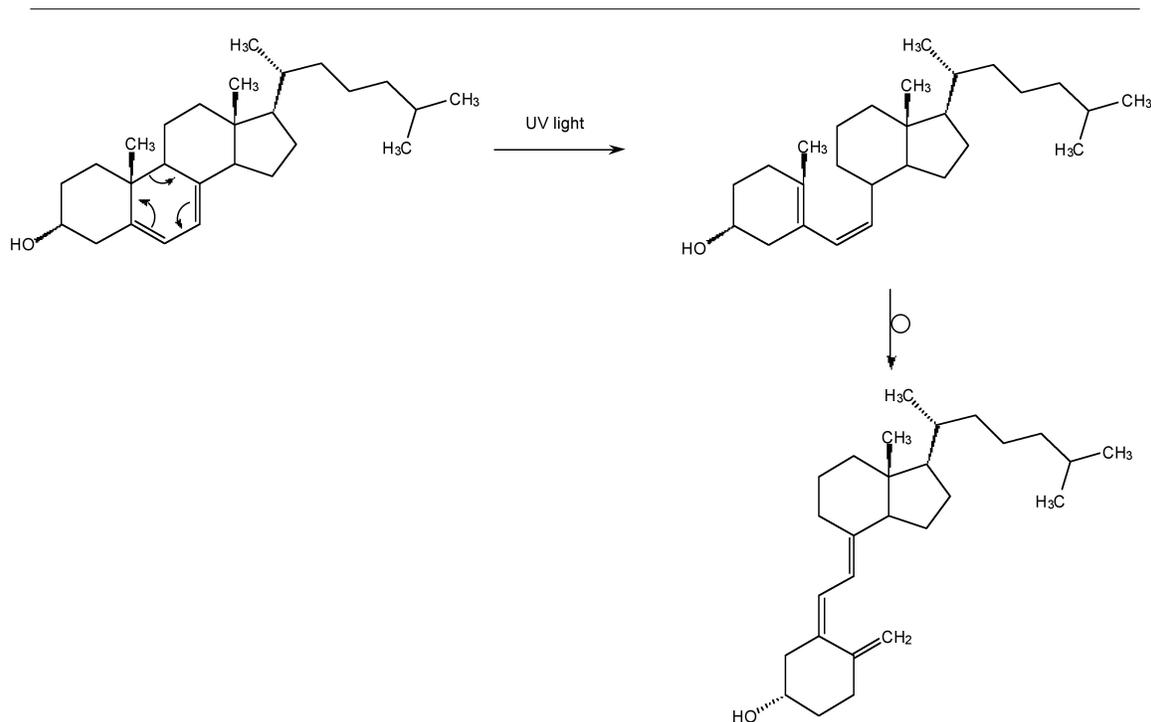
Metal ozanides, which contain the ozonide anion (O<sub>3</sub><sup>-</sup>) are explosive and must be stored at cryogenic temperatures. Ozonides for all the alkali metals are known. KO<sub>3</sub>, RbO<sub>3</sub>, and CsO<sub>3</sub> can be prepared from their respective superoxides.



### 9.2.1 Ozone as a modulator of life on Earth

The Earth's atmosphere acts as a source of  $O_2$  and a repository of  $CO_2$ , but it also acts as a shield for life. First, nearly all meteorites burn up on entry because of the high temperatures generated by the friction of the atmosphere. Second, the atmosphere acts as a shield for high energy UV radiation.

Although UV radiation converts 7-dehydrocholesterol into vitamin D3 in the skin (Figure 9.28), and is therefore useful, high energy UV destroys living cells. In fact the darkening we call a suntan is actually the body's mechanism for preventing further UV damage. Sun burn and skin cancer are caused by relatively weak UV light that reaches the Earth's surface, without the atmosphere we would be exposed to high energy UV that would be a hazard to all life on Earth. The Earth's "sun screen" is ozone ( $O_3$ ). And without ozone in the upper atmosphere there would be no life on Earth.



**Figure 9.28:** The conversion of 7-dehydrocholesterol (a derivative of cholesterol) to pre-vitamin D3 by photolysis by ultraviolet light, and its subsequent isomerization to vitamin D3.

The ozone layer is located in the lower portion of the stratosphere from approximately 10 km to 50 km above Earth, though the thickness varies seasonally and geographically. This layer contains over 91% of the ozone in Earth's atmosphere and absorbs 93-99% of the sun's high frequency ultraviolet light. The ozone decomposes photolytically to  $O_2$  and molecular oxygen, (9.14), and it is this reaction that accounts for the UV protection of the atmosphere. Ozone is naturally regenerated by the exothermic reaction of the molecular oxygen with  $O_2$ , (9.15).

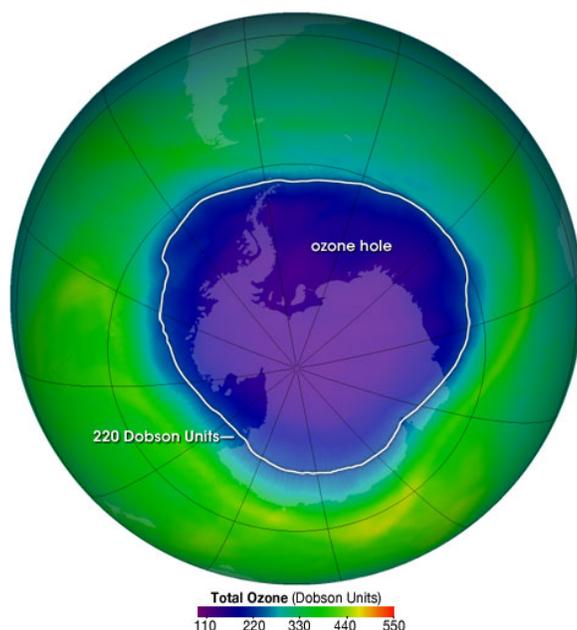




The balance between ozone formation and destruction is thus an important mechanism for the protection of living organisms on the planet. While the ozone layer had been relatively constant on Earth for millions of years, the last 70 have seen a dramatic change including the increase in the polar hole in the ozone layer. The ozone hole is defined geographically as the area where the total ozone concentration is less than 220 Dobson Units.

NOTE: One Dobson unit refers to a layer of ozone that would be  $10 \mu\text{m}$  (micrometre) that is  $1 \times 10^{-5} \text{ m}$  thick under standard temperature ( $25 \text{ }^\circ\text{C}$ ) and pressure (1 atmosphere).

The ozone hole has steadily grown in size and length of existence over the past two and half decades. At present the size of ozone hole over Antarctica is estimated to be about 30 million sq.km (Figure 9.29).



**Figure 9.29:** The concentration profile of ozone over Antarctica.

### 9.3 Water: The Fuel for the Medieval Industrial Revolution<sup>3</sup>

Despite the greatest industrial complex of the Roman Empire being the imperial grain mill at Barbegal near Arles in what is now southern France (Figure 9.30), and the knowledge of gearing used for the mill, the waterwheel (the power source of the Barbegal's power) was little used in the ancient world. This was probably due to the high slave population obviating the need for labor saving devices. However, it may also

<sup>3</sup>This content is available online at <http://cnx.org/content/m33813/1.1/>.

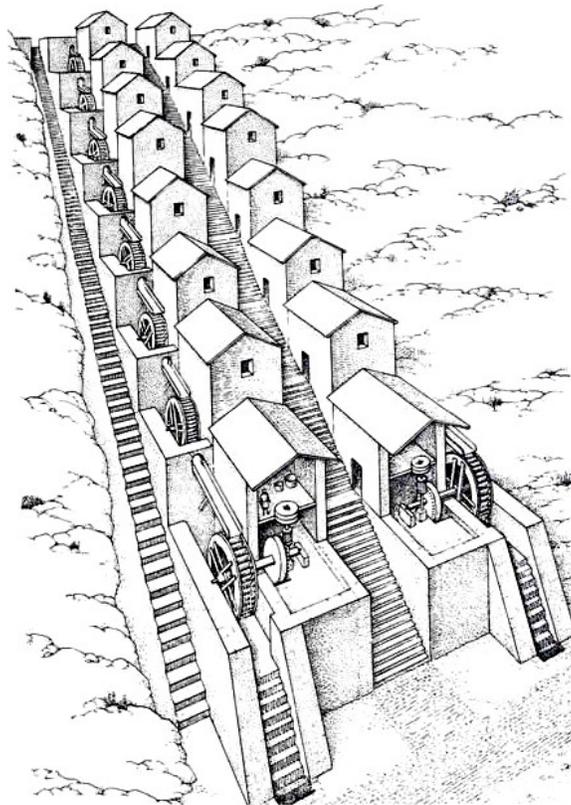
be that because the Roman Empire was very centralized, they could provide flour on a large scale from a few highly mechanized locations. Upon the fall of the Roman Empire, the knowledge of water power would have been lost were it not for the writing departments of churches and monasteries that continued to operate through the subsequent Dark Ages.



**Figure 9.30:** The Barbegal mill as it stands today.

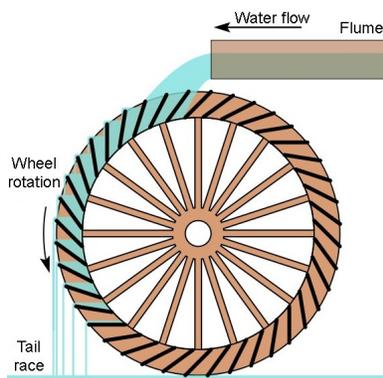
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The Barbegal mill is probably the first example of industrial mass production. It consisted of eight pairs of waterwheels positioned on a 65-foot slope (Figure 9.31). The wheels were turned by water that fell from a reservoir, which in turn was fed by a magnificent aqueduct. The sixteen wheels each powered two grindstones using a set of gear that allowed the horizontal shaft from the wheel to turn a vertical shaft on which the grindstones were positioned. Grain for the mill was imported from as far as Egypt, and the flour production was eight times that required for the local population of 10,000, resulting in an export business. Unfortunately, upon the fall of Rome the technology of waterpower almost ceased since the small city-states set up had no need for industrial complexes.



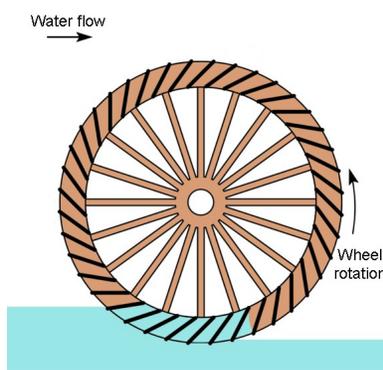
**Figure 9.31:** An artist's representation of the overshot waterwheels that are thought to have driven the 16 mills at Barbegal.

There are two general designs of waterwheel. The first is powered by water falling from above the wheel and is called an overshot wheel (Figure 9.32). The alternative design, the undershot wheel, relied on water flowing on a river or pond such that the current moved the paddles at the bottom of the wheel (Figure 9.33).



**Figure 9.32:** A schematic diagram of an idealized overshot water wheel.

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**Figure 9.33:** A schematic diagram of an idealized undershot water wheel.

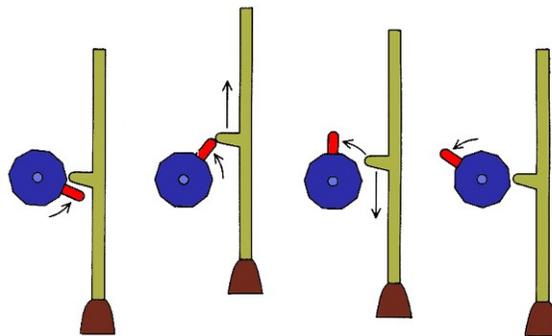
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Despite its fall from use, the waterwheel was not forgotten. Due to the writings of 14<sup>th</sup> century BC engineers, such as Vitruvius (Figure 9.34), whose texts had been preserved in the libraries in churches and monasteries across Europe, the waterwheel powered mills made a resurgence between the fifth and the tenth century. In most cases mills were owned by the church, since they had the knowledge (from ancient texts) to construct the mills and, possibly just as important, the literacy to develop the accounting system for their profitable use. The church would lease mills to farmers on a time usage, and they would take payment in flour. The owners of waterwheels and their mills were the first barons of industry post the Dark Ages. In fact, the fact that the Saxon word for an aristocrat is *Lord*, which means *loaf giver*, suggests the importance of the waterwheel. By the end of the tenth century the waterwheel was in widespread use across Europe. The Domesday Book (the nationwide census carried out by the Normans after the invasion of England) listed nearly six thousand grain mills in 1089.



**Figure 9.34:** A depiction of Vitruvius (right) presenting *De Architectura* to the Emperor Augustus.

Despite the large number of waterwheels, the gearing used up until the ninth century was little different to that described by Vitruvius and used at Barbegal. Then around 890 AD the monastery of St Gall a new device was attached to the waterwheel. Instead of gearing to transfer power from horizontal to vertical rotation, a piece of wood was set into the shaft driven by the waterwheel (Figure 9.35). What had been created was a cam, since as the shaft turns the protruding piece of wood its anything in its way. For example, the first recorded use, by the monks at St Gall, was to crush malt for beer. However, the cam could be made to trip a hammer with every rotation (pounding), or to act on a crank to turn a rotary motion into a horizontal back-and-forward motion (cutting), or to push down a level and activate a suction pump (raising water from a well), or operate a bellows (for a metal forge). The range of motions meant that waterpower could now be used for a wide range of industries. By the end of the tenth century there were waterwheels powering forge hammers, oil and silk mills, sugar cane crusher, tanning mills pounding leather, grinding stones, ore crushing mills (Figure 9.36), and as fulling mills for the rapidly expanding trans-European textile industry.



**Figure 9.35:** Schematic representation of the transformation of rotary motion into linear motion can be achieved by having a cam on the axle of the wheel

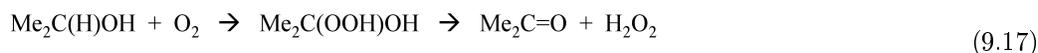
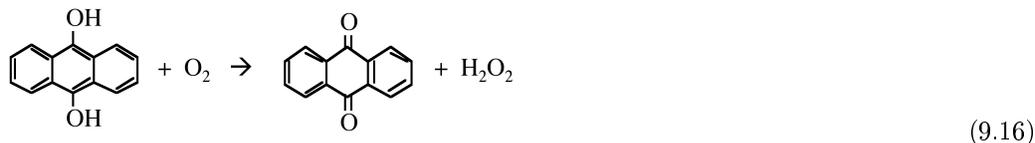


**Figure 9.36:** The cam principle as applied to a rock-crushing mill illustrated by Georgius Agricola in his book *De Re Metallica* (1556).

As a consequence of the waterwheel and the cam, the period between the tenth and fourteenth centuries has come to be known as the Medieval Industrial Revolution. It is interesting to note that water played a key role in the driving force during the next Industrial Revolution four hundred years later – the steam engine.

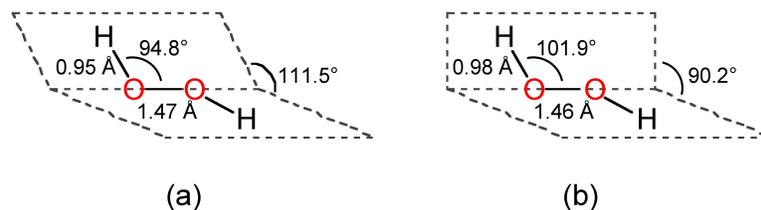
## 9.4 Hydrogen Peroxide<sup>4</sup>

Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is a very pale blue liquid but appears colorless in dilute solution. It is prepared by the oxidation of anthraquinol, e.g., (9.16). The hydrogen peroxide is extracted with water from the anthraquinone solution and the 20 - 40% solution is purified by solvent extraction. An alternative process involves the oxidation of isopropanol in either the vapor or liquid phase at 100 °C and ca. 15 atm, (9.17). The products are separated by fractional distillation.



In the gas phase  $\text{H}_2\text{O}_2$  adopts a gauche conformation (Figure 9.37), but there is only a low barrier to rotation about the O-O bond.

<sup>4</sup>This content is available online at <<http://cnx.org/content/m34995/1.1/>>.



**Figure 9.37:** Structure of hydrogen peroxide in (a) the vapor phase and (b) the solid (crystal) phase.

Hydrogen peroxide is a liquid at standard temperature and pressure (25 °C, 1 atm) due to the presence of strong hydrogen bonding similar to found in water. In fact, the liquid range for  $\text{H}_2\text{O}_2$  (Mp = -0.43 °C, Bp = 150.2 °C) is actually broader than water, and it is slightly more viscous than water. Hydrogen peroxide has a density of 1.44 g/cm<sup>3</sup>, and is 10<sup>6</sup> times less basic than water.

As with water,  $\text{H}_2\text{O}_2$  is a good solvent because of its polar nature and broad liquid temperature range, however, it is dangerous in its pure state due to its facile ( $\Delta H = -99$  kJ/mol) auto decomposition, (9.18), as well as its strong oxidizing nature.



Hydrogen peroxide is usually sold as 3 - 12% solution for home use; however, laboratory and certain industrial applications require 30% solutions.

**WARNING:** Hydrogen peroxide should be stored in a cool, dry, well-ventilated area and away from any flammable or combustible substances. It should be stored in a container composed of non-reactive materials such as stainless steel or glass (other materials including some plastics and aluminum alloys may also be suitable). Because it breaks down quickly when exposed to light, it should be stored in an opaque container, and pharmaceutical formulations typically come in brown bottles that filter out light.

Aqueous solutions are weakly acidic ( $K = 1.5 \times 10^{-12}$ ), (9.19). However, there is no exchange of oxygen atoms between  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}$  in the liquid phase.



As expected hydrogen peroxide is a strong oxidizing agent, (9.20), however, it can also act as a reducing agent, (9.21).



## 9.5 Hydrogen Peroxide Providing a Lift for 007<sup>5</sup>

In the pre-credit sequence of the 1965 film *Thunderball*, James Bond 007 (played by Sean Connery) uses a Jetpack to escape from two gunmen after killing Jacques Bouvar, SPECTRE Agent No. 6 (Figure 9.38).

<sup>5</sup>This content is available online at <<http://cnx.org/content/m34996/1.1/>>.

The Jetpack was also used in the *Thunderball* posters, being the "Look Up" part of the "Look Up! Look Down! Look Out!" tagline (Figure 9.39). The Jetpack returned in 2002 in *Die Another Day* (in which Pierce Brosnan played Bond) in the Q scene that showcased many other classic gadgets from previous Bond films.



**Figure 9.38:** James Bond 007 escaping from gunmen using a Jetpack (Copyright: Eon Productions).

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**Figure 9.39:** Original poster for *Thunderball* (Copyright Danjaq, LLC and Eon Productions).

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The Jetpack was actually a real fully functional device: the Bell Rocket Belt. It was designed for use in the US Army, but was rejected because of its short flying time of 21-22 seconds. Powered by hydrogen peroxide ( $H_2O_2$ ), it could fly about 250 m and reach a maximum altitude of 18 m, going 55 km/h. Despite its impracticality in the real world, the Jetpack made a spectacular debut in *Thunderball*. Although Sean Connery is seen in close-up during the takeoff and landings (Figure 9.40), the main flight was actually piloted by Gordon Yeager (Figure 9.41) and Bill Suitor (Figure 9.42).



**Figure 9.40:** Close-up shot of Sean Connery as James Bond landing the Jetpack. Note that the harness is not correctly attached, indicating this was a set-up shot for the film rather than a real flight. Presumably the crotch strap would have spoiled the lines of his suit. (Copyright: Eon Productions).

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**Figure 9.41:** American pilot Gordon Yeager (1927 – 2005).

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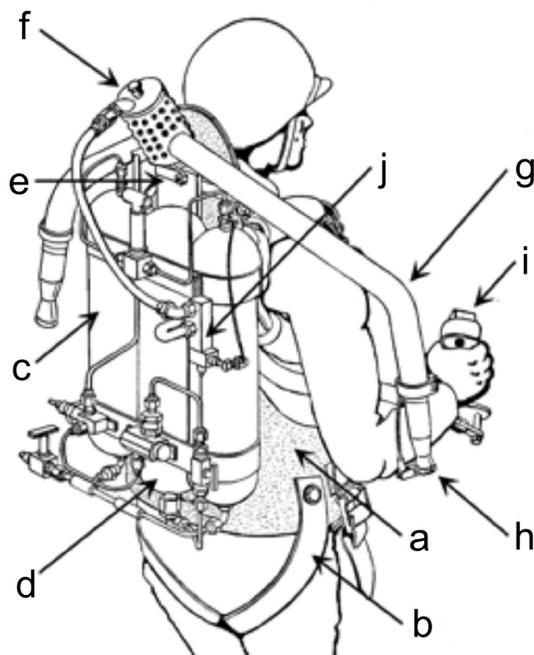


**Figure 9.42:** American rocket pack test pilot Bill Suitor (1944 - ).

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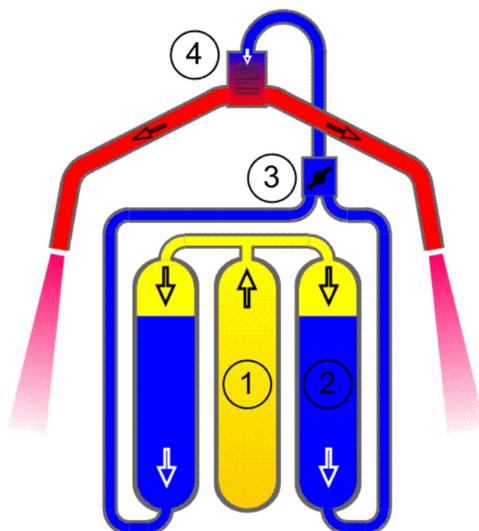
The Bell Rocket Belt is a low-power rocket propulsion device that allows an individual to safely travel or leap over small distances. All subsequent rocket packs were based on the construction design, developed in 1960-1969 by Wendell Moore. Moore's pack has two major parts:

1. Rigid glass-plastic corset (Figure 9.43a), strapped to the pilot (Figure 9.43b). The corset has a tubular metallic frame on the back, on which are fixed three gas cylinders: two with liquid hydrogen peroxide (Figure 9.43c), and one with compressed nitrogen (Figure 9.43d). When the pilot is on the ground, the corset distributes the weight of the pack to the pilot's back.
2. The rocket engine, able to move on a ball and socket joint (Figure 9.43e) in the upper part of the corset. The rocket engine consists of a gas generator (Figure 9.43f) and two pipes (Figure 9.43g) rigidly connected with it, which end with jet nozzles with controlled tips (Figure 9.43h). The engine is rigidly connected to two levers, which are passed under the pilot's hands. Using these levers the pilot inclines the engine forward or back and to the sides. On the right lever is the thrust control turning handle (Figure 9.43i), connected with a cable to the regulator valve (Figure 9.43j) to supply fuel to the engine. On the left lever is the steering handle, which controlled the tips of jet nozzles.



**Figure 9.43:** Diagram of the Bell rocket pack (Adapted from US Patent 3,243,144 (1966)).

The operating principle of the Jetpack is shown in Figure. The hydrogen peroxide cylinders and compressed nitrogen cylinder are each at a pressure of ca. 40 atm or 4 MPa). To operate the pilot turns the engine thrust control handle, and opens the regulator valve (3 in Figure 9.44). Compressed nitrogen (1 in Figure 9.44) displaces liquid hydrogen peroxide (2 in Figure 9.44), which enters the gas generator (4 in Figure 9.44). In the gas generator, the hydrogen peroxide contacts the catalyst and is decomposed. The catalyst consists of thin silver plates, covered with a layer of samarium nitrate. The resulting hot high-pressure mixture of steam and gas enters two pipes, which emerge from the gas generator. These pipes are covered with a layer of heat insulator to reduce loss of heat. The hot gas enters the jet nozzles, where first they are accelerated, and then expand, acquiring supersonic speed and creating reactive thrust. The whole construction is simple and reliable; the rocket engine has no moving parts. The pack has two levers, rigidly connected to the engine installation. Pressing on these levers, the pilot deflects the nozzles back, and the pack flies forward. Accordingly, raising this lever makes the pack move back. It is possible to lean the engine installation to the sides (because of the ball and socket joint) to fly sideways.



**Figure 9.44:** The operating principle of rocket engine.

## 9.6 Comparison of Sulfur to Oxygen<sup>6</sup>

### 9.6.1 Size

Table 9.6 summarizes the comparative sizes of oxygen and sulfur.

Element	Atomic radius (Å)	Covalent radius (Å)	Ionic radius (Å)	van der Waal radius (Å)
Oxygen	0.48	0.66	1.40	1.52
Sulfur	0.88	1.05	1.84	1.80

**Table 9.6:** Comparison of physical characteristics for oxygen and sulfur.

### 9.6.2 Electronegativity

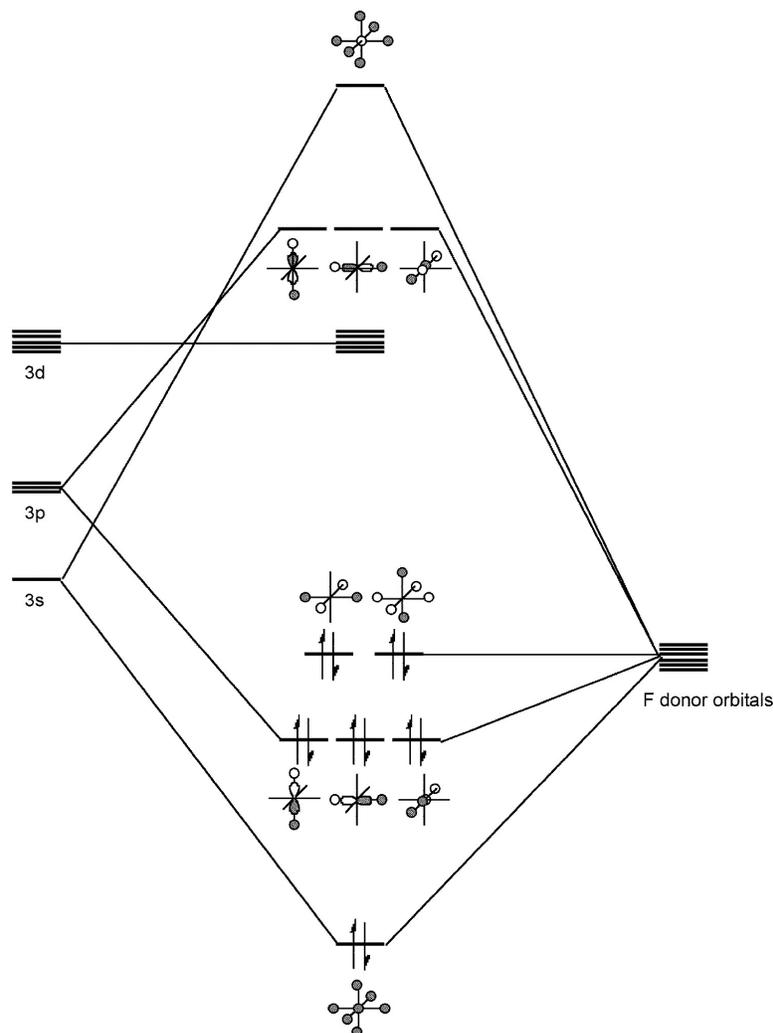
Sulfur is less electronegative than oxygen (2.4 and 3.5, respectively) and as a consequence bonds to sulfur are less polar than the corresponding bonds to oxygen. One significant result in that with a less polar S-H bond the subsequent hydrogen bonding is weaker than observed with O-H analogs. A further consequence of the lower electronegativity is that the S-O bond is polar.

<sup>6</sup>This content is available online at <<http://cnx.org/content/m34977/1.1/>>.

### 9.6.3 Bonds formed

Sulfur forms a range of bonding types. As with oxygen the -2 oxidation state prevalent. For example, sulfur forms analogs of ethers, i.e., thioethers R-S-R. However, unlike oxygen, sulfur can form more than two covalent (non-dative) bonds, i.e., in compounds such as SF<sub>4</sub> and SF<sub>6</sub>.

Such hypervalent compounds were originally thought to be due to the inclusion of low energy *d* orbitals in hybrids (e.g.,  $sp^3d^2$  for SF<sub>6</sub>); however, a better picture involves a combination of *s* and *p* orbitals in bonding (Figure 9.45). Any involvement of the *d* orbitals is limited to the polarization of the *p* orbitals rather than direct hybridization. In this regard SF<sub>6</sub> represents the archetypal hypervalent molecule. Finally, sulfur can form multiple bonds, e.g., Me<sub>2</sub>S=O.

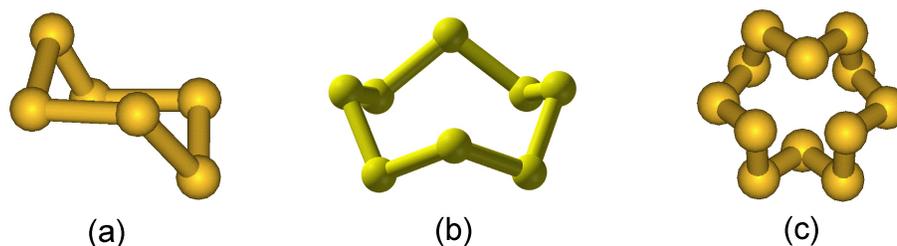


**Figure 9.45:** Molecular orbital diagram for SF<sub>6</sub>.

### 9.6.4 Catenation

Catenation is defined as the ability of a chemical element to form a long chain-like structure via a series of covalent bonds. Oxygen's extent of catenation is limited to ozone ( $O_3$ ) and peroxides (e.g., R-O-O-R). In contrast, the chemistry of sulfur is rich in the formation of multiple S-S bonds.

While elemental sulfur exists as a diatomic molecule (i.e.,  $S_2$ ) in the gas phase at high temperatures, sulfur vapor consists of a mixture of oligomers ( $S_3$  to  $S_8$ ) as a temperature dependant equilibrium. In the solid state the formation of  $S_n$  dominates, and sulfur exists as a range of polymorphs in which extended S-S bonding occurs in either rings of 6 to 20 atoms (e.g., Figure 9.46) or chains (catenasulfur).



**Figure 9.46:** Structures of two polymorphs of sulfur: (a) cyclohexasulfur  $S_6$ , (b) cyclooctasulfur  $S_8$ , and (c) cyclododecasulfur  $S_{12}$ .

The higher level of catenation for sulfur is due to the greater strength of a S-S bond (226 kJ/mol) as compared to the O-O bond (142 kJ/mol). In general the homoleptic bond strength is expected to decrease going down a period of the Periodic Table. The reason for the unexpected weakness of the O-O bond is that the electronegative oxygen atoms repel each other and thus weaken the bond.

## 9.7 Chalconide Hydrides<sup>7</sup>

### 9.7.1 Dihydrides

The hydrides of sulfur, selenium and tellurium are all extremely toxic gases with repulsive smells. Hydrogen sulfide ( $H_2S$ ) is very toxic, in fact it is more than 5x as toxic as HCN (Table 9.7). Hydrogen sulfide is considered a broad-spectrum poison, meaning that it can poison several different systems in the body, although the nervous system is most affected. It forms a complex bond with iron in the mitochondrial cytochrome enzymes, thereby blocking oxygen from binding and stopping cellular respiration. Exposure to low concentrations can result in eye irritation, a sore throat and cough, nausea, shortness of breath, and fluid in the lungs. Long-term, low-level exposure may result in fatigue, loss of appetite, headaches, irritability, poor memory, and dizziness.

Concentration (ppm)	Biological effect
	<i>continued on next page</i>

<sup>7</sup>This content is available online at <<http://cnx.org/content/m34642/1.1/>>.

0.00047	Threshold.
10–20	Borderline concentration for eye irritation.
50–100	Eye damage.
100–150	Olfactory nerve is paralyzed and the sense of smell disappears, often together with awareness of danger.
320–530	Pulmonary edema with the possibility of death.
530–1000	Stimulation of the central nervous system and rapid breathing, leading to loss of breathing.
800	Lethal concentration for 50% of humans for 5 minutes exposure (LC50).
+1000	immediate collapse with loss of breathing, even after inhalation of a single breath.

**Table 9.7:** Toxicity levels for hydrogen sulfide.

Each of the hydrides is prepared by the reaction of acid on a metal chalcogenide, e.g., (9.22) and (9.23). The unstable  $\text{H}_2\text{Po}$  has been prepared by the reaction of  $\text{HCl}$  on  $\text{Po}$  metal.



The thermal stability and bond strength of the dihydrides follows the trend:



While  $\text{H}_2\text{Se}$  is thermodynamically stable to  $280^\circ\text{C}$ ,  $\text{H}_2\text{Te}$  and  $\text{H}_2\text{Po}$  are thermodynamically unstable.

All the dihydrides behave as weak acids in water. Thus, dissolution of  $\text{H}_2\text{S}$  in water results in the formation of the conjugate bases, (9.25) and (9.26), with dissociation constants of  $10^{-7}$  and  $10^{-17}$ , respectively.



### 9.7.2 Sulfanes

The propensity of sulfur for catenation means that while the hydrides of oxygen are limited to water ( $\text{H}_2\text{O}$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), the compounds  $\text{H}_2\text{S}_n$  where  $n = 2 - 6$  may all be isolated. Higher homologs are also known, but only as mixtures. All of the sulfanes are yellow liquids whose viscosity increases with increased chain length.

A mixture of lower sulfanes is prepared by the reaction of sodium sulfides ( $\text{Na}_2\text{S}_n$ ) with  $\text{HCl}$ , (9.27). From this mixture the compounds  $\text{H}_2\text{S}_n$  where  $n = 2 - 5$  are purified by fractional distillation. However, higher sulfanes are made by the reaction of either  $\text{H}_2\text{S}$  or  $\text{H}_2\text{S}_2$  with sulfur chlorides, (9.28) and (9.29).





## 9.8 Oxides and Oxyacids of Sulfur<sup>8</sup>

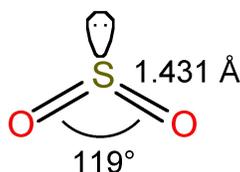
NOTE: Alternative spellings of sulfurous and sulfuric acids are based upon the traditional UK spelling of sulphur, i.e., sulphurous and sulphuric acid.

### 9.8.1 Sulfur dioxide and sulfurous acid solutions

The combustion of sulfur results in the formation of gaseous sulfur dioxide, (9.30).



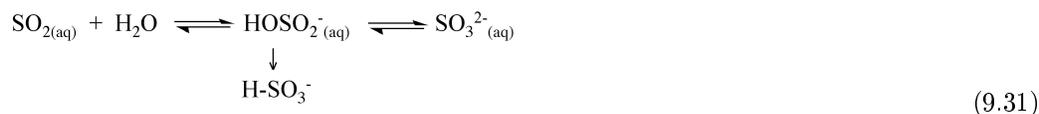
The bent structure of  $\text{SO}_2$  is shown in Figure 9.47, and as a consequence of the  $\text{sp}^2$  hybridization the molecule is polar.



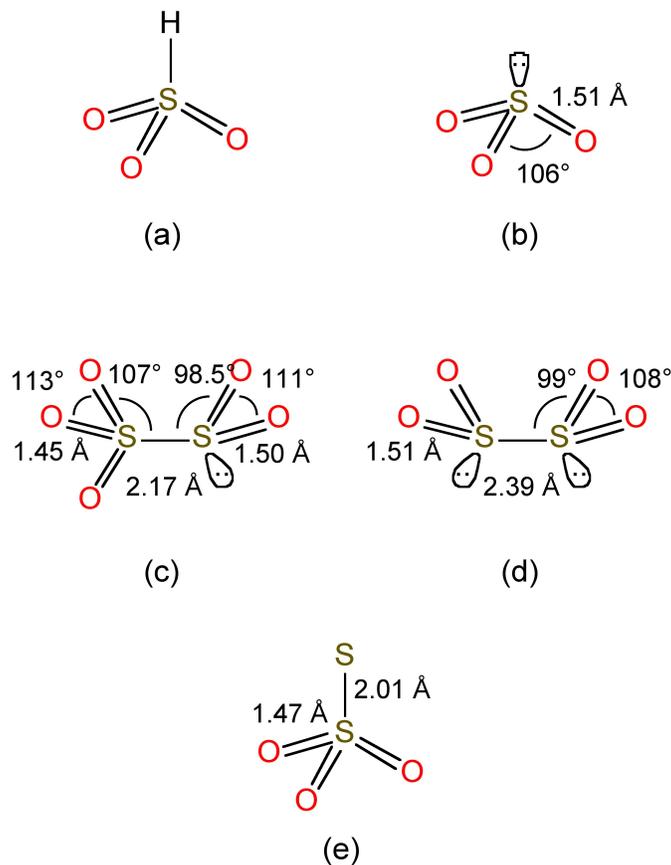
**Figure 9.47:** The structure of sulfur dioxide.

The modest boiling temperature of  $\text{SO}_2$  ( $-10^\circ\text{C}$ ) means that it is readily liquefied and easily kept as a liquid at room temperature under a slight pressure. The liquid is associated by dipole-dipole attractions due to the polar nature of  $\text{SO}_2$ . Liquid  $\text{SO}_2$  is a good solvent due to the polarity of the molecule; as a consequence it readily solubilizes polar compounds and salts. It is also convenient since it is easy to remove from reaction products by evaporation.

Sulfur dioxide is soluble in water forming aqueous solutions where most of the  $\text{SO}_2$  is maintained as a hydrogen-bonded hydrate, in a similar manner to that observed for aqueous solutions of carbon dioxide. At equilibrium in neutral water (no added base) a small fraction reacts, to give a mixture of bisulfite ( $\text{HSO}_3^-$ , Figure 9.48a) and sulfite ( $\text{SO}_3^{2-}$ , Figure 9.48b), (9.31). The free acid does not exist.



<sup>8</sup>This content is available online at <<http://cnx.org/content/m34990/1.1/>>.

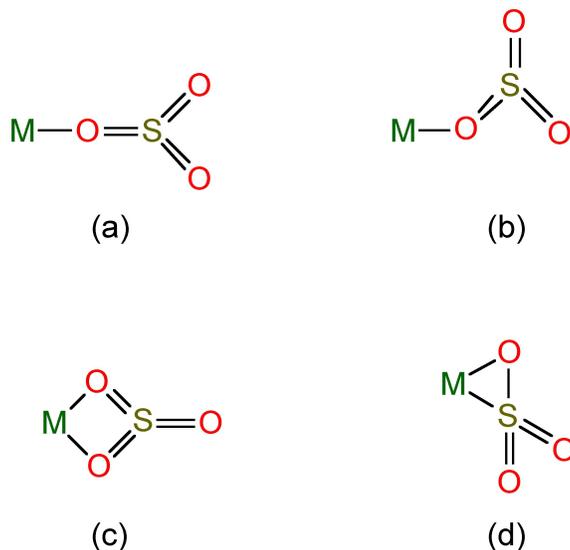


**Figure 9.48:** The structures of the (a) bisulfite, (b) sulfite, (c) disulfite, (d) dithionite, and (e) thiosulfate anions.

Bisulfite undergoes a further equilibrium, (9.32), to form disulfite, whose structure is shown in Figure 9.48c.

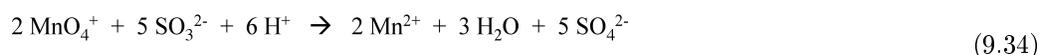
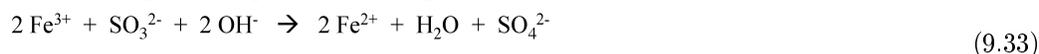


Salts of these anions are known, and complexes of the sulfite ion are known (Figure 9.49), while  $\text{SO}_2$  itself can act as a ligand to heavy metals.



**Figure 9.49:** The structural modes of sulfite coordination.

The bisulfite ion has strong reducing properties, e.g., (9.33) and (9.34).



Bisulfite is also reduced by zinc in the presence of additional  $\text{SO}_2$ , (9.35), to form the highly reducing dithionite anion (Figure 9.48d). Reaction of bisulfite with elemental sulfur yields the thiosulfate anion (Figure 9.48e), (9.36).

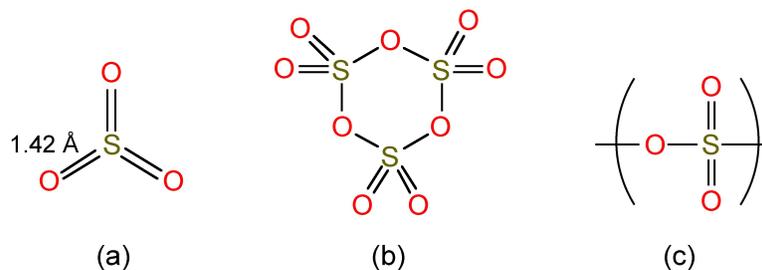


### 9.8.2 Sulfur trioxide and sulfuric acid

Oxidation of sulfur dioxide in the presence of a catalyst (e.g., platinum) yields sulfur trioxide, (9.37), which may be condensed to a liquid at room temperature ( $\text{Bp} = 45^\circ\text{C}$ ).



Liquid  $\text{SO}_3$  exists as a mixture of monomer and trimers (Figure 9.50a and b), while as a solid ( $\text{Mp} = 16.9^\circ\text{C}$ ) it forms polymers (Figure 9.50c).



**Figure 9.50:** The structure of (a) monomeric, (b) trimeric, and (c) polymeric sulfur trioxide.

The reaction of SO<sub>3</sub> with water results in the formation of sulfuric acid, H<sub>2</sub>SO<sub>4</sub>, as a viscous, hydrogen bonded liquid. Sulfuric acid is a strong protic acid, which in dilute solutions (in water) reacts as a dibasic acid, (9.38), forming bisulfate (HSO<sub>4</sub><sup>-</sup>) and sulfate (SO<sub>4</sub><sup>2-</sup>) anions. A large number of salts are known for both anions. In addition, sulfate is known to act as a monodentate or bidentate ligand in coordination complexes.



The dissolution of SO<sub>3</sub> in concentrated sulfuric acid yields very corrosive, *fuming* sulfuric acid, which contains some pyrosulfuric acid, (9.39).



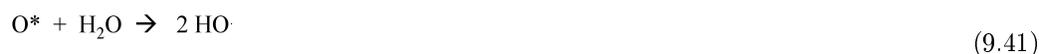
**Warning:** The corrosive properties of sulfuric acid are accentuated by its highly exothermic reaction with water. Burns from sulfuric acid are potentially more serious than those of comparable strong acids (e.g., hydrochloric acid), as there is additional tissue damage due to dehydration and particularly secondary thermal damage due to the heat liberated by the reaction with water.

### 9.8.3 Sulfur as a source of atmospheric pollution and acid rain

Sulfur dioxide is formed as a pollutant during the combustion of sulfur containing fuels, in particular coal. While the emission of SO<sub>2</sub> itself leads to concerns it is its conversion to sulfuric acid in the form of acid rain that has been of concern for several decades. The pathway for the formation of sulfuric acid in the atmosphere is dependant on whether the reaction occurs in dry atmosphere or in clouds and rain.

#### 9.8.3.1 Gaseous reactions in a dry atmosphere

In the dry atmosphere, gaseous sulfur dioxide reacts with the hydroxide radical (formed by the photochemical decomposition of ozone, (9.40) and (9.41)) in the presence of a non-reactive gas molecule such as nitrogen, (9.42). The sulfurous acid, thus formed reacts with oxygen to generate sulfur trioxide, (9.43), which reacts with water to form sulfuric acid, (9.44).

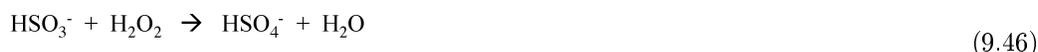
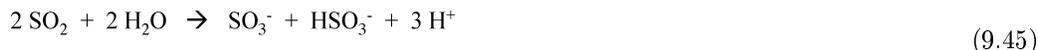




Measurements indicate that the conversion rate of  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$  is 4% per hour on a clear sunny day, but the rate is slower during the winter.

### 9.8.3.2 Liquid phase reactions in clouds and rain

In the liquid phase  $\text{SO}_2$  reacts directly with water, (9.45). The bisulfite ( $\text{HSO}_3^-$ ) is oxidized by hydrogen peroxide forming a forming bisulfate ( $\text{HSO}_4^-$ ) solution, (9.46).



Water soluble hydrogen peroxide is formed by the oxidation of water, (9.47).



The  $\text{HO}_2$  radical is formed by the photolysis of organic carbonyl compounds, e.g., formaldehyde in (9.48) and (9.49).



The conversion rate is independent of pH is very fast: almost 100% per hour in summer. However, the conversion is limited by the supply of hydrogen peroxide, which is often present in much lower levels than  $\text{SO}_2$ . Thus, a reduction in sulfur dioxide emissions does not always correlate with a reduction of wet acid deposition.

## 9.9 Sulfur Halides<sup>9</sup>

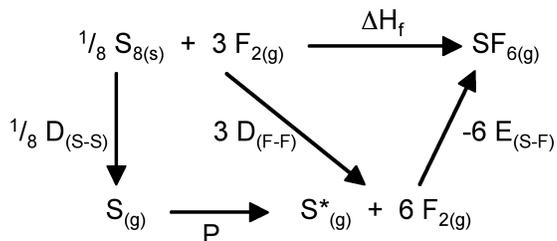
### 9.9.1 Sulfur hexafluoride

Sulfur hexafluoride ( $\text{SF}_6$ ) is a gas at standard temperature and pressure (25 °C, 1 atm). The most common synthesis involves the direct reaction of sulfur with fluorine yields  $\text{SF}_6$ .



It should be noted that while  $\text{SF}_6$  is highly stable,  $\text{SCl}_6$  is not formed. The explanation of this difference may be explained by a consideration of the Born-Haber cycle shown in Figure 9.51. A similar cycle may be calculated for  $\text{SCl}_6$ ; however, a combination of a higher dissociation energy for  $\text{Cl}_2$  and a lower S-Cl bond energy (Table 9.8) provide the rational for why  $\text{SCl}_6$  is not formed.

<sup>9</sup>This content is available online at <<http://cnx.org/content/m34973/1.1/>>.

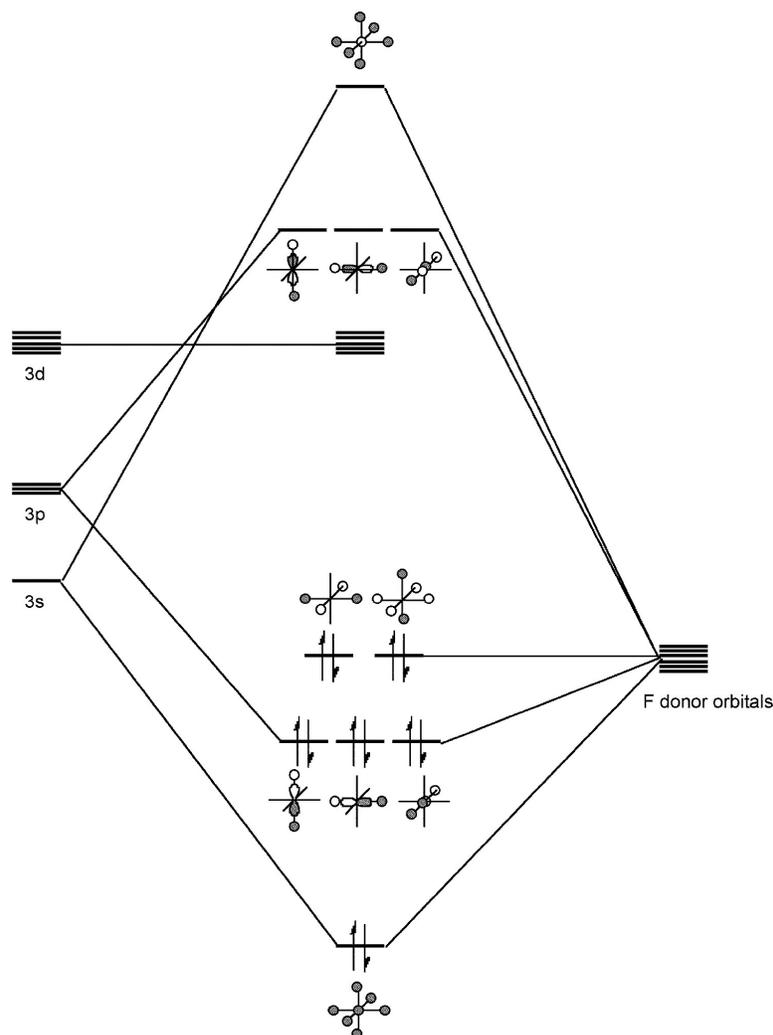


**Figure 9.51:** Born-Haber cycle for the formation ( $\Delta H_f$ ) of  $\text{SF}_6$ : where  $D_{(X-Y)}$  = dissociation energy for X-Y bond,  $E_{(S-F)}$  = S-F bond energy, and  $S^*$  indicates 6 coordinate sulfur.

Bond dissociation energy	kJ/mol	Bond energy	kJ/mol
$D_{(F-F)}$	158	$E_{(S-F)}$	362
$D_{(Cl-Cl)}$	262	$E_{(S-Cl)}$	235

**Table 9.8:** Comparison of diatomic bond dissociation and S-X bond energy for the fluorine and chlorine analogs.

The S-F bond length (1.56 Å) is very short and consistent with  $\pi$ -bonding in addition to  $\sigma$ -bonding. Like  $\text{SiF}_6^{2-}$ ,  $\text{SF}_6$  is an example of a hypervalent molecule (Figure 9.52).



**Figure 9.52:** Molecular orbital bonding in SF<sub>6</sub>.

Sulfur hexafluoride is an unreactive, non toxic compound. Its inert nature provides one of its applications, as a spark suppressor. The hexafluoride is generally resistant to chemical attack, e.g., no reaction is observed with potassium hydroxide (KOH) at 500 °C. The low reactivity is due to SF<sub>6</sub> being kinetically inert due to:

- Coordination saturation precluding associative reactions with nucleophiles.
- Strong S-F bond (360 kJ/mol) limiting dissociative reactions.

Thermodynamically SF<sub>6</sub> should react with water ( $\Delta H = -460$  kJ/mol), but the rate factors are too great. Sulfur hexafluoride can be reduced with sodium in liquid ammonia, (9.51), or with LiAlH<sub>4</sub>. In each of these reactions the mechanism involves the formation of a radical, (9.52). The reaction with sulfur trioxide yields SO<sub>2</sub>F<sub>2</sub>, (9.53), however, the reactions with carbon or CS<sub>2</sub> only occur at elevated temperatures (500 °C) and

pressure (4000 atm).

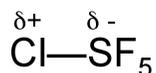


### 9.9.2 Sulfur monochloride pentafluoride

Although the hexachloride is unknown, it is possible to isolate the monochloride derivative ( $\text{SF}_5\text{Cl}$ ) by the oxidative addition of Cl-F across  $\text{SF}_4$ .



Sulfur monochloride pentafluoride is a gas (Bp =  $-21^\circ\text{C}$ ), but unlike  $\text{SF}_6$  it is fairly reactive due to the polarization of the S-Cl bond (Figure 9.53), and as a consequence it reacts with water, (9.55).



**Figure 9.53:** Polarization of the S-Cl bond in  $\text{SF}_5\text{Cl}$ .

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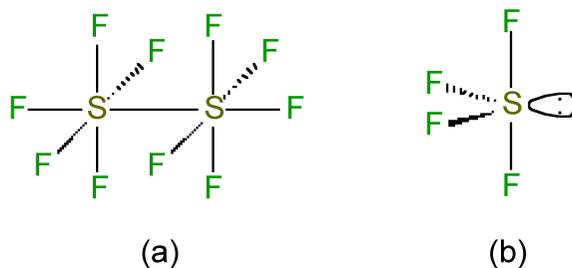
### 9.9.3 Sulfur pentafluoride

Although  $\text{SF}_5$  does not exist as a stable molecule, the gaseous dimer  $\text{S}_2\text{F}_{10}$  (Bp =  $29^\circ\text{C}$ ) may be isolated from the photochemical hydrogen reduction of  $\text{SF}_5\text{Cl}$ , (9.56).



While the sulfur is octahedral in  $\text{S}_2\text{F}_{10}$  (Figure 9.54a) the S-S bond is weak and long ( $2.21 \text{ \AA}$  versus an expected  $2.08 \text{ \AA}$  for a single S-S bond). Despite the apparently weak S-S bond,  $\text{S}_2\text{F}_{10}$  shows almost no reactivity at room temperature; however, the S-S bond undergoes homoleptic cleavage at high temperatures. The resultant  $\text{SF}_5^{\cdot}$  radicals disproportionate to give highly reactive fluoride radicals, (9.57), which is the source of the highly oxidative properties of  $\text{S}_2\text{F}_{10}$ .





**Figure 9.54:** Structures of (a)  $S_2F_{10}$  and (b)  $SF_4$ .

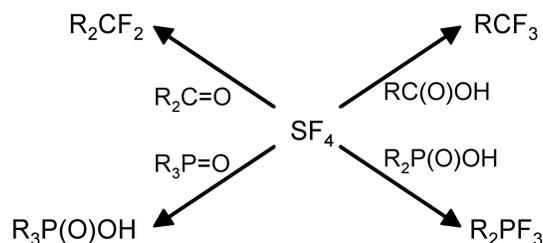
The  $SF_5\cdot$  fragment is stabilized by the addition of an alkyl radical, and thus, there are a large number of  $RSF_5$  derivatives known. Unlike, the chloride analog, these are very stable.

### 9.9.4 Sulfur tetrafluoride

Sulfur tetrafluoride ( $SF_4$ ) is prepared from sulfur dichloride and sodium fluoride in acetonitrile solution at 70 - 80 °C.



The structure of  $SF_4$  (and its substituted derivatives  $RSF_3$ ) is based upon a trigonal bipyramidal structure with one of the equatorial sites being occupied by a lone pair (Figure 9.54b). Unlike the hexafluoride, sulfur tetrachloride is a highly reactive compound. It hydrolyzes readily, (9.59), and is a useful fluorinating agent (Figure 9.55).



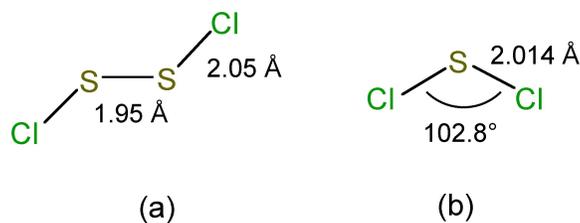
**Figure 9.55:** Examples of the use of  $SF_4$  as a fluorinating agent.

### 9.9.5 Sulfur chlorides

The chlorination of molten sulfur yields the fowl smelling disulfur dichloride ( $S_2Cl_2$ ). If the reaction is carried out with a catalyst such as  $FeCl_3$ ,  $SnI_4$  or  $I_2$ , an equilibrium mixture containing sulfur dichloride ( $SCl_2$ ) is formed. However, the dichloride dissociates readily, (9.60), although it can be isolated as a dark red liquid if it distilled in the presence of  $PCl_5$ . The reaction of chlorine at  $-80\text{ }^\circ\text{C}$  with  $SCl_2$  or  $S_2Cl_2$  allows for the formation of  $SCl_4$  as a yellow crystalline compound which dissociates above  $-31\text{ }^\circ\text{C}$ . Sulfur chlorides are readily hydrolyzed. Sulfur chlorides are used to dissolve sulfur (giving species up to  $S_{100}Cl_2$ ) for the vulcanization of rubber.



In the vapor phase  $S_2Cl_2$  has  $C_2$  symmetry (Figure 9.56a) while that of  $SCl_2$  has  $C_{2v}$  symmetry (Figure 9.56b).



**Figure 9.56:** Structures of (a)  $S_2Cl_2$  and (b)  $SCl_2$ .

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