

12.7: Group VIA- Chalcogens

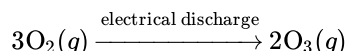
As we approach the right-hand side of the periodic table, similarities among the elements within a group become greater again. This is true of group VIA. Except polonium, which is radioactive and usually omitted from discussion, all members of the group form X^{2-} ions when combined with highly electropositive metals. The tendency to be reduced to the -2 oxidation state decreases significantly from top to bottom of the group, however, and tellurium shows some metallic properties. The group VIA elements are called **chalcogens** because most ores of copper (Greek *chalkos*) are oxides or sulfides, and such ores contain traces of selenium and tellurium. Atomic properties of the chalcogens are summarized in the table.

Table 12.7.1: Properties of the Group VIA Elements

| Element | Symbol | Electron Configuration | Usual Oxidation State | Radius/pm | |
|-----------|--------|--|-----------------------|-----------|--------------------|
| | | | | Covalent | Ionic (X^{2-}) |
| Oxygen | O | [He]2s ² 2p ⁴ | -2 | 66 | 140 |
| Sulfur | S | [Ne]3s ² 3p ⁴ | +6, +4, -2 | 104 | 184 |
| Selenium | Se | [Ar]4s ² 3d ¹⁰ 4p ⁴ | +6, +4, -2 | 117 | 198 |
| Tellurium | Te | [Kr]5s ² 4d ¹⁰ 5p ⁴ | +6, +4, -2 | 135 | 221 |

| Symbol | Ionization Energy/MJ mol ⁻¹ | | | Density/ g cm ⁻³ | Electro-negativity | Melting Point (in °C) |
|--------|--|--------|-------|-----------------------------|--------------------|-----------------------|
| | First | Second | Third | | | |
| O | 1.320 | 3.395 | 5.307 | 1.43×10 ⁻³ | 3.5 | -218 |
| S | 1.006 | 2.257 | 3.367 | 2.06 | 2.5 | 119 |
| Se | 0.947 | 2.051 | 2.980 | 4.82 | 2.4 | 217 |
| Te | 0.876 | 1.800 | 2.704 | 6.25 | 2.1 | 450 |

At ordinary temperatures and pressures, oxygen is a gas. It exists in either of two allotropic forms: O₂, which makes up 21 percent of the earth's atmosphere, or O₃ (ozone), which slowly decomposes to O₂. O₃ can be prepared by passing an electrical discharge through O₂ or air:

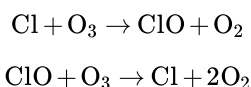


This reaction occurs naturally as a result of lightning bolts. O₃ is also produced by any device which produces electrical sparks. You may have noticed its distinctive odor in the vicinity of an electric motor, for example.

Ozone is formed in the earth's stratosphere (between altitudes of 10 and 50 km) by ultraviolet rays whose wavelengths are shorter than 250 nm:



The ozone itself absorbs longer-wavelength ultraviolet radiation (up to 340 nm), preventing these harmful rays from reaching the earth's surface. Otherwise these rays would increase the incidence of human skin cancer and cause other environmental problems. In recent years convincing evidence has been obtained to show that nitrogen oxide emissions from supersonic transport (SST) airplanes (which fly in the stratosphere) can reduce the concentration of ozone. Similar conclusions have been drawn regarding chlorofluorocarbons (sometimes referred to as CFCs) used as propellants in aerosol hair sprays and deodorants. Once in the atmosphere, a photochemical reaction causes atomic chlorine to be broken off from CFCs. This atomic chlorine can then participate in a catalytic ozone depleting reaction:



Atomic chlorine is regenerated, meaning that each CFC molecule has the potential to deplete large amounts of ozone. In the 1980s, it was determined that use of chemicals such as CFCs were thinning stratospheric ozone. This is also when the "ozone hole" over Antarctica was discovered. In response to the depletion of ozone, and the danger presented by it, the Montreal Protocol on Substances that Deplete the Ozone Layer was signed by leaders of multiple countries, with the goal to phase out production and use of CFCs and other chemicals harmful to the ozone layer. Today, 191 countries have signed the protocol, and while it is projected to take until 2075 for ozone levels to return to normal, the Montreal Protocol has so far proven a success^[1].

O₃ is also an important component of photochemical smog. It is produced when O atoms (formed by breaking N—O bonds in NO₂) react with molecules according to Eq. 12.7.1. O₃ is a stronger oxidizing agent than O₂. It reacts with unsaturated hydrocarbons (alkenes) in evaporated gasoline to produce aldehydes and ketones which are eye irritants. Rubber is a polymeric material which contains C=C bonds, and so it too reacts with O₃. Further, ground level ozone and the accompanying smog has proven a significant health concern, irritating and damaging the respiratory system and also having links to asthma^[2]. So ozone is beneficial when in the upper atmosphere, but has adverse effects when at ground level.

Sulfur occurs in a variety of allotropic forms. At room temperature the most stable form is rhombic sulfur. This yellow solid consists of S₈ molecules (seen in the Jmol below) packed in a crystal lattice which belongs to the orthorhombic system (listed on the page discussing crystal systems).

Figure 12.7.1 S₈ molecule: The initial ball and stick model can be manipulated in three dimensional space. Click on VdW radii to see a space filling model of the same molecule.

When heated to 96°C, solid rhombic sulfur changes very slowly into monoclinic sulfur, in which one-third of the S₈ molecules are randomly oriented in the crystal lattice. When either form of sulfur melts, the liquid is at first pale yellow and flows readily, but above 160°C it becomes increasingly viscous. Only near the boiling point of 444.6°C does it thin out again. This unusual change in viscosity with temperature is attributed to opening of the eight-membered ring of S₈ and formation of long chains of sulfur atoms. These intertwine and prevent the liquid from flowing. This explanation is supported by the fact that if the viscous liquid is cooled rapidly by pouring it into water, the amorphous sulfur produced can be shown experimentally to consist of long chains of sulfur atoms.

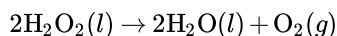
Both selenium and tellurium have solid structures in which the atoms are bonded in long spiral chains. Both are semiconductors, and the electrical conductivity of selenium depends on the intensity of light falling on the element. This property is utilized in selenium photocells, which are often used in photographic exposure meters.

Selenium is also used in rectifiers to convert alternating electrical current to direct current. Compounds of selenium and tellurium are of little commercial importance, and they often are toxic. Moreover, many of them have foul odors, are taken up by the body, and are given off in perspiration and on the breath. These properties have inhibited study of tellurium and selenium compounds.

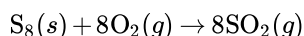
Chemical Reactions and Compounds

Oxygen Since oxygen has the second largest electronegativity among all the elements, it is found in the −2 oxidation state in most compounds. Important oxides have already been discussed in sections dealing with the elements from which they form, and so we will deal only with unusual oxidation states of oxygen here. One of these is the +2 state found in OF₂, the most common compound in which oxygen is combined with the more electronegative fluorine. We have already mentioned the −½ and −1 states observed in alkali-metal superoxides and peroxides, but one important peroxide, hydrogen peroxide (H₂O₂), has not yet been discussed.

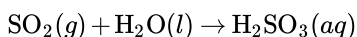
H₂O₂ can be prepared by electrolysis of solutions containing sulfate ions. H₂O₂ is a weak acid, and it can serve as an oxidizing agent (oxygen being reduced to the −2 state) or as a reducing agent (oxygen being oxidized to the 0 state). Like the peroxide ion, the H₂O₂ molecule contains an O—O single bond. This bond is rather weak compared with many other single bonds, and this contributes to the reactivity of H₂O₂. The compound decomposes easily, especially if exposed to light or contaminated with traces of transition metals. The decomposition



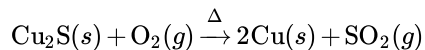
can occur explosively in the case of the pure liquid. **Sulfur** Although this element is only sixteenth in abundance at the surface of the earth, it is one of the few that has been known and used throughout history. Deposits of elemental sulfur are not uncommon, and, because they were stones that would burn, were originally called brimstone. Burning sulfur produces sulfur dioxide,



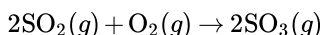
This colorless gas has a choking odor and is more poisonous than carbon monoxide. It is the anhydride of sulfurous acid, a weak diprotic acid:



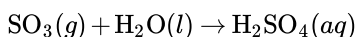
SO₂ is also produced when almost any sulfur-containing substance is burned in air. Coal, for example, usually contains from 1 to 4% sulfur, and so burning coal releases SO₂ to the atmosphere. Many metal ores are sulfides, and when they are heated in air, SO₂ is produced. Copper, for example, may be obtained as the element by heating copper(I) sulfide:



Since SO₂ is so poisonous, its release to the atmosphere is a major pollution problem. Once in the air, SO₂ is slowly oxidized to sulfur trioxide, SO₃:

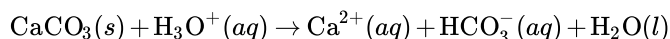


This compound is the anhydride of sulfuric acid, H₂SO₄:



Thus if air is polluted with SO₂ and SO₃, a fine mist of dilute droplets of can form. All three substances are very irritating to the throat and lungs and are responsible for considerable damage to human health.

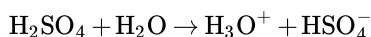
The natural mechanism for removal of sulfur oxides from the air is solution in raindrops, followed by precipitation. This makes the rainwater more acidic than it would otherwise be, and acid rain is now common in industrialized areas of the United States and Europe. Acid rain can slowly dissolve limestone and marble, both of which consist of CaCO₃:



Thus statues and buildings made of these materials may be damaged.

Despite the fact that a tremendous amount of sulfur is released to the environment by coal combustion and ore smelting, this element is not usually recovered from such processes. Instead it is obtained commercially from large deposits along the U.S. Gulf Coast and from refining of sour petroleum. Sour petroleum contains numerous sulfur compounds, including H₂S, which smells like rotten eggs. The deposits of elemental sulfur in Texas and Louisiana are mined by the **Frasch process**. Water at 170°C is pumped down a pipe to melt the sulfur, and the latter is forced to the surface by compressed air. Most of the H₂S or S₈ obtained from these sources is oxidized to SO₂, passed over a vanadium catalyst to make SO₃, and dissolved in water to make H₂SO₄. In 2005 an estimated 190 billion kg of H₂SO₄ was produced in the world, making H₂SO₄ one of the most important industrial chemicals. About half of it is used in phosphate fertilizer production^[3].

Pure H₂SO₄ is a liquid at room temperature and has a great affinity for H₂O. This is apparently due to the reaction:



Formation of H₃O⁺ releases energy, and the reaction is exothermic. Concentrated H₂SO₄ is 93% H₂SO₄ and 7% H₂O by mass, corresponding to more than twice as many H₂SO₄ as H₂O molecules. Since many H₂SO₄ molecules still have protons to donate, concentrated H₂SO₄ also has a great affinity for H₂O. It is often used as a drying agent and can be employed in condensation reactions which give off H₂O.

1. ↑ "Montreal Protocol-One Page Factsheet." Environmental Protection Agency. 6 September 2007.
http://www.epa.gov/ozone/downloads/MP20_FactSheet.pdf
2. ↑ Kenneth Olden. "Statement on Health Effects of Air Pollution before the Senate Committee on Health, Education, Labor and Pensions, Subcommittee on Health. Department of Health and Human Services. 3 September 2003.
www.hhs.gov/asl/testify/t020903.html
3. ↑ Bala Suresh and Yoshio Inoguchi. "Sulfuric Acid". SRI Consulting. July 2006.
<http://www.sriconsulting.com/CEH/Pub...orts/781.5000/>

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