

12.7.1: Cultural Connections- Sulfur

Hernan Cortes (1485-1547) was a Spanish conquistador who was responsible for the fall of the Aztec empire. In 1518, Cortes left with a fleet of 11 ships and 500 men to explore and secure inner Mexico for Spain. Cortes entered Aztec territory and was peacefully received by the emperor Moctezuma II. Moctezuma offered the Spaniards gold and took them into the



Figure 1. Hernan Cortes

heart of the city. This enticed the Spanish even more to take over the territory for what they believed was vast quantities of gold. Many battles took place with the Aztecs, and over time Cortes needed more gun powder for his army. Spain, being across the ocean, would not be a quick source that he needed to win this war. As a result, he had his men make the gun powder. The main ingredients of gunpowder are Carbon and Sulfur. Carbon was easy to come by, but Sulfur was not. Cortes sent an expedition of men on a treacherous mission to the top of Popocatepetl, an active volcano. Volcanoes are a good source of sulfur because they emit sulfur dioxide.

Sulfur has many similarities with the elements in its group. This group is 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.

Properties of the Group VIA Elements

Table 1.

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

Table 2.

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

Sulfur occurs in a variety of allotropic forms. At room temperature the most stable form is rhombic sulfur. This yellow solid consists of S_8 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 1 S_8 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 S_8 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 S_8 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.

Chemical Reactions and Compounds

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,

$S_8(s) + 8O_2(g) \rightarrow 8SO_2(g)$ This colorless gas has a choking odor and is more poisonous than carbon monoxide. It is the anhydride of sulfuric acid, a weak diprotic acid: $SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$ SO_2 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 SO_2 to the atmosphere. Many metal ores are sulfides, and when they are heated in air, SO_2 is produced. Copper, for example, may be obtained as the element by heating copper(I) sulfide: $Cu_2S(s) + O_2(g) \xrightarrow{\Delta} 2Cu(s) + SO_2(g)$ Since SO_2 is so poisonous, its release to the atmosphere is a major pollution problem. Once in the air, SO_2 is slowly oxidized to sulfur trioxide, SO_3 : $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ This compound is the anhydride of sulfuric acid, H_2SO_4 : $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$ Thus if air is polluted with SO_2 and SO_3 , 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 $CaCO_3$:

$CaCO_3(s) + H_3O^+(aq) \rightarrow Ca^{2+}(aq) + HCO_3^-(aq) + H_2O(l)$ 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 H_2S , 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 H_2S or S_8 obtained from these sources is oxidized to SO_2 , passed over a vanadium catalyst to make SO_3 , and dissolved in water to make H_2SO_4 . In 2005 an estimated 190 billion kg of H_2SO_4 was produced in the world, making H_2SO_4 one of the most important industrial chemicals. About half of it is used in phosphate fertilizer production^[1].

Pure H_2SO_4 is a liquid at room temperature and has a great affinity for H_2O . This is apparently due to the reaction

$\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HSO}_4^-$ Formation of H_3O^+ releases energy, and the reaction is exothermic. Concentrated H_2SO_4 is 93% H_2SO_4 and 7% H_2O by mass, corresponding to more than twice as many H_2SO_4 as H_2O molecules. Since many H_2SO_4 molecules still have protons to donate, concentrated H_2SO_4 also has a great affinity for H_2O . It is often used as a drying agent and can be employed in condensation reactions which give off H_2O .

References

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