Group VI

The elements of Group VI are:

	symbol	electron configuration
oxygen	O	$[He]2s^2 2p^4$
sulphur	S	$[Ne]3s^2 3p^4$
selenium	Se	$[Ar]3d^{10} 4s^2 4p^4$
tellurium	Te	$[Kr]4d^{10} 5s^2 5p^4$
polonium	Po	$[Xe]4f^{14} 5d^{10} 6s^2 6p^4$

Appearance

The first element of this Group, oxygen, is the only gas, and is colourless and odour-less. Sulphur is a pale yellow, brittle solid. Selenium can have either an amorphous or a crystalline structure; the amorphous form can be red or black, and the crystalline form can be red or grey. Tellurium is a silvery-white colour with a metallic lustre. Polonium is a naturally radioactive element.

Selenium and tellurium are rare elements with few uses, and along with polonium will not be considered further here.

General Reactivity

Oxygen and sulphur are highly electronegative elements - the electronegativity of oxygen is second only to that of fluorine. Their general reactivity is therefore dominated by their ability to gain electrons.

There is a transition down the Group from non-metallic to more metallic properties, so that oxygen is a non-metal and tellurium a metalloid. All the elements except polonium form M^{2-} ions.

There is a marked difference between oxygen and the other members of the Group. This arises from

(a) the small size of the O atom which enables it to form multiple bonds

(b) its inability to expand its valence shell like the other elements as it has no accessible d-orbitals

(c) its high electronegativity, which enables it to participate in hydrogen-bonding.

Occurrence and Extraction

Oxygen occurs widely as the free element in the form of O_2, comprising 21% of the air by volume. It also occurs as O_3, ozone, at high altitudes in the ozone layer. In the combined form it is found in very many minerals, and also in water. Oxygen is obtained industrially by the fractional distillation of liquid air. It is stored under pressure in cylinders.

Sulphur is found as the free element and also as metal sulphide ores and a number of sulphates. Native sulphur is brought to the surface from underground deposits by the Frasch Process, which uses superheated water to melt the sulphur and force it upwards.

Physical Properties

The covalent and ionic radii increase going down the Group, as electrons occupy shells with higher quantum numbers.

Oxygen occurs as 2 gaseous allotropes, O_2 (dioxygen or more commonly oxygen) and O_3 (trioxygen or ozone). Oxygen is the more common. It condenses to a pale blue liquid at -183°C which is paramagnetic. Ozone is a pale blue, pungent gas which condenses to an inky-blue liquid at -112°C. The ozone layer in the upper atmosphere is an important shield against harmful ultra-violet radiation from the sun.

Sulphur has several allotropes, the 2 main ones being rhombic and monoclinic sulphur. These both consist of S_8 molecules.

Chemical Properties

Oxygen is a very reactive oxidising agent, principally in combustion and respiration reactions. Ozone is also a highly reactive and powerful oxidising agent which can cleave the C=C double bond.

Sulphur is reactive in all its forms. It burns in oxygen with a blue flame to form sulphur dioxide, SO_2, a pungent, choking gas. With elements of lower reactivity it acts as an oxldising agent and forms sulphides - this reaction can be vigorous with some metals, especially if the metal is finely divided. Sulphur is not as strong an oxidising agent as oxygen.

Oxides

The most important oxides of sulphur are sulphur dioxide, SO_2, and sulphur trioxide, SO_3. SO_2 forms when sulphur is burnt in air or oxygen, and as all fossil fuels contain sulphur it is formed when they burn and contributes to the problem of acid rain. It is a colourless, toxic, pungent gas and dissloves in water to give sulphurous acid, H_2SO_3. The salts of this acid contain the sulphite ion, SO_3^{2-}. This ion has an important oxidising reaction to the thiosulphate ion, $S_2O_3^{2-}$, which is used for the titrimetric determination of iodine.

Sulphur trioxide is a volatile white solid that reacts violently with water.

Pure sulphuric acid, H_2SO_4, is a colourless, viscous liquid. It is a chemically important reagent as it behaves as an acid, an oxidising reagent and a dehydrating agent. It is also cheap, so is widely used in industry.

Halides

The only halide of oxygen is oxygen difluoride, OF_2, which is a colourless, toxic gas.

Sulphur has numerous halides, the most important being sulphur hexafluoride, SF_6, and disulphur dichloride, S_2Cl_2.

Compounds with hydrogen

The most important of these is water, H_2O, one of the most versatile of chemicals. It can act as a Bronsted acid or base, a Lewis base, an oxidising agent and a reducing agent.

Hydrogen peroxide, H_2O_2, is a pale blue liquid resembling water in its physical properties as both are extensively hydrogen-bonded. It has a strong oxidising ability and this makes it useful industrially.

Hydrogen sulphide, H_2S, is commonly known as “bad egg gas” because of its smell. It dissolves readily to form a weakly acidic solution, and is a strong reducing agent.

Oxidation States and Electron Affinities

The oxidation number of oxygen in its compounds is almost always -2. The oxidation numbers of sulphur range from -2 to +6, but the most common are -2, +4 and +6. This wide range is partly due to sulphur’s ability to accommodate extra electrons in its valence shell by using available d-orbitals.

The 1st electron affinity (electron gain) is exothermic, but the 2nd is strongly endothermic and so overall the formation of O^{2-} is endothermic. This is usually compensated by a high lattice enthalpy. Remember that electron affinities are quoted as -E kJ mol^{-1}.

Industrial Information

Sulphuric acid is of immense industrial importance. Because it has three chemical functions and is very cheap to produce, sulphuric acid is used at some stage of the manufacture of most products. It is said that the economic prosperity of a country can be assessed by its consumption of sulphuric acid. It is manufactured by the Contact Process.

Hydrogen peroxide is used to bleach hair and textiles, as a mild disinfectant and in pollution control.

Sulphur hexafluonde can be ionized by electric fields and so is widely used as a gaseous insulator in transformers and electrical switch gear.

Further Information

For further information look up the individual elements.

Data

	Atomic Number	Relative Atomic Mass	Melting Point/K	Density/kg m^{-3}
O	8	15.9994	54.8	1.429
S	16	32.066	386	2070
Se	34	78.96	490	4790
Te	52	127.60	722.7	6240

Electron Affinity/kJ mol^{-1}

$O \rightarrow O^-$	+141
$O^- \rightarrow O^{2-}$	-703
$S \rightarrow S^-$	+200.4
$S^- \rightarrow S^{2-}$	-694

Ionisation Energies/kJ mol^{-1}

	1st	2nd	3rd	4th
O	1313.9	3388.2	5300.3	7469.1
S	999.6	2251	3361	4564
Se	940.9	2044	2974	4144
Te	869.2	1795	2698	3610

	5th	6th	7th
O	10989.3	13326.2	71333.3
S	7013	8495	27106
Se	6590	7883	14990
Te	5668	6822	13200

	Atomic Radius/nm	Covalent Radius/nm	Ionic Radius/nm (M^{2-})
O	0.0604	0.066	0.138
S	0.1035	0.104	0.184
Se	0.116	0.117	0.198
Te	0.1432	0.137	0.221