Inorganic Chemistry
Lesson 13
Chalcogens, or oxygen family

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1 Sulfur

The major difference between oxygen and sulfur is that the former has is an extremely low boiling temberature, and is a gas at normal conditions, whereas the latter is a yellow low melting solid insoluble in water. It is solid because, in contrast to oxygen, sulfur atoms do not like to form double bonds with each other[1], and, since sulfur in a free form is divalent, like oxygen, it forms large circular molecules S_8, where each atom of sulfur is connected with other two, and they form an eight member ring.

If we compare chemical properties of oxygen and sulfur, we find some important similarities. Thus, both elements form hydrides (H_2O and H_2S). Hydrogen sulfide is a gas with a very strong unpleasant odor. It is a veak acid, and it reacts with very active metals, for example, sodium:

$$2\,\mathrm{Na} + 2\,\mathrm{H_2S} \longrightarrow \mathrm{NaSH} + \mathrm{H_2} \tag{1}$$

in the same way water reacts with sodium:

$$2\,\mathrm{Na} + 2\,\mathrm{H_2O} \longrightarrow \mathrm{NaOH} + \mathrm{H_2} \tag{2}$$

The compound NaSH is called "sodium hydrosulfide", by analogy with sodium hydroxide (NaOH). Reactions of sulfur with sodium, calcium, zinc, and even iron powder yield sulfides, which look like oxides of the same metal.

$$2\,\mathrm{Na} + \mathrm{S} \longrightarrow \mathrm{Na_2S} \tag{3}$$

$$\mathrm{Ca} + \mathrm{S} \longrightarrow \mathrm{CaS} \tag{4}$$

$$\mathrm{Zn} + \mathrm{S} \longrightarrow \mathrm{ZnS} \tag{5}$$

[1]This is a general rule: bigger and heavier atoms prefer to form single bonds with light atoms, whereas light atoms love to form double and even triple bonds when possuble.

$$Fe + S \longrightarrow FeS \tag{6}$$

These reactions are very violent, and they remind similar reactions with oxygen, e.g.:

$$Ca + O \longrightarrow CaO \tag{7}$$

Obviously, in these reactions the metals are being oxidized, which means sulfur is an oxidizer (in other words, it plays the role of oxygen in these reactions). Sometimes, the reactions between sulfur and metals are even more violent than the reactions of the same metal and oxygen. Thar occurs for two reasons. Firstly, since sulfur is a solid (a liquid at elevated temperature)rraction is larger than the amount of oxugen atoms, which makes the reaction faster. Secondly, many sulfides do not form a solid film that protect a metal from further reaction. As a result, such a metal as aluminium vigorously reacts with sulfur:

$$2\,Al + 3\,S \longrightarrow Al_2S_3 \tag{8}$$

whereas its seems inert towards oxygen (actually, it oxidizes instantly when it comes in a contact with oxygen, however, a thin film of aluminium oxide Al_2O_3 is very dense and hard, so aluminium doesn't burn in oxygen.

Sulfides of some metals, such as sodium or calcium, are soluble in water, and, being salts, they participate in exchange reactions, such as:

$$Na_2S + H_2SO_4 \longrightarrow H_2S + Na_2SO_4 \tag{9}$$

Although sulfur is an oxidizer, it is a less strong oxidizer than oxygen. As we already know, oxygen oxidizes sulfur: it burns in oxygen yielding sulfur dioxide:

$$S + O_2 \longrightarrow SO_2 \tag{10}$$

This oxide is a gas with a strong and unpleasant odor (an odor of burning matches). Sulfur dioxide is an acidic oxide, it reacts with water, and a moderate sulfurous acid forms as a result:

$$SO_2 + H_2O \rightleftharpoons H_2SO_3 \tag{11}$$

This reaction is reversible, which means it is impossible to make a concentrated sulfurous acid, because it slowly decomposes back onto the dioxide (SO_2) and water.

Sulfur dioxide can be oxidized further at elevated temperature and in the presence of some catalysts. The product of this reaction is sulfur trioxide:

$$SO_2 + O_2 \longrightarrow SO_3 \tag{12}$$

Sulfur trioxide is a liqud that reacts with water explosively. The propduct of this reaction is a sulfuric acid:

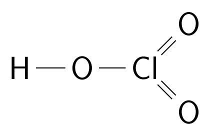
$$SO_3 + H_2O \longrightarrow H_2SO_4 \tag{13}$$

We are already familiar with this acid, which is one of the most common and most important product of chemical industry. It is a strong acid. 100% acid (anhydrous), is a viscous liquid high density liquid. It avidly absorbs water from atmosphere, so an open glass with sulfuric becomes heavier upon standing. Due to its high affinity towards water, sulfuric acid reacts with many organic materials, including sugar, paper, or wood and converts them into carbon. That makes sulfurin acid especially dangerous, because it is corrosive not only due to its acidity, but also because it destroys organic materials causing their dehydration. An video with this reaction is available online: `https://www.youtube.com/watch?v=xK4z_YhtTBM`.

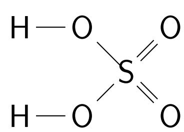
Salts of sulfuric acid are called sulfates.

1.1 Sulfates and acid salts

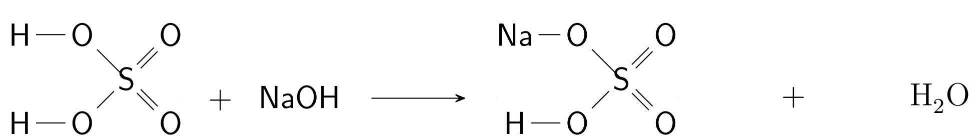
As we already know, acids are the compounds that can donate a hydrogen in a reaction with metals (left of hydrogen in a reactivity series) or with bases. Depending on the acid type, they can donate either one or several hydrogens. Thus, a chloric acid has just one hydrogen atom it can donate:



In contrast, sulfuric acid has two acidic hydrogens:



We know each hydrogen atom in sulfuric or similar acid can be substituted with a metal atom, however, is it an "all-or-nothing" process, or such a substitution can be performed stepwise? Let's imagine we took two water solutions. One solution (solution A) contains 40 grams of sodium hydroxide (NaOH), another solution (solution B) contains 98 grams of sulfuric acid (H_2SO_4). Note that the mass of sodium hydroxide in the solution A and the mass of sulfuric acid in a solution B are numerically equal to the masses of one NaOH and H_2SO_4 molecules (40 Da and 98 Da, accordingly). That means the number of NaOH molecules in a solution A is equal to the number of H_2SO_4 molecules in a solution B. What will happen when we mix these solutions together? Clearly, the amount of NaOH molecules is not sufficient to substitute all hydrogen atoms in the sulfuric acid. In our case, the reaction goes according to the following equation:

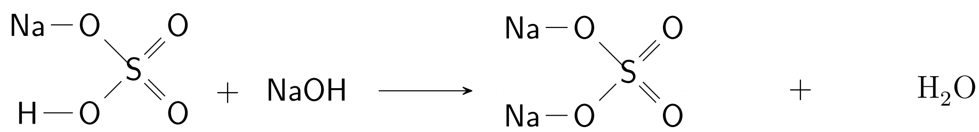


Sulfuric acid ???

As we can see, the product of this reaction can simultaneously be considered a salt (it contains a metal atom and an acidic residue) and an acid (the molecule still contains a hydroxide atom that can be substituted is a reaction with a base or a metal). That type compounds are called *acid salts*.

Acid salts are the salts having at least one active (replaceable) hydrogen.

The fact that active hydrogen is still present in the acid salts, a prefix “hydro” is added to its name. For example, the above acid salt ($NaHSO_4$) is called “sodium *hydro*sulfate”.[2] Acid salts inherit some properties of acids. Thus, sodium hydrosulfate is capable of reacting with one more molecule of sodium hydroxide to produce sodium sulfate and water:



Sodium hydrosulfate Sodium sulfate

The acid salt everybody is familiar with is a baking soda (aka sodium hydrocarbonate, aka sodium bicarbonate). Its formula is $NaHCO_3$, and it contains one carbonate residue per one sodium atom (as opposed to 1/2 carbonate residue per one sodium in Na_2CO_3).

Important! The term “acid salt” is somewhat misleading: acid salts are not necessarily acidic. Thus, whereas a sodium hydrosulfate solution is acidic (according to a pH paper), a baking soda solution is not. We will discuss that in more details next year.

1.2 Chalcogens, or oxygen family

Besides sulfur, there are two other elements that behave similarly. These elements (we are not familiar with them yet) are called **Selenium (Se)** and **Tellurium (Te)**. Since they have common properties, all of them are found in sulfur containing ores, especially in copper ores. The Greek name of copper is *chalkos*, hence the common name for this group ***Chalcogens***.

Their common properties of chalcogen compounds can be summarized in the Table 2.

Table 2. Chalcogen hydrides and oxo acids

Valence	S	Se	Te	Generalized formula
Hydride	H_2S	H_2Se	H_2Te	H_2X
IV	H_2SO_3	H_2SeO_3	H_2TeO_3	H_2XO_3
VI	H_2SO_4	H_2SeO_4	H_2TeO_4 (H_6TeO_6)	H_2XO_4

[2]Sometimes, a prefix “bi” is used instead of the prefix “hydro”, so the alternative name of sodium hydrosulfate is “sodium *bi*sulfate”, because such a salt contains two times more acidic residue per one metal atom as compared with ordinary salts.

2 General properties of chalcogens

The properties of chalcogens can be summarized using the same approach as we already used for halogens.

1. All chalcogens form binary compounds with metals. Chalcogen's valence in these compounds is ***always equal to two.***

   Examples: Na_2S, Al_2Se_3, CaO.

2. Metal chalcogenides are salts (except oxides). The same rule as the one we devepoled for halogenides works for chalcogenides too: if one chalcogeniide (e.g. sodium silfide) is soluble in water, sodium selenide ot telluride will be soluble too. Accordingly, if silver selenide is insoluble, silver sulfide or telluride is insoluble too. **Examples:** CuO is insoluble in water; CuS and CuSe are insoluble too.

3. All chalcogens form binary compounds with hydrogen with a general formula H_2X, where X is chalcogen. All these compounds (except H_2O) are acids. Their acidity is low, but, similar to halogen hydrides, ***acidity of hydrogen chalcogenides increases with the increase of chalcogen's atomic mass:*** thus, H_2Se is more acidic than H_2S.

4. All chalcogens (except oxygen) form binary compounds with oxygen (obviously, oxygen cannot form an oxide with itself). Sulfure, selenium and tellurium form two type oxides, where their valence is either four or six. Accordingly, these oxides produce two different acids (sulfur*ic vs* sulfur*ous*, selen*ic vs* selen*ous* etc).

Homework

1. Compare the properties of chalcogens and halogens summarized duriung last two lessons. What is the general approach to the description of the properties of these two classes of elements? Do you think this approach can be expanded onto other classes?

2. A 10 g piece of copper ore (a mixture of copper sulfide and other rocks, mostly calcium silicate) was finely ground and mixed with an excess of 10 % hydrochloric acid. The gas formed in this reaction was collected and bubbled through the solution of 100g of silver nitrate in 5000 mL of water, and all the gas was absorbed. The precipitate was collected and dried. Its mass was 15 g. Find the content of copper in the ore.