Inorganic Chemistry
Lesson 4
Oxygen. Oxides.
Chemical equations and some simple calculations.

October 8, 2017

1 On the term "Inorganic chemistry"

Now we are ready to start learning about the properties of the most important chemical elements, as well as about the major classes of *inorganic compounds*.

> **"Inorganic compounds" are the chemical substances containing no carbon atoms.[1] Accordingly, carbon containing compounds, except the simplest ones, such as carbon dioxide or baking soda, are called "organic compounds".**

> *Initially, chemists believed that the compounds living organisms are composed of can be produced only by living organisms themselves. For example, in XIX century, chemists were able to purify sugar from sugar cane, and determine the composition of sugar: they quickly realized that sugar is composed of carbon, hydrogen and oxygen. However, despite numerous attempts, they were unable to combine carbon, hydrogen and oxygen back to obtain sugar. After numerous unsuccessful attempts to prepare sugar, as well as other compounds found in living organisms, chemists came to a conclusion that two different realms of chemical compounds exist, namely "organic compounds" (i.e. the compounds derived from living organisms), and "inorganic compounds" (i.e., all others). Accordingly, chemistry was divided onto two different disciplines, organic and inorganic chemistry. Although subsequent studies demonstrated that there is no impassable abyss between inorganic and organic compounds (during the second half of XIX century chemists prepared many organic compounds from inorganic ones), the division of chemistry onto "inorganic" and "organic" appeared to be convenient, so these terms are still in use. As you have probably understood, during this year, we are studying inorganic chemistry, because this discipline lays a foundation for understanding chemistry as whole.*

[1] Strictly speaking, inorganic compounds contain no carbons directly connected by a chemical bond.

Joseph Priestly
1733-1804

Carl Wilhelm Scheele
1742-1786

2 Discovery of oxygen

In late XVIII century, chemists noticed that some compounds upon heating can produce gases (they called all of them “air”). However, they didn’t know how to collect it for more detailed studies. A British clergyman Joseph Priestley and Swedish pharmacist Carl Wilhelm Scheele were among the first scientists who started to study gases systematically. Although they worked independently of each other, their experiments were essentially the same. They both studied mercury oxide (HgO), a red scale that forms when mercury[2] is being baked on open air, and both Priestly and Scheele were able to collect the gas that formed when mercury oxide decomposed.

> *Actually, Scheele did that first, in 1772, but he didn’t published his results until 1777. Priestly published his findings in 1775, so he is generally regarded as a discoverer of oxygen. In addition, Scheele found that saltpeter (potassium nitrate, KNO_3) also produced oxygen when being heated.*[3]

Scheele called the gas "fire air" because it supported combustion. Priestly, who also made similar experiments, noted that candles burned brighter in the new gas he discovered that

[2]Mercury is the only metal that is a liquid at normal temperatrure. Its chemical symbol is Hg (chort for “hydrargirum”, literally “liquid silver”, from Greel "hydron" - water, and Latin “argentum” - silver).

[3]Scheele was an outstanding chemist, he discovered a tungstic acid (the substance tungsten had been subsequently prepared from). He discovered hydrogen cyanide (“prussic acid”), and even described its taste (believe you or not, it was common among early chemists to taste chemical substances they prepared) and managed to survive after that. He was a really remarkable man, and that is absolutely unfair that due to a five years long delay with publication of his results the priority in discovery of oxygen is usually given to Priestly.

in air. He also observed that a mouse was more active and lived longer while breathing it. After breathing the gas himself, 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."

3 Preparation of oxygen

The simplest way to prepare oxygen in laboratory conditions is a *decomposition* of some compound that contains too many oxygen atoms, or of the compound where oxygen atoms are not bound tightly to other atoms. Mercury oxide is an example of the second type compounds. When heated, it decomposes onto the elementary substances (mercury and oxygen), according to the equation (1):

$$2\,HgO \longrightarrow O_2 + 2\,Hg \tag{1}$$

As we already know, Scheele obtained oxygen by heating saltpeter.[4] The reaction was as follows (2):

$$2\,KNO_3 \longrightarrow 2\,KNO_2 + O_2 \tag{2}$$

Arguably, the most convenient and safe way to prepare oxygen chemically is a decomposition of dilute solution of hydrogen peroxide[5] in a presence of manganese dioxide,[6] according to the equation (3):

$$2\,H_2O_2 + MnO_2 \longrightarrow 2\,H_2O + O_2 + MnO_2 \tag{3}$$

The equations (1) - (3) show us the examples of *decomposition reactions.*

Decomposition reaction is a chemical reaction where some chemical compound produces more simple substances (i.e. simpler compounds or even elementary substances).

One may ask: "The same formula is found in the left and the right part of the equation (3)*! Why cannot we simply remove MnO_2 from both sides of that equation? " Actually, we can remove it from the equation, but we cannot remove MnO_2 from the reaction mixture, because, although it is not being consumed during this reaction, the decomposition of H_2O_2 will not go in the absence of MnO_2, or, strictly speaking, this reaction will go extremely slowly.* ***The substances that accelerate some chemical reaction without being consumed during that are called "catalysts". Manganese dioxide catalyzes a decomposition of hydrogen peroxide.***

Of course, these reactions are not suitable for large scale preparation of oxygen. In industry, oxygen is prepared by distillation of liquid air: briefly, since nitrogen boils easier than oxygen, the liquid air is allowed to boil until all nitrogen evaporates, so the remainder is pure oxygen.

[4] An inorganic fertilizer and a component of gunpowder.
[5] Dilute hydrogen peroxide (H_2O_2) is sold in pharmacies as a local antiseptic.
[6] Manganese dioxide (MnO_2) can be found in some (non-rechargeable) batteries

4 Properties of oxygen

4.1 Physical properties of oxygen

At normal pressure and temperature, oxygen is a gas. It is slightly more dense then air, so it can be collected and stored (although for a short time only) in vertically standing open flasks or bottles. At $-183\,^{\circ}\mathrm{C}$ it becomes a blue liquid, and below $-219\,^{\circ}\mathrm{C}$ it is a solid. Liquid oxygen can be stored in Dewar vessels. Oxygen is the most abundant element in the Earth crust, hydrosphere and atmosphere, and the third abundant element in the Universe. Due to its high chemical reactivity it exists predominantly in a chemically bound state. Free oxygen was found only in the Earth atmosphere, its formation was a result of the activity of primordial living organisms (mostly green-blue algae).

4.2 Chemical properties of oxygen

Experiment 8

Fill a conical flask with oxygen. Take a steel spoon and put a small piece of charcoal there. Using a candle, ignite a charcoal. It is burning very slowly, so the bright spot on its surface is almost invisible. Immerse the spoon into the oxygen flask. What do you see? After combustion has stopped, add a little lime water[7] *to the flask, shake it and leave it for 10-20 minutes. Describe your observations.*

As we can see, combustion of carbon (a charcoal) is much more active in oxygen than in air: in oxygen, charcoal burns violently, producing flares and sparks. In oxygen, charcoal shines glaringly, and gradually disappears until nothing is remaining in the spoon. Obviously, since neither new solid nor new liquid is formed, it is reasonable to conclude the product of combustion of carbon is gas. Unfortunately, we cannot see this gas directly, because it has no color. However, we can detect it indirectly: when we add lime water to the flask, the liquid becomes turbid. From previous experience we know[8] that, lime water forms solid calcium carbonate ($CaCO_3$) in the presence of gaseous carbon dioxide. In our case, turbidity of lime water serves as a good indication of carbon dioxide (CO_2) formation during our experiment. Chemists call such a trick a *qualitative reaction*: if you cannot see some compound A directly, you can add a compound B that is known to produce color, or gas, or something of that kind during the reaction with A.

Figure 2: Combustion of charcoal in oxygen.

A quantitative reaction is a chemical reaction that produces some effect (color change, gas evolution, sediment formation, etc) that can be

[7] "Lime water" is a water solution of calcium hydroxide

[8] Actually, you don't. Only I do. However, upon having read this text you will know that too, so I believe I have a right to write *we* know

seen directly. Quantitative reactions are widely used to detect certain chemical compound.

Now we are ready to draw the schemes of the reactions that took place during our Experiment **8** (Equation (4)):

$$C + O_2 \longrightarrow CO_{2(g)} \tag{4}$$

and interaction of carbon dioxide with lime vater (a solution of calcium hydroxide, $Ca(OH)_2$ (5):

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_{3(s)} + H_2O \tag{5}$$

The letters 'g' and 's' denote formation of gas or sediments, accordingly.

In other words, we demonstrated that combustion of carbon in oxygen is a chemical reaction, and we identified its product. Let's see if other substances react with oxygen similarly.

Experiment 9

(This experiment must be done in open air, because the gaseous products that form have unpleasant odor.) Fill a conical flask with oxygen. Take a steel spoon and put a small amount of sulfur into it.[9] *Ignite the sulfur. Sulfur's flame is faint blue. Immerse the spoon into the oxygen flask. How did the flame change?*

In this case the reaction can be described by the equation (6):

$$S + O_2 \longrightarrow SO_{2(g)} \tag{6}$$

No qualitative reactions are needed to detect a compound that forms during this reaction (SO_2), because of its strong and unpleasant smell that resembles a smell of burning matches.[10] In this case, the product of sulfur combustion is also a gas.

Figure 3: In an oxygen atmosphere, sulfur's fire is glaringly blue.

Experiment 10 (thought one)

Unfortunately, we cannot do this experiment, because phosphorus is a regulated compound in the US.[11] That is why we have to limit ourselves with a *thought experiment*. Had we used phosphorus instead of sulfur in the Experiment **9**, we also would see a bright fire (in this case, a fire would be white). However, in addition to that, we would observe a formation of thick white

[9] Sulfur is a yellow powder, non-toxic and insoluble in water. It is used, for example, in matches or for fireworks.

[10] Actually, this compound, SO_2 forms when you use matches, hence the smell.

[11] Some people use it to convert some over-the-counter medicine into a strong narcotics, so a special permit is necessary to purchase and handle this substance.

fog that would gradually precipitate on flask's walls and bottom. This white compound is a *phosphorus oxide* (P_2O_5), and the reaction can be described by the equation (7):

$$4\,P + 5\,O_2 \longrightarrow 2\,P_2O_{5(s)} \tag{7}$$

During the previous experiments, we used the substances that can burn in open air. The only effect we observed was acceleration and intensification of their combustion in pure oxygen. However, does that mean that every substance that are not combustible in open air cannot burn in pure oxygen?

Experiment 11

Figure 4: Burning of a steel rope in pure oxygen

Fill a conical flask with oxygen. Take a steel wire rope, untwist its end, and put a small piece of charcoal in between the threads. Using a gas torch, incandesce the end of the rope, along with the charcoal, and immediately immerse it into the oxygen flask. What do you see?

Not only we see a bright fire and a disappearance of a steel rope (Fig. 4), we also see formation of some fine red dust that precipitates on flask's walls. This dust is a common rust, or *ochre*, a red pigment that is being used by humans since prehistorical times (Fig. 5)[12] This reaction occurs according to the equation (8):

$$4\,Fe + 3\,O_2 \longrightarrow 2\,Fe_2O_3 \tag{8}$$

Figure 5: Cave of Altamira prehistorical painting of a bison. Red color is ochre (Fe_2O_3)

[12] When iron is being heated in air, or when temperature of combustion is not high enough, the major product is a mixture of iron (II) oxide and iron (III) oxide. Its net formula is Fe_3O_4.

4.3 Appollo 1 fire.

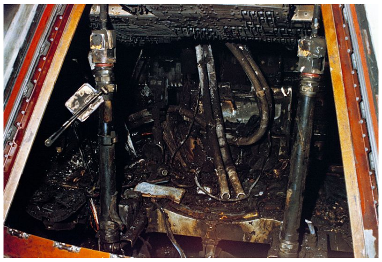

Figure 6: Apollo 1 cabin's interior after fire.

As we can see, some substances that are believed to be non-combustible are capable of burning in pure oxygen. One tragic incident may serve as a demonstration of that fact. On January 27, 1967, a cabin fire during a launch pad test destroyed completely the interior of the U.S. Apollo lunar command module. All three members of the crew, Command Pilot Virgil I. Grissom, Senior Pilot Edward H. White II, and Pilot Roger B. Chaffee, had burnt alive. Among the reasons of so quick and fatal propagation of fire was named Apollo's purely oxygen atmosphere (in contrast to the atmosphere used, for example, in Soviet space ships, or later American space ships).

5 Oxides. Oxidation.

In all above experiments, oxygen reacted with some material, and the products were composed of some element and oxygen. Reactions between oxygen and other substances[13] belong to the class of reactions that are called *oxidation* reactions. The chemical compounds formed by oxygen and some element are called *oxides*.[14]

> **Oxides are binary compounds formed by some element and oxygen. All elements, except fluorine, helium, neon, and argon, can form oxides.**

Oxides are the important class of chemical compounds. Many of them are formed during combustion of some element (such as iron, magnesium, carbon) in oxygen. Alternatively, oxides can be prepared indirectly. For example, calcium oxide (CaO), a major component of a concrete mixture, is being prepared in industrial scale *via* calcination of limestone (calcium carbonate), according to the equation (9):

$$\mathrm{CaCO_3} \longrightarrow \mathrm{CaO} + \mathrm{CO_{2(g)}} \tag{9}$$

It is is necessary to note that some elements do not burn in oxygen, and their oxides are prepared only indirectly. We will learn about that in more details later.

6 Schemes and equations of chemical reactions. Simple calculations.

As you have already seen, to describe reactions we can use either schemes or equations. What is the difference between them? Let's consider a reaction of combustion of phosphorus in oxygen. As we already know, during this reaction oxygen and phosphorus are being consumed, and phosphorus (V) oxide is formed. That can be described by a scheme (10)

[13] except fluorine.

[14] Interestingly, that means water, from chemist's point of view, is actually a "hydrogen oxide".

$$P + O_2 \longrightarrow P_2O_5 \tag{10}$$

From this scheme, you can see the starting materials ("reactants") and products of this reaction. In other words, schemes provide a *qualitative* description of chemical reactions. However, if you look at this scheme you will see that the number of atoms in the left and right side are different: there is one phosphorus and two oxygen atoms in the left side, and two phosphorus atoms and five oxygens in the right side of this scheme. Therefore, the scheme is not suitable for doing chemical calculations. For example, let's try to solve a following problem:

Problem 1.

> **Calculate the amount of phosphorus (V) oxide formed as a result of combustion of 31 g of phosphorus.**

Obviously, we cannot obtain all needed information from the scheme (10), because the number of atoms in right and left sides of the scheme is not equal. To make them equal, we modify the scheme (10) as follows:

$$4\,P + 5\,O_2 \longrightarrow 2\,P_2O_5 \tag{11}$$

Since left and right sides contain the same number of atoms, we can call it "equation", not a "reaction scheme".

> *The way we place coefficients before each formula is straightforward for those who studied math (and LCM/GDP in particular): there are two oxygens in the left side of the scheme* (10)*, and five oxygen in the right side; the LCM for 2 and 5 is 10. Therefore, the coefficient before O_2 should be 10/2=5. Accordingly, the coefficient before P_2O_5 should be 10/5=2. Finally, since there are two P_2O_5 in the right side, we must put 4 before phosphorus in the left side to make the amount of phosphorus atoms equal.*

Using the equation (11), we easily can solve our problem. We simply need to reword the problem as follows:

Problem 1 (reworded)

> One phosphorus atom weigh 31 Da, therefore, four atoms in the left side of the equation (11) weigh 124 Da. They produce two molecules of P_2O_5 that weigh $2 \times (31 \times 2 + 16 \times 5) = 284$ Da If 284 Da of P_2O_5 is produced from 124 Da of phosphorus, how much P_2O_5 will be produced from 31 g of phosphorus?

Obviously, a problem of that kind requires just elementary school math skills. To solve it, let's write a proportion:

$$\frac{124 \text{ Da}}{31 \text{ g}} -> \frac{284 \text{ Da}}{x} \tag{12}$$

By re-organizing the equation, we get:

$$x = 284 \text{ Da} \times \frac{31 \text{ g}}{124 \text{ Da}} = 71 \text{ g (grams of phosphorus (V) oxide).} \tag{13}$$

That is how chemists calculate the amount of chemicals needed for some reaction, and the amount of products.

To summarize,

> **For qualitative description of chemical reactions, we need to write just a reaction scheme. However, to calculate the amount of substances consumed or formed during some chemical reaction, we need to draw a chemical equation. In the reaction schemes, we do not care about material balance between the left and right sides. In contrast, chemical equations contain equal amount of atoms of each type in the left and sides.**

Homework

1. Draw chemical equations of the oxidation reactions between oxygen and the following elements: (a) magnesium, (b) calcium, (c) silicon, (d) boron, (e) hydrogen, (f) zinc.

2. You placed iron shavings into the sealed vessel filled with oxygen, and ignited them. Assuming that excess of iron was taken (some iron was left unreacted), what the final pressure in the vessel will be? Will the result be the same in you took sulfur?

3. A sealed vessel contains 10 g of oxygen and 64 g of copper wire. After heating, the wire was converted into some black powder with a formula CuO. (a) What is a chemical name of this compound? (b) Draw the chemical equation of this reaction. (c) Had all copper been converted into CuO, or some amount of copper metal remained unchanged? (d) What the total mass of a solid material will be by the end of the experiment?

4. Propylene has a formula C_3H_6. Please write a scheme of the reaction of propylene combustion, assuming that the combustion is complete (only water and carbon dioxide are the products of this reaction). Write the *equation* of propylene combustion. What is the difference?

5. During complete combustion of ethyl alcohol (C_2H_6O) only water and carbon dioxide (CO_2) are produced. Draw a chemical equation of this reaction, and calculate the amount of water formed after complete combustion of 20 g of ethyl alcohol.

6. Find and fix errors in the below equations:

$$\mathrm{Mg + O_2 \longrightarrow MgO} \tag{14}$$

$$\mathrm{C + O_2 \longrightarrow CO_3} \tag{15}$$

$$\mathrm{CH_4 + O_2 \longrightarrow CO_2 + H_2O} \tag{16}$$

$$\mathrm{C_2H_2 + O_2 \longrightarrow CO_2 + H_2O} \tag{17}$$

As usual, I would be grateful if you sent me your homework by evening of next Saturday. My e-mail is mark.lukin@gmail.com.