INORGANIC CHEMISTRY
Lesson 3
Dalton's atomic theory. Composition of molecules. Valence.

September 30, 2018

1 ...standing on the shoulders of giants

Dalton's ideas can be summarized as follows.

1. Matter is not infinitely divisible. It is composed of a large but finite number of extremely small ultimate particles (now we call them atoms and molecules).
2. Atoms of a given type are identical in size, mass, and other properties; atoms of different elements are different in some fundamental way (for example, they have different mass).
3. Substances that cannot be decomposed onto more simple substances are called elementary or simple substances. The atoms of a given elementary substance are identical.
4. Atoms combine in simple whole-number ratios to form composite substances, or chemical compounds.
5. Matter cannot be created or destroyed by chemical means; the only changes chemists can produce consist in separation, combination or rearrangement of atoms.

It would be correct to say that chemistry became a science only after these seemingly simple ideas had been formulated. Indeed, according to Dalton, small number of different atom (*elements*) combine with each other to form a huge variety of molecules of different kinds, and the rules that govern formation of these molecules depend of the types of the atoms involved in the interaction. To reveal these rules, and to show how the properties of molecules depend upon atomic composition is the main subject of chemistry, according to Dalton[1]. Yes, this theory was a major breakthrough, however, his work was based upon several major discoveries made by his great predecessors. Among these discoveries, two laws, which were initially derived experimentally, deserve a separate attention.

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[1] Now, after two hundred years, it is still remaining the major goal of chemistry.

1.1 Law of conservation of mass

The idea that matter, which is composed of indestructible atoms, cannot be created or destroyed seems obvious to all present-days people, however, *does this idea follow from our every-days experience?* Of course, no.

Experiment 6

> *Weigh a candle and write down its weight. Light the candle and leave it for 20 minutes. Then put it out, and weigh the candle again. How did its weight change?*

From our everyday's experience, we may conclude the candle's weight decreases during combustion, and our experiment confirms that.

Experiment 7

> *Weigh a nail and record its weight. Leave it in a moist place. After one year, weigh it again. Can you see a difference?*

In that case, the mass of the nail *increases* when it rusts.

This, as well as many similar phenomena were interpreted by ordinary peoples and by scientists as an indication that *matter is not necessarily conserved during chemical reactions*, and this wrong belief was common among people until late XVIII century. The roots of this error were obvious: during their experiments, early scientists were unable to accurately measure all reactants (the substances participating in a chemical reaction) and all products (the substances that are formed during the reaction). Thus, during the Experiment **6** some gaseous products form, which have not been taken into account. As a result, we (as well as early scientists) observed a "disappearance" of matter. Similarly, in the Experiment **7** the increase of the nail's weight was due to its reaction with atmospheric moisture. Early scientists, who did not understand the processes of rust formation, interpreted that reaction as some spontaneous "creation" of matter from nothing. In early and mid-XVIII century, chemists proposed the idea that such a visible "disappearance" or "formation" of matter was a result of experimental errors. Nevertheless, the first comprehensive study of that issue was made only in late XVIII century by an outstanding French chemists Antoine-Laurent de Lavoisier. He made systematic studies of various chemical reactions in sealed vessels, when any possibility of loss of matter was eliminated. He found, for example, that, when a piece of wood was burned to ashes on open air, its mass decreased. However, when a similar piece was burned in a sealed vessel, the mass

Antoine-Laurent de Lavoisier (1743-1794), a father of modern chemistry.

of the vessel remained unchanged. This, as well as a large number of others, meticulously planned and carefully performed experiments allowed Lavoisier to conclude that *"nothing is lost, nothing is created, everything is transformed"*.

> **During chemical reactions, matter cannot be created or destroyed.** This law is known as "Lavoisier's law".

This idea became one of the pillars of Dalton's theory. Indeed, we can speak about conservation of matter if, and only if its building blocks, atoms, cannot be created or destroyed.[2]

1.2 Law of definite proportions

The number of chemical reactions known to scientists is much greater that the number of chemical substances. That means that almost every chemical substance can be obtained *via* several different ways. Thus, you can obtain carbon dioxide (a gas used to produce soda water or coke) by burning charcoal, or by adding vinegar to baking soda, or by adding hydrochloric acid to limestone, or by dissolving baking powder in water, or by adding baking soda to boiling water, and so on. In all cases, carbon dioxide will be obtained, however, does it mean the chemical composition of this gas will be the same? Again, the answer on this question was not obvious to early chemists. To clarify that issue, another French chemist, Joseph Proust, performed a series of meticulous experiments, and convincingly demonstrated that each chemical compound always contains exactly the same proportion of elements *independently on the way it had been prepared*.

Joseph Proust (1754-1826), a discoverer of the law of definite proportions.

2 Elements and molecular formulas

Elements are the atoms of a certain type. Simple substances (a term used by Dalton, which is currently widely used in non-English literature) are also called *"elements"*. One has to see a difference between two meanings of the word "element". Let me give just one example to demonstrate this idea. In late XVIII century, Lavoisier and his colleagues decided to determine a composition of diamond. They bought a diamond, put it under glass bell and heated it under sunlight using a big magnifying glass. To their big surprise, the diamond turned black, ignited and burned completely. The only product of combustion of diamond was carbon

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[2] Of course, we speak about chemical reactions only. Discovery of atomic reactions demonstrated that atoms can be destroyed. Note, however, that Dalton made a very vise reservation: he never declared atoms are not possible to destroy, he said it is impossible *by chemical means*.

dioxide, the same gas that forms during combustion of ordinary charcoal. That experiment demonstrated that diamond, as well as ordinary charcoal or graphite is composed of the same *atom type* (carbon). However, does it mean charcoal, graphite and diamond are the same *substance*? Of course, no. These are *different substances composed of the same type of atoms.* Their properties are different because the same atoms (i.e carbon atoms) are organized differently in diamond, charcoal and graphite. Whereas the number of different molecules known to chemists exceeds many millions, the number of elements is very limited. Only 118 elements are currently known, and only 80 of them are stable (non-radioactive). The number of elements chemists can work with barely exceeds 90. However, we even don't need to memorize the names of each of them (at least, for now). To start learning Chemistry, we need no know the names of several essential elements. Below is the list of elements you need to remember (Table 1), because we will discuss them during this year. There are few things you need to know about them for the beginning: a name, an atomic symbol, and a mass. A mass of each element is (approximately) multiple of a mass of the lightest atom, hydrogen[3], so we will use hydrogen's mass as an atomic mass unit.[4]

Jons Jacob Berzelius
(1779-1848),
a developer of modern
chemical formula notation.

Table 1. Most common elements and their atomic masses

Element's name	Element's symbol	Atomic mass, Da
Aluminium	Al	27
Calcium	Ca	40
Carbon	C	12
Chlorine	Cl	35
Copper	Cu	64
Hydrogen	H	1
Iron	Fe	56
Nitrogen	N	14
Oxygen	O	16
Silver	Ag	108
Sodium	Na	23
Sulfur	S	32
Tin	Sn	119
Zinc	Zn	65

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[3] It is not a coincidence, there is an important law behind that, and we will talk about that later.

[4] Currently, a little bit more precise mass unit is being used by chemists, namely, 1/12 of mass of a carbon atom. We will discuss the reason for that during the lesson devoted to isotopes.

2.1 Atomic mass unit, or Dalton

The atomic mass unit has its own specific name, **dalton**, or **Da**. This name had been chosen in a recognition of John Dalton's immense contributions into creation of modern chemistry. Initially, 1 Da was set to be equal to the mass of one hydrogen atom. Currently, a little bit different value is being used: one dalton is equal to 1/12 of mass of a carbon atom. The reason for that is purely technical. We will discuss that during the lesson devoted to isotopes.

2.2 Molecular formulas

Using the symbols from the Table 1, we can write *chemical formulas* instead of full name of substances. Not only that makes our life easier, it allows us to describe chemical substances more correctly. Thus, instead of writing *"a molecule of water is composed of one oxygen atom and two hydrogen atoms"* we can simply write: H_2O. The superscript symbols denote the number of each atom type is the molecule. Other examples of chemical formulas are: Al_2O_3, Na_2O, H_2CO_3, CuO etc. (These formulas are shown just to give you an impression on how chemical formulas look like. You do not need to memorize them.) Using such formulas, we can draw chemical equations to describe, for example, a chemical reaction we did during the Experiment **3** (5):

$$\mathrm{CaCl_2 + Na_2SO_4 = CaSO_4 + 2\,NaCl} \tag{1}$$

Note, a number before a molecular formula indicates that more than onle molecule is formed. In this particular case, two molecules of sodium chloride are formed[5]

2.3 Molecular formula and molecular mass

Obviously, since there is nothing in molecules except the atoms they are composed of, the mass of some molecule is equal to the sum of masses of the atoms the molecule is built from. Although that is intuitively clear, it may probably be useful to give an explicit definition.

> **A mass of molecule, or its molecular mass, is a sum of masses of the atoms a molecule is composed of.**

For example, the mass of Al_2O_3 is equal to $27 \times 2 + 16 \times 3 = 102$ Da, mass of calcium chloride is $40 + 35 \times 2 = 110$, mass of sodium sulfate is $23 \times 2 + 32 + 16 \times 4 = 142$, mass of nitrogen is $14 \times 2 = 28$, etc.

3 Valence

As you probably have noticed, some molecules contain lower case indexes ("coefficients"). That means the number of atoms can be different in different molecules. For example, "H_2O"

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[5] NaCl, table salt, is called "sodium chloride". We will not memorize the names of all compounds in advance. We will discuss the names for each class of chemical compounds when we will be studying each of them.

(i.e. a chemical formula of water) means there are two hydrogen atoms and one oxygen atom in each water molecule.

Is the composition of molecules arbitrary, or there is some law that defines it? If such a law does exists, then is it possible to predict composition of molecules?

Yes, it is possible to predict molecule's composition, and to derive chemical formula. That can be done based of some property of atoms called *valence.* To demonstrate the concept of valence, let's try to answer a following question using a common sense.

> *We know that a compound formed by hydrogen and chlorine has a formula HCl, a compound formed by hydrogen and oxygen has a formula* H_2O*, a compound formed by silver and oxygen has a formula* Ag_2O*. Using this information, can you predict a formula of a compound containing silver and chlorine?*

It is intuitively clear that, since oxygen binds to two atoms of hydrogen, valence of oxygen is as twice as big as valence of hydrogen. H_2O and Ag_2O formulas are similar, that means silver has the same valence as hydrogen. Since one atom of chlorine binds to one atom of hydrogen, their valences are the same. However, that means one atom of chlorine would add to one atom of silver,so the formula should be AgCl.

> **Ability of some atom to bind to a certain number of other atoms is called valence.**

It had been experimentally established that hydrogen has minimal possible value of valence. Therefore, its valence is assumed to be equal to one. Based on that, an alternative definition of valence can be proposed.

> **Valence is the ability of some atom to bind to a certain number of hydrogen atoms.**

Oxygen is capable of binding to two hydrogen atoms, nitrogen binds to three hydrogen atoms, and carbon binds to four hydrogen atoms. Therefore, valence of these elements is two, three, and four, accordingly. Using this information, we can predict, for example, that a compound formed by oxygen and carbon has a formula CO_2. It is necessary to note, however, that the same element may have different valence when it is bound to different atoms. Thus, sulfur is divalent when it is bound to hydrogen, but it may be either tetra- or even hexavalent when it is bound to oxygen. We will discuss that in details later.

Homework

1. Try to memorize symbols and names of the elements (and, if possible, their atomic masses) from the above table. They are being used very commonly, so it is very useful to know them. You will need to know them during subsequent lessons.

2. Calculate a molecular mass (in Daltons) of following compounds: CuO, SO_2, SO_3, NO_2, Na_2O.

3. Two substances have identical molecular masses. A first substance contains only nitrogen atoms, the second one contains oxygen and carbon[6]. Can you draw formulas of both of them?

4. A molecular mass of the product of combustion of sulfur is as twice as big as the atomic mass of sulfur. Can you draw the formula of this product?

5. A molecular formula of glucose is $C_6H_{12}O_6$. Is there more oxygen (by weight) in one gram of water than in one gram of glucose?

6. In all compounds listed below sulfur is divalent. Please, tell what is valence of a second element in each formula: Al_2S_3, ZnS, Na_2S, CS_2.

7. Copper forms two compounds with oxygen.[7] Their formulas are Cu_2O and CuO. What is the valence of copper in each of them?

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[6] To solve this problem, you need to know that, whereas in most molecules carbon's valence is four, in some other molecules (rarely) it can be equal to two

[7] such compounds are called "oxides"

Lesson 4
Chemical bonds and structural formulas.
October 7, 2018

4 Structure of molecules

The concept of valence allows us to make some important conclusions about structure of molecules. Indeed, if we know that oxygen, being divalent, interacts with monovalent substances to give chemical compounds with general formula X_2O, it is reasonable to suggest that happens because each atom X forms one *chemical bond* with other atoms, but each oxygen atom can form two chemical bonds. It can be represented graphically, using solid lines for each chemical bond:

$\mathrm{H{-}O{-}H}$, or $\mathrm{Na{-}O{-}Na}$, or $\mathrm{Ag{-}O{-}Ag}$

Obviously, since hydrogen, sodium, and silver are monovalent, only one solid line can start from H, Na, or K atom. Oxygen is divalent, therefore, two lines come to (or go from) each oxygen atom. When oxygen is bound to itself, or to another atom with valence greater that one, it can form a *double bond*, which is shown in chemical formulas as a double line.[8] For example, a molecule of carbon dioxide, a gas used for preparation of soda water, can be drawn as follows:

$\mathrm{O{=}C{=}O}$

In other words, molecules are not random clods. Their structure is strictly defined, and can be drawn based on chemical laws.

> **Atoms in molecules are connected together *via* chemical bonds. A graphical representation of molecular structure that shows chemical bonding within the molecule is called a *structural formula*.**

Structural formulas can help us to predict the composition of chemical compounds, especially of binary ones.[9] For example, if some element X is divalent, its binary compound with a monovalent element Y has a structure:

$\mathrm{Y{-}X{-}Y}$

which means the formula of this compound is Y_2X (or XY_2, which is the same). The examples are H_2O, Ag_2O, $CuCl_2$.

If both X and Y are divalent, the structure of the binary compound is:

$\mathrm{X{=}Y}$

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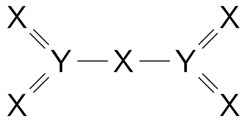
[8] triple bonds are also possible between two atoms whose valence is equal or greater than three. Quadrupole bonds are not possible. We will discuss it in more details next year.

[9] Binary compounds are the compounds formed by two different elements. CuO, CO_2, or Fe_2O_3 are the examples of binary compounds.

Accordingly, its chemical formula will be XY. The examples are CuO, CaO, MgO. If the atom Y is tetravalent, the structural formula is:

$\mathrm{X{=}Y{=}X}$

That corresponds to the chemical formula X_2Y (or YX_2, which is the same). The examples are CO_2, SO_2. A situation when a valence of one element is odd, but a valence of another element is even is a little bit more tricky. Thus, when the element X is divalent, and the element Y is pentavalent, a structural formula will be:



The examples of such compounds are N_2O_5, P_2O_5.

You have probably noticed that in all above formulas, every chemical bond that starts from one atom ends at another one. There is no “free” valences (i.e. the chemical bonds that go to nowhere) in molecules. However, does it mean that the molecule like those listed below do not exist?

$\mathrm{H{-}S{-}}$, or $\mathrm{Na{-}O{-}}$, or $\mathrm{Ag{-}O{-}}$

Actually, it doesn’t. Yes, such particles may exist. However, such a particle would be very active. It would try to use its “free valence” (i.e. a broken chemical bond) to bind to another particle of the same or different type. That means such a particle cannot form a bulk substance.

> **In stable chemical compounds, there are no chemical bonds that go to nowhere.**

5 Valence of different elements. Polyvalence

Why different elements have different valence? Actually, the chemists answered this question only in the middle of XX century, after the atomic structure had been determined, and quantum mechanics had been developed. We will definitely talk about that ... later. For now, we study the foundations of chemistry, and we simply have no time or sufficient factual background to dive into the details of electronic structure of atoms. What you currently need is to know that some elements have a certain valence when they are chemically bound to other atoms. Below is the table that lists most common elements and their valences. That is pretty sufficient for a while.

Table 2. Most common elements, their atomic masses and common valences[10]

Element's name	Element's symbol	Atomic mass	Valence
Hydrogen	H	1	1
Sodium	Na	23	1
Silver	Ag	108	1
Calcium	Ca	40	2
Copper	Cu	64	2 (1)
Magnesium	Mg	24	2
Iron	Fe	56	3 or 2
Oxygen	O	16	2
Tin	Sn	119	2 (4)
Zinc	Zn	65	2
Aluminium	Al	27	3
Phosphsorus	P	31	3, 5
Carbon	C	12	4 (2)
Nitrogen	N	14	3, 4, 5
Silicon	Si	28	4
Sulfur	S	32	2, 4, 6
Chlorine	Cl	35	1, 3, 5, 7

As you can see from this table,[11] some elements (such as sodium or hydrogen) always have the same valence, whereas the valence of others may vary. These elements are called *polyvalent* , or *multivalent*. Their valence depends on the type of the molecules they are a part of. For example, valence of chlorine is always 1 when it is bound to hydrogen, but it can be 3, 5, or 7 when chlorine is bound to oxygen. Usually, most multivalent elements, such as sulfur, chlorine, or nitrogen, have lower valence when bound to metals (sodium, iron, tin), and higher valence when bound to oxygen, or chlorine. We will discuss all of that later, and for now, try to memorize the above table. The valence state of polyvalent elements is denoted using Roman numbers. For example, a compound with a formula Fe_2O_3 (iron is trivalent there) is called "Fe (III) oxide".

6 Structural formulas and reaction schemes

Structural formulas allows a better understanding of what is going on during chemical reactions. Thus, using structural formulas, the reaction scheme **1** from lesson 2 can be redrawn as follows:

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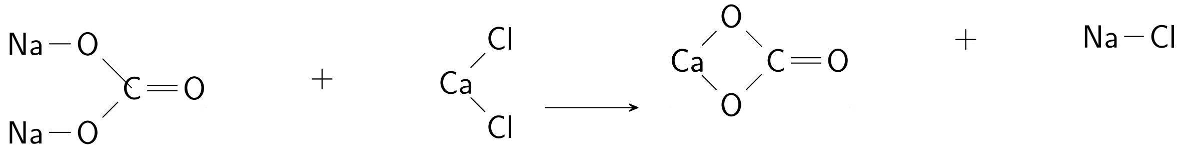
[10] Sometimes, very infrequently, they may have valences not listed in this table. However, these are just rare exceptions; rare valent states are shown in parentheses

[11] this table lists the same elements as the Table 1 (Lesson 3) does; three more elements have been added: magnesium (Mg), phosphorus (P) and silicon (Si).



Sodium carbonate

Calcium chloride

Calcium carbonate

Sodium chloride

As we can see from this scheme, only two types of bonds had been affected during this reaction: the bonds between sodium and oxygen, and the bonds between calcium and chlorine. Other bonds (the bonds between sulfur and oxygen) remained unaffected. That means that, in these particular reaction conditions, the latter bonds are stable (do not break).

> **In molecules, different chemical bonds have different stability. Depending on reaction conditions, some bonds break easily, whereas others remain unchanged. As a rule, just one (or few) chemical bond is affected during a certain reaction.**

It is very important to understand the reasons for stability or instability of chemical bonds in molecules. That will allow us to understand mechanisms of chemical reactions and to predict which compounds react with each other, and what the reaction products are.

Homework

1. Try to memorize valences of the elements from the table 2.
2. Using the table 2, draw structural formulas for each compound from the is list and find correct coefficients in the formulas: Al_xS_y, Cu_xCl_y, Sn_xS_y, Ca_xN_y, Ca_xCl_y, Zn_xN_y, Al_xCl_y, Ag_xCl_y, H_xN_y, Mg_xN_y, Mg_xC_y, Al_xP_y, Ca_xSi_y, Si_xC_y, Si_xP_y, P_xO_y, P_xS_y (for polyvalent elements, draw separate formulas for each valence state).
3. Draw structural formulas and calculate percentage (by mass) of: (a) phosphorus in a compound formed by phosphorus (III) and magnesium; (b) sulfur in a compound formed by sulfur (II) and aluminium; (c) zinc in a compound formed by zinc and chlorine[12].
4. * Becides iron (II) oxide (FeO) and iron (III) oxide (Fe_2O_3), one more iron oxide exists with formula Fe_3O_4. This oxide usually forms when iron is being heated at open air. Try to draw its structural formula and explain what is the valence of iron in it. Oxygen is always divalent[13].
5. * Which of two binary compounds contains more oxygen by weight, sodium oxide Na_2O, or iron (II) oxide FeO?

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[12] When chlorine forms compounds with zinc or other metals, and no other elements are there, chlorine is always monovalent.

[13] The problems denoted by an asterisk are more challenging.

6. * When sugar is heated in a glass flask, it melts, and if heating continues, the liquid becomes brown, then it becomes a viscous solid, and finally it converts into carbon (similar to charcoal). The vapors that form during this process can be collected as a colorless liquid. Chemical analysis shows this liquid is water. There is nothing in sugar but water and carbon, hence the name, “carbohydrate”. Calcullate the amount of water one can obtain from 100 grams of sugar. The formula of sugar is $C_{12}H_{22}O_{12}$.

   Calculate the amount of water that can be obtained from another sugar (another carbohydrate), arabinose, that has the formula $C_5H_{10}O_5$. Which compound contains more water (in percents)?

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.

Lesson 5
Oxygen. Oxides.
Chemical equations and some simple calculations.
October 14, 2018

7 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.[14] 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.*

8 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[15] is being baked

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

[15] 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).

Joseph Priestly
1733-1804

Carl Wilhelm Scheele
1742-1786

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.*[16]

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 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."

9 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

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[16] 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.

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 (2):

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

As we already know, Scheele obtained oxygen by heating saltpeter.[17] The reaction was as follows (3):

$$2\,\mathrm{KNO_3} \longrightarrow 2\,\mathrm{KNO_2} + \mathrm{O_2} \tag{3}$$

Arguably, the most convenient and safe way to prepare oxygen chemically is a decomposition of dilute solution of hydrogen peroxide[18] in a presence of manganese dioxide,[19] according to the equation (4):

$$2\,\mathrm{H_2O_2} + \mathrm{MnO_2} \longrightarrow 2\,\mathrm{H_2O} + \mathrm{O_2} + \mathrm{MnO_2} \tag{4}$$

The equations (2) - (4) 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 (4)! 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.

10 Properties of oxygen

10.1 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 °C it becomes a blue liquid, and below −219 °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.

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[17] An inorganic fertilizer and a component of gunpowder.

[18] Dilute hydrogen peroxide ($\mathrm{H_2O_2}$) is sold in pharmacies as a local antiseptic.

[19] Manganese dioxide ($\mathrm{MnO_2}$) can be found in some (non-rechargeable) batteries

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).

10.2 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[20] *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[21] 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 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 (5)):

$$C + O_2 \longrightarrow CO_{2(g)} \tag{5}$$

and interaction of carbon dioxide with lime vater (a solution of calcium hydroxide, $Ca(OH)_2$ (6):

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_{3(s)} + H_2O \tag{6}$$

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[20] “Lime water” is a water solution of calcium hydroxide

[21] 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

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.[22] *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 (7):

$$S + O_2 \longrightarrow SO_{2(g)} \tag{7}$$

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.[23] 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.[24] 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 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 (8):

$$4\,P + 5\,O_2 \longrightarrow 2\,P_2O_{5(s)} \tag{8}$$

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

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

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

[24] 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.

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)[25] This reaction occurs according to the equation (9):

$$4\,\mathrm{Fe} + 3\,\mathrm{O_2} \longrightarrow 2\,\mathrm{Fe_2O_3} \tag{9}$$

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

10.3 Appollo 1 fire.

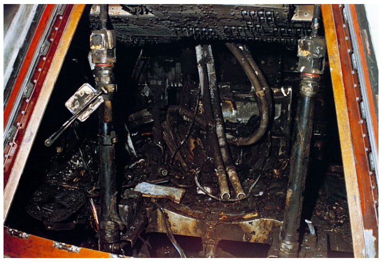

Figure 6: Apollo 1 cabin's interior after fire.

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).

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[25] 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.

11 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[26] belong to the class of reactions that are called *oxidation* reactions. The chemical compounds formed by oxygen and some element are called *oxides*.[27]

> **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 (10):

$$CaCO_3 \longrightarrow CaO + CO_{2(g)} \tag{10}$$

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.

12 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 (11)

$$P + O_2 \longrightarrow P_2O_5 \tag{11}$$

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.**

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[26] except fluorine.

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

Obviously, we cannot obtain all needed information from the scheme (11), because the number of atoms in right and left sides of the scheme is not equal. To make them equal, we modify the scheme (11) as follows:

$$4\,\mathrm{P} + 5\,\mathrm{O_2} \longrightarrow 2\,\mathrm{P_2O_5} \tag{12}$$

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* (11)*, 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 (12), 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 (12) 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:

$$\frac{124\ \mathrm{Da}}{31\ \mathrm{g}} - > \frac{284\ \mathrm{Da}}{x} \tag{13}$$

By re-organizing the equation, we get:

$$x = 284\ \mathrm{Da} \times \frac{31\ \mathrm{g}}{124\ \mathrm{Da}} = 71\ \mathrm{g}\ \text{(grams of phosphorus (V) oxide).} \tag{14}$$

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:

$$\mathrm{Mg} + \mathrm{O_2} \longrightarrow \mathrm{MgO} \tag{15}$$

$$\mathrm{C} + \mathrm{O_2} \longrightarrow \mathrm{CO_3} \tag{16}$$

$$\mathrm{CH_4} + \mathrm{O_2} \longrightarrow \mathrm{CO_2} + \mathrm{H_2O} \tag{17}$$

$$\mathrm{C_2H_2} + \mathrm{O_2} \longrightarrow \mathrm{CO_2} + \mathrm{H_2O} \tag{18}$$

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.