INORGANIC CHEMISTRY
Introduction

September 15, 2019

1 What does Chemistry study?

Until recently, the answer on this question was pretty straightforward.

> **Chemistry is a science dealing with the structure, properties and interconversion of substances.**

However, with the advent of new branches of chemistry such as biochemistry, geochemistry, physical chemistry, chemical physics etc, the borders of the realm of chemistry become somewhat blurry, however, by and large, the above definition remains valid. This definition contains one word that is not intuitively clear; this word is “substance”. Let’s discuss it in more details.

1.1 Chemical substances.

1.1.1 Physical bodies and chemical substances.

The world around us is full of what we call “material objects”. Each of them can be characterized by coordinate (position in space), size, mass, volume, shape (if they are solids), surface (if they are liquids or solids), etc. When we consider such an object as a single entity (i.e. we do not go into the details of its internal structure), we call it physical body (or physical object). All physical objects are composed of some material (or matter), which can be either homogeneous or heterogeneous. What does that mean? Let’s look at the piece of granite. Granite is a mineral with a granular structure (actually, the Latin word “granite” means “granular”), and if you look at the surface of granite, for example at a granite countertop, you can clearly see colorless semi-transparent grains, non-transparent white or colored grains, and highly brilliant sheet-like threads. These three components of granite can be separated; moreover, they also exist in nature as separate minerals called quartz, feldspar, and mica, accordingly. That means different regions in a piece of granite have different properties and different nature. In other words, granite is ***heterogeneous*** (in Latin this word literally means “of non-uniform nature”). In contrast, as soon as you identified a grain of quarts within a piece of granite, every part of this grain will have the same properties, and these properties will be indistinguishable from the properties of quartz obtained from other sources (for example, from sources of natural quartz). Quartz, mica, feldspar, and other materials of that type are called ***homogeneous*** (i.e. “of uniform nature”) substances.

Homogeneous substances are what chemistry primarily deals with.

Figure 1: Granite (top) and its components: mica (left), feldspar (center), and quartz (right)

1.1.2 Extensive and intensive properties

. To describe some object or substance means to describe a set of its properties. When we are describing the properties of some physical object, it is logical to start with the description of its size and shape. Obviously, a one kilogram copper ball and a two kilogram copper ball are two different objects with different properties (for example, with different masses). However, from the chemist’s point of view the properties of these two objects are identical: when you put them into an kiln, they melt at the same temperature, if you heat them further, they start to boil at the same temperature too. They have the same hardness and the same electrical resistance. If you decide to cut them onto smaller pieces, the melting and boiling points of such pieces, their density, specific heat capacity will remain unchanged.

> The properties that depend on the size of some object are called ***extensive***, whereas the properties that are size-independent are called ***intensive***.

Obviously, when we are describing physical bodies (objects) we use mostly extensive (size dependent) characteristics, whereas the properties of substances (i.e. the materials these objects are composed of) are intensive.

1.1.3 Physical and chemical properties of substances.

1.1.4 Physical properties.

We know that water freezes at 0°C and boils at 100°C; its density is 1 g per cubic centimeter, its specific heat capacity[1] is 4181.3 J/(kg·K), and its refractive index[2] is 1.333 (*Frankly speaking, even if you didn't know that before, don't worry, that is not too important for now*). If we decide to determine some of the above properties of water, no water will be lost (i.e. converted to another substance during such measurement). Indeed, we can cool water below 0°C to observe its freezing, but the ice that we obtain is just another state of water, and it will thaw back when heated to room temperature. We can put water into a *refractometer*[3] to measure how fast does light propagates in it, but water will remain unchanged during such an experiment. The same is true for all other properties of water listed above (as well as for many other properties of that type). These properties are the properties of water itself, and they are called ***physical properties*** of water. A set of physical properties serves a characteristic of each substance; it is the substance's "fingerprint".

1.1.5 Chemical properties.

It is also known that water, when mixed with quicklime[4] forms slack lime. When water vapors come into contact with hot iron, two new substances, the iron rust, and a hydrogen gas are formed. When water is added to burning magnesium metal, a burst of fire occurs, and lustrous and compact piece of magnesium metal turns into a white voluminous powder. During all these processes water disappears, and some new substances are generated instead. The ability of some substance to interact with another substance (or substances) to produce new substances, as well as the ability of a substance to decompose (to give new substances) is called a ***chemical property***.

> **Physical properties are used by chemists to characterize newly discovered substances or to identify already known ones.**
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> **Chemical properties of substances are what Chemistry studies.**

1.1.6 Pure substances and mixtures.

If different substances have different physical properties, they can be easily separated when they are mixed together. Thus, when a thin powder of charcoal is suspended in water, we can separate such a mixture either by filtration or by centrifuging. In the first case the separation takes place because liquid water is able to flow through the filter, but solid charcoal particles cannot, in the second cases the components of the mixture separate because they have different density. If iron and sulfur powders are mixed together, we can

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[1] i.e. the amount of heat needed to increase temperature of one kilogram of the substance one degree.

[2] Refractive index of transparent materials is the number that describes how fast light propagates through them.

[3] Refractometer is a device that measures refraction index of liquids.

[4] Quick lime, or calcium oxide, is a substance known to humans since antiquity; it is widely used for construction (masonry).

separate iron using a magnet. Not only heterogeneous mixtures are possible to separate. Sugar dissolves in water, and the resulting solution is a homogeneous substance. However, since water and sugar have different boiling temperatures the components of this solution can be easily obtained back: leave this solution in an open cup for several days, all water will evaporate, and the solid residue will be the sugar. Note, in all those examples the separation takes place due to the difference in physical properties of the components of the mixture. In other words, we separate the mixture by physical means. If some substance that can be separated onto other substances by physical means is called a mixture of substances or just a mixture, otherwise it is called a pure substance.

Preparation, characterization and study of pure substances is what majority of chemists are doing.

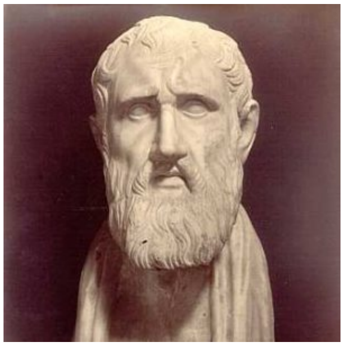
1.2 Compounds, simple substances and elements.

The fact that pure substances cannot be separated on components by physical means does not necessarily mean they cannot be separated at all. When you place a piece of sugar into a test tube and heat it, sugar melts, then its color changes to brown. If heating continues, the liquid becomes more and more dark and viscous, and finally it becomes a black solid. In addition to that, some vapors evolve that condense on the walls of the test tube to form a transparent odorless liquid. Further analysis shows that the solid formed is carbon, and the liquid is water. The same reaction made in a closed vessel yields the same products (water and carbon), which means that water and carbon are the products of decomposition of sugar, and no reaction between sugar and air takes place. However, there were no carbon and water in the piece of sugar before we started to heat it: sugar is clearly a pure substance, not a mixture. Indeed, it is impossible to obtain sugar just by mixing water with carbon. That means that, although sugar is a pure substance, it nevertheless can be converted onto other substances by chemical means (in this concrete case, decomposed at high temperature).

Pure chemical substances that can be decomposed on other substances are called ***complex substances***, or ***compounds***. Sugar can be decomposed, therefore it is a chemical compound (or just a compound). Since water is obtained as a result of decomposition of some compound, does that mean water is not a compound? Not necessarily. Although water is very hard to decompose, it still can be decomposed, for example by electric current. When two wires connected to positive and negative sources of voltage are immersed into water bubbles of gas start to form at their surface, and, if we continue this process long enough, all the water will disappear. What these gases are is not important now (we will talk about that later), but this experiment demonstrates that water can be decomposed on new substances, which means water is a compound, not an element. What about another product of decomposition of sugar? Numerous attempts made by early chemists to decompose it failed, so the chemists came to a conclusion that it is a substance that cannot be decomposed, i.e. a ***simple (elementary) substance***, or an ***element***. Chemical substances that cannot be decomposed onto components are called simple substances or elements. Each simple substance is composed from the atoms of a certain type. Although English literature uses the later term (“element”) almost exclusively, the two terms are not full synonyms, and many books written in French, German, Russian, etc make a distinction between them. We will learn later why.

1.3 Divisibility of matter. Atoms.

1.3.1 Ancient Greece, geometry, philosophy and real life.



Zeno (490-430 BC)

The idea that everything around us is composed of atoms seems pretty straightforward now, but is this idea really obvious? Actually, no, because nothing in our "big world" suggests the matter cannot be divisible infinitely. The first man who proposed the idea of *atoms* was a really non-trivial thinker, and the history of this concept deserves a special consideration.

The word "atom" (literally "indivisible") is of Greek origin, and the Greeks came to this idea as a result of abstract considerations. Ancient Greeks were good mathematicians and brilliant philosophers (actually, they were the first philosophers). They gave a start to abstract geometry, and, importantly, they created a concept of geometrical point, line and plane. The key idea of mathematical point is that (i) it is the object without size, and (ii) all other mathematical objects are the sets containing infinite amount of points. That means any segment of finite length can be divided onto two halves, the same can be done with the halves, and this process can be repeated infinitely. That idea looked fine in the abstract mathematical world, but an attempt to apply it to the real world lead to problems. Thus, Zeno of Elea, a Greek philosopher, concluded:

> **"Motion cannot exist because before that which is in motion can reach its destination, it must reach the midpoint of its course, but before it can reach the middle, it must reach the quarterpoint, but before it reaches the quarterpoint, it first must reach the eigthpoint, etc. Hence, motion can never start."**

Democritus (460-370 BC)

Since this idea, that looked logically incontrovertible, came into a clear conflict with our everyday experience, Democritus, another Greek philosopher, started to meditate about a possibility of infinite division in a real world. He concluded that would be impossible, because infinite division produces nothing, and because something cannot come from nothing. Democritus concluded that every real object can be divided only a finite number of times, and that atoms are the smallest objects everything in our world is made from. According to him, only a part of space is occupied by atoms, and the rest is void. Although the theory of Democritus helped to answer part of questions, one more step had to be made to convert it into a real chemical theory. That step was made more than two thousand years later, and we will talk about it during our next lesson.

Homework

Answer the following questions.

1. What is substance? Explain the difference between physical bodies and chemical substances.

2. Below is a list:
   ”a nail, clay, a brick, a snowflake, a knife, copper wire, brass, ivory, water, wood, a plain, a metal rod, an iceberg, a segment, a tusk, sugar, salt, aspirin, mercury, the Earth, vinegar, Mercury, a Tylenol tablet, ice.”
   Which items in this list are (i) chemical substances; (ii) physical bodies; (iii) mathematical objects?

3. Choose some pure compound you can find in your kitchen, for example, table salt or baking soda, oil, butter, etc. Provide a detailed description of their physical properties. Describe as many properties as you can.

4. Although Democritus is considered a grandfather of atomic theory, his concept was not popular in ancient Greece or Rome, and he was essentially forgotten until XVIII century. In your opinion, why did that happen? (A hint. What is the difference between the definition of atoms given by Democritus, and the current definition?)

2 Strengths and weaknesses of the Democritus atomic theory

Although Democritus’s serendipitous discovery of atomic theory laid a foundation for contemporary physics and chemistry, his theory was not popular among his contemporaries. It would be incorrect to attribute that fact to poor education or narrow-mindedness of Ancient Greek and Roman philosophers – many of them, such as Plato, Aristotle, Titus Lucretius Carus, were brilliant thinkers, who were open to logically correct arguments, and who were perfectly capable of understanding and appreciating non-trivial ideas. It would be more correct to attribute low popularity of the Democritus’s idea to the internal weaknesses of the theory itself. To check that, let’s look again at the main theses of the Democritus’s atomic theory. It says:

1. Atoms are perfectly solid and indivisible; it is impossible to create, destroy or change them.

2. Atoms are infinite in number and various in size and shape.

3. Atoms exist in a void; they are in motion, repelling one another when they collide or combining into small or large bodies by means of tiny hooks and barbs on their surfaces, which may become entangled or detangled, depending on external conditions.

Now let’s see how this theory can explain some phenomena around us.

Experiment 1

> *Take a piece of paraffin (for example, a piece of a candle) and put it into the glass test tube. Affix the tube in the holder and heat it gently using the gas torch or heat gun. You will see that white solid paraffin gradually melts yielding slightly turbid liquid. Now pour it onto a flat glass surface. The liquid freezes immediately giving solid paraffin.*

Could Democritus explain this phenomenon based on his theory? Of course, he could. He would say: *"Obviously, in solid paraffin, the atoms hold each other tightly because of their shape. Heat breaks part of these bonds, and paraffin melts. However, when paraffin cools down all broken connections restore, and paraffin freezes back."* That would sound quite reasonable; moreover, present-days scientists explain this process similarly, although using somewhat different terms.

Experiment 2

> *Take a teaspoon of table salt and dissolve it in a minimal amount of water. You may heat water gently to accelerate the process, although heating is not necessary. We see that the crystals of salt gradually disappear, and the resulting liquid remains clear, transparent and colorless. Put the liquid into a pyknometer*[5] *and record its weight. Then empty the pyknometer and fill it with water. You will see that the solution of salt weighs more then the same volume of water. Now put few drops of the solution on a glass plate and heat gently using a heat gun. You will see that water evaporates, and that small white crystals form.*

Again, Democritus would be perfectly able to explain these two experiments using his theory: *"The atoms of salt hold each other tightly via multiple hooks on their surface. When water is added, water atoms wedge between the atoms of salt to give a liquid which is more dense then water, because it contains a mixture of light water atoms and heavier atoms of salt. When we are heating this liquid, lighter water atoms escape, and the remaining salt atoms restore linkages between each other to form solid crystals."* "Again, this explanation is almost correct.

As we can see, the theory of Democritus is perfectly capable of explaining such phenomena as melting, crystallization, dissolution, evaporation, condensation, and similar processes. During these processes, the substances change their state, or mix together, or separate, but their chemical composition remains the same: liquid paraffin is still paraffin, and the salt dissolved in water is still table salt. These processes are called **physical processes**.

Physical processes are the processes that change the form of some substance, but not its chemical composition.

Democritus's theory explains such phenomena quite well. Does that mean Democritus's ideas were being rejected by Greek philosophers undeservedly? No. There are many phenomena it fails to explain.

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[5] A small bottle with exactly known volume. It is used to determine density of liquids.

Experiment 3

> *Weigh 1.47 grams of calcium chloride dihydrate*[6]*, place it into a test tube or a flask, add 5 mL of water and stir gently until all solid dissolves. Weight 1.42 grams of sodium sulfate*[7] *place it into a test tube or a flask, add 10 mL of water and stir gently until full dissolution. When both liquids became clear, mix them in a conical flask or in a beaker. Describe what you observe. Using a Buchner funnel and Bunsen flask*[8] *(Figure 1), filter the slurry formed, collect the solid and leave it to dry. Take few drops of the filtrate, put it on a glass plate and warm it gently using a heat gun. Describe the solid residue you obtain.*

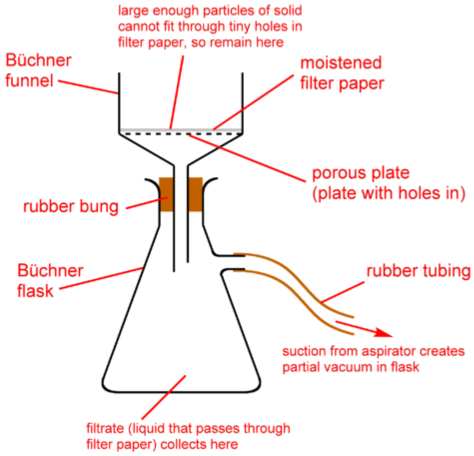

Figure 2: Vacuum filtration apparatus

The solid precipitate we obtained is a natural mineral, gypsum[9]. Its properties are different from the properties of starting materials we took. Indeed, whereas both calcium chloride and sodium sulfate are soluble in water, gypsum is not, and this fact is sufficient to conclude that some new substance has been formed during our experiment. Moreover, the solid we obtained after evaporation of sulfate also is a new substance: it is ordinary table salt. We can summarize our observations by the following equation[10] (57):

$$\text{Sodium sulfate} + \text{Calcium cloride} = \text{Calcium sulfate} + \text{Soduim chloride} \tag{1}$$

Had Democritus been asked to explain this process using his theory, he would have encountered a serious problem. Of course, he could be perfectly able to explain the process of dissolution of sodium sulfate or calcium chloride. However, he would be totally unable to

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[6] It is a water-soluble crystalline solid, which is being used for example as a medicine for treatment of hypocalcaemia.

[7] White water-soluble crystalline solid. It was used during XVII-XIX centuries as a laxative

[8] Buchner funnel and Bunsen flask are the parts of laboratory apparatus used for filtration.

[9] Gypsum is a material drywalls in your home are made from.

[10] Actually, that is not exactly how chemists write chemical equations. They use chemical formulas, not words. We will learn how to draw chemical formulas a little bit later.

explain the formation of sodium chloride and gypsum (as well as disappearance of sodium sulfate and calcium chloride). Remember, Democritus's atoms are impossible to create or destroy, and each substance is composed from its own type of atoms, according to him. However, if we assume some special gypsum "atoms"[11] do exist in nature, the question arises where these atoms have been before we started our experiment? They could be neither in sodium sulfate nor in calcium chloride, because these two are pure substances, not mixtures, and because both of them are water soluble, but gypsum is not. In addition, it is not clear from the Democritus's theory why sodium sulfate or calcium chloride *alone* cannot produce gypsum, but their combination can? And, finally, one more important question remains: where sodium sulfate and calcium chloride "atoms" have gone?

We see Democritus's theory fails to explain the processes where some substances are being consumed and new substances form instead. This type processes are called **chemical reactions**.

Chemical reactions are the processes of transformation of one (or several) chemical substances to other, new substances.

Experiment 4

> *Place a small piece of chalk into a glass test tube and add few milliliters of dilute hydrochloric acid. You will see the bubbles of some gas will start to evolve immediately, and chalk will be dissolving gradually.*

Experiment 5

> *Dissolve few grams of sodium carbonate*[12] *in 100 mL of water. Add few drops of dilute alcoholic solution of phenolphtalein*[13] *to it and stir gently. The colorless solution will immediately turn pink.*

The experiments **4** and **5** serve as other examples of chemical reactions. Dissolution of some material which is known to be insoluble, evolution of gas, color change - all are the traits of chemical reactions. This list is not exhaustive, moreover, sometimes the traits of a chemical reaction are hard to see (in that case chemists use special methods - we will learn about some of them later).

All these phenomena are totally impossible to explain using the original atomic theory, and that was the main reason the Democritus theory was rejected by most prominent thinkers and passed into oblivion for about two thousand years. However, it was not completely forgotten.

2.1 From Deomcritus's "atoms" to modern "molecules"

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[11] We use quotation marks because the actual term *atom* is not applicable here.

[12] Sodium carbonate is also called "washing soda". It can be prepared by heating ordinary baking soda in an oven

[13] Phenolphtalein is a synthetic compound that was used in past as laxative

Robert Boyle (1627–91), one of the first modern chemists.

We demonstrated that the idea of indivisible and indestructible atoms as building blocks for matter was not useful for explanation of chemical reactions. The next question is, could this theory be improved or amended? Initially, philosophers didn't believe it was possible, so the atomic theory was totally abandoned, and absolutely different concepts were proposed instead. Different candidates for the universal material were proposed by philosophers, including fire, or air, or earth, or water. Aristotle attempted to combine these ideas into a single theory: according to him, air, fire, earth, and water, when mixed in different proportions, form all other substances in our world. However, by XVII century, early chemists, such as Robert Boyle, started to learn more about properties of matter and about chemical reactions, they realized that chemical substances are probably composed of some particles of various sorts, although they avoided to call them "atoms", and used other words, such as "corpuscula", or "molecula".[14] The latter term became more and more popular, and became commonly accepted by XIX century. In English, the word "molecula" transformed to "a molecule".

The reason for inventing this new term (instead of an old word "atom") was as follows. *Whereas atoms cannot be formed, changed or destroyed during chemical reactions, molecules can.* In other words, molecules have the same properties as old Democritus's "atoms" had, except one, namely, they can be changed (actually, Democritus "atoms" were what we currently call "molecules", the only difference is that his "atoms" were unchangeable).

John Dalton (1766–1844), a developer of modern atomic and molecular theory.

And what about the term "atom"? It was not fully abandoned. Chemists realized that, whereas most molecules are able to change during chemical reactions, the building blocks the molecules are composed of are unchangeable by chemical means. To name these building blocks, chemists decided to use the old name "atoms" (which was absolutely correct, because real atoms are chemically indivisible). The idea that matter is composed of atoms which are grouped in "small ultimate particles" (which we now call "molecules") was formulated in early XIX century by British chemist John Dalton.

Dalton's theory made a revolution in chemistry, and it lead to an explosive progress of chemical knowledge. This theory deserves a separate attention, and we will devote the next Section to it.

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[14] In Latin, the suffix "ula" plays a diminutive role, so "corpuscula" means "an extremely minute body" ("corpus" means "a body"), and "molecula" means "an extremely minute mass".

Homework

1. During this class (see **Experiment 3**), we filtered out the crystals of gypsum and left them to dry. We also collected the filtrate, which contained another product of this reaction, namely, table salt. I left it to evaporate in the flask, and by the next Sunday it will be completely dry. During our next class we will weigh dry gypsum and table salt we obtained today. Could you predict what the masses will be? Use the following data for your calculations. We took 1.47 grams of calcium chloride dihydrate and 1.42 grams of sodium sulfate. Assume that the masses of one molecule of starting and final compounds are as follows. Calcium chloride: 147 arbitrary units (a.u.)[15], sodium sulfate: 142 a.u., gypsum: 172 a.u., sodium chloride: 58.5 a.u. *Please keep in mind that in this reaction one molecule of calcium chloride reacts with one molecule of sodium sulfate yielding one molecule of gypsum and* two *molecules of salt.* You need to take that fact into account in your calculations.
2. I believe you were able to solve the first problem easily (it is not as formidable at seems). However, to solve this problem you had to make some implicit assumptions. Try to formulate them explicitly. Which law can be derived from our experiment?

3 Dalton's atomic theory. Composition of molecules. Valence.

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

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[15] So far, we do not care what does a.u. mean. We can perfectly do all computations without knowing what a.u. is equal to.

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[16]. 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.

3.0.1 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,

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

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

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 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.[17]

3.0.2 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.

3.1 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

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[17] 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.*

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 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[18], so we will use hydrogen's mass as an atomic mass unit.[19]

Figure 3: Jons Jacob Berzelius
(1779-1848),
a developer of modern
chemical formula notation.

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

[19] 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 Section devoted to isotopes.

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

3.1.1 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 Section devoted to isotopes.

3.1.2 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** (57):

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

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[20]

---

[20] 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.

3.1.3 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 $27\times2+16\times3 = 102$ 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.

3.2 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" (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[21]. 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.[22] Their formulas are Cu_2O and CuO. What is the valence of copper in each of them?

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:

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

---

[21] 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

[22] such compounds are called "oxides"

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.[23] For example, a molecule of carbon dioxide, a gas used for preparation of soda water, can be drawn as follows:

$O{=}C{=}O$

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.[24] For example, if some element X is divalent, its binary compound with a monovalent element Y has a structure:

$Y{-}X{-}Y$

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

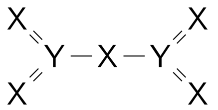
If both X and Y are divalent, the structure of the binary compound is:

$X{=}Y$

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

$X{=}Y{=}X$

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.

---

[23] 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.

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

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.**

4.1 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.

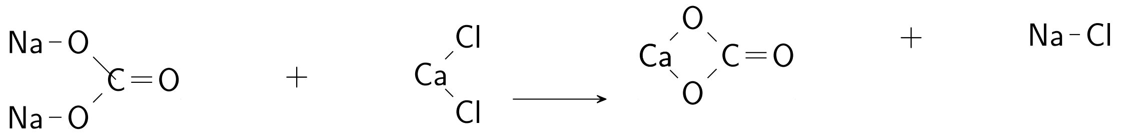
Table 2. Most common elements, their atomic masses and common valences[25]

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,[26] 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".

4.2 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 Section 2 can be redrawn as follows:



Sodium carbonate

Calcium chloride

Calcium carbonate

Sodium chloride

---

[25] 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

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

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[27].

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[28].

5. * Which of two binary compounds contains more oxygen by weight, sodium oxide Na_2O, or iron (II) oxide FeO?

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)?

---

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

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

5 Oxygen. Oxides. Chemical equations and some simple calculations.

5.1 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.[29] 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.*

5.2 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[30] is being baked on open air, and both Priestly and Scheele were able to collect the gas that formed when mercury oxide decomposed.

---

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

[30] 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

> *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.*[31]

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."

5.3 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 (3):

$$2\,\mathrm{HgO} \longrightarrow \mathrm{O_2} + 2\,\mathrm{Hg} \tag{3}$$

---

[31] 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.

As we already know, Scheele obtained oxygen by heating saltpeter.[32] The reaction was as follows (4):

$$2\,\mathrm{KNO_3} \longrightarrow 2\,\mathrm{KNO_2} + \mathrm{O_2} \tag{4}$$

Arguably, the most convenient and safe way to prepare oxygen chemically is a decomposition of dilute solution of hydrogen peroxide[33] in a presence of manganese dioxide,[34] according to the equation (5):

$$2\,\mathrm{H_2O_2} + \mathrm{MnO_2} \longrightarrow 2\,\mathrm{H_2O} + \mathrm{O_2} + \mathrm{MnO_2} \tag{5}$$

The equations (3) - (5) 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* (5)*! 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.

5.4 Properties of oxygen

5.4.1 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 °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. 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).

---

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

[33] Dilute hydrogen peroxide (H_2O_2) is sold in pharmacies as a local antiseptic.

[34] Manganese dioxide (MnO_2) can be found in some (non-rechargeable) batteries

5.4.2 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[35] *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[36] 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 5: 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 (57)):

$$C + O_2 \longrightarrow CO_{2(g)} \tag{6}$$

and interaction of carbon dioxide with lime vater (a solution of calcium hydroxide, $Ca(OH)_2$ (7):

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_{3(s)} + H_2O \tag{7}$$

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.

---

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

[36] 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

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.[37] *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 (8):

$$S + O_2 \longrightarrow SO_{2(g)} \tag{8}$$

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.[38] In this case, the product of sulfur combustion is also a gas.

Figure 6: 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.[39] 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 (9):

$$4\,P + 5\,O_2 \longrightarrow 2\,P_2O_{5(s)} \tag{9}$$

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

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?

---

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

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

[39] 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 7: Burning of a steel rope in pure oxygen

Not only we see a bright fire and a disappearance of a steel rope (Fig. 7), 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. **??**)[40] This reaction occurs according to the equation (10):

$$4\,\mathrm{Fe} + 3\,\mathrm{O_2} \longrightarrow 2\,\mathrm{Fe_2O_3} \tag{10}$$

5.4.3 Appollo 1 fire.

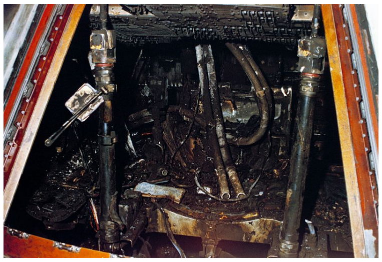


Figure 8: Apollo 1 cabin's interior after fire.

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).

5.5 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[41]

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[40] 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.

[41] except fluorine.

belong to the class of reactions that are called *oxidation* reactions. The chemical compounds formed by oxygen and some element are called *oxides*.[42]

> **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 (11):

$$\mathrm{CaCO_3 \longrightarrow CaO + CO_{2(g)}} \tag{11}$$

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.

5.6 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 (12)

$$\mathrm{P + O_2 \longrightarrow P_2O_5} \tag{12}$$

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 (12), because the number of atoms in right and left sides of the scheme is not equal. To make them equal, we modify the scheme (12) as follows:

$$\mathrm{4\,P + 5\,O_2 \longrightarrow 2\,P_2O_5} \tag{13}$$

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

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

> *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* (12)*, 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 (13), 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 (13) 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:

$$\frac{124\text{ Da}}{31\text{ g}} -> \frac{284\text{ Da}}{x} \tag{14}$$

By re-organizing the equation, we get:

$$x = 284\text{ Da} \times \frac{31\text{ g}}{124\text{ Da}} = 71\text{ g (grams of phosphorus (V) oxide).} \tag{15}$$

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:

$$\mathrm{Mg} + \mathrm{O_2} \longrightarrow \mathrm{MgO} \tag{16}$$

$$\mathrm{C} + \mathrm{O_2} \longrightarrow \mathrm{CO_3} \tag{17}$$

$$\mathrm{CH_4} + \mathrm{O_2} \longrightarrow \mathrm{CO_2} + \mathrm{H_2O} \tag{18}$$

$$\mathrm{C_2H_2} + \mathrm{O_2} \longrightarrow \mathrm{CO_2} + \mathrm{H_2O} \tag{19}$$

6 Oxides in nature. Acidic oxides. Acids.

6.1 Oxides in nature.

As we already know, oxygen is the most abundant element in the Earth crust: it constitutes about 49% of Earth lithosphere (by mass), and 20% of atmosphere (by volume).[43] Taking into account that water is actually a hydrogen oxide, oxygen is a major component of Earth hydrosphere too (please, calculate the oxygen content in water by yourself). Oxygen exists in a chemically bound form everywhere except in the Earth atmosphere, and various oxides are among the most abundant forms of chemically bound oxygen on the Earth. Besides water, such oxides are iron oxides (which are found in a form of magnetite, hematite, goethite, limonite, etc, see Fig. 9), aluminum oxide, silicon dioxide (in a form of quartz, opal etc).

Figure 9: Monument valley. Arizona and Utah sandstones are red due to a large content of iron oxide.

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[43] The rest is nitrogen (79%) and remaining 1% are other gases, mostly argon, water vapors and CO_2

6.2 Acidic oxides

Although we couldn't do the Experiment 10 (combustion of phosphorus) for formal reasons, we can experiment with the product of phosphorus's combustion, namely, with phosphorus (V) oxide. Let's look at this compound closer. Phosphorus (V) oxide, P_2O_5 is a white powder that quickly turns into a sticky and viscous mass when left at open air. To understand why does it happen, let's do an experiment.

Experiment 12

Pour about 100 mL of water into a large beaker. Add approximately a quarter teaspoon of P_2O_5[44]*. Describe your observations.*

As we have seen, phosphorus (V) oxide interacts with water violently. Is that a chemical reaction? Yes, an attempt to get P_2O_5 back, for example, by evaporation of water, would be unsuccessful: you will never be able get the same white powder back. Therefore, it would be correct to conclude that some chemical reaction occurs between water and P_2O_5, and the resulting compound dissolves in the excess water. What can we say about that solution? Let's take an indicator paper[45] and immerse it into the liquid we prepared. The paper will immediately become red. That is an indication that the liquid we prepared is an acid. A new substance we prepared from P_2O_5 is a *phosphoric acid* (H_3PO_4), and the reaction equation is as follows:

$$P_2O_5 + 3\,H_2O = 2\,H_3PO_4 \tag{20}$$

Phosphoric acid is a representative of the second important class of chemical compounds. This class is called ***acids***.

> *Now we can explain why* P_2O_5 *becomes a semi-solid viscous mass when exposed to an open air: it simply reacts with atmospheric water vapors. The substances that absorb water vapor from the atmosphere are called* ***hygroscopic****. Some of them are used as drying agents, for example, to reduce humidity during transportation of some sensitive objects of art.*

Besides P_2O_5, some other oxides also produce acids during their reaction with water. Such oxides are called *acidic oxides.* Among the oxides we are already familiar with, sulfur (IV) oxide and carbon (IV) oxide are acidic oxides. Their reactions with water produce sulfurous and carbonic acids, respectively:

$$SO_2 + H_2O = H_2SO_3 \tag{21}$$

$$CO_2 + H_2O = H_2CO_3 \tag{22}$$

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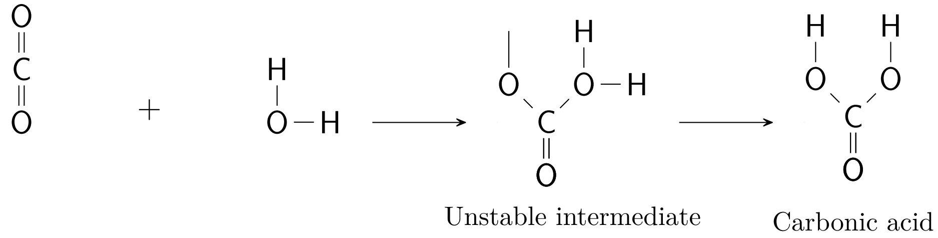
[44] Obviously, one must wear goggles during this experiment, as well as during all other experiments in the lab.

[45] An indicator paper is a paper stained with a mixture of special dyes. These dyes can change their color depending on the acidity on the media the paper is immersed in.

Some oxides, such as silicon dioxide, do not react with water directly. Nevertheless, they still can be converted into acids using some indirect procedure. Therefore, SiO_2 and similar oxides also considered acidic oxides.

Oxides that can be converted into acids are called 'acidic oxides'.

To understand how oxides form acids, let's look at the mechanism of that reaction. To do that, let's redraw the equation 65. On the scheme below the structural formulas of each molecule are shown. In addition, some odd molecule is shown in the middle of the scheme. What this molecule is?



As you can see, this molecule (labeled as "Unstable intermediate") is "wrong": in this molecule, one oxygen is trivalent, and another oxygen has a bond that goes to nowhere (i.e. it is not connected to any atom). As we already know, such molecules are impossible (or, more correctly, they are very unstable, so they don't live long). Why did I draw a structure of this short-living species? Because this odd structure reflects the actual mechanism of this reaction. You have probably noticed that the left part of this "unstable intermediate" resembles a carbon dioxide molecule, and the upper-right part resembles water, and that is not just a coincidence. This molecule forms as a result of the attack of CO_2's carbon by a water oxygen, and this is a first step of the reaction between carbon dioxide and water. However, since the intermediate molecule cannot live long, it needs to rearrange into some more stable molecule. That is achieved by jumping of a hydrogen atom from one oxygen to another. As a result, we get a molecule that contains three divalent oxygens, one tetravalent carbon, and two monovalent hydrogens i.e. the carbonic acid.[46]

Addition of water to the oxides of other elements proceeds according to the same mechanism: the reaction starts with the attack of the element's atom in the oxide by water oxygen atom, followed by hydrogen's jump to another oxygen. Importantly, the valence state of each atom is always preserved in the reactions of that type: if we take, for example, carbon (IV) oxide, the carbon atom in carbonic acid will be also tetravalent. Similarly, since phosphorus in pentavalent in P_2O_5 it remains pentavalent in phosphoric acid. The reason is obvious: as you can see from the scheme of the reaction between CO_2 and H_2O, during this reaction only rearrangement of the existing bonds takes place, so the number of chemical bonds remains the same.

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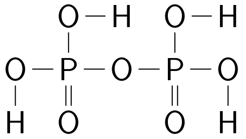
[46] Actually, this scheme is a little bit oversimplified. To draw a fully correct scheme of this reaction, we need to learn more about the electronic structure of atoms and molecules. We will return to this scheme later.

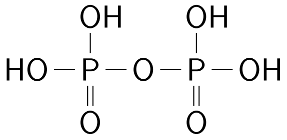
6.3 Simplified, or condensed structural formulas

As we can see on the previous scheme, structural formulas of bigger molecules become more and more complicated. To save our time, it is convenient not to draw all bonds explicitly. For example, we all know that hydrogen is always monovalent, so, when one atom of hydrogen is attached to oxygen, the oxygen atom can form just one more bond. In other words, a fragment “O-H” behaves as some composite monovalent atom. Since many compound exist that contain an “O-H” fragment, it is convenient not to draw this fragment explicitly, but to show it as a single “atom”. By using this trick, many formulas can be significantly simplified. Thus, instead of drawing this:



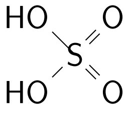
“Pyrophosphoric acid”

we can draw that:



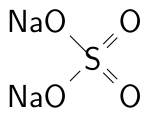
“Pyrophosphoric acid”

I believe you agree that the later formula looks nicer, and it is easier to draw and understand. Structures of other acids can be simplified in the same way. Thus, sulfuric acid can be drawn as follows:



Sulfuric acid

The same trick can be done with other compound. For example, a structure of sodium sulfate (Na_2SO_4) can be depicted as:



Sodium sulfate

In future, we will use simplified structural formulas when it is possible. There are other ways to make them even simpler, and will learn about that later.

6.4 Acids.

As we already demonstrated, some oxides (which are called "acidic oxides") produce acids when react with water. Acids form a second important class of inorganic compounds.

Definition 0.

Acids are compounds having a sour taste.

Although it sounds a little bit childish, the above definition is quite correct. The reason is simple: we have receptors on our tongue that detect acidity. Of course, that does not mean we must taste every chemical to check if it is an acid. In contrast, one of the most strict safety rules is: never taste anything in the lab! This rule saved thousands and thousands lives of chemists, and it must be strictly obeyed. To check if some substance is an acid, we use an "artificial tongue": either an indicator paper or a special electronic device called "pH-meter". Taking into account all said above, more common and strict definition of the term "acids" is:

Definition 1.

Acids are the substances having a pH value below 7 as measured by an indicator paper or a pH-meter.

Although this definition looks more "scientific", I hate such type definitions: it refers to the term "pH" that we haven't discussed yet. However, in this case, it is acceptable, because our tongue can sense "pH" directly, so for us a term "acid" is as natural as, for example, the term "red" is.

A common property of acids is their ability to react with some metals.

Experiment 13

Pour ca 5 mL of dilute sulfuric acid into a test tube. Carefully drop a granule of zinc into the acid. Describe your observations.

As we see, bubbles of some gas start to form on zinc surface immediately after we immersed zinc into the acid. This gas is hydrogen, and the equation of this reaction is as follows:

$$Zn + H_2SO_4 = ZnSO_4 + H_{2(g)} \tag{23}$$

During this reaction, zinc *replaces* or *substitutes* hydrogen atom in the H_2SO_4 molecule. Accordingly, this type reaction is called “replacement” or “substitution reaction”. This reaction is possible because sulfuric acid has the hydrogen atom it can easily donate. It can be demonstrated that that property (an ability to donate hydrogen) is a common property of all acids. Based on that, a more scientific definition of the term “acids” can be proposed:

Definition 2.

Acids are compounds having hydrogen atoms that can be substituted by active metals.[47]

Under “active metals” I mean such metals as zinc, iron, tin, magnesium. Some other metals, such as silver, copper, gold, mercury, platinum, do not react with common acids. Due to low reactivity, some of them, especially gold and platinum, are called “noble metals”.

> ***Oxides, acids, and the origin of oxygen’s name.*** *As you can see, acids are formed during the reaction between some acidic oxide (SO_2, SO_3, N_2O_5) and water, and many acids contain oxygen as an essential component. In XVIII century, by the moment oxygen had been discovered, chemists believed that every acid must contain oxygen, which was considered to be an essential and indispensable component of every acid. That is why Antoine Lavoisier coined the term “oxygen”. This term was based on two Greek words, “oxys” (acidic, literally, “sharp’) and “gonos” (literally “begetter”). Soon after that, the acids containing no oxygen had been discovered. However, chemists decided to preserve the name “oxygen” for this element.*

6.5 Nomenclature of acids

Now, when we know what the acids are, I believe it is a good moment to discuss how to name them. The acid’s name depends on its composition (whether it contains oxygen or not) and on the element’s valence (under ’element’, I mean the non-oxygen and non-hydrogen atom, a central atom in an acid).

> **Rule 1.** (for non-oxygen acids):
> *The name of an acid with a formula H-X, where ’X’ is some atom is formed by addition of the prefix ’hydro’ and the ending ’ic’ to the element’s name, followed by a word ’acid’.*
> **Examples** Hydrochloric (*hydro*-chlor-*ic*) acid (HCl) is formed by chlorine (Cl), hydroiodic (*hydro*-iod-*ic*) acid (HI) is formed by iodine.
> **Rule 2.** (for oxygen containing acids)
> *If the element can exists in one valence state only (such as silicon), the name of*

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[47] This definition is very close to that used in university textbooks, although it still is imprecise. However, for the beginning, it is quite satisfactory.

its oxygen containing acid is formed by adding the ending 'ic' to the element's name, followed by a word 'acid'.
Example Carbonic (carbon-*ic*) acid, H_2CO_3.
Rule 2a. (when the element may exist in two different valence states.)
For the acids where the element has a highest possible valence, the rule 2 still works. When the element's valence is lower, an ending 'ous' is added instead of 'ic'.
Examples. In sulfuric (sulfur-*ic*) acid (H_2SO_4), sulfur has a valence of 6; in sulfurous (sulfur-*ous*) acid (H_2SO_3) sulfur has a lower valence (it is tetravalent). Other examples are phosphoric/phosphorous acids (H_3PO_4 and H_3PO_3, accordingly), or nitric/nitrous acids (HNO_3 and HNO_2).

Since most elements have either one or two valence states, the above rules are sufficient to name most acids. However, more than two valence states are possible for several elements (for example, chlorine). Specifically for those elements, one more rule was proposed.

Rule 3.(for the elements existing in more than two valence states.)
The prefix 'per' and 'hypo' are used to denote highest and lowest element's valence states in its acids.
Example. Chlorine can be mono-, tri-, penta-, and heptavalent. In addition, it forms a non-oxygen acid. Accordingly, a full set of acids formed by chlorine is as follows: hydrochloric (HCl), *hypo*chlor*ous* (HClO, chlorine is monovalent), chlor*ous* (HCO_2, chlorine is trivalent), chlor*ic* ($HClO_3$, chlorine is pentavalent), and *per*chlor*ic* ($HClO_4$, chlorine is heptavalent).

Now we are ready to discuss properties of acids in more details. We will devote the next lessons to that.

Homework

1. Draw the chemical equations of the reaction between water and the following acidic oxides: (a) N_2O_5, (b) N_2O_3, (c) SO_3, (d) Cl_2O_5, (e) P_2O_3. Draw structural formulas of the acids formed during these reactions.

2. Draw the chemical equations of the reactions between (a) hydrochloric acid and magnesium, (b) sulfuric acid and iron, (c) tin and dilute nitric acid[48], (d) Aluminum and hydrochloric acid.

3. At room temperature and under atmospheric pressure, two grams of hydrogen occupy 22.4 L.[49] Will you be able to inflate a balloon up to 50 cm diameter using 50 grams of zinc and an unlimited amount of a hydrochloric acid? In your calculations, assume

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[48] it is important that nitric acid is dilute, because only dilute nitrous acid reacts with metals as other acids do.

[49] Actually, this is a general law: if a mass of one molecule of some gas is X Da, then X *grams* of this gas will occupy a volume of 22.4 L at standard temperature and pressure. We will talk about this law a little bit later.

the balloon has a spherical shape and the pressure inside the balloon is approximately atmospheric.

4. 38 grams of sulfur trioxide (SO_3) have been added to 200 mL of water. The obtained solution of the acid was added to 32 grams of iron. Will the iron dissolve completely? What will be the volume of hydrogen that forms during this reaction?

7 Chemical calculations.

7.1 Mole

One of the most common operations any chemist is doing routinely is as follows: "How much of the substance A is needed to produce a substance B?", or "How much of the substance B is needed to react with the substance A?"

For example, consider the following reaction:

$$\mathrm{Zn} + \mathrm{H_2SO_4} \longrightarrow \mathrm{ZnSO_4} + \mathrm{H_{2(g)}} \tag{24}$$

In this reaction, zinc (atomic weight 65 Da) interacts with sulfuric acid (molecular weight 98 Da). Obviously, since one molecule of zinc[50] reacts with one molecule of sulfuric acid, we may replace Daltons with grams, and conclude 65 *grams* of zinc are needed to react with 98 *grams* of sulfuric acid. In other words, the amount of particles (molecules) in 65 grams of zinc is equal to the amount of particles in 98 grams of sulfuric acid. Generally speaking, from the chemist's point of view, the amount of matter in 65 grams of zinc and in 98 grams of H_2SO_4 is the same. Indeed, we chemists are more interested in looking at molecules, and we do not care too much about their weight, because it is the number of molecules that matters, not their weight. That is why for us it is much more convenient to measure matter not in grams, but in other units that take into account the number of molecules. This unit is called a *mole*.

One mole of any substance is the amount of this substance in grams that is numerically equal to the molecular weight of this substance in daltons. For example, the molecular weight of hydrogen (H_2) is 2 Da, and, accordingly, one mole of hydrogen weighs 2 grams. Accordingly, one mole of nitric acid (HNO_3, MW = 63) is 63 grams, one mole of calcium carbonate ($CaCO_3$, MW = 100 Da) is 100 grams, and so on.

The concept of mole is one of the most fundamental chemical concepts. It makes chemical calculations much easier, and we will be using this concept very frequently.

Homework

1. Draw the structural formulas of the following compounds:

   HNO_3, H_3BO_3, Cr_2O_3, Cl_2O_7, C_2H_6, K_2SO_4.

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[50] Since metals do not form polyatomic molecules, for our purposes, zinc atom and zinc molecule is the same thing. This is true for all other metals.

Based on these structural formulas, decide which compounds from this list are acids, and name these acids using the rules we discussed in the class (the rules are available in the previous class reading materials).

2. Draw structural formulas for the following acids:

   a) phosphoric acid, b) nitric acid, c) chloric acid[51], d) sulfurous acid, e) silicic acid.

3. Iodine is the element that can exist in four different valence states. Can you tell, what is the relationship between the term "periodic acid" and the term "periodicity"?

4. A 20 g sample of the mixture of quartz sand[52], iron shavings, and graphite was treated with dilute sulfuric acids, and the gas formed was collected. When evolution of the gas has ceased, more acid has been added to the sample, but no reaction was observed after that. The total volume of the gas was 4 L. What is the content of iron shavings (in percents) in the mixture[53]?

5. You have four pieces of different metals: calcium, magnesium, iron, and zinc. The mass of each piece is 40 g. Which piece contains the biggest and the smallest number of atoms? If you add an excess of dilute H_2SO_4 to each piece, what will be the volume of hydrogen that forms in each case?

8 Salts and their reactions. Reaction of active metals with water. Bases, basic oxides, and their interaction with acids.

8.1 Nomenclature of salts

Before we started to discuss reactions of salts, and methods of their preparation, we need to know how to name them. Since salt are composed of some acidic residue[54] and a metal atom (or atoms), it would be logical to derive salt's name from the names of corresponding acids and metals. That is exactly what chemists do. The salt nomenclature (naming rules) are simple and straightforward. The rules are as follows.

Rule 1. (for non-oxygen acids):
The name of a salt formed by some metal and some non-oxygen acid is formed by combining the metal's name and the name of the acid. The prefix 'hydro' is removed, and the ending 'ic' is replaced with 'ide'
Examples Hydrochloric (*hydro*-chlor-*ic*) acid (HCl) and sodium form a salt named 'sodium chlor*ide* (NaCl).

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[51] Chlorine is pentavalent in chloric acid.

[52] Quartz is a crystalline silicon oxide.

[53] At room temperature and under atmospheric pressure, two grams of hydrogen occupy 22.4 L.

[54] Acidic residue is what is remaining when one or several hydrogens have been removed from the acid's molecule.

Calcium and hydrochloric acid form calcium chloride $CaCl_2$.[55]
Rule 2. (for oxygen containing acids)
In salts formed by 'ic' acids, the ending 'ic' is replaced with 'ate'.
Examples Carbonic (carbon-*ic*) acid, H_2CO_3 and sodium form a salt named 'sodium carbon*ate* (Na_2CO_3).
Sulfur*ic* acid and calcium from a salt named 'calcium sulf*ate* ($CaSO_4$).
Rule 2a. (for 'ous' acids).
In salts formed by 'ous' acids, the ending 'ous' is replaced with 'ite'.
Examples. Sulfur-*ous* acid (H_2SO_3) and sodium from a salt named 'sodium sulf*ite* (Na_2SO_3).
Nitr*ous* acid (HNO_2) and potassium from a salt named potassium nitr*ite* (KNO_2).

Since the acids whose name starts with 'hypo' or 'per' also can form salts, a separate rule exists for that type acids. This rule is simple.

Rule 3.(for the acids whose names begin with 'per' or 'hypo'.)
If acid's name starts with the prefixes 'per' or 'hypo', such a prefix is preserved in the salt's name.
Examples. A salt formed by sodium and *hypo*chlor*ous* acid (HClO) acid is called 'sodium *hypo*chlor*ite*' (NaClO). A salt formed by sodium and *per*chlor*ic* acid ($HClO_4$ is called 'sodium *per*chlor*ate*' ($NaClO_4$).

We are almost finished with the rules. There is one more rule; it deals with a situation when a metal can exist in more than one valence state. For example, iron can be either di- or trivalent, and, accordingly, it can from two different salts with hydrochloric acid. Their formulas are $FeCl_2$ and $FeCl_3$. As we can see, both these salts are 'chlorides'. Two alternative ways exist to create unique names for each of them. Firstly, we can show metal's valence using a Roman number.

Rule 4a.
When more than one valence states is possible for some metal, its valence can be indicated with a Roman letter after the metal name.
Examples. The name of $FeCl_2$ is 'iron (II) chloride'. The name of $FeCl_3$ is 'iron (III) chloride'.

Another possibility is to add the ending 'ous' or 'ic' to the *Latin* name of the metal. The meaning of these prefixes is the same as for acids: lower valence is denoted by 'ous', whereas higher valence by 'ic'.

Rule 4b.
When some metal is in a lower valence state, that fact can be indicated by adding the ending 'ous' to its Latin name. For metals in a higher valence state, the

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[55] In school, you may be requested to include numerals into the salt's name. For example, instead of 'calcium chloride' ($CaCl_2$) you should say 'calcium *di*chloride', instead of 'aluminum chloride' ($AlCl_3$) you should say 'aluminum *tri*chloride', etc. Although that is not incorrect, chemists prefer not to do that. During our lessons we will not use numerals unless that is absolutely necessary.

ending 'ic' is used.
Examples. A Latin name of iron is 'ferrum', therefore $FeCl_2$ is called 'ferr*ous* chloride', and $FeCl_3$ is called 'ferr*ic* chloride'. In Latin, copper's is called 'cuprum', therefore, their salts have names 'cuprous chloride' (CuCl), and 'cupric chloride' ($CuCl_2$).

This is an almost exhaustive set of rules. Most salts are named according to them. I neither expect nor want you to memorize all these rules, I presented them just to demonstrate that the rules are relatively simple. However, in future, you will use these rules frequently, and you know where can you find them: they will always be at our school's web site. The most frequently used rules are Rule 1 and Rule 2, sometimes, a Rule 4a. We will need them right now, during this lesson.

8.2 Reactions of salts with metals. More on the reactivity series.

Experiment 15a

Pour 5 mL of the solution of copper (II) sulfate ($CuSO_4$) into a test tube, and immerse an iron rod into it. Describe your observations.

After 5 minutes, the rod becomes reddish; the red film become more and more thick, and finally it peels off like a red sponge. It is easy to demonstrate that this is a copper metal. If we wait long enough we can see that a blue color of the copper sulfate solution gradually disappears, and the solution becomes pale greenish. This color belongs to another salt, iron (II) sulfate. Obviously, a chemical reaction occurs, and we can write the following equation for it:

$$\mathrm{Fe} + \mathrm{CuSO_4} = \mathrm{FeSO_4} + \mathrm{Cu} \tag{25}$$

As in the case of iron and sulfuric acid, a substitution reaction occurs, however, instead of elementary hydrogen, another simple substance, copper, is formed. Is such a reaction common for an arbitrary salt-metal pair? Let's try to think logically. Since a chemical reaction will hardly go into the opposite directions under the same conditions, swapping the sides in the equation 25 would lead to the equation describing the reaction that doesn't go normally. Actually, this consideration is totally correct: it is easy to demonstrate that reaction is not possible.

Experiment 15b

Pour 5 mL of the solution of iron (II) sulfate ($FeSO_4$) into a test tube, and immerse a piece of copper wire into it. Do you see any reaction?

As we expected, no reaction takes place.

Maybe, this reaction is specific to copper sulfate only? Let's check that.

Experiment 15b

Pour 5 mL of the solution of silver nitrate ($AgNO_3$), and immerse a piece of copper wire into it. What do you see?

We see that lustrous crystals quickly form on the copper surface, and that the colorless solution becomes green-blue. It is easy to demonstrate that the crystals we obtained are a silver metal. With regard to the color, it is characteristic for most copper salts, so we can conclude some copper salt, is formed. Indeed, a chemical analysis can demonstrate a new salt forms, a copper nitrate. The equation of this reaction is as follows:

$$\mathrm{Cu} + 2\,\mathrm{AgNO_3} = \mathrm{Cu(NO_3)_2} + 2\mathrm{Ag} \tag{26}$$

Again, similar to the of iron and copper sulfate case, a new metal and a new salt form. It is easy to demonstrate that the opposite reaction wouldn't go.

Do those reaction have anything in common? Yes. First of all, these reactions are *substitution reactions*. Secondly, in each of those reaction, one metal substitute another in its salt. Thirdly, there reactions go in one direction (copper sulfate reacts with iron), and do not go in another (iron sulfate does not react with copper). It is also easy to demonstrate that the acidic residue does not affect this reaction: for example, copper chloride and copper sulfate react similarly. All of that can be summarized as follows: copper *salts* react with iron to produce copper *metal*, silver *salts* react with copper to produce silver *metal*. It can be demonstrated that other metals, such as zinc, tin, etc, produce silver in the reaction with silver nitrate, but gold or platinum do not react with $AgNO_3$. Can we summarize all these facts in some simpler rule? We can try. To do that, let's look at the reactivity series again.

Reactivity series of metals
K, Na, Li, Ca, Mg, Al, Ti, Mn, Zn, Cr, **Fe**, Co, Ni, Sn, Pb (H) **Cu**, W, Hg, **Ag**, Au, Pt

As we can see, the metals we experimented with are arranged in the following order (in terms of their reactivity): iron is left of copper, and copper is left of silver. It can be easily demonstrated that rule is general: all metals left of tin are able to substitute it from tin salts, all metals left of gold can substitute it from gold salts, and so on. This is a general rule the reactivity series was built on. And it can be summarized as follows:

> **More active metals substitute less active metals from their salts. The opposite reaction does not go.**

8.3 Reactivity series and hydrogen

Let's look again at these two equations:

$$\mathrm{Fe} + \mathrm{CuSO_4} = \mathrm{FeSO_4} + \mathrm{Cu} \tag{27}$$

and

$$\mathrm{Fe} + \mathrm{H_2SO_4} = \mathrm{FeSO_4} + \mathrm{H_2} \tag{28}$$

Clearly, they have much in common: both of them are substitution reactions, in both of them one element substitutes another element from its compound. The only difference is that in the first case iron reacts with salt, and in the second case it reacts with acid. This comparison explains why did we put hydrogen into the reactivity series: the metals left of hydrogen are more active than hydrogen, and they substitute hydrogen from acids (in the same manner they substitute, for example, copper or silver from their salts). In contrast, the metals left to hydrogen are less active, so they cannot substitute it from acids.
The reactivity series is a first example of an empiric law that allows us not only to describe chemical reactions, but also to predict their outcome. There are many similar law in chemistry that make it not just a random collection of facts, but a systematic science. We will learn many of them during this and the next year.

8.4 On the very left part of the reactivity series.

As we already know, all metals left of hydrogen are able to react with acids to produce hydrogen. The closer to the left end of the series they are, the more actively they react with acids. Thus, almost no reaction takes place between acetic acid and iron; zinc does react with acetic acid, although very slowly; magnesium reacts with acetic acid very actively. In other words, active metals are capable of substituting hydrogen even from the molecules that are not willing to easily donate hydrogen. What about more active metals, the metals left of magnesium? Those metals (shown in bold below) are so active that they react too violently even with acetic acid.

Reactivity series of metals
K, Na, Li, Ca, Mg, Al, Ti, Mn, Zn, Cr, Fe, Co, Ni, Sn, Pb (H) Cu, W, Hg, Ag, Au, Pt

We know water contains hydrogen, but its hydrogen is not too active (at least, no hydrogen is formed when water is added to zinc or iron). We also know that common metals are not capable of substituting hydrogen from water. Let's see if active metals can do that.

Figure 10: Reaction of sodium with water. A liquid sodium ball in the left is partially covered with a water mist.

Experiment 16

Pour 100 mL of water into a glass beaker. Take approximately 1/4 gram of sodium metal, carefully drop it into the beaker, and immediately cover the beaker with a glass funnel. Attach a test tube to the narrow end of the funnel as shown on the Fig. 10 . When the reaction is complete, remove the test tube (do not flip it) and bring a burning candle to the tube's neck. Describe your observations.

We can see sodium's behavior differs dramatically from what we expect from a metal. It reacts with ordinary water, a compound we usually consider inert (not active) in normal conditions, and some gas is formed during that reaction. The reaction is so violent, that the sodium melts and collapses into a lustrous ball on the water surface.[56] As we demonstrated, the gas formed during this reaction is combustible,[57] and it is lighter than air (it goes up, and it stays in the test tube when its neck is pointing down). We will see later that are the properties of hydrogen. We can conclude therefore that reaction of sodium with water produces the same gas we obtained during the reaction between zinc and hydrochloric acid, i.e. hydrogen. Had we tried to evaporate the remaining liquid in the beaker,[58] we would obtain a white soapy substance with a formula 'NaOH'. Therefore, the equation of this reaction can be written as follows:

$$2\mathrm{Na} + 2\,\mathrm{H_2O} = \mathrm{H_2} + 2\mathrm{NaOH} \tag{29}$$

In this equation, one compound (NaOH) has a formula we have never seen before. It is not an oxide, not a salt, and not an acid. We have never dealt with a compound of such a type before. Definitely, NaOH belongs to a new type of compounds.

8.5 Hydroxides, bases and alkali.

A compound with a formula NaOH can be represented as an analog of sodium oxide $\mathrm{Na_2O}$, where one sodium atom has been replaced with a hydrogen atom:

$\mathrm{Na-O-Na}$

Sodium oxide

$\mathrm{Na-O-H}$

Sodium *hydr*oxide

It is intuitively clear why we call it "hydroxide": in this substance, one oxygen's valence is occupied by a hydrogen atom, and this diatomic particle, which is called a "hydroxy group", forms a compound with the atom of metal (in this concrete case, sodium).

> **Hydroxides are the compounds with general formula $\mathrm{M(OH)}_n$, where M denotes some element, and 'n' (a number of hydroxy groups) is equal to the element's valence. Hydroxides, form another major class of inorganic compounds.**

Examples of hydroxides are calcium hydroxide $\mathrm{Ca(OH)_2}$, magnesium hydroxide $\mathrm{Mg(OH)_2}$, aluminum hydroxide $\mathrm{Al(OH)_3}$.

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[56] Density of sodium is smaller than the density of water, so sodium does not sink in water.

[57] Sometimes, sodium becomes so hot during this reaction that the gas ignites spontaneously.

[58] We will not do that for safety reasons.

8.5.1 Nomenclature of hydroxides

In contrast to acids, there is almost nothing you need to remember about names of hydroxides. The hydroxide's name is created by combining the element's name and the word "hydroxide", in the same way we did in the end of the previous section. A situation is a little bit more complicated for the elements that can exist in more than one valence state. As a rule, such elements can form more than one hydroxide. In that case, you must denote the element's valence with a Roman numeral. For example iron forms two hydroxides: iron (II) hydroxide ($Fe(OH)_2$), and iron (III) hydroxide ($Fe(OH)_3$).
That's all what we need to know about hydroxides naming rules.

8.5.2 Preparation of hydroxides. Part I.

Our observations we made during the Experiment 16 can be generalized: it is natural to expect other metals in the left part of the reactivity series are able to react with water. This our hypothesis is correct, and it is easy to prove experimentally that potassium, lithium, calcium, as well as some other active metals not included in the reactivity series[59] produce hydrogen and hydroxides during their reaction with water according to the scheme:

$$\mathrm{Me + H_2O \longrightarrow H_2 + Me(OH)_n} \tag{30}$$

where Me denotes some active metal, and 'n' is the metal's valence. **Reaction of active metals with water is the first method to obtain hydroxides.** Is it the only method? Apparently, no. Alternative ways to prepare of hydroxides exist.

Experiment 17

Place approximately 10-20 grams of calcium oxide[60] *into a glass beaker or a steel bowl. Add approximately 10 mL of water to it. What happens to the solid? Carefully touch an external surface of the beaker. What do you feel?*

> We can see that during this experiment a thin white powder of calcium oxide absorbs water and swells. The volume of the solid increases, and large amount of heat evolves. The reaction mixture becomes so hot that water we added starts to boil, and a cloud of steam forms above the beaker. The compound that forms during this reaction is calcium hydroxide ($Ca(OH)_2$). Since ancient times, it is being used to prepare a mortar, or a lime slurry. Until XIX century, when modern cement had been invented, slaked lime was vital and indispensable for construction. The equation of this reaction is:
>
> $$\mathrm{CaO + H_2O = Ca(OH)_2} \tag{31}$$

---

[59] Remember, we are dealing with a short version the reactivity series: some other metals, besides potassium, sodium, lithium and calcium, are capable of reacting with water to produce hydrogen and hydroxides.

[60] Calcium oxide (CaO) is known under a name "quick lime".

Due to its practical importance, this reaction has its own name: “slaking”,[61] and, accordingly, the technical name of calcium hydroxide is “slaked lime”.

Ancient people started to use slaked lime long before a concrete had been discovered. They used it to prepare lime mortar, a paste to bind bricks or stone construction blocks together. During several months after the construction ended, the binding mixture was becoming harder and harder, and eventually it converted into some artificial stone. An astonishing longevity of ancient Roman aqueducts and bridges (for example, the aqueduct at the figure 2), which had been built more than two thousand years ago, and, nevertheless, remain virtually unchanged, may serve as a perfect demonstration of an excellent quality of the lime mortar cement. During this and the next Section we will learn about the chemistry behind that phenomenon.

Calcium oxide is not the only oxide capable of formation of hydroxides. Many other oxides, such as sodium oxide or potassium oxide, react with water. The equation of the reaction of sodium oxide and water is as follows:

$$Na_2O + H_2O = 2NaOH \tag{32}$$

The reaction between metal oxides and water is the second way to prepare hydroxides.

8.6 Soluble hydroxides and their properties. Bases. Alkali.

Now it is a time to look at the properties of the compounds we prepared during the experiments 16 and 17.

8.6.1 Sodium hydroxide.

Sodium hydroxide (NaOH), also known as lye is a white highly hygroscopic solid with a slippery feeling upon contact.[62] It is highly soluble in water; its dissolution is a highly exothermic process. Accordingly, sodium hydroxide belongs to a family of compounds called “soluble hydroxides”. Another common name for soluble hydroxides is “alkali”.

Soluble metal hydroxides are called “alkali”.

A solution of NaOH corrodes skin, paper, fabric, and many other materials changes the color of a standard indicator paper to deep blue, which corresponds to pH values above 13. Addition of few drops of the phenolphtalein[63] solution produces a purple color. This

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[61] This term refers only to the reaction of calcium oxide and water. No special term exist for the reaction of other oxides.

[62] Actually, you should never touch it! It is very corrosive, so in a case of contact with your skin you must immediately rinse it with large amount of water until a slippery feeling disappears.

[63] An indicator. This substance is colorless, but it becomes purple when a common pH paper becomes deep-blue.

is indication that sodium hydroxide is *basic.* Basicity is a common property of soluble hydroxides, such as potassium hydroxide (KOH) and lithium hydroxide (LiOH).

8.6.2 Calcium hydroxide.

In contrast to sodium hydroxide, calcium hydroxide is poorly soluble in water. However, its water solution, a so called "lime water",[64] is also basic, because it produces a pink color when a colorless solution of phenolphtalein is added to it. Other moderately soluble hydroxides, such as silver hydroxide (AgOH) have similar properties.

8.6.3 Properties of soluble hydroxides. Reaction with acids ("Neutralization").

Thus we have learned that the alkali are "basic". We also know acids are "acidic". So far, we do not fully understand what does it mean, however, we know that a standard indicator paper becomes red in an acid media, and it becomes deep-blue in a basic media. We also know that an indicator dye, phenolphtalein, becomes pink in a presence of a base. In connection to that, it is interesting to see what happens when an acid and a base are mixed together.

Experiment 18.

Pour 100 mL of 4% solution of sodium hydroxide into a glass beaker and add few drop of phenolphtalein solution to it. Using a pipette, gradually add a 3.7 % dilute solution of hydrochloric acid to the beaker. When a pink color disappeared, record the volume of the HCl solution you added. Pour the solution obtained into a porcelain bowl and evaporate on open fire. What did you obtain?

Interestingly, during this experiment, exactly 100 mL of the HCl solution are needed for the pink color to disappear. What conclusion can be drawn from that fact? You have probably noticed that the concentration of both solutions was chosen in such a way that equal volumes of NaOH and HCl solutions contained equal number of NaOH and HCl molecules. Indeed, the molecular weight of NaOH in 40 Da ($23 + 16 + 1 = 40$), and the molecular weight of HCl is approximately 37 ($35.5 + 1 = 36.5$). That means, 100 mL of 4% NaOH solution contain 4 g of NaOH; the same volume of 3.7% HCl solution contains 3.7 g of HCl, and these amounts are proportional to the molecular masses of NaOH and HCl, accordingly. In other words, by the end of our experiment, one HCl molecule have been added per one NaOH molecule. What we obtained as a result of that addition? Clearly, the solution is not basic any more: a pink color of phenolphtalein had disappeared. Is it acidic? No. An indicator paper immersed into the solution does not become red.

It is easy to demonstrate that, when the order of addition changes (in other words, if 100 mL of a 4% NaOH solution will be added to 100 mL of 3.7% HCl solution), the result will be the same.

That means an acid and a base, when mixed together, "destroy", or "eliminate" each other: an acid eliminates "basicity", and a base eliminates "acidity". Such a mutual elimination is called "neutralization".

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[64] We are already familiar with it. Do you remember what we used it for?

An acid and a base react with each other. Such a reaction is called "neutralization". The resulting solution is neither acidic nor basic; it is "neutral".

What is a product of the neutralization reaction? Evaporation of the solution obtained in the Experiment 18 yields white crystals having a cubic shape. The shape of the crystals, their density, hardness, melting temperature, and other physical properties[65] are totally identical to the properties of common salt. Therefore, we can conclude the product of this reaction is sodium chloride (NaCl), and the reaction's equation is as follows:

$$\mathrm{NaOH + HCl = NaCl + H_2O} \tag{33}$$

(The fact that the second product of this reaction is water also can be confirmed experimentally. However, we are not doing that because of the lack of time.)

Other hydroxides react with hydrochloric acid similarly. For example, calcium hydroxide produces calcium chloride ($CaCl_2$):

$$\mathrm{Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O} \tag{34}$$

Other acids are also react with the bases in the same way. Thus, potassium sulfate is formed in the reaction between potassium hydroxide and sulfuric acid:

$$\mathrm{2KOH + H_2SO_4 = K_2SO_4 + 2H_2O} \tag{35}$$

Numerous experiments demonstrated that every acid and every hydroxide can react with each other to produce salt and water, and this is a fundamental property of every base and every acid.[66] These observations had been summarized by a Swedish chemist Svante Arrhenius, who proposed a first definition of the term "bases".

Bases are the compounds that are capable of donating a hydroxy group in reaction with acids. Acids are the compounds donating hydrogen in a reaction with bases. The products of the reaction between an acid and a base (a neutralization reaction) are salt and water.

Historically, this is a first definition of the terms "acid", "base" and "salt". Current definitions of the terms "acid" and "base" are somewhat broader. However, since these old definitions work perfectly for our purposes, we will stick with them during this school year.

Figure 11: Svante Arrhenius
(1859-1927)
A men who proposed the first definition of "acids" and "bases".

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[65] Of course, we have neither an opportunity nor time to do all those measurement in the class, but, have we done that, we would obtain exactly the same results.

[66] Of course, when the acid is too weak and the hydroxide is poorly soluble, such a reaction would be too slow to be detected.

8.6.4 Reaction of bases with acidic oxides.

If we pour transparent lime water in a glass beaker and blow bubbles through it, the water will become turbid in few minutes. What happens during this reaction? In this reaction, carbon dioxide you exhale react with calciun hydroxide according to the equation:

$$\mathrm{Ca(OH)_2 + CO_2 = CaCO_3 + H_2O} \tag{36}$$

The salt that forms during this reaction is calcium carbonate, aka calk, or limestone, of marble. Since this compound is insoluble in water, even small amount of CO_2 are sufficient to turn a clear and transparent lime water (i.e. $Ca(OH)_2$ solution into a turbid suspension. More importantly, a solid $Ca(OH)_2$ is also capable of reacting with atmospheric CO_2, which leads to a gradual conversion of soft, semi-soluble slaked lime ($Ca(OH)_2$) into a rock-solid limestone ($CaCO_3$).

As we can see, in this reaction, a salt, is formed not in a reaction between an acid and a base, but in the reaction between an *acidic oxide* and a *base.*
Again, that is a common property of all bases:

Bases are capable of reacting with both acids and acidic oxides to form salts. The same salt is formed in the reaction with an acid and a parent acidic oxide.

A question. Do you understand now the chemical mechanism of the astonishing longevity of Antique Roman aqueducts, bridges and buildings?

8.7 Bases and basic oxides.

From the section 2.2, we know that some metal oxides are capable of reacting with water, and the metal hydroxide is a major product of such a reaction. In connection to that, it is interesting to compare that reaction with the reaction we studied during the Section 6 (section 2). As we already know, the product of the reaction between phosphorus (V) oxide and water is phosphoric acid:

$$\mathrm{P_2O_5 + 3\,H_2O = 2\,H_3PO_4} \tag{37}$$

Let's compare it with a reaction between calcium oxide and water (equation 31). Since phosphorus (V) oxide produces an acid, we call it, as well as all other oxides of that type, an "acidic oxide". Accordingly, it would be logical to introduce a term "basic oxide" to denote an oxide that produces a base in reaction with water.

Basic oxides are the oxides that react with water to produce a base.

8.7.1 Reaction of basic oxides with acids.

In the previous section, we found that acids and acidic oxides yield the same product in a reaction with acids. What about the bases and the basic oxides?

Experiment 19.

Put 1-2 grams of calcium oxide into a glass beaker. Add 10 mL of dilute acetic acid to it. When the reaction stopped, put the beaker on a how plate and gently evaporate to dryness.[67] *What did you obtain?*

The solid we obtained is a salt called “sodium acetate”. It is the same salt you would obtain, had you taken calcium hydroxide instead of calcium oxide. Again, we can experiment with a various basic oxides and acids, and the result will be the same:

> **Acids are capable of reacting with both bases and basic oxides to form salts. The same salt is formed in the reaction with an base and a parent basic oxide.**

You have probably noticed that the above statement mirrors the statement from the section 3.4: the only difference between them is that the words “acid” and “base” have been swapped.[68] Such a symmetry is not merely a coincidence. Let’s talk about that during the next lesson.

Homework

1. A tin-led alloy or silver can be used as a solder to connect copper parts together. Imagine you have two copper vessels. One of them was made using a tin-led solder. Silver was used to solder the parts of another vessels. Can these vessels be used to store dilute hydrochloric acid?

2. Brass is a copper and zinc alloy. Depending on a zinc/copper ratio, it may have different properties. You have brass shavings with unknown zinc content. You took 5 grams of those shavings and added 200 mL of 20% HCl[69] to them. You used an apparatus (similar to that we used for preparation of oxygen) that allowed you to collect all gas that forms during that reaction. When the reaction was complete (evolution of the gas ceased) you measured the gas volume, and found that 0.4 L of some gas was formed. Can you determine a zinc content (in percents) in the brass using these data? For your calculations, you can use the fact that at room temperature and under atmospheric pressure, two grams of hydrogen occupy 22.4 L.[70]

3. It is a good time to start summarizing what we learned during previous lessons. Please, answer, how many major classes of inorganic compounds have we currently learned? Can you list them, and briefly describe their properties?

4. Since we are starting to discuss properties of various chemical compounds (we already know almost all major classes of inorganic compounds), we need to practice in naming

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[67] Actually, we will not do this experiment, because it should be done either in the fume hood or on open air: although the vapors of acetic acid are not toxic, they have a very unpleasant odor.

[68] That is what I actually did: I used copy-past to save time.

[69] ‘20%’ means that 100 mL of solution contains 20 grams of HCl.

[70] Generally speaking, if a mass of one molecule of some gas is X Da, then X *grams* of this gas will occupy a volume of 22.4 L at room temperature and atmospheric pressure. This is a general law named ‘Avogadro’s’ law (after its discoverer, Amedeo Avogadro).

them. Please, name the following compounds:
a. $Al(OH)_3$
b. $FeSO_3$
c. H_3PO_4
d. $MgCO_3$
e. CuOH
f. Al_2O_3
g. $Sn_3(PO_4)_2$
h. K_2SO_3

5. Write formulas and name the compounds formed during the reaction between:
a. Silver hydroxide and nitric acid.
b. Calcium and oxygen.
c. Sodium hydroxide and sulfur (VI) oxide.
d. Magnesium and hydrochloric acid.
e. Iron (II) oxide and hydrochloric acid.
f. Carbon and oxygen.
g. Iron and dilute sulfuric acid.[71]
h. Silicon oxide and potassium hydroxide.

6. Propose a reaction scheme (draw each equation separately) for the following transformation:
a.

$$Ca \longrightarrow CaO \longrightarrow Ca(OH)_2 \longrightarrow Ca_3(PO_4)_2 \tag{38}$$

b.

$$S \longrightarrow SO_2 \longrightarrow MgSO_3 \tag{39}$$

c.

$$C \longrightarrow CO_2 \longrightarrow Na_2CO_3 \tag{40}$$

d.

$$Na \longrightarrow NaOH \longrightarrow Na_3PO_4 \tag{41}$$

7. Propose three different reactions to prepare each of the following compounds:
a. Calcium chloride.
b. Iron (II) sulfate.
c. Aluminum nitrate.

8. Propose four different reactions to prepare sodium phosphate Na_3PO_4.

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[71] When polyvalent metals, such as iron, react with acids, a salt is formed where the metal has the lowest possible valence.

9. You took 20 grams of calcium oxide, added 300 mL of 10% HCl, and evaporated the solution obtained to dryness. What is the formula of the solid you obtained? What is its mass?
10. A piece of zinc reacted with dilute hydrochloric acid in the apparatus that allowed you to collect all the gas formed. The zinc dissolved completely, and the volume of gas you collected was 35L. What is the amount of the second product formed during this reaction? What was the amount of zinc taken?[72]
11. Pont du Gard aqueduct was built 2000 years ago. It is still rock-stable. What chemical reaction is behind its outstanding stability? (A hint: we discussed this reaction in the class).

If you want to draw structural formulas using your computer, you may try to download a free program that does it. To install this progtam on your computer, go to the download page: `http://www.simulations-plus.com/software/medchem-designer/` and press a **Download** button.

> **This software is provided by a company that develops more sophisticated software for researchers and industry, so it is safe to download this program.**

To complete downloading procedure, ask the questions about you. I myself just typed my home address and answered all questions pretending I am a school student. It worked.

9 Water: a base or an acid? Interrelation between bases and acids. Classification of chemical reactions. Exchange reactions. Preparation of salts, acids, hydroxides. Genetic linkage between major classes of inorganic compounds.

9.1 Water: a Janus molecule

In Roman mythology, Janus (aka Ianus Bifrons, i.e. "Janus the two-faced") was a god of time and transitions, of beginnings and endings, of doors and gates. He was usually depicted as having two faces, directed to the future and to the past. The first month of a year, "Ianuarium" (January) was named after him.

During the previous lesson, we learned about the Arrhenius' definition of acids and bases. It says:

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[72] Just to remind you. In this problem, you should use the Avogadro's law: if a mass of one molecule of some gas is X Da, then X *grams* of this gas will occupy a volume of 22.4 L at room temperature and atmospheric pressure.

Figure 13: Janus, a two-faced Roman god.

Bases are the compounds capable of donating a hydroxy group in reaction with acids. Acids are the compounds donating hydrogen in a reaction with bases.

In connection to that, it is interesting to look at water. Which class of inorganic compounds does it belong to? On the one hand, during the reaction with active metals it behaves as an acid: it forms a hydrogen gas and some metal-containing compound.

$$2Na + 2\,H_2O \longrightarrow H_2 + 2NaOH \tag{42}$$

On the another hand, this reaction leads to formation of a hydroxy containing compound, i.e. a base. In that sense, water can be considered a “Janus molecule”, a molecule with two faces. It can donate hydrogen, thereby demonstrating an acidic behavior, however, such a donation would inevitably lead to formation of a hydroxy group, which is a typical property of a base. In other words, water is simultaneously a base and an acid, and, therefore, it is neither the former nor the later. Water is *neutral*, and its formation is a final result of any reaction between an acid and a base.[73] As we have seen during the previous lesson, the basic and acidic oxides also participate in similar reactions.

To summarize, reactions between the following classes of compounds lead to formation of a salt and water:

1. **Reaction between acids and bases:**

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O \tag{43}$$

2. **Reaction between acidic oxides and bases:**

$$SO_3 + 2NaOH \longrightarrow Na_2SO_4 + H_2O \tag{44}$$

3. **Reaction between basic oxides and acids:**

$$Na_2O + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O \tag{45}$$

As you can see, all three reactions yield the same products, sodium sulfate and water. Obviously, other acids, bases and oxides behave similarly. This is a fundamental property of most oxides, acids, bases.

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[73] Of course, I mean the acids and the bases that fit the Arrhenius definition.

9.2 Four major types of chemical reactions.

Before we continue to move further, let's take a break and discuss reaction types. We have already learned about many chemical reactions, and we will learn about many more reactions in future. It would be senseless and useless to start to mechanically memorize each of them. Instead of memorizing, and to avoid possible confusion, it is desirable to introduce some general terminology to describe chemical reactions, and to separate them onto several classes.

Overwhelming majority of chemical reactions fit four *abstract basic types*. In our case, "abstract" means that the concrete nature of reactants or products does not matter for this classification: instead of formulas of concrete chemical compounds, we denote the reactants and products using Latin letters 'A', 'B', etc. Using such a notation, four generic chemical equations can be written, each of them defining some basic type of chemical reaction. All chemical reactions we are already familiar with, as well as most chemical reactions we will study in future belong to one of those four types. These types are listed below.

9.2.1 Synthesis, or addition.

$$\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C} \tag{46}$$

In this chemical reaction, two (or more) different molecules combine together to produce a single compound. Oxidation of elementary substances is the example of such a reaction. Concrete examples are:

1. Combustion of carbon:

$$\mathrm{C} + \mathrm{O_2} \longrightarrow \mathrm{CO_2} \tag{47}$$

2. Combustion of magnesium:

$$\mathrm{Mg} + \mathrm{O_2} \longrightarrow \mathrm{MgO} \tag{48}$$

9.2.2 Decomposition.

$$\mathrm{A} \longrightarrow \mathrm{B} + \mathrm{C} \tag{49}$$

In this reaction, some compound decomposes onto two or more substances (elementary substances or compounds). We already know many examples of that type reaction. Below are two of them:

1. Decomposition of mercury oxide:

$$\mathrm{HgO} \longrightarrow \mathrm{O_2} + \mathrm{Hg} \tag{50}$$

2. Decomposition of hydrogen peroxide:

$$\mathrm{H_2O_2} \longrightarrow \mathrm{H_2O} + \mathrm{O_2} \tag{51}$$

9.2.3 Substitution, or replacement.

$$A + BC \longrightarrow AC + B \tag{52}$$

On this scheme, 'BC' and 'AC' denote some molecules composed of two parts: B and C, or A and C, accordingly. A, B, and C can be either a single atom, or a group of atoms. As we can see from the scheme, during this reaction, called a "substitution reaction", or "replacement reaction"[74] some atom or group of atoms substitutes an atom, or a group of atoms from another compound. Two new substances are formed as a result. During two previous lessons, we have learned about many examples of the substitution reaction. Two typical examples are shown below.

1. Reaction of iron with sulfuric acid:

   $$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2 \tag{53}$$

   In this reaction, iron *replaces*, or *substitutes* hydrogen from the sulfuric acid molecule: 'A' is Fe, and 'B' is hydrogen, and 'C' is SO_4, a sulfuric acid residue (sulfate).

2. Substitution of silver from silver nitrate by a copper metal:

   $$AgNO_3 + Cu \longrightarrow Cu(NO_3)_2 + Ag \tag{54}$$

   In this reaction, a silver atom is being substituted by copper from a silver salt.

9.2.4 Exchange.

$$AB + CD \longrightarrow AC + BD \tag{55}$$

The exchange reaction[75] is a reaction between two *compounds*. In that reaction, the molecules 'AB' and 'BC' exchange their constituents, so two new 'hybrid' compounds AC and BD are formed as a result. The neutralization reaction we discussed in the previous section is a typical example of the exchange reaction.

$$NaOH + HCl \longrightarrow NaCl + H_2O \tag{56}$$

This type reaction (exchange, or "double replacement") is among the most common reactions salts are participating in. It is being widely used to prepare all types of inorganic compounds, including salts, bases and acids.

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[74] The former term is being used by scientists, the latter term is popular in school textbooks.

[75] Again, for some unknown reason, school textbooks use a different name for this reaction: a "double replacement reaction". In scientific literature, this name is used rarely.

9.3 Exchange reactions between salts, bases, and acids.

After having defined major reaction types, we can continueour study of reactions of major types of inorganic compounds.

As we already know, bases and acids are capable of participating in exchange reactions. Are the exchange reactions specific only to these three classes of inorganic compounds? No.

During the Section 2, we made an experiment when calcium chloride and sodium carbonate reacted to produce two new salts. The equation of that reaction was as follows:

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2\,NaCl \qquad (57)$$

The products of that reaction were calcium carbonate and sodium chloride. In other words, during that experiment, two salts, $CaCl_2$ and Na_2CO_3, reacted with each other to produce two new salts, calcium carbonate ($CaCO_3$) and sodium chloride (NaCl). Since both the reactants and the products of this reactions are salts, we can conclude not every pair of salts are capable of participating in the exchange reaction. Indeed, as far as calcium carbonate and sodium chloride are the *products* of the reaction 57, they cannot serve as the *reactants* in the inverse reaction. In other words, if you take calcium carbonate and sodium chloride, you will never obtain calcium chloride and sodium carconate: the reaction 58 is not possible.

$$CaCO_3 + 2NaCl \neq CaCl_2 + Na_2CO_3 \qquad (58)$$

That means, depending on the type of reactants and products, some exchange reactions proceed to completion, whereas others do not go at all. Why does it happen? Unfortunately, we cannot give a full and detailed answer right now: our theoretical background is insufficient so far. However, we can try to develop some empirical rules to predict an outcome of (at least) some exchange reactions.

Experiment 20.

Into four test tubes, pour 3 mL of the following dilute solutions: (i) silver nitrate; (ii) calcium chloride; (iii) copper sulfate; (iv) sodium carbonate. To these test tubes, add ca 3 mL of dilute solutions of: (i) sodium chloride; (ii) sodium phosphate; (iii) sodium hydroxide; (iv) sulfuric acid.

As we can see some reaction takes place in each of four test tubes: some sediments are formed in the first three test tubes, and some gas is formed in a fourth one. Let's discuss these reactions separately.

9.3.1 Reaction between two salts (test tubes 1 and 2).

Reactions in the first and second test tubes can be described by the equations (100) and (60).

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3 \qquad (59)$$

$$3CaCl_2 + 2Na_3PO_4 \longrightarrow 2Ca_3(PO_4)_2 + 6NaCl \qquad (60)$$

The sediments are poorly soluble salts, silver chloride and calcium phosphate, accordingly. These two reaction, as well as the reaction between $CaCl_2$ and Na_2SO_4 (equation 57), proceed to full completion. Numerous experiments with various salts allowed chemists to propose the following empirical rule:

> **When at least one product of an exchange reaction between two salts is poorly soluble in water, such a reaction proceeds to completion, and a new insoluble salt is formed.**

Can we predict if a salt is soluble in water? Yes, we can. A solubility theory had been developed that explains why some salts are easily soluble, whereas others are not. This theory predicts a solubility of new salts quite well. We will discuss this theory in due time. Meanwhile, you can use the empirical table below to predict solubility of salts. This table summarizes some of experimental observations made by chemists during XIX century.

Solubility chart of salts formed by some metal (columns) and an acidic residues (rows).

	Li	Na	K	Ca	Mg	Al	Fe (II)	Fe (III)	Zn	Pb	Cu (I)	Cu (II)	Hg (II)	Ag
Cl	s	s	s	s	s	s	s	s	s	M	I	s	s	I
NO_3	s	s	s	s	s	s	s	s	s	s	s	s	s	s
ClO_4	s	s	s	s	s	s	s	s	s	s	s	s	s	s
S	s	s	s	D	s	D	s	s	I	I	I	I	I	I
SO_3	s	s	s	M	s	D	M	D	M	I	M	D	D	M
SO_4	s	s	s	I	s	s	s	s	s	I	M	s	s	M
PO_4	s	s	s	I	I	I	I	I	I	I	I	I	I	I
SiO_3	s	s	s	I	I	I	I	D	I	I	I	I	D	D
CO_3	s	s	s	I	D	I	I	D	I	I	I	I	I	I

In this table, 's' means the salt is soluble, 'M' means it is marginally soluble, 'I' means it is (virtually) insoluble. 'D' means such a salt decomposes in a presence of water. For example, from this table, we can conclude sodium chloride (NaCl) is soluble in water, whereas silver chloride (AgCl) is not, that sodium sulfide (Na_2S) is soluble, but silver sulfide (Ag_2S) is not, etc.

Interestingly, some salts (for example, nitrates NO_3 or perchlorates ClO_4) are soluble independently on the metal type, whereas other salts (for example, phosphates PO_4 or silicates SiO_3) are mostly insoluble. That is very important, because overwhelming majority of rocks and minerals Earth crust is composed of are phosphates, silicates, or carbonates of various metals.

9.3.2 Reaction between a salt and alkali (test tube 3).

In that test tube, a salt, copper (II) chloride, and a base, sodium hydroxide, had been mixed together, and that resulted in a formation of some new insoluble compound. This compound is copper (II) hydroxide ($Cu(OH)_2$, and the equation of this reaction is as follows:

$$CuCl_2 + 2\,NaOH \longrightarrow Cu(OH)_2 + 2\,NaCl \qquad (61)$$

Copper (II) hydroxide belongs to the last class of inorganic compounds called *insoluble hydroxide*. Actually, hydroxides of most metals, including iron, zinc, aluminum, magnesium, tin, lead, etc, are insoluble, and the reaction between a salt of such a metal and an alkali represents a general method for preparation of insoluble hydroxides.

> **Salts and alkali can react with each other to produce a new salt and a new hydroxide if that hydroxide is insoluble.**

Below are other examples of such a reaction:

$$\mathrm{FeCl_3 + 3NaOH \longrightarrow Fe(OH)_{3(s)} + 3\,NaCl} \tag{62}$$

$$\mathrm{MgCl_2 + 2\,NaOH \longrightarrow Mg(OH)_{2(s)} + 2\,NaCl} \tag{63}$$

$$\mathrm{Al_2(SO_4)_3 + 6\,NaOH \longrightarrow 2\,Al(OH)_{3(s)} + 6\,NaCl} \tag{64}$$

9.3.3 Reaction between a salt and an acid (test tube 4).

We observed no precipitate formation in the fourth test tube. Instead of that, we saw gas evolution, and the reaction's equation is as follows:

$$\mathrm{Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + CO_{2(gas)} + H_2O} \tag{65}$$

At first glance, this reaction has little in common with the first three. However, it can be demonstrated that reaction is also an exchange reaction, and two, not three products are formed initially. Actually, this reaction is a two step reaction. These two steps are:

$$\mathrm{Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2CO_3} \tag{66}$$

$$\mathrm{H_2CO_3 \longrightarrow CO_{2(gas)} + H_2O} \tag{67}$$

In other words, during the first step (equation 66), a new salt, sodium sulfate, and a new acid, carbonic acid, are formed, so this reaction is a typical exchange reaction. However, carbonic acid is very unstable, and it undergoes a decomposition reaction within few seconds (equation 67). As in the case of hydroxides, this reaction is general.

> **Salts and acids can react with each other to produce a new salt and a new acid if that acid is unstable, volatile, or insoluble.**

Below are the examples.

$$\mathrm{2\,NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HCl_{(gas)}} \tag{68}$$

Hydrochloric acid forms in a reaction between NaCl and H_2SO_4 because HCl is volatile, and escapes from the reaction mixture after formation. Some acids, such as a silicic acid (H_2SiO_3) are poorly soluble in water, therefore, they also can be prepared via an exchange reaction. A silicic acid forms a white loose precipitate.

$$\mathrm{Na_2SiO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2SiO_{3(s)}} \tag{69}$$

9.4 Insoluble hydroxides: bases or acids? Amphoteric compounds.

Look at the formulas of copper or zinc hydroxides. They have much in common with $Ca(OH)_2$. Are they basic too? It is not easy to tell, because they are insoluble, so you cannot use an indicator (phenolphtalein or a pH-paper) to answer this question. However, as we already know, an intrinsic property of each base is its ability to form a salt with an acid, and, conversely, every acid is capable of reacting with a base to produce a salt. Let's test if insoluble hydroxides are bases or acids.

Experiment 21.

Add 3 mL of dilute solution of aluminium sulfate ($Al_2(SO_4)_3$) to each or two test tubes. To each test tube, gradually add 5% NaOH solution until a white loose precipitate is formed. After that, add 5 mL of the same NaOH solution, to the first test tube; to the second test tube, add 5 mL of 5% solution of HCl.

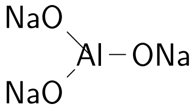
The reaction that takes place after initial addition of NaOH is quite understandable: like in the experiment 20, an insoluble hydroxide (in this case, aluminium hydroxide, $Al(OH)_3$, is formed, according to the equation 64). However, what we observe after that is somewhat counter-intuitive: the loose precipitate that formed initially disappears after addition of both NaOH and HCl. In other words, a newly prepared compound, $Al(OH)_3$, reacts both with the base and with the acid. Does it mean this compound is a base and an acid simultaneously? No. Actually, aluminium hydroxide is a weak base in a presence of a strong acid (such as HCl), and it is a weak acid in a presence of a strong base (in our case, NaOH). These two reactions can be described by the equations:

$$2\,Al(OH)_3 + 6\,HCl \longrightarrow 2\,AlCl_3 + 3\,H_2O \tag{70}$$

and

$$2\,Al(OH)_3 + 6\,NaOH \longrightarrow 2\,Na_3AlO_3 + 3\,H_2O \tag{71}$$

A new compound with a formula Na_3AlO_3 has a name "sodium aluminate", and, based on the name and the equation, we can conclude it is a salt. Indeed, it is a salt. Its formula can be drawn as:



Sodium aluminate

and it possesses all properties of common salts. However, again, it would be incorrect to call aluminium hydroxide a base or an acid. This type compounds demonstrate acidic or basic behavior only in a presence of strong bases or acids, accordingly. These compounds are called *amphoteric*.

> **Amphoteric substances are the molecules that, depending on a situation, can act either as a weak acid or as a weak base.**

Many (although not all) insoluble hydroxides are amphoteric. As a rule, when a hydroxide of some metal is amphoteric, a corresponding metal and its oxide is also amphoteric. For example, aluminium metal reacts both with acids and alkali, and hydrogen gas is produced in both cases. We will discuss that in more details during a Section devoted to aluminium.

9.4.1 Decomposition of insoluble hydroxides

A common property of insoluble hydroxides is their ability to decompose onto water and an oxide at high temperature. Thus, a blue cupric hydroxide ($Cu(OH)_2$) turns black when being heated:

$$Cu(OH)_2 \longrightarrow CuO + H_2O \tag{72}$$

9.5 Two classes of elements. Metals and non-metals.

All elements we have been dealing with can be subdivided onto two major types. The first type elements (we call them "metals"), such as sodium, zinc, iron or copper, form oxides, salts, hydroxides, but they do not like to form compounds with each other. Indeed, whereas zinc chloride, zinc oxide or zinc sulfide can be easily prepared, no "zinc sodiide", or "sodium zincide" (a putative zinc-sodium compound) is possible.

> **A common property of all metals is the ability to form at least one basic or amphoteric oxide or hydroxide.**

Another group pf elements demonstrate quite different properties. They form various binary compounds with metals and with each other. In addition, they are capable of forming more complex multiatomic molecules. These metals are called "nonmetals". The examples of nonmetals are oxygen, chlorine, carbon, hydrogen.

> **Most nonmetals form acidic oxides.**

Of course, there are some exception from this rule. For example, oxygen does not form acidic oxides, simply because it cannot oxidize itself. However, it is a typical nonmetal.

9.6 Genetic linkage between different classes of inorganic compounds.

Now we are ready to summarize the knowledge we obtained during this semester.

1. All elements can be subdivided onto two types, metals and nonmetals.
2. Metals are capable of forming compounds with nonmetals.
3. Nonmetals cam form binary compounds with each other and with metals; oxides are the most important binary compounds.
4. Most oxides react (directly or indirectly) with water to produce acids or bases. Accordingly, these oxides are called acidic or basic.

5. Acids and bases react with each other. The major product of such a reaction is called "salt".

6. Salts can also be formed in the reaction between a metal and an acid, between an acidic oxide and a base, and between an acid and a basic oxide.

7. Two salts can react with each other in solution, and two new salts can be produced, provided that at least one product of such a reaction is insoluble.

8. Some compounds can behave either as an acid or as a base. Such compounds are called "amphoteric".

9. Metals are the elements capable of forming at least one basic or amphoteric oxide. Oxides of nonmetals are always acidic.

That is a brief summary of what we know by now, and that is a core of inorganic chemistry.

It is easy to see that each type of inorganic compound is linked to other types: it begets compounds from other classes, and it can be begotten by a substance belonging to a progenitor class. That means a *genetic linkage* ("an ancestor - descendant linkage") exists between different classes of inorganic compounds. For example, some (not all) genetic linkages between different copper containing substances can be depicted as follows.

$$\mathrm{Cu} \longrightarrow \mathrm{CuO} \longrightarrow \mathrm{CuSO_4} \longrightarrow \mathrm{Cu(OH)_2} \longrightarrow \mathrm{CuO} \tag{73}$$

It is possible to draw a general scheme (a graph) showing all genetic linkages between different classes of inorganic compounds, however, I would like you to do that by yourself. try to do that, and let's discuss it during the next Sunday.

Homework

1. Please, list all classes of inorganic compounds we currently know.

2. As we know, hydroxides can be prepared in a reaction between basic oxides and water. That means, a basic oxide is a parent substance for a corresponding hydroxide. In other words, a genetic linkage exists between basic oxides and hydroxides. List as many genetic linkages between different classes of inorganic compounds as you can (please, keep in mind that every compound can have several parent substances)? Can you draw a scheme summarizing all genetic linkages between each class?

3. Below, several compounds are listed. To which class of inorganic compound each of them belongs? Name each compound.
   a. $Ca(OH)_2$
   b. $FeSO_4$
   c. H_2SO_4
   d. Na_2SO_3
   e. $Zn(OH)_2$
   f. Fe_2O_3

g. Na_2SO_4
h. $MgSO_4$

4. You need to prepare the following salts: (i) NaCl, (ii) AgCl, (iii) HgS, (iv)$MgSO_4$, (v)$CaCO_3$, (vi)$Al_2(SiO_3)_3$, (vii)$NaClO_4$. Using the solubility chart, can you tell which of those salts can be prepared via the exchange reaction between two salts? Which salts should be taken as the reactants in each case? Write equations of each reaction.

5. Write equations of the reactions that would allow you to perform the following transformations:

   (a)
   $$AlCl_3 \longrightarrow Al(OH)_3 \longrightarrow Al_2O_3 \longrightarrow Al_2(SO_4)_3 \tag{74}$$

   (b)
   $$S \longrightarrow SO_2 \longrightarrow CaSO_3 \longrightarrow Ca(OH)_2 \tag{75}$$

   (c)
   $$AlCl_3 \longrightarrow Al(OH)_3 \longrightarrow Al_2O_3 \longrightarrow Al_2(SO_4)_3 \tag{76}$$

6. Look at the equations below:

   (a)
   $$Zn + H_2SO_4 \longrightarrow ZnSO_3 + H_2O \tag{77}$$

   (b)
   $$MgO + H_2 \longrightarrow Mg(OH)_2 \tag{78}$$

   (c)
   $$6\,NaOH + 2\,H_3PO_3 \longrightarrow 2\,Na_3PO_4 + 3\,H_2O \tag{79}$$

   (d)
   $$H_2 + KOH + PO_3 \longrightarrow K_3PO_4 + H_2O \tag{80}$$

   Some of those equations contain errors. Fix the errors and draw correct equations. Explain.

7. How can you prepare copper (II) chloride starting from copper metal? Draw equation(s).

8. Prepare potassium carbonate from sodium carbonate.

9. Starting from sodium chloride and sulfuric acid, prepare zinc chloride. You may use any zinc containing compound you want.

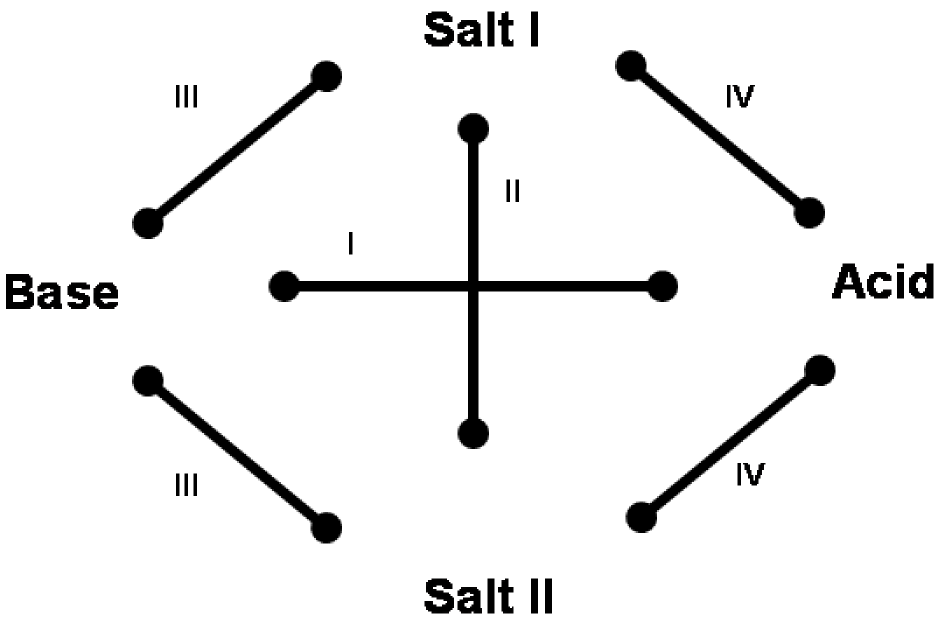
10. You have three test tubes, each of which contains one of the following solutions: (i) zinc chloride, (ii) sodium chloride, (iii) silver nitrate. The test tube labels have been wiped out by accident, and you need to restore them. To do that, you can use any glassware you want (test tubes, etc). You also can choose one additional chemical (any chemical on your choice). What chemical will you choose? How concretely will you do the analysis? Draw equations of each reaction.

10 Genetic linkage between major classes of inorganic compounds. Part II.

I think it a good time to summarize our current knowledge of inorganic chemistry.

10.1 Reactions between acids, bases, and salts. A summary.

A whole set of the reaction between acids, bases, and salts can be summarized using the below scheme:



Scheme 1.

In these scheme, solid lines show interactions between two reactants (salt + salt, base + acid, etc). Below are the examples.

10.1.1 Acid + Base (Type I reaction).

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O \qquad (81)$$

In this reaction, salt and water are formed.

10.1.2 Salt I + Salt II (Type II reaction).

$$Na_2SO_4 + Ca(NO_3)_2 \longrightarrow CaSO_{4(s)} + 2\,NaNO_3 \tag{82}$$

Two new salts are formed in this reaction, when at least one of two salts is insoluble.

10.1.3 Base + Salt (Type III reaction).

$$AlCl_3 + 2NaOH \longrightarrow Al(OH)_{3(s)} + 3\,NaCl \tag{83}$$

A new hydroxide is formed in this reaction if that hydroxide is insoluble. Alternatively, even a soluble hydroxide can be obtained in that reaction, provided that a new salt is not soluble in water. For example, this reaction was used in Antiquity and Middle Ages to produce alkali:[76]

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow 2\,NaOH + CaCO_{3(s)} \tag{84}$$

10.1.4 Acid + Salt (Type IV reaction).

As in the case of hydroxides, a new acid can be obtained in a reaction of its salt with another acid. For that, a new acid has to be either insoluble (as a silicic acid):

$$Na_2SiO_3 + H_2SO_4 \longrightarrow H_2SiO_{3(s)} + Al(OH)_3 + Na_2SO_4 \tag{85}$$

or volatile (as HCl):

$$2\,NaCl + H_2SO_4 \longrightarrow 2\,HCl_{(g)} + Na_2SO_4 \tag{86}$$

A new acid can also be formed when a salt that forms in the reaction precipitates:

$$Ca(ClO_4)_2 + H_2SO_4 \longrightarrow CaSO_{4(s)} + 2\,HCLO_4 \tag{87}$$

That is a brief summary of the reactions between acids, bases, and salts, which constitute lion's share of inorganic reactions. To make your life easier, below a combined solubility table of acids, bases, and salts is shown. This table will help you to predict the outcome of the type I-IV reactions.

---

[76] We already know how can calcium hydroxide (a slaked lime) be obtained from limestone.

Solubility chart of acids, bases and salts. Metals are shown in columns, and acidic residues in rows.

	H	Li	Na	K	Ca	Mg	Al	Fe (II)	Fe (III)	Zn	Pb	Cu (II)	Hg (II)	Ag
OH	-	s	s	s	M	I	I	I	I	I	I	I	D	D
Cl	s	s	s	s	s	s	s	s	s	s	M	s	s	I
NO_3	s	s	s	s	s	s	s	s	s	s	s	s	s	s
ClO_4	s	s	s	s	s	s	s	s	s	s	s	s	s	s
S	s	s	s	s	D	D	D	I	D	I	I	I	I	I
SO_3	s	s	s	s	I	M	I	I	D	M	I	D	D	M
SO_4	s	s	s	s	s	s	s	s	s	s	I	s	s	M
PO_4	s	s	s	s	I	I	I	I	I	I	I	I	I	I
SiO_3	I	s	s	s	I	I	I	I	D	I	I	I	D	D
CO_3	D	s	s	s	I	D	I	I	D	I	I	I	I	I

In this table, 's' means the compound is soluble, 'M' means it is marginally soluble, 'I' means it is (virtually) insoluble. 'D' means a compound decomposes in a presence of water, or it doesn't exist. From this table, we see that lead hydroxide, silicic acids and calcium silicate are insoluble, nitric acid, sodium hydroxide and sodium phosphate are soluble, whereas mercury hydroxide, carbonic acid and calcium sulfide decompose in water.

Experiment 21. "Silicate gardens."

Figure 12: Pont du Gard aqueduct in Southern France. Built about 2000 years ago, it is still almost functional.

Into a glass beaker, pour a concentrated solution of sodium silicate, dilute it with an equal volume of water, add stir thoroughly. Into this solution, drop few crystals of the following salts: copper (II) nitrate, nickel (II) sulfate, iron (II) sulfate, and chromium (II) chloride. Leave the beaker for half an hour. What do you see?

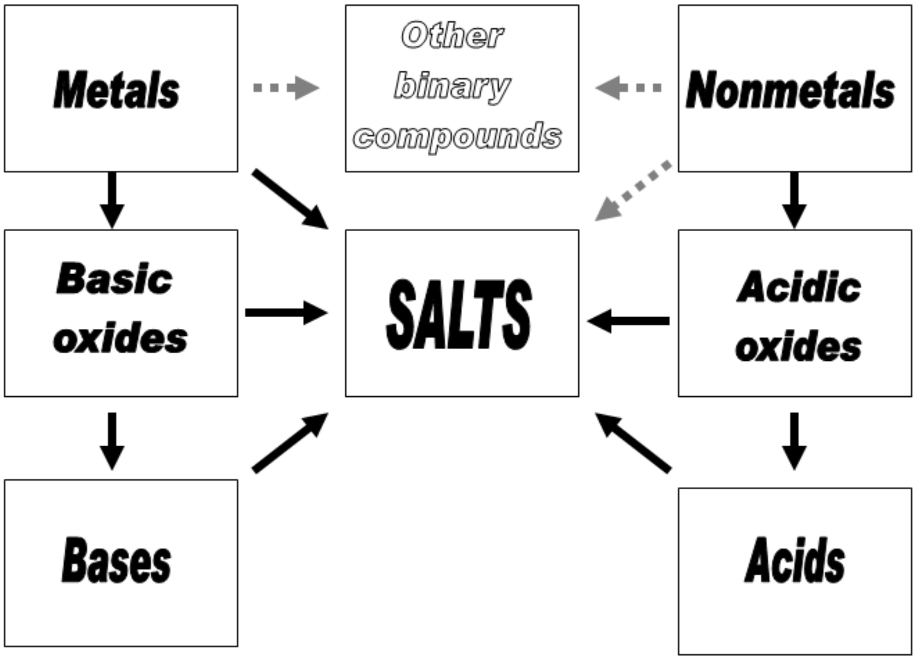
All salts used for this experiment are soluble in water, however, the corresponding silicates are not. As a result, a thin

Figure 14: Silicate gardens.

membrane of insoluble silicate starts to form around the crystals immediately after we dropped them into the Na_2SiO_3 solution. Such a membrane is partially permeable, so an outside water can penetrate into a membrane, and dissolve the salt As a result, the pressure inside the membrane increases, and beautiful colored stalagmites of copper (or nickel, or iron, or chromium) silicates start to grow. *(Please, write the equations of these reaction by yourself.)*

10.2 Genetic linkage between inorganic compounds.

A diagram of genetic linkages between different types of inorganic compounds is shown below. On this diagram, solid arrows indicate the genetic linkages we already know. Indeed, a metal, for example, magnesium, can produce salt in a reaction with acid, or with another salt, for example, tin sulfate. It also can produce an oxide in a reaction with oxygen. Similarly, a non-metal can produce acidic oxide in a reaction with oxygen; this acidic oxide reacts with water to produce an acid, or with alkali to produce a salt, etc.



Scheme 2.

This is an almost complete set of genetic linkages between major classes of inorganic compounds. In addition, some nometals are capable of reacting with metals to produce salts directly. Thus, sodium metal burns in chlorine to produce a ordinary table salt, NaCl. We haven't studied that type reactions yet, so the corresponding reaction is shown with a gray dashed arrow on the scheme 2. Some binary compounds exists that do not completely meet a definition of a salt. We will devote some time to those compounds in future.

Homework

1. Based on the solubility table, and using the information from the Web, try to predict which other salts can be used for making silicate gardens. If you e-mail this information before Jan 4, we probably can try those salts during the next class. Of course, I expect to get a detailed arguments supporting your choice: just to name a salt is not enough.
2. As a rule, metal ores found in Earth crust are the salts of a metal and some inorganic acid. These salts had been formed in young Earth's crust, when metal rich solutions were coming into contact with some concentrated salt or acid, so a new salt precipitated. Based on a solubility chart, try to predict which metals were likely to form deposits, and what the composition of their ore is? Which metals are likely to form mixed ores?
3. To 3.8 grams of sodium carbonate, 200 grams of 20% sulfuric acid were added. The gas formed during that reaction was collected and bubbled through a solution of 10 grams of calcium hydroxide in water in such a way that all the gas was absorbed. The solid formed during the bubbling was filtered out, dried and weighed. What was the weight of the solid obtained?
4. How can you perform the following transformations:

$$\mathrm{S} \longrightarrow \mathrm{SO_2} \longrightarrow \mathrm{K_2SO_3} \tag{88}$$

$$\mathrm{NaCl} \longrightarrow \mathrm{HCl} \longrightarrow \mathrm{CaCl_2} \tag{89}$$

$$\mathrm{P} \longrightarrow \mathrm{P_2O_5} \longrightarrow \mathrm{Ca_3(PO_4)_2} \tag{90}$$

   Draw separate equations for each step in the above schemes.

My e-mail is mark.lukin@gmail.com ©Mark Lukin

11 Classification of elements. Groups of elements. Halogens.

As we already know, all elements can be subdivided onto metals and nonmetals. Such a classification is intuitively clear: everyone understands what a metal is. Indeed, all metals (except mercury) are:

1. solids;
2. non-transparent;

3. lustrous. More precisely, they have metallic luster ("metallic luster" is a specific term; it is known in physicts that reflection of light from metals is different from reflection of light from other lustrous surfaces[77];
4. conductive. They have high electrical and thermal conductivity, and these two traits are not separable from each other;
5. usually, although not allways, metals are malleable (i.e. they can be shaped by pounding with a hammer)[78].

These properties forms an unseparable set. If some element possess *all* these properties, it is a metal. Accordingly, the elements that are devoid of at least one of these properties are not considered metals. However, this is a "physicist's point of view" on metals. Is this classification arbitrary, or it has some chemical applications? To answer that, let's look at metals and nonmetals from chemist's point of view.

11.1 Metals. Chemist's point of view.

Majority of chemical elements are metals. They all have some basic common physical properties: metallic luster, high thermal and electrical conductivity, non-transparency, and malleability. Such a similarity is not just a coincidence. There is an important fundamental reason for that, and this reason lies is the structure of the atoms of metals. One important consequence of that is the following: **metals do not like to make chemical compounds with each other**. Of course, you can take, for example, 23 grams of sodium (monovalent; atomic weight 23 Da) and 20 grams of calcium (divalent; atomic weight 40 Da), and to melt them together. However, the resulting substance will be not a new compound with a formula Na_2Ca, but just an *alloy*, i.e. a mixture of two substances, and its properties would be similar to the properties of the starting metals. Definitely, if all elements in our Universe were metals, it would be a very boring and tiresome world.

What brings diversity to our world is the interaction of metals with *nonmetals*. Firstly, all metals a capable of forming binary compounds with almost every nonmetal. Thus, reaction of magnesium with oxygen, sulfur, or chlorine produce magnesium oxide, sulfide, and chloride, accordingly.

$$\mathrm{Mg + O_2 \longrightarrow MgO} \tag{91}$$

$$\mathrm{Mg + S \longrightarrow MgS} \tag{92}$$

$$\mathrm{Mg + Cl_2 \longrightarrow MgCl_2} \tag{93}$$

Interestingly, these compounds are either salts (MgS or $MgCl_2$), or they can be converted into salts in a reaction with acids (MgO). That is a fundamental property of metals that allows us to discriminate between metals and nonmetals.

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[77] For example, a light reflected from water can be absorbed by so called polarisation light filters, a trick that is being widely used in photography. In contrast, a light reflected from a metal surface cannot be absorbed by these filters.

[78] Sometimes, metals can be fragile at low temperatures.

Metals are the elements that can produce salts in a reaction their oxides and an acid.

However, as we already know, that does not mean all metal oxides are basic. They (for example, zinc or iron (III) oxides) can equally be amphoteric. What is important for us is the ability of such an oxide to react with acids.

In addition, one has to keep in mind the following. As we know, some metals exist in different valence state. For example, two oxides are possible for copper (Cu_2O and CuO). As a rule, *lower valence oxides are more basic than the higher valence oxides.* For example, iron (II) oxide (FeO) is basic, whereas iron (III) oxide (Fe_2O_3) is amphoteric. Therefore, the above rule can be re-phrased as follows.

If an element X forms at least one basic or amphoteric oxide, the element X is a metal, otherwise it is a nonmetal.

11.2 Nonmetals.

In contrast to metals, the nonmetals alone are capable of forming a wide range of chemical compounds. They love to react with each other, and with metals. Almost every nonmetal is capable of forming binary compounds with other nonmetals, and almost every nonmetal (except fluorine, helium, neon and argon) can form oxides.

Oxides formed by nonmetals are acidic.

Does that mean *all* oxides of nonmetals are capable of generating acids in a reaction with water? No. One of the most important examples is *carbon monoxide* (CO), which does not react with water, and cannot be converted in a salt in a reaction with a base. Another example is a nitrogen (I) oxide (N_2O), a gas that is being widely used as a propellant and for anesthesia. However, both carbon and nitrogen are nonmetals, because they form no basic or amphoteric oxides. That can be summarized as follows:

Nonmetals are the elements that form neither basic nor amphoteric oxides.

11.3 "Metalloids": what is that?

The term "metalloid" has a bad karma. On the eve of inorganic chemistry, there was no term "nonmetal", and the term "metalloid" was used instead. In other words, all elements were subdivided onto metals and *metalloids*. That was counter-intuitive and misleading. Indeed, the suffix "-oid" means "similar to", or "resembling", so the word "metalloid" literally means "resembling a metal". Of course, that was not true: for example, can we seriously speak about any similarity between oxygen and magnesium? That is why this term was gradually dropped, and the term "nonmetal" was proposed instead.

Nevertheless, some new textbooks started to use the term "metalloid", although its modern meaning is different. It is used for some nonmetals that possess one or several traits of metals. For example, such elements as silicon or germanium are hard solids with a high melting point; they have a metal luster and moderate electrical conductivity, which is much lower that a conductivity of true metals. However, despite their visible similarity with metals, from chemist's point of view they are nonmetals. Thus, silicon or germanium compounds are very similar to carbon compounds. A comparison of silicon and carbon shows that both elements form oxides:

$$\mathrm{C + O_2 \longrightarrow CO_2} \tag{94}$$

$$\mathrm{Si + O_2 \longrightarrow SiO_2} \tag{95}$$

These oxides are acidic:

$$\mathrm{CO_2 + 2\,NaOH \longrightarrow Na_2CO_3 + H_2O} \tag{96}$$

$$\mathrm{SiO_2 + 2\,NaOH \longrightarrow Na_2SiO_3 + H_2O} \tag{97}$$

The acids can be generated from their salts:

$$\mathrm{Na_2CO_3 + 2\,HCl \longrightarrow H_2CO_3 + 2\,HCl} \tag{98}$$

$$\mathrm{Na_2SiO_3 + 2\,HCl \longrightarrow H_2SiO_3 + 2\,HCl} \tag{99}$$

11.4 Groups of elements.

As we can see from the above equations, there is a striking similarity between the chemical reactions of carbon and silicon compounds. Such a parallelism is not merely a coincidence: all chemical elements can be split onto groups based on their chemical properties. That means, the two major classes of elements, metals and nonmetals, contain smaller sub-classes, and each element in a certain sub-glass (or a group) have something in common with other members of that group. That observation was made in XIX century, and it made the life of chemists much easier: they realized that chemistry is not a random collection of facts about various reactions between various elements and their compounds, but some systematic discipline, which can be understood by humans. Starting from the next lesson, we will learn about the essential groups of elements, including halogens, chalcogens, and alkaline metals.

11.5 "Halos" means "salt"

We already know that addition of the sodium chloride solution to the solution of silver nitrate yields a precipitate of a salt called silver chloride:

$$\mathrm{NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3} \tag{100}$$

Is such a reaction specific to the table salt (NaCl), or some other compounds behave similarly? Let's look at the compounds formed by the elements we never discussed before, sodium bromide and sodium iodide.

Experiment 22.

In three glass beakers, put approximately 1 gram of sodium chloride, sodium bromide, and sodium iodide. Add 50 mL of water to each beaker and stir. What do you see? Pour 2 mL of the each liquids into separate test tubes and add 1 mL of silver nitrate solutions to each of them. Describe what you see. Leave all three tubes under bright lamp or sunlight for a short period of time. Do you see any change?

As we expected, sodium chloride produced a voluminous white AgCl precipitate, which is insoluble in water. Sodium bromide and iodide behave similarly.

$$\mathrm{NaBr + AgNO_3 \longrightarrow AgBr + NaNO_3} \tag{101}$$

$$\mathrm{NaI + AgNO_3 \longrightarrow AgI + NaNO_3} \tag{102}$$

When exposed to sunlight, all three salts behave similarly: all three white precipitates turn gray and then black. In all three cases, the same product, a fine silver powder is formed, which, as well as all finely divided metals, is black.[79] The reactions are as follows:

$$\mathrm{2\,AgCl \longrightarrow 2\,Ag + Cl_2} \tag{103}$$

$$\mathrm{2\,AgBr \longrightarrow 2\,Ag + Br_2} \tag{104}$$

$$\mathrm{2\,AgI \longrightarrow 2\,Ag + I_2} \tag{105}$$

These three reactions are dramatically facilitated by light. It is the reaction 103 that allowed us to see the faces of our grand-grand parents when they were young, to see historical XX century events, to watch old movies, because that reaction is a core chemical reaction of the wet photography. For us, these three reactions are a good demonstration of the commonality between all three compounds.

However, what about other metals? Do bromides and iodides of other metals behave similarly to their chlorides too? Actually, yes. For example, we know calcium chloride is soluble in water, and its bromide and iodide are easily soluble too. The same can be said about magnesium, iron, copper, zinc chlorides, bromides and iodides. The striking similarity between those compounds allows us to formulate the following rule:

> **If a chloride of some metal is easily soluble in water, its bromide and iodide are soluble too. The exceptions to this rule are extremely rare.**

Due to the ability of the three elements, chlorine, bromine, and iodine, to form salts with all metal, these three elements were combined into a separate group, which was named “halogens”, from two Greek words, “halos” (“salt”) and “gignomay” (“come to be”), literally “salt begetters”. Accordingly, the word “halogenides” is used as an umbrella term of all salts formed by halogens. For example, instead of writing: “potassium chloride, bromide, and iodide are white solids”, we can write “potassium halogenides are white solids”.

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[79] Actually, finely divided metals are among the most black materials in the world.

11.6 Hydrogen chloride and hydrochloric acid, or "acidum salis".

What about the binary compounds formed by halogens and nonmetals? As we know, hydrogen chloride is a compound whose aqueous solution are strongly acidic (accordingly, its name is "hydrochloric acid"). Since hydrogen chloride is a gas, it can be prepared from sodium chloride and sulfuric acid: as we know, exchange reactions between a salt and an acid can lead to formation of a new salt and a new acid when the latter is being removed from the reaction mixture, by formation of either a precipitate (as the silicic acid, H_2SiO_3), or a gas (like HCl). The equation of this reaction is as follows:

$$2\,\mathrm{NaCl} + \mathrm{H_2SO_4} \longrightarrow 2\,\mathrm{HCl_{gas}} + \mathrm{Na_2SO_4} \tag{106}$$

This reaction was the first practical method for the preparation of the hydrochloric acid: gaseous HCl that forms in this reaction can be collected and bubbled through water. It dissolves in water vigorously to form *acidium salis*, or hydrochloric acid.

Like HCl, hydrogen bromide and chloride are gases that are highly soluble in water. Their solutions are called hydrobromic and hydroiodic acids, accordingly. These two acids are very strong and corrosive, even stronger than HCl is. Hydroiodic acid is among the strongest acids currently known.

11.7 Fluorine, the fourth halogen.

Besides the three halogens (Cl, Br, and I), one more element was discovered whose properties are similar to halogens. Its name is fluorine. Like other halogens, it forms salts with all metals, although their properties are somewhat different. Like HCl, hydrogen fluoride (HF) is an acid, although it is not as strong as other hydrogen halogenides are. By its properties, fluorine stays a little bit apart from chlorine, bromine and iodine, however, there are several important reasons to consider it a halogen. We will discuss them a little bit later.

11.8 Preparation of elementary halogens.

Pure halogens can be prepared from their binary compounds by taking away the second element. For example, chlorine can be prepared from hydrogen chloride and potassium permanganate:

$$16\,\mathrm{HCl} + 2\,\mathrm{KMnO_4} \longrightarrow 5\,\mathrm{Cl_{2(gas)}} + 2\,\mathrm{MnCl_2} + 2\,\mathrm{KCl} + 8\,\mathrm{H_2O} \tag{107}$$

In this reaction, potassium permanganate, which serves as a "depot form" of oxygen (as we can see, it is an oxygen rich molecule), donates oxygen to HCl. Since oxygen binds to hydrogen very actively, it takes it from chlorine, and free chlorine atoms form. These chlorine atoms bind together, and a diatomic chlorine molecule forms. The same reaction can be used to produce bromine and iodine, but not fluorine. Why? As we can see from the above reaction, to prepare a halogen in its free form, we need some chemical that binds hydrogen more avidly than the halogens themselves do. It is possible to find such a chemical for HCl. Hydrogen bromide and hydrogen iodide (in that order) give their hydrogen even easier. However, no chemicals were found that take hydrogen from HF to give F_2. The reason is simple: fluorine is the most active element in the Universe. It reacts with other elements, both metals and nonmetals so vigorously, that such bonds are almost impossible to break. As a result, fluorine containing compounds prefer to participate in exchange reactions, but not in dissociation reactions.

> **Fluorine is the most chemically reactive element in the Universe. It reacts vigorously with most known materials. Even oxygen burns in fluorine.**

In connection to that, every person who is capable of critical thinking must ask: "If fluorine binds so strongly to other elements than how did people manage to prepare it in a pure form?" This question deserves a separate chapter. We will discuss it during the next class.

Homework

1. Read "Ask a Foolish Question" by Robert Sheckley. You can find it, for example, at the Project Gutenberg page `http://www.gutenberg.org/files/33854/33854-h/33854-h.htm`[80].

2. Read the above Classwork materials. Answer the following questions:

   1. Some solid ('A') has been prepared by heating an element X in an oxygen atmosphere. This solid is insoluble in water, however, it dissolves in aqueous hydrochloric acid or in aqueous sodium hydroxide. Is the element X a metal or a nonmetal?

   2. Evaporation of the solution prepared from hydrochloric acid and the solid 'A' (from the problem 1) produced some colorless crystalline solid. It was dissolved in water, and the solution obtained was poured into four test tubes. To each of those tubes, aqueous solution of one of the following chemicals were added: magnesium sulfate (to the tube No 1), sodium carbonate (to the tube No 2), sodium sulfide (to the tube No 3), and potassium phosphate. No precipitate was observed in the first test tube, whereas white precipitates were observed in the test tubes 2-4. We know for sure that the element X is one of the elements listed in the table 1 in a CW 3. Can you name the element X?

3. How would you do the following transformations?

   (a)
   $$ZnCl_2 \longrightarrow Zn(OH)_2 \longrightarrow ZnSO_4 \longrightarrow ZnS \qquad (108)$$

   (b)
   $$Si \longrightarrow SiO_2 \longrightarrow CaSiO_3 \qquad (109)$$

   (c)
   $$AlCl_3 \longrightarrow Al(OH)_3 \longrightarrow Al_2O_3 \longrightarrow Al_2(SO_4)_3 \qquad (110)$$

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[80] This link, as well as all other urls are clickable.

Each arrow corresponds to a separate chemical equation, for example, the first step in the scheme 108 can be written as:

$$\mathrm{ZnCl_2} + 2\,\mathrm{KOH} \longrightarrow \mathrm{Zn(OH)_2} + 2\,\mathrm{KCl} \tag{111}$$

Of course, you can choose any auxiliary chemicals you want. For example, instead of KOH you can use NaOH.

4. (a) Find the physical properties of all halogens on Internet[81]: their atomic masses, boiling and melting points. Arrange halogens in order where one of those properties increases.

   (b) Which halogen is the most chemically reactive? Arrange halogens according to its chemical activity.

   (c) Which conclusions can you draw from the results you obtained in (a) and (b)?

5. Glauber's salt, or *sal mirabilis* (Lat. "miraculous salt") was first prepared in 1625 by the German apothecary Johann Rudolf Glauber, who discovered its laxative properties. During the Industrial Revolution, when the need in Glauber's salt increased (it appeared to be a useful starting material for chemical industry), its large scale synthesis was performed by mixing an ordinary salt (table salt) with sulfuric acid in open tanks. Although this method was convenient, it was abandoned soon, because people from nearby houses started to complain that all their iron goods started to rust. Why did it happen? Draw chemical equations of the corresponding chemical reactions.

6. 25 grams of potassium chloride and 100 grams of sulfuric acid were placed into the flask. Immediately after that, the hose was attached to flask's neck, and the gas that formed during this reaction was bubbled through the solution of 12 grams of sodium hydroxide in 200 mL of water. All the gas has been absorbed by the NaOH solution (no bubbles escaped). When evolution of the gas has ceased, few drops of the phenolphtalein solution were added to the liquid. Will the solution turn pink or not?

7. How would you do the following transformations?

   (a)

$$\mathrm{NaCl} \longrightarrow \mathrm{HCl} \longrightarrow \mathrm{Cl_2} \tag{112}$$

   (b)

$$\mathrm{CaBr_2} \longrightarrow \mathrm{HBr} \longrightarrow \mathrm{AlBr_3} \tag{113}$$

12 Preparation of elementary halogens (continued). Reaction of halogens.

Besides usage of oxygen rich compounds as $\mathrm{KMnO_4}$, $\mathrm{KClO_3}$ and others, another general way exists to generate halogens from their salts. This procedure is called **electrolysis** (literally "decomposition by electricity").

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[81] The data from the current version of Wikipedia are correct.

12.1 Prefaration of chlorine

Experiment 23.

Put approximately 2-5-grams of table salt into a 250 mL glass beaker, and add 200 mL of water there. Stir the mixture until all salt dissolved. Attach insulated wires to a standard 9 V battery and mark positive and negative wires. Strip the opposite ends of each wire (about 3-5 cm) from the insulation. Put both ends of the wires into the NaCl solution and describe your observations.

Before we continue, let's introduce three more terms. In chemistry and physics, positive wire end is called **anode**, and negative is called **cathode**. Remember that, because we will use these terms many times.

> **An electic wire used to make contact with some nonmetallic media, be it a liquid, a solid, a human body, or a vacuum, is called "electrode". A positive electrode is called "anode", a negative electrode is called "cathode".**

As we can see, bubbles of some gas are formed both at the anode and the cathode. Is it the same gas, or they are different? If we collect these these gases, we can easily see that the gas formed at the cathode has no odor, no color, and it is combustible. It is easy to see that gas is hydrogen. It is easy to see that the gas formed at the anode is quite different, simply because of its unpleasant smell resembling the smell of bleach. That gas is an elementary chlorine. Moreover, it easy to see the amount of chlorine formed on the anode is much smaller that the amount of hydrogen on the cathode. If you look carefully at the copper anode, you can see its color changing. Obviously, some reaction takes place at the anode that leads to its corrosion. To eliminate corrosion, let's replace the copper anode with a small piece of platinum wire. As we expected, platinum, which is among the most inert metals, does not corrode (its surface remains clear and shiny), and the amount of chlorine bubbles increases dramatically.

What is going on during this process? Obviously, when an electric current passes through sodium chloride, it decomposes onto chlorine, which we can see (the bubbles) and smell (a bleach smell). But what is the second product? Isn't it logical to conclude that the second product is a sodium metal? But, if that is the case, why we don't see it? To answer this question, let's repeat the Experiment 23, but let's add few drops of phenolphtalein into the NaCl solution. We will see that immediately after connecting the electrodes to the battery a pink coloring starts to form near the cathode. That means the solution becomes basic. Now we can reconstruct all the processes in our apparatus.

Firstly, when an electric current passes through the NaCl solution, sodium chloride, initially, decomposes onto the elements:

$$2\,\mathrm{NaCl} \longrightarrow 2\,\mathrm{Na} + \mathrm{Cl}_{2\mathrm{gas}} \tag{114}$$

An interesting feature of this reaction is that the products are separated in space: chlorine is formed at the anode, whereas sodium is formed at the cathode. Both substances are extremely reactive, so a major part of chlorine immediately reacts with the copper electrode to form copper chloride or other compounds:

$$\mathrm{Cl}_2 + \mathrm{Cu} \longrightarrow \mathrm{CuCl}_2 \tag{115}$$

If we need to obtain pure chlorine, the anode's copper must be replaced with some more inert material, for example, platinum. That allows us to see a considerable amount of chlorine bubbles, and to feel its smell. But what is going on at the cathode? why do we see hydrogen bubbles instead of sodium? The reason is obvious. As we already know, sodium metal is so reactive that it violently reacts with water to form sodium hydroxide and hydrogen. That is exactly what happens at the cathode: immediately after its formation every single sodium metal reacts with water to produce hydrogen (a gas we see) and NaOH (a purple phenolphtalein color). Therefore, the net result the **electrolysis** reaction is the formation of a chlorine gas at the anode, and sodium hydroxide and hydrogen at the cathode:

$$2\,\mathrm{NaCl} + 2\,\mathrm{H_2O} \longrightarrow \mathrm{Cl_2} + \mathrm{H_2} + \mathrm{NaOH} \tag{116}$$

This process is general. All salts can be decomposed in such a way. In all cases, metals (or the products of their reaction with water) are formed at the cathode, and acidic residues are transformed at the anode. We cannot afford a luxury to discuss this process in details now, so let's return to its discussion in due time.

Decomposition of salts by means of the electric current is called electrolysis.

Interestingly, liquid NaCl can be subjected to electrolysis too. Sodium chloride melts at 801 °C*, and, when the electric current passes through the molten NaCl, sodium metal formed at the cathode has nothing to react with. As a result, we get pure chlorine gas at the anode, and pure sodium metal at the cathode. That is an industrial way to prepare large amount of these two elementary substances. Sir Humphry Davy, a brilliant British chemist, was a first person who isolated some alkaline metals in using electrolysis.*

12.2 Preparation of bromine and iodine

Both bromine and iodine can be prepared similarly. Since iodine is a solid, it forms a black film on the anode, which peels off easily.

12.3 Preparation of fluorine

Since fluorine is much more reactive even that chlorine, it cannot be prepared by the electrolysis of the sodium fluoride solution, simply because it would immediately react with water to generate oxygen and hydrogen fluoride[82]

$$\mathrm{F_2} + 2\mathrm{H_2O} \longrightarrow 4\,\mathrm{HF} + \mathrm{O_2} \tag{117}$$

That means the result of such a reaction would be the formation of hydrogen at the cathode and *oxygen*, (not fluorine) at the anode. To obtain elementary fluorine, we must exclude water.

Fortunately, that is possible to do, because, in contrast to HCl or HBr, anhydrous HF is not a gas, but a liquid. Many salts, including potassium fluoride, are soluble in liquid HF, so

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[82] Please, pay attention to that fact: fluorine is so reactive that it takes hydrogen even from oxygen. It is the only element capable of doing that.

Sir Humphry Davy (1778-1829),
a person who first used electrolysis for isolation of some elements.

Henry Moissan (1852-1907),
a discoverer of fluorine.

its electrolysis can produce elementary fluorine. Unfortunately, that is not the only obstacle chemists had to overcome to prepare pure fluorine. The main difficulty was an extreme reactivity of fluorine: since it reacts with almost every material, its collection and storage is a formidable task. In addition, due to its high activity, fluorine is extremely dangerous. Several chemists, including Sir Humphry Davy, attempted to isolate it, and some of those attempts were almost fatal. It was probably a reason why Davy died so prematurely. A person who succeeded in isolation of pure fluorine was a French chemist Henri Moissan, who was awarded a Nobel Prize for that achievement in 1906.

12.4 Reaction of halogens with other elements

As we already know, halogens are very reactive substances. One of the most common halogen reaction is a formation of binary compounds. Thus, such metals as copper or iron burn in gaseous chlorine to produce chlorides:

$$2\,\mathrm{Fe} + 3\,\mathrm{Cl_2} \longrightarrow 3\,\mathrm{FeCl_3} \tag{118}$$

$$\mathrm{Cu} + \mathrm{Cl_2} \longrightarrow \mathrm{CuCl_2} \tag{119}$$

(Obviously, such active metals as sodium react with chlorine even more vigorously, and the product of such a reaction is a metal chloride.)

Not only metals are capable of reacting with chlorine. Some moderately active non-metals, such as phosphorus, ignite spontaneously in chlorine. The product of that reaction is phosphorus (III) chloride PCl_3

$$2\,\mathrm{P} + 3\,\mathrm{Cl_2} \longrightarrow 3\,\mathrm{PCl_3} \tag{120}$$

Unfortunately, we cannot perform all these spectacular experiments in the class, because a special protective equipment is needed for that. However, you can watch some of those experiments on YouTube. In the Homework section, some links are provided.

12.5 Halogens and oxidation

As we can see, reaction of most metals and some nonmetals with halogens are vigorous, and they yield corresponding binary compounds (halogenides). In that sense, they have much in common with the reactions between oxygen and other elements (i.e. the combustion reaction, a.k.a. **oxidation reaction**). Therefore, the chemists realized the term "oxidation" is equally applicable to the reactions of halogens with metals and less active nonmetals.

> **Reactions of halogens with metals and less active nonmetals are the oxidation reactions. Like oxygen, halogens serve as oxidizers in that type reactions. Fluorine is the strongest oxidizer among all elements.**

If we compare, for example, the reaction between magnesium and oxygen and the reaction between magnesium and chlorine, we will see that in both cases a zero valence magnesium becomes divalent.

$$\mathrm{Mg} + \mathrm{O_2} \longrightarrow 2\,\mathrm{MgO} \tag{121}$$

$$\mathrm{Mg} + \mathrm{Cl_2} \longrightarrow \mathrm{MgCl_2} \tag{122}$$

That is a common trait of all oxidation reactions.

> **A valence of the element that has been subjected to oxidation always increases. Conversely, when a valence of at least one atom has increased during some reaction, such a reaction is an oxidation reaction.**

In connection to that, it is interesting to look at the exchange reactions between acids, salts and bases we studied recently. As you have probably noticed, valences of all atoms in totally preserved for all reactants and products of those reactions. That observation deserves to be emphasized:

> **Exchange reactions between acids, bases, or salts are not oxidation reactions.**

12.5.1 Chlorine or oxygen: what is stronger?

As we can see, chlorine can oxidize even the elements that seem not to react with oxygen. Does it mean it is a stronger oxidizer? Actually, no. There are two reasons why chlorine's apparent reactivity seems higher. Firstly, whereas chlorides of some elements are volatile or low melting solids, their oxides are hard and high melting compounds. For example, aluminium, which is a very active metal judging by its position in the reactivity series, does not ignite in air when heated. However, it ignites and violently burns in the chlorine atmosphere. The explanation is simple. Aluminium reacts with oxygen almost instantly, however, its product, $\mathrm{Al_2O_3}$ forms a very dense and hard film on the metal's surface, so the bulk aluminium becomes protected from further oxidation. In contrast, dry aluminium chloride is a low melting solid that provides no protection for the piece of aluminium metal. As a result, combustion of aluminium in chlorine lasts until all chlorine or all aluminium is consumed.

The second reason for high activity of halogens is in their monovalence. That means, in F_2, Cl_2, Br_2 and I_2, halogen atoms are connected to each other just with a single bond. which is easy to break[83]. In contrast to halogens, oxygen is divalent, so the O_2 molecule is much more stable. Therefore, much more energy is needed to break the oxygen molecule apart.

These two reasons make oxygen less active then chlorine or bromine are. However, oxygen is more active oxidizer. We can make that conclusion because, whereas it can form oxides with chlorine, bromine, or iodine (but not with fluorine), no chlorides, bromides or iodides of oxygen can be prepared.

12.6 High valence halogen oxides and oxo acids.

As we already know, overwhelming majority of elements form oxides. As a rule, their oxides have low stability, which is understandable, taking into account high halogen's activity: they do not "like" to be oxidized, when they are bound to oxygen, they donate an oxygen atom easily to other elements. In contrast to oxides, most oxygen containing acids generated from halogen oxides much more stable. A Table 1 summarize all acids formed by chlorine, bromine, and iodine.

Table 1. Halogen oxo acids

Valence	Cl	Br	I	Generalized formula
I	$HClO$	$HBrO$	HIO	HXO
III	$HClO_2$	$HBrO_2$	-	HXO_2
V	$HClO_3$	$HBrO_3$	HIO_3	HXO_3
VII	$HClO_4$	$HBrO_4$	HIO_4 (H_5IO_6)	HXO_4

As we can see, in these acids, the valence of halogen atoms varies from 1 to 7, and it always takes only odd values. The maximal valence is 7 for all of them (fluorine is the sole exception).

12.7 General properties of halogens

Now we can summarize some common properties of halogens.

1. All halogens form binary compounds ("halides", a.k.a "halogenides") with metals. Halogen's valence in halogenides is ***always equal to one.***

   Examples: $NaCl$, $AlBr_3$, CaF_2.

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[83] Obviously, for oxidation to occur, oxidizer's molecule must fall apart first.

2. Metal halides are salts. As a rule, if chloride of some metal is soluble, the same is true for its bromide or iodide. If one halogenide of some metal is insoluble, other halides are insoluble too.[84]

   Examples: $CuCl_2$ is soluble in water; $CuBr_2$ and CuI_2 are soluble too. AgCl is insoluble in water; AgBr and AgI are also insoluble.

3. All halogens form binary compounds with hydrogen with a general formula HX, where X is halogen. All hydrogen halogenides are acids. ***Acidity of hydrogen halogenides increases with the increase of halogen's atomic mass.***

4. All halogens form binary compounds with oxygen. Chlorine, bromine, and iodine (but not fluorine) form a series of oxygen containing acids. ***The maximal valence of halogen's atom in those acids is 7; in other acids the valence assumes only odd values.***

Homework

1. Watch the following YouTube videos[85]:
   (a) `http://www.youtube.com/watch?v=UHxXmHg2_yk`
   (b) `http://www.youtube.com/watch?v=EvtyMr5EvBY`
   (c) `http://www.youtube.com/watch?v=edLpxdERQZc`

   Describe what you seen, and draw the equations of these reactions.

2. Is the reaction between sulfuric acid and zinc an oxidation reaction? If yes, which atom is being oxidized?

3. Although fluorine is capable of oxidizing almost every material, dry fluorine can be safely stored in steel cylinders. Can you tell why?

4. How many ways to prepare copper bromide in one step can you propose? Draw chemical equations for each of them.

5. Do the following transformations:

   (a)
   $$Br_2 \longrightarrow AlBr_3 \longrightarrow AgBr \tag{123}$$

   (b)
   $$NaCl \longrightarrow Cl_2 \longrightarrow PCl_3 \tag{124}$$

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[84] Sometimes, that doesn't work for fluorine.

[85] If you open an electronic version of this document at our web site, you can click at the links directly

13 Chalcogens, or oxygen family. 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[86], 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:

$$2\,\mathrm{Na} + 2\,\mathrm{H_2S} \longrightarrow \mathrm{NaSH} + \mathrm{H_2} \tag{125}$$

in the same way water reacts with sodium:

$$2\,\mathrm{Na} + 2\,\mathrm{H_2O} \longrightarrow \mathrm{NaOH} + \mathrm{H_2} \tag{126}$$

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.

$$2\,\mathrm{Na} + \mathrm{S} \longrightarrow \mathrm{Na_2S} \tag{127}$$

$$\mathrm{Ca} + \mathrm{S} \longrightarrow \mathrm{CaS} \tag{128}$$

$$\mathrm{Zn} + \mathrm{S} \longrightarrow \mathrm{ZnS} \tag{129}$$

$$\mathrm{Fe} + \mathrm{S} \longrightarrow \mathrm{FeS} \tag{130}$$

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

$$\mathrm{Ca} + \mathrm{O} \longrightarrow \mathrm{CaO} \tag{131}$$

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:

$$2\,\mathrm{Al} + 3\,\mathrm{S} \longrightarrow \mathrm{Al_2S_3} \tag{132}$$

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[86] 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.

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:

$$\mathrm{Na_2S + H_2SO_4 \longrightarrow H_2S + Na_2SO_4} \tag{133}$$

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:

$$\mathrm{S + O_2 \longrightarrow SO_2} \tag{134}$$

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:

$$\mathrm{SO_2 + H_2O \rightleftharpoons H_2SO_3} \tag{135}$$

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:

$$\mathrm{SO_2 + O_2 \longrightarrow SO_3} \tag{136}$$

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

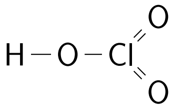
$$\mathrm{SO_3 + H_2O \longrightarrow H_2SO_4} \tag{137}$$

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`.

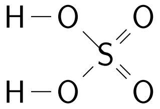
Salts of sulfuric acid are called sulfates.

13.0.1 Sulfates and acid salts

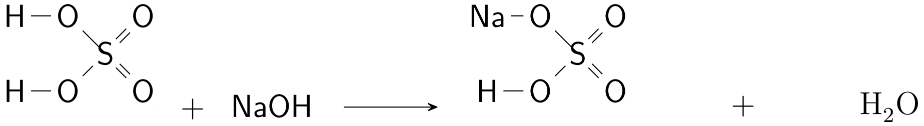
As we already know, acids are the compounds that can donate a hydrogen in a reaction with metals (left of hydrogen in a reactivity series) or with bases. Depending on the acid type, they can donate either one or several hydrogens. Thus, a chloric acid has just one hydrogen atom it can donate:



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".[87] 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:

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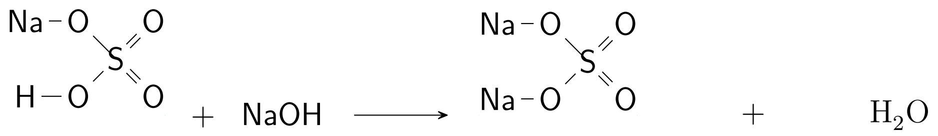
[87] Sometimes, a prefix "bi" is used instead of the prefix "hydro", so the alternative name of sodium hydrosulfate is "sodium *bi*sulfate", because such a salt contains two times more acidic residue per one metal atom as compared with ordinary salts.



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.

13.1 Other chalcogens

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

13.2 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.

14 A general approach towards the description of classes of elements. Pnictogens

You have probably noticed that when we were outlining the common traits of halogens and chalcogens we used the same approach: we did a comparison by comparing the composition and properties of some key compounds these elements form. In other words, if some elements form a set of compounds with similar formulas and similar properties, these elements are likely to belong to the same class, or group. Let's summarize this procedure.

1. Both halogens and chalcogens form binary compounds with metals, and, if we take sodium as an example[88], all sodium halogenides have a formula NaX, where X is

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[88] It is convenient to use sodium because it is active (so it forms binary compounds with almost all non-metals), and it is *always* monovalent.

halogen, whereas all sodium chalcogenides have a formula Na_2X. In general, the stoichiometry[89] of binary compounds with metals is a useful characteristic of elements.

2. A composition and properties of binary compounds with hydrogen (these compounds are called *hydrides*) is also a trait that can be helpful for element classification. Thus, all halogens form hydrides with a general formula HX, and all these hydrides are moderate or strong acids. All chalcogens form binary compounds with hydrogen with a general formula H_2X, and these hydrides are veak acids (except water, which is amphoteric: as we already know, in some cases it behaves as a weak acid, in some cases it is a weak base) where X is chalcogen. All these compounds (except H_2O) are acids.

3. Oxides of elements are also a good tool for classification: all elements, except oxygen, fluorine, and three other elements[90] form oxides, which are either acidic (form acids in a reaction with water), basic (form bases in reaction with water), or amphoteric. A general formula of oxides in the same (with minor exceptions) for all elements belonging to the same group.

Using this scheme, let's identify other groups of elements.

14.1 Pnictogens, or nitrogen family

The element belonging to that group are nitrogen, phosphorus, as well as three other elements, **Arsenic (As)**, **Antimony (Sb)**, and **Bismuth (Bi)**.

The name of this family comes from Greek word *pnígein*, meaning "to choke", or "to suffocate". The reason for that is obvious: a nitrogen gas does not support respiration. Nitrogen, as well as other pnictogens produce toxic gases (ammoina H_3N, phosphine H_3P, arsine H_3As, and stibine H_3Sb) when combined to hydrogen. All of them are trivalent in their hydrogen compounds, and can be either tri or pentavalent in oxides or some other compounds with active nonmetals. The Table 3 summarizes the properties of their key compounds:

Table 3. Pnictogen hydrides and oxo acids

Valence	N	P	As	Sb	Generalized formula
Hydride	H_3N	H_3P	H_3As	H_3Sb	H_3X
Oxides:					
III	N_2O_3	P_2O_3	As_2O_3	Sb_2O_3	X_2O_3
V	N_2O_5	P_2O_5	As_2O_5	Sb_2O_5	X_2O_5
Acids:					
III	HNO_2	H_3PO_3	H_3AsO_3	H_3SbO_3	H_3XO_3
V	HNO_3	HPO_3 (H_3PO_4)	H_3AsO_4	H_3SbO_4	H_3XO_4

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[89] In the case is you forgot this word, just a reminder: this word means both the chemical composition of substances and the part of chemistry that studies it.

[90] We will talk about them later this year.

Homework

1. Sodium sulfide is contaminated with some amount of sodium selenide. A sample of this mixture was dried and weighed. Its mass was 10.11 g. This sample was dissolved in 100 mL of water, a solution of 30 g of $AgNO_3$ in 200 mL of water was added. The precipitate was collected by filtration and dried. Its mass was 21,3 grams. What was the content of Na_2Se in the sample?