Inorganic Chemistry
Lesson 5
Oxides in nature. Acidic oxides. Acids.

October 22, 2017

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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).[1] 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. 1), aluminum oxide, silicon dioxide (in a form of quartz, opal etc).

Figure 1: Monument valley. Arizona and Utah sandstones are red due to a large content of iron oxide.

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.

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

Experiment 12

Pour about 100 mL of water into a large beaker. Add approximately a quarter teaspoon of P_2O_5[2]*. 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[3] 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:

$$P_2O_5 + 3\,H_2O = 2\,H_3PO_4 \tag{1}$$

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:

$$SO_2 + H_2O = H_2SO_3 \tag{2}$$

$$CO_2 + H_2O = H_2CO_3 \tag{3}$$

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.

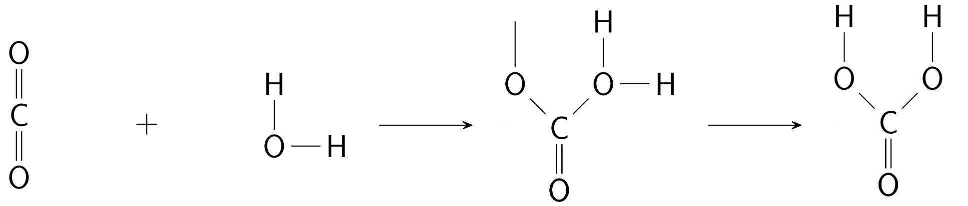
Oxides that can be converted into acids are called 'acidic oxides'.

To understand how oxides form acids, let's look at the mechanism of that reaction. To do that, let's redraw the equation 3. On the scheme below the structural formulas of each

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

[3] 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.

molecule are shown. In addition, some odd molecule is shown in the middle of the scheme. What this molecule is?



Unstable intermediate

Carbonic acid

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.[4]

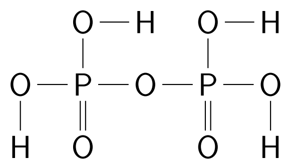
Addition of water to the oxides of other elements proceeds according to the same mechanism: the reaction starts with the attack of the element's atom in the oxide by water oxygen atom, followed by hydrogen's jump to another oxygen. Importantly, the valence state of each atom is always preserved in the 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.

2.1 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

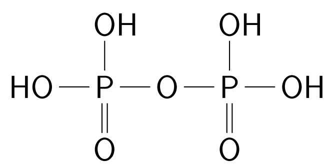
[4]Actually, this scheme is a little bit oversimplified. To draw a fully correct scheme of this reaction, we need to learn more about the electronic structure of atoms and molecules. We will return to this scheme later.

explicitly, but to show it as a single "atom". By using this trick, many formulas can be significantly simplified. Thus, instead of drawing this:



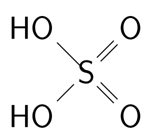
"Pyrophosphoric acid"

we can draw that:



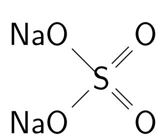
"Pyrophosphoric acid"

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.

3 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:

$$\mathrm{Zn + H_2SO_4 = ZnSO_4 + H_{2(g)}} \tag{4}$$

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.[5]

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.*

3.1 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 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).

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

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[6], (d) Aluminum and hydrochloric acid.

3. At room temperature and under atmospheric pressure, two grams of hydrogen occupy 22.4 L.[7] 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 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?

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

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

[7] 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.