

INORGANIC CHEMISTRY

Lesson 14

Halogens. Oxidation.

January 14, 2018

1 Preparation of elementary halogens (continued).

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

1.1 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 electric 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 phenolphthalein 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.

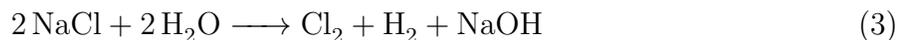
Firstly, when an electric current passes through the NaCl solution, sodium chloride, initially, decomposes onto the elements:



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:



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 phenolphthalein 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:



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



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

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.

1.2 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.

1.3 Fluorine

Since fluorine is much more reactive even than 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 fluoride¹

¹Please, 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.



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



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 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.

2 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:



(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 nonmetals, such as phosphorus, ignite spontaneously in chlorine. The product of that reaction is phosphorus (III) chloride PCl_3



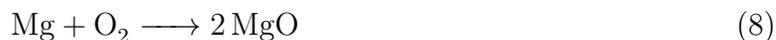
Unfortunately, we cannot perform all these spectacular experiments in the class, because a special protective equipment is needed for that. However, you can watch some of those experiments on YouTube. In the Homework section, some links are provided.

3 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.



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.

3.1 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, 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 break². 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 than 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.

4 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 summarizes 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).

²Obviously, for oxidation to occur, oxidizer's molecule must fall apart first.

5 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, AlBr₃, CaF₂.

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.³

Examples: CuCl₂ is soluble in water; CuBr₂ and CuI₂ 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 videos⁴:

(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.

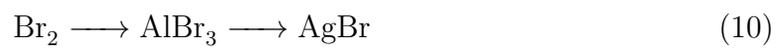
2. Is the reaction between sulfuric acid and zinc an oxidation reaction? If yes, which atom is being oxidized?
3. Although fluorine is capable of oxidizing almost every material, dry fluorine can be safely stored in steel cylinders. Can you tell why?
4. How many ways to prepare copper bromide in one step can you propose? Draw chemical equations for each of them.

³Sometimes, that doesn’t work for fluorine.

⁴If you open an electronic version of this document at our web site, you can click at the links directly

5. Do the following transformations:

(a)



(b)



My e-mail is mark.lukin@gmail.com