Inorganic Chemistry
Lesson 13
Classification of elements. Metals and nonmetals. Metalloids. Groups of elements. Halogens.

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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[1];
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)[2].

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.

[1]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.

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

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.

$$Mg + O_2 \longrightarrow MgO \tag{1}$$

$$Mg + S \longrightarrow MgS \tag{2}$$

$$Mg + Cl_2 \longrightarrow MgCl_2 \tag{3}$$

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.

> **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.**

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.

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:

$$C + O_2 \longrightarrow CO_2 \tag{4}$$

$$Si + O_2 \longrightarrow SiO_2 \tag{5}$$

These oxides are acidic:

$$CO_2 + 2\,NaOH \longrightarrow Na_2CO_3 + H_2O \tag{6}$$

$$SiO_2 + 2\,NaOH \longrightarrow Na_2SiO_3 + H_2O \tag{7}$$

The acids can be generated from their salts:

$$Na_2CO_3 + 2\,HCl \longrightarrow H_2CO_3 + 2\,HCl \tag{8}$$

$$Na_2SiO_3 + 2\,HCl \longrightarrow H_2SiO_3 + 2\,HCl \tag{9}$$

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.

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:

$$NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3 \tag{10}$$

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.

$$NaBr + AgNO_3 \longrightarrow AgBr + NaNO_3 \tag{11}$$

$$NaI + AgNO_3 \longrightarrow AgI + NaNO_3 \tag{12}$$

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.[3] The reactions are as follows:

$$2\,AgCl \longrightarrow 2\,Ag + Cl_2 \tag{13}$$

$$2\,AgBr \longrightarrow 2\,Ag + Br_2 \tag{14}$$

$$2\,AgI \longrightarrow 2\,Ag + I_2 \tag{15}$$

These three reactions are dramatically facilitated by light. It is the reaction 13 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".

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:

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

$$2\,NaCl + H_2SO_4 \longrightarrow 2\,HCl_{gas} + Na_2SO_4 \tag{16}$$

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.

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.

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:

$$16\,HCl + 2\,KMnO_4 \longrightarrow 5\,Cl_{2(gas)} + 2\,MnCl_2 + 2\,KCl + 8\,H_2O \tag{17}$$

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`[4].

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)

   $$ZnCl_2 \longrightarrow Zn(OH)_2 \longrightarrow ZnSO_4 \longrightarrow ZnS \quad (18)$$

   (b)

   $$Si \longrightarrow SiO_2 \longrightarrow CaSiO_3 \quad (19)$$

   (c)

   $$AlCl_3 \longrightarrow Al(OH)_3 \longrightarrow Al_2O_3 \longrightarrow Al_2(SO_4)_3 \quad (20)$$

   Each arrow corresponds to a separate chemical equation, for example, the first step in the scheme 18 can be written as:

   $$ZnCl_2 + 2\,KOH \longrightarrow Zn(OH)_2 + 2\,KCl \quad (21)$$

   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[5]: their atomic masses,

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

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

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)
$$NaCl \longrightarrow HCl \longrightarrow Cl_2 \tag{22}$$

   (b)
$$CaBr_2 \longrightarrow HBr \longrightarrow AlBr_3 \tag{23}$$

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