Inorganic Chemistry
Lesson 10
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.

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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:

> **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.**

Figure 1: Janus, a two-faced Roman god.

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.

$$2Na + 2\,H_2O \longrightarrow H_2 + 2NaOH \tag{1}$$

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.[1] 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:**

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

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

$$SO_3 + 2NaOH \longrightarrow Na_2SO_4 + H_2O \tag{3}$$

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

$$Na_2O + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O \tag{4}$$

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.

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.

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

2.1 Synthesis, or addition.

$$A + B \longrightarrow C \tag{5}$$

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:
$$C + O_2 \longrightarrow CO_2 \tag{6}$$

2. Combustion of magnesium:
$$Mg + O_2 \longrightarrow MgO \tag{7}$$

2.2 Decomposition.

$$A \longrightarrow B + C \tag{8}$$

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:
$$HgO \longrightarrow O_2 + Hg \tag{9}$$

2. Decomposition of hydrogen peroxide:
$$H_2O_2 \longrightarrow H_2O + O_2 \tag{10}$$

2.3 Substitution, or replacement.

$$A + BC \longrightarrow AC + B \tag{11}$$

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"[2] 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.

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

1. Reaction of iron with sulfuric acid:

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2 \tag{12}$$

   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:

$$AgNO_3 + Cu \longrightarrow Cu(NO_3)_2 + Ag \tag{13}$$

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

2.4 Exchange.

$$AB + CD \longrightarrow AC + BD \tag{14}$$

The exchange reaction[3] 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.

$$NaOH + HCl \longrightarrow NaCl + H_2O \tag{15}$$

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.

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 Lesson 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:

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2\,NaCl \tag{16}$$

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

[3]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.

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 16, 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 17 is not possible.

$$CaCO_3 + 2NaCl \neq CaCl_2 + Na_2CO_3 \tag{17}$$

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.

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 (18) and (19).

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3 \tag{18}$$

$$3CaCl_2 + 2Na_3PO_4 \longrightarrow 2Ca_3(PO_4)_2 + 6NaCl \tag{19}$$

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 16), 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.

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:

$$CuCl_2 + 2\,NaOH \longrightarrow Cu(OH)_2 + 2\,NaCl \tag{20}$$

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:

$$FeCl_3 + 3NaOH \longrightarrow Fe(OH)_{3(s)} + 3\,NaCl \tag{21}$$

$$MgCl_2 + 2\,NaOH \longrightarrow Mg(OH)_{2(s)} + 2\,NaCl \tag{22}$$

$$Al_2(SO_4)_3 + 6\,NaOH \longrightarrow 2\,Al(OH)_{3(s)} + 6\,NaCl \tag{23}$$

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:

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + CO_{2(gas)} + H_2O \tag{24}$$

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:

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2CO_3 \tag{25}$$

$$H_2CO_3 \longrightarrow CO_{2(gas)} + H_2O \tag{26}$$

In other words, during the first step (equation 25), 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 26). 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.

$$2\,NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HCl_{(gas)} \tag{27}$$

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.

$$Na_2SiO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2SiO_{3(s)} \tag{28}$$

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.

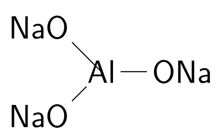
The reaction that takes place after initial addition of NaOH is quite understandable: like in the experiment 20, an insoluble hydroxide (in this case, aluminium hydroxide, $Al(OH)_3$, is formed, according to the equation 23). However, what we observe after that is somewhat counter-intuitive: the loose 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:

$$2\,Al(OH)_3 + 6\,HCl \longrightarrow 2\,AlCl_3 + 3\,H_2O \tag{29}$$

and

$$2\,Al(OH)_3 + 6\,NaOH \longrightarrow 2\,Na_3AlO_3 + 3\,H_2O \tag{30}$$

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 lesson devoted to aluminium.

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:

$$Cu(OH)_2 \longrightarrow CuO + H_2O \tag{31}$$

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.

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.

$$Cu \longrightarrow CuO \longrightarrow CuSO_4 \longrightarrow Cu(OH)_2 \longrightarrow CuO \tag{32}$$

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)

$$AlCl_3 \longrightarrow Al(OH)_3 \longrightarrow Al_2O_3 \longrightarrow Al_2(SO_4)_3 \tag{33}$$

(b)

$$S \longrightarrow SO_2 \longrightarrow CaSO_3 \longrightarrow Ca(OH)_2 \tag{34}$$

(c)

$$AlCl_3 \longrightarrow Al(OH)_3 \longrightarrow Al_2O_3 \longrightarrow Al_2(SO_4)_3 \tag{35}$$

6. Look at the equations below:

   (a)
   $$Zn + H_2SO_4 \longrightarrow ZnSO_3 + H_2O \tag{36}$$

   (b)
   $$MgO + H_2 \longrightarrow Mg(OH)_2 \tag{37}$$

   (c)
   $$6\,NaOH + 2\,H_3PO_3 \longrightarrow 2\,Na_3PO_4 + 3\,H_2O \tag{38}$$

   (d)
   $$H_2 + KOH + PO_3 \longrightarrow K_3PO_4 + H_2O \tag{39}$$

   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.

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