Ministry of Education and Science of Ukraine
Kyiv National University of Construction and Architecture

CHEMISTRY

TUTORIAL

Recommended by the academic council of the Kyiv National University of Construction and Architecture as a tutorial for applicants of the first (bachelor) level of higher education in the specialties 192 "Construction and civil engineering" and 161 "Chemical technology and engineering"

Kyiv 2024

УДК 54(075.8)
Х46

Autors: V. Grechanyuk, A. Kozyrev, I. Grechanyuk, O. Matsenko, T. Vitovetska, V. Chornovol, Y. Kovalchuk;

Reviewers: Lyudmila Oleksenko, Doctor of Chemical Sciences, professor of the Department of Physical Chemistry of Taras Shevchenko Kyiv National University;

Oleksandr Zaslavskyi, Doctor of Chemical Sciences, Academic Secretary of the Ukrainian State Scientific Research Institute "Resurs";

Oksana Berdnyk, Candidate of Technical Sciences, Assistant professor, Kyiv National University of Civil Engineering and Architecture

Approved at the meeting of the academic council of the Kyiv National University of Construction and Architecture, protocol N 19 dated 23 february 2024.

Chemistry: tutorial / V. Grechanyuk, A. Kozyrev, I. Grechanyuk et al. – Kyiv:
Х46 KNUCA, 2024. – 212 p.

ISBN 978-966-627-264-8

Contains the main theoretical material in general and inorganic chemistry within the discipline for applicant of higher education in construction and related specialties, including the manufacturing of materials. Contains test questions for self-work.

Intended for applicant of higher education of specialties 192 "Construction and civil engineering" and 161 "Chemical technologies and engineering".

Хімія: навчальний посібник / В. Гречанюк, А. Козирєв, І. Гречанюк та ін. –
Х46 Київ: КНУБА, 2024. – 212 с.

Містить основний теоретичний матеріал із загальної та неорганічної хімії в межах дисципліни для здобувачів вищої освіти будівельних та споріднених спеціальностей, зокрема виробництва матеріалів. Містить контрольні запитання для самостійної роботи.

Призначено для здобувачів вищої освіти спеціальностей 192 «Будівництво та цивільна інженерія» та 161 «Хімічні технології та інженерія».

УДК 54(075.8)

ISBN 978-966-627-264-8

Contents

Introduction

Chemistry is one of the fundamental sciences, containing not only theoretical information, but also of great practical importance. Chemistry allows us to predict the properties of materials, understand the mechanism of their changes under the influence of the environment and ways to achieve the desired properties. It combines all these aspects into one complex and considers them from the point of view of the structure of matter, chemical bonds, properties of individual molecules, atoms, chemical elements and electronic structure. Chemistry not only describes nature, but also provides a set of laws, principles and rules for the exploration of unexplored areas.

For many decades, chemistry has been studied by students of construction, technical and other specialties at the Kyiv National University of Construction and Architecture. During this time, the foundations of the traditional university chemistry course were laid, which became advanced, especially in the field of metal corrosion, chemistry of building materials and silicates.

Unfortunately, chemistry in Ukraine existed in some isolation from European and American traditions, primarily due to the language barrier. This is not very noticeable at the high academic level, but is strongly felt at the student level. This can be seen in the order of presentation of the material, terminology and explanations. Today, Ukraine makes great efforts to move closer to the European Union, the United States of America and the Commonwealth of Nations, but protects its own traditions and advantages. This tutorial is one of such effort.

This is the first educational publication of the Kyiv National University of Civil Engineering and Architecture in chemistry in English, which uses the traditional Ukrainian structure of presentation of the discipline, but modern English terminology. It contains theoretical material of the discipline Chemistry for students of specialty 192 “Construction and Civil Engineering” and part of a much more advance course General and Inorganic Chemistry for students of specialty 161 “Chemical Technologies and Engineering”. At the same time, it may be useful to other students who study chemistry at the frontier of the Ukrainian and English traditions, both foreign students in Ukraine and Ukrainian students abroad.

The English language and terminology in this textbook are at the level of peer-reviewed scientific journals, and the chemical nomenclature meets international standards.

As a result of studying chemistry using this textbook, students should:

- know and understand the essence and mechanisms of chemical phenomena and processes;
- know and apply the basic theories, methods and principles of chemistry as a natural science;
- know the chemical bases and principles of manufacturing modern building materials;
- correctly use professional terminology and basic concepts of chemistry.

A team of authors worked on the book:

- Professor V. Grechanyuk is the team leader and author of , and Chapter 6 Thermochemistry and chemical thermodynamics, Chapter 13 General characteristics of Mg/Ca-group elements, and Chapter 14 General characteristics of Al- and Si-group elements;
- Professor A. Kozyrev is the team coordinator and the author of Chapter 10 Red-ox reactions, Chapter 11 Electrochemistry, and Chapter 12 General characteristics of metals;
- Professor I. Grechanyuk is the author of Chapter 8 Dissociation and Electrolytes and Chapter 9 Hydrolysis of Salts.
- Associate Professor O. Matsenko is the author of Chapter 1 Basic concepts and laws of chemistry, Chapter 2 Atomic structure and electrons, and Chapter 3 Periodic trends and periodic table of the elements;
- Associate Professor T. Vitovetska is the author of Chapter 5 Classification of inorganic compounds;
- Associate Professor V. Chornovol is the author of Chapter 4 Molecular structure and types of chemical bonds and Chapter 7 Solutions;
- Associate Professor Y. Kovalchuk is the author of Chapter 15 Basics of chemistry of binding materials.

The authors are sincerely grateful to colleagues and reviewers and welcome any feedback regarding the content of the book.

Chapter 1. Basic concepts and laws of chemistry

1.1. Basic concepts of chemistry

Even ancient Greek philosophers believed that substances consist of very small particles called atoms. However, they could not prove it experimentally. More specific ideas about atoms arose much later, as a result of the development of experimental physics and chemistry. At the end of the 18th and the beginning of the 19th centuries. Thanks to the rapid development of chemistry and physics, the basis for the quantitative development of the atomic-molecular theory was created by scientists works from various countries.

Atomic-molecular theory in chemistry was finally established only in the middle of the 19th century. At the international congress of chemists in Karlsruhe (Germany) in 1860, concepts of definitions of molecule and atom were adopted.

The main thesis of this theory, which were formed at the end of the 19th century, are as follows:

1. All substances consist of atoms or molecules. A molecule is the smallest particle of a substance that remains its chemical properties.
2. Molecules consist of atoms that combine with each other in certain ratios. An atom is the smallest chemically indivisible particle of matter.
3. Atoms and molecules are in continuous movement.
4. Molecules of simple substances consist of the same atoms, and molecules of complex substances consist of different atoms.
5. During a chemical reaction, there is a change in the composition of molecules and reshuffle of atoms, as a result of which molecules of new compounds are formed.
6. The properties of molecules depend not only on their composition, but also on the way atoms are bonded to each other.

Modern science has developed, clarified and added the classical atomic-molecular theory, and some of its provisions have been revised, for example, thesis on the indivisibility of atoms.

The main concepts of modern atomic-molecular theory are: molecule, atom, chemical element, simple and complex substances.

A **molecule** is the smallest particle of a given substance that possesses its chemical properties. The molecule chemical properties are determined by its composition and chemical structure. These are actually existing particles characterized by size, mass, qualitative (atomic) and quantitative composition (that is described using chemical formulas).

An **atom** is an electrically neutral, chemically indivisible particle of matter consisting of a positively charged nucleus and negatively charged electrons moving around it. Like molecules, atoms are real particles that are characterized by their mass, size, nuclear charge, and electron shell structure. Another words, an **atom** is the smallest particle of a chemical element that is a part of the molecules of simple and complex substances. The chemical properties of an element are determined by the structure of its atom.

Atoms and molecules are very small particles. This makes it impossible (complicates) to use the absolute values of their mass. Therefore, in chemistry, as in other natural sciences, not absolute, but relative masses values of atoms and molecules are used. Since 1961 year, it has been accepted to use the carbon unit as a unit of measurement of atomic masses, which is now called the atomic mass unit (a.m.u.).

An atomic mass unit corresponds to 1/12 of the Carbon ^{12}C isotope mass. The absolute mass of an atom of this isotope, equal to $19.93 \cdot 10^{-27}$ kg, is taken as 12 a.m.u. It follows that the absolute value of a.m.u. is equal to $1.66 \cdot 10^{-27}$ kg. Thus, the **relative atomic weight** (Ar) is the ratio of the absolute mass of an atom to 1/12 of the mass of ^{12}C atom.

In the modern periodic system of elements, the average values of relative atomic masses of elements are given, taking into account the mass fractions of their isotopes that occur in nature.

Relative molecular mass is the absolute mass ratio of a molecule to 1/12 of an atom mass of the Carbon ^{12}C isotope. Relative masses are dimensionless quantities.

In practice, molecular masses are found by adding the atomic masses of the elements that make up the molecule of a given substance, for example:

$$Mr(H_2O) = 1 \cdot 2 + 16 \cdot 1 = 18 \text{ a.m.u.}$$

Ions (from the Greek ion that mean which goes) is monoatomic or polyatomic particles that carry an electric charge. Positive ions are called cations (from the Greek kation that mean the one that goes down), negative – anions (from the Greek anion that mean the one that goes up). In the free state, they exist in the gas phase (in plasma).

Chemical reactions occur between substances, and since they are made of atoms, molecules, or ions, **chemical reactions** are interactions between individual atoms, molecules, or ions. In practice (in the laboratory and in production), reactions are carried out with macroquantities of substances (grams, kilograms, tons), each of which consists of a huge number of simple chemical particles (molecules, atoms, ions). To separate micro- and macroportions of chemical compounds in chemistry, the concept of a substance amount was introduced – a physico-chemical quantity that characterizes a macroportion of this substance, just as the number of particles characterizes a microportion of a substance (for example, two atoms of oxygen, seven molecules of ammonia). The unit of quantity of a substance in the SI system is "mole".

A **mole** is taken as a unit of substance amount is the amount of substance containing Avogadro's number ($6{,}02\cdot10^{23}$) of structural, formula units (FU). **Formula units** are real particles, such as atoms, molecules, ions, radicals. Mole allows you to count atoms, molecules, etc. in portions of $6{,}02\cdot10^{23}$ (N_A) particles. For example, 1 mole of hydrogen consists of N_A molecules of H_2 or $2N_A$ atoms of hydrogen.

A **mole** is the amount of a substance that contains the same number of formula units (structural elements, elementary objects) as there are atoms in 12 g of the Carbon C isotope. Formula units are atoms, molecules, and ions.

$$\nu = \frac{m}{M};$$
$$m = \nu M;$$
$$M = \frac{m}{\nu}.$$

The **molar mass** of a substance is the ratio of a given portion mass of a substance to the amount of the substance.

The numerical value of the molar mass (expressed in g/mol) for a monoatomic simple substance is equal to the relative atomic mass of a given element, and for any compound – to its relative molecular mass.

For example, atomic oxygen: A_r (O) = 16.00 a.m.u., M(O) = 16.00 g/mol. Sulfuric acid H_2SO_4: M_r (H_2SO_4) = 98.00 a.m.u., M(H_2SO_4) = 98.00 g/mol.

1.2. Substances and compounds

Only atoms of inert gases exist in nature in an unbound individual (simple)state. All other elements are combined into compounds due to chemical bonding forces.

A **compound** is a type of matter that has a rest mass. It consists of elementary particles: electrons, protons, neutrons, mesons, etc.

Chemistry mainly studies matter organized into atoms, molecules, ions and radicals. Such substances are classified into simple and more complex chemical compounds.

Simple substances are formed by atoms of one chemical element and therefore are the form of its in a free state, for example, sulfur, iron, ozone, diamond.

Compounds are formed by various elements and can have a constant composition (stoichiometric compounds or daltonides) or variable within certain limits (non-stoichiometric compounds or bertholides).

Simple substances should be distinguished from the concepts of atom and chemical element. Since simple substances are the form of elements in a free state, each element can correspond to several simple substances (alotropic forms), which can differ in the composition of molecules (for example, Oxygen it is molecular oxygen O_2 and ozone O_3) or in crystal lattice (for example, Carbon it is diamond, graphite, carbine, fullerene). And this leads to the fact that with the same chemical properties, allotropic forms of simple substances have different physical properties.

Compounds are chemical compounds are formed by the interaction of atoms of various elements. Therefore, they must be distinguished from mechanical mixtures. The main difference between mechanical mixtures and chemical ones is the possibility of separation of simple substances included in the composition of mixtures during magnetization, extraction, filtering, etc.

The qualitative and quantitative composition of chemical compounds is described by chemical formulas based on the valency (oxidation state) of the elements that make up the compound.

A **chemical formula** is a symbol of the composition of substances using chemical symbols and indices (numbers) indicating the number of atoms of each element.

The formula of a substance is determined according to the rule: the product of valence by the number of cations (the total number of valences) is equal to the product of valence by the number of anions that make up the molecule of the substance. For example:

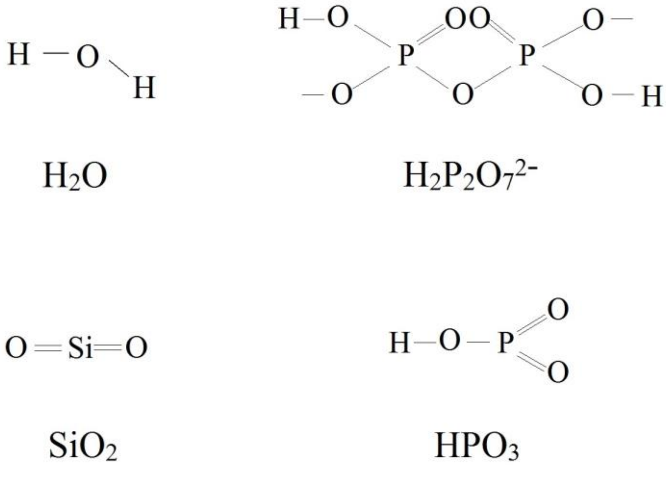
$$\overset{I}{H}\overset{I}{Cl}(1\cdot 1=1\cdot 1),$$
$$\overset{I}{K}\overset{I}{NO_3}(1\cdot 1=1\cdot 1),$$
$$\overset{I}{H_2}\overset{II}{SO_4}(1\cdot 2=2\cdot 1),$$
$$\overset{I}{K_3}\overset{III}{PO_4}(1\cdot 3=3\cdot 1),$$
$$\overset{III}{Fe}\overset{I}{(OH)_3}(3\cdot 1=1\cdot 3),$$
$$\overset{II}{Ca_3}\overset{III}{(PO_4)_2}(2\cdot 3=3\cdot 2).$$

Formulas are classified:

1. empirical formulas indicate the qualitative and quantitative composition of the compounds: H_2O, H_2SO_4, SiO_2;

2. structural formulas show the relationships of atoms in a molecule, and help determine the number of chemical bonds in molecules;

3. graphic (or valence) formulas allow you to determine the number of valence bonds in atoms with a conventional graphic representation of compounds, but do not have any important information (Fig 1.1);



H_2O $H_2P_2O_7^{2-}$

SiO_2 HPO_3

Fig. 1.1. Structural formulas of H_2O, $H_2P_2O_7^{2-}$, and graphic (or valence) formulas of SiO_2, HPO_3.

4. electronic formulas show the electronic structure of atoms and molecules: H:H, H:Be:H, (where the dots represent electrons).

Chemical reactions are the transformation of one or more starting substances (reagents) into other substances (reaction products) that differ from them in chemical composition and structure. They are spontaneously when mixing or physical contact of reagents, during heating, with the participation of catalysts, under the influence of light, etc. Chemical reactions are denote using chemical equations that take into account the laws of economy of mass and charges.

Chemical reactions are processes with the participation of the electron shells of atoms. Nuclear reactions (which are studied by physics) are processes with the participation of atomic nuclei. That is, the object of chemistry is only those processes that do not lead to a change in the atomic nucleus.

Based on the change in the number of initial and final substances, reactions are classified into the following types: combination, decomposition, substitution, and exchange.

Reactions that result in the formation of one new substance from two or more substances are called combination reactions.

Reactions that result in the formation of several new substances from one substance are called decomposition reactions.

Reactions between simple and complex substances, as a result of which atoms of a simple substance replace atoms of one element of a complex substance, are called substitution reactions.

Reactions in which molecules of two substances exchange their constituents to form molecules of two new compounds are called exchange reactions (Table 1.1).

Table 1.1.

Main types of chemical reactions

Type of reaction	**Scheme of the reaction**	**Examples**
Combination	$A + B \rightarrow AB$	$H_2 + Cl_2 \rightarrow 2HCl$
Decomposition	$AB \rightarrow A + B$	$2KClO_3 \rightarrow 2KCl + 3O_2\uparrow$
Substitution	$AX + B \rightarrow BX + A$	$Zn + 2HCl \rightarrow ZnCl_2 + H_2\uparrow$
Exchange	$AX + BY \rightarrow BX + AY$	$ZnS + 2HCl \rightarrow ZnCl_2 + H_2S\uparrow$

The vast majority of chemical reactions occur in gases or liquids (especially solutions), where chemical particles are much more mobile. Reactions in solids are very rare. These include, for example, solid-phase polymerization of monomers in a crystalline or glassy state under the influence of radioactive radiation or accelerated electrons.

The course of reactions is accompanied by the breaking of some chemical bonds and the formation of others. The thermal effect of reactions is determined by the difference in the energy of formation of new bonds and the energy lost when breaking previous ones. The thermal energy released during the formation of 1 mole of a substance from simple substances is called the heat effect.

Reactions with the release of heat are called exothermic, and reactions with heat absorption are called endothermic. Chemical reactions that show the thermal effects of reactions are called thermo-chemical reactions.

For example, exothermic reaction:

$$SO_3 + H_2O \rightarrow H_2SO_4 + Q\ (89\ \text{kJ}).$$

Endothermic reaction:

$$CaCO_3 \rightarrow CaO + CO_2 - Q\ (117\ \text{kJ}).$$

There are irreversible and reversible reactions. Irreversible ones go to the end until at least one of the starting substances is used up. As a rule, these are reactions with the release of a precipitate, the release of gas, or the formation of a low-active substance. Reversible reactions go in two mutually opposite directions. During such reactions, no one of the reactants is not completely consumed.

For example, irreversible reactions:

$$NaCl + AgNO3 \rightarrow AgCl\downarrow + NaNO_3;$$
$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2\uparrow;$$
$$2HNO_3 + Ca(OH)_2 \rightarrow Ca(NO_3)_2 + 2H_2O.$$

Reversible reactions:

$$CaSO_3 + H_2O \leftrightarrow H_2SO_3 + CaO.$$

Reactions can be shown by external influences: precipitation, change of color, or create of gas.

1.3. Main laws of chemistry

Stoichiometry is a part of chemistry that studies the mass, quantitative and volumetric relationships between reacting substances.

The basis of stoichiometry are the following stoichiometric laws:

1. law of conservation of mass or principle of mass conservation;
2. law of conservation of energy;
3. law of definite proportions (in Ukrainian tradition it called principle of permanent composition);
4. law of multiple proportions;
5. law of combining volumes (or Gay-Lussac's law);
6. Avogadro's law;
7. law of equivalents.

They are the foundation of the atomic-molecular theory, which is the basis of all chemistry.

The stoichiometric laws of chemistry were once formulated in relation to molecules, and therefore are valid only for the molecular form of a substance. For non-molecular structures, stability of composition is not a criterion for the formation of chemical compounds. Therefore, today the stoichiometric laws of chemistry are formulated taking into account the unity of molecular and non-molecular forms of matter.

The **law of conservation of mass** was formulated step by step, initially on the basis of philosophical hypotheses. It was finally discovered by Lavoisier through a series of experiments in 1773.

Today its formulation is as follows: **the mass of substances that enter into a reaction is equal to the mass of substances that are formed as a result of the reaction**.

From the point of view of atomic-molecular theory, this law is explained as follows: the mass of substances is the sum of the masses of their constituent atoms. Since the atoms themselves do not change during chemical reactions, their total number does not change; the corresponding mass remains constant.

The law of conservation of mass of substances is a special case of a more general principle of nature: matter is eternal, it does not disappear and does not arise from nothing, but only changes from one form to another. The law of conservation of mass of a substance underlies reactions between different substances. Based on it, you can make various calculations based on the equations of chemical reactions.

It should be noted that in some cases it does not seem to work. For example, when burned, many substances become lighter. This has confused chemists in the past, but in reality it is only an illusion of breaking the law. Everything becomes clear if we take into account the mass of gases formed.

Almost all chemical reactions are accompanied by a heat effect, but this is not a violation of the law of conservation, since there is a relationship between the mass of a substance and its energy, known as the Einstein equation:

$$E = mc^2,$$

where E is energy, m is mass, and c is speed of light in vacuum, which is $2.99 \cdot 10^8$ m/s.

If energy is released as a result of a reaction, then the mass of the reaction products should become less than the mass of the starting substances by an amount equivalent to the energy released. Based on the magnitude of the thermal effect of a chemical reaction, the decrease or increase in the mass of the products of any reaction is calculated. Calculations have shown that as a result of a chemical reaction, the mass of substances changes insignificantly. Currently, even the most advanced scales cannot measure such a change.

For example, the change in mass during the decomposition of 1 mole of $KClO_3$with 2537 J of heat is $2.8 \cdot 10^{-14}$ kg.

The composition of compounds, as is known, is not random. In 1808, Proust formulated the **law of constancy of composition**. After several clarifications, it looks like this: **any pure substance of molecular structure, regardless of the method of its preparation, has a stable qualitative and quantitative composition**. However, the composition of a compound without a molecular structure is not constant and depends on the conditions of preparation and pre-treatment.

For example, ammonia, directly synthesized from simple substances, obtained by the decomposition of ammonium salts, and also obtained by the action of acids on nitrides of active metals, is one and the same compound. They cannot be identified and therefore it is designated the same in all three reaction equations.

$$N_2 + 3H_2 \rightarrow 2NH_3;$$
$$(NH_4)_2CO_3 \rightarrow 2NH_3 + CO_2 + H_2O;$$
$$Na_3N + 3H_2O \rightarrow 3NaOH + NH_3.$$

Regardless of manufactured methods, the composition of the ammonia molecule is always constant and unchanged: there are three hydrogen atoms for one nitrogen atom.

Today, a number of substances of non-molecular structure are known: oxides, carbides, sulfides, nitrides, silicides and other crystalline inorganic compounds. Their composition depends on production conditions. Titanium oxide actually has a composition ranging from $TiO_{0.7}$ to $TiO_{1.3}$. It is the phase, consisting of a huge number of atoms (on the order of Avogadro’s number), that determines the properties of this compound. In an ammonia molecule consisting of only four atoms, changes in composition are excluded.

Thus, there are compounds of constant and variable composition. The former are traditionally called daltonides, and the latter are called bertolides. Compounds with constant composition is discribe by simple formulas with whole stoichiometric indices, for example H_2O, HCl, C_6H_6.Compounds with variable composition do not correspond to stoichiometric ratios and have fractional stoichiometric indicators. These include many alloys, ceramics and minerals.

Calculations of elements mass fractions in a substance are using the formula:

$$W = \frac{nA_r}{M_r},$$

where W is the mass fraction of the element (in fractions), n is the number of atoms of the element, A_r is the relative atomic mass of the element, and M_r is the relative molecular mass of the substance.

The **law of multiple proportions** complements the law of constant composition. According to it, **the masses of atoms in compounds with a molecular structure are related to each other as small integers**. For example, 1 to 2, 2 to 1 or even 2 to 7. This is clearly visible when one element forms several compounds. For example, nitrogen oxides N_2O, NO, N_2O_3, NO_2, and N_2O_5.

This is explained by the fact that each molecule really contains a certain number of atoms that are connected to each other.

Gases are relatively easy to study. In 1811, Avogadro explained the simple relationship between the volumes of gases observed in chemical reactions and established the law: **the same volume of gases under the same conditions contains the same number of molecules**. This simple law had many important consequences and gave us insight into the chemical nature of matter.

First of all, it was found that the molar volume of any gas according to this law is 22.4 liters under normal conditions (at 1 atmosphere and 273 K). Therefore, the molecular weight of any gas can be calculated from its relative density.

Relative density is the ratio of the mass of 1 liter of gas to the mass of 1 liter of another known gas (H_2, O_2, etc.). For example, if you determine the molecular weight of a gas whose density is 1.96 and use the known density of air 1.29 g/l, then the relative density of the gas is 1.96/1.29 = 1.5. Then the molecular weight of the unknown gas is 1.5 times greater than the molecular weight of air (29 g/mol).

To find the molecular masses of gases under non-standard conditions, the Mendeleev-Clapeyron equation is used:

$$PV = \frac{mRT}{M},$$

where P is pressure, V is volume, T is temperature, and R is universal gas constant.

Using this equation requires careful attention to units of measurement. If R=8.31 J/(mole·K), then the pressure should be in Pascal (Pa), the volume in m^3, the mass in grams, and the temperature in Kelvin.

Another important consequence of Avagadro's law is its number. The same volume of gas contains the same number of molecules, while in 1 mole of gas there are $2.06 \cdot 10^{23}$ of them.

The same number is contained in 1 mole of any substance, but in the case of liquids and solids they have various volumes.

It is known that compounds react with each other in certain ratios, but these equations take into account stoichiometric coefficients. If we take them into account, the equations take the form of the **law of equivalents**, which was discovered by Richter in 1792. **Substances react and are formed as a result of reactions in equivalent quantities**. That is, literally 1 equivalent of any substance reacts with 1 equivalent of another and forms 1 equivalent of the product.

An equivalent is a some amount of a substance, similar to a mole, but taking into account the stoichiometric coefficients in reactions.

The chemical equivalent of an element is the amount of it that combines with one mole of hydrogen atoms or replaces the same amount of hydrogen in compounds.

For example, in the compounds HCl, H_2O, NH_3, CH_4, per 1 mole of hydrogen atoms there are 1 mole of chlorine atoms, 1/2 mole of oxygen atoms, 1/3 mole of nitrogen atoms and 1/4 mole of carbon. .

Based on the definition, the dimension of the equivalent or amount of a substance will be equal to a mole, and the equivalent of hydrogen will be equal to 1 mole of atoms. In the compounds HCl, H_2O, NH_3, CH_4, the equivalent of chlorine, oxygen, nitrogen and carbon is 1 mol, 1/2 mol, 1/3 mol, 1/4 mol, respectively. The equivalent of an element (in moles) in a compound is easily calculated using the formula:

$$E = \frac{1}{z},$$

where E is the equivalent of the element, z is the valence of the element in the compound.

The use of equivalents may seem difficult, but they are widely used in industry, for equivalent concentrations of solutions and in some physical calculations. Using equivalents, you can avoid numerous calculations of reaction equations and stoicheometric coefficients.

The amount of a substance of one equivalent has a certain mass. Molar mass equivalent is the mass of 1 equivalent expressed in grams (g/mol).

The molar mass of the equivalent of an element in a compound, equal to the ratio of its molar mass to the oxidation state of this element in the compound, taken modulo, or to its valence:

$$M_E = \frac{M}{z},$$

where M_E is the equivalent mass of the element, M is the mass of a mole of the element, z is the valence of the element in the compound.

So equivalent masses of chlorine, oxygen, nitrogen, and carbon in tem compounds with hydrogen are:

M_E(Cl) = 35.5/1 = 35.5 g/mol;

M_E(O) = 16/2 = 8 g/mol;

M_E(N) = 14/3 = 4.66 g/mol;

M_E(C) = 12/4 = 3 g/mol.

The concept of equivalents also applies to compounds.

An equivalent of a compound is the amount of it that reacts without a residue with one equivalent of hydrogen or with one equivalent of any other substance.

In red-ox reactions, the equivalent mass of the oxidizing agent or reducing agent is determined by the number of electrons added (or lost).

In the equation of molar mass equivalent of a compound, z factor depends on its nature.

For an oxide, z is twice the number of oxygen atoms. For an acid it is equal to its basicity. It must be taken into account that the basicity of the acid is determined by the specific reaction. For example:

$$H_2SO_4 + NaOH \rightarrow NaHSO_4 + H_2O \text{ (basicity is 1);}$$
$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O \text{ (basicity is 2).}$$

For a hydroxide z is equal to its acidity. The acidity of the hydroxide is also determined by the reaction. For example:

$$Cr(OH)_3 + HCl \rightarrow Cr(OH)_2Cl + H_2O \text{ (acidity is 1).}$$

For salts, z is equal to the product of the number of cations and their ionic charge.

You can find it easier. For all inorganic compounds, z is equal to the valence of the first atom in the formula multiplied by its number (which is the index).

The molar mass of hydrogen equivalent is 1 g and under normal conditions has a volume of 11.2 liters.

The molar mass of oxygen equivalent is 8 g and under normal conditions has a volume of 5.6 liters.

Test questions

1. State the main provisions of the atomic-molecular theory.
2. Define the concepts: atom, molecule, chemical element, simple and complex substance.
3. Define the concept of equivalent, formulate the law of equivalents, define its mathematical notation.
4. What is the essence of the law of conservation of mass of matter?
5. What is the essence of the law of constancy of composition? By what criteria compound is classified as a daltonides or bertolides?
6. Formulate Avogadro’s law and its consequences.
7. Define the concept of “normal conditions” in terms of pressure and temperature values in different units of measurement.

Chapter 2. Atomic structure and electrons

2.1. Structure of the atom according to Bohr theory

Until the end of the 19th century, atoms were known as impartible particles. Over time, when new experimental data accumulated, such ideas had to be abandoned, since all the facts proved that atoms have a complex structure. For example, Rutherford, observing the passage of alpha particles through a thin metal plate, discovered that a small part of them deviates from its path towards the negative pole. Based on this experiment, Rutherford predicted that the atom contains positively charged particles.

The presence of β-rays (negatively charged particles) and γ-rays (X-rays are neutral particles that have a very high penetrating power) was also discovered.

Based on these facts, Rutherford proposed the planetary theory of the structure of atoms. According to his theory, an atom consists of a positively charged nucleus, very small in size. Almost all the atom mass is concentrated in the nucleus. Electrons that form the electron shell of an atom move around the nucleus. Because the atom as a whole is electroneutral, the total electrons charge must be equal to the charge of nucleus.

However, Rutherford's theory had certain weaknesses. Firstly, he used the laws of the macrocosm for his theory, which could not reflect the true structure of the atom. In addition, Rutherford believed that an electron, moving in an orbit, emits energy. But if this were so, then after some time the electron would have to fall onto the nucleus of the atom, but this does not happen.

Therefore, taking all this into account, Bohr used the laws of quantum mechanics and proposed his theory, the main provisions of which he formulated in the form of postulates:

1. An electron can rotate around the nucleus not in any, but only in certain allowed stationary orbits.
2. Moving along stationary orbits, an electron does not emit energy.
3. Energy radiation is only when an electron moves from an orbit further away from the nucleus to an orbit closer to the nucleus. At the same time, a quantum of light is emitted, which is equal to the difference in the energy of the atom in the initial and final state.

An atom is the smallest part of a chemical element that retains its properties. All substances construct from atoms, but an atom is not the smallest part of matter, but construct of a large number of smaller particles, called elementary particles, which have various nature and properties.

Protons, neutrons, electrons, and positrons are the most important of the several hundred known elementary particles that determine the properties of an element. **Protons** (p)are particles that have a mass equal to 1 (1 carbon unit) and an elementary positive charge of $4.8 \cdot 10^{-10}$ electrostatic units. **Neutrons** (n) are particles that do not have a charge, but have a mass equal to 1 a.u. **Electrons** (ē)are particles that have a negative electric charge equal to the charge of a proton and a mass equal to 1/1840 of the mass of a proton ($9.1 \cdot 10^{-28}$ g). **Positrons** (e+) are particles that have a positive charge equal to the charge of an electron and the same mass.

Table 2.1

Relative mass and charge of elementary particles

Elementary particle	Charge	Mass, c.u.
Neutron (n)	none	1
Protons (p)	+1	1
Electrons (ē)	–1	1/1840
Positrons (e^+)	+1	1/1840

ThepositivechargeofthenucleusisdeterminedbythenumberofprotonsinthenucleusandisequaltotheserialnumberoftheelementinthePeriodictable.

Takingintoaccountthequantitativecharacteristicsofprotonsandneutrons, they are written using symbols:

$$_1p^1{}_0n^1.$$

The upper index denotes the mass of the particle, the lower index the charge.

Since atoms are electron-neutral particles, they have the same number of negatively charged electrons as protons. Electrons continuously turning around the nucleus in orbits located at energy levels and sublevels. Elements differ from each other in the number of elementary particles that make up an atom. Electrons form the so-called electron shell of an atom. Thus, the simplest element hydrogen can be represented as an element with a positively charged nucleus (+1), around which one electron (-1) rotates (Fig. 2.1).

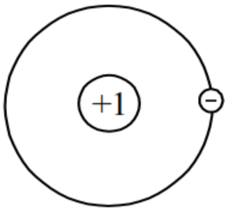


Fig. 2.1. Nuclear model of the hydrogen atomstructure

Electrons are held in an atom at a certain distance from the nucleus due to the action of two forces: the force of electrostatic attraction of the nucleus, which holds them in a positive electric field, and the centrifugal force resulting from the rotation of the electron around the nucleus at enormous speed. The balance of these two forces prevents an electron to fall onto the nucleus or break away from the atom.

Constantly moving, electrons fill a certain part of the space around the nucleus, forming the electron shell of the atom, consisting of energy levels and sublevels.

The maximum number of electrons that can be present at an energy level is determined by the formula:

$$N = 2n^2 ,$$

where n is the ordinal number of the energy level.

The movement of elementary particles with very low mass and speed close to the speed of light does not obey the laws of classical Newtonian mechanics. To characterize the behavior of microparticles, Planck's quantum mechanics was used, based on the idea of discrete motion and energy emission, occurring not continuously, but in portions, the so-called energy quantum. The energy of each portion of such radiation depends on the oscillation frequency according to the formula:

$$E = h\nu$$

where h is Planck’s constant, equal to $6.626 \cdot 10^{-34}$ J·s, ν is the oscillation frequency depending on the radiation wavelength λ (λ=1/ ν).

Bohr, using the basic principles of quantum mechanics, calculated the possible orbits of electron motion in the hydrogen atom. According to his calculations, the possible radii of motion of electrons in a hydrogen atom are expressed as squares of integers:

$$1^2 : 2^2 : 3^2 : \ldots : n^2.$$

These radii correspond to the so-called energy levels that determine the energy of the electron. The further the energy level is from the nucleus, the higher its energy. An electron moving in the first level has the lowest energy; As the ordinal number of the level increases, the electron energy increases.

When rotating at the level closest to the nucleus, the electron does not emit energy and the atom is in the so-called **normal (non-excited) state**.

Electrons can move to a higher energy level when receiving energy from the outside in an amount corresponding to the difference in energy levels. For example, for a transition from level 1 to level 2, the energy difference is:

$$\Delta E = E_1 - E_1$$

An atom in which an electron has moved to a higher energy level is in the so-called excited state. When the electron returns to the previous level, its energy is emitted and the atom returns to its normal (unexcited) state.According to these ideas, the electron shell of an atom is filled with electrons gradually, starting from the first level.

2.2. Quantum numbers of the atomic electronic state

A study of the properties of an electron showed that it simultaneously has the properties of a corpuscle (particle) with a certain mass and at the same time has the properties of a wave, as evidenced by the phenomenon of electron beam diffraction. Such properties lead to the fact that the electron, rotating around the nucleus at high speed, fills a certain space, forming an electron cloud. These electron clouds are different for electrons located in different sublevels and are called orbitals. Each electron is characterized by quantum numbers that are used to describe it.

Being at different distances from the nucleus, electrons form layers of electrons, which are called energy levels. The energy level number is determined by the **principal quantum number** *n* and takes integer values from 1.

The principal quantum number *n* characterizes the energy level, that is, the energy value of the level, and can have the value of a number of integers from 1 to n. Accordingly, energy levels are designated by capital letters of the Latin alphabet, starting with *K* (*K*, $n = 1$; *L*, $n = 2$; *M*, $n = 3$, etc.).

The principal quantum number is equal to the number of the period in which the element is located and characterizes:

1. the energy reserve of the electron at this energy level (for example, if $n = 3$, then the electron is on the third energy level and its energy reserve is greater than that of electrons at the first and second levels, but less than at the fourth);
2. the distance of an electron from the nucleus of an atom (atomic radius).

However, quantum mechanical calculations show that within one level the energy of electrons differs slightly from each other, and each energy level is further split into energy sublevels.

The number of sublevels corresponds to the level number. So, at the first level there is only one sublevel (s), at the second level there are two sublevels (s, p), at the third there are three sublevels (s, p, d), at the fourth there are four (s, p, d, g).

The second quantum number is the **azimuthal (secondary, orbital) quantum number** *l*. At the energy level, electrons can rotate in either circular or elliptical orbits. In this case, their energy reserves will be different. Therefore, within a level there are energy sublevels. The orbital quantum number indicates the possible number from 0 to $(n – 1)$.

Accordingly, sublevels are designated by lowercase letters of the Latin alphabet, starting with s (s, p, d, f). At the energy level *K* ($n = 1$), the orbital number has the value $l = n – 1 = 0$, that is, only one value and therefore there will be only one sublevel at the first energy level.

At the second level $n = 2$, which means the side quantum number can take on two possible values: for $l = 0$ it is sublevel s, and for $l = 1$ it is sublevel p

The energy sublevel is characterized by the orbital quantum number l. For each level n, the orbital quantum number can take values from 0 to $n – 1$. For example, for $n = 3$ its value is 0, 1 or 2.

The orbital quantum number characterizes:

1. Energy reserve of an electron at a sublevel;

2. Form of electron orbital motion:

An atomic orbital having a spherical symmetry shape is called an s-orbital, and the electrons in it are called s-electrons.

Atomic orbitals having the shape of an irregular figure eight are called p-orbitals, electrons located on it are called p-electrons.

The four-leaf clover-shaped atomic orbitals are called d-orbitals, and the electrons in it are called d-electrons.

The f-orbitals, which contain f electrons, have a more complex shape.

Magnetic quantum number (m_l) characterizes the number of orbitals contained in a sublevel:

The magnetic quantum number can take values from $-l$ to 0 and up to $+l$.

For example, at the first energy level (n=1), $l = n - 1$=0, m_l can only take one value, which is 0, so there can only be one s-orbital at this sublevel.

If $n = 2$ (second energy level), l is 0 and 1 (two sublevels), so m_l can take three values: 0 for the first s-sublevel with one s orbital, and for the second sublevel it is –1, 0 and +1, that are three p orbitals.

If $n = 3$ (third energy level), l is 0, 1 and 2, so m_l can take three values: 0 for the first s-sublevel with one s orbital, –1, 0 and +1 for the secondp-sublevel with three p orbital, and –2, –1, 0, +1, +2 for the third d-sublevel with five d orbitals.

The **spin quantum number** (m_s) characterizes the direction of rotation of the electron around its axis and can take values –1/2 and +1/2.Two electrons in the same orbital can only have antiparallel (opposite spins, that is, directions of rotation, indicated by opposite arrows ↑↓) because electrons with parallel spins repel each other.

The electron spin s shows that the electron can also rotate around its axis. There are only two such possible directions of rotation: clockwise and counterclockwise, so quantum mechanics gives two values for the electron spin: +1/2 and –1/2.The rotation of an electron around its own axis is similar to the movement of electric current in a closed circuit and causes the appearance of a magnetic field, the lines of force of which are directed in space according to the screw rule.

The magnetic field lines of two electrons with antiparallel spin are directed in opposite directions and can close. Therefore, such electrons can exist in the same orbital. The third electron cannot exist in the same orbital because it would be repelled by one of the electrons of the pair.

Therefore, the spin of an electron shows that there cannot be more than two electrons in one orbital. If this is a pair of electrons rotating around their own axis in opposite directions (electrons with antiparallel spin), then a stable electronic configuration is formed.

2.3. Multi-electron atoms

The located of electrons in the orbitals of an atom is determined by several rules, including the Pauli principle, Hund's rule, and Klechkovsky's rules. These rules are used to compile electronic formulas that describe the electron shells of atoms according to the modern theory of their structure.

According to the **Pauli principle, there cannot be two electrons in an atom with the same values of all four quantum numbers**.

According to this principle, the maximum number of electrons in an orbital, sublevel, or level can be calculated. So, in the s-orbital there cannot be more than 2 electrons, in the p-orbital – no more than 6, in the d-orbital – no more than 10. Therefore, the maximum number of electrons that can be in the first energy level is 2, in the second energy level – 8, at the third – 18, etc.

Klechkovsky's rules (called also Aufbau principle) determine the order in which the orbitals are filled.

The first rule: with increasing nuclear charge, electrons fill the orbitals in the order of increasing the sum of the principal and azimuthal quantum numbers, that is, $n + l$.

The second rule: if this sum is equal, then the sublevels of orbitals with the smaller principal quantum number n are filled first.

In multi-electron atoms, energy levels and sublevels are filled with electrons depending on their energy in the following sequence:

$$1s \rightarrow 2s \rightarrow 2p \rightarrow 3s \rightarrow 3p \rightarrow 4s \rightarrow 3d \rightarrow 4p \rightarrow 5s \rightarrow 4d \rightarrow 5p...$$

Hund's rule is about filling equivalent orbitals with electrons.

When composing electronic formulas for atoms of elements, we must remember that the number of electrons is equal to the positive charge of the nucleus, that is, the atomic number of the element. Denoting energy levels with numbers corresponding to the main quantum number, sublevels with letters of the Latin alphabet (s, p, d, f), and the number of electrons at a sublevel in the form of an exponent above the sublevel, we obtain the electronic formula of the atom.

For example, element No. 1 hydrogen H has one proton in the nucleus (nuclear charge +1), respectively, one electron rotates around the nucleus at the s-sublevel of the first level. Thus, the electronic formula of element No.1 (H) is $1s^1$.

The next element, helium, has a nuclear charge of +2, therefore two electrons revolve around it. Therefore its electronic formula (He) is $1s^2$.
This is the maximum number of electrons that can be in the first level and its only s-sublevel. Therefore, the first row of the Periodic Table consists of only two elements.

With a further increase in the order number of an element, that is, its nuclear charge and the number of electrons, these electrons are forced to occupy sublevels of the next energy level. Thus, element No. 3 lithium has one electron in the second level, and element No. 4 beryllium has two electrons. After the 2s sublevel is completely filled, 2p electrons appear.

The electronic formula of element No.3 (Li) is $1s^2 2s^1$;

for element No.4 (Be) it is $1s^2 2s^2$;

for element No.5 (B) it is $1s^2 2s^2 2p^1$;

for element No.6 (C) it is is $1s^2 2s^2 2p^2$;

and so on until element number No.10 (Ne) wit formula $1s^2 2s^2 2p^6$, wich is last in this row.

Elements of the third period will have electrons already at the third energy level. For example, element No.11 Na has electronic formula $1s^2 2s^2 2p^6 3s^1$.

Thus, each chemical element has its own unique serial number of the Periodic Table, which is equal to the number of electrons and precisely determines the location of these electrons by energy levels. There are no vacancies in the Periodic Table, at least up to element number 110. At the same time, atoms of chemical elements with such high atomic numbers are unstable and decay by nuclear processes.

Today, all chemical elements are known, except for unstable ones. And for all (even those not found), their electronic structure is known, and therefore certain chemical properties.

The most important information that can be learned from the electronic structure is the number of electrons that can participate in the formed chemical bonds. First of all, these are unpaired electrons, which are called valence.

There is another form of writing electronic formulas in the form of energy cells, which is good for understanding the possible chemical properties of elements. An energy cell is schematically designated by a cell. For a cell, we have three quantum numbers n, l and ml, which are the coordinates of a specific orbit in which the electron rotates in the atom. The electrons in these cells are shown by the arrows pointing up ↑ and down ↓. These arrows show the direction of the magnetic field lines (spin) of the electrons, and their number corresponds to the number of electrons in the orbit.

So, for the s sublevel this is the bottom cell, which can be occupied by up to two electrons, which corresponds to the formula s^2. And for sublevels p and d, the number of cells is 3 and 5, respectively (Fig 2.2).

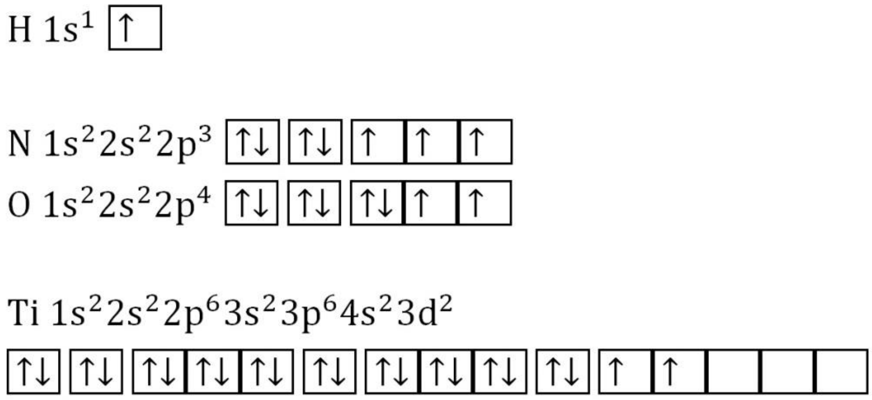


Fig. 2.2. Electronic graphic formulas of hydrogen, nitrogen, oxygen and

The filling of these sublevels with electrons is carried out in accordance with Hund's rule: **when energy cells within a sublevel are filled with electrons, the electrons are located so that their total spin is maximum**. Therefore, we first designate the arrows pointing up (that is, spin +1/2), and only then pointing down.

The number of unpaired electrons that an atom has or may have corresponds to its valence. Variable valency is characteristic of atoms with incompletely filled energy levels, which is why electron pairs can be destroyed when energy is supplied from the outside.

Atoms of elements, entering into a chemical interaction, depending on the structure of the external energy level, lose electrons (usually metals) or gain them (non-metals).The ability of an atom of an element to give up electrons is characteristic of metals, and the ability to acquire electrons is characteristic of non-metals. Ionization energy is used to compare metallic properties of an element, and electron affinity or relative electronegativity is used to compare nonmetallic properties.

To compile electronic formulas, information from the periodic table is used. For example, the electronic formula of sulfur is characterized by the distribution of electrons over three energy levels (third period) and the presence of six electrons at the outer level (sixth group). Its electronic form:

$$_{16}S\ 1s^2 2s^2 2p^6 3s^2 3p^4.$$

Graphic representation of the external energy level is possible in several ways (Fig. 2.3.).

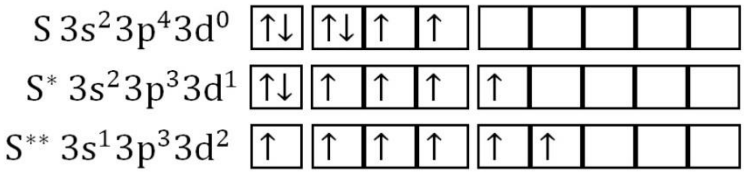


Fig. 2.3. Electronic graphic formulas of sulfur in normal and excited states

The valence of sulfur is equal to the number of unpaired electrons. When receiving energy from the outside, some electrons can move to higher sublevels, which will lead to a change in the number of unpaired electrons, that is, a change in valence. As we can see, sulfur can have a valency of 2 (normal state), 4 or 6 (excited states).

The oxidation state of sulfur in compounds, that is, the hypothetical charge of an atom if all its bonds with other atoms were completely polarized, can take the following values: –2, 0, +2, +4, +6. For example, in the compounds H_2S, S, SO (unstable compound), SO_2 and H_2SO_3, SO_3 and H_2SO_4.

Test questions

1. What is the essence of Bohr's postulates?
2. Which state of the atom is called normal and which is called excited?
3. What are quantum numbers? How many quantum numbers describe an electron? Name each of them.
4. Define the principal quantum number. What are its values for an atom in normal and excited states?

5. Define azimuthal quantum number. How are its possible values related to the principal quantum number?

6. Define magnetic quantum number. How are its values related to the azimuthal quantum number?

7. Define spin quantum number. What values of this number are possible for the electron of an atom?

Chapter 3. Periodic trends and periodic table of the elements

3.1. Periodic law

In the past, some elements were known to have similar properties. For example, sodium and potassium, calcium and magnesium, or chlorine, bromine and iodine. However, it was not clear why this was the case. The classification of elements was of great interest. In 1869, Mendeleev solved this problem with the discovery of the periodic law.

There are several formulations of the periodic law.

The first was Mendeleev's formulation, based on the atomic mass of chemical elements. According to it, the properties of substances (chemical elements) change periodically as atomic masses increase.

However, according to this formulation, atoms with the same atomic mass should have the same properties, but this is not the case. In addition, there is a violation of the order of chemical elements in the periodic table (Ar and K, Th and Pa, Te and I, Co and Ni).Moreover, this formulation cannot explain the existence of isotopes at all. However, thanks to this formulation, Mendeleev was able to predict elements unknown at the time.

The modern formulation (nuclear) is that chemical properties change periodically as the charge of the atomic nucleus increases. Thus, the shortcomings of the old formulation were corrected. There are no contradictions in it: the increase in the charge of the nucleus is continuous, and the change in chemical properties is periodic. According to this formulation, the order of arrangement corresponds to the charge of the nucleus: first Ar 18 and then K 19, first Co 27 and then Ni 28.

The flaw of this formulation is that the nucleus of an atom does not directly affect chemical properties.

The third and most accurate formulation is electronic. The chemical properties of elements are determined by their electronic structure. It is electrons that take part in chemical processes.

Thus, periodic changes with increasing atomic number are explained by changes in the electronic structure. The number and place of a chemical element in the periodic table corresponds to the chemical properties of the element.

A chemical element is a type of atom with the same electronic structure that determines its chemical properties. The electronic structure is naturally determined by the charge of the nucleus, that is, the number of protons that make up the nucleus. In addition to protons, there are also neutrons in the nucleus.

The mass of a proton and a neutron (nucleons) in chemistry is taken as a unit – 1 a.u.m. Protons have a charge of +1, neutrons are electrically neutral. As for electrons, the mass of each of them is very small, so in chemistry the mass of an electron is neglected.

Atomic mass is the sum of protons and neutrons in the nucleus:

$$A = Z + N,$$

where Z is the sum of protons, and N is the sum of neutrons.

The mass of an atom is determined by the mass of the nucleus and is an integer. But despite the fact that the mass of individual atoms is a whole number, the atomic masses of chemical elements are mostly fractional numbers.

The periodic table does not indicate the masses of individual atoms, but rather the masses of atoms of chemical elements. The term "chemical element" includes several atoms with the same electronic structure, and then the atomic mass of a chemical element is the average mass of all atoms.

For example, the chemical element chlorine Cl. In nature, it occurs in two forms: chlorine atoms with a mass of 35 ($_{17}Cl^{35}$) make up 75% of all chlorine, and with a mass of 37 ($_{17}Cl^{37}$) – 25%.Both types of atoms belong to the same chemical element and therefore have the same properties.

On average, among 100 natural chlorine atoms, 75 atoms will be Cl 35 and 25 will be Cl 37 atoms. Their average mass, taking into account the distribution, is 35.50. However, there are no chlorine atoms with a mass of 35.5 Cl.

Thus, as we see, the chemical properties of elements are determined by the electronic structure, which depends on the number of electrons, which is equal to the number of protons. These quantities correlate with the mass of the atom, but are not equal to it.

Special terms are used to designate atoms that have certain similar properties.

Isotopes are atoms that contain the same number of protons but different numbers of neutrons.

Isobars are atoms containing different numbers of protons and neutrons, but the same mass number.

Isotones are atoms that contain the same number of neutrons but different numbers of protons.

3.2. Electronic formulas of atoms of chemical elements

Analysis of the electronic structures of atoms made it possible to find the same periodic dependencies that Mendeleev found when studying the chemical properties of elements:

1. one period includes elements whose atoms have the same number of energy levels, but a different number of electrons at the external energy level, and therefore their properties change over the period from active metals (group IA is alkali metals) to non-metals (each period ends with inert gases);
2. the number of elements in each period is determined by the maximum possible number of electrons at the energy level, which is filled with atoms of the elements of this period;
3. the number of electrons in the outer energy level of atoms of elements of the main subgroups (except He) is equal to the number of the group in which the element is located;
4. one subgroup includes elements whose atoms have the same structure of external energy levels and, accordingly, similar chemical properties.

The electron shells of inert gases have completely filled outer levels and sublevels, that is, each cell contains two electrons. This is a very stable electronic structure, and it is almost impossible to destroy it. That is why atoms of inert gases do not form valence bonds and do not form compounds similar to other elements of the periodic table.

All chemical elements of the periodic table are divided into four categories:

s-elements are elements of the first and second main subgroups.

p-elements are elements of the main subgroups from IIIA to VIIA.

d-elements are elements of side subgroups. There are ten such subgroups. The first side subgroup is the Sc subgroup.

f-elements are lanthanides and actinides. There are 14 subgroups.

The abbreviated electronic formulas of s-elements are designated as ns^1 (IA), ns^2 (IIA). p-elements are designated np^{1-6} (IIIA-VIIIA).The abbreviated electronic formula for side group elements is $(n-1)d^{1-10}$. The abbreviated electronic formula for lanthanides and actinides is $(n-2)f^{1-14}$. For example:

$_{23}V 1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$;

$_{29}$Cu $1s^22s^22p^63s^23p^63d^{10}4s^1$;

$_{74}$W $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4f^{14}5s^25p^65d^45f^06s^2$.

In last case n = 6, n – 2 = 4 ($4f^{14}$) , n – 1 = 5 ($5d^4$).

For all lanthanides, the last part of the formula is $5s^25p^65d^1$.

$_{103}$Lr ...$5s^25p^65d^{10}5f^{14}6s^26p^66d^17s^2$.

In this case n=7, n – 2 = 5 ($5f^{14}$), n – 1 =6 ($6d^1$).

For a number of chemical elements, the theoretical electronic formula does not correspond to the practical one. This applies primarily to d-elements and f-elements and is explained by the stable electronic configurations. More stable are fully and half filled sublevels, for example d^0, d^5, d^{10} or f^0, f^7, f^{14}.

Therefore, in some elements, electrons skip certain sublevels. For example:

$_{24}$Cr $1s^22s^22p^63s^23p^63d^44s^2$.

In the case of gold, the theoretical formula of $_{79}$Au is $5d^96s^2$, but the real formula is $5d^{10}6s^1$.

This phenomenon does not have a complete explanation and has not been fully studied. There are known cases when the movement of electrons in some atoms has no explanation. For example, lanthanum should theoretically be with its own group of elements, that is, together with the lanthanides. That is, the same with actinium. However, in reality this is not the case.

Thus, we must clearly understand that the distribution of electrons according to quantum numbers is only a model.

3.3. Changing the size of atoms in the periodic table

Angstrom units are used to indicate the size of an atom.

$$1\text{Å} = 10^{-8}\text{cm} = 10^{\,-10}\text{m}.$$

Another widely used unit of measurement of atomic size is called the nanometer.

$$1\text{nm} = 10^{-9}\text{m} = 0.1\text{Å}.$$

For example: an iron atom has a size (atomic radius) of 1.24 Å, lithium 1.52 Å, cesium 2.655 Å.

If an atom transforms into an ion, its size will increase or decrease. If an atom gives up electrons, that is, turns into a cation, its size will decrease. If it accepts electrons and becomes an anion, then vice versa.

For example, anion O^{-2} has ionic radius 1.4 Å, but atom of oxygen has atomic radius 0.6 Å.

In the period from the first element to the subsequent ones, the size of the atom decreases as the charge of the nucleus increases. In the second and third periods, a decrease in atomic sizes is observed in all 8 elements. In periods IV and V, a decrease in atomic radius is observed in 18 elements, and in period VI – in 32 elements. There are 14 lanthanides included in this period. They also have a reduction in the size of the atoms and this phenomenon is called lanthanide contraction. For lanthanides and actinides, this compression is called f-compression (4f, 5f).

The compression of lanthanides greatly affects the size of the atoms of the following chemical elements. For example, the size of Hf is much smaller than expected. Therefore, the noble metals as Au and Pt, which come after the lanthanides, are chemically passive due to the small size of the atoms.

The size of the atoms also varies depending on the subgroup. In the main subgroups, the size of atoms increases due to an increase in the number of energy levels. The size of the atom should decrease due to the increase in nuclear charge ($_3Li$, $_{87}Fr$). But with an increase in the number of energy levels, the effect of shielding of the nucleus occurs, which leads to an increase in its size.

In side subgroups, the size of the atom increases when moving from the first to the second element Ti, Zr, Hf, and when moving from the second to the third, the size of the atoms does not change, because this is compensated by lanthanoid compression. Thus Hf is more passive than Zr because hafnium has a higher charge and is the same size as zirconium.

3.4. Energy characteristics of chemical elements

Quantitative characteristics of the activity of chemical elements are the following energy characteristics: ionization energy, electron affinity energy, electronegativity, which are calculated per mole of atoms in energy units (eV, electronvolts).

Ionization energy (E_i) is the energy required to remove an electron from a neutral atom.

For example, for element of the II period:

$$Li^0 - 1e \rightarrow Li^+ - E_i\,(Li);\ E_i\,(Li) = 5.39\ eV$$
$$F^0 - 1e \rightarrow F^+ - E_i\,(F);\ E_i\,(F) = 17.42\ eV$$

For lithium, this process is real in chemical reactions, since Li has an oxidation state of +1. But for fluorine it is not real, since F in compounds is never positive. Although this process is not natural for chemical reactions, it can be caused physically (in ionization tubes).

The ionization energy of metals is lower than the ionization energy of non-metals, since metals are those elements that easily give up electrons, and non-metals are those elements that attach them. The activity of a metal can be characterized by its ionization energy: the lower the ionization energy, the more active the metal.

As for non-metals, their activity is measured by the **electron affinity energy** (E_{af}) which shows how much energy is released as a result of the addition of one electron to a neutral atom.

$$Li^0 + 1e \rightarrow Li^- + E_{af}\,(Li)$$
$$F^0 + 1e \rightarrow F^- + E_{af}\,(F)$$

The process of reducing Li to an atom is not a natural process. This practically never happens, so E_{af} (Li) ≈ 0.

Fluorine attaches electrons very energetically and has a high electron affinity.

The activity of nonmetals can be characterized by the value of affinity: the greater the affinity, the stronger the properties of the nonmetal will be and the stronger the oxidizing agent will be. Thus, the activity of metals is determined by ionization energy, and the activity of nonmetals by electron affinity energy. But along with metals and non-metals, there are intermediate chemical elements to which both ionization energy and affinity energy can be applied. The general energy characteristic in this case is the one that combines the ionization energy and the electron affinity energy and is called electronegativity (χ).

Electronegativity is a characteristic of all chemical elements; it is the sum of the absolute values of ionization energy and electron affinity energy.

$$\chi = E_i + E_{af};$$

$$\chi(\text{Li}) = E_i(\text{Li}) + E_{af}(\text{Li}) = 5.39 \text{ eV}.$$

Electronegativity of metals, as a rule, is much smaller than that of non-metals. It includes the values, which shows how easily or hard an atom gives up an electron and which shows how energetically an atom attaches electrons.

For convenience, the electronegativity of lithium is taken to be 1. If we take F, then it has the highest electronegativity of all the elements, equal to 4.

Metals more reactive than Li have electronegativity below 1. For example, in $\chi(\text{Cs}) = 0.7$.

Atomic size is related to electronegativity and is the inverse of electronegativity. For example, F has the highest electronegativity and smallest atomic radius, and Cs has the largest atomic radius and smallest electronegativity.

The electronegativity of period II elements varies linearly from Li to F (Table 3.1).

Table 3.1

Relative electronegativity of elements of period II

	Li	Be	B	C	N	O	F
χ	1.0	1.5	2.0	2.5	3.0	3.5	4.0

The concepts of ionization energy, electron affinity and electronegativity do not apply to helium, argon and neon.

It should be noted that ionization energy and electron affinity should not be confused as the same values for inverse processes.

1. $\text{Li}^0 - 1\text{e} \rightarrow \text{Li}^+ - E_i\,(\text{Li})$;
2. $\text{Li}^+ + 1\text{e} \rightarrow \text{Li}^0 + E_i\,(\text{Li})$;
3. $\text{Li}^0 + 1\text{e} \rightarrow \text{Li}^- + E_{af}\,(\text{Li})$.

Process 1 and process 2 are inverse to each other and for them the energies will indeed be the same, but with the opposite sign. In terms of electron affinity, in the case of process 3, an electron is added to an atom rather than an ion.

The electronegativity of hydrogen is 2.2.

3.4. Oxidation state

Oxidation state is a fundamental quantity in inorganic chemistry.

The oxidation number is the hypothetical charge that would appear on an atom of a chemical compound if the pairs of electrons that share it with other atoms were completely shifted towards more electronegative atoms.

The oxidation state of atoms in molecules that consist of identical atoms is always equal to 0. However, if there are different atoms in the molecule, the more electronegative one accepts electrons and receives a negative oxidation state. An atom with less electronegativity donates electrons and receives a positive oxidation state. Moreover, both values are equal in modulus.

In fact, the real charges of atoms are much smaller, but in chemistry this is inconvenient to use, because in many cases the real charges are not integers, but fractions. Therefore, in the case of Fe_2O_3, for example, it is customary to mentally subtract 3 electrons from the Fe atom and make it +3. In the case of oxygen, we add electrons to –2.

To determine the oxidation state, you must first find the sign of the oxidation state. This is possible using the electronegativity value.

$$H^{+0.18}Cl^{-0.18} \rightarrow H^{+} + Cl^{-}.$$

Based on the number of the most typical oxidation states (that is, those in which the element forms stable compounds), elements can be divided into two groups:

1. elements that have mainly one stable oxidation state, that is, only +1, only +2 or only +3;
2. elements that have several oxidation states, for example for nitrogen it is –3, –2, –1, 0 +1, +2, +3, +4, +5.

In this classification, for those elements that can have several oxidation states, it is customary to distinguish certain categories: higher, lower positive, lower negative, intermediate.

The highest oxidation state has the largest positive value, which is always equal to the group number of the periodic system, and is an important quantitative characteristic of this element in its compounds. The highest degree of oxidation in compounds, as a rule, occurs in the most excited state of the atom.

Metals and nonmetals have lower positive oxidation states in their compounds with more electronegative elements due to the minimum number of unpaired electrons they have in their outer shell in their normal (unexcited) state.

Nonmetals have lower negative oxidation states in their compounds with less electronegative elements (usually metals and hydrogen) due to the minimal number of electrons they have in their outer shell in normal state.

Their valency is usually equal to:

$$Z = N - 8,$$

where N is the group number in the periodic table.

Some elements have **intermediate oxidation states** due to a certain number of unpaired electrons (between minimum and maximum) in intermediate excited states.

All elements (metals and non-metals) in any positive oxidation state have a corresponding oxygen compound (oxides and hydroxides). Non-metallic elements also correspond to the corresponding hydrogen compounds (hydrides). Their structure and properties are predetermined by the chemical composition of the compound.

There are certain patterns of changes in the degree of oxidation of elements over periods. In each of them, from left to right, there is an increase in the maximum possible positive values from +1 to +8. Among non-metals there is also a reduction in the maximum possible negative values from –4 to –1. Moreover, the sum of the absolute values of the lowest negative and highest positive oxidation states of elements of one group is always equal to eight.

The oxidation state of some atoms in some compounds is difficult to determine clearly. For example, the oxidation state of the Ferrum in Fe_3O_4. Based on the fact that the oxidation state of oxygen is -2, we can assume that the oxidation state of all Fe atoms together is +8, therefore the oxidation state of each of them is +8/3. Indeed, in some cases the oxidation state may be a fractional number. However, it can also be said that in the Fe_3O_4 molecule there are two Fe +3 atoms and one Fe +2 atom. This is also a correct description.

In the compound hydrogen peroxide (H_2O_2), each oxygen atom is bonded to one hydrogen atom and another oxygen atom (H–O–O–H). The bond between oxygen, as identical atoms, does not affect the oxidation state. Therefore, the oxidation state of oxygen in such a compound is –1, which is very unusual. The same is observed for many organic compounds where there are bonds between carbon atoms.

Oxidation states are a unique quantitative characteristic of an element, and changes in oxidation states of elements in groups of the periodic table reflect the periodicity of changes in the chemical properties of elements and their compounds with increasing atomic numbers. The magnitude of the oxidation states of elements makes it possible to predict the most important chemical properties of both simple substances of this element and a whole group of elements - electronic analogues, namely:

- acid-base properties of oxides and hydroxides;
- re-dox properties of elements and their compounds;
- properties of hydrides (oxygen-free acids).

In addition to the concept of oxidation state, another classical concept called valency is widely used in chemistry.

The **valency** of an atom in a molecule is the number of electron pairs with which the atom is connected to other atoms. The number of electron pairs (bonds) that an atom can form is equal to the number of its unpaired electrons at the outer (valence) energy level. The polarity of the chemical bonds formed is not taken into account, so the valency has no sign.

For example, in the nitrogen compound N_2, the valence is 3 and the oxidation state is 0, since both atoms have the same electronegativity. However, in ammonia NH_3, where nitrogen also has 3 common electron pairs, the valence is 3, and the oxidation state of nitrogen is –3.

The fact is that oxidation state and valence are completely different concepts, although they are often numerically equal.

Valence is determined by the number of atomic orbitals involved in a chemical bond. Each nitrogen atom has three valence orbitals p_x, p_y, p_z, so the nitrogen atom in a nitrogen molecule has a valence of three. The number of oxidation state always has a sign, but the valence never has it. Numerically, the oxidation state is determined mainly by electronic formulas.

Valences are used to describe atoms in compounds: divalent atom, trivalent, etc. In the event that one atom can have different valence, and therefore form several compounds, they are written with the indication of its valence in Roman numerals. For example, FeO called Ferrum oxide (II), and Fe_2O_3 Ferrum oxide (III).

Test questions

1. Describe the structure of the periodic table of elements. What is a period, group, and subgroup.

2. What is the essence of the period of the periodic table? Why do periods have different numbers of elements? Which periods are smaller and which are larger than others? In what period are the lanthanides found?

3. How and why do the properties of elements and their compounds change with increasing atomic number? Show this using the example of the second and fourth periods.

4. How do the properties of elements and their compounds change within side subgroups?

5. Define the concept of oxidation state. In what cases is its value is zero?

6. Define the concept of valence. What is the difference between valence and oxidation state?

7. What is electronegativity? How does the electronegativity of atoms of elements change within a period or subgroup?

Chapter 4. Molecular structure and types of chemical bonds

4.1. Types of chemical bond and its characteristics

Chemical elements are found in nature mainly in the form of simple or complex substances, the atoms of which are connected by chemical bonds. Only inert gases (helium, neon, argon, krypton and xenon), some metals (Cu, Ag, Au) and non-metals (C, S) exist in nature in a free state. Inert gases have a complete external energy level, which is characterized by great stability. The so-called noble metals have a small atomic radius and a relatively large positive charge of the nucleus, and therefore they strongly retain electrons and their chemical activity is limited. Under normal conditions, carbon and sulfur are not very active elements and therefore they are found in nature in a free state.

The outer levels of atoms of other elements (I-VII groups) are incomplete and unstable. In the process of chemical interaction, they are rearranged and completed due to the fact that unpaired electrons of different atoms form electron pairs that are shared by two or more atoms or are shifted to one of the atoms. Thus, with the help of a chemical bond, the formation of molecules occurs.

A chemical bond is the interaction of two or more atoms, resulting in the formation of a chemically stable compound (molecule or crystal).

When a chemical bond is formed between atoms, the energy of the system decreases compared to the sum of the energies of the isolated atoms from which it is formed. This is a condition for the formation of a chemical bond. That is, the formation of molecules from atoms is accompanied by a gain of energy, since under normal conditions the molecular state is more stable than the atomic state. The main characteristics of a chemical bond are its energy, length (internuclear distances), angle between bonds (valence angles).

The length of a chemical bond (*l*) is the distance between the nuclei of the atoms that form the bond. The bond length is measured in nanometers (nm), and 1 nm = 10^{-9}m). It has a value of the order of 0.1-0.2 nm. Thus, it was experimentally determined that the bond length between atoms in the H_2 molecule is 0.074 nm, N_2 – 0.110 nm, and O_2 – 0.121 nm. The chemical bond is stronger the shorter the distance between the atoms in the molecule.

The regularities of changes in the values of internuclear distances coincide with the regularities of changes in the atomic (ionic) radii of elements by periods and groups of Periodic table. As the radii of the atoms between which the bond is formed increases, its length increases. Thus, for molecules of halogens and hydrogen halides: the bond length Cl_2is0.200 nm,HCl –0.128nm, Br_2 – 0.229nm, HBr – 0.141nm,I_2 – 0.267nm, HI – 0.162nm.

With an unchanged valence state, the internuclear distance for this type of bond is practically constant in different compounds. When going from a single bond to a multiple bond, the bond length decreases. For example, the length of a single bond C–C is 0.154 nm, double C=C is 0.134 nm, and triple C≡C is 0.120 nm.

The angle between the imaginary lines that pass through the nuclei of chemically bonded atoms is called the **bond angle.** Valence angles depend on the nature of the atoms and the nature of the chemical bond. It was experimentally established, for example, that in a triatomic water molecule, the hydrogen atoms are at the same distance (0.096 nm) from the oxygen atom, that is, in the H_2O molecule, the O–H bond length is 0.096 nm. The valence angle is 104.5°.

Chemical bond energy ***(E)*** *is a* measure of the strength of the bond between atoms in a molecule, is the amount of energy that must be expended to break the bond. Chemical bond energy is measured in kilojoules per mole of substance (kJ/mol). The higher the bond energy, the stronger it is.

Comparing the length and bond energy in molecules, for example, hydrogen halides ($E_{H–Cl}$ = 426 kJ/mol, $E_{H–Br}$ = 364 kJ/mol, $E_{H–I}$ = 239 kJ/mol), we conclude that with an increase in the bond length, its strength decreases.

An increase in the number of bonds between the same atoms increases the bond energy between them, but this increase is not proportional to the increase in the number of bonds. For example, the energy of a C–C single bond is 347 kJ/mol, a double C=C bond is 606 kJ/mol, and a triple C≡C bond is 831 kJ/mol.

The length and energy of a chemical bond, valence angles, as well as other physical and chemical properties of a substance directly depend on the nature of the electron density distribution in the molecule and determine its geometry.

The chemical connection between atoms is carried out by valence electrons: in the elements of the main subgroups (s- and p-elements), these are electrons of the last (external) energy level, in the elements of secondary subgroups (d-elements), these are the s-electrons of the last and d- electrons of the penultimate energy levels. For example: in the Ca atom, two s-electrons of the outer energy level are valence, in Mn – two s-electrons of the outer and five d-electrons of the penultimate energy level.

Bond direction and geometry of molecules. The electrical properties of molecules depend on the arrangement of atoms in the molecules and the spatial orientation, which is determined by which electrons participate in the formation Bond direction and geometry of molecules. The electrical properties of molecules depend on the arrangement of atoms in the molecules and the spatial orientation, which is determined by which electrons participate in the formation of a covalent bond. If we take a molecule consisting of two AB atoms, for example HCl (Fig. 4.1), then it is formed from a hydrogen atom, which has one s-electron, and a chlorine atom, which has one unpaired p-electron in its outer energy level. A covalent bond between them will be formed when the electron clouds of the s-electron of hydrogen and the p-electron of chlorine overlap. The HCl molecule is a linear molecule.

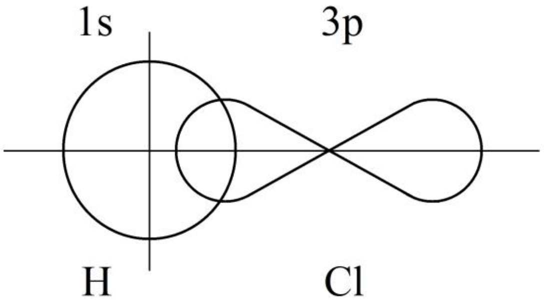


Fig. 4.1. Scheme of the formation of a hydrogen chloride molecule

In the formation of a chemical bond, only electrostatic Coulomb forces are important, the carriers of which are electrons and atomic nuclei. According to modern ideas, the chemical bond has an electrical nature, but the mechanism of its formation is different.

There are the following main types of chemical bonds: covalent, ionic, hydrogen, and metallic.

4.2. Covalent bond and its properties

A covalent bond is a chemical bond that is carried out due to shared electron pairs belonging to two atoms at the same time, and each atom donates one electron to form a pair. Molecules of such substances as H_2, O_2, Cl_2, N_2 and others are formed due to covalent bonds.

It is characteristic that during the formation of shared electron pairs, the atoms that make up the molecule have a supposedly complete outer electron shell, which is similar to the shell of the nearest inert gas. Valence electrons of atoms are depicted as dots placed next to the symbol of a chemical element, and the shared electron pair standing between atoms is indicated by two dots on the diagrams:

$$H\cdot + \cdot H \rightarrow H : H.$$

There are two mechanisms of covalent bond formation: exchange and donor-acceptor.

A covalent bond by the exchange mechanism arises due to the overlapping of one-electron clouds (orbitals) of unpaired electrons with antiparallel spins that belong to the interacting atoms.

Let us consider the mechanism of formation of a covalent bond by the exchange mechanism using the example of the formation of a hydrogen molecule from atoms:

$$H\cdot + \cdot H \rightarrow H_2 ;\ \Delta H = -346 \text{ kJ/mol}.$$

The electronic configuration of a hydrogen atom is $1s^1$, that is, there is one unpaired electron in the outer energy level. The nucleus of an isolated hydrogen atom is surrounded by a spherically symmetric electron cloud.

Initially, when hydrogen atoms with oppositely directed spins come together, attractive forces prevail between them, as a result of which a gradual decrease in the energy of the system is observed. The energy minimum, which is 4.5 eV (binding energy), corresponds to such a state of the system when the forces of attraction and repulsion are balanced. After that, repulsive forces prevail, which leads to a sharp increase in the energy of the system.

The formation of a hydrogen molecule, in addition to a change in the energy of the system, is accompanied by a change in the density of electron clouds. When atoms approach a certain distance, their electron clouds partially overlap.

The greatest overlapping of electron clouds is carried out along the line connecting the nuclei of two atoms. The stronger the chemical bond, the greater the overlap of electronic orbitals. As a result of the formation of a chemical bond between two hydrogen atoms, each of them reaches the electronic configuration of an atom of the noble gas helium.

A quantitative assessment of the chemical bond in the molecule of any chemical compound can be obtained based on the solution of Schrödinger's equation. This was done for the first time in 1927 by Heitler and London for the hydrogen molecule – the simplest of the existing molecules. They calculated two quantitative characteristics of the bond energy and length.

If the distance between nuclei was 0.106 nm for hydrogen atoms approaching collision, then after overlapping of electron clouds (formation of H_2 molecule) this distance (bond length) is 0.074 nm (Fig. 4.2).

The results of these calculations were in good agreement with experimental data and were the basis for calculations of chemical bonding in polyatomic molecules.

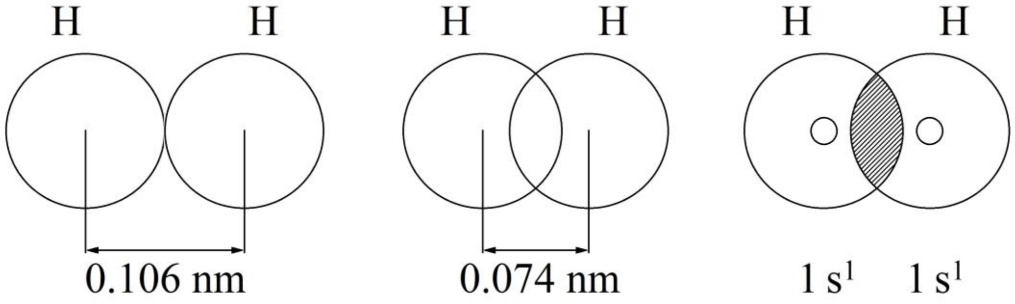


Fig. 4.2. Scheme of the overlapping of electronic orbitals of atoms during the formation of a hydrogen molecule

The main properties of a covalent bond include: saturation; multiplicity; directionality in space; polarity.

Saturationis the ability of atoms to form a number of chemical bonds limited by the number of orbitals.

An atom of each element forms a certain number of covalent bonds with other atoms. Thus, the atoms of elements of the second period, which have four orbitals at the outer energy level (one s- and three p-), form bonds, the number of which does not exceed four. Atoms of elements of other periods with a larger number of orbitals at the outer energy level can form a larger number of bonds.

For example, nitrogen and phosphorus atoms, despite having the same number of valence electrons (five), form a different maximum number of bonds in compounds: phosphorus - five, nitrogen - four. This is explained by the fact that there are free d-orbitals $3s^2 3p^3 3d^o$ at the outer energy level of the phosphorus atom, one of which can be transferred to one of the unpaired electrons from the 3s-orbital: $3s^1 3p^3 3d^1$.

In the nitrogen atom at the outer energy level, there are no vacant orbitals (because it is an element of the second period) to which an electron from the 2s orbital could move. Therefore, a nitrogen atom can form no more than four bonds.

As a result of the saturation of the covalent bond, molecules have a certain composition: H_2, HCl, H_2O, NH_3, etc., that is, all unpaired electrons of atoms participate in the formation of a molecule.

The multiplicity of a covalent bond is the number of shared electron pairs that bond atoms together when the bond is formed.

A bond between two atoms with the help of one common electron pair is called **simple** (or single), two electron pairs – **double**, three electron pairs – **triple**. For example, in the molecules of hydrogen H_2, chlorine Cl_2, bromine Br_2, iodine I_2, the atoms are connected by a single bond (H–H, Cl–Cl, Br–Br, I–I), in the molecule of ethylene C_2H_4 there is a double bond (C=C), in the nitrogen molecule N_2 – triple (N≡N).

Polarity of molecules are distinguished by the distribution of electric charges between atoms in a molecule. At the same time, the mutual location of the shared electron pair between the atoms in the molecule is taken into account. If the covalent bond is formed by the same atoms, then the electron pair is placed at the same distance from them and the centers of positive and negative charges in such a molecule will be at the same point. Such a molecule is called **non-polar**.

If one of the atoms is able to attract electrons more strongly (is more electronegative), then the electron pair will be shifted to it and the molecule will have two poles (polar molecule). The greater the electronegativity of one of the atoms, the more polar the molecule will be. The degree of polarity is determined by the dipole moment, which is equal to the product of the magnitude of the elementary electric charge ($4.8 \cdot 10^{-10}$ el. st. unit) by the distance between the charges in angstroms Å (10^{-8} cm). In Fig 4.3 shows the location of the shared electron pair relative to the axis of symmetry for molecules formed by atoms of different natures.

According to the degree of displacement of the common electron cloud, the bond in the molecule can be non-polar, polar or ionic. Non-polar and ionic bonds are extreme cases of polar covalent bonds.

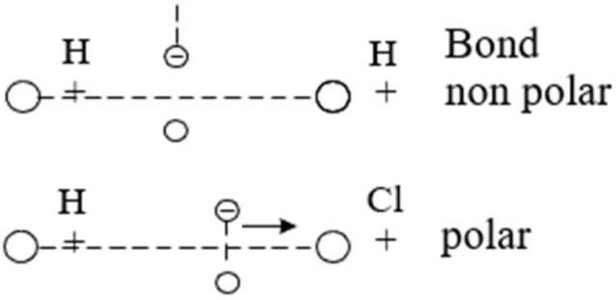


Fig. 4.3. Displacement of the electron pair in H_2, HCl and NaCl molecules

During chemical reactions, for example, during the burning of sodium in chlorine, the unpaired electrons of the s-orbitals of the sodium atom and the p-orbitals of the chlorine atom form a common electron pair, which is completely shifted to the chlorine atom, as a more electronegative element.

In molecules of organic compounds, the degree of polarity will depend on the spatial arrangement of atoms and on the substituent included in its composition. Thus, benzene is a non-polar molecule, but its derivatives will already have a different degree of polarity (Fig. 4.4).

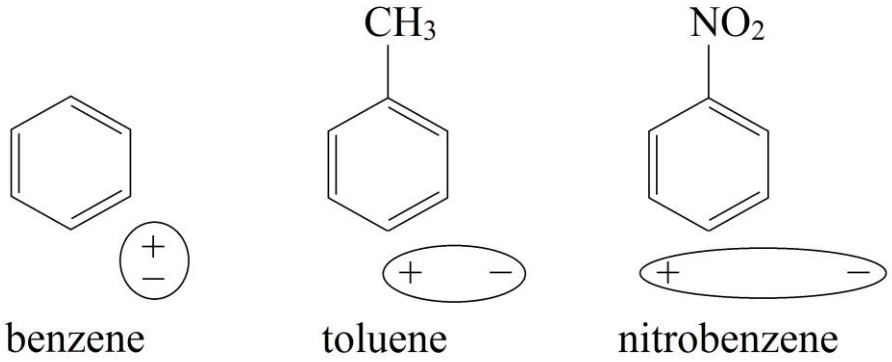


Fig. 4.4. The effect of substituents on the polarity of benzene molecules

Therefore, there is no fundamental difference in the mechanisms of formation of ionic, covalent polar and covalent nonpolar bonds. They differ only in the degree of polarization of shared electron pairs. The nature of the chemical bond is the same.

The value of the difference in the values of the relative electronegativity (symbolized as χ) of the atoms forming the bond is used to estimate the polarity of the bond. The greater the value of $\Delta\chi$, the stronger the polarity of the bond, i.e., the greater the degree of ionicity of the bond.

If $\Delta\chi = 0$ thebond is non-polar covalent bond.

If $0 < \Delta\chi < 2.0$ the bond is covalent polar.

If $\Delta\chi > 2.0$ the bond is not covalent, but ionic.

Extremely high value of $\Delta\chi$ in the CsF compound ($\Delta\chi = 3.24$).

In fact, bonds are not 100% ionic. It has been experimentally determined that even in such a compound as CsF, the ionic bond is expressed only by 89%, so we talk about the degree or share of ionicity of the bond. In many compounds, the bond between atoms has an intermediate character between ionic and covalent.

4.3. Donor-acceptor mechanism of covalent bond formation

A covalent bond by the donor-acceptor mechanism occurs due to an unshared electron pair that is at the outer energy level of one of the interacting atoms and the free orbital of another atom. An example of the implementation of the donor-acceptor mechanism is the formation of the ammonium ion during the interaction of ammonia $NH_4^+$with hydrogen chloride HCl according to the reaction:

$$NH_3 + HCl \rightarrow NH_4Cl;$$
$$NH_3 + H^+ \rightarrow NH_4^+.$$

In the ammonia molecule, the nitrogen atom (N $1s^2 2s^2 2p^3$) at the outer energy level has an unshared pair of electrons (three unpaired electrons form three covalent bonds with the unpaired electrons of three hydrogen atoms) and an unshared $2s^2$ electron pair. The H^+ hydrogen ion has a free 1s orbital, denoted by empty square.

When the NH_3 molecule interacts with the H^+ ion, a covalent bond occurs between them due to inseparability donor-acceptor (Fig 4.5).

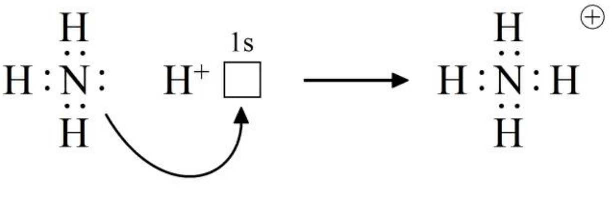


Fig. 4.5. Scheme of formation of donor-acceptor bond, examples of ammonia

The atom that provides its lone pair of electrons for the formation of a bond is called **a donor** (in this case, nitrogen). An atom that has a free orbital and accepts an electron pair is called **an acceptor** (in this example, a hydrogen ion).

Most often, metal ions with vacant orbitals play the role of acceptors: Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{3+}, Fe^{2+}, Fe^{3+}, etc. Donors of electron pairs can be neutral molecules (H_2O, NH_3) or negatively charged ions F^-, Cl^-, Br^-, I^-, CN^-, etc.

The donor-acceptor mechanism of covalent bond formation is especially important in the formation of coordination compounds, which is why it is sometimes called a coordination bond.

In fact, a donor-acceptor bond can be considered a variant of a covalent bond, which differs in that before the formation of a shared pair of electrons, this pair completely belonged to one of the atoms (donor of the electron pair) that formed the bond. The second atom or ion (acceptor) joins the free electron pair of another atom.

The donor-acceptor bond occurs in the molecules of many complex compounds. For example, the complex zinc ion $[Zn(NH_3)_4]^{2+}$ is formed due to the addition of the zinc (II) ion to the free $2s^2$ electron pair of nitrogen in the ammonia molecule, which is the donor, and the zinc ion is the acceptor (Fig. 4.6).

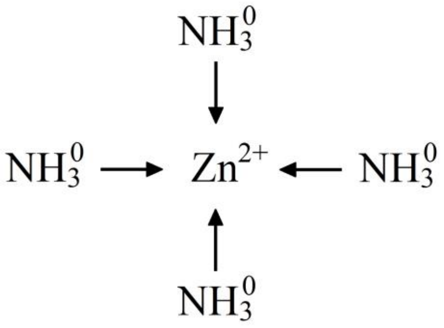


Fig. 4.6. Scheme of formation of complex zinc ion with ammonia

The donor-acceptor bond in the diagrams is indicated by an arrow (→) going from the donor to the acceptor.

4.4. Method of valence bonds and hybridization of atomic orbitals

The ideas of Heitler and London about the mechanism of formation of a chemical bond were developed by Slater and Pauling for polyatomic molecules and formed the basis of the method of valence bonds.

It, along with another method (molecular orbitals), is used in the modern theory of chemical bonding. The main provisions of the method of valence bonds:

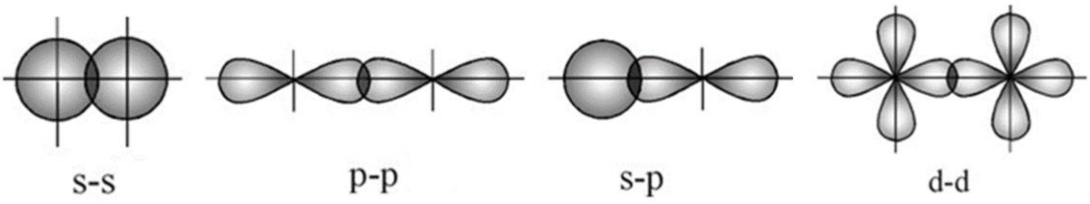
1. A covalent bond is formed by two electrons with oppositely directed spins belonging to two atoms. It is localized between two atoms - two-electron and two-centered.

2. A covalent bond is formed as a result of overlapping atomic electron clouds. At the same time, the electron density is maximal in the space between atoms. Thanks to this, the forces of attraction between the atom's nucleus and electrons increase. This leads to a decrease in the potential energy of the system, that is, to the formation of a chemical bond.

3. A covalent bond is formed in the direction in which the overlap of atomic electron clouds is maximal.

The mechanism of formation of a covalent bond by the exchange mechanism in chlorine and hydrogen chloride molecules from the positions of the valence bonds method can be presented as follows: the electronic configuration of hydrogen atoms H – $1s^1$ and chlorine – Cl $1s^12s^22p^63s^23p^5$ shows that their outer energy levels contain one unpaired electron each. When the atoms approach, the orbitals of these electrons overlap, forming common electron pairs.

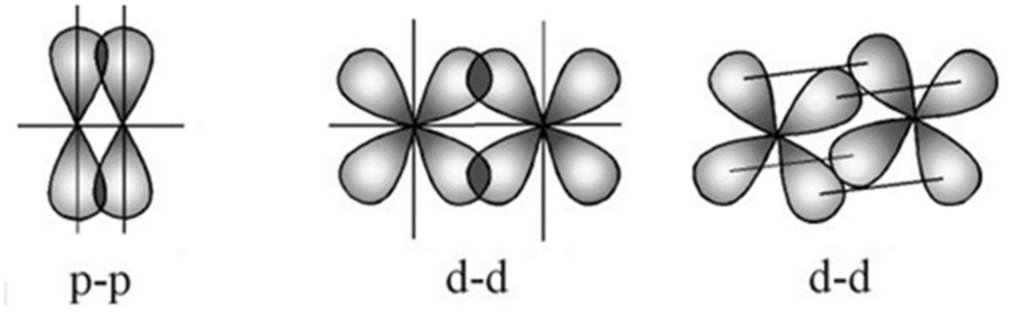
Depending on the method of overlapping electronic orbitals, the following are distinguished: σ- (Fig. 4.7), π- (Fig. 4.8a,b) and δ- (Fig. 4.8c) bonds.



a b c d

Fig. 4.7. Schemes of the formation of σ-bonds due to the overlap of s-s (a), p-p (b), s-p (c) and d-d (d) electronic orbitals

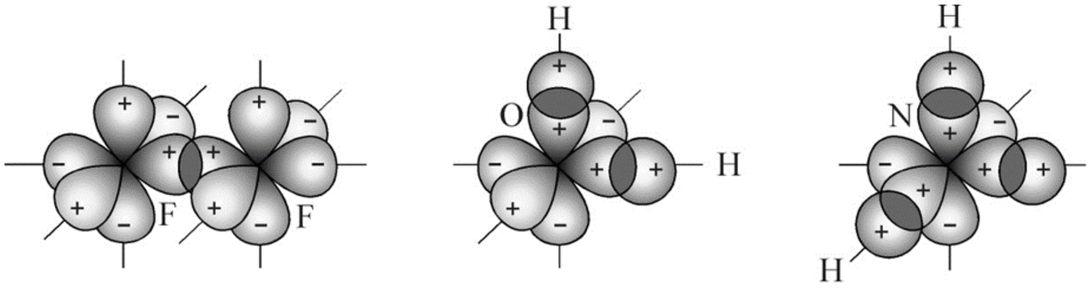
As we can see in Fig. 4.7., electronic orbitals overlaps in various ways, but in all cases in σ-bonds the area of overlap is located on a straight line between the nuclei of atoms.



a b c

Fig. 4.8. Schemes of the formation of π-bonds (a, b) and δ-bond (c) due to the overlap of p-p (a) and d-d (b, c) electronic orbitals

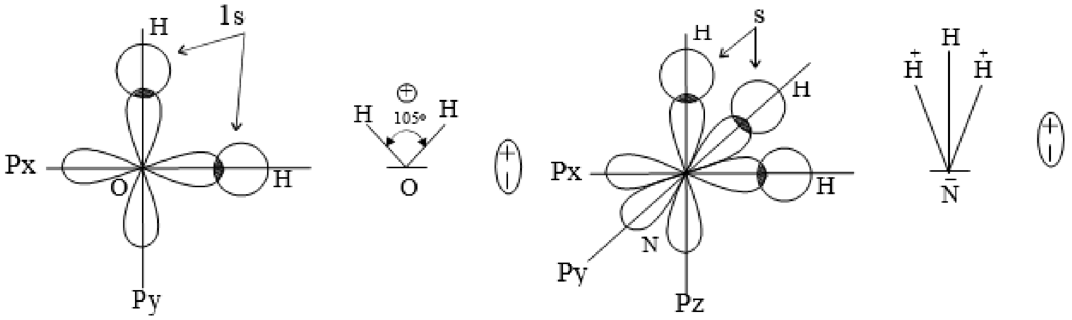
Examples of the formation of σ-bonds in fluorine, water, and ammonia molecules are shown in Fig. 4.9.



a b c

Fig. 4.9. Schemes of the formation of chemical bonds in molecules: F_2 (a), H_2O (b), and NH_3 (c)

When a water molecule is formed, two hydrogen atoms join an oxygen atom (AB_2 type molecule), which has two unpaired p-electrons, each of which forms a polar covalent bond with the s-electrons of hydrogen. But the two p-electrons of oxygen are directed along the coordinate axes and the angle between the two covalent bonds should be 90°. In fact, due to the repulsion of hydrogen ions from each other, this angle is slightly larger than a straight line and is 104.5°. As a result of the one-sided arrangement of hydrogen atoms, the center of positive charges will be near the hydrogen atoms, and the center of negative charges will shift to the oxygen atoms. That is, the water molecule is a strongly polar molecule (Fig. 4.10).



H_2O NH_3

Fig. 4.10. Formation of H_2O and NH_3 molecules

For a molecule of AB_3 type (for example, NH_3), three p-electrons of nitrogen and s-electrons of hydrogen atoms participate in the formation of a bond between nitrogen and hydrogen atoms. Nitrogen has a greater electronegativity than hydrogen, and therefore the ammonia molecule will also be polar (Fig. 4.10).

A chemical bond is formed when overlapping orbitals have the same symmetry about the bond line. It follows from the symmetry conditions that electrons of s-orbitals can participate only in the formation of σ-bonds, electrons of p-orbitals – in the formation of σ- and π-bonds, and electrons of d-orbitals - in the formation of σ-, π- and δ-bonds. Ways of overlapping *f*-orbitals are even more diverse. Despite the different forms of the original valence orbitals, the bonds formed with their participation are equivalent. Slater and Poling explained this phenomenon by the **hybridization** of valence orbitals, which consists in the fact that orbitals of different symmetry, which do not differ much in energy, form hybridized orbitals. During hybridization, the initial shape and energy of the orbitals change and new orbitals are formed, but already of the same shape with the same energy. The number of hybridized orbitals is equal to the number of orbitals involved in hybridization.

Hybridized orbitals are asymmetric and more elongated on one side of the nucleus in the direction of the formation of chemical bonds and therefore lead to better overlapping of electronic orbitals. As a result, the chemical bond formed with the participation of a hybridized orbital is stronger than that formed due to the electrons of individual original orbitals. Therefore, hybridization is associated with an energy gain due to the formation of stronger bonds and a more symmetrical distribution of electron density in the molecule.

The type of hybridization is determined by the type and number of orbitals involved in hybridization. If the hybridized orbitals form one s- and one p-orbital, then it is said about sp-hybridization and sp-hybridized orbitals, and if one s- and three p-orbitals, then it is said about sp^3-hybridization and sp^3-hybridized bonds and etc.

sp-hybridization is combination of one s- and one p-orbital with results in two s-hybridized orbitals placed symmetrically at an angle of 180º (Fig. 4.11). The bonds that are formed with the participation of the electrons of these orbitals are also located at an angle of 180º. This type of hybridization takes place during the formation of halides of elements of the II group of the periodic system: Be(II), Zn(II), Cd(II), Hg(II), the atoms of which in the valence state have unpaired s- and p-electrons. In molecules of elements of other groups, for example O=C=O, H–C≡C–H, σ-bonds are formed by sp-hybrid orbitals of the Carbon atom.

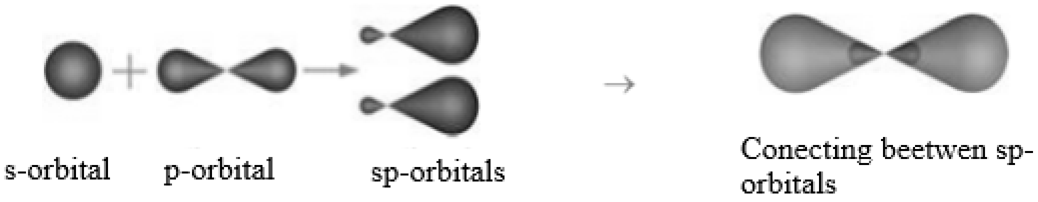


Fig. 4.10. Scheme of sp-hybridization

sp^2-hybridization iscombination of one s- and two p-orbitals leads to the formation of sp^2-hybridized orbitals located at an angle of 120º (Fig. 4.11). The bonds formed by the electrons of these orbitals are placed at the same angle. This type of hybridization is characteristic of molecules of elements of the III group of the periodic system, the atoms of which in the excited state have electronic structures ns^1 np^2 that form hybrid bonds. Molecules BF_3, BCl_3, $AlCl_3$, AlF_3 are compounds that contain sp^2-hybridized bonds. For example, the BCl_3 molecule has the shape of a flat triangle due to the sp^2-hybridization of the orbitals of the Boron atom.

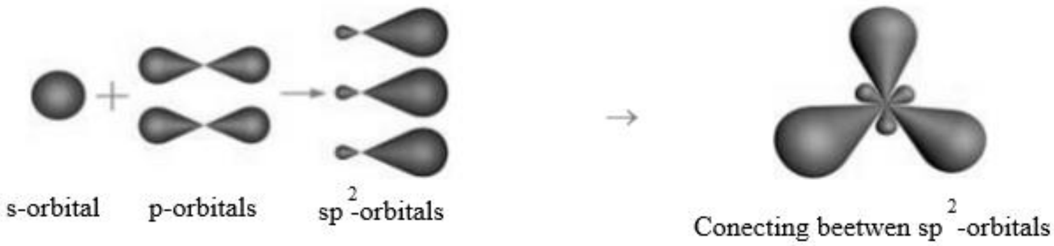


Fig. 4.11. Scheme of sp^2-hybridization

In the atoms of elements of the II group of the periodic system, sp^2-hybridized orbitals are formed if the valence s-orbital is not filled with an electron pair, and this atom forms three σ-bonds. Molecules with sp^2-hybridization also form elements of other groups, for example, carbon in ethylene C_2H_4.

sp^3-hybridizationis combination of four orbitals: one s-orbital and three p-orbitals leads to sp^3-hybridization, in which the four hybridized orbitals are symmetrically oriented in space to the four vertices of the tetrahedron, i.e. at an angle of 109º28' (Fig. 4.12). The tetrahedral arrangement of bonds and the shape of the tetrahedron are characteristic of many compounds of tetravalent carbon, for example, in CH_4, CCl_4 molecules. Examples of compounds of elements of other groups of the periodic system, in which the tetrahedral structure is due to sp^3-hybridization of the valence orbitals of the central atom, are ions BeF_4^{2-}, BF_4^-, PO_4^{3-}, SO_4^{2-}, ClO_4^-.

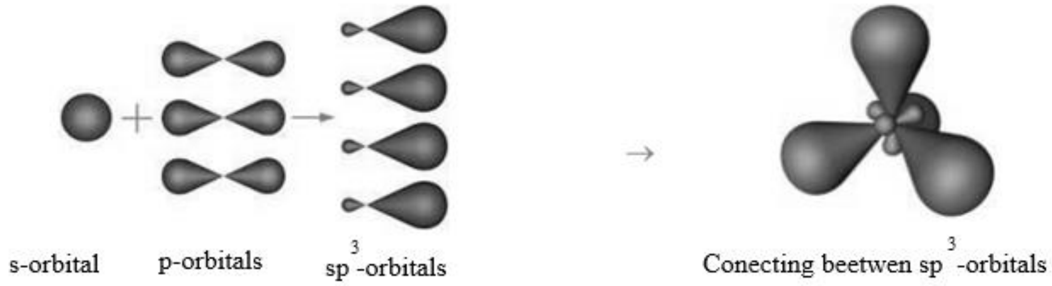


Fig. 4.12. Scheme of sp^3-hybridization

In addition to those considered above, other types of hybridization of valence orbitals and corresponding spatial configurations of molecules are also possible. In the elements of the third and subsequent periods, d- and f-orbitals can participate in the formation of hybridized bonds. The combination of one s-, three p- and one d-orbital leads to sp^3d-hybridization. This corresponds to the spatial orientation of the sp^3d-hybridized orbitals to the vertices of the trigonal bipyramid. In the case ofsp^3d^2-hybridization six sp_3d_2 -

hybridized orbitals are oriented to the vertices of the octahedron. The octahedral structure of the SF_6 molecule, $[SiF_6]^{2-}$, $[Fe(CN)_6]^{3-}$ ions, and many others is explained by sp^3d^2 hybridization of the atomic orbitals of the central atom. The orientation of the seven orbitals to the vertices of the pentagonal bipyramid corresponds to sp^3d^3– or sp^3d^2f-hybridization of the valence orbitals of the central atom of the molecule. The chemical bond between the atoms in the molecule is localized, that is, the electron pair belongs to two atoms at the same time (two-centered bond). However, sometimes during the formation of a chemical bond, electron pairs can be located between several atoms (a multicenter bond) so that it is impossible to determine which atoms individual pairs of electrons belong to. Such connections are called non-localized.

4.5. Ionic bond

This type of connection is based on the ideas that atoms of metals and non-metals, which are opposite in properties, connect to each other as a result of the electrostatic interaction of oppositely charged particles - ions. Ions are formed from atoms during the transition of electrons of a metal atom to the outer shell of a non-metal atom. So, a molecule of sodium chloride is formed by the reaction:

$$2Na + 2Cl_2 \rightarrow 2NaCl.$$

Schematically, the mechanism of formation of an ionic bond can be represented as follows:

$$NaO - 1e \rightarrow Na^+;$$
$$Cl_2 + 2e \rightarrow 2Cl^-;$$
$$2Na^+ + 2Cl^- \rightarrow 2NaCl.$$

Thus, the transfer of an electron from a sodium atom to a chlorine atom produces charged particles with a completed electron shell similar to that of the nearest inert gas, which is a stable electronic configuration. The vast majority of salts are formed by the ionic type of bond.

The formed combinations of NaCl ions are ionic associates. In the form of molecules, they exist only in a gaseous state (at high temperatures). The form of existence of ionic compounds under normal conditions is solid crystalline substances.

A characteristic feature of an ionic bond (as opposed to a covalent bond) is its unsaturation and non-directionality in space. Therefore, Na^+ ions, for example, can interact with $Cl^–$ ions in any direction, attracting a certain number of them. This leads to the formation of not simple molecules, but ionic crystals consisting of a large number of ions. Molecules in this case are absent. For example, in a NaCl crystal, each Na^+ ion interacts with six $Cl^–$ ions and vice versa (Fig. 4.13).

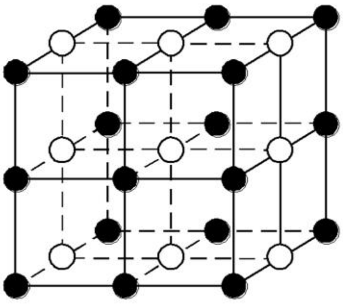


Fig. 4.13. Structure of NaCl crystals

Crystal lattices of ionic compounds consist of regularly arranged positively and negatively charged ions.

The ionic bond energy is determined by the Coulomb forces of attraction of oppositely charged ions. It depends on the values of the ionization energy of the metal atom and the electron affinity of the non-metal atom. The smaller the first value and the larger the second, the more energetically favorable is the formation of an ionic compound, the higher is the bond energy.

Thus, in a number of NaF–NaCl–NaBr–NaI salts, the bond energy decreases. This is explained by a decrease in the electron affinity in the series from F to I. A similar conclusion is given by the value of ΔBEH of the atoms forming the bond.

Ionic substances are formed during the combination of not only monoatomic, but also polyatomic multicharged ions, for example, NaOH, $Ba(OH)_2$, KNO_3, Na_2HPO_4, $Al_2(SO_4)_3$are ionic compounds. Their crystal lattices contain the following ions: Na+ and $OH^–$, Ba^{2+} and $OH^–$, K^+ and $NO_3^–$, Na+ and $HPO_4^{2–}$, Al^{3+} and $SO_4^{2–}$, respectively.

Ionic compounds form atoms of elements that differ sharply in electronegativity values. For example, compounds of metals of the I and II groups of the main subgroups with non-metals of the VI and VII groups of the main subgroups: oxides, halides, sulfides, hydroxides and oxygen-containing salts of these metals.

4.6. Hydrogen bond

A hydrogen bond is characteristic of molecules that include hydrogen combined with atoms of very electronegative elements as fluorine, oxygen, nitrogen, etc. (Fig. 4.14).

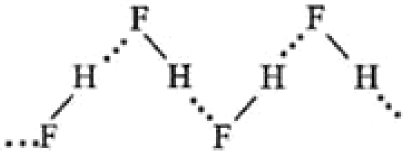


Fig. 4.14. Scheme of formation of a hydrogen bond between H-F molecules

It is formed between molecules as a result of interaction of hydrogen ions of one of the molecules with electronegative atoms of another molecule. In such molecules, the binding electron pair is strongly shifted towards the electronegative atom, which acquires a negative charge. A hydrogen ion, having a small size and a strong positive charge, can be attracted to the electron shell of neighboring molecules and form a bond. Thus, in water molecules, a rather strong hydrogen bond is formed between hydrogen and oxygen ions of neighboring molecules, which gives water a number of abnormal properties (liquid state, high specific heat capacity, and others).

From the point of view of the valence bond method, the hydrogen bond is three-centered, since one electron orbital of hydrogen provides a bond with three atoms. This relationship is characterized by directionality in space and saturation.

The stronger the hydrogen bond, the greater the electronegativity of the partner atom and the smaller its size. It is characteristic, first of all, for compounds of fluorine, as well as oxygen, to a lesser extent – for nitrogen, chlorine and sulfur. Accordingly, the energy of the hydrogen bond also changes. Thus, the energy of the H···F hydrogen bond is about 40 kJ/mol, the H···O bond is 20 kJ/mol, and H···N is 8 kJ/mol.

Hydrogen bond is weaker than ionic and covalent. Its energy is 8-40 kJ/mol, that is, approximately 15-20 times less than the energy of a covalent bond. For comparison, the hydrogen bond energy of O–H···O ice is 20 kJ/mol, which is only 4.3% of the covalent H–O bond energy.

At the same time, the hydrogen bond plays an important role in the association of molecules, crystallization, formation of crystal hydrates, dissolution of compounds and other chemical processes. In ammonia, the lone electron pair of nitrogen and the polarity of the N–H bond determine the formation of a hydrogen bond between NH_3 molecules. Therefore, ammonia liquefies quite easily and has a high boiling point.

Due to the ability to form hydrogen bonds and enter into a donor-acceptor interaction, liquid HF, H_2O, NH_3 are good ionizing solvents. Hydrofluoric acid, unlike its counterparts HCl, HBr, HI, does not exhibit the properties of a strong acid.

Hydrogen bonds are classified into intermolecular, intramolecular and interatomic.

The mechanism of formation of an **intermolecular hydrogen bond** (using the example of a water molecule) is explained as follows: H atoms in the H_2O molecule are connected to O atoms by means of a polar covalent bond. Shared electron pairs are strongly shifted to the atom of the electronegative element (to the oxygen atom). As a result, the O atom acquires a significant effective negative charge, and the hydrogen atom almost loses its electron cloud. An electrostatic interaction occurs between the hydrogen proton of one water molecule and the negatively charged oxygen atom of another water molecule, which leads to the formation of a hydrogen bond. In addition, the occurrence of a hydrogen bond is also determined by the donor-acceptor interaction, since the hydrogen atom has a vacant orbital, and the atom of an electronegative element has an unshared electron pair.

Due to the formation of hydrogen bonds, water molecules are associated and have an openwork spatial structure (Fig. 4.15). This leads to abnormally high temperatures of melting ice and boiling water.

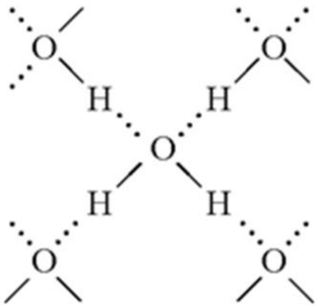


Fig. 4.15. Scheme of formation of hydrogen bonds in ice structure

The formation of hydrogen bonds leads to such an arrangement of water molecules when they come into contact with each other with their opposite poles. Molecules form layers, and each of them is bound to three molecules belonging to the same layer and to one molecule from a neighboring layer. The structure of ice belongs to the least dense structures, it has voids, the size of which slightly exceeds the size of the H_2O molecule.

During the melting of ice, only part of the hydrogen bonds is destroyed. Therefore, at temperatures close to 0°C, liquid water contains the remains of the ice structure and individual molecules that have broken off from them. The latter can also be located in the voids of "ice" aggregates, as a result of which a denser packing of molecules is achieved. That is why, during the melting of ice, the volume of water decreases, and its density increases. In the process of heating water, hydrogen bonds continue to break, which leads to a decrease in the volume of water and an increase in its density. In the temperature range from 0 to 4°C, this effect prevails over thermal expansion, so that the density of water continues to increase. However, when heated above 4°C, the influence of thermal motion of molecules prevails and the density of water decreases. Therefore, water has the maximum density at 4°C.

When water is heated, part of the heat is spent on breaking hydrogen bonds (the energy of breaking a hydrogen bond in water is about 25 kJ/mol). This explains the high heat capacity of water. Hydrogen bonds between water molecules are completely broken only when water turns into steam. At 20°C, about half of the hydrogen bonds remain in liquid water.

A hydrogen bond can occur not only between atoms of different compounds, but also between atoms of the same molecule. Most often, an intramolecular hydrogen bond is formed in the molecules of organic compounds that contain the groups OH^-, NH^{2-}, NO^{2-}, etc.

Hydrogen bonds are especially common in the molecules of proteins, nucleic acids and other biologically important compounds, and therefore these bonds play an important role in the chemistry of life processes.

4.7. Metallic bond

A metallic bond is a multicenter bond that exists in metals and their alloys between positively charged ions and valence electrons shared by all atoms.

In metals, the ionization energy of atoms is lower than in non-metals. Therefore, in them, valence electrons are easily detached from individual atoms and become common to the entire crystal. This is how positively charged ions and electron gas – a collection of mobile electrons – are formed. In a metal crystal, shared electrons bind many ions together.

A metallic bond is similar to a covalent bond. The basis of the formation of these bonds are the processes of formation of shared valence electrons. However, in compounds with a metallic bond, the valence electrons are shared by the entire crystal, and in compounds with a covalent bond, they are shared only by two neighboring atoms. At the same time, the metallic bond is somewhat similar to the ionic one, because there are ions in the nodes of the crystal lattices.

The metallic bond is non-directional because the valence electrons are distributed almost uniformly throughout the crystal. Despite the fact that there are positive ions in the nodes of crystal lattices, crystal lattices of metals are quite stable. This stability is due to the electrostatic attraction of ions and generalized electrons that continuously move between ions. The energy of a metallic bond is lower than the energy of a covalent bond.

The metallic bond due to the presence of free electrons (electron gas) determines the characteristic general properties of metals and alloys, in particular thermal and electrical conductivity. The melting and boiling points of various metals have a wide range of values: for example, the melting point of the lowest-melting metal mercury is 39.9°C, and the most refractory tungsten is 3380°C.

Metallic bonding is characteristic of metals in solid and liquid states and determines all physical and chemical properties of metals and alloys. In the vapor state, metals are monoatomic.

Test questions

1. Define the covalent bond type and describe the mechanism of its formation. Supply examples of compounds that are formed with this type of bond.
2. What is different in covalent polar and non-polar bonds? Supply examples of both of them.
3. Define the donor-acceptor mechanism of covalent bond. How does it differ from covalent? Supply examples of compounds with donor-acceptor bonds.
4. Define ionic bond? How does it differ from covalent? Supply examples of compounds with ionic bonds.
5. Why are molecules polar and non-polar? Supply examples of both cases. What type is a water molecule?
6. Define hydrogen bond and describe it. Supply examples of compounds with hydrogen bonds.
7. Define a metallic bond and describe it. Supply examples of compounds with metallic bonds.

Chapter 5. Classification of inorganic compounds

All known substances can be formal classified into simple and complex. About 400 simple substances (taking into account all modifications) are known. All simple substances are classified into metals and non-metals. Complex substances are inorganic or organic in nature. Inorganic substances are classified by the number of elements that form compounds: two-element (binary), three-element, and multi-element.

The whole set of inorganic compounds is classified into four main classes: oxides, bases (hydroxides), acids, and salts.

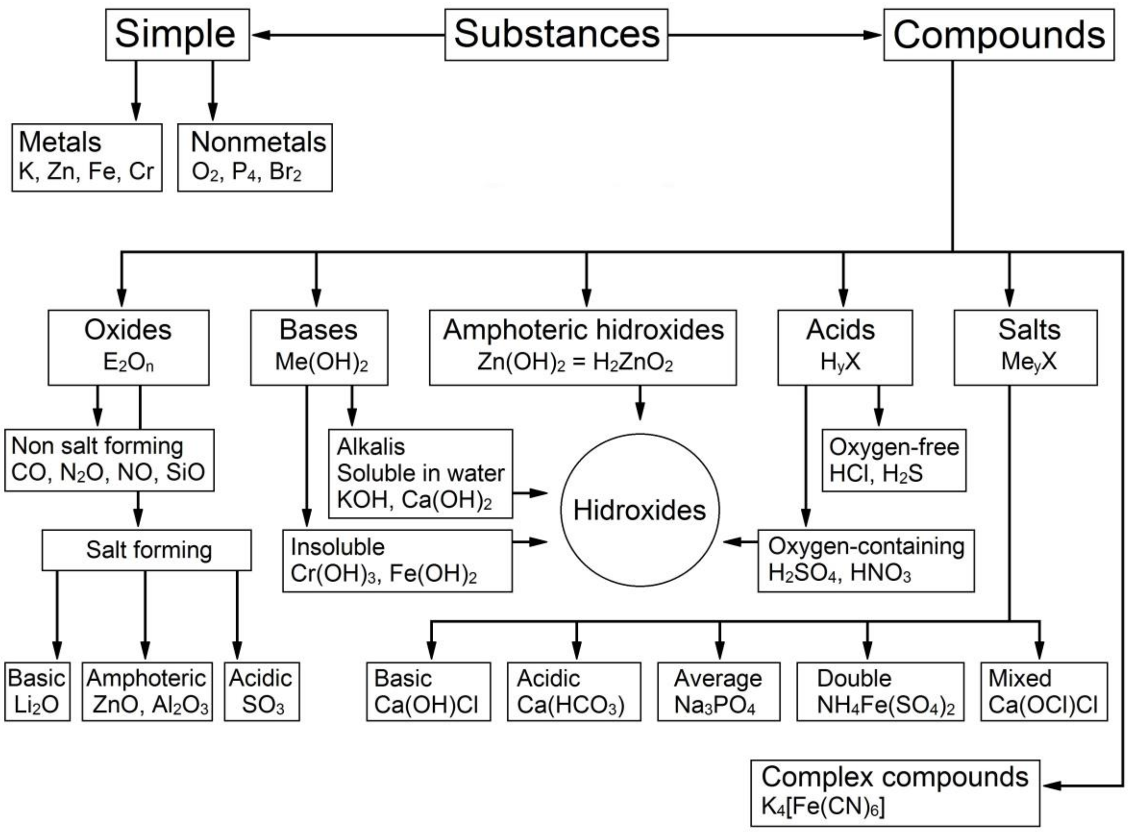


Fig. 5.1. Classification of inorganic substances

Binary compounds are formed by atoms of two elements. Compounds of metals with nonmetals are classified by the type of nonmetals. Compounds of metals with metals are called intermetallics (intermetallics).

The most important binary compounds are halides, which can be considered as salts of the corresponding oxygen-free acids, and oxides.

Hydrolysis of binary compounds leads to the formation of the corresponding hydrogen-containing compounds of nonmetals and hydroxides:

$$FeBr_3 + 3H_2O \rightarrow Fe(OH)_3\downarrow + 3HBr;$$
$$Na_2O + H_2O \rightarrow 2NaOH;$$
$$Al_2S_3 + 6H_2O \rightarrow 2Al(OH)_3\downarrow + 3H_2S;$$
$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2\downarrow + 2NH_3;$$
$$CaH_2 + H_2O \rightarrow Ca(OH)_2\downarrow + H_2;$$
$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2\downarrow + C_2H_2.$$

The hydrolysis of some binary compounds is irreversible.

Three-element compounds are bases, acids and some salts. Another bases, acids, salts, complex compounds and some non-electrolytes are multi-element compounds.

5.1. Simple substances. Metals and non-metals

The classification of simple substances into metals and non-metals is due to the difference in the structure of atoms.

In the Periodic Table, nonmetals are located in the upper right part above the diagonal B–At, and metals are located below it. Elements located near the diagonal have amphoteric properties.

When moving to each subsequent element of the main subgroup or period of the Periodic Table, a smooth change in metallic and non-metallic properties occurs.

Metals are s-elements of groups IA and IIA, all d- and f-elements and p-elements IIIA (except B), IVA (Ge, Sn, Pb), VA (Sb, Bi), VIA (Po), VIIA subgroups . The remaining 22 elements are non-metals.

The classification of elements into metals and non-metals is not very precise. Some elements, depending on conditions, may exhibit properties of metals or non-metals (Be, Ge, Sn, Pb). They are called amphoteric.

Few simple substances are found in nature in their pure form. These are inert gases, low-active metals, some non-metals (carbon, sulfur) and atmospheric gases oxygen and nitrogen. Oxygen is very active, but its quantity is too large for it to fully enter into any chemical reactions.

5.2. Oxides

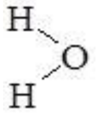
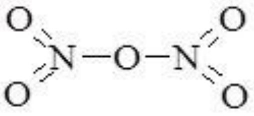
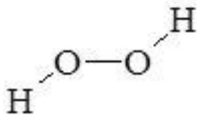
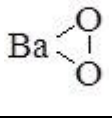
Inorganic substances include oxides, hydroxides, acids, salts and complex compounds.

Oxides are polyatomic substances consisting of two elements, one of which is oxygen in the -2 oxidation state. In oxides there is no bond between oxygen atoms. Compounds having such a compound are called peroxides, the oxidation state of oxygen in them is –1, they belong to the class of hydrogen peroxide salts H_2O_2 (Table 4.1).

The chemical (systematic) name of oxides consists of two words: the first is the name of the element in the nominative case, the second is oxide. If an element can form several oxides, then in the name of the oxide after the name of the element the degree of its oxidation is indicated in parentheses (in Roman numerals, without the “–” or “+” signs). Sometimes oxides of the composition EO are called monoxides, $EO_2$are dioxides, etc. Some oxides have trivial names (Table 4.1).

Table 5.1

Some binary compounds of elements with oxygen

Formula	Graphical formula	Name
H_2O		Hydrogen oxide, water
CO_2	O=C=O	carbon (IV) oxide, carbon dioxide
N_2O_5		nitrogen (V) oxide, nitrogen pentoxide, nitrican hydride
H_2O_2		Hydrogen peroxide
BaO_2		Barium peroxide

The main methods for producing oxides

1. The interaction of simple substances with oxygen, accompanied by the release of heat and light, is called combustion:

a) metals:

$$4Al + 3O_2 \rightarrow Al_2O_3;$$
$$2Cu + O_2 \rightarrow 2CuO.$$

In this way it is impossible to obtain alkali metal oxides, which, when reacting with oxygen, form peroxides or super-oxides:

$$2Na + O_2 \rightarrow Na_2O_2;$$
$$K + O_2 \rightarrow KO_2.$$

therefore, oxides of such elements are obtained by other methods:

$$Na_2O_2 + 2Na \rightarrow 2Na_2O;$$
$$4KO_2 \rightarrow 2K_2O + 3O_2.$$

b) nonmetals:

$$2H_2 + O_2 \rightarrow 2H_2O;$$
$$C + O_2 \rightarrow CO_2.$$

2. Interaction of complex substances with oxygen:

a) inorganic:

$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2;$$
$$2SO_2 + O_2 \rightarrow 2SO_3.$$

b) organic:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O;$$
$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O.$$

3. Thermal decomposition (thermolysis) of compounds:

a) oxides:

$$2PbO_2 \rightarrow 2PbO + O_2;$$
$$2N_2O_5 \rightarrow 4NO_2 + O_2.$$

b) hydroxides:

$$Cu(OH)_2 \rightarrow CuO + H_2O;$$
$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O.$$

c) acids:

$$4HNO_3 \rightarrow 4NO_2 + 2H_2O + O_2;$$
$$H_2SO_3 \rightarrow SO_2 + H_2O.$$

d) salts:

$$CaCO_3 \rightarrow CaO + CO_2;$$
$$NH_4NO_3 \rightarrow N_2O + 2H_2O.$$

There are specific methods for extracting some oxides, they were considered when studying the corresponding elements.

The **classification of oxides** is based on their chemical properties and ability to react with water, bases and acids.

All oxides are classified into salt-forming and non-salt-forming (indifferent) (Fig. 4.1).

Non-salt-forming (indifferent) oxides do not form salts in reactions with acids and bases. There are 4 such oxides: carbon oxide (II) CO, silicon oxide (II) SiO, nitrogen oxide (I) N_2O, nitrogen oxide (II) NO. However, the known method for producing sodium formate is based on the reaction:

$$CO + NaOH \rightarrow HCOONa \text{ (under pressure 15 atmospheres).}$$

Salt-forming oxides in reactions with acids or bases form salts:

$$CaO + H_2SO_4 \rightarrow CaSO_4 + H_2O;$$
$$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O.$$

Among salt-forming oxides, basic, acidic and amphoteric oxides are classified.

The physical properties of oxides can be very diverse. In nature, oxides are found in gaseous (N_2O, CO_2), liquid (H_2O, SO_3) or solid (metal oxides) states.

The **basic oxides** are oxides, the hydrates of which are bases. The main ones are oxides of alkali (Li, Na, K) and alkaline earth (Ca, Sr, Ba) metals, as well as oxides of Cu (II), Fe (II), and Fe (III). In them, an ionic chemical bond is mainly realized, according to n. in. they are all solids.

The chemical properties of basic oxides are similar to those of bases.

1. Interaction with water to form alkalis:

$$Na_2O + H_2O \rightarrow 2NaOH;$$
$$CaO + H_2O \rightarrow Ca(OH)_2.$$

Cu (II), Fe (II) and Fe (III) oxides do not interact with water.

2. Interaction with acids to form salts and water:

$$Li_2O + 2HCl \rightarrow 2LiCl + H_2O;$$
$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O.$$

3. Interaction with acidic and amphoteric oxides with the formation of salts:

$$K_2O + CO_2 \rightarrow K_2CO_3;$$
$$Na_2O + Al_2O_3 \rightarrow 2NaAlO_2;$$
$$FeO + SO_3 \rightarrow FeSO_4;$$
$$BaO + ZnO \rightarrow BaZnO_2.$$

4. Interaction with amphoteric hydroxides with the formation of salts and water:

$$Na_2O + Al(OH)_3 \rightarrow 2NaAlO_2 + 3H_2O.$$

5. Participation in red-ox reactions:

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe;$$
$$3CuO + 2NH_3 \rightarrow 3Cu + N_2 + 3H_2O.$$

Acidic oxides are oxides whose hydrates are acids. These oxides are also called acid anhydrides. Oxides of non-metals and metals in high (from +5 to +7) oxidation states are acidic. In acidic oxides, a covalent polar chemical bond is realized; under normal conditions they are in the gaseous (CO_2, SO_3), liquid (N_2O_5, Cl_2O_7) or solid (P_2O_5, Mn_2O_7) state.

The chemical properties of acid oxides are similar to those of acids.

1. Interaction with water to form acids:

$$SO_3 + H_2O \rightarrow H_2SO_4;$$
$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4.$$

Acidic oxides formed by elements in an intermediate state of oxidation in this case form two acids:

$$2N^{+4}O_2 + H_2O \rightarrow HN^{+3}O_2 + HN^{+5}O_3;$$
$$2Cl^{+6}O_3 + H_2O \rightarrow HCl^{+5}O_3 + HCl^{+7}O_4.$$

2. Interaction with alkalis with the formation of salts:

$$CO_2 + Ca(OH)_2 \rightarrow Ca(HCO_3)_2;$$
$$SO_3 + 2NaOH \rightarrow Na_2SO_4 + H_2O.$$

Acidic oxides formed by elements in an intermediate state of oxidation in this case form two salts:

$$2N^{+4}O_2 + 2NaOH \rightarrow NaN^{+3}O_2 + NaN^{+5}O_3 + H_2O.$$

3. Interaction with basic and amphoteric oxides with the formation of salts:

$$P_2O_5 + 3Na_2O \rightarrow 2Na_3PO_4;$$
$$SO_3 + ZnO \rightarrow ZnSO_4.$$

4. Interaction with amphoteric hydroxides with the formation of salts and water:

$$3N_2O_5 + 2Al(OH)_3 \rightarrow 2Al(NO_3)_3 + 3H_2O.$$

5. Interaction in solutions with average salts of the corresponding acids with the formation of acid salts (if possible):

$$CO_2 + CaCO_3 + H_2O \rightarrow Ca(HCO_3)_2.$$

6. Participation in red-ox reactions:

$$C^{+4}O_2 + C^0 \rightarrow 2C^{+2}O;$$
$$4Cr^{+6}O_3 + C^{-4}{}_2H_5OH \rightarrow 2Cr^{+3}{}_2O_3 + 2C^{+4}O_2 + 3H_2O;$$
$$S^{+4}O_2 + 2H_2S^{-2} \rightarrow 3S^0 + 2H_2O;$$
$$Mn^{+4}O_2 + 4HCl^{-1} \rightarrow Mn^{+2}Cl_2 + Cl^0{}_2 + 2H_2O.$$

Amphoteric oxides, depending on conditions, exhibit the properties of basic or acidic oxides. They are formed only by metals of secondary subgroups that are in intermediate oxidation states, as well as beryllium Be and aluminum Al. In amphoteric oxides, an ionic-covalent chemical bond is realized. Under normal conditions they are all solids.

The chemical properties of amphoteric oxides include the properties of both acidic and basic oxides.

1. They do not react with water. Therefore, amphoteric hydroxides are obtained by other methods (as it shown in the section on amphoteric hydroxides).

2. Like basic oxides, they react with acids and acidic oxides to form salts:

$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O;$$
$$Cr_2O_3 + 3SO_3 \rightarrow Cr_2(SO_4)_3.$$

3. Like acidic oxides, they react in the melt with bases and basic oxides to form salts:

$$ZnO + 2KOH \rightarrow K_2ZnO_2 + H_2O;$$
$$Al_2O_3 + Na_2O \rightarrow 2Na_2AlO_2.$$

Water can also be considered an amphoteric oxide, since upon dissociation it forms H^+ and OH^- ions:

$$H_2O \leftrightarrow H_+ + OH^- \text{ or } H_2O + H_2O \leftrightarrow H_3O^+ + OH^-.$$

and reacts with acidic and basic oxides to form acids or bases, respectively.

The use of oxides is considered in the study of the chemistry of elements.

5.3. Bases

Bases are compounds consisting of a metal atom and a hydroxyl group.

The systematic names of bases and amphoteric hydroxides are compiled similarly to the names of the corresponding oxides – from the name of the element (indicate its oxidation state if necessary) and the word hydroxide (the name of the OH^- anion): NaOH is sodium hydroxide, $Ca(OH)_2$ is calcium hydroxide, Fe $(OH)_3$ is iron(III) hydroxide.

For some bases, trivial (historical) names have been preserved: NaOH is called caustic soda, caustic soda, KOH is caustic alkali, $Ca(OH)_2$ is slaked lime.

All bases are solids. Water-soluble bases are called alkalis (hydroxides of alkali and alkaline earth metals). These are ionic compounds. The remaining bases are insoluble in water, and the bonds in them are covalent-ionic.

The main methods for producing oxides

1. Interaction of active metals with water:

$$2K + 2H_2O \rightarrow 2KOH + H_2;$$
$$Ba + 2H_2O \rightarrow Ba(OH)_2 + H_2.$$

2. Interaction of active metal oxides with water:

$$Na_2O + H_2O \rightarrow 2NaOH;$$
$$CaO + H_2O \rightarrow Ca(OH)_2.$$

3. Electrolysis of aqueous solutions of salts of active metals:

$$2NaCl + 2H_2O \rightarrow 2NaOH + Cl_2 + H_2.$$

Only alkalis can be obtained by these methods.

4. Interaction of salts with aqueous solutions of alkalis:

$$CuSO_4 + 2NaOH \rightarrow Cu(OH)_2 + Na_2SO_4;$$
$$Fe(NO_3)_3 + 3KOH \rightarrow Fe(OH)_3 + 3KNO_3;$$

$$K_2SO_4 + Ba(OH)_2 \rightarrow 2KOH + BaSO_4.$$

Insoluble bases can be obtained in this way. Alkalis can be obtained provided that a poorly dissociated (water, gas) compound is formed in the reaction.

Note that none of the listed methods makes it possible to obtain the hydroxides $AgOH$ and $Hg(OH)_2$, since they immediately decompose into the corresponding oxide and water:

$$2AgNO_3 + 2NaOH \rightarrow Ag_2O\downarrow + 2NaNO_3 + H_2O.$$

The **chemical properties of bases** are mainly explained by their ability to decompose into a metal ion and a hydroxyl group.

1. In aqueous solutions, water-soluble bases (alkalis) dissociate almost completely:

$$MeOH \leftrightarrow Men^{+} + OH^{-},$$

and due to the formation of OH^{-} ions, they change the color of the indicators (see pH), insoluble bases do not change the color of the indicator.

2. They react with aqueous solutions of acids to form salts and water. This reaction in the case of using alkalis is called a neutralization reaction:

$$Fe(OH)_2 + H_2SO_4 \rightarrow FeSO_4 + 2H_2O;$$
$$NaOH + HCl \rightarrow NaCl + H_2O.$$

When using polyacid bases ($Ca(OH)_2$, $Ba(OH)_2$) or polybasic acids (H_2SO_4, H_3PO_4) in this reaction, depending on the ratio of the reagents, the formation of medium, acidic or basic salts is possible (see Salts).

3. Alkalis react with amphoteric hydroxides to form complex compounds (see Complex compounds):

$$NaOH + Al(OH)_3 \rightarrow Na[Al(OH)_4].$$

With an excess of alkali, the same reaction will take a different path:

$$3NaOH + Al(OH)_3 \rightarrow Na_3[Al(OH)_6].$$

However, in a melt (without an aqueous medium), the same reaction will occur with the separation of water:

$$NaOH + Al(OH)_3 \rightarrow NaAlO_2 + 2H_2O;$$
$$3NaOH + Al(OH)_3 \rightarrow Na_3AlO_3 + 3H_2O.$$

The products of these reactions can be understood as salts of metaaluminate ($HAlO_2$) and orthoaluminate (H_3AlO_3) acids, respectively.

4. When alkalis fuse with amphoteric oxides, salt and water are formed:

$$2KOH + Al_2O_3 \rightarrow 2KAlO_2 + H_2O;$$
$$6KOH + Al_2O_3 \rightarrow 2K_3AlO_3 + 3H_2O.$$

5. Alkalis react with acid oxides to form salts and water:

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$
$$6KOH + P_2O_5 \rightarrow 2K_3PO_4 + 3H_2O$$

With an excess of acidic oxide in the case of multivalent alkalis, the formation of acidic salts is possible:

$$Ca(OH)_2 + CO_2 \rightarrow Ca(HCO_3)_2.$$

6. Alkalis react with salts provided that one of the reaction products (precipitate or gas) leaves the reaction medium:

$$3NaOH + FeCl_3 \rightarrow Fe(OH)_3\downarrow + 3NaCl;$$
$$Ca(OH)_2 + 2NH_4Cl \rightarrow CaCl_2 + 2NH_3\uparrow + 2H_2O.$$

With a lack of alkali, the formation of basic salts is possible (see Salts).

7. When heated, metal hydroxides decompose into the corresponding oxides and water:

$$Ca(OH)_2 \rightarrow CaO + H_2O;$$
$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O.$$

Alkali metal hydroxides do not decompose even when melted.

5.4. Acids

Acids are compounds in which the hydrogen atoms included in their composition can be replaced by metal atoms to form salts:

$$2HCl + 2Na \rightarrow 2NaCl + H_2;$$
$$H_2SO_4 + Fe \rightarrow FeSO_4 + H_2.$$

Acids are classified according to various criteria (Fig 5.2).

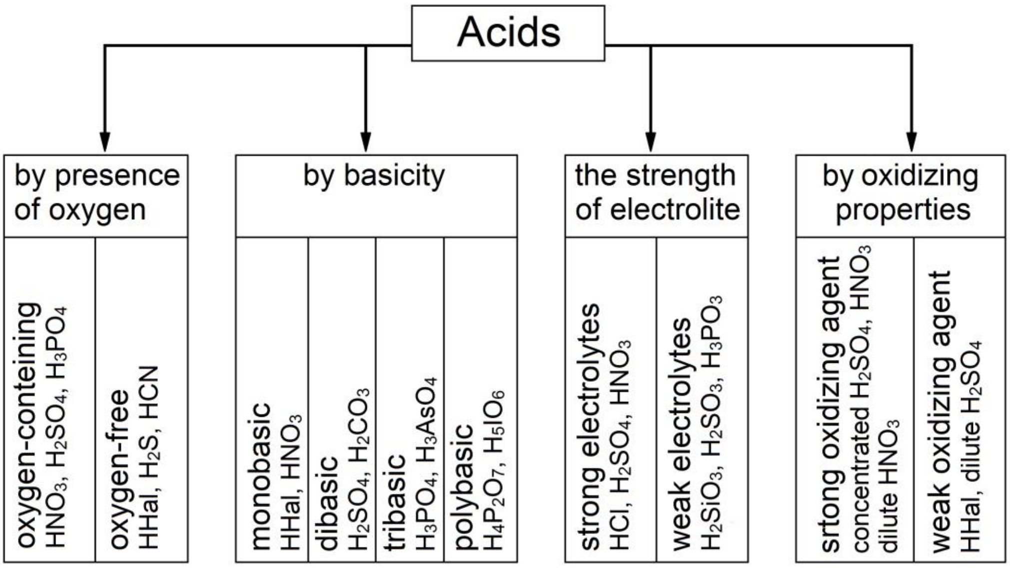


Fig. 5.2. Classification of inorganic acids

There are two common types of acid nomenclature: chemical (systematic or rational) and trivial. The first is most often used in scientific literature, and the second in industry and common life. There is no clear division of areas of their use.

According to the modern Ukrainian chemical nomenclature, the systematic names of acids consist of two words, the second of which is acid. The root of the first word comes from the name of the acid-forming element with the addition of the suffix -at- (nitric acid HNO_3 – a compound of Nitrogen N, carbonic acid H_2CO_3 – a compound of Carbon C, etc.). In the case of an oxygen-containing acid, this word may include an indicator of the degree of oxidation of the element. If the element that forms the acid is in the maximum degree of oxidation, it is usually not indicated ($H_2S^{+6}O_4$ – sulfuric acid), otherwise the degree of oxidation is indicated in parentheses ($H_2S^{+4}O_3$ – sulfuric (IV) acid).

The first word of the name of an oxygen-free acid comes from the name of the element with the addition of the suffix -id- (sulfuric acid H_2S, iodide acid HI).

Rational names have been preserved for some of the most important acids along with systematic names. In these names, different degrees of oxidation of elements that form acids are indicated by prefixes and/or suffixes: $H_3P^{+3}O_3$ is phosphate, $H_3P^{+5}O_4$ is orthophosphate, $H_2S^{+4}O_3$ is sulfite, $H_2S^{+6}O_4$ is sulfate, $HCl^{+1}O$ – hypochlorite, $HCl^{+3}O_2$ is chloric acid, $HCl^{+5}O_3$ is chlorate acid, and $HCl^{+7}O_4$ is perchlorate acid.

Graphic formulas of acids, which show the relative positions of atoms and bonds, show several patterns. In oxygen-containing acids, Hydrogen atoms are connected to the atom of the acid-forming element through Oxygen atoms. In oxygen-containing acids, the molecules of which contain 2 or more atoms of the acid-forming element, these atoms are connected through oxygen atoms (Fid 5.3):

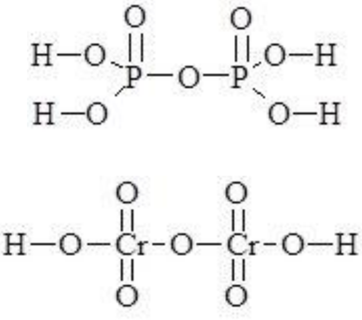


Fig. 5.3. Graphic formulas of $H_4P_2O_7$ and $H_2Cr_2O_7$

It should be remembered that the number of hydrogen atoms does not always coincide with the basicity of the acid, since basicity is determined only by the hydrogen atoms bonded to the central atom through oxygen.

This is shown even more clearly in the molecules of higher carboxylic acids, which contain a lot of hydrogen atoms, but are monobasic: oleic acid $C_{17}H_{33}COOH$, stearic acid $C_{17}H_{35}COOH$.

The main methods for producing acids

1. Oxygen-free acids can be synthesized by direct interaction of a non-metal with hydrogen:

$$H_2 + Hal_2 \rightarrow 2HHal;$$
$$H_2 + S \rightarrow H_2S.$$

2. Oxygen-containing acids are formed by the interaction of acidic oxides (anhydrides) with water:

$P_2O_5 + H_2O \rightarrow H_3PO_4$;
$SO_3 + H_2O \rightarrow H_2SO_4$;
$ClO_2 + H_2O \rightarrow HClO + HClO_2$.

3. Acids whose anhydrides do not react with water are obtained from their salts by exchange reactions:

$Na_2SiO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2SiO_3$.

Some other acids can also be obtained in this way, provided that the reaction produces gaseous, sparingly soluble or difficultly dissociated compounds:

$NaCl_{(t)} + H_2SO_{4(t)} \rightarrow HCl + NaHSO_4$;
$FeS + 2HCl \rightarrow FeCl_2 + H_2S$.

4. Anoxic and oxygen-containing acids can be obtained by hydrolysis of the corresponding halogens or anhydrides:

$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$;
$POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$;
$PBr_3 + 3H_2O \rightarrow H_3PO_3 + 3HBr$;
$SO_2Cl_2 + 2H_2O \rightarrow H_2SO_4 + 2HCl$;
$P_2S_3 + 6H_2O \rightarrow 2H_3PO_3 + 3H_2S$;
$P_2S_5 + 8H_2O \rightarrow 2H_3PO_4 + 5H_2S$.

5. Some acids can be obtained by red-ox reactions:

$Cl_2 + H_2O_{(hot)} \rightarrow HCl + HClO_3$;
$Cl_2 + H_2O_{(cold)} \rightarrow HCl + HClO$;
$3P + 5HNO_3 + 2H_2O \rightarrow 3H_3PO_4 + 5NO$;
$S + 2HNO_3 \rightarrow H_2SO_4 + 2NO$.

Under normal conditions, acids are solids (silicate H_2SiO_3, borate H_3BO_3, orthophosphate H_3PO_4) or liquids (sulfate H_2SO_4, nitrate HNO_3). As a rule, acids are highly soluble in water (except H_2SiO_3). Aqueous solutions of gaseous hydrogen compounds with some non-metals (HHal, H_2S, HCN) are also acids.

Acid solutions have a sour taste, are corrosive, and corrode fabric and skin.

The **chemical properties of acids** can be divided into two groups:

The first, common to all acids, is associated with the presence of hydronium ions H_3O^+ in their solutions.

The second, specific, characteristic of specific acids (in particular, qualitative reactions), taken into account when studying the corresponding elements.

Here we consider only those common to all acids.

The H^+ ion, which is necessarily present in aqueous solutions of all acids in the form of H_3O^+, can, on the one hand, enter into red-ox reactions, being reduced to molecular hydrogen H_2, and on the other hand, it can interact with negatively charged or neutral particles, which have lone pairs of electrons (acid-base interaction).

Red-ox reactions are the interaction of acids with metals, which stand next to Hydrogen in the series of standard electrode potentials:

$$2Me + 2nH^+ \rightarrow 2Me^{n+} + nH_2.$$

All non-oxidizing acids react according to this scheme.

Acid-base reactions occur with basic oxides and bases, and also with average, basic and sometimes with acidic salts with the formation of new salts:

$$H_2SO_4 + CaO \rightarrow CaSO_4\downarrow + H_2O;$$
$$HCl + NaOH \rightarrow NaCl + H_2O;$$
$$2HNO_3 + BaCO_3 \rightarrow Ba(NO_3)_2 + CO_2\uparrow + H_2O;$$
$$4HBr + (CuOH)_2CO_3 \rightarrow 2CuBr_2 + CO_2\uparrow + 3H_2O;$$
$$H_2SO_4 + 2KHSO_3 \rightarrow K_2SO_4 + 2SO_2\uparrow + 2H_2O.$$

Polybasic acids, which are in excess in the reaction mixture, react with medium salts to form acid salts:

$$Ca_3(PO_4)_2 + 4H_3PO_4 \rightarrow 3Ca(H_2PO_4)_2;$$
$$KOH + H_2SO_4 \rightarrow KHSO_4 + H_2O.$$

A special case of acid-base interactions are color reactions with indicators.

When heated, oxygen-containing acids split water to form anhydrides:

$$2H_3PO_4 \rightarrow P_2O_5 + 3H_2O;$$
$$4HNO_3 \rightarrow 4NO_2 + 2H_2O + O_2.$$

5.5. Amphoteric hydroxides

Along with typical bases and acids, there is a large group of hydroxides that can react with acids (show the properties of bases) or with bases (show acidic properties) to form salts and water – these are amphoteric hydroxides.

They include hydroxides of metals of the main subgroups (beryllium Be, aluminum Al) and many metals of secondary subgroups of the Periodic Table, which are in intermediate oxidation states: $Be(OH)_2$, $Al(OH)_3$, $Zn(OH)_2$, $Cr(OH)_3$, $Pb(OH)_2$, etc.

For example, the amphotericity of zinc hydroxide $Zn(OH)_2$ is shown in its dissociation diagram (Fig 5.4).

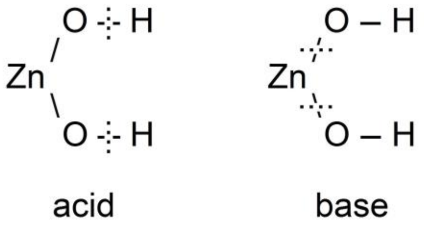


Fig. 5.4. Scheme of $Zn(OH)_2$ dissociation

$$Zn(OH)_2 \leftrightarrow [ZnOH]^+ + OH^- \leftrightarrow Zn^{2+} + 2OH^-;$$
$$H_2ZnO_2 \leftrightarrow HZnO_2^- + H^+ \leftrightarrow ZnO_2^{2-} + 2H^+.$$

Due to the same amount of H^+ and OH^- ions formed, amphoteric hydroxides do not change the color of the indicators.

Amphoteric hydroxides are prepared in the same way as water-insoluble bases, by reacting salts with alkalis:

$$Al_2(SO_4)_3 + 6NaOH \rightarrow 2Al(OH)_3 + 3Na_2SO_4.$$

The resulting amphoteric hydroxide can dissolve in excess alkali.

$$NaOH + Al(OH)_3 \rightarrow Na[Al(OH)_4].$$

To prevent this, it is taken in smaller quantities than calculated.

The **chemical properties of amphoteric hydroxides** include those of both acids and bases.

1. Acidic properties are revealed in reactions with aqueous solutions of alkalis:

$$H_2ZnO_2 + 2NaOH \rightarrow Na_2[Zn(OH)_4].$$

The reaction can also occur in the melt state:

$$H_2ZnO_2 + 2NaOH \rightarrow Na_2ZnO_2 + 2H_2O.$$

2. The main properties are revealed in reactions with acids:

$$Zn(OH)_2 + HCl \rightarrow ZnCl_2 + 2H_2O.$$

This can be represented schematically as the transformation of $Zn(OH)_2$ in aqueous solutions depending on the pH of the medium:

$$\text{In } H^+ \ [Zn(H_2O)_4] \leftrightarrow Zn(OH)_2 \leftrightarrow [Zn(OH)_4]^{2-} \text{ in } OH^-.$$

Amphoteric hydroxides are not very strong as acids or bases, and their strength in these cases may vary. When heated, they tend to decompose relatively.

5.6. Salts

Salts are compounds formed by cations of metals (Me^{n+}) or ammonia NH^{4+} and anions of acidic residues An^{m-}: Me_mAn_n, where *n* and *m* are the charges of the cation and anion, respectively.

The classification of salts is based on the fact that salts can be considered as products of the replacement of hydrogen atoms in acid molecules with metal cations (ammonia), or as a product of the replacement of hydroxyl groups in bases with anions of acid groups (Fig5.1).

If these replacement is complete, normal (average) salts are formed:

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O.$$
$$Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O.$$

Simple salts also include metal peroxides (Na_2O_2, BaO_2), binary compounds of metals with nonmetals (except oxides), mixed oxides (Fe_3O_4or $Fe(FeO_2)_2$, Pb_3O_4or $Pb(PbO_2)_2$, etc.).

In the case of incomplete replacement of hydrogen atoms in an acid molecule, acidic salts are formed:

$$H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O.$$

Acidic salts form only polybasic acids (H_2CO_3, $H_2C_2O_4$, H_2SO_4, H_2S, H_3PO_4, etc.).

In the case of incomplete replacement of hydroxo groups in the base molecule, basic salts are formed:

$$Al(OH)_3 + 2HCl \rightarrow (AlOH)Cl_2 + 2H_2O.$$

Basic salts form only polyacidic bases ($Ca(OH)_2$, $Al(OH)_3$, $Fe(OH)_2$, $Fe(OH)_3$, etc.).

Mixed salts are formed by one metal cation and anions of different acids:

$$Ca(OH)(OCl) + HCl \rightarrow Ca(OCl)Cl + H_2O.$$

Double salts are formed by different cations and anion of the same acid:

$$KHSO_4 + NaOH \rightarrow KNaSO_4 + H_2O.$$

A special type of salts are complex compounds, discussed below.

Salt nomenclature uses the name of the salts from the constituent parts in the formula: first the name of the cation, then the name of the anion in general. For example, NaCl is sodium chloride, and CaS is calcium sulfide.

In the case of metal cations with variable valence, after their name in the genitive case, the valency of the cation is indicated in parentheses in Roman numerals. For example, $FeSO_4$ is iron (II) sulfate, $CrCl_3$ is chromium (III) chloride.

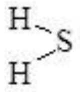
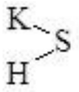
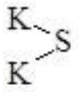
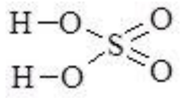
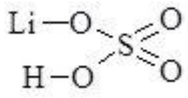
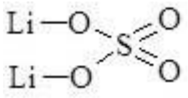
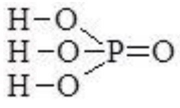
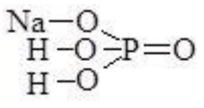
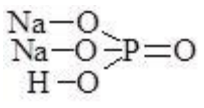
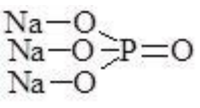
The prefix hydrogen is used in the names of acid salts indicating the number of hydrogen atoms. For example, $NaHCO_3$ is sodium bicarbonate, and $Ca(H_2PO_4)_2$ is calcium dihydrogen phosphate.

The names of cations or anions of double or mixed salts are given in the order in which they are written in the formula. For example, $KAl(SO_4)_2$ is potassium aluminum sulfate, $NH_4Fe(SO_4)_2$ is iron(III) ammonium sulfate, Ca(OCl)Cl is calcium hypochlorite chloride, and BiSCl is bismuth(III) sulfide chloride.

When writing graphic formulas of salts, the graphic formulas of the corresponding acids are taken as a basis, replacing the hydrogen atoms in them with metal cations (Table 4.2).

Table 5.2

Graphic formulas of some salts

Acid	Graphic formula	Acidic salt		Averege salt
H_2S				
H_2SO_4				
H_3PO_4				

The main methods for producing salts

The most important reactions for obtaining salts are considered when describing oxides, bases, and acids.

1. Salts can be obtained by interaction simple metal and non-metal substances:

$$2K + Cl_2 \rightarrow 2KCl;$$
$$Fe + S \rightarrow FeS.$$

2. By interaction metals with acids:

$$Mg + 2HCl \rightarrow MgCl_2 + H_2;$$
$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2.$$

3. By interaction metals with salts:

$$Cu + HgCl_2 \rightarrow CuCl_2 + Hg\downarrow;$$
$$Fe + CuSO_4 \rightarrow FeSO_4 + Cu\downarrow.$$

4. By interaction salt with salts:

$$Ba(NO_3)_2 + Na_2SO_4 \rightarrow BaSO_4\downarrow + 2NaNO_3;$$
$$NH_4Cl + AgNO_3 \rightarrow NH_4NO_3 + AgCl\downarrow.$$

5. By interaction salts with bases:

$$CuSO_4 + 2NaOH \rightarrow Cu(OH)_2\downarrow + Na_2SO_4;$$
$$FeCl_3 + 3KOH \rightarrow Fe(OH)_3\downarrow + 3KCl.$$

6. By interaction salts with acids:

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2\uparrow + H_2O;$$
$$FeS + 2HNO_3 \rightarrow Fe(NO_3)_2 + H_2S\uparrow.$$

7. By thermal decomposition of salts:

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2\uparrow;$$
$$2KNO_3 \rightarrow 2KNO_2 + O_2\uparrow.$$

There are still many ways to obtain salts, but when choosing one method or another, one should first of all take into account its rationality.

Acidic salts are obtained by the same methods as medium ones, but at the same time they take a significant excess of the acid component:

$$NaOH + H_2SO_4 \rightarrow NaHSO_4 + H_2O;$$
$$Ca(OH)_2 + CO_2 \rightarrow Ca(HCO_3)_2.$$

By acting on an averege salt with an acid, you can turn it into an acidic one:

$$K_3PO_4 + 2H_3PO_4 \rightarrow 3KH_2PO_4;$$
$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl.$$

Basic salts are obtained similarly, but in excess they take the base:

$$Ca(OH)_2 + HCl \rightarrow Ca(OH)Cl;$$
$$2Cu(OH)_2 + CO_2 \rightarrow (CuOH)_2CO_3 + H_2O.$$

By acting a base on average salt, it can be turn it into a basic one:

$$Al_2(SO_4)_3 + 2NaOH \rightarrow 2Al(OH)(SO_4) + Na_2SO_4;$$
$$Bi(NO_3)_3 + 2KOH \rightarrow Bi(OH)_2NO_3 + 2KNO_3.$$

Double salts are prepared by the action of another acid on a basic salt:

$$Ca(OH)Cl + HClO \rightarrow Ca(OCl)Cl + H_2O.$$

Mixed salts are formed by the action of acid salts of other bases:

$$KHSO_4 + NaOH \rightarrow KNaSO_4 + H_2O.$$

The physical properties of salts are generally similar. Under normal conditions, all salts are crystalline solids with high melting points. The type of chemical bond in them is ionic. The color of the salts varies from colorless to dark brown.

According to their solubility in water, they are easily soluble ($NaCl$, NH_4NO_3), poorly soluble ($PbCl_2$, $CaSO_4$) and insoluble ($AgCl$, $CaCO_3$, $BaSO_4$).

The **chemical properties of salts** are very diverse. They interact with metals, non-metals, acids, bases and each other. These reactions are taken into account when studying methods for producing salts.

A very important chemical property is the **hydrolysis of salts**, that is, decomposition under the influence of water.

Pure water has a neutral environment, aqueous solutions of acids create an acidic environment, and bases create an alkaline environment.

Aqueous solutions of salts have different effects on the environment. Solutions of salts that are formed by strong acids and weak bases have an acidic environment. Conversely, solutions of salts that are formed by weak acids and strong bases (alkalis) have an alkaline environment.

Salts formed by both weak ones decompose completely. However, salts formed by both strong ones do not hydrolyze at all.

For example:

$$CuCl_2 + 2H_2O \leftrightarrow Cu(OH)_2\downarrow + 2HCl;$$
$$K_2S + 2H_2O \leftrightarrow H_2S + 2KOH.$$

These reactions are reversible and occur only partially.

Salts formed by a weak acid and a weak base (CaC_2, Ca_3P_2, Al_2S_3, $(NH_4)_2CO_3$, NH_4CN, CH_3COONH_4) hydrolyze irreversibly:

$$Al_2S_3 + 6H_2O \rightarrow 2Al(OH)_3\downarrow + 3H_2S;$$
$$CH_3COONH_4 + H_2O \rightarrow CH_3COON + NH_4OH.$$

5.7. Complex compounds

As mentioned earlier, as a result of some reactions, compounds are formed whose structure and properties are clearly not included in the classes of inorganic substances we have considered so far.

These substances are complex compounds. They are formed by the interaction of such inorganic substances as salts, acids, and bases:

$$FeCl_2 + 6KCN \rightarrow K_4[Fe(CN)_6] + 2KCl;$$
$$Al(OH)_3 + 3NaOH \rightarrow Na_3[Al(OH)_6];$$
$$AgNO_3 + 2NH_3 \rightarrow [Ag(NH_3)_2]NO_3;$$
$$Au + HNO_3 + 4HCl \rightarrow H[AuCl_4] + NO + 2H_2O.$$

The foundations of the doctrine of complex compounds were laid by Werner in 1893.According to his coordination theory, every complex compound contains a complex ion formed by a central atom, called a complexing agent, and surrounding neutral molecules or ions called ligands.The total number of bonds of the central atom with ligands is its coordination number (Fig. 5.5). The complexing agent and ligands form the inner sphere of the complex, or complex ion, which is indicated in square brackets when written. Outside the complex ion there is an outer sphere formed by cations or anions. There are complex compounds without an outer sphere.

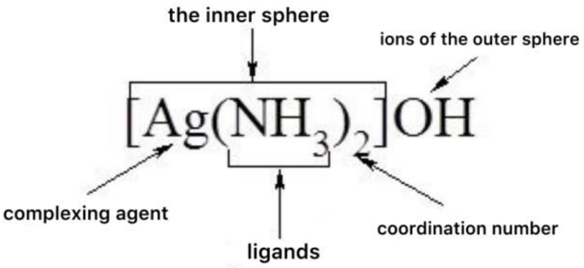


Fig. 5.5. Scheme of complex compounds name

Their modern definition is based on the structure of complex compounds.

Complex compounds are called complex compounds that contain a complex ion consisting of complexing agents and ligands and capable of independent existence in solution and/or in melt.

Typical complexing agents are *d*- and *f*-elements and their cations: Cr, Fe, Mn, Ag^{+}, Cu^{2+}, Hg^{2+}, Zn^{2+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, Co^{3+}, Ni^{2+}, Pt^{4+}, etc.

Cations of *s*- and *p*-elements (Be^{2+}, Al^{3+}, Sn^{4+}, Pb^{4+}) and atoms of nonmetals (N, P, Si, B) can also be complex formers.

Ligands can be neutral molecules (H_2O, CO, NH_3, C_6H_6) or acid anions. The ligand must contain an atom with an unshared electron pair.

The inner sphere of complex compounds can be neutral or charged (positive or negative):

$[Ni(CO)_4]$ – neutral inner sphere,

$K_4[Fe(CN)_6]$ – negatively charged inner sphere (complex anion),

$[Ag(NH_3)_2]Cl$ – positively charged inner sphere (complex cation).

If the inner sphere is neutral, there is no outer sphere. If it is charged, then the outer sphere has the same charge, opposite in sign. Most often, the outer sphere is formed by cations of alkaline and alkaline earth metals, ammonium, anions of oxygen-free and oxygen-containing acids, hydroxo groups of OH^{-}.

Let us consider the mechanism of formation of chemical bonds between the complexing agent and ligands using the example of $[Zn(NH_3)_4]Cl_2$.

The structure of the outer electronic level of the Zn atom is represented by the formula $3d^{10}4s^2$, and that of the Zn^{2+} ion by $3d^{10}4s^0$:

$K_4[Fe(CN)_6]$ – negatively charged inner sphere (complex anion),

$[Ag(NH_3)_2]Cl$ – positively charged inner sphere (complex cation).

If the inner sphere is neutral, there is no outer sphere. If it is charged, then the outer sphere has the same charge, opposite in sign. Most often, the outer sphere is formed by cations of alkaline and alkaline earth metals, ammonium, anions of oxygen-free and oxygen-containing acids, hydroxo groups of OH^-.

Let us consider the mechanism of formation of chemical bonds between the complexing agent and ligands using the example of $[Zn(NH_3)_4]Cl_2$ (Fig 5.6).

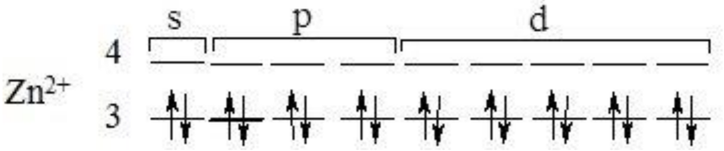


Fig. 5.6. Scheme of complexing agent Zn^{2+} electron structure

The outer electronic level of the Zn^{2+} ion has free orbitals that can be involved in the formation of chemical bonds by the donor-acceptor mechanism. One s- and three p-orbitals of the fourth electronic level of the Zn^{2+} ion are used to form four such bonds.

NH_3 molecules (ligands) carry a lone pair of electrons on the nitrogen atom, which they provide as donors for the formation of bonds with the Zn^{2+} ion, that is, the acceptor.

Thus, four bonds arise between Zn^{2+} ions and NH_3 molecules according to the donor-acceptor mechanism (Fig. 5.7).

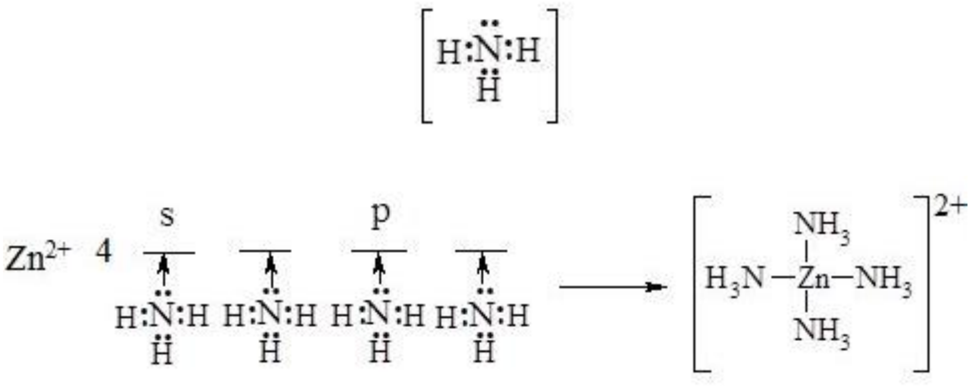


Fig. 5.7. Scheme of ligand NH_3 structure

By this mechanism, bonds are formed in all complex compounds. The connection between the inner and outer spheres is carried out by the ionic mechanism.

In aqueous solutions, complex compounds (except those consisting only of the inner sphere) almost completely dissociate and are strong electrolytes:

$$K_2[PtCl_6] \leftrightarrow 2K^+ + [\ PtCl_6]_2^-;$$
$$[Ag(NH_3)_2]Cl \leftrightarrow [Ag(NH_3)_2]^+ + Cl^-.$$

Complex ions dissociate to a very small extent by the first degree, and by each subsequent one even less:

First stage: $[Ag(NH_3)_2]^+ \leftrightarrow [Ag(NH_3)]^+ + NH_3$;
Second stage: $[Ag(NH_3)]^+ \leftrightarrow Ag^+ + NH_3$.

The coordination formula of a complex compound can be determined using double exchange reactions. Thus, Platinum Pt forms complex compounds of the composition $PtCl_4{\cdot}6NH_3$, $PtCl_4{\cdot}4NH_3$, $PtCl_4{\cdot}2NH_3$, $PtCl_4{\cdot}2KCl$. If $AgNO_3$ is applied to solutions of these compounds, then an AgCl precipitate is formed only in the first two cases, and in the second – only 1/2 chlorine. It is obvious that in the compound $PtCl_4{\cdot}6NH_3$ all chlorine atoms are contained in the outer sphere, and its formula is $[Pt(NH_3)_6]Cl_4$. Similarly, $PtCl_4{\cdot}4NH_3$ contains two chlorine atoms in the outer sphere and its formula is $[Pt(NH_3)_4Cl_2]Cl_2$. The compound $PtCl_4{\cdot}2NH_3$ has the formula

$[Pt(NH_3)_6Cl_4]$. K^+ ions can be detected in the $PtCl_4{\cdot}2KCl$ solution, that is, its formula is $K_2[PtCl_6]$.

The great role of natural complex compounds in the processes of photosynthesis (chlorophyll is a complex compound of magnesium), biological oxidation, respiration and enzymatic catalysis (hemoglobin is a complex compound of Ferrum (III)). Vitamin B_{12} is a complex compound of cobalt (II).

Test questions

1. What are oxides? What groups are oxides classified into? What compounds do amphoteric oxides interact with?
2. How are bases classified? Supply examples of chemical reactions for properties of amphoteric hydroxides.
3. How are acids classified? Supply examples of obtaining acids (laboratory methods).
4. How obtain acidic and basic salts with chemical reactions? Supply few examples.
5. Write all possible chemical reactions between magnesium hydroxide and orthophosphoric acid.
6. What are peroxides? Supply some examples of such compounds.
7. Write the structural formulas of the following compounds: Cr_2O_3, $Ba(OH)_2$, H_3PO_4, $Al_2(SO_4)_3$, $NaHCO_3$, $KMnO_4$.

Chapter 6. Thermo-chemistry and chemical thermodynamics

6.1. Basic concepts of thermodynamics

Thermodynamics studies the mutual transformations of different types of energy, in connection with the transfer of energy between them in the form of heat and work. One of the terms often used in thermodynamics is **system**. This word refers to a body or a group of interacting bodies that are conditionally separated from the environment. If in a system there is no interface, then the system is called homogeneous. If a system consists of two or more parts, separated from each other, such a system is called heterogeneous. A system that does not interact either materially or energetically with the environment, that is, the energy and volume in it are constant, is called isolated. An open thermodynamic system is a system that interacts with its environment.

The terms **component** and **phase** are also commonly used.

In thermodynamics, a component is one of a collection of chemically independent constituents of a system. The number of components represents the minimum number of independent chemical species necessary to define the composition of all phases of the system.

A phase is a region of material that is chemically uniform, physically distinct, and (often) mechanically separable. In a system consisting of ice and water in a glass jar, the ice cubes are one phase, the water is a second phase, and the humid air is a third phase over the ice and water. The glass of the jar is another separate phase.

A phase transition (or phase change) is the physical process of transition between one state of a medium and another. Commonly the term is used to refer to changes among the basic states of matter: solid, liquid, and gas. A phase of a thermodynamic system and the states of matter have uniform physical properties. During a phase transition of a given medium, certain properties of the medium change as a result of the change of external conditions, such as temperature or pressure. This can be a discontinuous change. For example, a liquid may become gas upon heating to its boiling point, resulting in an abrupt change in volume. The identification of the external conditions at which a transformation occurs defines the phase transition point.

Of course, not every impact leads to a phase transition. However, the impact necessarily leads to changes in the system. These changes are reflected using certain characteristics, which are called system parameters. These include temperature, volume, pressure and many others.

The most fundamental parameter is the internal energy of the system.

The internal energy of a thermodynamic system is the energy contained within it, measured as the quantity of energy necessary to bring the system from its standard internal state to its present internal state of interest, accounting for the gains and losses of energy due to changes in its internal state. It includes the thermal energy, that is the constituent particles kinetic energies of motion. The internal energy of an isolated system never be change.

The internal energy of a thermodynamic system is the energy contained within it, measured as the quantity of energy necessary to bring the system from its standard internal state to its present internal state of interest, accounting for the gains and losses of energy due to changes in its internal state. It includes the thermal energy, that is the constituent particles kinetic energies of motion. The internal energy of an isolated system never be change.

Thermodynamics defines internal energy macroscopically, for the body as a whole. It cannot be measured absolutely. However it can be measured in changes in the internal energy. The processes that change the internal energy are transfers, into or out of the system, of matter, or of energy, as heat, or by thermodynamic work. The internal energy depends only on the internal state of the system and not on the particular choice from many possible processes by which energy may pass into or out of the system.

The unit of energy in the International System of Units is the joule (J). The internal energy relative to the mass with unit J/kg is the specific internal energy. The corresponding quantity relative to the amount of substance with unit J/mol is the molar internal energy.

The characterization of processes that occur in systems is based on universal fundamental principles, which are called the laws of thermodynamics. They state empirical facts, but also form the basis of calculations.

Thermodynamics studies processes as phenomena that lead to changes in parameters. The thermodynamics parameters ones are temperature (T), pressure (p), volume (V), and concentration. They are all related to each other and to more fundamental quantities, such as internal energy and others, which will be discussed later. Since processes in which all parameters change simultaneously are very difficult to describe, simpler ones are often distinguished, where one or more parameters are constants. For example, a process in which the temperature does not change (T = const) is called isothermal. A process in which the volume does not change (V = const) is called isochoric. A process in which the pressure is constant (p = const) is called isobaric. The latter case is often encountered in chemistry, since most chemical reactions are been in an open glasses, at a pressure of one atmosphere.

6.2. First law of thermodynamics

The first law of thermodynamics is a special case of the law of conservation of energy at rest it is related to the processes that are accompanied by work and allocation, absorption or by reproducing heat. The law of conservation of energy says that it is impossible to build a machine that you I would do a job out of nothing. Such a machine is called a perpetual motion machine of the first kind.

It is impossible to create a machine that would produce the effect of work without the expenditure of energy. This consequence of the law of conservation of energy is called the first law of thermodynamics.

Based on the law of conservation of energy, the first law of thermodynamics can also be formulated as follows: with all possible mutual transformations of different types of energy, the transition of energy of one type to another occurs in strictly equivalent quantities.

The internal energy of an isolated system is a constant value.

The first law of thermodynamics establishes the relationship between heat Q, energy ΔU and work A create by the system:

$$\Delta U = Q - A,$$

or

$$Q = \Delta U + A.$$

By internal energy of a system we mean the sum of the potential energy of interaction of all parts of the body with each other and the kinetic energy of their movement. It consists of the energy of rotational and translational motion of molecules, the energy of intramolecular vibrational motion of atoms and their groups, the formation of molecules, the energy of rotation of electrons in atoms, nuclear energy, the energy of atoms, and the energy of intermolecular interaction. interaction, etc. Internal energy is the total energy reserve of a system without taking into account the kinetic energy of the system as a whole and its positional potential energy.

The absolute values of internal energy are unknown, but it is important to know its change. Thermodynamic functions, the values of which depend only on the state of the system, are called state change functions. Internal energy is a function of the state, its change in the process is recognized both in this state U_2 and in the initial state U_1:

$$\Delta U = U_1 - U_2.$$

The change in internal energy during its transition from one object to another can be considered in the form of two parts. One of them is the form of energy transfer due to chaotic motion and the collision of molecules of two bodies. The measure of such energy is heat. The second part includes forms of energy transfer as a result of the ordered movement of objects under the influence of any forces. The measure of this energy is work.

The work is done in various ways, but it always has external signs. Of the various types of work, work against the external environment, which creates pressure, that is, expansion work, is of particular importance in thermodynamics. In chemical reactions, the only effective force is the external pressure p when the volume changes ΔV (expansion). Based on this, we can calculate the amount of work A:

$$A = p\Delta V = p(\,V_2 - V_1).$$

Based on the fact that in an isobaric process p = const, the heat supplied to the system is equal to:

$$Q = \Delta U + p\Delta V;$$
$$Q = (U_2 - U_1) + (p\Delta V_2 - p\Delta V_1);$$
$$Q = (U_2 + p\Delta V_2) - (U_1 + p\Delta V_1).$$

Thus, the change in internal energy and the work of expansion at constant pressure together can be considered as another parameter of the system.

$$U + pV = H.$$

If we denote it this way, we have:

$$Q = H_2 - H_1 = \Delta H.$$

As we see, the thermal effect in this case is denoted by a new thermodynamic quantity ΔH, called **enthalpy**. Like internal energy, enthalpy is a state function, that is, its change depends only on the initial and final state of the system, and does not depend on the way of change.

$$\Delta H = H_2 - H_1.$$

Thus, in an isobaric process, the thermal effect is equal to the change in the enthalpy of the process:

$$Q = \Delta H\ (p = const).$$

Under other circumstances (not an isobaric process), enthalpy is equal to the heat effect that would be without pressure change.

In an isochoric process (V = const), the heat transferred to the system is equal to:

$$Q = \Delta U + p\Delta V\ (V = const).$$

Since during an isochoric process there is no change in volume, then $p\Delta V = 0$. Therefore, the heat effect during an isochoric process is equal to the change in the internal energy of the process:

$$Q = \Delta U\ (V = const).$$

Hess's law of constant heat summation, also known simply as Hess' law, is a relationship in physical chemistry named after Hess, who published it in 1840. **Hess's law states that the heat effect of chemical reactions depends only on this and the initial state of the reacting substances, but does not depend on the path of the process**. This law is a special case of the first law of thermodynamics and applies only to reactions under isochoric or isobaric conditions.

In thermodynamics, it is accepted that the heat absorbed by a system is considered a positive quantity. In fact, we are harming ourselves in the place of reagents. If the chemicals in a reaction absorb heat, there is less heat in the laboratory, but this is recorded as an increase in heat (within the reaction).

In thermo-chemistry, the laws of which were formulated earlier than thermodynamics, these quantities are traditionally used as opposites. In thermo-chemistry, processes of heat release (heating of the laboratory) are called exothermic, and are denote as positive. And the absorption of heat (cooling) is called an endothermic process and is denote as negative.

$$Q_{in\ thermodinamic} = -Q_{in\ thermochemistry}.$$

Based on Hess's law, the thermal effect will be the same regardless of the reaction path. Let's look at this using the example of the combustion reaction of coal. The starting materials are oxygen and carbon, the reaction product is carbon dioxide.

The transformation of the initial reagents into the reaction product can be realized in two ways: directly to CO_2 or through the intermediate stage of CO formation. In both cases, each reaction, reduced by coefficients to one mole of a substance, is characterized by a heat effect. If these are isobaric conditions, then by enthalpy.

$$\text{C (solid)} + \text{O}_2 \text{ (gas)} \rightarrow \text{CO}_2 \text{ (gas)} \qquad \Delta H_1,$$

or

$$\text{C (solid)} + 1/2\text{O}_2 \text{ (gas)} \rightarrow \text{CO (gas)} \qquad \Delta H_2,$$
$$\text{CO (gas)} + 1/2\text{O}_2 \text{ (gas)} \rightarrow \text{CO}_2 \text{ (gas)} \qquad \Delta H_3.$$

Hess's law allows us to find the connection between these three processes using a simple equation:

$$\Delta H_1 = \Delta H_2 + \Delta H_3.$$

The calculation of the heat effects of chemical reactions is based on Hess's law. Since the values of thermodynamic functions depend on external conditions (temperature and pressure), they are usually used under standard conditions. This means a standard temperature of 25°C (298.15 K) and a standard pressure of 1 atmosphere (101.3 kPa).All heat and physical quantities under standard conditions are called standard and are designated by 0 and 298.For example, standard enthalpyΔH^0_{298}.The standard enthalpy of formation of a complex substance is the effect of the reaction of formation of 1 mole of a certain compound from simple substances under standard conditions. The enthalpy of formation of all simple substances is zero.

In thermo-chemical equations, the state of aggregation is indicated for all substances and compounds, since the enthalpy of formation of gas and liquid, for example, is not the same. Thanks to this, by the way, it is possible to find the enthalpy of the phase transition.

Standard enthalpies of formation of substances are measured or calculated. They are known as ΔH^0_{298}, kJ/mol. Their values are in thermodynamic tables. Using the data in the table, you can calculate the heat effect of any chemical reaction if the standard enthalpies of formation of all compounds in the reaction are known.

To calculate the thermal effects of reactions, a corollary of Hess's law is used: the heat effect of a reaction is the difference between the sum of the standard enthalpies of formation of the reaction products and the sum of the standard enthalpies of formation of the starting substances, per 1 mole.

In mathematical form:

$$\Delta H^0 = \left(\sum n\Delta H^0_{298}\right)_{products} - \left(\sum n\Delta H^0_{298}\right)_{initial},$$

where ΔH^0–heat effect of the reaction under standard conditions, and n is the designation of the stoichiometric coefficients of the reaction products and starting reagents.

6.3. Second law of thermodynamics

The second law of thermodynamics is a physical law based on universal empirical observations about the transformations of heat and energy, which it complements the first law. The first law of thermodynamics allows us to solve issues related to the determination of effects in various chemical and physical processes. But the first law does not answer the question in which direction the real process is going and under what conditions there is equilibrium. The answer to these questions is in the second law of thermodynamics.

In nature, processes have a one-way direction: water falls down, heat moves from a hot body to a cold one, diffusion is directed to an area of low concentration. All these processes are spontaneous.

Spontaneous processes are processes that gone in a system without outside intervention. Processes that cannot gone on their own, without outside intervention, are called non-independent.

The second law of thermodynamics is related to the reversibility of these processes. All processes are classified into irreversible and reversible.

Irreversible processes are those processes after which the system and environment cannot be returned to their previous state.

All spontaneous processes are irreversible. They flow only in one direction until they reach equilibrium, and then stop. For example, the transfer of heat from a hotter object to a less hot one ends after their temperatures equalize.

Reversible processes are processes after which the system and environment can be returned to a previous state. Reversible processes gone in the forward and reverse directions. In the reverse process the system goes through the same intermediate states as in the forward, but in the reverse order.

Looking at the phenomena of irreversibility of thermal processes, one can give different formulations of the second law of thermodynamics, but they are all logically related to each other.

For example, heat cannot by itself move from a less heated body to a more heated one (by Clausius).

A process whose only result is work is impossible. However, a process is possible whose only result is a change in heat (by Thomson).

It is impossible to build such a machine, all of whose actions would be reduced to doing work and corresponding cooling of the heat source (by Ostwald).

Heat is converted into work in any machine, but at the same time there is always also irreversible cooling. This part of the heat cannot be used for work. That is, all the heat cannot be converted into work, since it is partially consumed in the environment.

The mathematical form of the second law of thermodynamics for reversible and irreversible processes is as follows:

$$\Delta S > \frac{\Delta Q}{T} \text{ in reversible process,}$$

$$\Delta S = \frac{\Delta Q}{T} \text{ in irreversible process,}$$

where, ΔS is a function that was introduced by Clausius (1865) and called **entropy**.

Entropy characterizes the molecular disorder of a system and will change with decrease in temperature. Boltzmann showed that entropy is associated with a large number of different microscopic ways of realizing a particular macroscopic situation:

$$\Delta S = k\mathrm{lg}W,$$

where W is the number of different microscopic ways of realizing a specific macroscopic situation, and k is Boltzmann constant:

$$k = \frac{R}{N},$$

where R is the gas constant, N is Avogadro’s number.

Similar to internal energy, the change in entropy in any process depends on the initial and final state of the system and is defined as:

$$S_2 - S_1 = \Delta S.$$

Standard entropy values are used for thermodynamic calculations. Entropy S^0 is calculated at a temperature of 298 K and a pressure of 101.3 kPa. It is based on the third law of thermodynamics: the entropy of any crystalline substance in the form of an ideal solid with a temperature of absolute zero is equal to zero.

Standard entropy values can be found in thermodynamic reference books. The entropy value of the process under standard conditions is determined based on Hess's law:

$$\Delta S^0 = \left(\sum n\Delta S^0_{298}\right)_{products} - \left(\sum n\Delta S^0_{298}\right)_{initial},$$

where ΔS^0 is the entropy value of the process under standard conditions.

6.4. Thermodynamic potentials

Any chemical system changes towards a state with minimum energy and maximum disorder. This uses a new function called free energy. It shows these factors.

For an isobaric-isothermal process, this function looks like ($H - TS$) is called the isobaric potential, or Gibbs free energy, and is denoted G:

$$\Delta G = \Delta H - T\Delta S.$$

For any isochoric-isothermal process, the function ($U - TS$) is called the isochoric potential, or Helmholtz free energy, and is denoted F:

$$\Delta F = \Delta U - T\Delta S.$$

Since the quantities U, H, S, T, p, V are functions of the state, it follows from the relationship that F and G will also be functions of the state, that is, changes in the isochoric and isobaric potentials during the process do not depend on the way of the process, but only on initial and final states of the system.

The isochoric potential, or Helmholtz free energy, is a criterion for the direction of the process and equilibrium in the system under isochoric-isothermal conditions, and the isobaric potential, or Gibbs free energy, is under isobaric-isothermal conditions.

Based on this, the principle of minimum and maximum of new energy can be used. In any systems that are at a constant volume and temperature, only processes with decrease in the Helmholtz free energy can gone ($\Delta F < 0$), and its minimum value is in the equilibrium state ($\Delta F = 0$).

Similarly, the Gibbs energy is a criterion in systems that are under constant pressure and temperature. In such systems, only processes with decrease in the Gibbs free energy can gone ($\Delta G < 0$), and its minimum value is in the equilibrium state ($\Delta G = 0$).

These parameter findings are very important for technologists because free energy calculations allow one to predict whether a reaction will proceed spontaneously, whether it will remain in an equilibrium state, or whether it will spontaneously proceed in the opposite direction. Gibbs energy is widely used in chemistry, for solutions, melts, solid state reactions and heterogeneous reactions such as corrosion.

Helmholtz energy is used much less frequently, mainly for calculations of gas systems.

In order to find out whether a reaction will gone under isobaric-isothermal conditions, you need to calculate the enthalpy and entropy of the reaction, as shown above, and then use formula for ΔG. If the temperature differs from 25°C, you can take this into account by changing the value of T. Of course, entropy and enthalpy also change with temperature, but not dramatically. Therefore, this can be neglected.

If $\Delta G<0$ the reaction will gone spontaneously. If $\Delta G>0$ the reaction is impossible. If $\Delta G=0$, this means that the system is in equilibrium and will not change without external influence.

Of course, ΔG can also be found directly using reference handbooks (Table 6.1).

For any chemical reaction:

$$\Delta G^0_{reaction} = \left(\sum n\Delta G^0_{298}\right)_{products} - \left(\sum n\Delta G^0_{298}\right)_{initial}.$$

Table 6.1 contains standard thermodynamic values for some chemical compounds that are used in construction. They can be used for simple calculations of changes in thermodynamic parameters for chemical reactions and approximate determination of the temperature of thermodynamic equilibrium. For all chemical compounds, their state of aggregation is indicated: crystalline (c), solid (s), liquid (l), or gas (g). As is easy to see in the example of water, a change in the state of aggregation leads to a change in all thermodynamic parameters. There are no simple substances in this table, since the thermodynamic parameters of their formation under standard conditions are zero. It should be noted that entropy values are traditionally written in units other than enthalpy and free energy. This should be taken into account when calculations.

Table 6.1

Standard thermodynamic values for certain chemical compounds

Compound (state)	$\Delta H^0_{f,298}$, kJ/mole	ΔS^0_{298}, J/(mole·K)	$\Delta G^0_{f,298}$, kJ
Al_2O_3 (c)	–1676.0	50.9	–1582.0
$Al_2(SO_4)_3$ (c)	–3442.0	239.2	–3101.0
CH_4 (g)	–74.8	186.2	–50.8
CO (g)	–110.5	197.5	–137.1
CO_2 (g)	–393.5	213.7	–394.4
$CaCO_3$ (c)	–1206.9	92.9	–1128.8
$CaCl_2$ (c)	–795.0	113.8	–750.2
CaO (c)	–635.5	39.7	–604.2
$Ca(OH)_2$ (c)	–986.6	76.1	–896.8
$CaSiO_3$ (s)	–1584.0	82.0	–1499.4
$CaSO_4$ (c)	–1433.3	85.9	–1319.2
$CaSO_4 \cdot 2H_2O$ (s)	–2033.7	193.9	–1794.0
H_2O (g)	–241.8	188.7	–228.6
H_2O (l)	–285.8	70.1	–237.2
H_2SO_4 (l)	–814.2	156.9	–690.3
SiO_2 (c)	–910.9	41.8	–856.7
NaCl (c)	–411.1	72.1	–384.0
KCl (c)	–435.9	82.6	–408.0
Na_2SO_4 (c)	–1384.6	149.9	–1266.8
NaOH (c)	–425.6	64.4	–380.7
KOH (c)	–425.8	79.3	–380.2
Na_2SiO_3 (s)	–1519.5	114.2	–1432.2

From formula of ΔG it is clear that the possibility of a reaction is determined by two factors (entropy and enthalpy factors). Firstly, reactions with negative enthalpy values, that is, those that lead to the release of heat (exothermic), are spontaneously. Secondly, reactions with an increase in entropy (for example, the transformation of solids into liquids or gases, the formation of solutions) are spontaneous. If both factors coincide, the reaction gone easily. If they are in opposition, temperature becomes critical.

Four cases are possible:

1. $\Delta H<0$, $\Delta S>0$, then both parts of the formula are negative, which means $\Delta G<0$. These are reactions that release heat and increase entropy. For example, burning wood.

2. $\Delta H<0$, but $\Delta S<0$, then $\Delta G<0$ only at certain values of T, which are less than critical. These are processes with a decrease in entropy, for example, crystallization. When heated to a critical temperature, precipitation stops.

3. $\Delta H>0$, but $\Delta S>0$, then $\Delta G<0$ only at certain values of T, which are higher than critical. These are processes that absorb heat, for example, the melting of a solid. The critical temperature in this case is the melting point.

4. Finally, $\Delta H>0$, $\Delta S<0$. Such processes can never happen.

In reversible reactions, each of the two (direct and reverse) has its own change in free energy parameters. At the equilibrium point they are equal.

It should be noted that entropy is very sensitive to any changes in the system, including temperature. Therefore, all simple calculations are very approximate. Only at temperature $T = 0$, ΔS does not depend on any changes in the system and the transition of the system does not lead to its change. According to this principle, called the third law of thermodynamics, absolute zero temperature cannot be reached by any process involving a change in entropy; you can only get closer to it.

6.5. Chemical kinetics

Chemical kinetics, also known as reaction kinetics, is the part of physical chemistry that is concerned on rates of chemical reactions. It is different from chemical thermodynamics, which deals with the direction of reaction but in itself tells nothing about its rate. Chemical kinetics includes investigations of how conditions influence the speed of a chemical reaction, its mechanism and transition states, as well as the construction of mathematical models.

It should be noted that the rate of a chemical reaction is the change in the concentration of compounds over time. It is measured in units of concentration per time. For example, in moles/liter per minute.

Prime factor is nature of the reactants. Acid/base reactions, formation of salts, and ion exchange are usually fast. Formation of covalent bond large molecules are slower. The strength of bonds in reactant molecules also influence the rate of their transformation.

The physical state (solid, liquid or gas) of the reactant is also an important factor in the rate of change. When the reactants are in the same phase, thermal motion causes them to come into contact. However, when they are in separate phases, the reaction is limited by the interface between them. This means that the finer a solid or liquid reactant is, the greater its surface area per unit volume and the more contact it has with another reactant, the faster the reaction occurs.

In a solid, only those particles that are at the surface can be involved in a reaction. Crushing a solid into smaller parts means that more particles are present at the surface, and the frequency of collisions between these and reactant particles increases, and so reaction is faster.

The reactions are due to collisions of reactant particles. The frequency with which the molecules or ions collide depends positive upon their concentrations. For example, combustion is faster in pure oxygen than in air (21% oxygen).This rule is called the **law of mass action**.

For reaction A + B → AB:

$$v = kC_A^n C_B^m,$$

where *k* is the reaction rate constant, *C* is the molar concentration of reactants and *n*, *m* is the partial orders of reaction for this reactants. The partial order for a reactant can only be determined experimentally. It is often not indicated by its stoichiometric coefficient.

In general, this formula looks like:

$$v = \prod kC_i^{n_i}.$$

Temperature usually has a significant effect on the rate of a chemical reaction. A simple rule of thumb (van't Hoff) says that for every 10 °C increase in temperature, the reaction rate increases by 2-4 times. For biological systems, α (temperature coefficient) is often in the range of 1.5 to 2.5.

For more complex calculations, you need to use the Arrhenius equation and the active collision model.

In the active collision model, not all collisions lead to changes in molecules, but only some of them. To do this, molecules must have a certain energy. This explains why wood does not always burn, although its combustion reaction is thermodynamically possible. A fire requires initiation, and then it can sustains itself.

Temperature directly affects the energy of molecules. It also increases their speed and collision frequency, but this is less important than the impact effect.

The effect of temperature on the reaction rate constant obeys the **Arrhenius equation**:

$$k = Ae^{-\frac{E_a}{RT}},$$

where A is the pre-exponential factor, E_a is the activation energy, R is the molar gas constant and T is the absolute temperature.

Another factor that affects the reaction rate is catalysis, that is, the effect of a catalyst. A catalyst is a substance that changes the rate of a chemical reaction, but subsequently remains chemically unchanged. A catalyst increases the rate of a reaction by providing a new reaction mechanism with a lower activation energy. In reversible reactions, the catalyst does not affect the equilibrium position, since it equally accelerates both the reverse and forward reactions.

Pressure is significant only in reactions involving gases. In these cases it replaces concentration.

The rate of a reversible reaction is the difference between the rate of the forward and reverse reaction. At the equilibrium point they are equal. Thus, from the point of view of the observer, the system does not change, however, both chemical reactions continue to occur, but cancel each other out.

Of course, any change in factors affecting the rate of at least one of these reactions will lead to a change in the equilibrium point. For example, a change in concentration, pressure (if it is a gas), temperature. This pattern is known as **Le Chatelier's principle**, also called Equilibrium Law. If the equilibrium of a system is disturbed by a change in one or more of the determining factors (as temperature, pressure, or concentration) the system tends to adjust itself to a new equilibrium by counteracting as far as possible the effect of the change.

Test questions

1. Define the first law of thermodynamics and the term internal energy. Explain why absolute values of internal energy are not used, but only changes in this quantity.
2. Define isochoric and isobaric processes and supply several examples. What thermodynamic values indicate the thermal effect of these processes.
3. Define Hess's law. How can it be used for calculations?
4. Define the second law of thermodynamics and write it in mathematical form and explain what entropy is.
5. Define the third law of thermodynamics and explain what absolute zero temperature is.
6. Define the thermodynamic potentials that determine isobaric and isochoric processes.
7. What are the thermodynamic reasons for a spontaneous chemical reaction and a state of equilibrium.

Test calculations

Find the change in enthalpy, entropy, and free energy under standard conditions (using Table 6.1) for the chemical reactions:

1. CaO (c) + H_2O (l) → $Ca(OH)_2$ (c)
2. $Ca(OH)_2$ + CO_2 (g) → $CaCO_3$ (c) + H_2O (l)
3. $Ca(OH)_2$ + SiO_2 (c) → $CaSiO_3$ (c) + H_2O (l)
4. $2NaOH$ (c) + SiO_2 (c) → Na_2SiO_3 (s) + H_2O (l)
5. $CaSO_4$ (c) + Na_2CO_3 (c) → $CaCO_3$ (c) + Na_2SO_4 (c)
6. $CaCl_2$ (c) + Na_2CO_3 (c) → $CaCO_3$ (c) + $2NaCl_2$ (c)
7. $CaSO_4$ (c) + $2H_2O$ (l) → $CaSO_4 \cdot 2H_2O$ (s)

Chapter7.Solutions

7.1. Basic concepts of solution theory and types of solutions

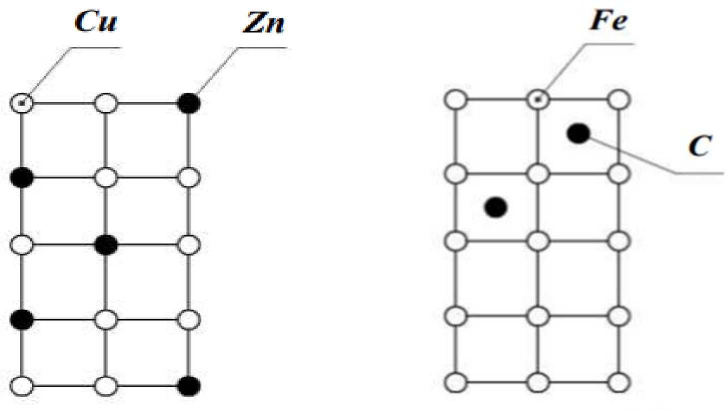
Suppose two substances are finely ground and mixed together. Chemical interaction can occur between these substances with the formation of a new compound and the system will become uniform (homogeneous) throughout the volume. If the starting substances do not interact with each other, then a mechanical mixture will be formed – a non-homogeneous (heterogeneous) system containing two or more phases. When mixing substances, you can get a homogeneous or heterogeneous system, which is called a solution. The composition of the solution, that is, the content of its components, can be changed within certain limits without disturbing its homogeneity.

Systems of two or more substances, in which one substance (or several) is evenly distributed in the form of very small particles in the volume of another, are called dispersed. A substance dispersed (evenly distributed) in the volume of another is called a dispersed phase. The continuous phase in which the dispersed phase is dispersed is called the dispersion medium. A solution of sugar in water is a dispersed system in which sugar is the dispersed phase and water is the dispersion medium.

According to the degree of dispersion, that is, depending on the linear size of the particles of the dispersed phase, dispersed systems are divided into **coarse-dispersed** (various suspensions, emulsions, soil, concrete, granite, smoke, fog, etc.), in which the particles have a size of more than 1 μm; **finely dispersed** (colloidal solutions - blood, hydrogen solutions of glue, gelatin, starch, sulfur, etc.) with the size of dispersed particles in the range of 1-100 nm and **true solutions** or **simply solutions** in which the dissolved substance is dispersed to the size of molecules or ions (less than 1 nm). In solutions, there is no distribution surface between the dispersed substance and the dispersion medium (solvent), so the solution is a homogeneous system. Therefore, **a solution** is a homogeneous, thermodynamically stable system of variable composition, which consists of two or more components. Depending on the aggregate state of the dispersion medium, solutions are divided into **gaseous** (mixtures of gases, for example air), **solid**(glass, alloys, co-crystals of KCl and KBr, etc.) and **liquid**, which are formed when dissolving gaseous (ammonia, hydrogen chloride, carbon dioxide), liquid (alcohol , acetone, sulfuric acid) or solid (salts, alkalis, etc.) substances in a liquid dispersion medium (**solvent**), such as water. The latter type of solution is the most important, since most biological, geological, and chemical processes occur with participation of liquid solutions. Solid solutions are divided into two types: substitution and penetration.

Substitution solid solutions are solutions in which atoms of one element replace atoms of another in the nodes of crystal lattices. Such solutions are formed only when the atoms of different elements are close in size and properties. For example, when copper is alloyed with zinc, copper atoms replace zinc atoms in the crystal lattice (Fig. 5.1a). In simple substances, atoms or molecules replace each other. Both cations and anions can be substituted in ionic crystals.

Solid solutions of penetration (rooting) are solutions in which atoms and ions are statistically located in the spaces between atoms and ions of the main substance. In solid rooting solutions, the atoms and ions of the solute occupy a free and regular system of points (internodes) of the crystal lattice of the solvent in a disorderly manner. The main condition for the formation of solid penetration solutions is the correspondence of the sizes of the penetration atoms to the sizes of the lattice-matrix voids. Typical representatives of solid penetration solutions are phases that are formed when nonmetal atoms enter the crystal lattice of transition metals, for example, the penetration of carbon atoms into the interstices of iron crystals during molten cast iron (Fig. 7.1b). The solubility according to the type of penetration, as a rule, is small and is equal to several percent, and only under special conditions it reaches 10%. In penetration solid solutions, in contrast to substitution solid solutions, the atoms that penetrate the matrix differ significantly in electronic structure, electronegativity, type of chemical bond, etc. Therefore, solid penetration solutions are characterized by a mixed covalent-metallic bond.



a b

Fig. 7.1. Solid solutions of substitution (a) and penetration (b)

Gaseous (aerated) solutions are usually called gas mixtures (for example, air). Since the solvent is a component whose concentration is significantly greater than the concentration of other components, the solvent in air is nitrogen.

The ability of a substance to mixing with another substance, to form homogeneous systems (solutions) **is called solubility**. If a sufficient amount of a crystalline substance that dissolves is introduced into a certain amount of solvent, then in such a system two mutually opposite processes take place at the same time: individual molecules or ions detach from the surface of the crystals of the substance that dissolves. Thanks to diffusion, the latter are evenly distributed throughout the entire volume of the solvent. At the same time as dissolution, the are also reverse process – crystallization. Particles of a dissolved substance that have passed into a solution are attracted to the surface of a substance that has not dissolved yet and crystallize. Dissolution and crystallization rates depend on the concentration of the solution and the temperature. Initially, the rate of dissolution exceeds the rate of crystallization. As the concentration of the solute in the solution increases, the rate of crystallization increases and there comes a point when the rates of dissolution and crystallization become the same. A dynamic equilibrium is established in the system, in which as many molecules are dissolved per unit of time as are released from the solution. A solution that is in equilibrium with a substance that dissolves (that is, at a given temperature, the substance in the solution no longer dissolves) is called a **saturated solution.**

A solution in which a solute can still dissolve at a given temperature is **called unsaturated.** Unsaturated solutions are divided into diluted in which the substance is dissolved relatively little (Fig. 5.2a) and concentrated in which the substance is dissolved in a sufficient amount, but less than in a saturated solution (Fig. 7.2b).

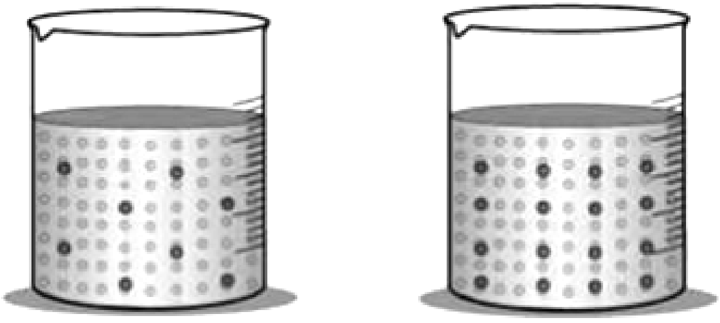

a b

Fig. 7.2. Dilute (a) and concentrated solutions (b)

By solubility, all substances are divided into **well soluble** (more than 10 g of the substance dissolves in 100 g of water), **poorly soluble** (less than 1 g of the substance dissolves in 100 g of water) and **practically insoluble** (less than 0.01 g of the substance dissolves in 100 g of water). Solubility depends on the nature of the solvent and dissolved substance, dissolution conditions (temperature, pressure, concentration, presence of other substances). The solubility of most solids decreases with a decrease in temperature, so when hot saturated solutions are cooled, the excess solute is released in the form of crystals. The release of a substance upon cooling a saturated solution is called crystallization (re-crystallization). Crystallization from solutions or re-crystallization is widely used to purify substances that dissolve in water or other solvents.

If the saturated solution is cooled carefully and slowly, crystallization may not occur. In this case, the resulting solution contains a much larger mass of solute than can be dissolved to form a saturated solution at a given temperature. Such a solution is called **supersaturated**. Supersaturated solutions are thermodynamically unstable systems. Instant crystallization occurs when the solution is shaken, dust gets into it, or a crystal of a solute is added. Supersaturated solutions easily form sodium chloride, sulfate and carbonate, sodium tetraborate (borax), etc.

The solubility of liquids in liquids can be complete or limited. Limited solubility is more common. With complete mutual solubility, liquids are mixed in any ratio (alcohol/water). Liquids with limited mutual solubility always form two layers. For example, when mixing aniline and water, there are always two layers: the upper layer consists mainly of water and contains aniline in small quantities (about 13%), the lower layer, on the contrary, consists mainly of aniline and contains about 5% of water. An increase in temperature leads to an increase in the mutual dissolution of liquids. The temperature at which the limited mutual solubility of liquids becomes unlimited is called the critical dissolution temperature. For the aniline–water system, it is equal to 168 °C. The solubility of gases in liquids is quite diverse. It is significantly affected by temperature and pressure: with increasing temperature, the solubility of gases decreases, and with increasing pressure, it increases.

The self-flow distribution of the substance that is dissolved between the molecules of the solvent is **called dissolution**. However, dissolution cannot be considered as a mechanical process because the properties of the solute and the solvent change when the solution is formed. This is evidenced by a number of factors. Prime, the volume of the solution is never equal to the sum of the volumes of the solvent and the dissolved substance. Second, dissolution is usually accompanied by the release or absorption of heat, and sometimes by a change in the color of the solution. In some cases, these effects are small, but in some cases they become very noticeable. For example, the dissolution of nitrates is accompanied by significant cooling of the solution, and the dissolution of sodium, potassium hydroxides, and sulfuric acid is accompanied by strong heating. When mixing 500 ml of water with 500 ml of ethyl alcohol, the volume of the resulting solution becomes equal to 940 ml instead of 1 liter (the volume decreases by 6%). This phenomenon is called contraction and is caused by the formation of hydrogen bonds between alcohol and water molecules. The dissolution of the white powder of dehydrated $CuSO_4$ is accompanied by the formation of a blue solution, and blue crystals of $CoCl_2$ – a pink solution. All these phenomena are caused by both physical and chemical changes in the general solution system.

The study of solutions contributed to the emergence of two theories of their formation: **physical and chemical** (both in second half of the 19th century). Representatives of the **physical theory of solutions**, the founder of which was van't Hoff, considered dissolution as a physical process: the solvent is some kind of indifferent medium in which the molecules of the dissolved substance are evenly distributed throughout the volume of the solution due to **diffusion forces**. At the same time, the intermolecular interaction between the particles of the dissolved substance and between the molecules of the solvent is excluded. **Proponents of the chemical theory** of solutions believed that there is a chemical interaction between the molecules of the components of the solution, which leads to the formation of a mixture of more or less stable compounds of solute particles with solvent molecules. Such an idea about solutions was first formulated by Mendeleev. For the development of the chemical theory of solutions were the works of Kablukov, Kurnakov, Kistiakovsky. Physical and chemical theories formed the basis of the modern theory of solutions. The dissolution process is a complex physical and chemical process. Depending on the nature of the components and conditions of solution formation (concentration, temperature, pressure), either physical or chemical phenomena may prevail. Physical phenomena include the simple distribution of solute molecules among solvent molecules, as well as interaction due to the forces of electrical nature: ion-dipole, dipole-dipole, interaction between ions of the opposite sign. Physical forces act at long distances and prejudice chemical forces that act at distances of the order of the diameter of molecules: rearrangement of electronic shells of atoms, molecules, ions. The totality of all processes that occur as a result of the appearance of a dissolved substance in a solvent is called **solvation**, for aqueous solutions – **hydration**.

Compounds of variable composition, which are formed as a result of the interaction of solvent molecules with particles of a dissolved substance, are called **solvates**. If the solvent is water, then the solvates are called **hydrates.**

When dissolving ionic compounds, the solvation process begins with the orientation of water dipoles relative to the ions in the crystal lattice, as it shown on example of sodium chloride in water (Fig. 7.3). Hydrogen bonds and van der Waals forces (orientation forces) operate between water molecules. Thus, water molecules behave as dipoles, that mean particles that have a negative charge on one side and a positive charge on the other (Fig. 7.3). An ion-dipole interaction occurs between sodium and chlorine ions, which are located on the surface of the sodium chloride crystal, and water molecules. Water molecules behave in such a way that they return to the Na^+ by a negative pole, and to the Cl^- by a positive pole of the dipole. An ion-dipole interaction occurs, as a result of which sodium and chlorine ions detach from the crystal, are surrounded by water dipoles (hydration), and diffuse into the solvent. In this way, the sodium chloride crystal disintegrates into hydrated ions, which form a homogeneous system water – solution.

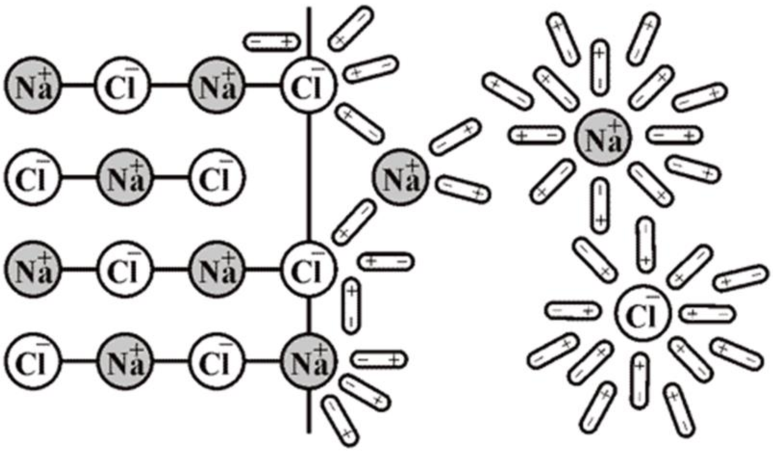


Fig. 7.3. Mechanism of dissolution of NaCl in water

Water molecules are held near the formed ions both due to electrostatic forces (opposite charges attract) and due to the formation of donor-acceptor bonds. It depends on the nature of the solvent and the solute. One of the consequences of hydration (solvation) is the ability of substances to bind a certain amount of water (solvent) when extracted from a solution: $BaCl_2 \cdot 2H_2O$, $CuSO_4 \cdot 5H_2O$, etc.

Substances whose crystals contain water molecules are called crystal hydrates, and the water that is part of the crystals of these substances is called crystallization water.

Crystal hydrates are unstable compounds in many cases, they lose water when heated. Water of crystallization, for example, from $Na_2CO_3 \cdot 10H_2O$ is already removed at room temperature. Dehydration of $CuSO_4 \cdot 5H_2O$ requires rather strong heating (about 100 °C), while the blue color of crystalline cuprum sulfate crystal hydrate changes to white in powdered dehydrated form. Often, after cooling, dehydrated substances add water from the air: the white powder of dehydrated $CuSO_4$ after storage in an open container acquires a blue color due to the formation of crystal hydrate $CuSO_4 \cdot 5H_2O$.

Energy effects of dissolution. The dissolution of substances is accompanied by thermal effects (ΔH_{diss}). Thus, during the dissolution of alkalis or acids in water, heat is released (exothermic process), and during the dissolution of many salts, it is absorbed (endothermic process).

According to the modern theory of solutions, dissolution is a set of physical and chemical processes, each of which is accompanied by a certain thermal effect:

1) destruction of the structure of the dissolved substance (destruction of crystal lattices), ionization occurs with heat absorption ($\Delta H_1 > 0$);

2) interaction of solvent molecules with particles of the dissolved compound – solvation (hydration), formation of solvates (hydrates) – a process accompanied by the release of heat ($\Delta H_2 < 0$);

3) distribution of solvated particles in the volume of the solvent – diffusion, occurring with heat absorption ($\Delta H_3 > 0$). Therefore, depending on the ratio of these thermal effects, the dissolution process can be exothermic (heat is released) or endothermic (heat is absorbed):

$$\Delta H_{diss} = \Delta H_1 + \Delta H_2 + \Delta H_3.$$

7.2. Concentration of solutions and methods of its expression

There are different ways of numerically expressing the composition of solutions: **fraction of dissolved substance** (mass, molar, volume), **concentration** (molar, molal, mass, normal, etc.).

The mass fraction of the dissolved substance (ω) is a physical quantity determined by the ratio of the mass of the dissolved substance (m_{solute}) to the mass of the solution ($m_{solution}$):

$$\omega = \frac{m_{solute}}{m_{solution}} \cdot 100\%.$$

The mass fraction of a solute is usually expressed in fractions of a unit or as a percentage.

The mole fraction of a dissolved substance (χ) is a physical quantity determined by the ratio of the number of moles of a dissolved substance ν_{solute} to the total number of moles of solute and solvent ($\nu_{\text{solute}} + \nu_{\text{solution}}$):

$$\chi = \frac{\nu_{\text{solute}}}{\nu_{\text{solute}} + \nu_{\text{solution}}}.$$

The volume fraction of the dissolved substance (φ) is a physical quantity determined by the ratio of the volume of the dissolved substance (V_{solute}) to the volume of the solution V_{solution}:

$$\varphi = \frac{V_{\text{solute}}}{V_{\text{solution}}}.$$

It should be remembered that when substances are mixed, the volume of the solution is not equal to the sum of the volumes of the dissolved substance and the solvent.

Concentration is the amount of dissolved substance (g, mol) in a certain amount (by mass or volume) of a solution (or solvent).

Molar concentration(C_M) is a physical quantity determined by the ratio of the number of moles of a dissolved substance (ν_{solute}) to the volume of the solution (V_{solution}):

$$C_M = \frac{\nu_{\text{solute}}}{V_{\text{solution}}} = \frac{m_{\text{solute}}}{M_{\text{solute}} \cdot V_{\text{solution}}}.$$

The unit of molar concentration is mol/liter. **The molarity** of the solution is denoted by the letter M. For example, a bimolar is 2 M solution of sulfuric acid contains2 mol/liter, i.e. 196.16 g of H_2SO_4 in 1 liter of solution. Solutions containing 0.1 mol/liter and 0.01 mol/liter solute in 1 liter are called decimolar and centimolar, respectively.

Molal concentration (C_m) is expressed as the number of moles of dissolved substance in 1 kg of solvent (mol/kg):

$$C_m = \frac{\nu_{\text{solute}}}{m_{\text{solvent}}} = \frac{m_{\text{solute}} \cdot 1000}{M_{\text{solute}} \cdot m_{\text{solvent}}}.$$

For example, if 98.08 g of H_2SO_4 (i.e. 1 mol) is dissolved in 1000 g of water, then such a solution is unimolar. The molality of the solution is denoted by the letter m (1 m, 0.02 m, etc.).

Molar equivalent (or a normal) concentration (C_N)is expressed as the number of equivalents of a dissolved substance contained in 1 liter of solution (mol-equiv/liter):

$$C_n = \frac{\nu_{\text{eq.solute}}}{V_{\text{solution}}} = \frac{m_{\text{solute}}}{M_{\text{eq.solute}} \cdot V_{\text{solution}}}.$$

Normality is denoted by the letters n or N (1 N is a uninormal, 0,001 N is a millinormal solutions). Normality and molarity of solutions coincide for monobasic acids (HCl, HNO_3, CH_3COOH) and monoacid bases (KOH, NaOH, NH_4OH). If the acid, for example, is tribasic, then the normality is three times greater than its molarity: a 1 M solution of H_3PO4 corresponds to the normality of this acid, which is equal to three, i.e. 1 M H_3PO_4 = 3 n H_3PO_4.

A feature of equinormal solutions (that is, solutions of the same normality) is that equal volumes of them interact without a residue. Thus, 20 ml of a 1 N solution of KOH interacts without a residue with 20 ml of a 1 N solution of any acid (HCl, H_2SO_4, H_3PO_4), since, according to the law of equivalents, substances interact with each other in amounts proportional to their equivalents. In the case of different normalities of the reacting solutions, the latter interact in volume ratios inversely proportional to their normalities. Mathematically, this can be expressed by the equation:

$$\frac{V_1}{V_2} = \frac{C_{H_2}}{C_{H_1}};$$

$$V_1 \cdot C_{H_1} = V_2 \cdot C_{H_2}.$$

Titer is the number of grams of dissolved substance in 1 ml of solutions

$$T = \frac{m}{V}, \text{g/ml.}$$

The titer is widely used in analytical chemistry to express concentrations in volumetric analysis (thirtimetry), hence its name.

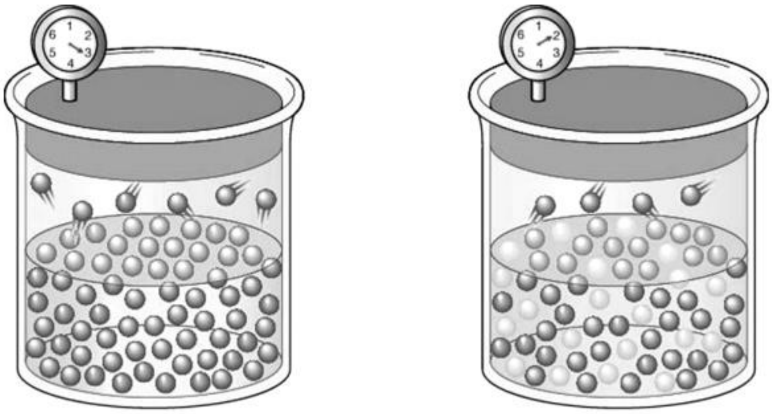
7.3. Properties of non-electrolyte solutions

A decrease in the pressure of the saturated vapor of the solvent above the solution explain by Raoult's laws.

The main issue of the thermodynamic theory of solutions is to establish the dependence of equilibrium properties of solutions on the composition and properties of their components. Let's establish the dependence of the saturated vapor pressure of the solvent and the dissolved substance on the composition of the solutions and the properties of the pure components for ideal solutions. **A solution in which the forces** of intermolecular interaction of individual components (for example, A–A, B–B, A–B) are the same and there is no chemical interaction between the components is called ideal. The formation of such a solution is accompanied by a zero thermal effect ($\Delta H = 0$); each component behaves in an ideal solution independently of the other components, and the properties of the solution under these conditions are determined only by the concentration of the solute. Properties of solutions that depend only on their concentration and do not depend on the nature of the dissolved substance are called **colligative**.

Consider the case when a pure liquid, for example, water, is contained in a closed vessel at a constant temperature. Individual molecules that have the greatest kinetic energy will overcome the surface tension and pass into the gaseous phase, that is, the liquid will evaporate. As the number of water molecules in the gaseous phase increases, so does the number of molecules that accidentally return to the liquid phase. There will inevitably come a time when the concentration of water molecules in the gaseous (vapor) phase will increase so much that the same number of molecules will return to the liquid. Equilibrium will occur when the number of water molecules that will pass from the liquid will be equal to the number of molecules that will return to the liquid from the gaseous (vapor) phase in the same unit of time. The equilibrium state of the liquid-vapor system at a certain temperature is characterized by the saturated vapor pressure. Saturated vapor pressure is also called vapor elasticity.

If, instead of water, a solution of any substance is introduced into the vessel, the balance will be disturbed. The total number of water molecules on the surface will decrease, so the number of water molecules that will have energy will also decrease accordingly necessary for the transition to the gaseous phase. At the same time, the same number of water molecules will return to the liquid. As a result, the concentration of water molecules in the vapor phase will decrease until the number of water molecules returning to water is equal to the number of water molecules moving from the solution to the vapor phase. Balance will come again. But now the concentration of water molecules in the gaseous phase will be lower than it was over pure water. Accordingly, the saturated vapor pressure will be lower. From this we can conclude that the pressure of saturated water vapor (solvent) above the solution is lower than the pressure of saturated water vapor (solvent) above pure water i.e., above pure solvent (Fig. 7.4).



a b

Fig. 7.4. Decrease in the saturated vapor pressure of the solvent above the solution (b) compared to the pure substance (a)

The dependence of the decrease in vapor pressure of solutions on their concentration is **expressed by Raoult's first law** (1887): the relative decrease in saturated vapor pressure above the solution is equal to the mole fraction of the dissolved substance, or the decrease in saturated vapor pressure above the solution is directly proportional to the mole fraction of the dissolved substance:

$$\frac{P_0 - P}{P_0} = \chi,$$

$$\Delta P = P_0 \cdot \chi,$$

where P_0 is the saturated vapor pressure of a pure solvent, P is the pressure of saturated vapor above the solution.$\Delta P = P_0 - P$ is a reduction of saturated steam pressure. And χ is the mole fraction of dissolved substance. It follows from this equation that the decrease in vapor pressure does not depend on the nature of the substance, but is determined only by the number of its moles in a certain amount of solvent, that is, its concentration.

Raoult's law, which was formulated on the basis of experimental results, can be derived analytically, assuming that the solvent vapor obeys the laws for ideal gases, and that there is no any specific interaction between the molecules of the solvent and the solute (ideal solutions). In fact, the properties of real solutions always differ from ideal solutions. However in many cases, at low concentrations, real solutions obey Raoult's law quite precisely, so they can be considered ideal without much error. Based on Raoult's law, a certain concentration of water vapor can be created in a closed vessel by adjusting the concentration of the solute accordingly. This makes it possible, for example, to test various materials, including construction materials, under conditions of different humidity.

The boiling point and freezing point (crystallization) of solutions depend on the vapor pressure of the solutions. A liquid boils when the saturated vapor pressure equals the external pressure. A decrease in the vapor pressure of the solution causes the boiling point or freezing point of the solution to rise compared to the corresponding temperatures for the pure solvent.

Investigating the boiling point and freezing point of dilute solutions of different concentrations, Raoult discovered that equimolar amounts of different substances dissolved in the same amount of a given solvent lower the freezing point and raise the boiling point of solutions by the same number of degrees. **He formulated his conclusions in the form of consequences from Raoult's law: an increase in the boiling point (ΔT_{boil}) or a decrease in the freezing point (ΔT_{freez}) of a solution is directly proportional to its molal concentration:**

$$\Delta T_{\text{boil}} = K_E \cdot C_m;$$
$$\Delta T_{\text{freez}} = K_K \cdot C_m.$$

where C_m is the molal concentration of the solution, K_E and K_K are the proportionality coefficients, which are called **ebullioscopic** and **cryoscopic constants**, respectively.

Substitute the value of the molal concentration from the equation into the equation, and we get:

$$\Delta T_{\text{boil}} = K_E \frac{m_{\text{solute}} \cdot 1000}{M_{\text{solute}} \cdot m_{\text{solvent}}};$$
$$\Delta T_{\text{freez}} = K_K \frac{m_{\text{solute}} \cdot 1000}{M_{\text{solute}} \cdot m_{\text{solvent}}},$$

where K_E and K_K are measured in degrees and show the elevation of the boiling point or the decrease of the freezing point of a unimolar solution compared to the corresponding temperatures of the pure solvent. The values of ebullioscopic and cryoscopic constants do not depend on the concentration and nature of the dissolved substance, but depend on the nature of the solvent.

The values of K_E and K_K for many standard solvents are in the reference literature.

In concrete works, when transporting concrete mixture in winter and in some other cases, calcium chloride, sodium chloride salts or their mixture are thereof is added to reduce the freezing point of mortars.

Determining the molecular weights of substances by lowering the freezing point or raising the boiling point of solutions is called **cryoscopy and ebullioscopy**, respectively. These methods are also used to find the composition of compounds, determine the degree of dissociation of electrolytes, study the processes of association and polymerization of substances in solutions.

Based on the previous equations, the molar mass of the dissolved substance is equal:

$$M_{\text{solute}} = \frac{K_E \cdot m_{\text{solute}} \cdot 1000}{\Delta T_{\text{boil}} \cdot m_{\text{solvent}}};$$

$$M_{\text{solute}} = \frac{K_K \cdot m_{\text{solute}} \cdot 1000}{\Delta T_{\text{freez}} \cdot m_{\text{solvent}}}.$$

7.4. Diffusion, osmosis and osmotic pressure

In the solution, the molecules of the solvent and the dissolved substance are in a state of continuous movement, and due to mutual diffusion, concentrations are equalized at any point in the solution (Fig. 7.5).

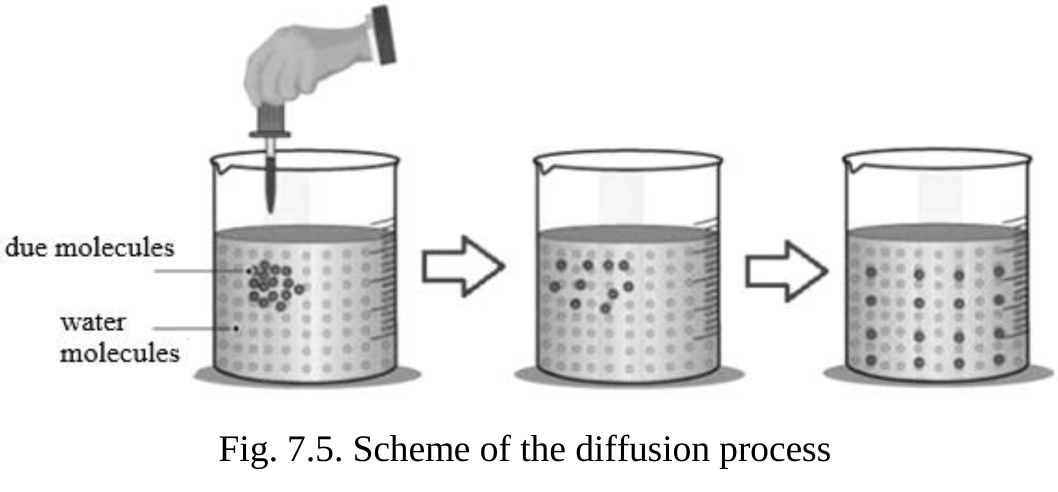


Fig. 7.5. Scheme of the diffusion process

The spontaneous process of substance transfer, as a result of which an equilibrium distribution of concentrations is established due to the disordered thermal movement of molecules, atoms, and ions in gases, liquids, or solids, is called **diffusion.** Diffusion occurs spontaneously and is accompanied by an increase in the entropy of the system.

Diffusion also occurs if a membrane is placed at the boundary of a solution and a pure solvent (or two solutions of different concentrations) – a partition that is permeable to only one component, usually the solvent, and impermeable to the dissolved substance. Solutions that are separated from the solvent by membranes are quite common in nature. Such membranes are called **semi-permeable** (Fig. 7.6).

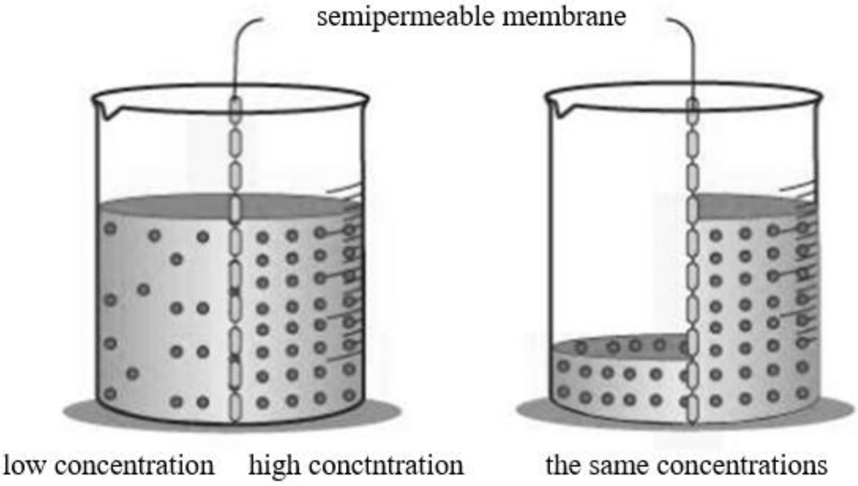


Fig. 7.6. Scheme of the osmosis process

Since the membranes are impermeable to the dissolved substance, equalization of the concentration in the vessel can be carried out only due to the diffusion of the solvent into the solution (or the solvent from a dilute solution to a concentrated one).

One-way spontaneous diffusion of solvent molecules through a semi-permeable membrane into a solution or from a solution with a low concentration to a solution with a high concentration is called osmosis, and the pressure that occurs in this case is called **osmotic pressure.** Osmosis can be observed in special devices called osmometers (Fig. 7.7).

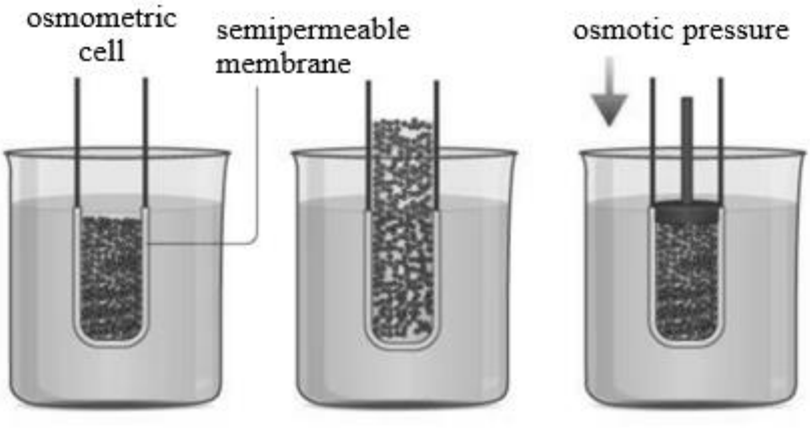


Fig. 7.7. Scheme of the osmometer

The main part of the osmometer is the osmometric cell, which is separated from the vessel with the pure solvent by a semi-permeable membrane that allows only solvent molecules to pass through. A cell with a concentrated solution is immersed in a vessel with a solvent. After some time, a significant increase in the liquid level in the tube is noted. The pressure that must be applied to equalize the liquid levels in the osmometric cell and vessel will be equal to the osmotic pressure of the solution.

The osmotic pressure P_{osm} of dilute solutions obeys the gas laws. Van't Hoff proposed a unified law for osmotic pressure in solutions (similar to the ideal gas law, also called the general gas equation, or unified Mendeleev-Clapeyron gas law):

$$P_{\text{osm}} = C_M \cdot R \cdot T \cdot 1000,$$

where C_M is a molar concentration (mol/liter), R is universal gas constant (8.314 $J \cdot K^{-1} \cdot mol^{-1}$), and T is absolute temperature.

The osmotic pressure of dilute solutions of non-electrolytes is directly proportional to molar concentration and absolute temperature.

From the Van't-Hoff equation, it can be concluded that the osmotic pressure of a dilute solution is equal to the pressure that the dissolved substance would exert, being in a gaseous state and occupying the same volume as the solution. Knowing the osmotic pressure of a dissolved substance, you can calculate its molar mass.

In order to extend colligative laws to concentrated solutions of non-electrolytes and dilute solutions of electrolytes, Van't-Hoff proposed to introduce a correction isotonic coefficient (i), which shows the degree of deviation of real solutions from ideal ones and is defined as the ratio of experimental and theoretical values. From the Van't-Hoff equation, it can be concluded that the osmotic pressure of a dilute solution is equal to the pressure that the dissolved substance would exert, being in a gaseous state and occupying the same volume. Knowing the osmotic pressure of a dissolved substance, you can calculate its molar mass.

In order to extend colligative laws to concentrated solutions of non-electrolytes and dilute solutions of electrolytes, Van't-Hoff proposed to introduce a correction coefficient i (isotonic coefficient), which shows the degree of deviation of real solutions from ideal ones and is defined as the ratio of experimental and theoretical values:

$$i = \frac{P_{\text{exp.}}}{P_{\text{theor.}}}.$$

Then the equation for electrolytes will look like this:

$$P_{\text{osm}} = iCRT$$

Taking into account the isotonic coefficient, the equation of Raoult's law for dilute solutions will take the following form:

$$\Delta T_{\text{boil}} = i \cdot K_E \frac{m_{\text{solute}} \cdot 1000}{M_{\text{solute}} \cdot m_{\text{solvent}}};$$
$$\Delta T_{\text{freez}} = i \cdot K_K \frac{m_{\text{solute}} \cdot 1000}{M_{\text{solute}} \cdot m_{\text{solvent}}}.$$

The isotonic coefficient for non-electrolytes dissolved in water is equal to one, and for electrolytes it is greater than one. Its value increases as the electrolyte dissolves. For solutions in which the association of solute molecules occurs, the isotonic coefficient is less than unity.

In practice, the isotonic coefficient can be found experimentally using one of the gas laws, and then used in all calculations for the same substance.

Test questions

1. What is a solution? Supply the classification of solutions?
2. What is the difference between the physical and chemical theory of solutions?
3. What is concentration? Supply the main types of denote of concentration units?
4. Define Raoult's law and state its consequences.
5. Define the concept of isotonic coefficient?
6. Define the concept of osmosis and osmotic pressure?
7. Define the phenomena cryoscopy and ebulioscopy?

Chapter8. Dissociation and electrolytes

8.1. Dissociation in solution of electrolytes

The laws of van't Hoff and Raoult are derived for ideal solutions in which chemical interaction between the components of the solution do not occur and dissociation or association of the dissolved substance does not occur. When studying solutions of acids, alkalis and salts, the solutions of which conduct an electric current, it turned out that these solutions show higher values of osmotic pressure, a decrease in the freezing point or an increase in the boiling point. The reason for the deviation from the laws of van't Hoff and Raoult in solutions of electrolytes is explained by the Swedish physicist and chemist Arrenius (1887) in the theory of electricity dissociation. He established a connection between the inability of electrolyte solutions to conduct electricity current and the deviation of their authorities from the laws of Raoult and van't Hoff. Electric materials are substances, solutions and melts that conduct electricity in a three-phase current. In this regard, for electrolytes, van't Hoff introduced the isotonic coefficient (i) into the equation, which shows how many times the osmotic pressure of the solution, a decrease in the freezing point or an increase in the boiling point, determined experimentally, is greater than the calculated one:

$$i = \frac{P_{\text{osm.exp.}}}{P_{\text{osm.theor.}}};$$

$$i = \frac{\Delta T_{\text{point.exp.}}}{\Delta T_{\text{point.theor.}}};$$

$$i = \frac{\Delta T_{\text{boiling.exp.}}}{\Delta T_{\text{boiling.theor.}}}.$$

Since electric current can only be carried by charged particles –positive (cation) or negative (anion), then in solutions electrolytes are ions, formed as a result of the dissociation of molecules according to the electrolyte. Electrolytic dissociation is the process of splitting electrolyte molecules into ions under the influence of polar solvent molecules.

The mechanism of electrolytic dissociation can be simplified as follows. Each of the ions located on the surface of the electrolyte crystal creates an electrostatic field around itself.

Polar molecules of the solvent, falling into the sphere of action of this field, are they cluster and form a salt shell around each ion (Fig. 8.1).

Between polar molecules of water and ions of molecules of a substance, a dipole-ionic bond arises, as a result of which the bonds between ions in the substance weaken and under the influence of these In the slow motion of the solvent molecules, the separation of the salt ions from each other is observed, i.e. from There is a solution to the problem. Molecules with polar bonds are also subject to dissociation, such as the dissociation of acids and hydroxides (bases).

Dissociation is affected not only by the size of the electrical permeability medium to high. Of great importance is the chemical interaction between the molecules of the dissolved substance and solvent (solution) that is accompanied by the release or absorption of lots of salts. That's why the same dissolved salts in water behave differently in different their solvents, although their partial permeability was the same.

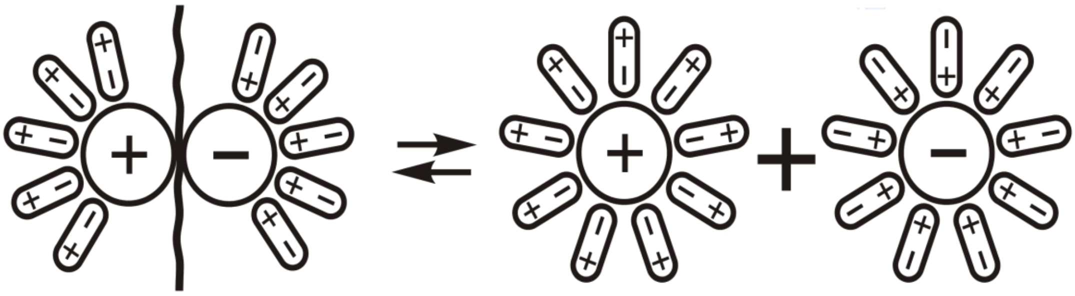


Fig. 8.1. Scheme of dissociation of electrolyte molecules with an ionic bond under the influence of polar solvent molecules

As a result of dissociation, not ions themselves are formed, but complexes of ions with solvent molecules (ion hydrates). For example, a hydrogen ion always combines with one water molecule in solution, forming a hydroxonium ion H_3O^+. However, in the equations of dissociation reactions, for simplification, the formulas of simple ions are mostly written, for example, in the form of H^+.

The main provisions of the Arrhenius theory are as follows:

- in any solvents with a fairly high dielectric constant electrolytes spontaneously dissociate to form oppositely charged ones ions;
- in the solution, a dynamic equilibrium is established between ions and non-dissociated molecules, that is, the dissociation process is reversible.

The quantitative equilibrium state is determined by the degree of dissociation of the electrolyte α, which is equal to the ratio of the number of molecules split into ions in the solution to the total number of molecules in the solution:

$$\alpha = \frac{\text{number of dissociated molecules}}{\text{total number of molecules}}.$$

The degree of dissociation is expressed as a fractional number or as a percentage and varies from 0 to 1 (0-100%). The degree of dissociation depends on the nature of the dissolved substance, the solvent in which the electrolyte is dissolved, and the temperature and concentration of the solution.

According to the degree of dissociation, electrons are divided into strong and weak. Strengths are electrolytes, the degree of dissociation of which is in 0.1 N aqueous solution exceeds 30%, weak – the degree of dissociation of which in 0.1 N aqueous solution Shy for 3%. The intermediate position ($3\%<\alpha<30\%$) is occupied by medium-sized electric vehicles, which for their Our powers are getting closer to the weak. Strong electrolytes include almost all salts, alkalis, some acids (HC1, $HCIO_4$, HNO_3 , H_2SO_4, etc.), to weak ones – most bases, amphoteric hydroxides, some acids You (H_2S, H_3BO_3, HSN, H_2SiO_3, etc.). With the analysis of electrical solutions.

The degree of their dissociation is increasing over time (Table 8.1). From table it is obvious that when dissociation slow down the dissociation degree αof weak electrolytes is reduced.

Table 8.1.

Effect of dilution (in four times) on the degree of dissociation and dissociation constant of acetic acid

Dilution, liter/mol-eq.	Degree of dissociation (α)	Dissociation constant (K_{dis})
13.57	0.0157	$1.845 \cdot 10^{-5}$
13.57×4	0.0319	$1.849 \cdot 10^{-5}$
13.57×4^2	0.0614	$1.851 \cdot 10^{-5}$
13.57×4^3	0.1190	$1.850 \cdot 10^{-5}$
13.57×4^4	0.2236	$1.850 \cdot 10^{-5}$

Solutions of strong electrolytes with a concentration less than 0.001 n are almost the input is dissociated into ions, that is, α practically becomes equal to 1.

For solutions of electrolytes, the magnitude of the osmotic pressure, lowering the temperature Restrictions and other authorities are determined by the joint purpose of by the separation of particles – ions and non-dissociable molecules. Arrhenius showed that the degree of electron dissociation can be related to isotonic van't Hoff coefficient i. As for the dissociation in the solution, N mole-balls of electron and degrees were found its dissociation increases α, then the number of dissociated molecules increases is αN, and the number of non-dissociable molecules will be:

$$N - N\alpha = N(1 - \alpha).$$

Each molecule breaks down into ions, based on this, in general, ions will be: αNn. The number of all particles (molecules and ions) will be:

$$\alpha Nn - N(1 - \alpha) = N[1 + \alpha(n - 1)].$$

Osmotic pressure is proportional to the number of particles, therefore, the observe osmotic pressure is proportional to $N[1 + \alpha(n - 1)]$. The calculated osmotic pressure is proportional to N. Then:

$$i = \frac{p_{\text{experiment}}}{p_{\text{calculated}}} = \frac{N[1 + \alpha(n - 1)]}{N} = 1 + \alpha(n - 1).$$

In the general case, for the electrolyte, which gives during the electrolytic dissociation of n ions.

$$\alpha = \frac{i - 1}{n - 1}.$$

The degree of dissociation α can take on different values, it increases with decreasing concentrations and equals units in an infinitely diluted solution (C → 0). This explains the characteristic change and what is observed during the diluted calculation of electrolytes that dissociate incompletely (acetate acid), namely: the efficiency increases with the dilution of the solution and in an infinitely diluted solution acquires borderline integer value. For example, for the NaCl bi-polar electrolyte, the isotonic coefficient in – thoroughly enlightened solutions up to 2, under the same conditions for $CaCl_2$ isotonic electrolyte the coefficient is 3.

8.2. Equilibrium in solutions of weak electrolytes

The distribution of electrons into weak and strong is conditional, but completely natural, that is, it corresponds to certain properties of solutions. Weak electrons are called electrons in which only dissociation is present in the soluble parts of molecules.

Since electrical dissociation is a reversible process, it subject to the law of the working masses. Constant balance for the dissociation reaction of acetic acid:

$$CH_3COOH \leftrightarrow CH_3COO^- + H^+;$$

$$K = \frac{C_{\text{cation}} \cdot C_{\text{anion}}}{C_{\text{molecule}}}.$$

The equilibrium constant in dissociation processes is called the dissociation constant. Polybasic acids are characterized by a graded nature of dissociation, and each degree of dissociation is characterized by its dissociation constant. For example, dissociation of H_3PO_4:

$H_3PO_4 \leftrightarrow H_2PO_4^- + H^+$ with constant K_1;
$H_2PO_4^- \leftrightarrow HPO_4^{2-} + H^+$ with constant K_2;
$HPO_4^{2-} \leftrightarrow PO_4^{3-} + H^+$ with constant K_3.

The values of the constants change in the order $K_1>K_2>K_3$. Separation of the second and third ions of the requires the consumption of energy. With an increase in the temperature of the concentration and dissociation of weak electrolytes is increase due to the fact that the dissociation of many weak electrons is an endothermic process.

When $K>10^{-2}$, electrolytes are considered strong. For medium-strength electrolytes (H_3PO_4, $Ca(OH)_2$, etc.) values of $K = 10^{-2}$-10^{-4}. Dissociation constants of weak electrolytes (NH_4OH, CH_3COOH) change in 10^{-5}-10^{-9}. Electrolytes for which $K = 10^{-9}$are called very weak.

For the solutions of weak electrolytes, Oswald established the relationship between the by the type of dissociation, degree of dissociation and molar concentration. For acetic acid, if the total concentration of electricity is C, and the degree of dissociation is α, then the number of cations, anions and non-producible molecules in the electrolyte those will be:

$$C_{\text{cation}} = C_{\text{anion}} = \alpha C;$$
$$C_{\text{CH}_3\text{COOH}} = (1 - \alpha)C.$$

Substituting the corresponding values into the equation, we determine the dissociation constant:

$$K_{\text{dis}} = \frac{\alpha^2 C}{1 - \alpha}.$$

Having accepted that the inverse of the concentration is the dilution $V = 1/C$, we obtain:

$$K_{\text{dis}} = \frac{\alpha^2}{(1 - \alpha)V}.$$

Formulas are a mathematical eform of Ostwald's law of dilation (for binary new electricity), according to which electric power of dissociation at constant temperature does not depend on concentration (dissolved solution) solution. Since the degree of dissociation in weak electrolytes is small, this value in the lower part of the equation can be neglected. Then, from re-introduction:

$$K = \alpha^2 C.$$

These equations are successfully applied to weak electorates in a wide range of dilutions, which indicates the independence of their properties from concentrations.

8.3. Solutions of strong electrolytes

The strong ones include such electrolytes, all the molecules of which are highly dissociable on ions not only in dilute but also in concentrated solutions.

According to calculations and experimental data, in solutions of strong electrolytes there are practically absente non-dissociation molecules. Therefore, it would be possible to expect that the isotonic coefficient for electrolyte NaCl is equal to 2 at any concentration of the solution, for electrolyte Na_2SO_4 – 3, etc. However, research has shown that in solutions of strong electrolytes, the coefficient *i* dependence from the concentration of the solution, and it becomes stronger with the reduction of the latter. A decrease in the isotonic coefficient with an increase in concentration for strong electrolytes are explained by the effect on thermodynamics of solution by intermolecular interactions between ions and molecules. The result of this interaction can formally be considered as a change in the degree of dissociation of a strong electrolyte, and, therefore, in the value of *i*.

Deviation from the law of effective masses, which causes a change in the dissociation constant during dilution, is taken into account by using a special value called activity instead of concentration. The concepts of activity and activity coefficient were introduced by D. Lewis (1916) for calculations of electrolytic interaction in solutions of strong electrolytes. The relationship between activity and concentration is described by the equation:

$$\alpha = \gamma C,$$

where γ– is the efficiency coefficient.

The coefficient of activity can be considered as a multiplier, the introduction of which in the formulas for ideal solutions allows to apply this expressions for real solutions. The activity can be used for osmotic pressure, temperature measurement and others.

For binary electrolytes, the activity equals:

$$a^2 = a_+ a_- \,,$$

and the equation for the average activity coefficient for a binary electrolyte is determined accordingly:

$$\gamma^2 = \gamma_+ \gamma_- \,,$$

where a_+ and a_-, γ_+ and γ_- are the activity and activity coefficient of the cation and anion, respectively.

With an infinitely large solution, the solutions are approaching to the ideal, the forces of interaction between the parts of the dissolved substance become very low and activity coincide with the concentration, and the coefficient of activity gone to be 1.

To take into account the total interaction of all substances in the calculation of the coefficient of activity Lewis and Rendall introduced the concept of ionic strength of a solution.

$$I = \frac{1}{2}\sum C_i n_i^2.$$

The ionic strength of the solution is related to the activity coefficient by the equation:

$$\ln\gamma = A\sqrt{I}\ ,$$

where A is a constant, the value of which is determined by the temperature, ion charge, and dielectric constant of the medium.

This equation expresses the **rule of ionic strength:** the activity coefficients of any electrolytes in solutions with the same ionic strength are the same (for dilute solutions, $I \approx 0.02$-0.05).

One of the tasks of the theory of solutions of strong electrolytes is to find a way calculation of the concentration of A in the equation, knowing the properties of ions and solutions. In addition, the theory considers the methods of calculation of properties that depend not only on the ionic ratio, but also from electric fields created by each other ions that interact with each other.

In calculation interaction between electric fields of ions is extremely complex problem. Therefore, it is possible to solve it by just entering a series of simple particles. In the theory of solutions of strong electrolytes, developed by Debye and Hückel (1923), the interaction of each ion with neighboring changes in the interaction of one (central) ion with the surrounding ions of another sign (opposite). As a result of such interaction, the actual number of particles that determine properties of the solution will be smaller and, accordingly, all powers will show themselves more weakly. The accumulation near the central ion of ions of the opposite sign is due to electrostatic forces of attraction and leads to the formation of the so-called ionic atmosphere.

The density of the ionic atmosphere, its radius, the rate of formation and destruction have a complex effect on the thermodynamic and conductive properties of the electrolyte solution. However, the influence of these factors can be quantified only for the simplest electrolytes and under the condition of their strong dilution.

Test questions

1. Why do solutions of electrolytes not obey laws of van't Hoff and Raoult?
2. What is the main principles of the theory of electrolytic dissociation?
3. Write the equation of the electrolytic dissociation of compounds: $Ca(OH)_2$, H_3PO_4 and write down the formulas of the dissociation constants for them.
4. Find the degree of dissociation of acetic acid (CH_3COOH) if the dissociation constant is $1.75 \cdot 10^{-5}$ and its concentration in the solution is 0.01 M.
5. Define the isotonic coefficient. How are the isotonic coefficient and the degree of dissociation related to each other?
6. Define Ostwald's law. Find the dissociation constant of acetic acid if the degree of dissociation of its solution is 0.0319 at a dilution of 54.28 l/mol-eq.
7. What are the main principles of the theory of solutions for strong electrolytes? Define the term activity in solution. How is it related to concentration?

Chapter9. Hydrolysis of salts

9.1. Electrical dissociation of water and hydrogen index

Although water is most often thought of as a substance that does not dissociate into ions, studies of purified water have shown that it has a slight electrical conductivity that increases with temperature. Thus, at 273 K, the specific electrical conductivity of water is $1{,}5 \cdot 10^{-6}$ $Om^{-1} \cdot m^{-1}$, and at 289 K it is equal to $6{,}2 \cdot 10^{-6}$ $Om^{-1} \cdot m^{-1}$.

The presence of electrical conductivity can be explained only by the fact that the molecules in although to a small extent, they still break down into ions, so pure H_2O is weak electrolyte. Proceeding from this, it is possible to write down the process of dissociation of water:

$$H_2O \leftrightarrow H^+ + OH^-,$$

or

$$2H_2O \leftrightarrow H_3O^+ + OH^-.$$

It should be noted that the ions that are formed have the formulaH_3O^-, but for simplicity, are used H^+ ions, since this does not affect the conclusions. The balance of the water dissociation process is characterized by the dissociation constant, which is generally determined by activity a:

$$K = \frac{a_{\mathrm{H}^+} a_{\mathrm{OH}^-}}{a_{\mathrm{H2O}}}.$$

Taking into account that at room temperature only one of approximately 108 water molecules dissociates into ions, for dilute solutions and for pure water the activities can be replaced by concentrations of *C*:

$$K = \frac{C_{\mathrm{H}^+} C_{\mathrm{OH}^-}}{C_{\mathrm{H2O}}}.$$

The concentration of H_2O molecules can be calculated by dividing the mass of 1 liter of water by its molar mass:1000/18 = 55.5 mol/l.

Considering this value to be constant, we can write:

$$C_{\mathrm{H}^+} C_{\mathrm{OH}^-} = K \cdot 55.5 K_w \, .$$

The value of K_W is called the ionic product of water. Since, according to the dissociation equation, the concentrations of H^+ and OH^- ions in water are the same, they can be determined by knowing the ionic product of water. If at a temperature of 295 K, the ion product of water is equal to 10^{-14}, then:

$$C_{\mathrm{H}^+} = C_{\mathrm{OH}^-} = \sqrt{K_w} = 10^{-7} \mathrm{mole/liter.}$$

During calculations related to aqueous solutions of strong concentrated electrolytes, not concentrations, but ion activities should be used:

$$a_{\mathrm{H}^+} = a_{\mathrm{OH}^-} = K_w.$$

The K_W constant depends on the temperature. Ionic product of water and the concentrations of H^+ and OH^- ions are dependence of the temperature (Table 9.1).

Table 9.1

Dependence of the ionic product of water on temperature

T, K	273	293	298	323	353	373
K_W, 10^{-14}	0,11	0,68	1,11	5,55	25,1	55,0
$C_{H^+} = C_{OH^-}$, 10^{-7}	0,34	0,78	1,05	2,44	5,02	7,4

Thus, in aqueous solutions, the concentrations of H^+ and OH^- ions at a constant temperature are interconnected. It is enough to indicate the content of any of them to determine the concentration of the other, using the constant value f ion product of water (10-14). The relationship between ion concentrations can be used to characterize the acidity and alkalinity of various environments. According to the theory of electrolytic dissociation, H+ ions are carriers of acidic properties, and OH^- ions are carriers of basic properties (Fig 7.1).

Therefore, the solution will be:

Neutral, if $a_{H+} = a_{OH^-} = 10^{-7}$

Acid, if $a_{H^+} > a_{OH^-}$

Alkaline, if $a_{H^+} < a_{OH^-}$

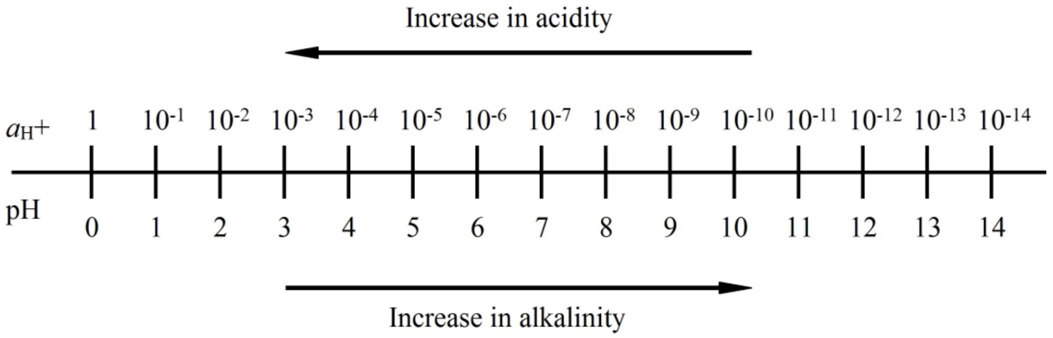


Fig. 9.1. Scale of decreasing hydrogen ion concentration and increasing in alkalinity and acidity

To characterize the acidity (alkalinity) of the environment, a specially introduced parameter is the hydrogen index or pH. The hydrogen indicator, or pH, is the decimal logarithm of the activity of hydrogen ions in the solution taken with the inverse sign:

$$\mathrm{pH} = \lg a_{\mathrm{H}^+} \,.$$

The hydrogen indicator determines the nature of the reaction of the solution.

For example, at a temperature of 295 K, the reaction of the solution is neutral at pH =7 ($a_{\mathrm{H}}^{+}= 10^{-7}$mol/l).

At pH < 7 ($a_{\mathrm{H}}^{+}> 10^{-7}$mol/l), the reaction of the solution is acidic, and at pH > 7 ($a_{\mathrm{H}}^{+}< 10^{-7}$mol/l), the reaction of the solution is alkaline.

A pH value of 7 corresponds to a neutral solution only at a temperature of 295 K (22°C). With a change in temperature, K_W and the concentration of H^+ ions in a neutral solution change. So, at temperature 353 K value of $K_W = 25.1 \cdot 10^{-14}$ and in a neutral solution the activity of hydrogen ions will $a_{\mathrm{H}}+ = 5 \cdot 10^{-7}$mol/l and pH = 6.3.

Based on the ionic product of water, it is possible according to known values activities of H^+ ions, calculate the activity of OH^- ions:

$$a_{\mathrm{OH}^-} = \frac{K_w}{a_{\mathrm{H}^+}} \,.$$

The hydrogen index is important for understanding most of the processes that take place in the liquid phase, since H^+ and OH^- ions are directly involved in many processes. In addition, these ions are homogeneous catalysts for many reactions. The value of pH can serve as a criterion for the strength of an acid or a base. In a series of acids, the stronger will be the one in which, at the same molar concentration, the activity of H^+ ions will be higher ($pH < 7$).

9.2. Hydrolysis of salts and constant of hydrolysis

Hydrolysis is the interaction of substances with water, in which the constituent parts of the substance interact with parts of water. This definition covers the hydrolysis of inorganic compounds: salts, carbides, halogens, metal halides and the hydrolysis of organic compounds - esters, fats, carbohydrates, proteins. Let's stop at the hydrolysis of salts.

Hydrolysis of salt is the chemical interaction of salt ions with water, which leads to the formation of a weak electrolyte, which contributes to the accumulation of H^+ or OH^- ions and, accordingly, to a change in the reaction of the salt solution environment. Let's write the salt hydrolysis equation in general form:

$$MA + H_2O \rightarrow MOH + HA,$$

where M^+ is a cation, A^- is anion, MOH is alkaline, and HA is acid

As we already know, the equilibrium of the reaction shifts in the direction of the formation of poorly dissociated substances, gases or slightly or poorly soluble substances. Salts formed with the participation of weak acids or weak bases are subject to hydrolysis. Salts, which are derivatives of strong acids and strong bases, do not hydrolyze, because their ions do not bind water ions (H^+ or OH^-) in a weak electrolyte, and therefore do not shift its ionic balance. Therefore, when such salts as KCl, $NaNO_3$, Na_2SO_4, $CaCl_2$, $Ba(NO_3)_2$, etc. are dissolved in water, the reaction of the medium remains neutral ($pH =7$).

Salts, which include multi-charged ions, are hydrolyzed step by step (by stages). At the same time, the hydrolysis of salt mainly occurs according to the first stage.

Depending on the nature of the salt, three types of salt hydrolysis are distinguished:

by cation– characteristic of salts formed by the cation of a weak base and the anion of a strong acid. For example: NH_4NO_3, $FeCl_3$, $Zn(NO_3)_2$, $CuSO_4$ and others.

by anion– characteristic of salts formed by the cation of a strong base and the anion of a weak acid. For example: Na_2CO_3, K_2SO_3, Na_3PO_4, $Ca(CH_3COO)_2$ and others.

by cation and anion – characteristic of salts formed by the cation of a weak alkaline and the anion of a weak acid. For example: $(NH_4)_2S$, $Al(CH_3COO)_3$, NH_4NO_2, $(NH_4)_2CO_3$and others.

Hydrolysis of the salt by cation occurs as a result of the salt cation binding hydroxide ions of water in the poorly dissociated electrolyte.

The strong acid that is formed does not bind H^+ ions. It is in the solution in the form of ions. Therefore, solutions of salts formed by the cation of a weak base and the anion of a strong acid have an acidic reaction of the environment ($pH < 7$).

The hydrolysis products of such salts, depending on the charge of the cation, are:

- a weak alkaline (if the salt is formed by a singly charged cation);
- alkaline salt (if the salt is formed by a multi-charged cation).

Example:

$$NH_4Cl + H_2O \leftrightarrow NH_4OH + HCl,$$

or

$$NH_4^+ + H_2O \leftrightarrow NH_4OH + H^+.$$

Hydrolysis of salts of multicharged weak bases occurs in stages with the formation of alkaline salts in the intermediate stages. For example, as a result of the hydrolysis of cuprum chloride (II) in the first step, cuprum hydroxochloride is formed:

$$CuCl_2 + H_2O \leftrightarrow CuOHCl + HCl,$$

or

$$Cu^{2+} + H_2O \leftrightarrow CuOH^+ + H^+.$$

After the second stage of hydrolysis, copper hydroxide (II) is formed:

$$CuOHCl + H_2O \leftrightarrow Cu(OH)_2 + HCl,$$

or

$$CuOH^+ + H_2O \leftrightarrow Cu(OH)_2 + H^+.$$

In the first stage, hydrolysis occurs to a much greater extent than in the subsequent ones. This is due to the fact that $CuOH^+$, which is formed by the first step, is a weaker base compared to $Cu(OH)_2$, which is formed by the second step. In addition, hydrogen ions H^+, which appear in the solution, cause the equilibrium of hydrolysis to shift to the left and greatly hinder its progress, therefore, the hydrolysis of salts of weak multicharged alkalines is practically determined by the first degree.

The greater the charge of the metal cation of the salt and the smaller its radius, the stronger it binds the hydroxide ions of water to a weaker alkaline and the greater the hydrolysis occurs. For example, Ferrum (II) salts ($FeCI_2$, $Fe(NO_3)_2$, etc.) are hydrolyzed to a much lesser extent than Ferrum (III) salts ($FeCI_3$, $Fe_2(SO_4)_3$, $Fe(NO_3)_3$, etc.).

Hydrolysis of salt by anion occurs as a result of the binding of H^+ water ions by the anion of the salt in the poorly dissociated electrolyte. The strong alkaline that is formed in this case does not bind hydroxide ions OH^-. Therefore, solutions of salts formed by the cation of a strong base and the anion of a weak acid have alkaline reaction of the medium ($pH > 7$). Examples of salts of this type can be soluble salts of common weak acids, such as acetate, phosphate, sulfite, carbonate (CH_3COONa, Na_3PO_4, Na_2SO_3, Na_2CO_3).

The hydrolysis products of such salts, depending on the charge of the anion, are:

- weak acid (if the salt is formed by a singly charged anion);
- acidic salt (if the salt is formed by a multi-charged anion).

Example:

$$CH_3COONa + H_2O \leftrightarrow CH_3COOH + NaOH,$$

or

$$CH_3COO^- + H_2O \leftrightarrow CH_3COOH + OH^- \text{ (pH >7).}$$

The hydrolysis reaction is reversible, due to the presence of weak electrolytes among the starting substances (H_2O) and reaction products (weak acid). The hydrolysis equilibrium is also strongly shifted to the left because water is a much weaker electrolyte than the weak acid produced by hydrolysis. Hydrolysis occurs to a greater extent, the weaker is the acid formed as a result of the course of this process.

Due to the hydrolysis of salts of weak acids, the concentration of free hydroxide ions OH^-, which give the solution an alkaline reaction, increases.

Salts of polybasic weak acids are hydrolyzed step by step with the formation of acid salts, for example:

$$Na_3PO_4 + H_2O \leftrightarrow Na_2HPO_4 + NaOH,$$

or

$$PO_4^{3-} + H_2O \leftrightarrow HPO_4^{2-} + OH^- \text{ (pH > 7).}$$

Hydroxide ions OH^- accumulated in the solution inhibit the dissociation of water, preventing the second stage of hydrolysis. However, with an increase in temperature and a strong dilution, hydrolysis partially occurs according to the second degree:

$$Na_2HPO_4 + H_2O \leftrightarrow NaH_2PO_4 + NaOH,$$

or

$$HPO_4^{2-} + H_2O \leftrightarrow H_2PO_4^- + OH^- \text{ (pH > 7).}$$

Hydrolysis according to the third degree, which is described by the equation:

$$NaH_2PO_4 + H_2O \leftrightarrow H_3PO_4 + NaOH,$$

or

$$H_2PO_4^{-} + H_2O \leftrightarrow H_3PO_4 + OH^{-}.$$

Practically it does not occur, because the $H_2PO_4^{-}$ ion binds the H^+ ions of water much more weakly than the PO_4^{3-} ion.

Indeed, as in the case of salts of weak alkalines, the hydrolys is of the first step always occurs to a much greater extent than the subsequent ones, since the anion of the acid (for example, PO_4^{3-}) has a greater negative charge than its acidic anions (for example, HPO_4^{2-}, $H_2PO_4^{-}$), and therefore binds hydrogen ions of water more strongly.

Salt hydrolysis by cation and anion occurs as result of the cation and anion of the salt binding each of the water ions (H^+ and OH^-) in poorly dissociated electrolytes. The hydrolysis of salts formed by the cation of a weak alkaline and the anion of a weak acid, for example $(NH_4)_2S$, $Al(CH_3COO)_3$, $Zn(NO_2)_2$, $(NH_4)_2CO_3$, etc., occurs quite completely, since two weak electrolytes are formed as a result of hydrolysis.

Example:

$$CH_3COONH_4 + H_2O \leftrightarrow CH_3COOH + NH_4OH,$$

or

$$CH_3COO^{-}+NH_4^{+}+ H_2O \leftrightarrow CH_3COOH + NH_4OH.$$

The reaction of solutions of such salts is determined by the strength ratio of the formed weak electrolytes. It can approach neutral if the dissociation constants of a weak acid and a weak alkaline are close to each other (for example, for ammonium acetate, the dissociation constants of the substances formed as a result of the reaction are practically the same ($K_{dis(CH3COOH)}=1.75\cdot10^{-5}$, $K_{dis(NH4OH)} =1.79\cdot10^{-5}$), then the CH_3COONH_4 solution has a pH ≈ 7.

During the hydrolysis of ammonium cyanide, the reaction of the medium will be alkaline,

$$NH_4CN + H_2O \leftrightarrow NH_4OH+ HCN;$$
$$NH_4^{+} + CN^{-}+H_2O \leftrightarrow NH_4OH + HCN(pH>7).$$

during the hydrolysis of ammonium cyanide, the reaction of the medium will be alkaline, since the dissociation constant of ammonium hydroxide ($K_{NH4OH} = 1,76 \cdot 10^{-5}$) significantly exceeds the dissociation constant of hydrocyanic acid ($K_{HCN} = 7,2 \cdot 10^{-10}$). On the contrary, the hydrolysis of ammonium formate causes a weak acidification of the solution,

$$HCOONH_4 + H_2O \leftrightarrow HCOOH + NH_4OH \ (pH < 7),$$

since formic acid dissociates to a greater extent ($K_{HCOOH} = 1,8 \times 10^{-4}$) compared to ammonium hydroxide.

Hydrolysis of salts formed by a multi-charged cation or anion takes place **stepwise** (mostly according to the first step).

The hydrolysis products of such salts, depending on the charges of the cation and anion, are:

- alkaline salt (if the salt is formed by a multi-charged cation);
- acidic salt (if the salt is formed by a multi-charged anion).

Example:

$$(NH_4)_2CO_3 + H_2O \leftrightarrow NH_4HCO_3 + NH_4OH.$$

At room temperature, the second stage of hydrolysis practically does not occur. However, when heating and adding water, the second and even partially the third stage of hydrolysis can occur. For example:

$$Fe(CH_3COO)_3 + H_2O \leftrightarrow Fe(OH)_3 + CH_3COOH.$$

The first stage of this reaction:

$$Fe(CH_3COO)_3 + H_2O \leftrightarrow FeOH(CH_3COO)_2 + CH_3COOH,$$

or

$$Fe^{3+} + 3CH_3COO^- + H_2O \leftrightarrow FeOH^{2+} + 2CH_3COO^- + CH_3COOH.$$

The chemical reaction at this stage occurs under any conditions, but then the reaction starts to slow down or even stops.

The second stage:

$$FeOH(CH_3COO)_2 + H_2O \leftrightarrow Fe(OH)_2CH_3COO + CH_3COOH,$$

or

$$FeOH^{2+} + 2CH_3COO^{-} + H_2O \leftrightarrow Fe(OH)_2^{+} + CH_3COO^{-} + CH_3COOH.$$

The third stage:

$$Fe(OH)_2CH_3COO + H_2O \leftrightarrow Fe(OH)_3 + CH_3COOH,$$

or

$$Fe(OH)_2^{+} + CH_3COO^{-} + H_2O \leftrightarrow Fe(OH)_3 + CH_3COOH.$$

The solution acquires a weakly acidic environment because $K_{dis(CH3COOH)} = 1.75 \cdot 10^{-15}$ is greater than $K_{dis(Fe(OH)3)} = 1.35 \cdot 10^{-12}$.

Many salts of this type hydrolyze irreversibly. An example of salts that **undergo complete hydrolysis** are salts of weak alkalines and very weak, unstable or volatile acids: Cr_2S_3, Al_2S_3, Fe $(CO_3)_3$, $Al_2(CO_3)_3$, $CuSiO_3$, Ag_2SiO_3, $Fe_2(SO_3)_3$, $SnCO_3$ and others. Their hydrolysis is accompanied by complete decomposition of the salt with the release of free acids and hydroxides.

Equations for reactions of complete hydrolysis of salts are written only in molecular form:

$$Al_2S_3 + 6HOH \leftrightarrow 2Al(OH)_3\downarrow + 3H_2S\uparrow.$$

Due to complete hydrolysis, these salts cannot be obtained from aqueous solutions.

$$2AlCl_3 + 3Na_2CO_3 + 3H_2O \leftrightarrow 2Al(OH)_3 + 3CO_2 + 6NaCl;$$
$$2Al^{3+} + 3CO_3^{2-} + 3H_2O \leftrightarrow 2Al(OH)_3 + 3CO_2.$$

For most salts, hydrolysis is a reversible process. Therefore, the hydrolytic equilibrium is quantitatively characterized by the degree of hydrolysis and the hydrolysis constant.

The degree of salt hydrolysis is the ratio of the number of hydrolyzed molecules to the total number of solute molecules.

We derive the salt hydrolysis constant as follows. Let's write down the hydrolysis equation:

$$MA + H_2O \leftrightarrow MOH + HA.$$

This chemical equilibrium corresponds to mathematic formula of the equilibrium constant:

$$K_{eq} = \frac{[\mathrm{MOH}][\mathrm{HA}]}{[\mathrm{MA}][\mathrm{H_2O}]}.$$

The concentration of water in the diluted solution is practically constant.

$$K_{eq}[\mathrm{H_2O}] = K_{hid}\ ;$$

$$K_{hyd} = \frac{[\mathrm{MOH}][\mathrm{HA}]}{[\mathrm{MA}]}.$$

The K_{hyd} value is called the hydrolysis constant. Its value indicates the ability of the salt to undergo hydrolysis. The hydrolysis constant can be calculated using the following equations.

For salt of a weak acid and a strong alkaline:

$$K_{hyd} = \frac{K_{\mathrm{H_2O}}}{K_{acid}}.$$

For salt of a weak alkaline and a strong acid:

$$K_{hyd} = \frac{K_{\mathrm{H_2O}}}{K_{alkaline}}.$$

For salt of a weak acid and a weak alkaline:

$$K_{hyd} = \frac{K_{\mathrm{H_2O}}}{K_{acid}K_{base}}.$$

The degree of hydrolysis is determined by the nature of the salt, its concentration and temperature. The nature of the salt is revealed in the value of the hydrolysis constant. The dependence on concentration is expressed in the fact that the degree of hydrolysis increases with dilution of solution. Indeed, let us have, for example, a solution of potassium cyanide. It establishes an equilibrium to which the constant corresponds:

$$\mathrm{KCN} + \mathrm{H_2O} \leftrightarrow \mathrm{HCN} + \mathrm{KOH},$$

$$K_{hid}(\mathrm{KCN}) = \frac{[\mathrm{KOH}][\mathrm{HCN}]]}{[\mathrm{KCN}]}.$$

Dilute the solution 10 times. At the first moment, the concentration so fall substances – KSN, HCN and KOH – decrease by 10 times. As a result, the numerator of the right-hand side of the hydrolysis constant equation will decrease by 100 times, and the denominator by only 10 times. But the hydrolysis constant, like any equilibrium constant, does not depend on the concentrations of substances. Therefore, the equilibrium in the solution will be disturbed. In order for it to be established again, the numerator of the fraction must increase, and the denominator must decrease, that is, some amount of salt must be additionally hydrolyzed. As a result, the concentrations of HCN and KOH will increase, and the concentration of KSN will decrease. Therefore, the degree of salt hydrolysis will increase.

The influence of temperature on the degree of hydrolysis follows from the principle of Le Chatelier. All neutralization reactions occur with the release of heat, and hydrolysis – with the absorption of heat. Since the yield of endothermic reactions increases with increasing temperature, the degree of hydrolysis also increases with increasing temperature.

It is clear from the above that to weaken hydrolysis, the solutions should be kept concentrated and at low temperatures. In addition, inhibition of hydrolysis is facilitated by acidification in the case of salts formed by a strong acid and a weak base, or by basification for salts formed by a strong base and a weak acid.

Test questions

1. Find the pH if the concentration of OH^- ions in the solution is 10^{-5} mol/l.
2. Find the concentration of H^+ and OH^- ions in a solution with pH = 5.
3. Define the term hydrolysis. What salts can be hydrolyzed?
4. Write the equation for the hydrolysis of salts $ZnCl_2$, K_2CO_3, Li_2S, and find the pH of their solutions.
5. Write the equation for the hydrolysis of salts $FeCl_3$, Na_2SO_3, Na_2S, and find the pH of their solutions.
6. Which of the $CrCl_3$, NaCl, Na_2CO_3 salts cannot be hydrolyzed and explain why?
7. The hydrolysis products of which salts are the insoluble compounds $Cu(OH)_2$ and H_2S? Write the reaction equations as examples.

Chapter 10. Red-ox reactions

10.1.General information about red-ox reactions

Reduction-oxidation reactions are those that occur with a change in the degree of oxidation of some reactant atoms. This happens due to the redistribution of electrons, that is, some atoms give up electrons and some others accept them. These two processes are closely related, occur synchronously and obey the law of conservation of matter (the total number of electrons does not change). Electron transfer can occur indirectly (as in galvanic cells) or directly between interacting molecules and ions.

In the simplest case, the change in oxidation states occurs due to the fact that substances pass from the state of a simple substance to a constituent part of a compound and vice versa. For example:

$$Mg + 2B \rightarrow MgB_2.$$

In simple substances, all atoms have an oxidation state of 0. In the composition of the MgB_2 compound, boron, as a more electronegative element, acquires a negative oxidation state, and magnesium, accordingly, is positive. That is, magnesium gives its electrons, and boron accepts them.

$$\begin{array}{l|l} Mg^0 - 2e \rightarrow Mg^{+2} & 1 \\ B^0 + 1e \rightarrow B^- & 2 \end{array}$$

Since magnesium has II valence, and boron in this compound has I valence, the number of electrons given and accepted is unequal. For balance, we should note (after the vertical bar) that their ratio is 1 to 2. This ratio corresponds to the stoichiometric coefficients in the reaction equation.

In red-ox reactions, it is very important to correctly determine the stoichiometric coefficients. To do this, use the electronic balance method.

1. First, the oxidation state of all elements in the starting compounds and reaction products is determined. Find the elements whose oxidation state changes during the reaction.

2. Then equations are written that show only the change in oxidation state. The number of electrons that enter and leave atoms is found. Since the actual number of electrons in the system is constant, these oxidation and reduction equations are adjusted using coefficients. These are numbers written

down after simplified reactions. They are also written in the basic reaction equation before the corresponding compounds.

3. If necessary, the amounts of other elements that do not change the oxidation state are equalized using other coefficients.

4. Lastly, the number of hydrogen and oxygen atoms is equalized, usually like water molecules. It should be noted that water is always present in aqueous solutions. Therefore, if necessary, its molecules should be added. However, you have to be very careful with this in melts, dry gases or other solvents. The important thing is that when heated, water turns into steam and gone from the reaction system as a gas.

$$2Na + S \rightarrow Na_2S,$$

$$\begin{array}{l|l} Na^0 - 1e \rightarrow Na^{+1} & 2 \\ S^0 + 2e \rightarrow S^{2-} & 1 \end{array}$$

It is easy to understand that all reactions in which simple substances enter or as a result of which they are formed are red-ox. However, they also include reactions involving compounds of elements having different valences. For example:

$$Fe_2O_3 + CO \rightarrow 2FeO + CO_2,$$

$$\begin{array}{l|l} Fe^{3+}+1e \rightarrow Fe^{+2} & 2 \\ C^{2+} - 2e \rightarrow C^{4+} & 1 \end{array}$$

When making electronic balances with gases, remember that most molecules consist of two atoms. This does not affect their oxidation number, since for all simple substances it is zero. However, this must be taken into account for the number of electrons come and gone. This can be done by writing down molecules and immediately doubling their number. For example:

$$S + O_2 \rightarrow SO_2,$$

$$\begin{array}{l|l} S^0 - 4e \rightarrow S^{+4} & 1 \\ O_2^0+4e \rightarrow 2O^{2-} & 1 \end{array}$$

In complex cases, choosing the coefficients is much more difficult than determining the electronic balance, so first the electronic equations are compiled, and then found ratio is already used to determine the coefficients. For example:

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$\begin{array}{l|l} Cu^0 - 2e \rightarrow Cu^{+2} & 3 \\ N^{+5} + 3e \rightarrow N^{+2} & 2 \end{array}$$

10.2.The most important oxidizing agents

Historically, the names oxidation and reduction were associated with the processes of oxidation of metals under the influence of air and their reduction to a pure state from compounds. On the example of iron:

$2Fe + O_2 \rightarrow 2FeO$ oxidation of Ferrum,
$FeO + C \rightarrow Fe + CO$ reduction of Ferrum.

Now oxidation is a process that leads to an increase in the degree of oxidation of an atom, even if oxygen or any oxygen-containing compounds do not participate in the reaction. Reduction, accordingly, is called a process that leads to a decrease in the degree of oxidation, even if the product of the reaction is another compound, and not a simple substance.

It can be seen that in the given reaction of iron oxidation with air oxygen, the iron itself is oxidized, but at the same time oxygen is reduced. In the second reaction equation, along with the reduction of Ferrum to iron, the oxidation of carbon to carbon monoxide occurs. Oxidation cannot occur without reduction and vice versa, that is why such reactions are called red-ox reactions.

It should be noted that all oxidation and reduction reactions belong to red-ox reactions. Their name with only one syllable is used to emphasize a process that is more important from a practical point of view. For example, if in the above example with iron oxide, the main task would be to obtain carbon monoxide, this reaction would be called carbon oxidation.

Combustion (wood, coal, oil, gasoline, etc.) is always a process of oxidation. In most organic compounds, carbon has an oxidation state of –1 or –4. This is explained by the fact that it is more electronegative than hydrogen.

However, if carbon has a bond with another carbon atom, then it is always non-polar covalent, that is, these electrons are not displaced to either of them. When interacting with oxygen, carbon acquires an oxidation state of 0 (amorphous carbon, or soot), then +2 (carbon monoxide) and then +4 (carbon dioxide). The latter occurs when the compound is completely burned.

High chimneys are made for more complete oxidation in the rising gas flow. Specifically, it converts carcinogenic smoke (soot) into a less toxic gas. The same applies to other devices. Residence time in the reaction space is very important for complete oxidation. Gaseous products that can quickly leave the reaction often lead to incomplete oxidation. For example, fires produce toxic carbon monoxide, which is more dangerous than dioxide. Incomplete oxidation is a serious problem in waste incineration and water treatment.

A substance that causes oxidation is called an oxidant. At the same time, she herself recovers. Conversely, a reducing agent causes reduction, but it itself is oxidized at the same time. However, oxidizing agent and reducing agent not only play a role in the red-ox reaction, but also a certain way of classifying chemical compounds.

Oxygen, ozone (O_3), hydrogen peroxide (H_2O_2), some salts of transition metals in very high degrees of oxidation ($KMnO_4$, $K_2Cr_2O_7$), as well as oxidizing acids (HNO_3 and concentrated H_2SO_4) are called strong oxidizers.

Consider the effect of strong oxidants on the same example of iron oxidation.

When oxidized by ozone in the reaction, it actually decomposes with the formation of oxygen and atomic oxygen, which is very reactive.

$$Fe + O_3 \rightarrow FeO + O_2,$$

$$\begin{array}{l|l} Fe^{0} - 2e \rightarrow Fe^{2+} & 1 \\ O^{0} + 2e \rightarrow O^{-2} & 1 \end{array}$$

A very similar mechanism is observed when hydrogen peroxide is oxidized. This unstable compound with oxygen in its uncharacteristic -1 oxidation state actually decomposes into water and atomic oxygen, which, in turn, reacts with iron.

$$Fe + H_2O_2 \rightarrow FeO + H_2O,$$

$$\begin{array}{l|l} Fe^{0} - 2e \rightarrow Fe^{2+} & 2 \\ O^{-1} + 1e \rightarrow O^{-2} & 1 \end{array}$$

In the case of compounds of transition metals in high degrees of oxidation, the reaction products are various compounds of the same metals in lower degrees of oxidation. Since for metals in low degrees the case of compounds of transition metals in high degrees of oxidation, the reaction products are various compounds of the same metals in lower degrees of oxidation. Since the formation of acidic residues is not typical for metals in low oxidation states, they will take the form of oxides or cations of the corresponding salts.

$$3Fe + 2KMnO_4 + H_2O \rightarrow 3FeO + 2MnO_2 + 2KOH,$$

$$\begin{array}{l|l} Fe^{0} - 2e \rightarrow Fe^{2+} & 3 \\ Mn^{+7} + 3e \rightarrow Mn^{+4} & 2 \end{array}$$

$$3Fe + K_2Cr_2O_7 + 7H_2SO_4 \rightarrow 3FeSO_4 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O,$$

$$\begin{array}{l|l} Fe^{0} - 2e \rightarrow Fe^{2+} & 3 \\ Cr^{+6} + 3e \rightarrow Cr^{+3} & 2 \end{array}$$

Oxidizing acids readily react with metals (even with those in the voltage range to the right of hydrogen), but without releasing hydrogen. Instead, the central atom of the acid residue is reduced to lower oxidation states. It should be noted that the composition of products strongly depends on the activity of metals and acid concentration. With very active metals (Li, Na, K), the sulfur of the acid is reduced to –2 (H_2S), and the nitrogen to +1 (N_2O), and in the case of dilute acid even to –3 (NH_3). In reactions with low-reactive metals, reduction occurs minimally, up to +4 oxidation state (NO_2, SO_2). Iron occupies an intermediate position.

$$3Fe + 8HNO_3 \rightarrow 3Fe(NO_3)_2 + 2NO + 4H_2O,$$

$$\begin{array}{l|l} Fe^{0} - 2e \rightarrow Fe^{2+} & 3 \end{array}$$

$$N^{+5} + 3e \rightarrow N^{+2} \quad \vert\, 2$$

$$Fe + H_2SO_4 \rightarrow FeSO_4 + SO_2 + 2H_2O,$$

$$\begin{array}{l|l} Fe^{0} - 2e \rightarrow Fe^{2+} & 2 \\ S^{+6} + 2e \rightarrow S^{+4} & 2 \end{array}$$

Noble metals (Au, Ag, Pt) do not react with most acids and do not remove hydrogen from them, but they do react with oxidizing acids.

$$Ag + 2HNO_{3(conc.)} \rightarrow AgNO_3 + NO_2\uparrow + H_2O,$$

$$\begin{array}{l|l} N^{5+} + 1e \rightarrow N^{4+} & 1 \\ Ag^{0} - 1e \rightarrow Ag^{+1} & 1 \end{array}$$

Aqua regia is a particularly strong oxidizing agent that reacts with noble metals. This is a mixture of nitric acid and hydrochloric acid, optimally in a molar ratio of 1:3. Aqua regia is a fuming liquid. Freshly prepared aqua regia is colorless, but it turns yellow, orange or red within seconds from the formation of nitrosyl chloride and nitrogen dioxide. It was named by alchemists because it can dissolve the noble metals gold and platinum, though not all metals.

Upon mixing of concentrated hydrochloric acid and concentrated nitric acid, chemical reactions occur.

$$HNO_3 + 3HCl \rightarrow NOCl + Cl_2 + 2H_2O.$$

Aqua regia dissolves gold, although neither constituent acid will do so alone. Nitric acid is a powerful oxidizer, which will actually dissolve a virtually undetectable amount of gold, forming gold (III) ions Au^{3+}.The hydrochloric acid provides a ready supply of chloride ions Cl^{-}, which react with the gold ions to produce tetrachloroaurate (III) anions $[AuCl_4]^{-}$, also in solution.

$$Au + 3HNO_3 + 4HCl \rightarrow H[AuCl_4] + 3NO_2 + 3H_2O,$$

$$\begin{array}{l|l} N^{5+}+1e \rightarrow N^{4+} & 3 \\ Ag^{0}-3e \rightarrow Au^{3+} & 1 \end{array}$$

Mercury is also an oxidizing agent in the formation of amalgams.

Amalgam is an alloy of mercury with another metal. It may be a liquid, a soft paste, or a solid, depending on the mercury content. These alloys are formed through metallic bonds. Almost all metals can form amalgams with mercury. The exceptions are iron, platinum, tungsten and tantalum. Silver-mercury amalgams are important in dentistry, and gold-mercury amalgam is used in the extraction of gold from minerals.

Mercury salts, compared to metallic mercury and amalgams, are highly toxic due to their solubility in water. The presence of these salts in water can be detected due to the readiness of mercury ions to form an amalgam with copper. A solution of the nitric acid salts being tested is applied to a piece of copper foil, and any mercury ions present leave a silver-colored amalgam stain. Silver ions leave similar stains, but are easily washed off, allowing silver and mercury to be identified.

Red-ox reaction in which mercury oxidizes copper:

$$Hg^{2+} + Cu \rightarrow Cu^{2+} + Hg,$$

$$\begin{array}{l|l} Hg^{2+}+2e \rightarrow Hg^{0} & 1 \\ Cu^{0}-2e \rightarrow Cu^{2+} & 1 \end{array}$$

10.3.The most important reducing agents

Strong reducing agents are hydrogen, active metals (Mg, Al are widely used), sulfides (H_2S, Na_2S), carbon in the form of activated carbon. Regenerators are also chemical compounds in the composition of fuel that are oxidized during combustion to CO_2, H_2O, etc.

The most important reducing agent is Hydrogen. The usual product of its oxidation is water, sometimes H^+ in an acid, or an OH^- group in a base.

$$Fe_2O_3 + 3H_2 \rightarrow 2Fe + 3H_2O,$$

$$\begin{array}{l|l} Fe^{3+}+3e \rightarrow Fe^{0} & 2 \\ 2H^{0}-2e \rightarrow 2H^{1+} & 3 \end{array}$$

In this role, it is used in both inorganic and organic chemistry.

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O,$$

$$\begin{array}{l|l} C^{4+}+8e \rightarrow C^{4-} & 1 \\ 2H^0-2e \rightarrow 2H^{1+} & 4 \end{array}$$

$$CH_2{=}CH_2 + H_2 \rightarrow CH_3{-}CH_3,$$

$$\begin{array}{l|l} 2C^{2-}+2e \rightarrow 2C^{3-} & 1 \\ 2H^0-2e \rightarrow 2H^{1+} & 1 \end{array}$$

In general, there are much fewer strong reducing agents on Earth than strong oxidizing agents, and they are very rarely found in their pure form. This is explained by the fact that the planet's atmosphere is filled with oxygen, that is, an oxidizing agent. Therefore, the restoration processes are technically more difficult.

Any fuel used in technology is a reducing agent. However, in some cases, when the engine is operating in a space where there is no access to air oxygen, the apparatus must also contain a supply of fuel oxidizer.

It should be noted that the roles of oxidizing agent and reducing agent in a red-ox reaction are relative roles. For example, oxygen is almost always an oxidizing agent. However, in the reaction with fluorine, it does not add electrons, as usual, but gives them away, since fluorine is a more electronegative element, that is, it is better at annexing shared electrons. As a result, the oxidation state of oxygen changes from 0 to +2, that is, oxygen in this exotic case is a reducing agent.

$$O_2 + 2F_2 \rightarrow 2OF_2,$$

$$\begin{array}{l|l} O_2{}^0-4e \rightarrow 2O^{2+} & 1 \\ F_2{}^0+2e \rightarrow 2F^{-} & 2 \end{array}$$

By the way, this unique compound with oxygen in the +2 oxidation state is not formally fluorine oxide, but should be called only oxygen fluoride.

When considering specific products of the red-ox react, one should take into account the most characteristic oxidation states, the stability of the compounds, as well as their state of aggregation. It should be taken into account that gases are particularly easy to escape from reacting space. Therefore various gaseous compounds formed very often, even if they are not very stable (for example, many nitrogen oxides).

Unstable compounds of elements in oxidation states that are not characteristic of them enter into reactions more easily, using every opportunity to achieve a more stable state. For example, phosphine PH_3 reacts more dramatically than ammonia NH_3.

In general, elements that can have different oxidation states are more capable of red-ox reactions than with only a few or only one possible valence. The most stable are active metals in the oxidation state +1 or +2, fluorine in the oxidation state –2, then silicon and carbon +4, aluminum +3 and oxygen –2.

An exotic case of a red-ox reaction are those reactions with oxidation and reduction of the same element. They are called self-oxidation and self-reduction reactions. As a result of the reaction, some of the atoms of the same element increase, and the other part decreases, the oxidation state. This is possible if the reaction products are more stable than starting compound. For example:

$$4KClO_3 \rightarrow 3KClO_4 + KCl,$$

$$\begin{array}{l|l} Cl^{5+} - 2e \rightarrow Cl^{7+} & 3 \\ Cl^{5+} + 6e \rightarrow Cl^{-} & 1 \end{array}$$

Such reactions often involve oxides that do not form salts and cannot form acids or bases directly.

$$H_2O + 2NO_2 \rightarrow HNO_3 + HNO_2,$$

$$\begin{array}{l|l} N^{4+} - 1e \rightarrow N^{5+} & 1 \\ N^{4+} + 1e \rightarrow N^{3+} & 1 \end{array}$$

The reverse process is also possible, when atoms of the same element in different oxidation stages manifest themselves in such a way that the number of their electrons becomes the same or, at least, to a lesser extent in relation to each other. For example:

$$C + CO_2 \rightarrow 2CO,$$

$$\begin{array}{l|l} C^{0}-2e \rightarrow C^{2+\ +} & 1 \\ C^{4+}+2e \rightarrow C^{2+} & 1 \end{array}$$

$$CH_4 + 2CO_2 \rightarrow C + 2CO + 2H_2O,$$

$$\begin{array}{l|l} C^{4-}-4e \rightarrow C^{0} & 1 \\ C^{4+}+2e \rightarrow C^{2+} & 2 \end{array}$$

In some cases, the composition of reaction products is determined not by the stability of the compounds, but by the ratio of the reagents. For example, in the latter case, an excess of CH_4 would shift the equilibrium towards the formation of simple carbon, and an excess of CO_2– towards the formation of monoxide. With certain quantities of reagents there would be only one reaction product, but with others this is impossible.

In cases where the coefficients show the actual ratio of the reactants, the products of the red-ox reaction are selected so that they correspond to these coefficients. For example, alternatives to the last reaction:

$$CH_4 + CO_2 \rightarrow 2C + 2H_2O,$$

$$\begin{array}{l|l} C^{4-}-4e \rightarrow C^{0} & 1 \\ C^{4+}+4e \rightarrow C^{0+} & 1 \end{array}$$

$$CH_4 + 3CO_2 \rightarrow 4CO + 2H_2O,$$

$$\begin{array}{l|l} C^{4-}-6e \rightarrow C^{2+} & 1 \\ C^{4+}+2e \rightarrow C^{2+} & 3 \end{array}$$

As we can see, the chemical nature of the reagents is the same, but the products are different. This depends on the ratio of the starting compounds in the reaction.

Test questions

1. Supply an equation for the oxidation of potassium with dilute nitric acid if it is known that the product of the reaction will be NH_3. Calculate the electronic balance and find the reaction coefficients. What will change in the reaction if a less active metal is taken instead of potassium?
2. Supply an equation for the oxidation of sodium with concentrate nitric acid if it is known that the product of the reaction will be N_2O. Calculate the electronic balance and find the reaction coefficients. What will change in the reaction if a less active metal is taken instead of sodium?
3. Supply an equation for the oxidation of tin with dilute nitric acid if it is known that the main product of the reaction will be NO. Calculate the electronic balance and find the reaction coefficients. What will change in the reaction if a more active metal is taken instead of tin?
4. Supply an equation for the oxidation of lead with concentrated nitric acid if it is known that the main product of the reaction will be NO_2. Calculate the electronic balance and find the reaction coefficients. What changes in the reaction if a more active metal is taken instead of lead?
5. Supply an equation for the oxidation of lithium with concentrated sulfuric acid if it is known that the main product of the reaction will be H_2S. Calculate the electronic balance and find the reaction coefficients. What will change in the reaction if a less active metal is taken instead of lithium?
6. Supply an equation for the oxidation of iron with concentrated sulfuric acid if it is known that the main product of the reaction will be pure S. Calculate the electronic balance and find the reaction coefficients. What will change in the reaction if a less active metal is taken instead of iron?
7. Supply an equation for the oxidation of copper with concentrated sulfuric acid if it is known that the main product of the reaction will be pure SO_2. Calculate the electronic balance and find the reaction coefficients. What will change in the reaction if a more active metal is taken instead of copper?

Chapter11. Electrochemistry

11.1. Electrode potential and reactivity series of metals

The interaction of any metal with the solution in which it is immersed is determined by the features of the metallic chemical bond. In the nodes of the crystal lattice, there are metal ions, and between them there is a common electron cloud.

Under the influence of polar molecules (for example, water), metal ions can undergo the same action as during dissociation and pass into solution. However, at the same time, excess electrons appear in the electron cloud, which creates a certain excess charge. In such conditions, the ions in the solution easily return to the metal surface and are difficult to separate. Over time, a dynamic equilibrium is establish according to the scheme: metal – metal ions (in solution).

Metal ions that have gone into solution will not move away from the surface in most cases, but will stay close to the surface. A so-called electric double layer will form at the metal/solution interface (Fig. 11.1).

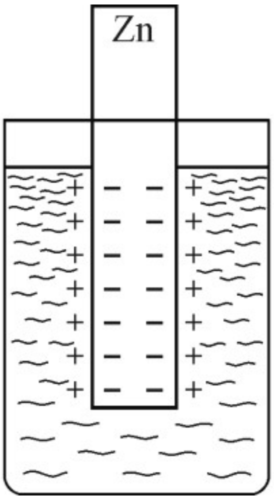


Fig. 11.1. Double electric layer

The dynamics of this process is determined by a certain property of the metal, which is related to its ability to enter the ionized state. It is called the electrochemical potential of the metal and depends on its nature and the concentration of its ions in the electrolyte solution.

In the case of contact between two such metals immersed in electrolyte solutions, a potential difference arises between them, which causes the transfer of electrons from one metal to another and a chemical process in the electrolyte solution that compensates for these changes. At the same time, the metal with a more negative value of the electrochemical potential realizes the transition of metal ions from the crystal lattice into the solution, and the excess electrons are redistributed between the two metals. Obviously, the process will be more intensive in the case of a large difference in electrochemical potentials, and less intensive in the case of their close values.

To compare the electrode potentials of different metals, the so-called **normal hydrogen electrode** is used. This is a plate made of an inert metal (platinum), immersed in sulfuric acid, near which hydrogen is passed so that its bubbles tightly cover its surface. In a pair of two electrodes, it behaves as if a hydrogen plate is immersed in an acid solution (Fig. 11.2). An equilibrium is established between the molecules in the bubbles and the ions in the solution:

$$H_2 \rightarrow 2H^+ + 2e.$$

The electrode potential of such a hydrogen electrode is taken as zero, and the potentials of other metals are calculated relative to it (Table 11.1).

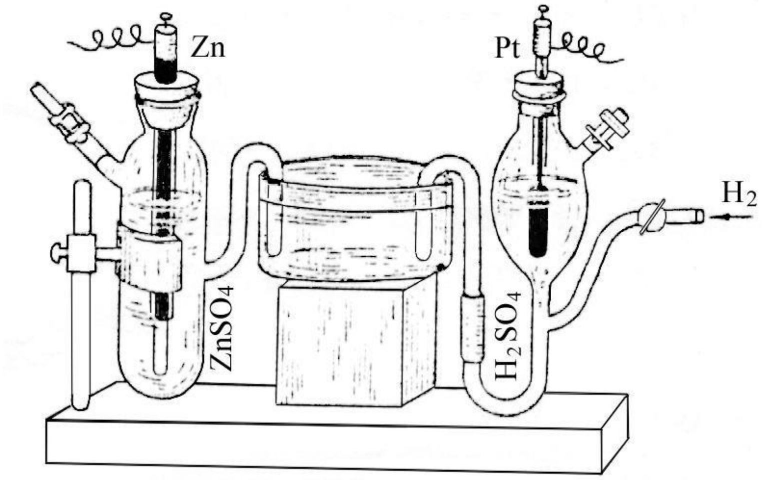


Fig. 11.2. Galvanic element for detection of normal potential of metals

All metals arranged in order of increasing values of their standard electrode potentials form the so-called **series of voltages.** This is a scheme that is convenient to use for determining the properties of metals. All metals by the value of the **normal electrode potential** can be divided into active (easily reduce H^+ ions to H_2 on the hydrogen electrode), medium and low activity, as well as passive (not capable of the normal potential of metals reducing hydrogen). The former occupy the distant between Lithium and

Aluminum, and the latter stand to the right of hydrogen. Lithium has the highest negative value among all metals (E_{Li} = –3.04 eV). The highest positive value is on gold (E_{Au} = +1.50 eV).

Table 11.1.

Values of standard electrode potentials of some metals

Li	Al	Zn	Fe	Sn	Pb	H_2	Cu	Ag	Hg	Au
Li^+	Al^{3+}	Zn^{2+}	Fe^{2+}	Sn^{2+}	Pb^{2+}	$2H^+$	Cu^{2+}	Ag^+	Hg^{2+}	Au^{3+}
–3.04	–1.70	–0.76	–0.44	–0.14	–0.13	0	+0.34	+0.80	+0.85	+1.50

It can be seen that the location of these metals corresponds to the chronology of their discovery and use. In ancient times, people knew silver and gold (because they are found in nature in a metallic state, sometimes in the form of nuggets). Over time, people learned to smelt copper, extract tin and lead from their compounds, and obtain their alloys (bronze). All these processes are quite simple and do not require significant energy consumption or special reagents. However, iron was already inaccessible to ancient peoples.

Iron occurs in nature only in the form of compounds, in particular oxides and sulfides. Its reduction to pure metal in the reaction with carbon takes place at high temperatures, which became achievable only at a certain stage of the development of science and technology. For a long time, iron remained the most active metal used by humans. Zinc began to be obtained in Europe only in the 18th century. This opened the way to the creation of sources of electric current and the study of electromagnetism.

Aluminum was obtained at the beginning of the 19th century, but for a long time it was expensive and exotic metal. A relatively simple method of obtaining it electrochemically was proposed only at the end of the 19th century. Thanks to this, it became possible to obtain other metals by displacing them from the corresponding compounds with metallic aluminum (aluminothermy).

Lithium, the most active of all metals, began to be widely used only in the 21st century. It is difficult and dangerous to work with it, but thanks to its record-breaking electrochemical potential, it allows you to create electrochemical devices with extremely high power (lithium batteries).

The electromotive force in a system consisting of two electrodes connected together and immersed in an electrolyte solution depends on the potential difference between the two electrodes. And those, in turn, depend on the concentration of ions of the corresponding metals in the solution, that is, on the concentration of the corresponding salts and the degree of their dissociation.

This dependence is determined by the Nernst equation:

$$E = E_0 + \frac{0.059 \lg c}{n},$$

where E is the potential of the metal at a certain concentration of its ions, E_0 is the normal potential, n is the valence of the metal ion, and c is the concentration of metal ions in the solution (in moles)

It is important to remember that the value of the electrode potential refers to the metal/ion pair, not the metal itself and is a quantitative sign of the transition from one state to another. In particular, for the Cr/Cr^{2+} pair E = –0.91 eV, and for Cr/Cr^{3+} pair E = –0.74 eV. This should be taken into account in calculations.

11.2. Chemical electricity sources

A galvanic cell is a chemical source of electricity that works on the principle of creating a flow of electrons as a result of two chemical reactions occurring on the surface of two electrodes connected by a conductor and a common electrolyte solution. Electrons move from a more active metal, which gradually dissolves in the electrolyte, to a less active one, on which the process of restoring ions from the solution takes place. A classic example of a galvanic cell is a pair of Zn and Cu in solutions of their salts.

On the more active electrode (zinc), the process takes place:

$$Zn^0 - 2e^- \rightarrow Zn^{2+}.$$

On the less active (copper):

$$Cu^{2+} + 2e^- \rightarrow Cu^0.$$

As we can see, the second process can occur only if excess electrons appear, and the first – only if they are removed from the crystal lattice of the metal. The speed of both chemical reactions is strictly related. The process will continue until the more active electrode is completely dissolved or the electrochemical chain is broken. The entire chemical reaction together can be shown by equation:

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu.$$

The scheme of the galvanic cell, taking into account the semi-permeable partition between the solutions of two electrolyte salts, is depicted as follows:

$$Zn|ZnSO_4 \,\vdots\, CuSO_4|Cu.$$

The electromotive force of a galvanic cell is calculated as the difference of their potentials (calculated according to the Nernst equation). For standard conditions, electromotive force of a zinc-copper element:

$$\varepsilon = 0.34 - (-0.76) = 1.103 \text{ volts}.$$

Concentration elements differ in that they are formed by two electrodes of the same metal, but immersed in solutions of different concentrations. The electrochemical process in such an element will lead to equalization of concentrations. For example, a zinc cell with two zinc electrodes, while c_1 and c_2 are not equal:

$$(-)\ Zn \mid ZnSO_4 \,\vdots\, ZnSO_4 \mid Zn\ (+).$$

In the part of the element with a lower concentration of ions, zinc goes into solution:

$$Zn - 2e^- \rightarrow Zn^{2+}.$$

In the part with a higher concentration of ions on the electrode, metallic zinc is released:

$$Zn^{2+} + 2e^{-} \rightarrow Zn.$$

From the point of view of electron balance, the first electrode works as an electron donor, and the second as an electron acceptor.

Accumulators are renewable chemical sources of electric current. In fact, these are ordinary galvanic elements, but such that their reaction can occur both in the forward and reverse direction (under the influence of an external source of direct electric current). For this, in both reactions, gases or liquids, compounds that decompose, enter into reactions, etc., should not be formed. In discharge mode, batteries generate electric current, like ordinary galvanic cells. In the charging mode, under the action of an external source of constant electric current, they return to their initial state.

Let's consider several examples of batteries.

An alkaline battery consists of an electrode made of Fe iron powder and a second electrode made of nickel hydroxide. Both electrodes are immersed in a concentrated KOH solution.

During discharge, that is, iron reduces hydroxide $Ni(OH)_3$ to $Ni(OH)_2$ according to the reaction:

$$Fe + 2Ni(OH)_3 \rightarrow Fe(OH)_2 + 2Ni(OH)_2.$$

When charging, iron returns to the metallic state:

$$Fe(OH)_2 + 2Ni(OH)_2 \rightarrow 2Ni(OH)_3 + Fe.$$

An alkaline battery when discharged at the terminals has $\varepsilon = 1.3$ V. When charged, the voltage is 1.8 V. It can withstand overloading and a long stay in a discharged state, is not afraid of shaking and has a relatively small mass. It is used on massive mechanisms. The disadvantage is its lower efficiency than the acid one and relatively large size.

An acid battery contains lead electrodes and a solution of sulfuric acid (30% H_2SO_4). One of the electrodes is metallic lead, the other is a paste of its oxide PbO_2 in the holes of the clip.

When the battery is discharged, the oxidation state are +2.

On the negative electrode:

$$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^{-}.$$

On the positive electrode:

$$Pb(SO_4)_2 + 2e^- + 2H^+ \rightarrow PbSO_4 + H_2SO_4.$$

When charging, the initial state is restored.

On the negative electrode:

$$PbSO_4 + 2e^- + 2H^+ \rightarrow Pb + H_2SO_4.$$

On the positive electrode:

$$PbSO_4 + SO_4^{2-} - 2e^- \rightarrow Pb(SO_4)_2.$$

One element of such a battery is capable of providing a current of 2 V. Serial connection of elements makes it possible to create batteries of different capacities (usually 6 or 12 V). Cars and tractors use batteries with a voltage of 12 V. In the electrical circuits of cars, batteries are used to start engines and when working at low speeds. When a certain number of engine revolutions is reached, the generator starts working, which not only provides the electrical system, but also charges the battery. Disadvantages of the acid battery are significant weight and low resistance of the plates to significant shaking.

11.3. Electrolysis

Electrolysis is a chemical reaction that is carried out under the influence of an electric current. The principle of individual components of this chemical reaction at the electrodes is the same as in the case of a galvanic cell, but the flow of excess electrons and their outflow is not ensured by the difference in electrochemical potentials of metals, but by an external source of direct current. Thanks to this, the reaction can be directed towards the formation of products that cannot be obtained in another way. The electrolysis method, in particular, makes it possible to obtain alkaline and alkaline earth metals, halogens, hydrogen, oxygen.

If two electrodes are immersed in a solution or melt of an electrolyte and a constant electric current is passed through them, the ions will acquire a directed movement. Anions will move to the positive electrode (anode), which has a shortage of electrons. There they will give electrons to the electrode. At the opposite end of the electrochemical circuit, the reverse process will occur. Cations will move to the negative electrode (cathode) containing an excess of electrons. There, cations will join them, turning into neutral molecules. Such a process is called reduction (as opposed to oxidation, for example, the transformation of a metal into an oxide). Even very high negative values of the electrochemical potential, as in Li, Na, or Al, will not prevent this, although more electrical energy will be required.

Electrolysis of salt melts is carried out in special furnaces that allow to achieve a liquid aggregate state.

The NaCl electrolysis reaction follows the scheme:

$$NaCl \rightarrow Na^+ + Cl^-.$$

At the cathode: $Na^+ + e^- \rightarrow Na$

At the anode: $Cl^- - 2e^- \rightarrow Cl_2$

If several anions or cations are present in the melt, competing processes occur. The more active the metal, the more difficult it is to recover it at the cathode. At close values, simultaneous recovery of several metals can occur. The processes occurring at the anode depend on the properties of the anions. The giving of electrons by oxygen-containing ions is, as a rule, accompanied by their decomposition with the release of oxygen. Anions containing only one atom (for example, chlorine ion) give up excess electrons and turn into a simple substance. In the latter case, this process is relatively easier.

Anodes are divided into insoluble (indifferent) and soluble.

Insoluble anodes are made of materials that do not participate in electrochemical reactions (graphite, platinum, iridium, etc.). The material of the electrode does not change in any way during electrolysis, but only serves as a conductor of electrons. Instead, processes take place on its surface that should compensate for the return of electrons. Oxidation of anions (acid residues or hydroxide ions) takes place. Acid residues that do not contain oxygen (HCl, H_2S, etc.) are oxidized to simple substances.

For example:

$$S^{2-} - 2e \rightarrow S.$$

Anions containing oxygen decompose with the release of molecular oxygen.

For example:

$$4OH^{-} - 4e^{-} \rightarrow 2H_2O + O_2.$$

Soluble anodes are metal anodes (Zn, Cu, Ag, Ni, etc.) that participate in electrochemical reactions. The source of electrons is actually the metal atoms themselves, which turn into positive ions. As a result, the electrode material dissolves in the solution.

For example:

$$Ni^{0} - 2e^{-} \rightarrow Ni^{2+}.$$

Soluble anodes are used to create coatings. The surface of the product, which is the cathode, is covered with the metal that makes up the anode.

During the electrolysis of aqueous solutions of various compounds, it should be borne in mind that H^+ and OH^- ions, which are formed in small quantities during the dissociation of water, may participate in the processes at the electrodes.

In aqueous solutions of salts of the most active metals (which are located in the range of voltages up to and including Al), the process of reducing hydrogen ions from water takes place at the cathode. At the anode, processes that require lower energy consumption also take place: first, simple ions are discharged - halides, S^{2-}, OH^-, and only then the oxidation of anions of oxygen-containing acids, such as SO_4^{2-}, NO_3^-, etc., occurs.

During the oxidation of hydroxide ions at the anode, a reaction occurs with the release of oxygen:

$$4OH^{-} - 4^{e-} \rightarrow 2H_2O + 2O^{0}.$$

Let's examine, for example, the electrolysis of an aqueous solution of $CuCl_2$. The solution of such a salt contains ions Cu^{2+}, Cl^-, as well as H^+, OH^-. Oxidation of Cl^- or OH^- to oxygen can occur on the anion. Chlorine oxidation predominates, in accordance with the order of anion discharge.

Thus, during the electrolysis of an aqueous solution of $CuCl_2$, the following processes occur at indifferent electrodes:

At the cathode: $Cu^{2+} + 2e^{-} \rightarrow Cu^{0}$;

At the anode: $2Cl^{-} - 2e^{-} \rightarrow Cl_2$.

That is, the processes will be implemented as shown in Fig. 11.3.

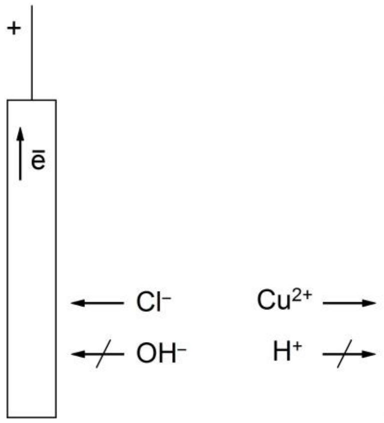


Fig. 11.3. Scheme of electrolysis of an aqueous $CuCl_2$ solution

During the electrolysis of an aqueous K_2SO_4 solution under the same conditions, other processes will be implemented (Fig. 11.4). Potassium is a very active metal, so its reduction at the cathode is less energetically beneficial than the reduction of hydrogen. The discharge of the sulfide ion at the anode is also a less energetically beneficial process than the reduction of OH^- to oxygen.

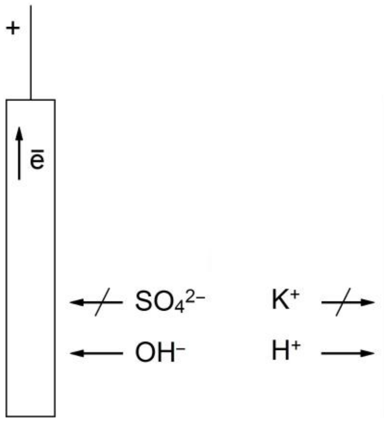


Fig. 11.4. Scheme of electrolysis of an aqueous K_2SO_4 solution

Thus, during the electrolysis of an aqueous solution of K_2SO_4, the following processes occur at indifferent electrodes:

At the cathode: $2H^+ + e^- \rightarrow H_2$;

At the anode: $4OH^- - 4e^- \rightarrow 2H_2O + O_2$.

As you can see, some salts are actually not susceptible to electrochemical decomposition during the electrolysis of their aqueous solutions due to the high activity of cations and the low energy benefit of discharging their anions. In this case, the electrochemical decomposition of water into hydrogen and oxygen (which, by the way, is one of the main methods of their industrial production) takes place. Obtaining pure alkali or alkaline earth metals is possible only from the melt, in the absence of any competition between ions.

Electrolysis on soluble electrodes occurs with the dissolution of the anode material. At the cathode, the order of ion discharge does not change. However, in some cases, if the ions of the anode material have high positive values of the electrochemical potential, this particular metal is regenerated at the cathode. This method is called the method of galvanostegy. It is used, in particular, for applying a nickel coating.

The main laws quantitatively describing electrolysis processes in terms of electric current consumption are Faraday's two laws.

Faraday's first law: the mass of the substance released at the electrode during electrolysis is proportional to the amount of current that passes through the electrolyte solution. In mathematical form:

$$m = Q = It,$$

where Q is the amount of electric current (in coulombs, Kl), I is the strength of the current (in amperes), t is the time it passes through the solution (in seconds).

Faraday's second law: equal amounts of electric current passing through solutions of different electrolytes during electrolysis release such masses of substances at the electrodes that are directly proportional to their equivalents. This is easily explained by the fact that a certain fixed number of electrons is transferred, so the reduction process takes place with a certain number of ions, but taking into account their valence. In mathematical form:

$$m = E\frac{It}{F},$$

where E is the equivalent, F is the Faraday number, which is 96,500 Kl.

As you can see, the Faraday number is the amount of electric current that, when passing through the electrolyte, releases 1 equivalent of the substance. However, in real processes, due to side processes, the mass of the separated substance can be much less than theoretically calculated. In addition, simultaneous release of several substances can occur. Therefore, they use the concept of a certain efficiency ratio: output by substance.

Test questions

1. Write the reactions on the electrodes of a galvanic cell with tin and zinc electrodes in a solution of their salts? How will the power of the galvanic element change if we replace the tin electrode with a copper one?
2. Write the reactions on the electrodes of a galvanic cell with lead and iron electrodes in a solution of their salts? How will the power of the galvanic element change if we replace the iron electrode with a zinc one?
3. Write the reactions on the electrodes of a galvanic cell with platinum and aluminum electrodes in a solution of their salts? How will the power of a galvanic cell change if a platinum electrode is replaced with a copper one?
4. Write the reactions on an inert anode and cathode during the electrolysis of an aqueous solution of lithium iodide. What will change if you use molten salt without water?
5. Write the reactions on an inert anode and cathode during the electrolysis of an aqueous solution of silver nitride. What will change if you use molten salt without water?
6. Write the reactions on an inert anode and cathode during the electrolysis of an aqueous solution of sodium hydroxide. What will change if you use molten hydroxide without water?
7. Write the reactions on an inert anode and cathode during the electrolysis of pure water. The presence of which salts does not cause any changes in the reaction?

Chapter12. General characteristics of metals

12.1. Metals as materials and element

A metals is a material that have some specific properties such as: when freshly prepared, polished, or fractured, shows a lustrous appearance, and conducts electricity and heat relatively well. Metals are typically ductile (can be drawn into wires) and malleable (they can be hammered into thin sheets). These properties are the result of the metallic bond between the atoms or molecules of the metal.

In physics, a metal is generally regarded as any substance capable of conducting electricity at a temperature of absolute zero, so many elements and compounds that are not normally classified as metals become metallic under high pressures. For example, iodine or hydrogen under extremely high pressure.

However in chemistry metals are only chemical elements such as iron, or their alloy (usually solid solutions) such as stainless steel. As chemical compounds metal have same specific properties due to metallic chemical bounds and libber electron in the crystalline structure of them. They give up electrons relatively easily, especially if their number at the external level is small, and accept them relatively poorly. The exception is d-elements, which are capable of both giving electrons and accepting them, and sometimes they are even better in the second.

Some elements have properties intermediate between metals and non-metals. They are located between them in the periodic table, conventionally between carbon and aluminum (boron, silicon).In chemistry, two elements arsenic and antimony that would qualify in physics as brittle metals are commonly instead recognized as metalloids due to their chemistry (predominantly non-metallic for arsenic, and balanced between metallicity and non-metallicity for antimony).

It should be noted that metallic properties are not synonymous with the activity of metals. Of course, sodium, potassium or calcium are metals with strong metallic properties, as well as very active metals. However, for example, gold is definitely a metal, but its chemical activity is low. Thus, the place of an element in the range of activities of metals does not allow finding its metallicity.

This can be explained by the fact that the characteristic metallic properties of the substance are determined by the metallic bonds in its structure, namely by the cloud of shared electrons. Due to this, an electric current can easily flow in the metal, as well as heat. This also makes plastic deformation possible, since the movement of electrons can compensate for changes in the crystal lattice. The electron cloud can be seen by its metallic sheen. Metals reflect light rays better than non-metals because the empty space between their atoms is partially filled by shared electrons.

Metals, as chemical elements, comprise 25% of the Earth's crust and are present in many aspects of modern techniques. The strength and resilience of some metals (bronzes, steels, and aluminum) has led to their frequent use. Precious metals were historically used as coinage and luxury.

The history of refined metals is thought to begin with the use of copper about 11 thousand years ago. Gold, silver, iron (as meteoric iron), lead, and brass were likewise in use before the first known appearance of bronze. Subsequent developments include the production of steel. Important milestone of metallurgy was discovery of sodium, the first light metal, in 1809. Latest advances include the development of aluminum and rare metal alloys.

There are a lot of method of classification of metals.

The term ferrous is derived from the Latin word meaning containing iron. This can include pure iron, such as wrought iron, or an alloy such as steel. Ferrous (black) metals are often magnetic, but not exclusively. Non-ferrous (colored) metals and alloys lack appreciable amounts of iron.

A white metal is any of range of white colored metals (or their alloys) with relatively low melting points. Such metals include zinc, cadmium, tin, antimony, lead, and bismuth, some of which are quite toxic.

While nearly all metals are malleable or ductile, a few (beryllium, chromium, manganese, gallium, and bismuth) are brittle. Arsenic and antimony, if admitted as metals, are also brittle.

Same metals called refractory. In materials science, metallurgy, and engineering, that mean a metal that is extraordinarily resistant to heat and wear (niobium, molybdenum, tantalum, tungsten, and rhenium). They all have melting points above 2000°C, and a high hardness at room temperature.

A heavy metal is any relatively dense metal or metalloid. As usual it mean more heavy than iron. All other metals are light metals.

In chemistry, the term base metal is used informally to refer to a metal that is easily oxidized or corroded, such as reacting easily with dilute hydrochloric acid (HCl) to form a metal chloride and hydrogen. Examples include iron, nickel, lead, and zinc.

$$Fe + HCl \rightarrow FeCl_2 + H_2\uparrow,$$
$$Ni + 2HCl \rightarrow NiCl_2 + 2H_2\uparrow.$$

Copper is considered a base metal as it is oxidized relatively easily, although it does not react with HCl.

The term noble metal is commonly used in opposition to base metal. Noble metals are resistant to corrosion or oxidation, unlike most base metals. They tend to be precious metals, often due to perceived rarity. Examples include gold, platinum, silver, rhodium, iridium, and palladium. Chemically, the noble metals are less reactive than most elements, have high luster and high electrical conductivity.

Some metals are amphoteric, that is, they can react with alkalis and bases, which leads to the formation of salts in which this metal is part of the anion. This is characteristic of metals that have high valences in compounds (at least three), as well as some medium and low-active metals with a valence of two or even one. Such are, for example, beryllium, aluminum, tin, lead, germanium and zinc.

If they react in aqueous solutions, complex salts are formed, for example:

$$Be + 2KOH + 2H_2O \rightarrow K_2[Be(OH)_4] + H_2\uparrow,$$
$$Pb + 4KOH + 2H_2O \rightarrow K_4[Pb(OH)_6] + H_2\uparrow,$$
$$2Al + 2KOH + 6H_2O \rightarrow 2K[Al(OH)_4] + 3H_2\uparrow,$$
$$2Al + 6KOH + 6H_2O \rightarrow 2K_3[Al(OH)_6] + 3H_2\uparrow.$$

In some cases, the reaction products may be different depending on the concentration of the reactants.

When interacting in a melt, the reaction products are ordinary salts:

$$Be + 2KOH \rightarrow K_2BeO_2 + H_2\uparrow,$$
$$2Al + 6KOH \rightarrow 2KAlO_2 + 2K_2O + 3H_2\uparrow,$$
$$Zn + 2KOH \rightarrow K_2ZnO_2 + H_2\uparrow.$$

Most metals do not dissolve in water, but many of them can react with it. All s-elements, except beryllium, react with water to form a base and hydrogen. At the same time, rubidium and cesium react with an explosion. In the case of potassium, sodium, and lithium, the actively released hydrogen can ignite:

$$2Na + 2H_2O \rightarrow 2NaOH + H_2\uparrow,$$
$$Ba + 2H_2O \rightarrow Ba(OH)_2 + H_2\uparrow.$$

p-elements, as a rule, cannot react with water, because their surface is covered with a chemically resistant oxide film. But if you remove this film or turn the metal into a powder, some of them are able to dissolve in water, for example, aluminum (can interact with water at room temperature) or gallium (can react when heated with water vapor):

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2\uparrow,$$
$$2Ga + 3H_2O \rightarrow Ga_2O_3 + 3H_2\uparrow.$$

Among the d-elements, only lanthanum reacts with water

$$2La + 6H_2O \rightarrow 2La(OH)_3 + 3H_2\uparrow.$$

The effect of water on metals increases in the presence of oxygen dissolved in it. At the same time, some low-reactivity metals that do not interact with H_2O under normal conditions can be oxidized by aerated water according to the scheme:

$$2Me + nH_2O + 0.5nO_2 \rightarrow 2Me(OH)_n.$$

12.2. Corrosion of metals

Corrosion is the process of chemical destruction of metals under the influence of the surrounding environment. This process occurs with all metals that can enter into a chemical interaction with oxygen, water and other substances contained in the air. In some cases, this process can be very slow due to the formation of a dense oxide film on the surface of the metal. This is observed, in particular, when aluminum and chromium are oxidized. Iron corrosion is especially important from a practical point of view. It happens quickly due to the fact that iron oxides are fragile and do not prevent the further destruction of the metal at all.

Corrosion causes significant damage due to the need to replace parts and mechanisms, as well as due to accidents, simple equipment, deterioration of product quality as a result of its contamination. Indirect damage, by the way, always outweighs direct damage. In some cases, the destruction of structural materials creates threats to the environment and human life.

Externally, metal corrosion manifests itself in the loss of metallic luster, the appearance of corrosion products on the surface, and also in the change of mechanical properties. However, it should be noted that the external signs of corrosion can be very different for different metals. For steel (iron alloys), such a sign is the appearance of rust (brown color).

Corrosive processes include the processes that occur between metal and substances present in the surrounding environment. First of all, it is oxidation of metals by air oxygen and interaction with water. Water can react as a liquid or as a vapor (in the presence of oxygen). Sea water contains a significant amount of dissolved salts. Groundwater and wastewater, as a rule, have a slightly alkaline or acidic environment. In addition, metals can be affected by gases (gas corrosion) and non-electrolyte substances (oil, organic solvents, waste products).

Several types of corrosion are distinguished by the nature of metal destruction. First of all: uniform, local and intercrystalline (Fig. 12.1).

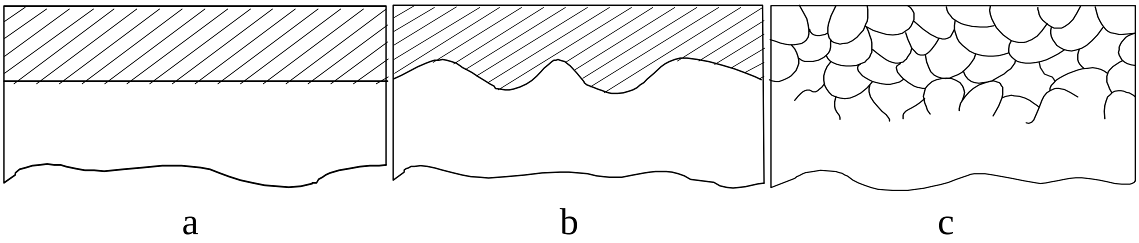


Fig. 12.1. Main types of corrosion: a – uniform corrosion; b – local; c – intercrystalline corrosion

Uniform corrosion occurs simultaneously over the entire plane of the metal. This happens in those cases when the metal is homogeneous in composition. It is relatively safe, as it slowly penetrates into the depths.

Local corrosion occurs in certain areas and develops unevenly. There are less and more damaged areas where corrosion penetrates deep. Local corrosion includes such varieties as point, spot, etc.

Intercrystalline (intergranular) corrosion occurs at the boundaries of metal crystals (metal grains) and quickly penetrates deep. It is especially dangerous due to the fact that it is hardly visible from the outside, but it leads to a violation of the integrity of the material. Its sign is that the metal loses its volumetric properties: electrical conductivity, thermal conductivity, acoustic properties, etc. It is detected by tapping (there is no characteristic metallic sound) and special methods.

According to the peculiarities of the course of chemical processes, two main types of corrosion are distinguished: chemical (gas) and electrochemical. Chemical corrosion is caused by non-electrolyte aggressive media, in particular gases. Electrochemical corrosion occurs when an electrochemical circuit is formed, consisting of two substances with different electrochemical potentials, in contact with each other and in contact with the electrolyte. It can be two metals immersed in a liquid or covered with condensate. However, it can also be the same metal, which has a different electrochemical potential at different points, for example, due to a difference in the concentration of ions in the solution or due to the flow of an external electric current.

Electrochemical corrosion, as a rule, is observed in the case of corrosion of a metal that has a coating of a different composition (for example, an iron surface covered with zinc, tin, nickel, chromium, etc.) or the composition of the metal contains impurities of other metals (heterogeneous alloys). In addition, it is observed at the border of two metal parts made of different materials. The electrochemical process takes place with the participation of both metals, but the source of electrons is the more active of them. It is its atoms that turn into ions and pass into the solution, that is, electrochemical corrosion of this particular material occurs. A less active metal serves as an electron acceptor, that is, it initiates corrosion, but does not destroy itself.

All coatings of one metal to another can be considered an electrochemical circuit or galvanic element, at least after the first scratches and violation of their integrity. According to the nature of the processes taking place, the coating can be divided into anodic (coating of metal with a more active metal) and catodic (coating of metal with a less active metal). In the first case, the coating itself corrodes over time. In the second, corrosion spreads deep into the material, and the coating remains intact (Fig. 12.2).

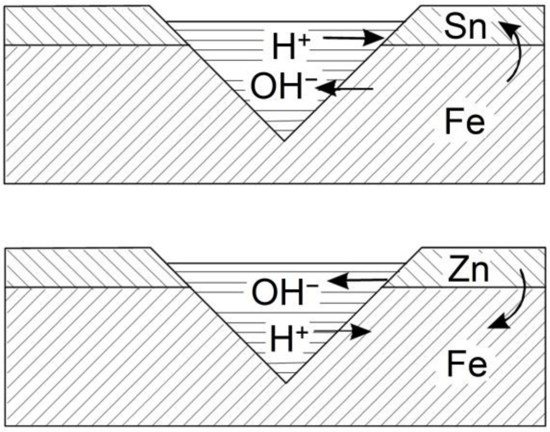


Fig. 12.2. Electrochemical corrosion of iron covered with tin and zinc coating

Protective protection consists in creating a galvanic element by attaching an auxiliary electrode made of a more active metal (anode) to the protected structure.

The same effect can be achieved by passing direct current from an external source so that the structure to be protected becomes the cathode (acquires an excess of electrodes) and the auxiliary electrode (usually scrap metal) becomes the anode.

Other methods of corrosion protection include those that insulate the material from the corrosive environment (polymer coatings, paints, varnishes), change the environment (cleaning from salts, corrosion inhibitors, etc.) or prevent the flow of electrochemical processes (use of non-electrolytes, removal of stray currents).

Corrosion inhibitors are volatile or soluble substances, in the presence of which the rate of corrosion is significantly reduced. Volatile inhibitors provide protection against atmospheric corrosion. They are often used as a component of packaging materials (wrapping paper for steel products, container material, etc.). Soluble inhibitors are used as components of lubricants or as additives in the aqueous medium in contact with the metal.

Inhibitors are adsorbed on the metal surface and act by inhibiting anodic or cathodic processes. Anodic processes are slowed down due to the passivation of metals by the formation of oxide films or layers of poorly soluble compounds on their surface. Such inhibitors are sodium dichromate, phosphates, sodium benzoate and other salts of benzoic acid. Cathodic processes are slowed down due to the reduction of the area of cathodic areas or inhibition of cathodic reactions. Such inhibitors are diethylamine, formaldehyde, urotropin and other organic substances containing oxygen, nitrogen and sulfur.

Test questions

1. Describe the corrosion processes on the surface of copper covered with a nickel after the partial destruction of the protective layer. Write the reaction equation of the cathodic process in this system.
2. Describe the corrosion processes on the surface of iron covered with chromium after the partial destruction of the protective layer. Write the reaction equation of the anodic process in this system.
3. Describe the corrosion processes on the surface of tin covered with silver after the partial destruction of the surface layer. Write the reaction equation of the cathodic process in this system.
4. Describe the corrosion processes on the surface of zinc covered with copper after the partial destruction of the surface layer. Write the reaction equation of the anodic process in this system.
5. Describe the corrosion processes in the contact zone of an iron and lead part in a weakly acidic water environment. Write the equation for the reaction at the anode in this system.
6. Describe the corrosion processes in the contact zone of an aluminum and zinc part in a weakly alkaline water environment. Write the equation for the reaction at the anode in this system.
7. Describe the corrosion processes in the contact zone of an iron and copper part in an aqueous aerated environment. Write the equation for the cathode reaction in this system.

Chapter 13. General characteristics of Mg/Ca-group elements

Magnesium (Mg) and calcium (Ca) belong to the s-elements of the main subgroup of the second group of the periodic table. At the outer energy level of the atoms of these elements, there are 2 electrons, so the elements of this subgroup are divalent.

13.1. Magnesium and its compounds

Magnesium is a fairly common element in nature (≈ 2 wt.%).

Magnesium is found in the form of minerals: magnesite $MgCO_3$, dolomite $MgCO_3 \cdot CaCO_3$, kainite $KCl \cdot MgSO_4 \cdot 3H_2O$, carnalite $KCl \cdot MgCl_2 \cdot 6H_2O$. Seawater contains the magnesium ion Mg^{+2}, which gives it a bitter taste. Magnesium is part of the chlorophyll of green plants.

Magnesium (Mg) is a silvery-white, very light metal that is coated in air with a thin layer of oxide, protecting it from further oxidation. Water decomposes magnesium slowly due to the formation of slightly soluble magnesium hydroxide. Magnesium reacts with acids to release hydrogen. Alkalis do not affect magnesium. When heated in air, magnesium burns to form magnesium oxide (MgO).

Magnesium is mainly used to produce light alloys, which are hard, strong and corrosion resistant.

Magnesium alloys Mg–Al–Zn; Mg–Mn; Mg–Zn–Zr are used in aircraft and automobile constructions.

Pure magnesium is used in metallurgy to produce other pure metals, such as titanium. In the production of magnesium alloys, it is used to remove oxygen and sulfur. Used in organic synthesis and synthesis of organic compounds.

Magnesium oxide MgO is obtained by decomposition of magnesite $MgCO_3$ when heated:

$$MgCO_3 \rightarrow MgO + CO_2.$$

MgO is burnt magnesia (with a melting point of about 3000°C), which is used for the manufacture of refractory crucibles, pipes, and bricks.

Caustic magnesite is a component of building materials (cement, concrete, etc.), one of two widespread magnesium binders (the second is caustic dolomite). Its chemical formula is MgO. It is obtained either by firing natural magnesite at a temperature of 600-800°C:

$$MgCO_3 \rightarrow MgO + CO_2\uparrow.$$

Caustic magnesite reacts with water to form magnesium hydroxide. The hardening of this material is based on this reaction. The reaction rate depends on additives and catalysts, which allows you to control the process.

Magnesium hydroxide $Mg(OH)_2$ is a slightly soluble white precipitate with basic properties. It is obtained by the action of alkali on a salt solution:

$$MgSO_4 + 2NaOH \rightarrow Mg(OH)_2\downarrow + Na_2SO_4.$$

There are few the most common compounds of magnesium. Magnesium sulfate $MgSO_4{\cdot}7H_2O$ is a bitter salt, dissolves well in water. Magnesium chloride $MgCl_2{\cdot}6H_2O$ is a colorless crystaline, soluble in water.

Magnesian cement MgOHCl is formed by the reaction:

$$MgO + MgCl_2 + H_2O \rightarrow 2MgOHCl,$$

and then polymerizes into chains: –Mg–O–Mg–O–Mg–.

The ends of the chains contain chlorine atoms or hydroxide groups.

Magnesian cement is a binding material, very hard, the strength of which in compression and bending exceeds cement stone from Portland cement. It is used to make sharpened wheels, millstones, slabs, and floors in industrial workshops.

Natural magnesium silicates are widely used:

Talc has the formula $3MgO{\cdot}4SiO_2{\cdot}H_2O$ and it is one of the softest minerals.

Asbestos $CaO\ {\cdot}3MgO\ {\cdot}4SiO_2$is a fibrous material that can withstand high temperatures (phase transitions begin at ≈ 900°C). It is a widely used thermal insulation material.

13.2 Calcium and its compounds

Calcium is quite common in the earth's crust (≈ 3 wt.%).It is found in nature in the form of limestone $CaCO_3$ (marble, chalk), gypsum $CaSO_4{\cdot}2H_2O$, phosphorite $Ca_3(PO_4)_2$ and various silicates.

Calcium metal is a white, hard metal that is lightweight and malleable. In air it becomes covered with an oxide layer, and when heated it burns with a red flame. It is an active metal that easily combines with sulfur, halogens, nitrogen, and when heated, it reduces many metals from their oxides. With water it is reacts slowly in the cold, but easily displaces hydrogen from the hot ones.

Calcium is used in metallurgy to extract uranium, chromium, zirconium, cesium, rubidium, remove oxygen from steel and dehydrate many organic compounds.

When heated in a hydrogen stream, calcium metal forms the hydride CaH_2. CaH_2 is a white salt-like substance that reacts violently with water, releasing hydrogen.

$$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + H_2\uparrow.$$

Calcium oxide CaO is a white, very fire-resistant substance (up to 2600°C). It is also called quicklime. Usually obtained by roasting (calcination) of $CaCO_3$:

$$CaCO_3 \rightarrow CaO + CO_2\uparrow.$$

This process is so widespread that the technological operation of heat treatment of roasting in English is usually called calcination (even if there is no calcium there).

Calcium hydroxide $Ca(OH)_2$ is an easily obtained product of the reaction of quicklime with water, which is called slaked lime. Due to its ease of preparation and reactive strength, it is the most common alkaline agent in chemistry. Lime is also a widely used binder.

The most important calcium salts are natural minerals: chalk (almost pure calcium carbonate), fluorspar (containing calcium fluoride), calcium chloride, and gypsum (calcium sulfate).

CaF_2 is used for the manufacture of enamels and in metallurgy as a flux.

$CaCl_2$ is one of those additives that are most often added to concrete to regulate its hardening process.

$CaSO_4$ is a crystalline hydrate in its normal state, which can lose water when heated. Over time, it can reattach water, turning into gypsum stone.

Calcium and carbonic acid H_2CO_3 form two salts: calcium carbonate $CaCO_3$ and bicarbonate $Ca(HCO_3)_2$, however, the latter exists only in aqueous solutions and has low thermal stability. Under natural conditions, calcium bicarbonate is formed by the action of water and CO_2 dissolved in it on rocks containing calcium carbonate.

$$CaCO_3 + H_2O + CO_2 \leftrightarrow Ca(HCO_3)_2.$$

With an increased concentration of CO_2 in water, the equilibrium of this reaction shifts to the right, i.e. water becomes an aggressive environment for $CaCO_3$. However, when water containing calcium hydrogen carbonate is boiled, CO_2 is released from it, the equilibrium of this reaction shifts to the left and the acid salt decomposes with the formation of a $CaCO_3$ precipitate.

This is an important factor that is taken into account in many technological processes and is the reason why water is considered as a potential source of sediment. For this, the concept of water hardness is used.

13.3. Hard water and methods of its control

Natural water containing a lot of calcium and magnesium salts is called hard, and water containing little of these salts is called soft. Water hardness is also determined by divalent iron and divalent manganese salts.

Water hardness resulting from the presence of salts of $Ca(HCO_3)_2$and $Mg(HCO_3)_2$ is called temporary, since it is easily eliminated. The hardness resulting from the presence of carbonates and some other salts of magnesium and calcium is called permanent. Non-carbonate water hardness is mainly due to the presence of sulfates and chlorides. The sum of all temporary and permanent hardness is the total water hardness.

Water hardness is expressed by the number of millimoles of calcium and magnesium ions in 1 liter of water. One mmol/liter (or mmol/kg) hardness corresponds to 20,04 mg/liter Ca^{2+} or 12,16 mg/liter Mg^{2+}:

$$T_v = \frac{m}{EV},$$

where *m* is the mass of substances (ions) causing water hardness or substances used to remove hardness, *E* is the molar mass of the equivalent of this substance, and *V* is the volume of water.

The hardness of natural water varies widely depending on geography and even changes with the seasons. In surface waters, carbonate hardness usually prevails (70-80% of the total).

Magnesium hardness of water rarely exceeds 30% of the total, but in some areas it reaches 60%. Water with a hardness of less than 3.0 mmol/dm³ is considered soft, and water with a hardness of more than 6.0 mmol/dm³ is considered hard.

The hardness of river waters of Ukraine increases from northwest to southeast. In the north, it is 2-3 mmol/dm^3, in the Dnieper it is 4-5 mmol/dm^3, and in the rivers of the Azov region it is 15-30 mmol/dm^3.

The hardness of sea water in the Black Sea is 65 mmol/dm^3, and in the ocean it is 130.5 mmol/dm^3. About 80% of it is magnesium hardness.

Temporary hardness is determined by titration of a certain volume of water with a solution of hydrochloric acid of the appropriate concentration. When a solution of hydrochloric acid is added to water containing salts of temporary hardness, it were the following reactions:

$$Ca(HCO_3)_2 + 2HCl \rightarrow CaCl_2 + 2CO_2\uparrow + 2H_2O;$$
$$Mg(HCO_3)_2 + 2HCl \rightarrow MgCl_2 + 2CO_2\uparrow + 2H_2O;$$

or in ionic form:

$$HCO_3^- + H^+ \rightarrow CO_2\uparrow + H_2O.$$

There are several reasons why water hardness should be taken into account. Firstly, water with high hardness forms sediment in steam boilers. The most dangerous in terms of sedimentation on the walls of heating equipment are calcium and magnesium sulfates $CaSO_4$ and $MgSO_4$, followed by $CaCO_3$ and $MgCO_3$. Secondly, such water is also unsuitable for use in construction. Thirdly, hard water prevents the use of surfactants, since hard water salts interact with them, forming insoluble compounds. Therefore, before use, water is usually cleared of hardness, that is, softened.

There are two main methods of water softening: thermal and chemical.

The thermal method for eliminating temporary hardness is based on the decomposition of hydrogen carbonates during heating, such as simple boiling. This process transforms highly soluble hydrogen carbonates into slightly water-soluble carbonates or insoluble bases, for example:

$$Ca(HCO_3)_2 \rightarrow CaCO_3\downarrow + CO_2 + H_2O;$$
$$Mg(HCO_3)_2 \rightarrow MgCO_3\downarrow + CO_2 + H_2O.$$

The chemical method of water softening is based on the treatment of water with various reagents: lime, soda ash, caustic soda, sodium phosphate, etc. In this case, precipitation of insoluble carbonates, hydroxides and phosphates is formed due to the following reactions:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O;$$
$$MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + CaSO_4\downarrow;$$
$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4;$$
$$3CaSO_4 + 2Na_3PO_4 \rightarrow Ca_3(PO_4)_2\downarrow + 3Na_2SO_4.$$

The method of eliminating water hardness using ion exchange has become widespread in technology. For this purpose, some natural and synthetic high-molecular compounds (ion exchangers) are used that are capable of exchanging the ions included in their composition for ions found in water. Based on the type of ionogenic groups in the composition of ion exchangers, a distinction is made between cation exchangers (insoluble acids) and anions (insoluble bases).

Among the natural mineral cationites, a group of aluminosilicates (zeolites, clays) should be noted, and among anionites – apatites $[Ca_5(PO_4)_3]F$, and hydroxoapatites $[Ca_5(PO_4)_3]OH$, which are able to exchange ions F^- , OH^- for Cl^-, SO_4^{2-}. Synthetic mineral ionites include weakly acidic aluminosilicates called permutites.

When using a cationite (for example, permutite $Na_2[Al_2Si_2O_8]\cdot nH_2O$) $Ca^{2+}$and Mg^{2+} ions are exchanged for Na^+ ions between aluminosilicate and hard water:

$$Ca(HCO_3)_2 + Na_2R \rightarrow 2NaHCO_3 + CaR;$$
$$CaSO_4 + Na_2R \rightarrow Na_2SO_4 + CaR.$$

Similarly, anions ensure the removal of SO_4^{2-}, CO_3^{2-} and another ions from water by exchanging them for OH^-:

$$SO_4^{2-} + R(OH)_2 \rightarrow RSO_4 + 2OH^-;$$
$$CO_3^{2-} + R(OH)_2 \rightarrow RCO_3 + 2OH^-.$$

Other methods are also used, for example, ultrasonic, electrochemical, magnetic. For drinking water, it is disinfected with chlorine or ozone.

Test questions

1. In the form of which minerals is magnesium found in nature?
2. Define the term caustic magnesite. For the production of what is this compound used in construction?
3. In the form of which compounds is calcium found in nature?
4. How is quicklime obtained? Write the reaction of its interaction with water.
5. What salts cause water hardness?
6. How to eliminate carbonate hardness of water?
7. How to eliminate non-carbonate hardness of water?

Chapter 14. General characteristics of Al- and Si-group elements

14.1. Aluminum and its compounds

The Al-group is the third group of the periodic table, which also includes boron, gallium, indium, and thallium. All elements in this group, with the exception of boron, are metals. They all have three electrons in their outer shell, so they have a valence of three in compounds. Their compounds do not have extreme alkaline or acidic properties. Aluminum compounds are well known as amphoteric.

Aluminum is the most common metal in the earth's crust, 8 wt.%. The raw materials of it are bauxite (32-60% alumina Al_2O_3), alunite $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 2Al_2O_3 \cdot 6H_2O$, and nepheline $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$.Aluminum was first extracted by Weller in 1827 by the action of metallic potassium on aluminum chloride.

Now aluminum is mined from Al_2O_3 by the electrolytic method. Since the melting point of pure Al_2O_3 is ~2050°C, a mixture of Al_2O_3 with cryolite$Na_3[AlF_6]$ is subjected to electrolysis. Due to this, the melting temperature is reduced to 960°C.

Aluminum is a silver-white metal, light, can be drawn into wire and into foil. The standard electrode potential of aluminum is $E = -1.66$ V, so it very active. But since there is an oxide film on the surface of aluminum, Al does not displace hydrogen from acids.

In aqueous solutions of alkalis, the oxide layer of aluminum dissolves and it reacts, forming salts that contain aluminum as an anion, for example sodium tetrahydroxoaluminate:

$$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na[Al(OH)_4].$$

Aluminum that has lost its protective film easily interacts with water, with releasing of hydrogen:

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2\uparrow.$$

Aluminum hydroxide can react with excess alkali to form sodium tetrahydroxyaluminate:

$$Al(OH)_3 + NaOH \rightarrow Na[Al(OH)_4].$$

The general equation for the dissolution of aluminum in an aqueous alkali solution:

$$2Al + 2NaOH \rightarrow 2\ Na[Al(OH)_4] + 3H_2\uparrow.$$

Aluminum is used for the production of alloys for aicraft, automobile and shipbuilding, instrument building, in the manufactures of dishes, cables, chemical equipment, and capacitors. It also used for annealing (saturation of the surface of steel and cast iron products with aluminum) for protecting the surface from oxidation under heating. In metallurgy, aluminum is used to extract calcium, barium, lithium and other metals by the aluminothermy method.

Aluminum oxide Al_2O_3 (alumina) find in nature in a crystalline state, forming the mineral corundum. Corundum has a high hardness (9.95 by the Mohs scale). It is used to make abrasive tools, and corundum with a micron grain size of up to 7 microns is used to suspensions for finishing surfaces (polishing).

Transparent Al_2O_3 crystals colored red or blue called ruby and sapphire. They are precious stones, but they are also used for technical purposes, as parts of precision instruments. Ruby crystals doped with Cr_2O_3 are used to produce quantum generators, called lasers.

$Al(OH)_3$ and Al_2O_3 have clear amphoteric properties.

$$Al(OH)_3 + 3NaOH \rightarrow Na_3[Al(OH)_6];$$
$$2AI(OH)_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6H_2O;$$
$$Al_2O_3 + 2KOH \rightarrow 2KAlO_2 + H_2O;$$
$$Al_2O_3 + 3SO_2 \rightarrow 2Al_2\ (SO_3)_3.$$

Aluminum salts (aluminates) undergo hydrolysis reactions, forming basic or intermediate salts. Aluminates $Al_2(SO_4)_3\cdot 18H_2O$ are used for water purification and paper production, and $KAl(SO_4)_2\cdot 12H_2O$ for leather tanning, and in the dyeing industry.

14.2. Silicon and its compounds

The silicon group includes carbon, silicon, germanium, tin (stanum), and lead (plumbum). Only carbon is a nonmetal, although graphite has metallic properties, such as luster. Tin and lead are not very reactive metals, and the rest are metalloids. All of them have a valence of four and sometimes (especially carbon) of two.

Silicon is one of the most common elements in the earth's crust (27 wt.%). It ranks second after oxygen. In nature, it is found only in compounds: in the form of silicon dioxide SiO_2, silicic acid and its salts (silicates).

Free silicon is obtained by calcining silicon dioxide with magnesium:

$$SiO_2 + 2Mg \rightarrow 2MgO + Si.$$

As a result, amorphous silicon is formed.

In the industry, silicon is extracted in electric furnaces according to the reaction:

$$SiO_2 + 2C \rightarrow Si + 2CO\uparrow.$$

Product contains 2-5% of impurities.

An even purer product is obtained by zone melting. Silicon is weakly active and reacts with oxygen, halogens and sulfur when heated. Acids (except for a mixture of hydrofluoric and nitrate acids) do not act on silicon, but alkalis react violently with it, forming silicate acid salts:

$$Si + 2KOH + H_2O \rightarrow K_2SiO_3 + 2H_2\uparrow.$$

Silicon carbide SiC (carborundum) is formed when a mixture of sand and coke is heated in electric furnaces.

$$SiO_2 + 3C \rightarrow SiC + 2CO\uparrow.$$

Carborundum (γ = 3,2 g/cm^3) is dark gray crystals, very hard, similar to diamond, in which half of the carbon atoms are replaced by silicon. It is used for the manufacture of grinding wheels, sanding paper, and for floors in workshops and stations. A mixture of carborundum and silicon powders is used to manufacture rods for electric furnaces.

At high temperature, silicon reacts with many metals, forming silicides:

$$4Mg + SiO_2 \rightarrow Mg_2Si + 2MgO.$$

Silicides produce a gas (silane), which spontaneously ignites in air:

$$MgSi + 4HCl \rightarrow 2MgCl_2 + SiH_4;$$
$$SiH_4 + 2O_2 \rightarrow 2SiO_2 + 2H_2O\uparrow.$$

Silicon chloride $SiCl_4$is obtained by heating a mixture of silicon dioxide with coal in a stream of chlorine:

$$SiO_2 + 2C + 2Cl \rightarrow SiCl_4 + CO\uparrow.$$

$SiCl_4$ is a liquid that enters into hydrolysis reactions, that mean it has properties as a salt of silicon as a metal:

$$SiCl_4 + 3H_2O \rightarrow H_2SiO_3 + 4HCl.$$

$SiCl_4$is used for the synthesis of organosilicon compounds.

When hydrogen fluoride interacts with silicon dioxide, a colorless gas SiF_4 with a pungent odor is formed.

$$SiO_2 + 4HF \rightarrow SiF_4\uparrow + 2H_2O;$$
$$SiF_4 + 3H_2O \rightarrow H_2SiO_3 + 4HF.$$

Hydrogen fluoride interacts with SiF_4 to form hexafluorosilicate acid:

$$SiF_4 + 2HF \rightarrow H_2SiF_6.$$

Summary process:

$$3SiF_4 + 3H_2O \rightarrow 2H_2SiF_6 + H_2SiO_3.$$

Hexafluorosilicate acid is similar in strength to sulfate H_2SO_4. Salts of hexafluorosilicate acid (fluorosilicates) are mostly soluble in water. Salts are used as a component in the production of cements and enamels. Soluble magnesium and aluminum fluorosilicates are used in construction. These substances make the surface of the building material waterproof.

Silicon dioxide SiO_2 is a very common in nature. It is found in the form of quartz. Transparent, colorless quartz crystals that have the shape of hexagonal prisms with hexagonal pyramids at the ends are called rock crystal. Rock crystal colored with impurities in purple color is called amethyst, and brownish - smoky topaz. One of the varieties of quartz is silicon. Fine-crystalline varieties of silicon include agate and jasper. Quartz is part of many rocks (granite, gneiss).

Ordinary sand consists of small grains of silicon. Pure sand is white, while colored sand (yellow or reddish) has some impurities.

Acids, except hydrofluoric acid, do not affect silicon dioxide. SiO_2 melts at 1610°C, forming glass. Amorphous SiO_2find very little in nature (crepel, kidelgur) at the bottom of the seas.

In construction and buildings, SiO_2 is used for the production of glass, fiberglass, cement, and brasives.

SiO_2 is an acidic oxide. It corresponds to weak, slightly water-soluble acids with the general formula $xSiO_2 \cdot yH_2O$. Orthosilicate H_2SiO_4, metasilicate H_2SiO_3 and a number of other acids were isolated in the free state. Since x and y can take on the values of numbers in the natural series, in nature there is a wide variety of salts of these acids, collectively called silicates.

Only sodium and potassium silicates, which are formed by fusing silicon dioxide with alkalis or potassium and sodium carbonates, dissolve in water:

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O;$$
$$SiO_2 + K_2CO_3 \rightarrow K_2SiO_3 + CO_2\uparrow.$$

Sodium and potassium silicates are called soluble glass, and their aqueous solutions are called liquid glass. Liquid glass can also be obtained by the reaction:

$$2Na_2SO_4 + 2SiO_2 + C \rightarrow 2Na_2SiO_3 + 2SO_2\uparrow +CO_2\uparrow.$$

Liquid glass is used for the production of acid-resistant cement, for plastering work, for impregnating fabrics, for the production of fire-resistant paints for wood, for strengthening weak soils, as a concrete hardening accelerator. Na_2SiO_3, K_2SiO_3 undergo hydrolysis. Natural silicates include silicates, including feldspars, micas, clays, asbestos, talc and rocks: granite, gneiss, basalt, shales. Emerald, topaz, and aquamarine gemstones are also natural silicate crystals.

The most important natural silicates are: kaolin $Al_2SiO_3 \cdot 2SiO_2 \cdot 2H_2O$, white mica $K_2O \cdot Al_2SiO_3 \cdot 2SiO_2 \cdot 2H_2O$, asbestos $CaO \cdot 3MgO \cdot 4SiO_2$.

Glass is also a synthetic silicate. It is produced at high temperatures in furnaces during melting:

$$Na_2CO_3 + CaCO_3 + 6SiO_2 \rightarrow Na_2O \cdot CaO \cdot 6SiO_2 + 2CO_2\uparrow;$$
$$Na_2CO_3 + CaCO_3 \cdot MgCO_3 + 6SiO_2 \rightarrow Na_2O \cdot CaO \cdot MgO \cdot 6SiO_2 + 3CO_2\uparrow.$$

When replacing soda with potash, fireproof glass is obtained:

$$K_2CO_3 + 6SiO_2 + CaCO_3 \rightarrow K_2O \cdot CaO \cdot 6SiO_2 + 2CO_2.$$

When glass is made, impurities in sand give it different colors: Cu^{+2} gives it green, Fe^{+2} gives it brown, and Co^{+2} gives it purple.

Quartz glass is pure sand without impurities, so it transmits ultraviolet radiation. Window glass does not transmit ultraviolet radiation.

Special decorative lead glass (crystal) is obtained by replacing soda with potash and adding lead oxide.

By pulling molten glass through narrow holes, thin (2-10 microns) fiberglass threads are obtained. This is a non-flammable fabric that has thermal, electrical and sound insulating properties and high chemical resistance.

The combination of fiberglass with synthetic resins makes it possible to obtain fiberglass, which is 3-4 times lighter than steel, but not inferior to it in strength. It is used to make pipes that are not subject to corrosion, are durable and can withstand very high pressure. They are used in the automotive, aviation, shipbuilding and construction industries.

Glass coatings are called enamels (opaque, fusible, designed to protect metals) and glazes (to cover ceramic products).

Water glass is an alkaline solution of sodium and potassium silicates. Unlike most silicate salts, they are soluble in water. They are obtained by fusing SiO_2 with alkalis or carbonates.

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O;$$
$$SiO_2 + K_2CO_3 \rightarrow K_2SiO_3 + CO_2\uparrow.$$

They are used for gluing cellulosic materials. Sodium and potassium silicates look like ordinary glass and are a transparent solidified melt. As a result of the hydrolysis of these salts, solid silicate acid is formed, that is, water glass can harden in air. For this reason, it is used to strengthen soils, make acid-resistant concrete, and impregnate fabrics that become refractory.

14.3. Aluminosilicates

Silicates containing aluminum are called aluminosilicates. The most important of them are feldspars, for example, orthoclase $K_2O\cdot Al_2O_3\cdot 6SiO_2$. Aluminosilicates are very common in nature. These include feldspars, micas, kaolin, etc. The most common rocks, granites and gneisses, are composed of crystals of quartz, feldspar and mica. Mica and asbestos are used as electrical and thermal insulation materials.

Aluminosilicates are insoluble in water and decompose by hydrofluoric acid, alkali melts and alkali metal carbonates. Some aluminosilicates react slowly with CO_2 and water, weathering under natural conditions to form quartz and other minerals.

Natural aluminosilicates, which do not contain the (OH) group and crystalline water, are refractory, thermally stable compounds. Mica has an unusual layered structure that breaks down into thin, flexible sheets.

Synthetic aluminosilicates are produced by hydrothermal synthesis by heating silicon oxides SiO_2 and aluminum Al_2O_3 with metal oxides.

Silicates and aluminosilicates are part of Portland cement. Its components are subject to hydration:

$$3CaO\cdot SiO_2 + nH_2O \rightarrow 2CaO\cdot SiO_2\cdot 2H_2O + Ca(OH)_2 + (n\text{-}3)H_2O;$$
$$2CaO\cdot SiO_2 + 2H_2O \rightarrow 2CaO\cdot SiO_2\cdot 2H_2O;$$
$$3CaO\cdot Al_2O_3 + 6H_2O \rightarrow 3CaO\cdot Al_2O_3\cdot 6H_2O;$$
$$4CaO\cdot Al_2O_3\cdot Fe_2O_3 + 10H_2O \rightarrow$$
$$3CaO\cdot Al_2O_3\cdot Fe_2O_3\cdot 6H_2O + Ca(OH)_2 + 2Fe(OH)_3.$$

Aluminosilicates form fine-grained sedimentary rocks called clay. They are dense when dry, but flexible and plasticity when moistened. A common clay mineral, kaolinite $Al_2O_3\cdot 2SiO_2\cdot 2H_2O$, which is formed during the weathering of aluminosilicates, is a raw material for the porcelain industry.

Sitall (what does mean Si and Al) is glass-crystalline material obtained by controlled crystallization of silicate melts with the formation of small crystals distributed in the material. The average size of the crystals is 1-2 microns. The amount of amorphous glass is small and is only a few percent. Thin layers of glass connect the crystals, forming a strong, dense structure.

To ensure fine crystallization of glass, catalysts are added to it, which leads to the formation of numerous centers of crystallization. Usually, the composition of sitalls is $MgO–Al_2O_3–SiO_2$ and $Li_2O–Al_2O_3–SiO_2$ systems, and TiO_2 is used as a catalyst.

Thanks to the fine-crystalline structure, these materials have high mechanical strength, chemical and thermal resistance, and are resistant to gas diffusion. In terms of hardness, some of the sitalls are close to hardened steel and 25 times higher than window glass.

Obtaining such materials from metallurgical slag is effective and environmentally beneficial. TiO_2, P_2O_5, CaF_2, ferrum and magnesium sulfates in the amount of 4-5% are used as catalysts. Products made from slag-sitalls are used in industrial, residential and road construction as floor tiles, material of stair treads, walls, pavements, etc. Foams made of such materials are effective thermal insulation materials.

Materials and products obtained from mineral clay by molding and then firing at high temperatures are called ceramics. Such technologies have been common known since ancient times. Today, a large number of various ceramic materials are used in construction: bricks, pipes, floor and roof tiles.

The main raw materials for the production of ceramics are natural aqueous aluminates (kaolins and clays). When water is added, they form a plastic mass. When this mass is heated to 550-600 C, water comes out of it and the structure of the clay is destroyed with the formation of mullite $3Al_2O_3 \cdot 2SiO_2$, which is a stone-like solid.

The reaction of decomposition of kaolinite with the formation of mullite can be simply described by the following equation:

$$3[Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O] \rightarrow 3Al_2O_3 \cdot 2SiO_2 + 4SiO_2 + 6H_2O.$$

However, it should be noted that ceramics is a more general term that includes pottery, porcelain, refractory and technical ceramics from oxides (alumina, beryllia, zirconia), non-oxides (carbides, borides, nitrides, silicides) and composites. Each of these groups has unique material properties.

Test questions

1. What are the main minerals of silicon and aluminum in nature? Which chemical elements are more and less common than them?
2. How is pure aluminum manufactured and why is this process different from manufacturing of steel?
3. Write reaction equations showing the amphoteric properties of aluminum oxide and hydroxide.
4. What compounds does silicon form with hydrogen and halogens?
5. What is water glass and how is it used in construction?
6. What are sitalls and how are they manufactured?
7. What are construction ceramic materials and how are they manufactured?

Chapter 15. Basics of chemistry of binding materials

15.1. General characteristics

A binder or binding agent is any material or substance that holds or draws other materials together. More narrowly, binders are liquid or dough-like substances that harden by a chemical or physical process.

Binders are classified as organic (bitums, glues, polymers) and inorganic (lime, cement, gypsum, liquid glass, etc.).

Based on their chemical resistance, binders are classified by the field of use: non-hydraulic, hydraulic, acid-resistant etc.

In construction and architecture, masonry and buildings, binders are usually inorganic compounds, that is, mineral binders.

Mineral binders are powdered materials that, when mixed with water, aqueous or other solutions, can form a doughy mixture that eventually turns into a stone-like body.

One of the most important properties of binders is their ability to bind heterogeneous inorganic and organic materials into a single strong monolith through adhesion.

Mineral binders are divided into hydraulic and air.

Hydraulic binders are able to continue to continue to cure and retain strength in air and water after pre-curing in air. This class of binders includes hydraulic lime, all types of cements: Portland cement, Roman cement, alumina, aluminate, slag cements.

Aerial (air) binders are able to harden and retain strength for a long time only in air. This class of binders includes gypsum and magnesia binders, aerial lime, soluble glass.

To characterize the properties of binders, the following indicators are used:

- The chemical composition of binders is determined by analytical chemistry experiments. The most important in the analysis of binders is the determination of the content of the following oxides: CaO, MgO, SiO_2, Fe_2O_3, Al_2O_3, SO_3.

- The mineral composition of binders is determined using a set of different methods of analysis: analytical chemistry, X-ray phase analysis, differential thermal analysis (DTA), infrared electroscopy, etc.

- The degree (fineness) of grinding is a characteristic of the dispersion of the powder of the material, which is expressed as a mass fraction as a percentage of the powder residue on the control sieves.

- Specific surface area is a characteristic that is related to the size of powder particles and is determined in m^2/kg.

Water demand is the mass of water as a percentage of the mass of the binder, which is used for mixing to acquire the desired plasticity of the dough.

Curing of binders is the transition of a viscous plastic system into a solid one. The beginning of curing is considered to be the time from the moment of mixing the powder with liquid until the moment the mixture loses mobility while maintaining plasticity. The end of curing is considered to be the time from the moment of kneading to the moment of transition of the system into a solid.

- Hardening is a spontaneous irreversible physicochemical process of interactions of a binder with water or an aqueous solution of salt, which leads to the formation of a plastic dough, which eventually turns into an artificial stone. The driving force of solidification is the chemical interaction of the minerals of the binder with water to form new phases of crystal hydrates.

- Hardening rate is the time it takes to achieve the required strength. The hardening of slaked lime lasts for years and decades. In gypsum binders, it is two hours. According to the rate of hardening, cements are divided into ordinary and fast-hardening with strength standardization, corresponding to the period of 7 and 28 days; 2 and 28 days.

Stability in various operating conditions is the ability to be in contact with fresh or mineralized water, alkalis, acids for a long time without significant loss of strength and weight of binder products, or to counteract the destructive effect of high temperature, or alternating freezing and thawing.

15.2. Aerial construction lime

It is a product that is obtained from limestone and limestone-magnesia carbonate rocks by firing to obtain mainly calcium oxide. The quality of aerial lime is assessed by various indicators, but the main one is the content of calcium and magnesium oxide in it (lime activity). The higher their content, the higher the quality of the lime. Depending on the content of magnesium oxide, the following types of air lime are distinguished: calcium with MgO not more than 5%, magnesia with 5-20% MgO and dolomite where content of MgO is from 20 to 40%.

Lime used for autoclaved products should not have more than 5% magnesium oxide. The activity of high-quality varieties of air lime reaches 93-97%. Lime differs in the rate of quenching. The quenching rate is the time from the moment of mixing lime with water until the maximum temperature is reached and it begins to decrease.

Limestone-magnesia carbonate rocks are used for the production of aerial lime: marble-like limestone, crystalline dense limestone, chalk, limestone tuff, shell limestone, dolomite. Marble is the purest raw material, but it is rarely used for lime production.

The most important technological operation in the production of aerial lime is firing. At the same time, physicochemical processes occur that determine the quality of lime. The firing goal is the maximum possible thermal dissociation of $CaCO_3$ and$MgCO_3{\cdot}CaCO_3$ into CaO, MgO and CO_2 with an optimal particle microstructure.

The decomposition reaction (decarbonization) of the main component of limestone, calcium carbonate, are to the following scheme:

$$CaCO_3 \leftrightarrow CaO + CO_2\uparrow$$

Theoretically, carbonization of 1 mole of $CaCO_3$ requires 179 kJ of heat.

The process of thermal dissociation of calcium carbonate is reversible. The direction of this chemical reaction depends on the temperature of the carbon dioxide partial pressure process.

Based on the fact that CaO and $CaCO_3$ by theirnature are in a solid state and their concentration is a constant value, the dissociation constant depends solely on the concentration of carbon dioxide. This can be shown in terms of the partial pressure of the gas. Consequently, in the system, the dynamic equilibrium established at the partial pressure P_{OC2}, determined for each temperature, does not depend on the amount of calcium carbonate and calcium oxide. This equilibrium pressure P_{CO2} is called the dissociation pressure.

Dissociation of $CaCO_3$ is only possible under conditions where the dissociation pressure is higher than the partial pressure of CO_2 in the environment.

At normal temperatures, the breakdown of calcium carbonate is not possible. The process of thermal dissociation begins slowly in a vacuum at a temperature of 600°C.With a further increase in temperature, the dissociation of $CaCO_3$ accelerates. So, at 880°C, the dissociation pressure reaches 0.1 MPa, which exceeds the external atmospheric pressure, so the decomposition of calcium carbonate in open space occurs intensively.

This phenomenon can be conditionally compared to the intensive release of steam from the entire volume of water (boiling), if the pressure of saturated steam over water becomes equal to the external pressure. At a temperature of more than 900°C, a temperature increases for every 100°C accelerates the decarbonization process by 30 times, which corresponds to the Van't Hoff rule on the effect of temperature on the rate of a chemical reaction.

The decomposition of $CaCO_3$ does not occur immediately in the entire mass of the granule, but begins from the surface and gradually moves to the middle. The speed of movement of the thermal dissociation zone depends on the firing temperature: at 800°C, the speed of movement of the dissociation zone is 2 mm, at 1100°C it is 14 mm per hour, that is in 7 times faster.

In manufacturing, the optimal firing temperature of $CaCO_3$ is in the range of 1000-1100°C.

Despite the fact that, according to the second law of thermodynamics, with an increase in the temperature of the technological process, the efficiency of fuel use increases, nevertheless, lime firing is not allowed to be carried out at a temperature greater than 1250°C.

The quality of construction air lime depends not only on the content of calcium and magnesium oxides in it, but also on the structure of the resulting compounds, which is marked by the size and shape of CaO and MgO crystals, as well as the size of the pores and their distribution in the mass of the substance. Decarbonization of limestone at low temperatures (800-850°C) leads to the formation of calcium oxide in the form of a spongy structure consisting of crystals 0.2-0.3 μm in size, which, as it were, are pierced with too thin capillaries about 8×10^{-3}μm in size.

The specific surface area of such lime reaches 50 m^2/g, which theoretically contributes to a rapid reaction with water. In reality, this does not happen, and the reason is that water moves too slowly through such small capillaries.

An increase in temperature to 900-1000°C lead to an increase in the size of CaO crystals with a decrease in the specific surface area to 5 m^2/g, which should adversely affect the reactivity of the substance. But high porosity in the mass of finished products creates the prerequisites for rapid penetration of water into the volume of lime lumps. Although calcinations at higher temperatures leads to an increase in CaO crystals, the specific surface area decreases as a result of shrinkage, which slows down the reaction with lime. Roasting results in the formation of $2CaO \cdot SiO_2$, $CaO \cdot Al_2O_3$, $CaO \cdot Fe_2O_3$ as a result of the interaction of the resulting calcium oxide with impurities that are always present in the $CaCO_3$ raw material (class A limestone has 5% of houseshock, class B has 18%, and class C has 50%).

The neoplasms in lime have a negative effect on the quality of the solution and products. Delayed quenching of such lime, which are in the products, lead to their destruction. Therefore, best of all use lime that is calcinated at a temperature that ensures the complete breakdown of the limestone and economy of fuel. The choice of the optimal temperature for burning lime depends on the admixtures of magnesium carbonate in the raw material. Unlike calcium carbonate, it decomposes at a lower temperature, starting around 400°C and completely within 600-650°C.

The reactivity of lime and MgO becomes less with increasing calcination temperature. Already at 1200°C, the result is highly burnt magnesium oxide called **periclase**, which does not have astringent properties. Sufficiently active magnesium oxide is obtained by firing dolomites or limestones with a high magnesite content at 850-950°C. Therefore, lime burned at a higher temperature than necessary for the decomposition of $MgCO_3$ hardens slowly and unevenly.

Lime calcination is carried out using various furnaces: shaft, rotating, fluidized bed, with special grates.

Rotary lime kilns have the advantage of obtaining high quality lime that contains no ash and reacts quickly with water. In such furnaces, soft limestone rocks are also burned, which is impossible to do in mine furnaces (chalk, tuff, etc.).In addition, rotary kilns have possibility of mechanization and automation of the process.

The next technological operation will be lime quenching. Calcium and magnesium oxides transform into hydroxides interacting with water:

$$CaO + H_2O \rightarrow Ca(OH)_2.$$

This process is spontaneous and full possible because the original CaO compound is obtained through an endothermic reaction. The lime slaking process generates a significant amount of heat, amounting to 65 kJ/mol, or 160 kJ per 1 kg of calcium oxide.

The lime quenching reaction is undulating and depends on the temperature and partial pressure H_2O. The process of dehydration is already possible at a temperature of 300-350°C, and the resulting CaO is re-quenched not completely and slowly. It can be prevent by adding of water. When quenching lime, it is competent to provide the temperature of 60-80°C to avoid overheating of the material and intensive process of CaO interaction with water.

It is assumed that when slaking lime, calcium oxide first dissolves in water, and then a precipitate of calcium hydroxide precipitates from the supersaturated solution. Steam hardening is also possible. In this case, water molecules directly attach to calcium oxide molecules, so, this is a solid-phase reaction. The high- and low-temperature calcined limes are hydrated in different ways. In the first case, lime react with water in the liquid phase with the transition of calcium oxide into solution. In the second case, due to the fact that lime has high porosity (up to 65%), CaO hydrates in the middle of the granules. Thus, the process of interaction of lime with water is influenced by the calcination temperature, the state of aggregation of water and quenching conditions, and temperature has a contradictory effect on the process. On the one hand, an increase in temperature reduces the solubility of $Ca(OH)_2$ and a film forms on the lime grains that have not yet reacted. But on the other hand, the diffusion of water through these films becomes faster. As a result, with an increase in temperature by 10°C, the quenching rate doubles.

Other cations have a negative effect on the solubility of $Ca(OH)_2$. The hydration process is also affected by the additions of NaCl, NH_4Cl, HNO_3, etc. They form poorly soluble substances with lime, which are deposited on the lime particles in the form of films that are poorly permeable to water, which slow down hardening. These include sulfates, phosphates and oxalates.

Slaked lime mixed with quartz sand and other fine aggregates is used to make slow-hardening mortars.

When mixed with water, hardening of slaked lime is realized in two ways: crystallization of calcium hydroxide Ca(OH)2 when lime solutions dry (hydrate hardening) and its subsequent carbonization (carbonate hardening). They can be shown by the following reactions:

$$CaO+H_2O \rightarrow Ca(OH)_2;$$

$$Ca(OH)_2 + CO_2 + nH_2O \rightarrow CaCO_3 + (n+1)H_2O.$$

The resulting calcium carbonate fuses with $Ca(OH)_2$ crystals, strengthens the lime mortar and doubles its water resistance.

In the case of using autoclave treatment, it is possible to implement another type of hardening called hydro silicate, which occurs under a pressure of 0.9-1.6 MPa, which corresponds to a temperature of 174.4-200°C. The solubility of $Ca(OH)_2$ drops quickly with a decrease in temperature, and at the same time the solubility of SiO_2 dramatically increase starting from 150°C. Under such conditions, calcium hydrosilicates are formed with the formulas $(0.8\text{-}1.5)CaO\cdot SiO_2\cdot(0.5\text{-}2.0)H_2O$.

Long-term autoclave treatment produces the Tobermory mineral $5CaO\cdot 6SiO_2\cdot 5H_2O$, which ensures high strength and durability of products.

The reaction of quartz filler with $Ca(OH)_2$ is possible under normal conditions, but for this purpose amorphous silica, slag, ash, fireclay and even finely ground quartz sand are used.

When processed in autoclaves, the strength of products first increases, and then begins to decrease with prolonged steaming. At the beginning of steaming, the increase in the strength of lime-silica products is determined by the intensive formation of highly dispersed particles of calcium hydrosilicate, which have significant astringent properties.But over time, the rate of appearance of hydrosilicates fades due to the fact that the reaction is heterogeneous and new formations interfere with the interaction of $Ca(OH)_2$ and SiO_2. On the other hand, there is a parallel process of increasing the size of hydrosilicate crystals, which leads to a decrease in the contact area between them and reduces the strength of products.

Thus, as we see, even such a relatively simple binder as lime has many aspects of its practical use that must be taken into account with carefully and precision.

15.3.Gypsum binders

Gypsum binders are the most effective in technical and economic terms. This is due to relatively low energy costs, full mechanization and automation of the technological process. They are a typical example of air binders.

They are powdered materials consisting of β-hemihydrate gypsum $CaSO_4\cdot 0.5H_2O$, obtained by firing gypsum stone$CaSO_4\cdot 2H_2O$ at a temperature of 120-160°C).

When heat treatment of dihydrate gypsum in a steam environment under pressure in autoclaves or aqueous solutions,α-hemihydrate sulfate is formed, which consists of large and dense crystals characterized by a reduced water demand comparatively with β-$CaSO_4 \cdot 0.5\ H_2O$.

This determines the dense structure of the hardened α-$CaSO_4 \cdot 0.5H_2O$ and high strength of gypsum. Highly roaste gypsum binders are made by firing gypsum stone at a high temperature (600-1000°C) followed by grinding the product. At this temperature, gypsum is almost completely dehydrated, and a certain amount of $CaSO_4$ undergoes thermal dissociation, with the formation of CaO, which activates the chemical interaction of the binder with water. Such a binder is called Estrich-gypsum, it is characterized by slow curing and hardening. The water requirement of such gypsum is 28-32%.It is characterized by high water and frost resistance compared to other binders.

Hardening of gypsum binders occurs as a result of the dissolution of semiaqueous calciumsulfate and the appearance of a saturated solution in which a hydration reaction occurs to form dihydrous calcium sulfate:

$$CaSO_4 \cdot 0.5H_2O + 1.5H_2O \rightarrow CaSO_4\ 2H_2O.$$

According to Le Chatelier's theory, when semi-aqueous gypsum is mixed with water, it dissolves to form a saturated solution. In solution, it reacts with water and turns into dihydrate. Based on the fact that the solubility of $CaSO_4 \cdot 0.5H_2O$ is 8 g/l, and $CaSO_4 \cdot 2H_2O$ is only 2 g/l, the solution can be supersaturated in relation to one and diluted in relation to the other. This means that conditions exist for the formation of crystals of both dihydrate and semi-aqueous substances.

This, in turn, leads to a decrease in the concentration of hemihydrate in the liquid phase and creates the possibility of dissolving new portions of this substance and the formation of a supersaturated solution of $CaSO_4 \cdot 2H_2O$.

As more and more gypsum dihydrate is separated from the solution, its crystals grow, intertwine, coalesce and cause the gypsum to harden and harden. The destruction of the structure of hardening gypsum leads to a dramatic drop in its strength.

According to Baikov's theory, the hardening process of semi-aqueous gypsum is divided into three periods.In the first period, as soon as gypsum is mixed with water, $CaSO_4 \cdot 0.5H_2O$ dissolves and a saturated solution is formed. In the second period, water interacts with semi-aqueous gypsum with its direct attachment to the solid. In the last period, colloidal bihydrate particles recrystallize to form larger crystals. The solution hardens and its strength increases.

In reality, the processes of the periods under consideration are shifted and superimposed on each other.

The basic theories of hardening of semi-aqueous gypsum were created later by other scientists (Budnikov, Rebinder and Segalova), but they have much in common with the theories of their predecessors.

Hydration of the total mass of semi-aqueous gypsum and crystallization of $CaSO_4 \cdot 2H_2O$ are practically completed within 20-40 minutes after mixing. The strength of gypsum increases significantly as the water dries, which no longer occurs due to hydration, but due to the evaporation of water. Gypsum dihydrate precipitates from the solution, which helps strengthen the contacts between crystalline intergrowths.

Products made from β- and α-semi-aqueous gypsum are characterized by high strength in dry conditions and fire resistance. It should be noted that steel reinforcement in gyproducts quickly corrodes. It should be noted that the steel reinforcement in it quickly collapses.

15.4.Magnesia binders

Magnesia binders include caustic magnesite and caustic dolomite. After firing and pumping, it is a powder, the main component of which is magnesium oxide MgO and, accordingly, MgO and CaO. To accelerate hardening, they are mixed with aqueous solutions of calcium chloride or calcium sulfate of a certain concentration. It is possible to use solutions of $ZnCl_2$, $FeSO_4$, etc.

To obtain caustic magnesite, magnesite MgCO3 is used, which in nature is found in crystalline state and less often in an amorphous state. During firing, a process of thermal dissociation occurs:

$$MgCO_3 \rightarrow MgO + CO_2\uparrow.$$

This process is possible already at 400°C, when the pressure generated by carbon dioxide is equal to the ambient pressure. In practice, to speed up the process, magnesite firing is carried out at temperatures above 600°C, but not more than 800°C.

At high temperatures, magnesium oxide becomes denser, recrystallizes and loses the ability to interact not only with water, but also with acids. This magnesium oxide is used to make fire bricks.

Construction products made from caustic magnesite using magnesium chloride are characterized by hygroscopicity.

According to Shelyagin, when MgO interacts with a solution of magnesium chloride, the rate of the chemical reaction of the formation of $3MgO \cdot MgCl_2 \cdot 6H_2O$ or $3MgO \cdot MgSO_4 \cdot 7H_2O$ increases due to improved solubility of caustic magnesite.

The higher the concentration of mixers, the slower the hardening and curing process occurs, but the final strength is greater. However, the use of solutions with a density of more than $1.3 \cdot 10^3$ kg/cm^3 leads to the formation of cracks and efflorescence. Caustic magnesite hardens quickly. After 7 days, its strength is within 90% of its maximum value.

Unlike other mineral binders, caustic magnesite produces high-quality mortars and concretes not only with mineral, but also with organic fillers (sawdust, shavings, bone).

Caustic magnesite is an air binder. In water or wet conditions its strength decreases quickly.

Caustic dolomite is produced by roasting dolomite $MgCO_3 \cdot CaCO_3$ at a temperature of 600-700°C, followed by grinding in ball mills. It consists of magnesium oxide MgO and calcium carbonate $CaCO_3$. If the thermal dissociation of dolomite occurs at a temperature of 750-850°C, then we obtain dolomite cement, which consists of MgO, CaO and $CaCO_3$. At a temperature of 900-950°C, dolomitic lime is obtained, consisting of magnesium and calcium oxides.

The products of dolomite firing at a temperature of 1400-1500°C are used for the manufacture of refractory materials.

Caustic dolomite is mixed with aqueous solutions of $CaCl_2$ or $MgSO_4$. It is characterized by a slow hardening time: the beginning is after 3-10 hours, the end is not earlier than 8-20 hours, it is less durable and also belongs to air binders.

Concretes based on caustic magnesite and caustic dolomite are destroyed in water due to the leaching of soluble $MgCl_2$ salt.

Caustic magnesite and dolomite are used to make xylolite, oribrolite and thermal insulation materials. Magnesia concretes with organic fillers have high impact strength.

15.5.Portland cement

Portland cement is a hydraulic binder obtained by finely grinding Portland cement clinker with gypsum ($CaSO_4 \cdot 2H_2O$), active and inactive additives. It was developed by Aspdin from other types of hydraulic lime in England in the early 19th century and became the most common type of cement. Its name comes from the Isle of Portland in England, or more precisely from the natural stone mined there, which looks something like concrete. Portland cement is widely used as the main ingredient of concrete, plaster and mortar. The basis of Portland cement is silicates (alite and belit).

Clinker is an intermediate product in the production of cement. It is manufactured by firing a finely dispersed mixture consisting of limestone, clay, and iron compounds, ensuring the predominance of highly basic calcium silicates. Gypsum, which is added to clinker during grinding, is necessary to regulate the hardening period. This makes it possible to create a technological pause in time and in the process of producing mortar or concrete before its use.

The properties of Portland cement are determined primarily by the quality of the clinker.

With the help of additives, an increase in corrosion resistance, a more complete passage of chemical reactions, savings in binders and an overall improvement in the quality of concrete are achieved.

The chemical composition of Portland clinker is determined by a special method. In this case, the amount of bound CaO and free SiO_2, Fe_2O_3 and Al_2O_3 is determined. Their total content is 95-97%. The composition of clinker in small quantities may include MgO, SO_3, TiO_2, Cr_2O_3, Mn_2O_3, Na_2O, K_2O, P_2O_5 and others.

The calcium oxide content increases the hardening rate of cement and gives concrete high final strength, while at the same time negatively affecting the water resistance of building products.

Cements with a high SiO_2 content in clinker are characterized by a longer hardening time and rapidly gain strength over a long period of time.

Aluminum oxide promotes rapid hardening of the solution. Excess Al2O3 impairs water, frost and sulfate resistance.

Ferrum (III) oxide Fe_2O_3reduces the sintering temperature and increases corrosion resistance.

Magnesium oxide is an undesirable component of clinker, leading to an uneven change in the volume of concrete.

Titanium oxide TiO_2 improves the crystallization of clinker, which leads to an increase in strength, but an excess (more than 5%) of this oxide worsens the quality of cement.

Trivalent manganese oxide Mn_2O_3 and chromium oxide Cr_2O_3 enter raw materials and waste with by-products, for example, blast furnace slag instead of the clay slag component. If the first (Mn_2O_3) does not significantly affect the properties of clinker, then Cr_2O_3 in small quantities (0.1-0.3%) increases the hardening rate, but in an amount of 1-2% it slows down this process.

Phosphorus (V) oxide P_2O_5 in an amount of 0.2-0.3% increases the strength of concrete, but at more than 2% it completely stops the crystallization of alite $3CaO \cdot SiO_2$ and the strength of concrete decreases sharply.

Cement clinker always contains K_2O and Na_2O. If their total amount exceeds 1%, then the solutions have unstable curing times.

The composition of cement clinker includes four most important clinker materials:

- alite (tricalcium silicate) $3CaO \cdot SiO_2$;
- belite (bicaclium silicate) $2CaO \cdot SiO_2$;
- tricalcium aluminate $3CaO \cdot Al_2O_3$;
- celite (tetracalciumaluminoferite) $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$.

The production of Portland cement consists of the production of clinker and its grinding with additives.

When obtaining clinker of the required mineralogical composition and quality of raw materials, the main thing is a carefully calculated ratio of the starting substances with the required dispersion, the homogeneity of the mixture of raw materials (sludge), and the correct firing and cooling regime. Compliance with the specified parameters will ensure the normal flow of the following technological processes.

Three methods of preparing a raw mixture from starting materials are used: wet (crushing, crushing, mixing of raw materials occurs in an aqueous environment), dry (materials are crushed and mixed in a dry state) and combined (preparing the mixture using a wet method, then dehydrating it to 16-18% water and granulation).

Each of these methods has positive and negative sides. In an aquatic environment, the grinding of raw materials is facilitated, high-quality mixing of the charge occurs, and working conditions are more favorable, however, fuel consumption for firing raw materials using the wet method is almost 2 times higher, and a long rotating kiln is also required. When using the dry method, the raw materials are dried after grinding.

The dry method is better when using limestone and clay of a homogeneous composition with a moisture content of 10-15%.

Today there is a tendency to combine the processes of fine grinding and grinding with drying.

Rotary kilns are most often used for firing the raw material mixture in both wet and dry production methods. The furnace body is a long steel drum mounted on a foundation with an inclination of 3-4°.

The furnace rotates by means of an electric motor at a speed of 0.5-1.2 revolutions per minute. The furnace is lined from the inside. Refractory materials for these purposes are selected mainly taking into account the temperature in different zones of the furnace.

The rotary kiln operates according to the following scheme: the raw material mixture (sludge) from the sludge accumulator is pumped into a distribution tank located above the kiln, and then fed into the kiln. Fuel is supplied from the opposite side.

Sludge, passing through the furnace, is exposed to various temperatures, which gradually increase, leading to physical and physicochemical changes and transformations. The nature of the processes occurring with the raw material mixture is determined by temperature. The wet rotary kiln is divided into six zones:

The first is the drying zone. It starts at low temperature and ends at 700°C. The water evaporates intensely, the sludge becomes compacted and clumps.

The second is the heating zone. In this zone, organic impurities burn out, kaolinite is dehydrated, and kaolinite anhydride $Al_2O_3 \cdot 2SiO_2$ is formed. With the loss of hydration water, the plasticity of the mass is lost and the lumps are destroyed. The temperature of the material at the end of the zone is 700-800°C.

The third is the calcination zone. This section of the furnace is about 20% of its length. This zone has the highest heat consumption. At a temperature of 900-1200°C, decarbonization of $CaCO_3$ is completed. The resulting calcium oxide CaO begins to interact with Al_2O_3, Fe_2O_3 and SiO_2.Fine grinding of raw materials and thorough mixing of components contribute to increasing the intensity of reactions in the solid state. During reactions in the solid state between CaO and the decomposition products of clays and their components, β-$CaO \cdot SiO_2$, $CaO \cdot Al_2O_3$ and $2CaO \cdot Fe_2O_3$ are formed.

The fourth is the zone of exothermic reactions, as well as the temperatures of formation of minerals that are important for the mineralogical composition of cement clinker. At 1300°C the following are formed: β-$2CaO \cdot SiO_2$, $3CaO \cdot Al_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. The formation of these minerals occurs with a significant release of heat (up to 420 kJ per 1 kg of clinker), which leads to an intense increase in temperature by 150-200°C.

The fifth is the sintering zone, which occupies 10-15% of the total length of the furnace. At a temperature of 1300-1450°C, sintering of materials begins in this zone, as a result of which up to 30% of the liquid phase is formed. Without a liquid phase, the formation reaction of the most important mineral alite $3CaO \cdot SiO_2$ due to the interaction of $2CaO \cdot SiO_2$ and CaO remaining after the formation of belite, tricalcium aluminate, celite in previous reactions.

Increasing the sintering temperature will help to increase the efficiency of the furnace and the complete assimilation of CaO, and on the other hand, leads to a deterioration in the quality of alite due to too strong an increase in crystals. Therefore, it is necessary to accurately maintain the optimal sintering temperature of the material.

The sixth is the cooling zone, the last part of the kiln 10-15% of its length, in which the clinker is cooled to 1100-1000°C. Below this temperature, $3CaO \cdot Al_2O_3$, $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ crystallize, the viscosity of the liquid phase increases and it solidifies in the form of glass.

Depending on the cooling rate, not only the content of the glassy phase changes, but also the size of the crystals. Slowly cooling clinker contains large crystals of magnesium oxide, which leads to an uneven change in the volume of concrete. As a rule, slowly cooled clinker is used to produce cement of lower activity with impaired sulfate resistance, which is explained by the low content of the glassy phase.

The final technological operation in the production of Portland cement is clinker grinding, that is, its fine grinding with gypsum, active and other additives.

The hardening rate of cement and its strength depend not only on the phase and chemical composition of the clinker, but also on the degree of its grinding. Ordinary Portland cement has a specific surface area of 300 m^2/kg, while quick-hardening cement has a specific surface area of 450 m^2/kg. The physical and mechanical properties of cement improve only to a specific surface area of 700-800 m^2/kg. After this limit, the strength and frost resistance of cement deteriorate and its shelf life is reduced. Increasing the specific surface area is not always economically feasible, since this requires a lot of electricity.

As a result of mixing cement with water, hydrolysis of alite and hydration of clinker materials occurs, which leads to hardening and hardening of the cement paste to form manufactured stone.

The transition of clinker materials into hydrates as a result of hydrolysis and hydration reactions is a complex physicochemical process. The composition of new formations is determined mainly by the chemical and mineralogical composition of cement, temperature conditions, and the ratio of solid and liquid phases.

Tricalcium silicate (alite) $3CaO{\cdot}SiO_2$ is the most important mineral of cement clay. Its content in clinker can range from 37 to 60%.

At normal temperature and the concentration of Ca(OH)2 in the liquid phase is up to 1.1 g/liter (in terms of CaO), alite with water forms a hydrosilicate of the composition $(0.8\text{-}1.5)CaO{\cdot}SiO_2{\cdot}(1\text{-}2.5)H_2O$. With an increase in the concentration of $Ca(OH)_2$ in the solution, the basicity of the hydrosilicate increases.

It is generally accepted that at the end of the process of hydration and hydrolysis of alite, a crystalline hydrate with the composition $3CaO{\cdot}2SiO_2{\cdot}3H_2O$ is formed according to the reaction:

$$2(3CaO{\cdot}2SiO_2) + 6H_2O \rightarrow 3CaO{\cdot}2SiO_2{\cdot}3H_2O + 3Ca(OH)_2.$$

The composition of the above reaction products may vary depending on the temperature and time of processing of concrete products in autoclaves.

The hydration of belite proceeds slowly with the formation of the same products as in the reaction with alite, but in a different ratio:

$$2(2CaO{\cdot}SiO_2) + 4\,H_2O \rightarrow 3CaO{\cdot}2SiO_2{\cdot}3H_2O + Ca(OH)_2.$$

$Ca(OH)_2$ crystals are much larger, the composition of the hydrosilicate changes over time, and the CaO/SiO_2 ratio increases.

Tricalcium aluminate interacts with water according to the following scheme:

$$2(3CaO\cdot Al_2O_3) + 21\ H_2O \rightarrow 4CaO\cdot Al_2O_3\cdot 13H_2O + 2CaO\cdot Al_2O_3\cdot 8H_2O.$$

Based on the fact that lime is present in Portland cement and is also formed by the interaction of alite with water, the hydration reaction of tricalcium aluminate proceeds as follows:

$$3CaO\cdot Al_2O_3 + Ca(OH)_2 + 12H_2O \rightarrow 4CaO\cdot Al_2O_3\cdot 13H_2O.$$

In the case of autoclaveheat treatment of concrete, another compound $3CaO\cdot Al_2O_3\cdot 6H_2O$ is formed.

When grinding cement clinker, gypsum is added to regulate the hardening time of concrete, which, together with tricalcium aluminate, forms calcium hydro sulphaaluminate, called ethringite:

$$3CaO\cdot Al_2O_3 + 3(CaSO_4\cdot 2H_2O) + 26H_2O \rightarrow 3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O.$$

Hydration of tetracalcium aluminum ferrite occurs according to complex patterns with the formation of various types of crystalline hydrates:

$$4CaO\cdot Al_2O_3\cdot Fe_2O_3 + 13H_2O \rightarrow 4CaO\cdot Al_2O_3\cdot Fe_2O_3\cdot 13H_2O;$$

$$4CaO\cdot Al_2O_3\cdot Fe_2O_3 + 10H_2O\rightarrow$$

$$3CaO\cdot (Al,Fe)_2O_3\cdot 6H_2O + Fe_2O_3\cdot 3H_2O + Ca(OH)_2.$$

It hardens very quickly. In a short period of time of 3 days, the degree of hydration of the mineral reaches 70%, but it adds the least strength to concrete.

15.6.Aluminous cement

Aluminous cement is a hydraulic, fast-hardening binding mineral material formed as a result of fine grinding of sintering products or melting of a raw material mixture consisting of bauxite Al_2O_3, limestone $CaCO_3$ and impurities of iron, titanium, potassium, and sodium compounds. Sintering temperature

1150-1250°C. When using the melting method, the temperature reaches 1550-1650°C.

The mineralogical composition of aluminous cement is represented mainly by $CaO \cdot Al_2O_3$, $12CaO \cdot 7Al_2O_3$, $CaO \cdot 2Al_2O_3$ and ferrites of various compositions. This cement contains 40-50% calcium aluminate alone, which basically provides high strength.

Depending on the Al_2O_3 content, aluminous cements are divided into three types:

- ordinary alumina containing about 50% Al_2O_3;
- high-alumina containing more than 60% Al_2O_3;
- especially pure, high-alumina cement containing more than 70% Al_2O_3.

Sometimes acidic granulated blast furnace slag is introduced into aluminous cement, which reduces the cost of the binder, reduces shrinkage and heat generation during hardening.

A rapid increase in strength is the main property of aluminous cement (grade strength is achieved after 3 days). The process of increasing strength lasts up to 3 years and amounts to 150% of the grade.

Aluminous cement is sensitive to hardening conditions. At a normal temperature of 20°C, the hydration process is possible according to the following schemes:

$$CaO \cdot Al_2O_3 + 10H_2O \rightarrow CaO \cdot Al_2O_3 \cdot 10H_2O;$$
$$2(CaO \cdot Al_2O_3 \cdot 10H_2O) \rightarrow 2CaO \cdot Al_2O_3 \cdot 8H_2O + 2Al(OH)_3 + 9H_2O.$$

The recrystallization process involves a deterioration in strength. To prevent this from happening, ground dolomite $CaCO_3 \cdot MgCO_3$ is added to the cement, forming a stable crystalline hydrate $(CaO, MgO)Al_2O_3 \cdot 11H_2O$.

Concrete based on alumina cement under the influence of environmental carbon dioxide enters into the following reaction:

$$3CaO \cdot Al_2O_3 \cdot 6H_2O + CO_2 \rightarrow 3CaCO_3 + Al_2O_3 \cdot 3H_2O + 3H_2O.$$

The carbonization process proceeds more intensely, the more porous the cement stone.

Carbonation of calcium hydroaluminates negatively affects their protective properties in relation to steel reinforcement.

The environment of alumina cement is quite alkaline (pH = 11.5-11.7), which makes it impossible to corrode steel reinforcement. But over time, due to carbonization, the pH of the concrete medium decreases to 9, and this leads to the inevitable destruction of the reinforcement.

To prevent corrosion, it is proposed to prepare high-density concrete and protect the reinforcement with a sufficient layer of concrete.

15.7.Concrete corrosion

Concrete corrosion is the destruction of cement stone material under the influence of the environment. This process varies depending on both the chemical and mineralogical composition and operating conditions.

Under conditions of use, cement stone can be exposed to water containing salts of various compositions and properties, waste from chemical and other enterprises, acids, gases, etc.

The study of the durability of concrete in various environments began when builders were confronted with the destructive effects of seawater in structures on foundations and Portland cement. Fundamental work on concrete corrosion was under the leadership of Moskvin.

He classified corrosion processes in cement concrete under the influence of an aqueous environment into three groups:

The first group is corrosion due to the dissolution of cement stone components under the influence of water of low temporary hardness.

The second group is corrosion under the influence of water, which contains substances that interact with the components of cement stone to form easily soluble compounds that are washed out with water, or substances that do not contribute to strength and are easily washed off.

The third group is corrosion, when in the pores and capillaries of the cement stone, due to an exchange reaction with its components, particles crystallize, which create internal stresses leading to it destruction.

However, this is not the only possible classification. Kind classifies corrosion of concrete under the influence of natural water into: curing, acid, magnesia, and magnesia-sulfate.

The first of them occurs under the influence of soft water. When alite interacts with water, in addition to other compounds, calcium hydroxide $Ca(OH)_2$ is formed. Its content in cement stone is 10-18% (in terms of CaO). As a result of leaching, the $Ca(OH)_2$ content in concrete decreases, and this leads to the decomposition of other cement stone compounds. A decrease in $Ca(OH)_2$ content by 15-30% leads to a loss of concrete strength by 40-50%.

Leaching corrosion becomes even more intense under the influence of water pressure. The risk of corrosion decreases if acid salts of calcium and magnesium are present in the water, and increases in the presence of NaCl or Na_2SO_4.To prevent concrete from deteriorating, it must be compacted, confined and bound with calcium hydroxide into a stable compound.

To do this, during the manufacturing of cement, amorphous silica SiO_2 is prudently added, which reacts with dissolved $Ca(OH)_2$:

$$Ca(OH)_2 + SiO_2 + mH_2O \rightarrow CaO \cdot SiO_2 \cdot nH_2O.$$

Another type of corrosion is associated with exchange reactions between the components of the cement stone and compounds present in the water. The process of destruction begins from the surface, when the products of new formations do not have astringent properties and this does not prevent further penetration of water inside. This corrosion includes acid, carbon dioxide and attack by certain salts.

Acid corrosion occurs under the influence of mineral and organic acids, which can be found in wastewater from industrial enterprises. Their activity depends on the pH of the environment. Concrete begins to deteriorate already at pH = 6.5. Soluble salts of strong acids and weak bases also create an acidic environment when hydrolyzed, where the pH is <7, and acid salts act in the same way.

Carbon dioxide corrosion is different from acid corrosion. Carbon dioxide CO_2, which is always present in air and water, forms carbonate acid H_2CO_3, reacts with $Ca(OH)_2$ in concrete. At the first stage, it forms an insoluble salt $CaCO_3$ filling the pores and sealing the concrete surface. Chemical processes continue and the average salt $CaCO_3$ is converted into a soluble acid:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3\downarrow + H_2O;$$
$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2.$$

As the temporary hardness of water increases, the intensity of carbon dioxide corrosion of concrete decreases.

To eliminate carbon dioxide corrosion during cement production, active additives (amorphous silica) are introduced, which react with Ca(OH)2 and form an insoluble salt:

$$Ca(OH)_2 + SiO_2 \rightarrow CaSiO_3\downarrow + H_2O.$$

On the other hand, where possible, carbonate rock backfills are placed around the concrete structure to protect against corrosion.

Magnesium corrosion of concrete is associated with the action of solutions of magnesium salts on it, which are always present in sea and ocean water, and sometimes in groundwater. In this case, magnesium salts interact with $Ca(OH)_2$, resulting in the formation of a soluble salt – flakes of calcium chloride and magnesium hydroxide, which are washed off with water:

$$Ca(OH)_2 + MgCl_2 \rightarrow CaCl_2 + Mg(OH)_2\downarrow.$$

Corrosion of this type is determined by the formation in the pores of hardened concrete of compounds larger in volume than the original substances. They press from the middle of the volume of the building product, internal stresses arise and the concrete collapses. This includes sulfate corrosion, when tricalcium hydroaluminate reacts with gypsum formed as a result of the interaction of $Ca(OH)_2$, concrete and Na_2SO_4, which may be in water:

$$3CaO \cdot Al_2O_3 \cdot 6H_2O + 3CaSO_4 + 25H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O;$$
$$Ca(OH)_2 + Na_2SO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2NaOH.$$

The resulting ettringite $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$ is 2.9 times larger in volume than $3CaSO_4 \cdot Al_2O_3 \cdot 6H_2O$.

To prevent the formation of ettringite, it is necessary to bind $Ca(OH)_2$ to a concentration not exceeding 460 mg/liter:

$$Ca(OH)_2 + SiO_2 \rightarrow CaSiO_3\downarrow + H_2O.$$

An effective measure to eliminate sulfate corrosion is a directed change in the composition of clinker of Portland cement, primarily a decrease in tricalcium aluminate.

Recently, a completely new method has been proposed to improve the stability of concrete. In this case, the products of the interaction of $Ca(OH)_2$ with SiF_4 or $MgSiF_6$ settle in the pores of concrete, compacting it:

$$Ca(OH)_2 + SiF_4 \rightarrow 2CaF_2\downarrow + SiO_2\downarrow + 2H_2O;$$
$$Ca(OH)_2 + MgSiF_6 \rightarrow 2CaF_2\downarrow + MgF_2\downarrow + SiO_2\downarrow + 2H_2O.$$

Test questions

1. What substances are called binders? Define their main types.
2. What properties of binders allow us to classify them into air and hydraulic?
3. How is building lime manufactured? Supply few chemical reactions as example.
4. What are the main types of gypsum binders? What properties do they have? Supply the chemical reactions that cause their hardening.
5. What is the raw material for Portland cement and how is it manufactured? What are the main methods of its manufacture?
6. What is glenosilicate cement? What is its raw material and how is it manufactured? Supply the chemical reactions.
7. What are the factors of concrete corrosion? What are the main types of corrosion in concrete? What are the methods for protecting concrete from corrosion?

List of recommended literature

1. Emelyanov B.M. Chemistry: textbook / B.M. Emelyanov, G.I. Berdov, O.O. Bondar, P.S. Shilyuk. – Kyiv: Phoenix, 2010. – 456 p. (in Ukrainian)
2. Chemystry 2e / P. Flowers, K. Theopold, R. Langley, S.F. Austin et al. – OpenStax College, 2015. https://openstax.org/details/books/chemistry-2e
3. Introductory Chemistry. LibreTexts / Open Education Resource (OER) LibreTexts Project – 2024. – 631 p. https://LibreTexts.org
4. Romanova N.V. General and inorganic chemistry. – Kyiv: "Perun", 2004. – 480 p.(in Ukrainian)
5. M. S. Slobodianyk General and inorganic chemistry: workshop / M. S. Slobodianyk, N. V. Ulko and others. – Kyiv: Lybid, 2004. – 336 p. (in Ukrainian)
6. Nedilko S.A. General and inorganic chemistry. Tasks and exercises / S.A. Nedilko, P.P. Popel. – Kyiv: Lybid, 2001. – 397p. (in Ukrainian)

Educational edition

Vira GRECHANYUK;
Artem KOZYREV;
Igor GRECHANYUK et al.

Chemistry

Tutorial

Комп'ютерна верстка *Т.І. Кукарєвої*

Підписано до друку 08.05.2024. Формат 60 × 84 1/16
Ум. друк. арк. 12,32. Обл.-вид. арк. 13,25.
Тираж 25 прим. Вид. № 16/І-24. Зам. № 29/1-24 .

Видавець і виготовлювач
Київський національний університет будівництва і архітектури

Проспект Повітряних Сил, 31, Київ, Україна, 03037

Свідоцтво про внесення до Державного реєстру суб'єктів
видавничої справи ДК № 808 від 13.02.2002 р.