Навчальне видання
Educational edition

A LABORATORY MANUAL Of Inorganic Chemistry For English-speaking students on speciality 211 – Veterinary medicine

ЛАБОРАТОРНИЙ ПРАКТИКУМ з неорганічної хімії для англомовних студентів зі спеціальності 211 – Ветеринарна медицина

Kyiv – 2019
Київ – 2019

УДК 546 (07)

Рекомендовано вченою радою агробіологічного факультету Національного університету біоресурсів і природокористування України
(протокол № 5 від 26 грудня 2019 р.)

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A Laboratory Manual of Inorganic Chemistry for English-speaking students on specialty 211 - Veterinary Medicine (Лабораторний практикум з неорганічної хімії для англомовних студентів зі спеціальності 211 – Ветеринарна медицина: Educational edition (Навчальне видання) / V. Kopilevich, L. Voitenko, V. Galimova, L. Abarbarchuk. Kyiv: NUBiP, 2019. – 161 pp.

Під редакцією професора Копілевича В.А.

За авторським редагуванням

У навчальному виданні коротко викладено основні теоретичні положення неорганічної хімії, необхідні для виконання лабораторного практикуму. Видання містить приклади тестів, завдання для самостійної роботи.

UDC 546 (07)
Recommended by the Scientific Council of Agrobiological faculty of National University of Life and Environmental Sciences of Ukraine
(Report # , . .2019).

The main theoretical notions of General Chemistry and description of lab training are expounded in manual. It includes test questions and tasks for students' self-control.

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INTRODUCTION

Inorganic chemistry is a fundamental subject, obligatory for teaching students received the specialties in the field of Veterinary Medicine of Universities of III-IV accreditation levels. This program was developed on the base of Educational Program of Subject “Inorganic chemistry” for “Veterinary Medicine” 211 Speciality (field “Veterinary Medicine”).

In modern society Chemistry is powerful source of productive powers. In particular, intensification of scientific and technological progress in agricultural and food production requires a rational use of chemical science achievement, intensification of ecological monitoring of economic activity.

So, the main aim of presented subject is the study of properties, preparation methods and use of chemical elements and their compounds, acquiring the skills for execution.

The main objectives of Inorganic chemistry are:

- Study the bases for subjects as the part of fundamental training for specialties in the field of Veterinary Medicine and Quality and Safety of Food Production;
- Creation of a scientific basis for study of professional-oriented and special subjects (Organic Chemistry, Biochemistry, Therapy etc.);
- Assimilation of general ideas of chemical experiments using semimicromethod.

In the result of Inorganic Chemistry study the student should:

To know: the classification of inorganic substances and ideas about genetic relationship between them; modern ideas on atomic structure and molecules; nature and characteristics of chemical bonds; general laws of chemical kinetics and chemical equilibrium; nature of solution formation and processes in solutions (electrolytic dissociation, hydrolysis); nature of processes with oxidation number changes; nature, structure, chemical properties of coordination (complex) compounds: structure of electronic shells, chemical properties, methods of preparation, distribution in the Environment, using in human life and, in particular, in agricultural production, bio-active chemical elements and their compounds; chemical models of biological processes; to receive the knowledge about classical and modern methods of chemical analyses, formation of skills of chemical analysis using the modeling objects, which will be increased on the real objects of Veterinary Medicine and Food Quality fields (plants, fertilizers, water, veterinary drags, foods etc.):

To know how to use the educational, methodical and reference literature sources in the field of bio-inorganic chemistry, to carry out calculations according to chemical reactions, to carry out chemical experiment by itself, to present results of experimental exercises in the form of protocol; to make calculations using the computers, to prepare equipment, dishes, reagents for analysis; to conduct qualitative and quantitative chemical analyses according to methodical rules; to carry out a mathematical processing of quantitative analyses, to estimate the inaccuracy of analysis; to present results of experimental exercises in the form of protocol.

According to Academic Curriculum of Specialist Training in Veterinary Medicine for this subject study**,** 3 modules are planned, including 60 hours of class time (15 – lectures, 45 – laboratory training), 15 hours of own training.

Control of knowledge and skills is realized in the form of defense of laboratory exercises in oral form, written control tests of theoretical knowledge and final written exam.

Teaching of subject is organized according to module-rating principle for more objective and ranked estimation of student's knowledge.

Per-Course for Inorganic Chemistry study:

Secondary school course of Chemistry.

The main tasks of “Inorganic Chemistry” subject on the assumption of its role in the system of interrupted training in the field of Veterinary Sciences are the following:

- study of subject foundations as the part of a fundamental training of specialists in the field of Veterinary Medicine;
- creation of theoretical and experimental foundations for a few professional-oriented and special subjects study;
- assimilation of the main practical skills for qualitative and quantitative analyses and mathematical calculation of their results;
- Awareness of a function of chemistry in the processes of agricultural production in the whole and in the field of Veterinary Medicine in particular.

In lectures the main attention is concentrated on study of the main laws, rules, principles, methods and terminology of Inorganic chemistry, which are further basis for training in professional-oriented and special subjects.

In general the laboratory experiments in Inorganic Chemistry course are directed to assimilation of skills for compelling of different types of chemical equations and methods of their realization. Herewith the problem situations, active forms of study are used including the system of intercoupling of related subjects and examples of everyday situations (chemistry for living).

The chapters for self-assimilation are of secondary importance, but they increase the outlook and erudition of future specialist.

Inorganic chemistry should be as pre-course for the following subjects and their chapters:

- **Organic Chemistry** – types of reactions; chemical bonds and theory of organic compounds’ structure;
- **Biochemistry** – molecules’ structure and chemical bond, ferments as nature catalysts, redox processes.
- **Therapy, Pharmacology and Toxicology** – properties of artificial drags composition and structure of biologically active and toxic compounds.

CHAPTER # 1. THE FOUNDATIONS OF ATOMIC-MOLECULAR STUDIES. THE LAWS AND CONCEPTS OF STOICHIOMETRY

Vocabulary

English	Українська назва	English	Українська назва
Artificial substances	*Штучні речовини*	*Equivalent*	*Еквівалент*
Drags	*Ліки*	*Relative atomic mass*	*Відносна атомна маса*
Pesticide	*Пестицид*	*Atomic mass unit (a.m.u.) or Carbonic unit*	*Відносна атомна одиниця маси або вуглецева одиниця*
Atom	*Атом*		
Mole	*Моль (кількість речовини)*		
Chemical element	*Хімічний елемент*		
Allotropy	*Алотропія*	*Relative molecular mass*	*Відносна молекулярна маса*
Valency (valence)	*Валентність*		
Electron shell	*Електронна оболонка*	*Relative atomic mass*	*Відносна атомна маса*
Phenomenon	*Явище*	*Avogadro's Number*	*Число Авогадро*
Molecule	*Молекула*	*SI*	*Міжнародна система одиниць вимірювання*
Indivisible participle	*Неподільна частинка*		

1.1 Subject and Tasks of Chemistry

Inorganic chemistry is one of the fundamental natural sciences. It takes part in the formation of man world view directly or indirectly that determinates him approach to Environment, understanding of its phenomena.

For the first time the determination of Chemistry as science was taken by M.V. Lomonosov: “Chemical science studies the properties and changes of bodies … bodies’ composition, explains the reasons of the chemical transformations of substances”. D.I. Mendeleev made original determination of chemistry: “Chemistry is a science about elements and these compounds”.

So, according to the modern ideas **Chemistry is a science about composition, structure, properties and transformations of natural and artificial substances and phenomena accompanied these transformations.**

Objects of chemical sciences are the Earth and its components, space bodies, water and solution, air and gases, plants, animals at al. Chemistry takes a central place among natural sciences and social production. It combines abstract physical and chemical ideas with biological and geological processes. Following chemical reactions causes biological changes.

Chemistry as science started from the 17th century when was used quantitative methods for studying of chemical reactions.

What place is take chemistry in Veterinary Medicine and Food Sciences? At first, the most of modern drags for veterinary needs are the artificial chemical substances. Now it is known more than 7 million organic and more than 100 000 inorganic substances, included 1500 pesticides, 4 000 drags, 38 000 potentially toxic substances and 50 000 commercial products or that which have a practical using. Secondly, medical diagnostics and treatment just as control of food quality and safety are based on results of analyses made chemical methods (gravimetry, volumetry et al).

The main notions of chemistry are:

- Atom;
- Molecule;
- Simple and complicated (complex) substances;
- Atomic and molecular mass;
- Mole and molecular volume;
- Valency of element and chemical equivalent.

According to advanced doctrines **atom** is a chemically indivisible participle of substance consisted from positive charged nucleus and negative changed electrons.

The main characteristics of atom are its weight (mass), size, composition, nucleus charge and structure of electronic shells.

Atomic mass changes from $1,67{\cdot}10^{-27}$ kg for Hydrogen H to $4,35{\cdot}10^{-25}$ kg for Kurchatovyi Ku; atomic nucleus consists from protons and neutrons, its radius are 10^{-14}-10^{-15} m.

Quantitative characteristics of atom are:

1) a nuclear charge (which is equal to number of chemical element in Periodical Table of Chemical Elements);
2) A relative atomic mass.

Chemical element is a kind of atom identical in nuclear charge.

Every element has own name and chemical symbol in Periodical Table of Chemical elements named D.I. Mendeleev. Chemical element saves without changes in chemical reactions crossing from one substance to other. Chemical elements are existing in the form of simple and complicated (complex) substances.

Simple substances are the substances form from the atom of one chemical element oft the form of existence of chemical element in the free state.

For example, Oxygen O_2, Hydrogen H_2, Silver Ag are the simple substances, while water H_2O, Silver Oxide Ag_2O are the complicated substances.

Now it is known 113-115 chemical elements with well-known properties and more than 500 simple substances. Why quantities of last one are more in some times that first one? Because there is a phenomenon of allotropy.

Allotropy is a possibility of chemical elements to exist in the form at least of two simple substances with different properties. This phenomenon is caused by two reasons:

1) Different number of atoms in molecule (for example Oxygen O_2 and Ozone O_3);
2) Formation of different crystalline forms (for example diamond, graphite and a few new artificial substances for Carbon C).

Molecule is a smallest participle of substance, which has its chemical properties. During chemical transformation molecules saves but during chemical reactions decomposed on atoms or groups of atoms forming new substances.

Relative atomic mass (A_r) of chemical element is named a physical value that equal to ratio of medium weight of element to 1/12 part of atomic weight of Carbon atom 12C. One-twelfth part of Carbon atomic weight ^{12}C is advanced off-system unit for atomic and molecular weights that named **atomic mass unit** (a.m.u.) or **Carbonic unit:**

1 a.m.u. = $(19{,}93 \cdot 10^{-27}$ kg$)$:12 = $1{,}66 \cdot 10^{-27}$ kg or $1{,}66 \cdot 10^{-24}$ g,

where $19{,}93 \cdot 10^{-27}$ kg – an absolute mass of Carbon atom ^{12}C. So calculating relative atomic masses it used next ratio:

$A_r = m_a$: 1 a.m.u. = m_a: $1{,}66 \cdot 10^{-27}$, where m_a- atomic mass in kg.

Relative molecular mass (M_r) is a physical value equal to ratio of medium isotope mass of molecule into 1/12 part of atomic mass of Carbon atom ^{12}C. Practically molecular mass is equal to sum of atomic masses of elements included to molecule.

1.2 Amount of substance. Mole. Avogadro’s Number. Molar mass

Three very important concepts - the mole, Avogadro’s number and molar mass - provide the basis for relating masses in grams to numbers of atoms. The first, the mole, is the SI unit for amount of substance. **The mole** is the amount of a substance that contains the same number of particles as the number of atoms in exactly 12 g of ^{12}C. The abbreviation for the mole is **mol**. The mole is a counting unit, like one dozen. In writing, a chemist might refer to 1 mol of Carbon, or 2 mol of Iron, or 2,567 mol of calcium. Amount of substance (in mol) is indicated as Greek letter υ.

The number of particles in a mole has been experimentally determinates in a number of ways. The best modern value is $6{,}022137 \cdot 10^{23}$ particles. This number is of such importance to chemistry that it is named in honor of the Italian scientist Amedeo Avogadro (1776-1856), whose ideas were crucial in the early understanding of chemistry. **Avogadro's number N_A**- $6{,}022137 \cdot 10^{23}$ - is the number of particles in exactly one mole of each pure substance. In most cases, Avogadro's number is rounded to $6{,}02 \cdot 10^{23}\ \frac{1}{mol}$ (or mol^{-1}).

Molar mass (M_m) is the mass in grams of one mole of pure substance (g/mol). Molar masses of elements contain equal numbers of atoms. One mole of a substance is one molar mass of this substance. An alternative definition of the mole is the amount of a substance that contains an Avogadro's number of particles of chemical units.

The molar mass is used as the conversion factor in chemical calculations. For a specific substance, a known number of grams can be converted into moles or a known number of moles can be converted into grams. Figure 1 shows the conversions of molar mass, moles, and Avogadro's number.

In general, mass of any chemical substance (in grams) is connected with amount of this substance by the next ratio:

$$\nu = \frac{m}{M_m}, \tag{1.1}$$

where ν - amount of any pure substance (mol or kmol);

m - mass of any pure substance (g or kg);

M_m - molar mass (g/mol or kg/kmol).

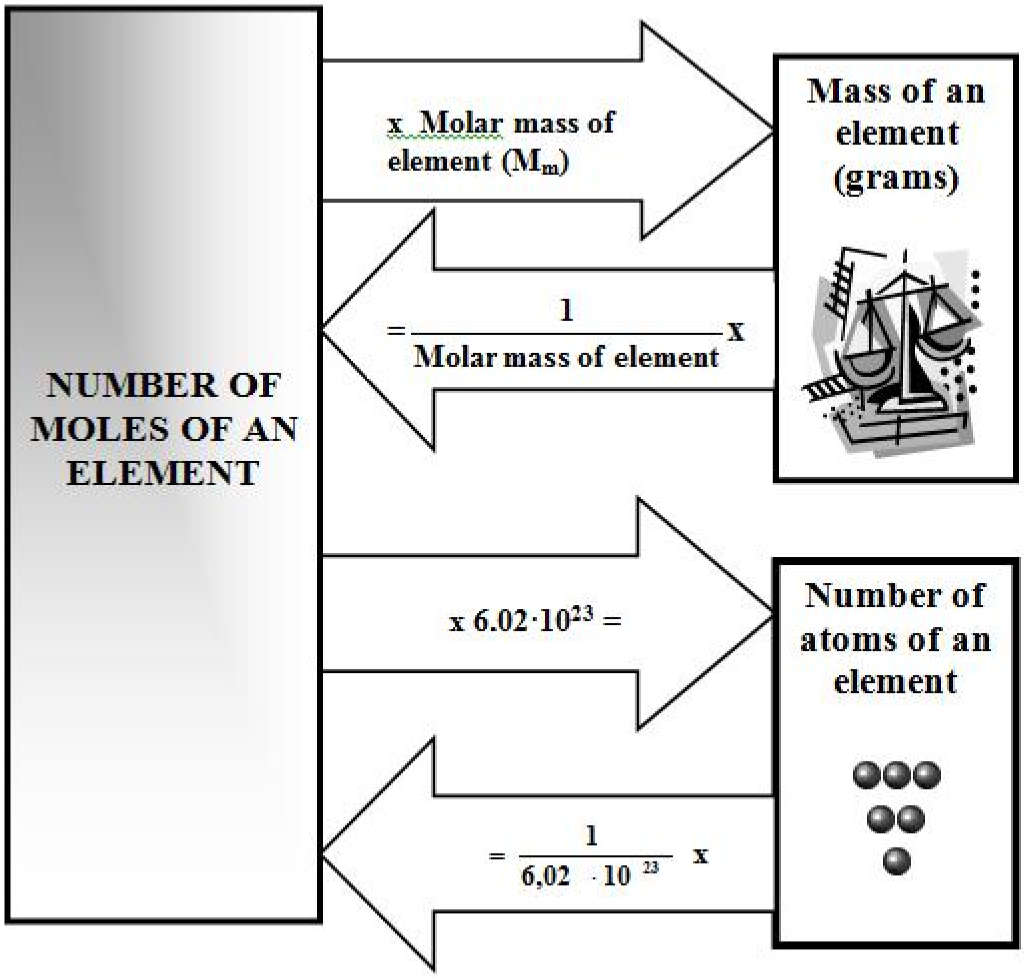


Figure 1.1. Relationships between mass, the number of moles, and the number of atoms of an element in the sample

EXAMPLES OF SOLUTION

1. To determine a relative molecular mass of Sodium Sulfate Na_2SO_4*.*

Relative molecular mass M_r is determined as sum of relative atomic masses A_r of elements in this compound:

$M_r(Na_2SO_4)=2Ar(Na)+A_r(S)+4A_r(O)=2\cdot23+32+4\cdot16=142$ c.u.

2. To determine molar mass of Calcium Nitrite $Ca(NO_3)_2$*.*

Molar mass of substance, expressed in grams, is numerically equal to relative molecular mass expressed in a.m.u. So, calculating relative molecular mass of $Ca(NO_3)_2$, we obtain:

$M_r(Ca(NO_3)_2)=A_r(Ca)+2A_r(N)+6A_r(O)=40+2\cdot14+6\cdot16=164$ c.u.

And molar mass of Calcium Nitrite is equal to 164 g/mol.

3. How many atoms and moles are contained in 60 g of Carbon ^{12}C*? Determine mass of one Carbon atom in grams.*

If mass of substance m and its molar mass M_m are known, we could determine the amount of substance (number of moles) in this mass:

M_m is equal to 1 mol;

m –“- x mol; and $\nu = x = \frac{m}{M_m}$.

Since m=60 g, M_m (C)=12 g/mol, then $\nu = x = \frac{60\,g}{12\,g/mol} = 5\,mol$.

Multiplying number of moles (5 moles) by Avogadro’s number N_A we determine the number of atoms in given mass of substance:

$N=\nu \cdot N_A=5 \cdot 6{,}02 \cdot 10^{23}=3{,}01 \cdot 10^{24}$ atoms.

Next step - to be divisible molar mass of Carbon M_m (C)=12 g/mol by Avogadro’s number N_A for calculation of mass of Carbon one atom in grams:

$$m(C) = \frac{M_m(C)}{N_A} = \frac{12\,g/mol}{6{,}02 \cdot 10^{23}\,1/mol} = 2{,}0 \cdot 10^{-23}\ g.$$

4. How many moles of Hydrobromide HBr are contained in 0,162 grams of this compound?

Determine a relative molecular mass of HBr:

$M_r(HBr)=A_r(H)+A_r(Br)=1+80=81$.

So, molar mass of HBr is equal to 81 g/mol. Calculate the number of moles in 0,162 g of HBr:

$$\upsilon = \frac{m}{M_m} = \frac{0{,}162g}{81g/mol} = 0{,}002\,mol.$$

5. For neutralization of acid it was used 6 moles of Calcium Hydroxide $Ca(OH)_2$. How many grams of $Ca(OH)_2$ are equal to such number of moles?

Calculate a molar mass of $Ca(OH)_2$:

$M_r(Ca(OH)_2)=40+2 \cdot 16+2 \cdot 1=74$ g/mol.

Mass of 6 moles: $m=\upsilon \cdot M_r$ =6 g·74 g/mol =444 g.

6. To calculate a mass part of Sodium in Sodium Sulfate Na_2SO_4.

Calculate a molar mass of Sodium Sulfate M_r (Na_2SO_4) = 142 g/mol. 1 mole of Sodium Sulfate contains 2 moles of Sodium atoms. Its mass is equal to: m =2 A_r (Na) = 2·23 = 46 g.

Mass part ω (Na) is the ratio of Sodium mass to total mass of substance:

$$\omega\ (\mathrm{Na}) = \frac{m\ (\mathrm{Na})}{m\ (\mathrm{Na_2SO_4})} = \frac{46\ \mathrm{g}}{142\ \mathrm{g}} = 0{,}324.$$

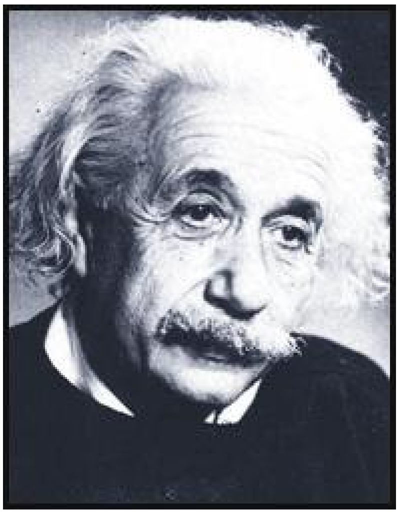
7. To determine a mass part of waterless salt in crystalline hydrate.

Molar mass of crystalline hydrate of blue vitriol $M_r(CuSO_4 \cdot 5H_2O)= M_r(CuSO_4)+5M_r(H_2O)=160+90=250$ g/mol? One mole of hydrate (250 g) contains 160 g of waterless salt. We calculate Mass part ω ($CuSO_4$) as ratio of Copper Sulfate mass to mass of hydrate:

$$\omega\ (\mathrm{CuSO_4}) = \frac{m(\mathrm{CuSO_4})}{m(\mathrm{CuSO_4 \cdot 5H_2O})} = \frac{160}{250} = 0{,}64\ (64\%).$$

1.3 The laws and concepts of Stoichiometry

Stoichiometry is the branch of chemistry dealing with mass relationships of elements in compounds and among reactants and products in chemical reactions. Accordingly, the calculations of the quantitative relationships between elements in compounds or between substances in chemical reactions are called ***stoichiometric calculations***. They are based on the laws of conservation of mass, of definite proportions, of multiple proportions, and also the gas laws - Gay-Lussac's law of combining volumes and the Avogadro’s law. The laws listed below are customarily considered to be the fundamental laws of stoichiometry.



A. Einstein (1879-1955)

In 1905, A. Einstein showed that the mass of a body (m) and its energy (E) are related as follows (**laws of conservation of mass**):

$$E = mc^2 \qquad (1.2)$$

where **c** is the speed of light in vacuum, **c** = $2.997925 \cdot 10^8$ ms^{-1} (or approximately 300000 $km \cdot s^{-1}$).

Energy is always liberated or absorbed in chemical reactions but very small masses that are impossible to measure correspond to the energies that are liberated or absorbed in it. This is why the mass defect in chemical reactions may be disregarded.

Situation differs in the case of nuclear reactions. Nuclear reactions involve changes in the nuclei of atoms whereas chemical reactions involve only the outermost electrons of atoms. Another significant difference between the two types of reactions is in the amount of energy liberated. Nuclear reactions involve energies a million times greater than those of chemical reactions. Due to this a significant amounts of matter are transformed into energy in a nuclear explosion or reaction.

The quantitative composition of many substances was studied from the end of the 18th century. This led to the establishment of **the law of definite proportions (**also called **the law of constant composition)** by a Frenchman, Joseph Proust, in 1797: ***The masses of the elements forming a given compound are always in a definite proportion that does not depend on how this compound was prepared.***

Many elements in combining with one another can form different substances each of which is characterized by a definite proportion of the masses of these elements. For instance, Nitrogen forms five compounds with Oxygen, **Table 1.1**. For example, one of them - Nitrogen monoxide - always contains 46,7% (mass) of Nitrogen and 53,3°/o (mass) of Oxygen. In studying such compounds, **J. Dalton** in 1803 established **the law of multiple proportions**: ***If two elements form several chemical compounds with each other, then the masses of one of the elements corresponding to the same mass of the other element in these compounds are in a simple integral proportion.***

Table 1.1. Mass ratio between elements in Nitrogen oxides

Oxide	Composition, % (mass)		Mass ratio of Oxygen on one part of Nitrogen	Ratio between quantity of Oxygen
	Nitrogen	**Oxygen**		
N_2O	63,7	36,3	1: 0,57	1
NO	46,7	53,3	1: 1,14	2
N_2O_3	36,9	63,1	1: 1,71	3
NO_2	30,5	69,5	1: 2,28	4
N_2O_5	25,9	74,1	1: 2,86	5

The laws of definite proportions and multiple proportions follow from the atomic and molecular concepts. Substances having a molecular structure consist of identical molecules. When several compounds are formed from two elements, the atoms of these elements combine with one another into molecules of a different, but definite composition, see **Table 1.1.**

Unlike the law of conservation of mass, whose correctness was completely confirmed by the discoveries made after its establishment, the laws of definite proportions and multiple proportions were found to be not so universal. In connection with the discovery of isotopes, it was found that the ratio of the masses of the elements forming a given substance is constant only provided that the isotopic composition of these elements is constant. A change in the isotopic composition of an element is attended by a change in the mass composition of the compound.

The laws of definite proportions (the law of constant composition) and multiple proportions were found to be not realizing also for **the compounds of varying composition (berthollides,** named in honor of understanding French chemist Claude Louis Bertollet). In these compounds, for each unit of mass of a given element there may be a varying mass of another element. For example, in a compound formed by Bismuth with Thallium (metal alloy), there may be from 1,24 to 1,82 units of mass of Bismuth per unit of mass of Thallium ($TlBi_{1,24-1,82}$). Compounds of varying composition are encountered also among other solids, for example oxides ($UO_{2,5-3,0}$, $FeO_{0,85-0,95}$), compounds of metals with Sulfur, Nitrogen, Carbon and Hydrogen ($TiH_{0,88-1,00}$).

Compounds of varying composition have an atomic structure instead of a molecular one, the formula only reflect the limits of the composition of the relevant substance. For many compounds of varying composition, the limits within which their composition may change have been found.

So, a conclusion can be made that compounds with molecular structure always have constant composition, otherwise the composition of compounds may change in some range (homogeneity area) that depend on conditions of its obtaining.

It follows from the law of definite proportions that elements combine with one another in strictly definite quantitative proportions. This is why the concepts of equivalent and equivalent mass were introduced in chemistry. At present an **equivalent of an element** is defined to be an amount of it such that combines with one mole of Hydrogen atoms or replaces the same number of Hydrogen atoms in chemical reactions.

For example, in the compounds HC1, H_2S, NH_3, and CH_4, the equivalents of Chlorine, Sulfur, Nitrogen, and Carbon are 1, 1/2, 1/3, and 1/4 mole, respectively. **The mass of one equivalent of an element is called its equivalent mass.**

For instance, in the above examples, the equivalent masses of Chlorine, Sulfur, Nitrogen, and Carbon are respectively 34,45, 32/2 = 16, 14/3 = 4,67, and 12/4 = 3 g/mol.

To determine the equivalent (or equivalent mass) of an element, we do not necessarily have to proceed from its compound with Hydrogen. The equivalent (equivalent mass) can be calculated using the composition of a compound of the given element with any other one whose equivalent (equivalent mass) is known. In addition to the concept of equivalent mass, it is sometimes convenient to use the concept of **equivalent volume**, i.e. the volume occupied in given conditions by one equivalent of the substance being considered. For example, in standard conditions, the equivalent volume of Hydrogen is 11,2, and that of Oxygen is 5,6 liters per mole. The concept of equivalents and equivalent masses also extends to compounds.

The equivalent of a compound substance is defined to be an amount of it such that reacts without any residue with one equivalent of Hydrogen or in general with one equivalent of any other substance.

The introduction of the concept "equivalent" into chemistry made it possible to formulate a law known as **the law of equivalents**: ***The masses (volumes) of substances reacting with one another are proportional to their equivalent masses (volumes):***

$$\frac{m_1}{m_2} = \frac{E_1}{E_2} \qquad (1.3)$$

The equivalent of a simple substance and the equivalent of an element (X) in compound (X_nY_m) are calculated as follows:

$$E_x = A_x / v_x \qquad (1.4)$$

The equivalent of a compound (X_nY_m) is calculated as follows:

$$E_{XnYm} = M_x / n_x v_x = E_X + E_Y \qquad (1.5)$$

A - atomic mass of element X,
M - molecular mass,
v - valency of atom X,
n - number of atom X in X_nY_m molecule.

1.4 Types of the chemical reactions

Chemical reactions are processes by which atoms or molecules are redistributed, resulting in different substances with unique properties. Chemical reactions are classified into different categories according to the mechanics of the reactions. The original elements or compounds involved in a chemical reaction are called reactants, and the chemicals that result are called products. Classification of types is presented in **Table 1.2.**

Table 1.2. Types of chemical reactions

Type	Scheme	Example
Synthesis (combination, construction, composition) reactions	X + Y = Z, where X, Y are elements or compounds; Z - new compound	$2\ H_2 + O_2 = 2H_2O$; $H_2O + SO_3 = H_2SO_4$; $K_2O + CO_2 = K_2CO_3$
Decomposition (desythesis, decomposition, deconstruction) reactions	XZ = X + Z	$2\ KClO_3 \xrightarrow{t} 3\ O_2\uparrow + 2\ KCl$; $6NaHCO_3 \xrightarrow{t} 3\ Na_2CO_3 + 3\ CO_2\uparrow + 3H_2O$; $2\ AgI \xrightarrow{t} 2\ Ag + I_2$
Single replacement (single displacement, single substitution, activity replacement) reactions	A + BX = B + AX	$2\ Mg + TiCl_4 \xrightarrow{t} Ti + 2\ MgCl_2$; $2\ Al + 6\ CaO \xrightarrow{t} Ca_3(AlO_3)_2 + 3\ Ca$;
Double replacement (double displacement or metathesis) reactions	AB + CD = AD + CB	$AgNO_3 + KCl = AgCl\downarrow + KNO_3$; $TiCl_4 + H_2O = 4\ HCl\uparrow + TiO_2\downarrow$; $HCl + NaOH = NaCl + H_2O$
Oxidation-reduction reactions (Red-Ox)	$A^z + n\ \bar{e} \rightarrow A^{(z-n)}$ $B^y - m\ \bar{e} \rightarrow B^{(y+m)}$	$2Na + S \rightarrow Na_2S$; $2\ KMnO_4 \xrightarrow{t} K_2MnO_4 + MnO_2 + O_2$
Acid-Base reactions (neutralization)	$H^+ + OH^- \rightarrow H_2O$ (in net ionic form)	$H_2SO_4 + 2\ NaOH = Na_2SO_4 + 2H_2O$

PRACTICE PROBLEMS

1. To determine relative molecular mass and molar mass of Potassium Orthophosphate K_3PO_4.

2. How many atoms and moles of atoms are contained in 64 g of Oxygen ^{16}O? To calculate a mass of one atom of Oxygen in grams.

3. How many moles of H_2SO_4 are contained in 4,9 grams of this substance?

4. How many moles of Sulfuric acid is it possible to prepare from 6,4 kg of Sulfur?

5. How many moles of slack lime $Ca(OH)_2$ is it possible to prepare from 0,1 g of chalk $CaCO_3$ if chalk completely changed into slack lime?

6. To calculate mass (in g) of molecules of Chlorine Cl_2, Carbonic gas CO_2, ammonia gas NH_3.

7. How many grams of Barium Sulfate $BaSO_4$ may be prepared from 6,1 g of salt $BaCl_2 \cdot 2H_2O$? To calculate the mass of Sulfuric acid used in this reaction.

8. Solution, contained 12,6 g of Nitric acid HNO_3, was mixed with 7,2 g of Caustic soda NaOH. What substance will be rest in surplus and in which quantity?

CHAPTER # 2. ATOMIC STRUCTURE

Vocabulary

English	Українська назва	English	Українська назва
Nucleus	*Ядро*	*Spin*	*Спін (електрону)*
Proton	*Протон*	*Unpaired (paired) electrons*	*Неспарені (спарені) електрони*
Neutron	*Нейтрон*		
Quantum of energy	*Квант енергії*	*Ground state*	*Стаціонарний (незбуджений) стан атому*
Oxidation number	*Ступінь окислення*		
Orbit	*Орбіта*	*Excited state*	*Збуджений стан*
Quantum figure	*Квантове число*		

2.1 General concepts

Atom is an electroneutral particle consisted of positive charged nucleus and negative charged electrons. Nucleus is a positive charged component of atom concentrated practically all its mass. Components of nucleus are s (*p*) and s (*n*). Sum of protons and neutrons is equal to relative atomic mass (A_r):

$$A_r = \sum p^+ + n^0$$

Nucleus charge of atom is equal to number of element in Periodical Table (Z):

Example: To consider structure of atom *Na:*

Z (*Na*) = 11

$A_r(Na) = 23$ $\quad {}^{23}_{11}Na$

Positive charge of atomic nucleus – 11

Number of electrons - 11

In nucleus: p^+-*11*

n^0-*12 (* $A_r - p^+$*)*

2.2 Evolutions of atomic concepts

> **Atomic theory is a scientific description of the nature of atoms. It combines elements of physics, chemistry, and mathematics. The theory has evolved over time, from the philosophy of atomism to modern quantum mechanics.**

The theory of atomic structure of the Universe started as a philosophical idea in ancient times in Greece and India. The word atom has origin from the Ancient Greek word *atomos*, means "indivisible".

According to atomism concept, matter consisted of the small discrete units. However, the theory was one of much explanation for matter and was not based on empirical data. In the V century, Democritus proposed matter consisted of indestructible, indivisible units called atoms. The Roman poet Lucretius recorded the idea, so it survived through the Dark Ages for later consideration.

Historically the scientific development of ideas about atomic structure passed some stages (Fig. 2.1).

Dalton's Atomic Theory. Up to the 18th century, there was no experimental evidence for the existence of atoms. No one knew how finely matter could be divided. Antoine Lavoisier formulated the law of conservation of mass in 1789 (see Chapter 1, p. 49), which states the mass of the products of a reaction is the same as the mass of reactants. Joseph Louis Proust proposed the law of definite proportions in 1799**.** These theories did not reference atoms, yet John Dalton built upon them to develop the law of multiple proportions, which states the ratio of masses of elements in a compound are small whole numbers. Dalton's law of multiple proportions drew from experimental data. He proposed each chemical element consists of a single type of atoms that could not be destroyed by any chemical means. His oral presentation (1803) and publication (1805) marked the beginning of the scientific atomic theory (Fig. 2.1). In 1811, A**.** Avogadro corrected a problem with Dalton's theory when he proposed equal volumes of gases at STP contain the same number of particles. Avogadro's law made it possible to accurately estimate the atomic masses of element and made clear there was a distinction between atoms and molecules.

Another significant contribution to atomic theory was made in 1827 by botanist Robert Brown, who noticed dust particles floating in water seemed to move randomly for no known reason. In 1905, Albert Einstein postulated the Brownian motion was due to the movement of water molecules. The model and its validation in 1908 by Jean Perrin supported atomic theory and particle theory.

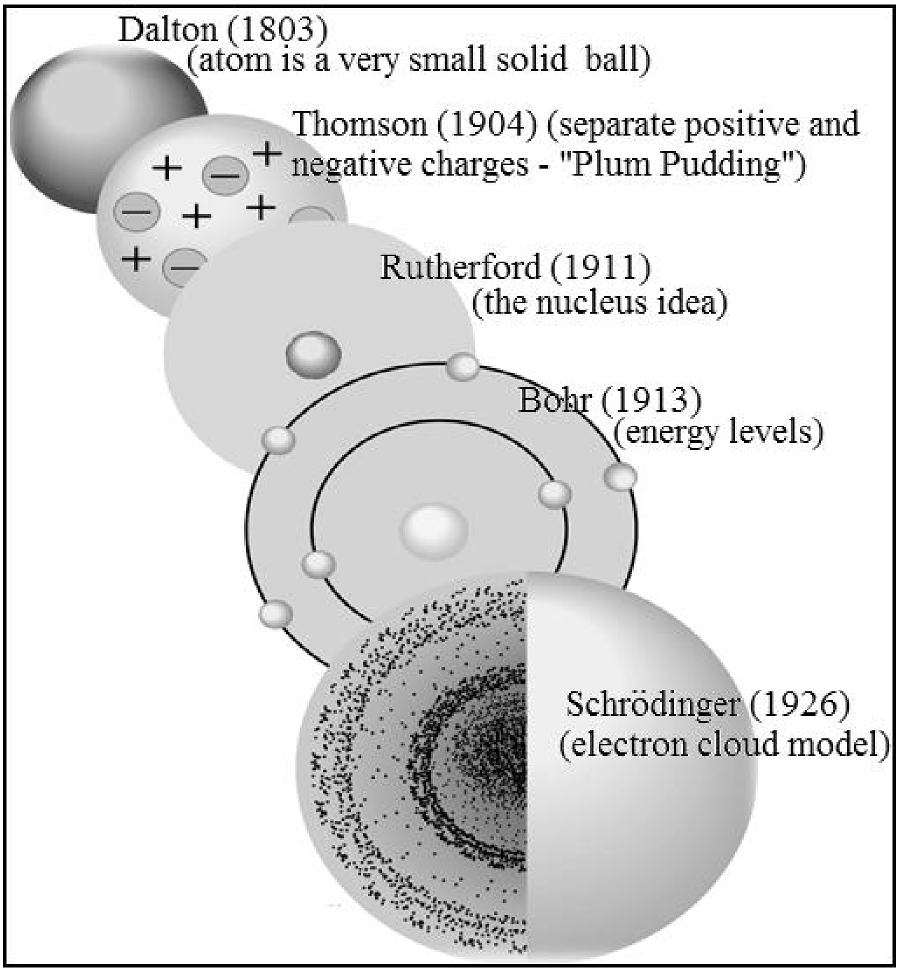


Figure 2.1. Evolution of atomic structure ideas

Plum Pudding Model and Rutherford Model. Rutherford proposed a planetary model of atoms, with electrons orbiting a nucleus like planets orbiting a star. Up to this point, atoms were believed to be the smallest units of matter. In 1897, J.J. Thomson discovered the electron. He believed atoms could be divided. Because the electron carried a negative charge, he proposed a plum pudding model of the atom, in which electrons were embedded in a mass of positive charge to yield an electrically neutral atom.

Ernest Rutherford, one of Thomson's students, disproved the plum pudding model in 1909. Rutherford found the positive charge of an atom and most of its mass was at the center or nucleus of an atom. He described a planetary model in which electrons orbited a small positive-charged nucleus.

Bohr Model of the Atom. According to the Bohr model, electrons orbit the nucleus at discrete energy levels. Rutherford was on the right track, but his model could not explain the emission and absorption spectra of atoms nor why the electrons didn't crash into the nucleus. In 1913, Niels Bohr proposed the Bohr model, which states electrons only orbit the nucleus. But this idea mismatched to the concepts of classic electrodynamics (Maxwell's theory). In accordance with one, moving electron must loss energy uninterruptedly and finally fall on nucleus. But in reality atoms and Universe exists without serious problems. Energy can radiates or absorbs when electron jumps from one orbit to another by separated portion - quantum of energy. But it turned out, that Bore's theory is valid absolutely only for atom of Hydrogen. The cause of this is in mechanistic approach to the nature of electron. Electron according to Bore's theory is like a very small ball. But further development of natural science in particular Einstein's research shows that micro-world has other laws than macro-world.

Quantum Atomic Theory. According to modern atomic theory, an electron could be anywhere in an atom, but it's most probable it is in an energy level. Bohr's model explained the spectral lines of hydrogen, but didn't extend to the behavior of atoms with multiple electrons. Several discoveries expanded the understanding of atoms. In 1913, Frederick Soddy described isotopes, which were forms of an atom of one element that contained different numbers of neutrons. Neutrons were discovered in 1932.

Louis de Broglie proposed a wave-like behavior of moving particles, which Erwin Schrodinger described using Schrodinger's equation (1926). This, in turn, led to the Heisenberg uncertainty principle (1927), which states it's not possible to simultaneously know both the position and momentum of an electron.

Quantum mechanics led to an atomic theory in which atoms consist of smaller particles. The electron can potentially be found anywhere in the atom, but is found with greatest probability in an atomic orbital or energy level. Rather than the circular orbits of Rutherford's model, modern atomic theory describes *orbitals* that may be spherical, dumb bell shaped, etc. For atoms with a high number of electrons, relativistic effects come into play, since the particles are moving speeds that are a fraction of the speed of light.

Electronic orbital is the part of space where the probability of electron being is 90% or where electron spends 90% of time. Schematically electronic orbital can be described by Fig. 2.2.

Modern scientists have found smaller particles that make up the protons, neutrons, electrons, although the atom remains the smallest unit of matter that cannot be divided using any chemical means.

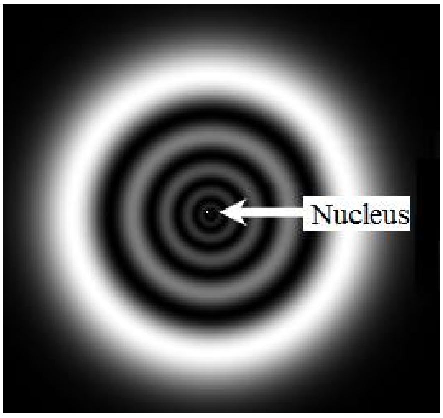


Figure 2.2. Cross-section of computed hydrogen atom orbital

Motion of electrons around nucleus is described by energy and structure of atomic orbital. State of electron is described by values of 4 quantum figures (Tables 2.1, 2.2).

Table 2.1. Names and physical content of quantum figures

Names	Symbol	What's determined?	Possible values
Main (Principal)	N, n	Orbital energy (main energy level)	Algebraic integers from 0 to ∞ (infinity)
Secondary (Azimuthal)	L	Orbital form (energy sub-level)	Algebraic integers from 0 to n-1
Magnetic	m_l	Spatial orientation of orbital	From $-l$ *to* $+l$ ($m_l=2l+1$)
Spin	m_s	Own magnetic moment of electrons	+ ½ and - ½

Table 2.2. Schematic description of atomic orbital

l		m_l	Quantity of orbitals	Schematic imagination
0	s	0	1	☐
1	p	-1 0 +1	3	☐☐☐
2	d	-2 –1 0 +1 +2	5	☐☐☐☐☐
3	f	-3 –2 –1 0 +1 +2 +3	7	☐☐☐☐☐☐☐

Example: To show a p-orbital:

l=1, m_l= -1; 0; +1;

p-orbital has 3 variants of space orientation (Fig. 2.3):

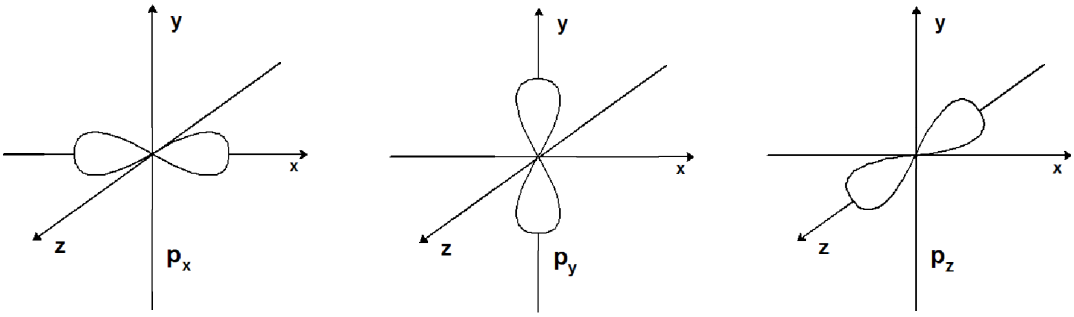


Figure 2.3. Spatial orientation of p-orbitals

2.3 Principles for distribution of electrons in atoms

Distributions of electrons in atoms on energy levels and sub-levels may be presented in the form of electronic formulas.

It may be compelled in the following way:

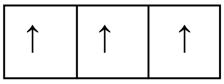
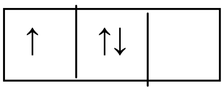
- Note Arabian figure, which indicates the main quantum figure (energy level);
- Note symbol of orbital, that determined electronic sub-level;
- Quantity of electrons on this sub-level is made by Arabian figure above it in the right upper corner.

Example: To show electronic formula of Nitrogen: $_7N$ $1s^2\,2s^2\,2p^3$. Atom of Nitrogen has 7 electrons, 2 - on the first level on *s*-sub-level, and 5 others – on the second level, *s* and *p*-sub-levels.

Principles, according to which the electrons are distributed in atoms, are shown in the Table 2.3.

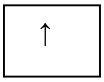
Table 2.3. General rules for electronic formulas compilation

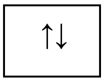
Name	Formulation	Using
Principle of energy minimum	Minimum of energy responds to the most stable state of electrons in atom	Electron occupies an atomic orbital with minimum energy
Pauli's Principle	Atom may not have two electrons with the same values of all four quantum figures	$N=2n^2$ (quantity of $\bar{e}$ on the level) Max quantity of $\bar{e}$ on the sub-level is equal to $2{\cdot}(2l+1)$ s=2; p=6; d=10; f=14
Rule of Klech-kowsky	Energy sub-levels are filled up according increasing of sum $n+l$	Indicate an order of sub-levels occupation

Rule of Hound	Summary spin value of electrons on sub-level must be maximum	Indicate an order of occupation of equal atomic orbitals:  Correctly  Incorrectly

In addition to electron formulas graphic pictures of electrons distributions in atoms is widely used. Orbitals are represented by rectangle

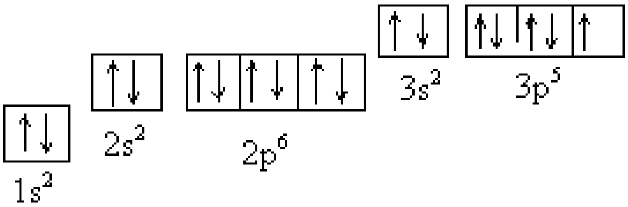
where may be unpaired electrons or paired electrons with antiparallel spins:



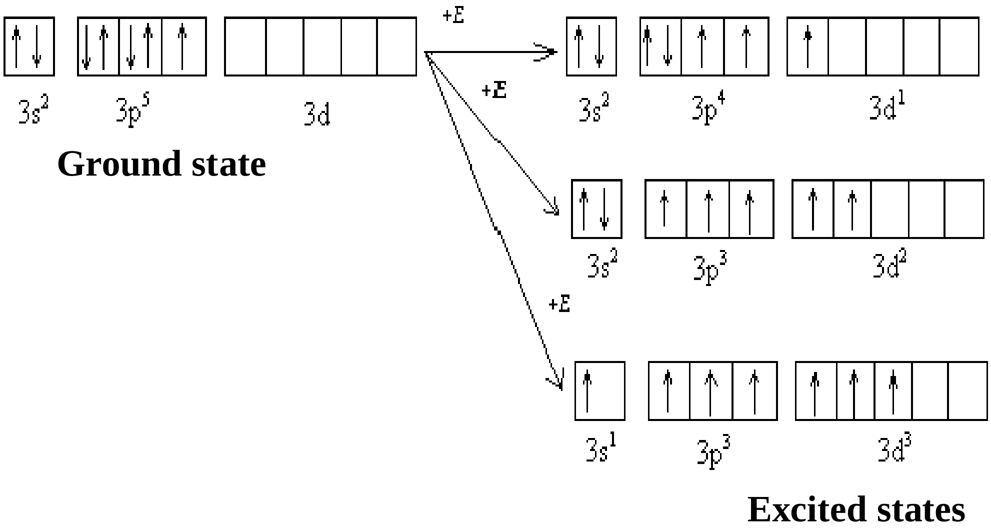


For each atom different quantity of electrons states, notable for energy, is possible. The most stable state of electrons in atom corresponds to minimum possible value of its energy. Such state is named as normal (ground) one. All other states are named as excited ones. Atoms may pass on to excited state if they have free orbitals and take energy from the outside. At the same time electrons may be separated.

Example. $_{17}Cl$ $\mathbf{1s^22s^22p^63s^23p^5}$



Electrons located on the last, third level, may go into free *d*-sublevel when atom was excited.



2.4 Valency and Oxidation numbers as function of electrons distribution

Using electron formulas, possible values of valency and oxidation numbers for chemical elements may be predicted.

In general case valency is equal to the quantity of unpaired electrons on the last (for s- and p-elements) and next to last (for d-elements) sub-levels.

According to this idea valency of Chlorine may be equal to **I** (normal state), **III** (the first excited state), **V** (the second excited state) and **VII** (the last, third excited state).

For estimation of oxidation number the theory of “**octet configuration”** must be used. It says that all atoms pressing towards to obtain the same configuration of the last electron shell are similar to noble (indifferent) gases. Why? Because the noble gases are the most stable chemical elements and they have 8 (excluding He) electrons on the last electron shell (ns^2np^6). Chemical elements may form configuration like noble gases giving up unpaired electrons to other atoms or joining them from other atoms. If after such operation atom has structure of last or next to last electron shell absolutely like noble gas it will be stable. If its configuration is not “ideal”, we may predict that such one is not stable and of course compounds included these atoms.

According to this theory, we may predict that in the first (normal) state atom of Chlorine may have three figures of oxidation number: -1 (when it joined one unpaired electron from any other atom); 0 (without interchange of electrons with other atoms) and +1 (when it lost one electron). Only the first figure of oxidation number will respond to an octet configuration of the last electron shell ($3s^23p^6$) and Cl^{-1} is a stable oxidation number for this chemical elements. Truly in nature this element exists only in the form of Chlorides where Chlorine has oxidation number –1.

Let's consider the first excited state of Chlorine atom. We see, that there are 3 unpaired electrons on the last electron shell. What can be said about possible degree of oxidation? The first possibility is to join 3 electrons from other atom and to have oxidation number –3. This state in not stable, because atom has not octet configuration. If it lost 3 elections, its configuration is more stable, because atom has two pairs of electrons.

Analogously it may be shown that oxidation numbers of Chlorine in the second and third excited states will be equal to +5 and +7. Oxidation number +5 is more stable than +1 and +3, but the most stable compounds respond to oxidation number +7.

Note, that valency and oxidation number are the different notions. Oxidation is the virtual figure, mathematical value. For example, in molecules H_2 and O_2 oxidation numbers are equal to 0, but valency is equal to 1 and 2 correspondingly.

PRACTICE PROBLEMS

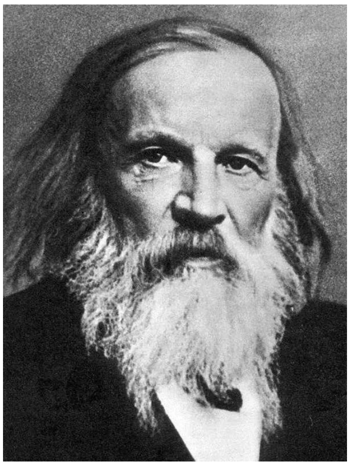
1. What does "dualism of electron nature" main?
2. What is spin and which values it may to have?
3. What's geometrical form of s, p and d-orbital?
4. To record an electron formulas of Potassium, Oxygen, Manganese.
5. How many valency electrons include atoms of elements № 12, 20, 32?

CHAPTER # 3. THE PERIODIC LAW AND PERIODIC TABLE OF CHEMICAL ELEMENTS

Vocabulary

English	Українська назва	English	Українська назва
Periodicity	*Періодичність*	*Lanthanide Series*	*Лантаноїди*
Small period	*Малий період*	*Actinide Series*	*Актиноїди*
Great period	*Великий період*	*Metal*	*Метал*
s-block	*Родина s-елементів*	*Non-metal*	*Неметал*
p-block	*Родина p-елементів*	*Noble gas, rare gas*	*Благородний газ*
d-block	*Родина d-елементів*	*Row (paired, unpaired)*	*Ряд (парний, непарий)*

3.1. Definition



D.I. Mendeleev (1834-1907)

Mendeleev’s principle of chemical periodicity is known as the periodic law: “The physical and chemical properties of the elements are periodic function of their atomic mass”.

Modern formulation:

“The properties of chemical elements, as well as the forms and properties of the compounds of the elements are periodic function of the nuclear charge of atoms of the chemical elements”.

3.2. Physical meaning of the chemical periodicity

Periodic changes of chemical properties of elements are stipulated by the correct repetition of electron configuration of external energy level (valency electrons) their atoms with nuclear charge increasing. Graphic inventing of a Periodic law is a periodic Table (see below). It is kept 7 periods and 8 groups.

Period is a horizontal row of elements in the Periodic Table with similar maximum value of the main quantum number of electrons. Period number indicates the number of energy levels in the atom of element.

Period can consist of 2 (first), 8 (second and third), 18 (fourth and fifth) or 32 (sixth) electrons, depending on the amounts of electrons on the external energy level. Seventh period is not completed.

All periods (except the first) are begun with alkaline metal (s-element), but are finished by noble gas (ns^2np^6).

Metallic properties are considered as an ability of atoms of elements to loss electrons easily, but non-metallic – to accept electrons. Filling of external *s*-sublevel is pointed out to metallic properties of atom, but shaping an external *p*-sublevel (from 5) intensifies non-metallic properties of atom. Atoms with completely formed, energy firm configuration of the external electronic layer (ns^2np^6) are chemically inert.

At great periods change of the properties from the active metal to the noble gas occurs more smoothly, than at small periods, since a shaping an internal (n-1) *d*-sublevel occurs at the conservation external ns^2-layer. Great periods consist of even and odd rows.

At even row of elements on the external layer ns^2- electrons, such metallic properties are dominated and their weakening with the growing of nuclear charge is not great; in odd rows the *np*-sublevel is formed, that explains a significant weakening of metal properties.

Groups – vertical rows of elements with similar valency number electrons, which is equal to group number. Main and secondary sub-groups are distinguished.

Main sub-groups consist of elements of great periods; valency electrons are placed on the external *ns*- and *np*-sublevels.

Secondary groups consist of elements of great periods only. Their valency electrons are on the external ns-sublevel and internal (n-1) *d*-sublevel (or (n-2) *f*-sub-level).

Depending on the sub-level, which is filled by valency electrons, the periodic system of elements is subdivided into:

s-block (elements of main sub-group of I and II groups);

p-block (elements of sub-groups of III-IV groups);

d-block (elements of secondary sub-groups);

f-block (lanthanides and actinides).

In the main subgroups from top to bottom the metallic properties are intensified, but non-metallic is weakened.

The number of the group shows the highest valency of element (except N, O, and F, elements of Copper sub-group and eighth group).

Formulas of the highest oxides are general for elements of main and secondary sub-groups (and their hydrates). At the highest oxides and hydrates – elements of I-III groups (except boron) the basic properties are dominated, but from IV till VII – acid (Table 3.1).

Table 3.1. General trends in periodicity

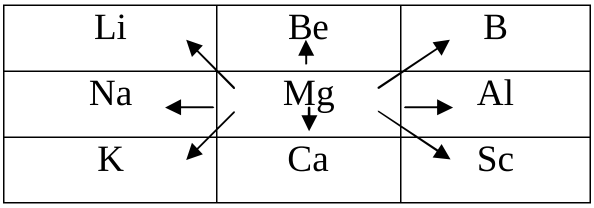
Group	I	II	III	IV	V	VI	VII	VIII (except noble gases)
Highest oxide	E_2O	EO	E_2O_3	EO_2	E_2O_5	EO_3	E_2O_7	EO_4
Hydrate of highest oxide	EOH	$E(OH)_2$	$E(OH)_3$	H_2EO_3	H_3EO_4	H_2EO_4	HEO_4	H_4EO_4

For the elements of main sub-groups formulas of Hydrogen compounds are general. Elements of main sub-groups of I-III groups form hard substances – hydrides (Hydrogen has oxidation number –1), but IV-VII – gaseous. Hydrogen compounds of main sub-group of IV group (EH_4) are neutral, V group (EH_3) – base and VII groups (H_2E and HE) – acids.

The properties of atom depend on the position of elements in the Periodic System, which is connected with structure of atoms.

Many characteristics of atoms are changed periodically, for example – electronegativity at the period is increased from left to right, but in sub-group is decreased; ionization energy – at the period increased, but in sub-group is decreased.

According to the position of element in the Periodic system it is possible to forecast its basic properties, as average of its neighbors:



3.3. The Periodic Table

The Periodic Table is an arrangement of the elements according to their atomic numbers so that elements with similar properties fall in the same column.

The length of each period in the Periodic table determinates by the sublevel being filled with electrons as shown in table 3.2. The first energy level holds only two electrons in its *1s* sublevel. Hydrogen and Helium are presented in the first period. The second main-energy level holds two electrons in *2s*-sublevel and six electrons in *2p*-sublevel. These eight electrons account for the eight elements presence in the second period. In eight elements of the third period, *3s*- and *3p*-sublevels are being filled.

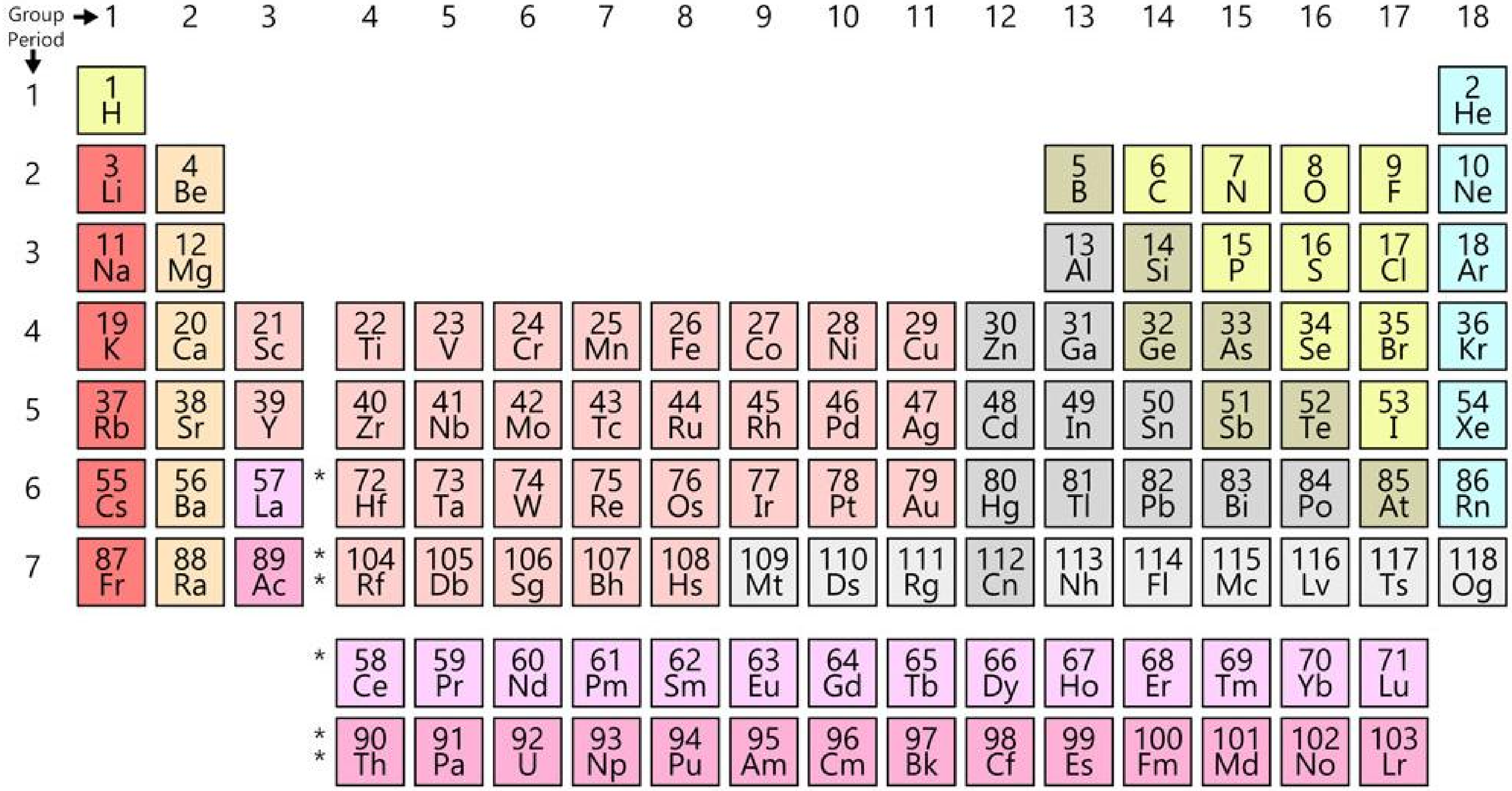
Table 3.2. Relationship between quantity of elements in period and sublevels being filled in the Periodic Table

Period Number	Number of Elements in Period	Energy Sublevels in Order of Filling
1	2	*1s*
2	8	*2s 2p*
3	8	*3s 3p*
4	18	*4s 3d 4p*
5	18	*5s 4d 5p*
6	32	*6s 4f 5d 6p*
7	23 (to date)	*7s 5f 6d* etc.

Filling *3d* and *4d*-sublevels in addition to *s* and *p* sublevels adds 10 elements to fourth and fifth periods, which therefore include totally 18 elements each. Filling *4f* sublevels in addition to *s*, *p*, *d* sublevels adds 14 elements to the sixth period, for totally of 32 elements in the sixth period. As new artificial elements are created, the 23 known elements in period 7 could be extended to 32.

The period of element can be determined from its electron configuration. For example, Arsenic (As) has the configuration [Ar]$3d^{10}4s^{2}4p^{3}$. The “4” in “$4p^3$” indicates that the highest one occupied energy level is the fourth energy level. Arsenic is therefore in the fourth period in the Periodic Table.

There are a lot of styles for presentation of Periodical Table of Chemical Elements (authors Stowe, Benfey, Zmaczynski, Gicuere - more details *http:/chemlab.pc.maricopa.edu/periodic/styles.html*). In Ukraine the most popular one is so-called “Short-Periodic” form, presented in **Appendix 1.** The Modern style of so-called “Long-Periodic” table is presented in Fig. 3.3.



Group → Period ↓	1	2	3		4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc		22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y		40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
				*	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
				**	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

Figure 3.3. “Long-Periodic” style of Periodic table

A science exhibit designer, Roy Alexander, to eliminate the confusion and apparent inconsistencies in the flat table by arranging the elements contiguously and continuously according to the atomic number without disturbing the accepted group, originated the improvement for learning and using the Periodic Table and property interrelationships previously found in the periodic chart (see Fig. 3.4).

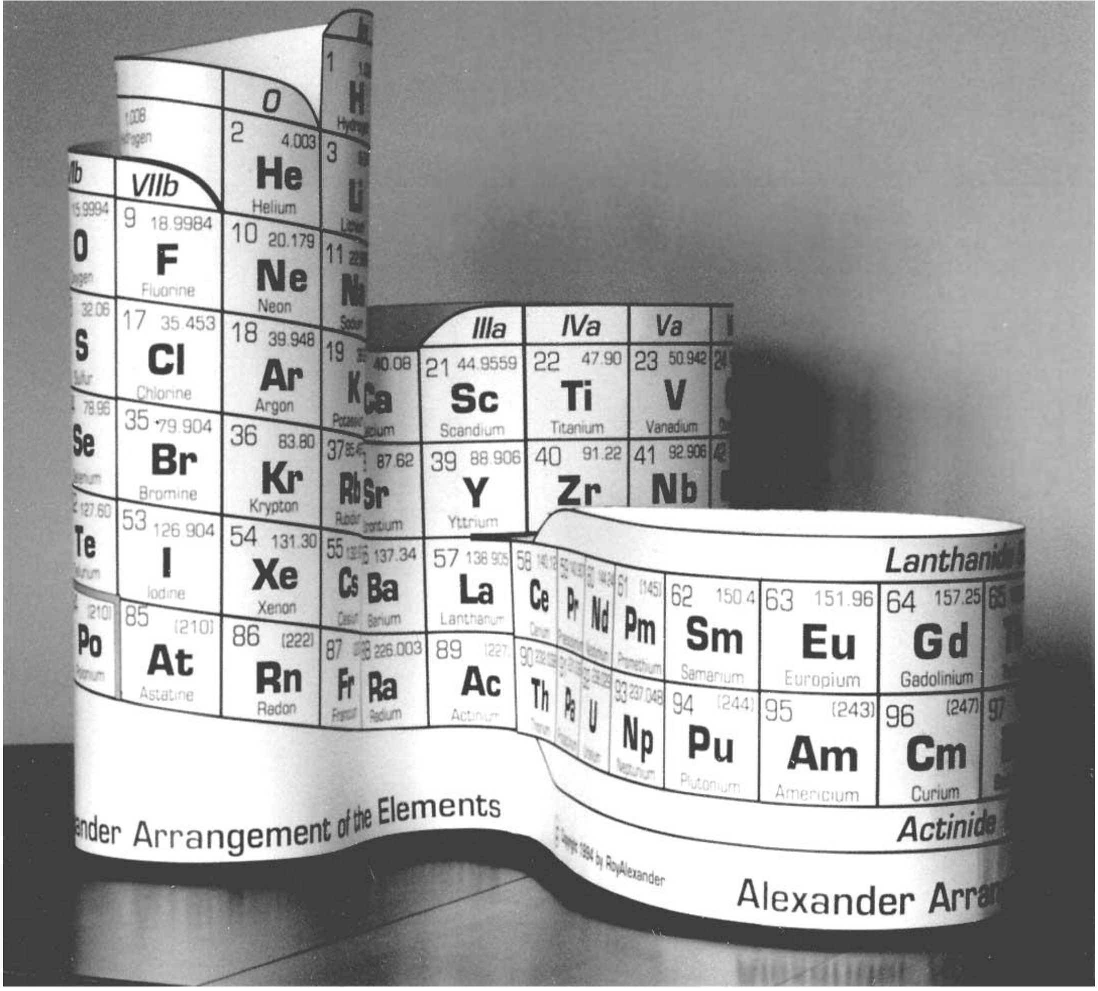


Figure 3.4. Roy Alexander Arrangement of the Elements

The resulting form has three parts looping outwards from a relatively central point. The elements in Groups 0 (VIII), Ia, IIa, IIIb, IVb, Vb, and VIIIb are in the narrowest and tallest part, which forms a tube in the upper part, topped by a “crown” of Hydrogen. From the lower part of this component the sides branch to a lengthier loop showing IIIa, IVa, Va, VIa, VIIa, VIII, Ib, and IIb groups. From the lower half of this, the third, and longest loop protrudes the *f*-block.

Printed as a flat sheet, it can be easily assembled into a 3-D model by teacher or student. All printed element data, therefore, have a common plane so their electron numbers can trace the elements without changing direction or leaving the surface.

PRACTICE PROBLEMS

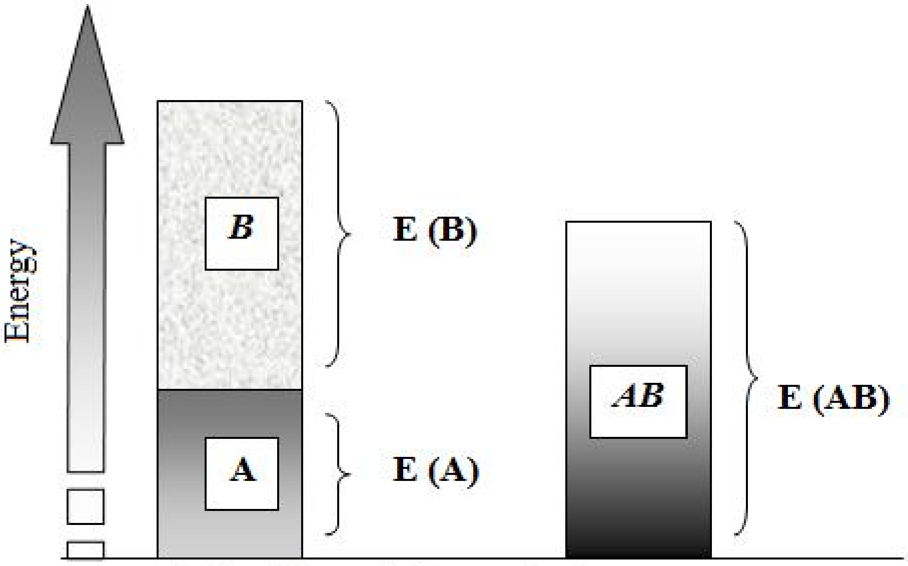
1. Without looking at the Periodic Table, give the group, period, and block in which the element that has the following electron configuration, is located: [Xe]$6s^2$.
2. Without looking at the Periodic Table, write the electron configuration for the element in the third period in Group 1. Is this likely to be more or less active than that described in question #1?
3. Without looking at the Periodic Table, give the group, period, and block in which the element with the following shorthand electron configuration is located: [Kr]$5s^1$.
4. How does the reactivity of the element in question # 1 compare with that in Group 1 of the same group?

CHAPTER # 4. CHEMICAL BONDING

Vocabulary

English	Українська назва	English	Українська назва
Electrostatic attraction	*Електростатичне притягування*	*Ionic bond*	*Іонний зв'язок*
Unpaired electron	*Неспарений електрон*	*Covalent bond*	*Ковалентний зв'язок*

Isolated and electrically neutral atoms are rare in nature. Ordinarily, only noble-gas atoms exist independently. Atoms of other elements are usually combined with each other or with atoms of different elements. A stable compound occurs when the total energy of the combination has lower energy than the separated atoms (Fig. 6).



$\sum (E(A) + E(B)) > E(AB)$
A, B - separated atoms;
AB - compound

Figure 6. Condition for chemical bond formation

Atoms are held together by electrostatic attraction between positively charged nuclei and negatively charged electrons. This attraction permits two atoms to be held together by a chemical bond, which is a link between atoms that results from the mutual attraction of their nuclei for electrons. Chemical bonds are classified by the way in which valency electrons are distributed around the nuclei of the combined atoms.

4.1 Types of Chemical Bonds

In previous chapter we described how atoms of main group elements could gain or lose electrons to form ions with noble-gas electron configurations. Metals tend to lose electrons to form positive ions, and non-metals tend to gain electrons to form negative ions. Many chemical compounds are composed of ions; in these compounds the chemical bond is an ionic one. **An ionic bond** is the *chemical bond resulting from electrostatic attraction between positive and negative ions*. If these is a **purely** ionic bond, one atom has completely given up one or more electrons, and another atom has gained them - as illustrated for two atoms that each have one unpaired electron at the top in **Figure 7**.

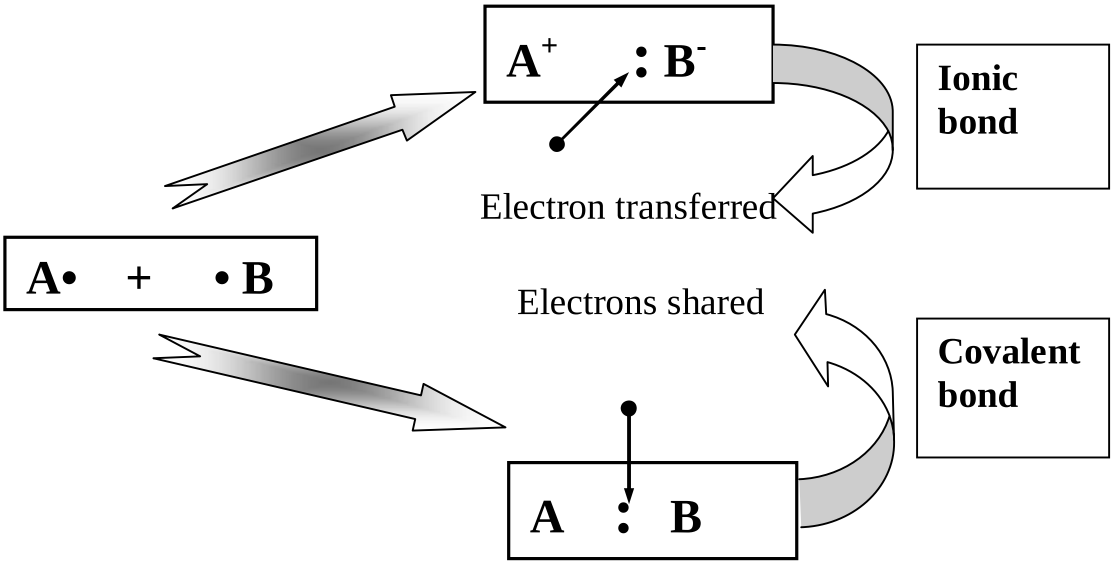


Figure 7. Two main types of chemical bond formation (in ionic bond, electrons are transferred from one atom to another, and positive and negative ions are formed. In covalent bond, an electron pair is shared between two atoms)

In the second major type of chemical bond, called covalent bond, neither bonding atom completely loses or gains an electron or electrons. A **covalent bond** is a chemical bond resulting from the sharing of electrons between two atoms. A covalent bond in which two electrons are shared is represented by a pair of electron dots, as shown at the bottom right-hand corner in Figure 7. In a purely covalent bond, the shared electrons are "owned" equally by the two atoms.

Chemical bonds between unlike atoms are never completely ionic and rarely completely covalent. Bonds can be anywhere in the range between the bonded atoms attract electrons.

The degree to which bonds are ionic or covalent can be estimated by comparing of electronegativity of the bonded atoms. The more two atoms differ in electronegativity, the more ionic the bond is between them. In other words, the electrons spend more time close to the bonded atom that attracts them more strongly and hence cause that atom partially resemble an anion and the other atom, a cation.

Figure 8 can be used to classify bonds according to electronegativity differences. The electronegativity (see **Appendix 7**) of one bonded atom is subtracted from that of the other. For example, the electronegativity difference between a Cesium (Cs) atom and a Fluorine (F) atom is 4,0 - 0,7 = 3,3. According to Figure 8, a Cesium-Fluorine bond is an ionic one. In fact it is one of the most highly ionic bonds known.

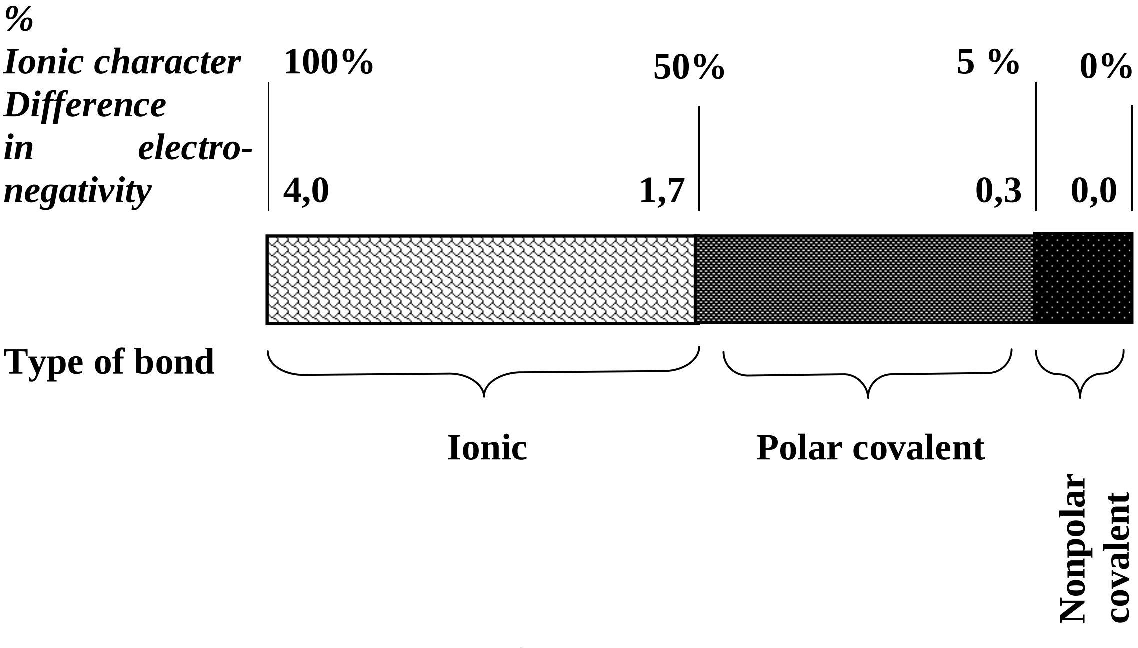
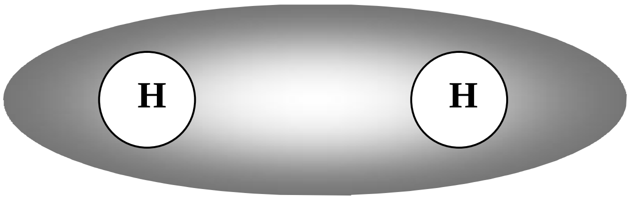


Figure 8. The variation of bond type with percent ionic character and the electronegativity difference between the bonded atoms

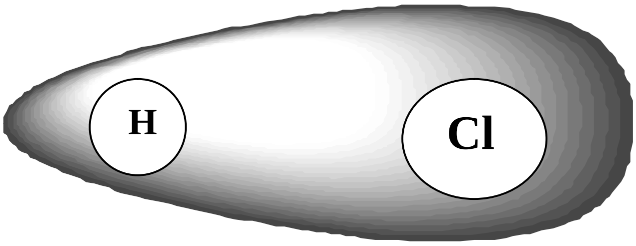
Bonds that have an ionic character of 50% or less are classified as covalent bonds. A bond between identical atoms is completely covalent. Hydrogen, for example, exists in nature not as isolated atoms, but as pairs of atoms held together by covalent bonds, H:H. The Hydrogen-Hydrogen bond has 0% ionic character. It is **nonpolar-covalent bond,** *a covalent bond in which the bonding electrons are shared equally by the bonded atoms, with a resulting balanced distribution of electrical charge.* Bonds having 0%-5% ionic character, corresponding to electronegativity differences of roughly 0 to 0,3, are generally considered as nonpolar covalent bonds. For example, because the electronegativity difference between Hydrogen (H) and Boron (B) is 0,1, they form a bond that is essentially nonpolar.

In bonds with significantly different electronegativities, the electrons are more attracted to the more electronegative atom. Such bonds are **polar,** meaning that they have an uneven distribution of charge. Covalent bonds having 5%-50% ionic character are classified as polar. A **polar-covalent bond** *is a covalent bond in which the united atoms have an unequal attraction for the shared electrons.*

Nonpolar and polar-covalent bonds are compared in the sketches in Figure 9 of the electron density in Hydrogen-Hydrogen and Hydrogen-Chlorine bonds. Hydrogen and Chlorine atoms combine to produce the compound known as Hydrogen Chloride (HCl). The electronegativity difference between Chlorine and Hydrogen atoms is 3,0 - 2,1 = 0,9, indicating formation of a polar-covalent bond. The electrons in this bond spend more of their time near more electronegative Chlorine atom than near the Hydrogen atom, as indicated in Figure 9b. Consequently, the Chlorine end of the bond has a relative surplus of electrons and a partial negative charge, indicated by writing δ-. The Hydrogen end of the bond then has an equal partial positive charge δ+.



a) Nonpolar-covalent bond



b) Polar-covalent bond

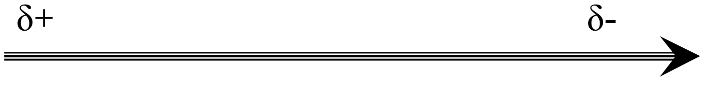


Figure 9. Comparison of the electron density in (a) a non-polar, Hydrogen-Hydrogen bond and (b) polar Hydrogen-Chlorine bond

In addition to ionic and covalent bond, there is a third major type of bond - metallic bond. In solid or liquid metals, metal atoms give up electrons, as in ionic compounds. The liberated electrons however, are free to move throughout the material, rather than being held in place in negative ions.

In general, atoms of non-metals form covalent bonds with each other, atoms of metals form metallic bonds with each other, and atoms of metals form ionic bonds with atoms of non-metals. There are many exceptions, however. One common and important exception is the formation of polar-covalent bonds between metals and non-metals that do not differ greatly in electronegativity.

Sample.

Use electronegativity differences and Figure 8, to classify bonds between Sulfur and the following elements: Hydrogen, Cesium, Chlorine, Magnesium, and Oxygen. Which atom in each bond will be more negative?

The electronegativity of Sulfur is 2,5 (see **Appendix 7**). The more electronegative end of atom in each bond will be the atom with the larger electronegativity.

Bond from Sulfur to	Electronegativity difference	Bond type	More electronegative atom
Hydrogen	2,5 - 2,1 = 0,4	Polar covalent	Sulfur
Cesium	2,5 - 0,7 = 1,8	Ionic	Sulfur
Chlorine	3,0 - 2,5 = 0,5	Polar covalent	Chlorine
Magnesium	2,5 - 1,2 = 1,3	Polar covalent	Sulfur
Oxygen	3,5 - 2,5 = 1,0	Polar covalent	Oxygen

4.2 Hydrogen Bonds

Hydrogen bonding differs from other uses of the word “bond” since it is a force of attraction a Hydrogen atom in one molecule and a small atom of high electronegativity (mostly Oxygen, Nitrogen, Fluorine) in another molecule. That is, it is an intermolecular force, not an intramolecular force as in the common use of the word “bond”.

When Hydrogen atoms are joined in a polar covalent bond with a small atom of high electonegativity, the partial positive charge on the Hydrogen is highly concentrated because of its small size.

Hydrogen bonding has a very important effect on the properties of water. Consider two water molecules coming close together (see Fig. 10).

Polar molecules, such as water molecules, have a weak, partial negative charge at one region of the molecule (the Oxygen atom in water) and a partial positive charge elsewhere (the Hydrogen atoms in water).

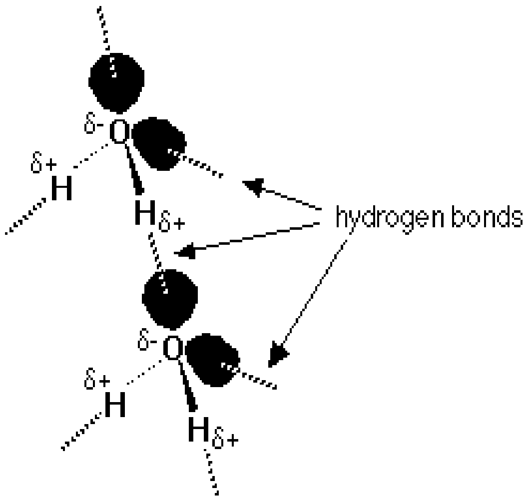


Figure 10. Formation of Hydrogen Bonds between water molecules

Thus when water molecules are close together, their positive and negative regions are attracted to the oppositely-charged regions of nearby molecules. The force of attraction, shown here as a dotted line, is a hydrogen bond. The δ+ Hydrogen is so strongly attracted to the electron pair that it is almost as if you were beginning to form a co-ordinate (donor-acceptor covalent) bond. Notice that each water molecule can potentially form four Hydrogen bonds. It doesn't go that far, but the attraction is significantly stronger than an ordinary interaction. Hydrogen bonds have about a tenth of the strength of an average covalent bond, and are being constantly broken and reformed in liquid water.

This is why the boiling point of water is higher than that of ammonia or Hydrogen Fluoride (see Fig. 11). In the case of Ammonia, the amount of hydrogen bonding is limited by the fact that each Nitrogen only has one electron pair. In a group of Ammonia molecules, there aren't enough electron pairs to go around to satisfy all the Hydrogens. In Hydrogen fluoride, the problem is a shortage of hydrogens. In water, there are exactly the right number of each. Water could be considered as the "perfect" Hydrogen bonded system.

The hydrogen bonds that form between water molecules account for some of the essential and unique properties of water:

The attraction created by hydrogen bonds keeps water liquid over a wider range of temperature than is found for any other molecule its size.

The energy required to break multiple hydrogen bonds causes water to have a high heat of vaporization; that is, a large amount of energy is needed to convert liquid water, where the molecules are attracted through their hydrogen bonds, to water vapor, where they are not.

Two outcomes of this:

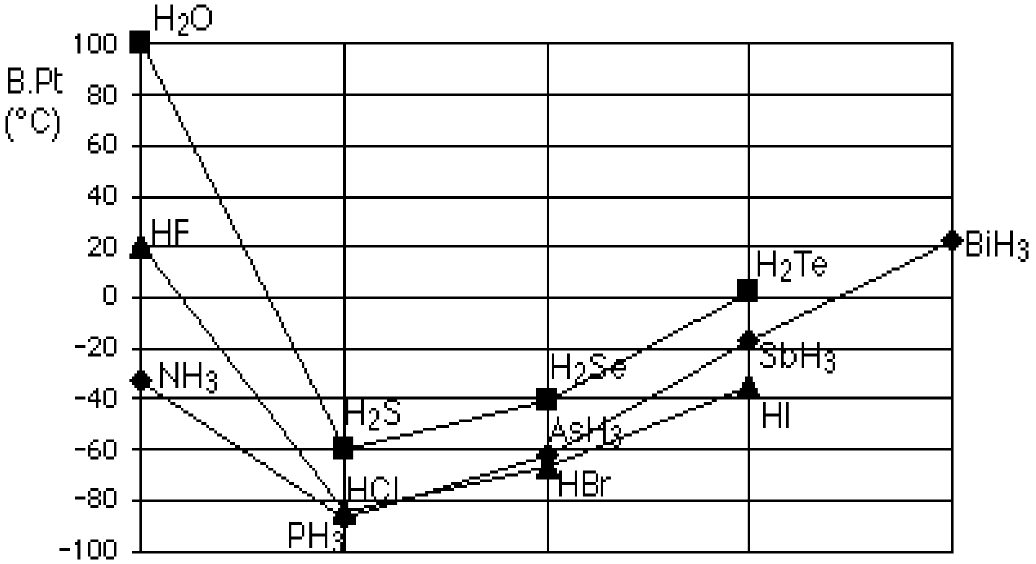


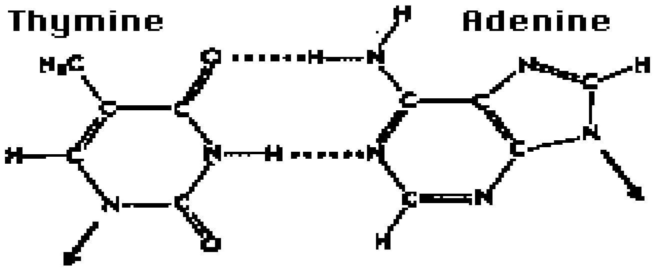
Figure 11. Depending of boiling-points (B.Pt) of double Hydrogen-contained compounds from nature of the second atom and presence of Hydrogen bonding

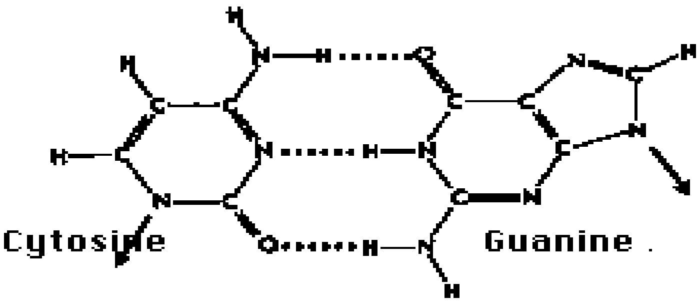
The evaporation of sweat, used by many mammals to cool themselves, achieves this by the large amount of heat needed to break the hydrogen bonds between water molecules.

Moderating temperature shifts in the ecosystem (which is why the climate is more moderate near large bodies of water like the ocean).

Multiple hydrogen bonds in alive objectes:

hold the two strands of the DNA double helix together:





hold polypeptides together in such secondary structures as the alpha helix and the beta conformation;

help enzymes bind to their substrate;
help antibodies bind to their antigen
help transcription factors bind to each other;
help transcription factors bind to DNA.

4.3 Why does Chemical Bond occur?

The fascinating variety of materials in the world around us is possible because chemical bonds unite atoms of the elements in so many different combinations. Some elements are found in nature only in chemical compounds. Even the atoms of elements that can be found in nature in uncombined form - such as Oxygen and Nitrogen in the air, of Gold and Copper in the Earth’s crust - do not exist as independent atoms. They are bonded together.

If their potential energy is lowered by the change, two atoms will form a chemical bond. Throughout nature, changes that decrease potential energy are favored. Books fall off desks, and the result is lower potential energy for the books. Most atoms have lower potential energy in bonds than as independent atoms.

Chemical-bond formation is often energy - releasing process. Experiments also show that the reverse - breaking chemical bonds - is often an energy-absorbing process. Atoms separated by breaking a chemical bond have a higher total potential energy than when they were bonded. Whether or not a given chemical reaction occurs spontaneously is partly dependent on whether or not forming new bonds in the products produced enough energy to break bonds in the reactants.

Covalent, ionic and metallic bond all decrease the potential energy of the combined atoms.

PRACTICE PROBLEMS

1. What are the three major types of bonds?
2. What is the role of electronegativity in the determination of the ionic or covalent character of a bond?
3. What type of bond would be expected between H and F; Cu and S; Br and I?
4. List the three bond pairs referred to in the previous question in order to increase ionic characters.

CHAPTER # 5. LABORATORY GLASSWARE, LABWARE AND RULES OF LABORATORY RESEARCH

Vocabulary

English	Українська назва	English	Українська назва
Test-tube	*Пробірка*	*Gooch crucible*	*Тигель Гуча*
Beaker	*Стакан*	*Cylinder*	*Циліндр (мірний)*
Walter's Crucible Holder	*Держач для тиглів Вальтера*	*Mortar*	*Ступка*
		Pestle	*Пестик*
Buchner Funnel	*Воронка Бюхнера*	*Spatula*	*Шпатель*
Clamp	*Зажим*	*Pump*	*Пробовідбірник (хімічний)*
Crystallizing Dish	*Кристалізатор*	*Erlenmeyer's flask*	*Колба Ерленмеєра*
Dropper Bottle	*Крапельниця*	*Volumetric flask*	*Мірна колба*
Cork	*Корок*	*Evaporation dish*	*Випарювальна чашка*
Florence flask	*Круглодонна колба*	*Pipette*	*Піпетка*
Forceps	*Пінцет*	*Filtering funnel*	*Воронка для фільтрування*
Glass jar	*Склянка*		

The most useful chemical glassware is presented in Fig. 12 and 13.

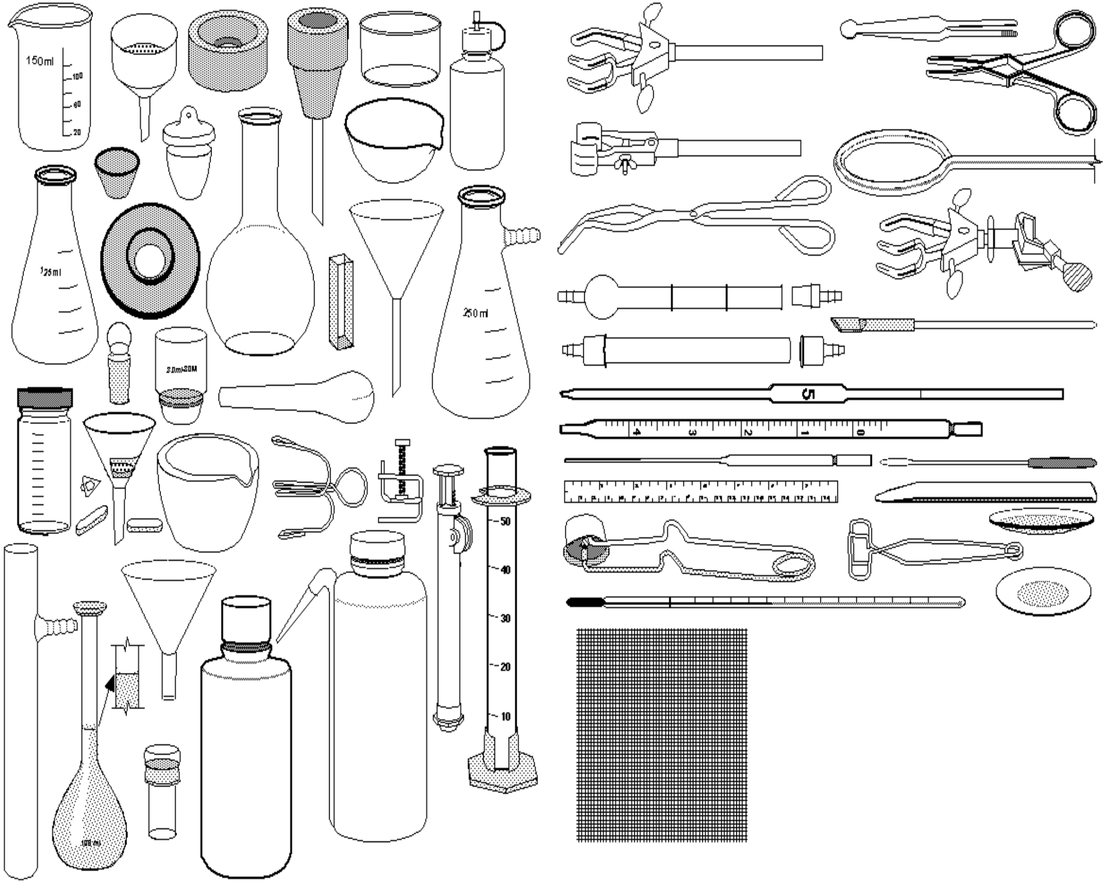
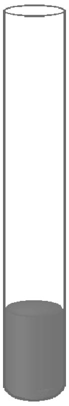
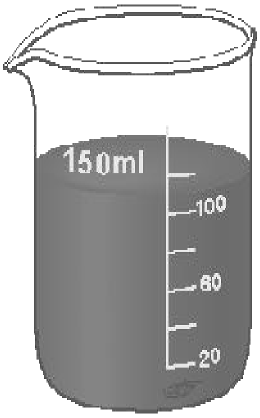


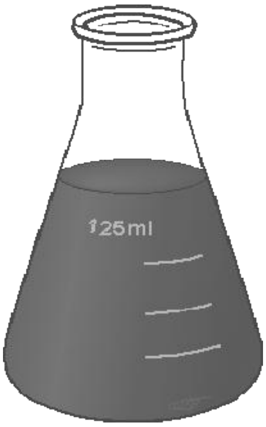
Figure 12. Chemical Glassware



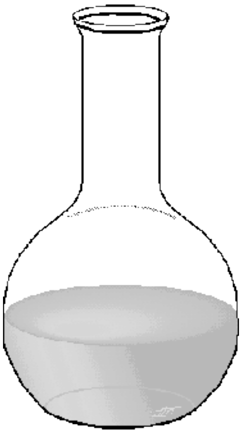
Test tube



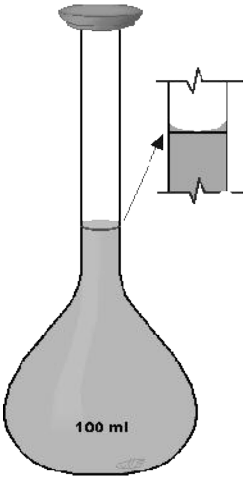
Beaker



Erlenmeyer Flask

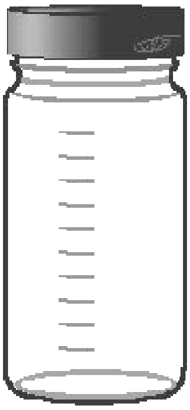


Florence Flask

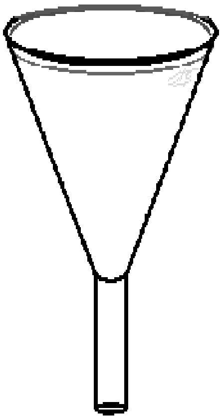


Volumetric Flask

Dropper Bottle

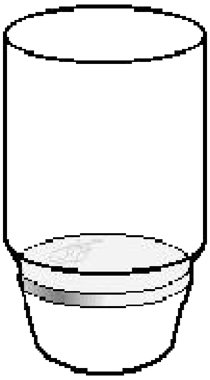


Glass Jar

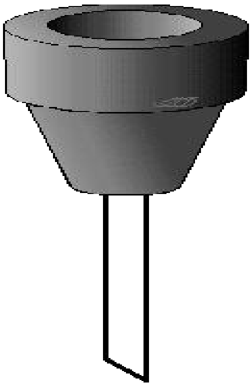


Filtering Funnel

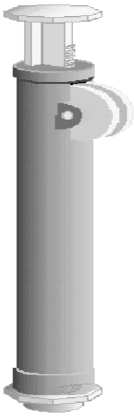
Buchner’s Funnel



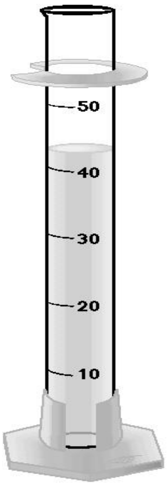
Gooch’s Crucible



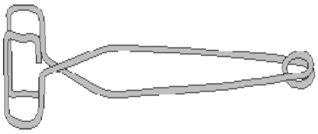
Walter’s Crucible Holder



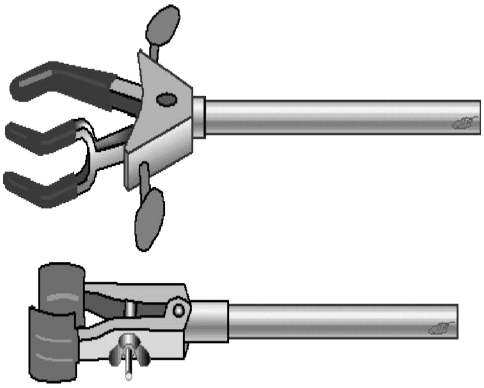
Pi-Pump



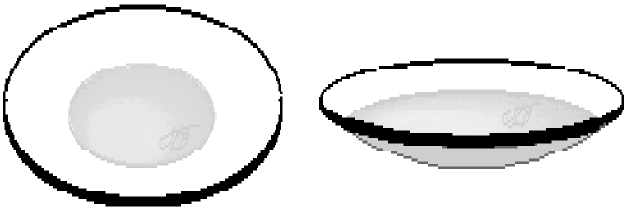
Graduated Cylinder



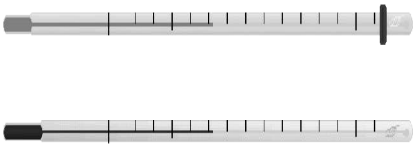
Test tube clamp



Clamps

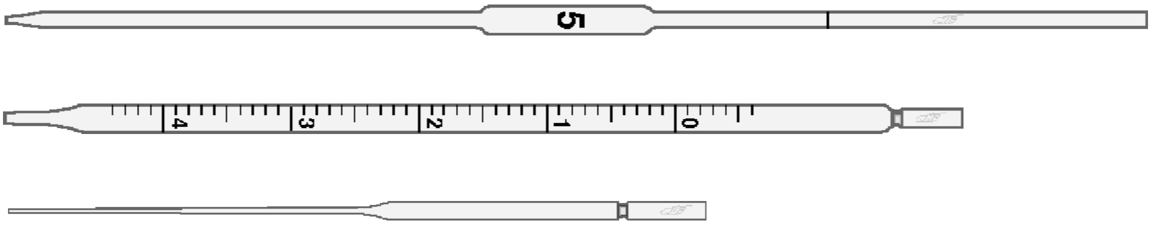


Watch glass



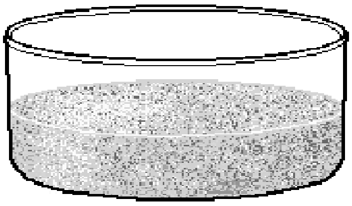
Thermometers

Spatulas



Volumetric pipettes

Evaporation dish Pestle and mortar Forceps



Crystallizing Dish as sand bath

Figure 13. Separate varieties of laboratory glassware

5.1 Chemical glassware

All chemical glassware is divided into several groups according to their use:

- *of general usage* (is used to carry out different chemical operations): test tubes, beakers, flat-bottom, round-bottom and conical flasks, Wurtz flasks (round-bottom with bleeder), crystallizer tanks, funnels, clock glass, weighing bottles;
- *measuring vessels*: graduated cylinders, measuring tubes, measuring pipettes, volumetric flasks;
- *of special use*: flasks, Kipp gas generator, vacuum filtering apparatus, consisting of Bunsen flask, Buchner funnel, trap flask, and water-jet pump;
- *porcelain ware and ware made from other materials*: spreading rods, mortars, evaporating dishes, crucibles and boats.

5.2 Chemical reagents and their storage

Reagents are individual substances, their solutions or mixtures of strictly determined composition, destined for laboratory works, scientific researches and chemical analysis.

Chemical reagents can be used in solid, liquid and gaseous state (as vapors). They are divided into several qualifications with characteristics, given in the Table 8, depending on the degree of purity.

Table 8. Analytical classification of chemicals

Qualification of reagent	Symbol	Contents of main substances, % (by mass)	Contents of separate admixtures, % (by mass)
Pure	p.	98	0,01- 0,5
Analytically pure	a.p.	Not less than 99	to 0,1
Chemically pure	c.p.	More than 99	to 0,1
Specially pure	s.p.	About 100	10^{-5}- 10^{-10}

Solid reagents are stored in glass and polyethylene boxes, liquids – in flasks. Depending on substance property boxes and flasks are closed with glass, polyethylene, and rubber or cork stoppers.

Hygroscopic substances are stored in weighing bottles, desiccators, soldered ampoules, and flasks with calcium Chloride tubes and in boxes with rubbed stoppers. Boxes stoppers can be covered with paraffin embedded. Reagents changing on light are stored only in dark-glass flasks.

Great amounts of gases are stored in gas storage tanks, small amounts - in gas burettes or gasometers.

5.3 Elementary operations carrying out

Balances and weighing

Chemical, pharmaceutical and analytical balances are usually used in chemical laboratories.

Chemical and pharmaceutical balances allow to determine the mass to a precision of 0,01 g and analytical one – that of 0,0001 g. Balances are equipped with the set of weights called the set of fractional weights. Weights from the set are taken with pincers.

For weighing the object put it on the left scale pan and put the weight on the right one. Chemical balances have the device called arrester supporting the scale pans in the non-working state. To bring the balances in the working state the arrester has to be put down. Take and put objects and fractional weights only when the arrester is lowered (non-working state). Weighing can be considered as completed if the deviation of pointer to the right and to the left from medium line becomes equal. After weighing put immediately the fractional weights back to the set.

Keep the following rules when weighing:

1. Do not put hot or wet objects on the scale pans. Work with liquids; avoid spilling of liquid on balances and fractional weights.
2. Do not put the substance being weighed directly on the scale pans, use special glassware (clock glass or weighing bottle) or filter paper.
3. Take fractional weights only with pincers and do not use the weights of another set of fractional weights.
4. After weighing put balances in the non-working state and do not leave anything on the balances.

Measurement of liquid reagents volume

Measurement of liquid reagents volume is carried out with the measuring vessels. Measuring graduates, measuring tubes, and volumetric flasks are used for the relatively rough measurement of liquid volume.

Burettes allow to measure the volume of flowing out liquid or the evolving gas to a precision of 0,1%. Volumetric flasks are used for preparation of solutions with necessary concentration or for diluting of solution to given extent. The precision of volume measurement is 0,12 - 0,20 %.

Measuring (Mohr's pipettes) and transfer pipettes are used in order to take precisely the volume. Measuring pipettes can be used to measure the total volume or its part.

Heating

Heating is often used in laboratories at conducting the chemical reactions; incineration, dehydration, melting of solid substances; evaporation and boiling of solutions.

For heating different devices are used: electrical plates, drying chambers, electrical furnaces (muffles), spirit burners, bathes. Depending on the substance properties and the purpose of heating, the different methods are used.

1. When substances are heated in test tubes, porcelain and metal crucibles for short time, and the open fire is used. Heating is done in the upper part of flame, fixing the test tube in the wooden holder. Liquids in the thermally sound glass or porcelain ware are heated on spirit burners through the asbestos net.
2. If the long-term heating at high temperature is necessary (incineration, melting etc.) the electrical plates (temperature up to 300^0C) and electrical furnaces (temperature 300 – 1000^0C) are used.

Incinerated substances are put to the porcelain, metal or alundum crucibles or boats.

3. If the heating of solutions (evaporating) is to be done in the narrow temperature interval, the bathes (water, sand, glycerine, oil or silicon) filled with liquid (sand) to 2/3 its volume are used. The vapors of boiling water produce heating; if glycerin or oil is used, the liquid produces the heating itself. Sand bath is used for long heating. Bathes allow getting the temperature up to 300^0C.

4. Drying and the heating in order to remove hygroscopic moisture at temperature to 110^0C are made in the drying chambers. Hygroscopic substances and substances decomposed at heating are dried in desiccators with the help of certain substances, taking water.

Drying is considered as completed if the crystals of substance taken with glass rod are poured from it when knocked slightly.

Separation of solid components from liquids

For separation of solid components from liquid ones the filtering and decantation are used. Filtering is the process of liquid separation from solid matter through the filtering material with the simultaneous detaining of the sediment on its surface.

When the aim of filtering is the obtaining of solid precipitate the plain filter is used. If it is necessary to get pure liquid the folded filter is used. For separation of fine-crystalline precipitate and for the acceleration of filtering the vacuum filtering or filtering with removal by suction is used. For the separation of heavy precipitate the decantation – pouring the liquid off the precipitate – is used.

If it is necessary to filter a hot solution, the special double-wall funnel with electric heating is used. It is the metal funnel with double wall, the heating element inserted between them. Ordinary funnel is inserted in this double-wall funnel and is heated. The filtering with heating by vapor is widespread operation in chemical laboratory. The funnel for such filtering is the glass double-wall one. The jet of steam is passed between its walls at filtering.

Filtering materials are: paper, cotton wool, glass wool, and fabric. Paper filters can be ordinary and quantitative (ashless). Filter is quantitative if the weight of ashes forming when it burns is less than 0,0001 g. Funnels and Shott’s crucibles (funnels with soldered pore glass partition) are used for aggressive liquids filtering.

Characteristics of paper filters are given in the Table 9.

Table 9. Characteristics of paper filters

Band color	Pore diameter, nm	Characteristic of paper and type of precipitate

Red or black	10	Wide pores, fast filtering, for rough precipitate
White	About 3	Medium pores, for large precipitate
Blue	1–2,5	Small pores, for fine precipitate
Green	Less than 1	High-density, for very fine precipitate
Yellow	3	Degreased paper

Rules of filtering

1. Correctly chosen filter must be 3 – 4 mm lower than the edge of funnel and fit closely to its walls.

2. Filter is moistened with small amount of distilled water.

3. Let the precipitate settle on the bottom of glassware and carefully, not disturbing it, pour off the liquid along the glass rod on the filter. Only the last portion of liquid is to be mixed with the precipitate.

4. Fill the funnel with liquid so that its level is 2 – 3 mm lower than the edge of filter.

5. When all the liquid flows down, wash the precipitate with washing liquid.

6. Vacuum filtering is carried out with the installation consisting of Bunsen flask, Buchner’s funnel, trap flask and water-jet pump. Filter must cover the whole perforated bottom of Buchner’s funnel and its edge must not rise up. Then turn on the pump and, when the air begins to penetrate through the bottom of funnel, pour off the liquid. Filtering is considered as completed if the drop does not hang from the spout of funnel. The mixture on the filter must not be mixed! The precipitate on the filter is distributed evenly and is concentrated with flat glass stopper. After the operation is finished pass the air in the flask and only then close the water-supply tap. It is necessary to take the substance from the Buchner’s funnel in the following way: disconnect the funnel from the flask, overturn it and knock out (blow out) the substance on the sheet of filter paper by light knocks.

Grinding

For solid substances grinding various mortars: porcelain, metal, agate are used most frequently. Metal mortars are used for rough grinding, porcelain – for finer grinding and agate – for very hard materials.

The very big pieces are firstly broken with hammer. The pieces of the walnut size can be ground in the mortar, filled with the substance to ¼ of its height. Grind carefully so that the substance does not throw out from the mortar. The size of the mortar must be chosen in accordance with the amount of substance. Mortars cannot be used for heating.

Dissolving of solid substances

Preparation of solutions is one of the most important operations of the inorganic synthesis. At preparing solutions the following rules are to be observed.

1. Solutions must be prepared using distilled water.

2. Usually the dissolving is carried out in glass or porcelain beakers, Erlenmeyer (conical) flasks, and other flasks. For the preparation of solutions with certain concentration measuring flasks are used. If the substance dissolves with the great heat production, the solution is prepared in thin-wall porcelain or thermally sound glassware.

The capacity of glassware where solution is prepared must be a little greater than the given volume. Each flask with solution must be provided with an etiquette or inscription.

3. Pour out small quantity of solvent in the glassware then pour the substance, mix and add the solvent in the amount, slightly less then necessary to prepare solution. Add the solvent to the given volume only after solid substance is completely dissolved. After all solvent is added, mix the solution thoroughly and, if necessary, filter before use it.

4. If the substance is hydrolyzed easily, add firstly the substance preventing from the hydrolysis and then dissolve.

Obtaining and drying of gases

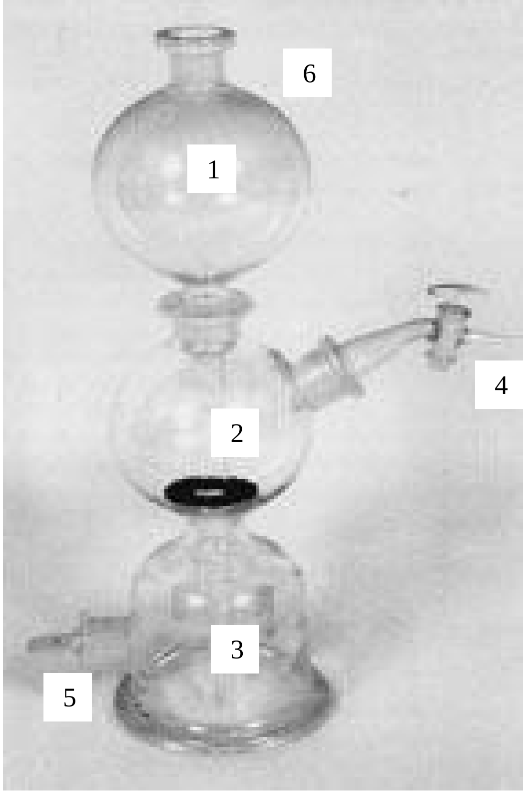
In the laboratory conditions gas can be obtained by the solid substance and solution interaction, by thermal decomposition of substances and from the gas storage tank with pressed gas.

The form and design of device for gas obtaining depends on the gas properties.

If the gas is obtained by solid substance decomposition, the latter is placed into the test tube, fixed horizontally so that the emitting moisture does not flow down to the place of heating.

If the gas is evolving when liquid reacts with solid substance, test tubes, Wurtz flasks, Kipp gas generator (Fig. 14) are used. In this case test tube or Wurtz flask is fixed vertically. Kipp gas generator is the device of non-stop action; it is used for obtaining of great amounts of gas.

Methods of gas collecting depend on gas properties. Gases, heavier than air, are collected in the open glassware. If the gas and the air are similar by mass, the gas is collected using the water displacement method. The possibility of gas interaction with water must be taken into account. If it reacts with water, other liquid, for example, the saturated solution of salt, must substitute water. Gases, lighter than air, are collected in open, overturned glassware.



The accompanying substances contaminated gases, industrial as well as obtained in laboratory, and gases, evolved from the water solutions, contain water. The purifying and drying of gases is carried out in special glassware: Tyshchenko's, Wulf's, Drexel's flasks, etc.

Figure 14. Kipp gas generator. 1 — upper bulb, 2, 3 — connected vessels, 4, 5 — tubules, 6 — throat.

Cooling

For substances, cooling in dry air after the incineration or melting, desiccators are used. The flowing water, ice, cooling mixtures are used for cooling in order to crystallize the solid substance. Pea-size pieces of ice (snow) are mixed with water to obtain the mess-like mass. To obtain the lower temperatures ice is mixed with Sodium Chloride: 1 part of ice to 0,3 parts of Sodium Chloride (temperature decreases to -21^{0}C) or 1 part of ice to 1,43 parts of five-watered calcium Chloride.

5.4 Safety rules during carrying out laboratory works

All experiments with poison, fugitive, inflammable substances and substances with a specific odor are to be carried out in ventilating hoods.

It is forbidden to smell evolving gases, stooping close to a vessel. If it is necessary to smell the gas, cautiously direct by hand the flow of air from vessel to nose.

It is forbidden to leave working electrical and gas equipment without supervision.

At pouring liquids, and also at heating of vessel with liquid it is forbidden to stoop above it or to direct its aperture on other people, in order to prevent hit of drops of a liquid on the face or clothes. If drops of a liquid hit on the face or the hands, it is necessary to wash them off immediately with water and to wipe with rag. The drops of concentrated acid are to be washed off with a plenty of water then injured places are to be washed with weak soda solution. The alkali is necessary to be washed off with water until skin will not be slip.

In case of a fire in laboratory use the fire extinguisher. For extinguishing benzene, alcohol or ether, it is necessary to use sand, strewing flame with it. In case of thermal burn (by flame of the burner or hot subjects) it is necessary to moisten the burnt place with strong solution of Potassium permanganate so that the skin became brown, or to put cotton wool moistened with liquid against burns. If burns are heavy, it is necessary to call for the doctor immediately.

It is strictly forbidden to eat, to smoke, to taste anything, to make the disorder in chemical laboratory.

After the end of the work in the laboratory it is necessary to check up, that gas, heating, measuring or other electrical equipment is switched off.

5.6 Rules for reagents and equipment use

Solutions and solid reagents are to be stored in glassware (flasks, boxes), covered with glass (ground), rubber or cork stoppers. All flasks with reagents are to be kept closed and are to be opened only when being used. Closing flasks do not confuse stoppers, or reagents will be contaminated and unfit. Before taking the flask with reagent from the shelf, read the etiquette with its name attentively; after using it is necessary to bring the flask back.

All flasks with reagents always must be provided with the etiquette with the substance name or chemical formula. For solutions the concentration should be marked. Reagents in the flasks without etiquette are to be excluded and exterminated.

If there is no instruction on the reagents dosage, it is necessary to take reagent as little as possible, namely: the amount that covers the bottom of the test tube of solid substance and 1-2 mL of solutions. It is not allowed to bring remains of reagents back to the glassware where they were taken from. After the using of reagent it is necessary to cover the box or flask with stopper immediately and bring it back to its place.

Solid substances are to be taken with dry and clean horn, porcelain, metallic spoons or spreading rods (shovels), after using they are to be wiped thoroughly (the best is with filter paper).

When liquid is poured from the flask, keep the flask so that etiquette is on the top in order the drops of reagent flowing down could not damage etiquette. Practically, it is necessary to take the flask so that etiquette is in your palm and to take off the last drop of reagent with the edge of glassware where reagent is poured in. Using pipette, it is necessary to wash it thoroughly before taking the reagent from other flask.

At diluting the concentrated acid (Sulfuric especially) it is necessary to pour acid in water, but not on the contrary.

Excess amounts of reagents containing poisonous substances are not allowed to be poured to the sewerage; they are to be poured in special flasks.

5.7 Rules for work carrying out and results design

At carrying out the laboratory works it is necessary to take all precautionary measures given in special instruction and in the methodical instructions.

Before the beginning of studies it is necessary to familiarize oneself with a theme of the work by the methodical instructions, textbooks and lecture notes. Before carrying out the laboratory work it is necessary to read attentively its description, to clarify vague questions with the instructor, to prepare all necessary required for carrying out practical work, and only after that begin its implementation.

During the work in chemical laboratory it is necessary to use special clothes - laboratory coat, and rubber gloves and mask if necessary. It is necessary to support cleanliness and order at the working place, it is not allowed to overload it with unnecessary subjects.

Before each laboratory work record in a logbook its title, date, description of an experimental section, figures and schemas of the necessary equipment. Give observations, corresponding equations of the reactions, calculations and conclusions. The laboratory work is considered as completed only after its defense before the teacher in individual order.

It is necessary to protect the methodical instructions, textbooks and logbook against spilling of solutions of acids, alkalis, salts and so on. It is forbidden to put flasks with reagents on the books and logbooks.

It is forbidden to carry out experiments, which are not stipulated by laboratory work without sanction of the teacher.

CHAPTER # 6. THE MAIN CLASSES OF INORGANIC COMPOUNDS

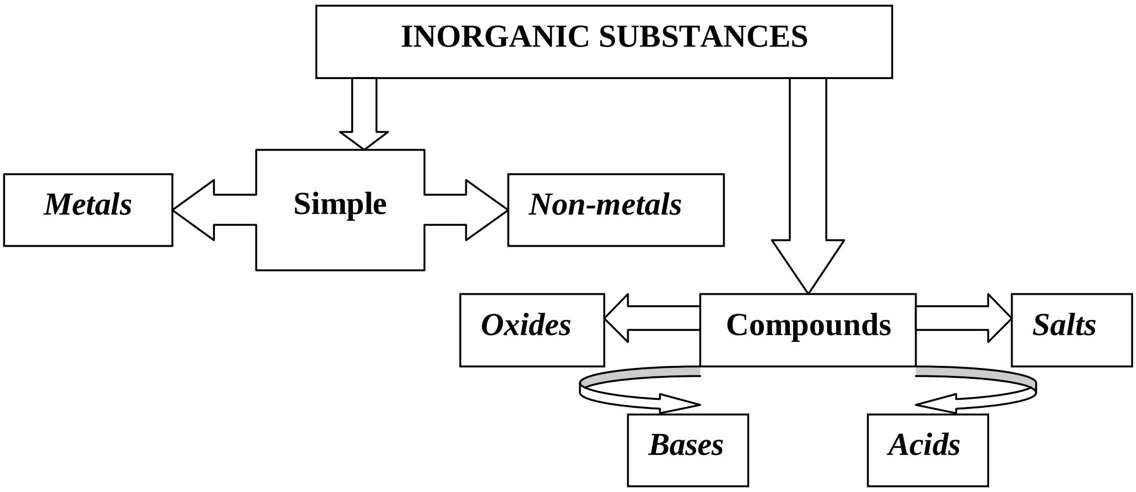
Vocabulary

English	Українська назва	English	Українська назва
Oxide	*Оксид*	*Basic salt, hydroxy salt*	*Основна сіль*
Hydroxide	*Гідроксид*	*Base*	*Основа*
Chemical compound	*Хімічна сполука*	*Noble/precious metal*	*Благородний метал*
Complex substance	*Складна речовина*	*Halogen*	*Галоген*
Simple substance	*Проста речовина*	*Chalcogen*	*Халькоген*
Salt	*Сіль*	*Alkali(ne) metals*	*Лужні метали*
Neutral [normal] salt	*Середня сіль*	*Alkaline-earth metals, earth metals*	*Лужноземельні метали*
Acid salt	*Кисла сіль*		

6.1Classification of inorganic substances

Simple substances consist of one-type atoms (atoms of one chemical element).

Complex (complicated) substances (or chemical compounds) consist of different type atoms (atoms of different chemical elements).



Non-metals include the next groups of chemical elements with closely related properties:

Noble (rare) gases - elements of VIII-A subgroup of Periodical Table (He; Ne; Ar; Kr; Xe; Rn);

Halogens - elements of VII-A subgroup of Periodical Table (F, Cl, Br, I, At);

Chalcogens - elements of VI-A subgroup of Periodical Table (O, S, Se, Te), except Po;

Elements of V, IV, III groups of Periodical Table - N, P, As, C, Si, B, H.

Metals include some groups of chemical elements with similar properties:

Alkali(ne) metals - elements of I-A subgroup of Periodical Table (Li, Na, K, Rb, Cs, Fr);

Alkaline-earth metals, earth metals - some elements of II-A subgroup of Periodical Table (Ca, Sr, Ba, Ra);

Family of Iron - Fe, Co, Ni;

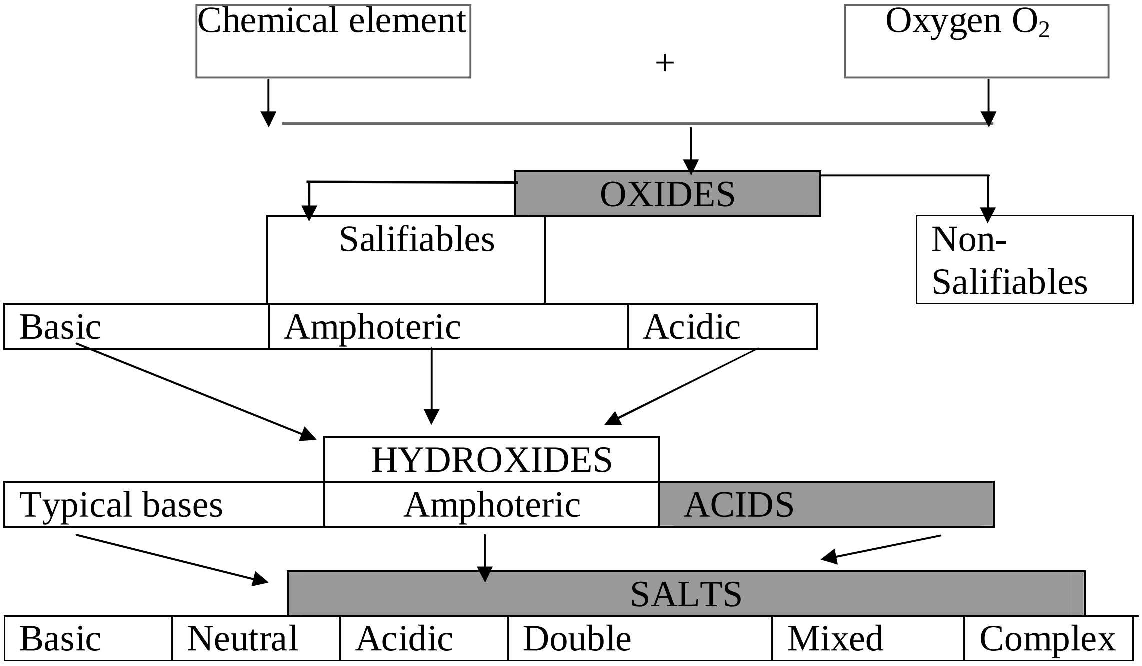
Family of noble metals *(Family of* Platinum*)* - Ru, Rh, Pd, Os, Ir, Pt;

Lanthanide Series - elements of periodical table from № 58 till № 71, their properties are very similar to element La (Lanthanum);

Actinide Series - elements of periodical table from № 90 till № 103, their properties are very similar to element Ac (Actinium).

6.2 Relation between main classes of inorganic substances

Scheme of relationships of classes



6.3 Oxides

Oxides - complex substances, consisting of two elements, one of them is Oxygen. Practically all elements (excepting three noble gases - He, Ar and Ne) may form oxides.

Classification of oxides:

Non-Salifiables	- non-salts forming (CO, N_2O, NO)
Salifiables	- salts forming, subdivided into:
	Basic - it is a metal oxides in which metals display low oxidation number +1, +2 (Na_2O, MgO, CuO);
	Amphoteric (for some metals with oxidation number +3, +4, sometimes +2) - ZnO, Al_2O_3, Cr_2O_3, SnO, PbO, MnO_2;
	Acidic - it is oxides of non-metals and some metals with oxidation number from +5 to +7 (SO_2, SO_3, P_2O_5, Mn_2O_7, CrO_3).

Preparation

1. Interaction of simple and complex substances with Oxygen:

$2Mg + O_2 = 2MgO$;
$4Al + 3O_2 = 2Al_2O_3$;
$S + O_2 = SO_2$;
$2H_2S + 3O_2 = 2SO_2 + 2H_2O$;
$2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O$;
$4FeS + 7O_2 = 2Fe_2O_3 + 4SO_2$.

2. Decomposition of some substances containing Oxygen (oxides, bases, acids, salts) on heating:

$4CrO_3 \xrightarrow{t} 2Cr_2O_3 + 3O_2$;
$Cu(OH)_2 \xrightarrow{t} CuO + H_2O$;
$2Fe(OH)_3 \xrightarrow{t} Fe_2O_3 + 3H_2O$;
$H_2CO_3 \xrightarrow{t} CO_2 + H_2O$;
$H_2SiO_3 \xrightarrow{t} SiO_2 + H_2O$;
$CaCO_3 \xrightarrow{t} CaO + CO_2$;
$2AgNO_3 \xrightarrow{t} 2Ag + 2NO_2 + O_2$.

Chemical properties

Basic oxides

1. Interaction with water. Oxides of alkaline (Li_2O, Na_2O, K_2O, Rb_2O, Cs_2O) and alkaline-earth (CaO, SrO, BaO) metals form soluble bases - **alkalis**:

$Li_2O + H_2O = 2LiOH$;
$Rb_2O + H_2O = 2RbOH$;
$CaO + H_2O = Ca(OH)_2$;
$BaO + H_2O = Ba(OH)_2$.

2. Interaction with acidic oxides forming the salts:

$K_2O + SO_2 = K_2SO_3$;

$SrO + N_2O_5 = Sr(NO_3)_2$;

$CuO + SO_3 = CuSO_4$;

$3BaO + P_2O_5 = Ba_3(PO_4)_2$.

3. Interaction with acids forming the salts and water:

$Na_2O + 2HNO_3 = 2NaNO_3 + H_2O$

$NiO + H_2SO_4 = NiSO_4 + H_2O$

$3MgO + 2H_3PO_4 = Mg_3(PO_4)_2 + 3H_2O$.

Other basic oxides do not react with water directly.

Acidic oxides

1. The most of acidic oxides reacts with water forming the acids (except a few oxides like SiO_2, MoO_3, WO_3):

$SO_3 + H_2O = H_2SO_4$;

$N_2O_5 + H_2O = 2HNO_3$;

$P_2O_5 + 3H_2O = 2H_3PO_4$;

$4NO_2 + O_2 + 2H_2O = 4HNO_3$.

2. Interaction with basic acids with forming the salts:

$N_2O_3 + Na_2O = 2NaNO_2$;

$P_2O_5 + 3CaO = 2Ca_3(PO_4)_2$;

$SO_3 + BaO = BaSO_4$.

3. Interaction with bases forming the salts and water:

$SO_3 + Ba(OH)_2 = BaSO_4 + H_2O$;

$N_2O_5 + 2KOH = 2KNO_3 + H_2O$;

$SiO_2+2NaOH = Na_2SiO_3 + H_2O$.

Amphoteric oxides

Term Amphoteric (from Greek) means *double-sided, mutual*. Therefore amphoteric oxides occupy a position between basic and acidic oxides and display corresponding chemical properties.

1. Interaction with basic and acidic oxides forming the salts:

$PbO + SO_3 = PbSO_4$;

$PbO + N_2O_5 = Pb(NO_3)_2$;

$Cr_2O_3 + 3SO_3 = Cr_2(SO_4)_3$;

$Cr_2O_3 + 3N_2O_5 = 2Cr(NO_3)_3$;

$Li_2O + PbO = Li_2PbO_2$;

$CaO + PbO = CaPbO_2$;

$3Li_2O + Cr_2O_3 = 2Li_3CrO_3$;

$Li_2O + Cr_2O_3 = 2LiCrO_2$;

$CaO + Cr_2O_3 = Ca_3(CrO_3)_2$;

$CaO + Cr_2O_3 = Ca(CrO_2)_2$.

2. Interaction with acids forming the salts and water:

$PbO + 2 HCl = PbCl_2 + H_2O$;

$Al_2O_3 + 2 H_3PO_4 = 2AlPO_4 + 3H_2O$.

3. Interaction with alkalis forming the salts and water:

$Cr_2O_3 + 6KOH = 2K_3CrO_3 + 3H_2O$;

$MnO_2 + 2NaOH = Na_2MnO_3 + H_2O$.

Peroxides may be shown as a peculiar group of Oxygen-contained compounds. Frequently peroxides are considered as salts of Hydrogen peroxide H_2O_2, where O_2^{-2} (-O-O-) is an analogue of acid residue. For example, BaO_2 - Barium peroxide includes Ba^{2+} and formally O^-.

6.4 Bases

Bases are complex substances, in which atoms of metals or ionic groups (for example, NH_4^+) are bonded with one or several hydroxyls groups.

Classification of bases: they are divided into two groups - soluble in waters (alkalis - LiOH, NaOH, KOH, RbOH, CsOH, FrOH, $Ca(OH)_2$, $Ba(OH)_2$, $Sr(OH)_2$) and insoluble (for example, $Fe(OH)_2$, $Cu(OH)_2$ etc.). Insoluble bases include amphoteric ones too ($Al(OH)_3$, $Cr(OH)_3$, $Zn(OH)_2$ etc.).

According to quantity of OH^- bases may be divided into:

One-acidic (NaOH);

Two-acidic ($Ca(OH)_2$);

Three-acidic ($Cr(OH)_3$) and so on.

Preparation

1. Interaction of alkaline and alkaline-earth metals and water forming alkalis and free Hydrogen:

$2K + 2H_2O = 2KOH + H_2$;

$Ba + 2H_2O = Ba(OH)_2 + H_2$;

2. Direct interaction of alkaline and alkaline-earth metals oxides and water forming the alkalis:

$Na_2O + H_2O = 2NaOH$;

$CaO + H_2O = Ca(OH)_2$;

3. Insoluble bases may be prepared by interaction between soluble salts of corresponding metals and alkali solution:

$Cu(NO_3)_2 + 2LiOH = Cu(OH)_2\downarrow + 2LiNO_3$;

$Fe_2(SO_4)_3 + 3Ca(OH)_2 = 2Fe(OH)_3\downarrow + 3CaSO_4$.

Chemical properties

1. Interaction with acidic oxides forming the salts and water:

$2LiOH + SO_3 = Li_2SO_4 + H_2O$;

$Ca(OH)_2 + N_2O_5 = Ca(NO_3)_2 + H_2O$;

2. Interaction with acids forming the salts and water:

$2LiOH + H_2SO_4 = Li_2SO_4 + 2H_2O$;

$Ca(OH)_2 + 2HNO_3 = Ca(NO_3)_2 + 2H_2O$;

3. Interaction with amphoteric oxides forming the salts and water:

$2KOH + ZnO = K_2ZnO_2 + H_2O$;

$3Ba(OH)_2 + Al_2O_3 = Ba_3(AlO_3)_2 + 3H_2O$;

4. Interaction with amphoteric hydroxides forming the salts and water:

$3NaOH + Cr(OH)_3 = Na_3CrO_3 + 3H_2O$;

$Ca(OH)_2 + Sn(OH)_2 = CaSnO_2 + 2H_2O$;

5. Alkalis react with some salts:

$2NH_4Cl + Sr(OH)_2 = 2NH_4OH + SrCl_2$;

$Fe_2(SO_4)_3 + 6LiOH = 2Fe(OH)_3 + 3Li_2SO_4$.

6.5 Acids

Acids are the complex substances, consisting from Hydrogen atoms and acid radical (residue).

According to quantity of H^+ *(basicity)* acids may be divided into:

One-basic (HCl, HNO_3, $HClO_4$, CH_3–COOH etc.);

Two-basic (H_2CO_3, H_2SO_3, H_2SO_4 etc.);

Three-basic (H_3BO_3, H_3PO_4, H_3AsO_4 etc.);

Four-basic (H_4SiO_4, $H_4P_2O_7$ etc.).

There are two types of acids depending on their chemical composition: *Oxyacids* - contain Oxygen (the most of acids - H_2CO_3, H_2SiO_3, HNO_3, H_3PO_4, H_2SO_3, H_2SO_4, $HClO_4$ etc.) and *Oxygen-free acids* (HF, HCl, HBr, HI, H_2S, H_2Se, HCN, HSCN etc.).

Oxyacids are hydrated forms of acidic oxides (anhydrides). The most of such oxides may react with water directly forming hydrates - acids. For example, Sulfuric acid is a hydrate of Sulfur (VI) oxide.

The total characteristics of the usual acids are presented in **Appendix 4.**

Preparation

1. Oxygen-free acids may be prepared by interaction between corresponding non-metals and free Hydrogen and following dissolution of gaseous products in water:

$H_2 + Cl_2 = 2HCl$;

$H_2 + S = H_2S$;

2. Oxygen-free acids are synthesized by action of strong acids **to** corresponding salts of Oxygen-free acids:

$CaF_2 + H_2SO_4 = CaSO_4 + 2HF;$

$FeS + 2HCl = FeCl_2 + H_2S;$

3. Interaction of acidic oxides (anhydrides) with water:

$SO_3 + H_2O = H_2SO_4;$

$Cl_2O_7 + H_2O = 2HClO_4;$

4. If anhydrides do not react with water directly, the corresponding acids may be prepared by action of strong acids to responding soluble salt of needed acid:

$H_2SO_4 + Na_2SiO_3 = Na_2SO_4 + H_2SiO_3;$

$2HCl + Na_2WO_4 = 2NaCl + H_2WO_4.$

Chemical properties

1. Interaction with basic oxides with formation of salts and water:

$2HNO_3 + CuO = Cu(NO_3)_2 + H_2O;$

$3H_2SO_4 + Fe_2O_3 = Fe_2(SO_4)_3 + 3H_2O;$

2. Interaction with amphoteric oxides with formation of salts and water:

$2HCl + ZnO = ZnCl_2 + H_2O;$

$6HClO_4 + Al_2O_3 = 2Al(ClO_4)_3 + 3H_2O;$

3. Interaction with bases with formation of salts and water:

$H_2CO_3 + Ca(OH)_2 = CaCO_3 + 2H_2O;$

$2H_3PO_4 + 3Mg(OH)_2 = Mg_3(PO_4)_2 + 6H_2O;$

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

$2HNO_3 + Pb(OH)_2 = Pb(NO_3)_2 + 2H_2O;$

$3H_2SO_4 + 2Cr(OH)_3 = Cr_2(SO_4)_3 + 6H_2O;$

5. Interaction with metals (Red Ox reactions):

$Zn + 2HCl = ZnCl_2 + H_2\uparrow;$

$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO\uparrow + 4H_2O;$

6. Interaction of weaker acid salts (metathesis or exchange reaction):

$FePO_4 + 3HNO_3 = Fe(NO_3)_3 + H_3PO_4;$

$H_2SO_4 + BaCl_2 = BaSO_4 + 2HCl.$

6.6 Amphoteric hydroxides

Amphoteric hydroxides are the hydrated forms of amphoteric oxides having weak basic and acidic properties.

Preparation

1. Interaction with acidic oxides forming **salts** and water (amphoteric hydroxides show properties of bases):

$Zn(OH)_2 + N_2O_5 = Zn(NO_3)_2 + H_2O$;

$2Cr(OH)_3 + 3SO_3 = Cr_2(SO_4)_3 + 3H_2O$.

2. Interaction with acids forming salts and water (amphoteric hydroxides show properties of bases):

$Zn(OH)_2 + 2HNO_3 = Zn(NO_3)_2 + 2H_2O$;

$2Cr(OH)_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 6H_2O$.

3. Interaction with basic oxides forming salts and water (amphoteric hydroxides show properties of acids):

for $Zn(OH)_2$: $H_2ZnO_2 + Li_2O = Li_2ZnO_2 + H_2O$

for $Cr(OH)_3$: $2HCrO_2 + BaO = Ba(CrO_2)_2 + H_2O$ or

$2H_3CrO_3 + 3BaO = Ba_3(CrO_3)_2 + 3H_2O$;

4. Interaction with bases forming salts and water (amphoteric hydroxides show properties of acids):

for $Zn(OH)_2$: $H_2ZnO_2 + 2LiOH = Li_2ZnO_2 + 2H_2O$

for $Cr(OH)_3$: $2HCrO_2 + Ba(OH)_2 = Ba(CrO_2)_2 + 2H_2O$ or

$2H_3CrO_3 + 3Ba(OH)_2 = Ba_3(CrO_3)_2 + 6H_2O$;

Depending on series of chemical reaction, names of amphoteric hydroxides are changed. For example, $Zn(OH)_2$ in reactions with acidic oxides and acids must be referred to "Zinc hydroxide", while in reactions with basic oxides and alkalis - "Zinc acid" (see **Appendix 4)**.

6.7 Salts

Salts - complex substances, which consist of metal atoms and acid residuals. This is a most multiple class of inorganic compounds. Sometimes salts may include positive charged group of atoms (for example, NH_4^+).

Classification of salts:

Varieties	**Characteristics**	**Examples**
Neutral (normal)	Include atoms of metal (or ionic group NH_4^+) and acid residue. Products of full substitution of Hydrogen atoms in acids to metal atoms	NaCl, $Ca_3(PO_4)_2$, K_3AlO_3
Basic	Include atoms of metal (or ionic group NH_4^+), hydroxyl OH^- and acid residue. Products of incomplete substitution of OH-groups of multi-acidic bases into acid residue	ZnOHCl, $(MgOH)_2SO_4$, $(MgOH)_3PO_4$, $FeOHBr_2$
Acidic	Include atoms of metal (or ionic group NH_4^+), ion H^+ and acid residue. Products of incomplete substitution of H^+ of multi-basic acids into atoms of metal or NH_4^+	$NaHCO_3$, $NH_4H_2PO_4$, $Ca(H_2PO_4)_2$, $KHSO_4$

Double	Include atoms of two different metals and acid residue	$NaKSO_4$, $KAl(SO_4)_2$, $NH_4Cr(SO_4)_2$.
Mixed	Include atoms of metal and two different acid residues	$CaCl(ClO)$
Complex	Contain complex cations or anions	$[Ag(NH_3)_2]Cl$, $Na_3[Co(NO_2)_6]$

Salts are entitled starting from the name of corresponding metal and acid residue (See **Appendix 4**). For example, $Ca_3(PO_4)_2$ - Calcium OrthoPhosphate, $NaNO_3$ - Sodium Nitrate, $KHSO_4$ - Potassium HydroSulfate, $FeOHCl_2$ - Iron (III) Hydroxy Chloride etc.

A few salts and chemical compounds or mixes have common names as household (domestic) chemicals or technical reactants. Sometimes names of such chemicals were given by Alchemists in great antiquity (for example, $BaSO_4$ (Barium Sulfate) - Heavy Spar, Aqua-regia - Mixture of conc. HNO_3 (1 volume) and conc. HCl (3 volumes) etc. (See **Appendix 12**).

Preparation

There are known a lot of methods for salts' preparations. The typical ones are mentioned below:

1. Interaction between metals and non-metals (Sulfur, Halogens):
   $Zn + S = ZnS$
   $2Bi + 3Cl_2 = 2BiCl_3$;
2. Interaction between salts and metals (according to relative activity of Metals, see **Appendix 11**):
   $CuSO_4 + Fe = FeSO_4 + Cu$;
   $Pb(NO_3)_2 + Zn = Zn(NO_3)_2 + Pb$;
3. Interaction between some salts and non-metals:
   $2FeCl_2 + Cl_2 = 2FeCl_3$;
   $2Na_2SO_3 + O_2 = 2Na_2SO_4$;
4. Interaction between basic oxides and acidic oxides:
   $CaO + CO_2 = CaCO_3$;
   $3Na_2O + P_2O_5 = 2Na_3PO_4$;
5. Interaction between acids and basic oxides:
   $H_2SO_4 + MgO = MgSO_4 + H_2O$;
   $6HCl + Fe_2O_3 = 2FeCl_3 + 3H_2O$;
6. Interaction between bases and acidic oxides:
   $Ba(OH)_2 + SO_2 = BaSO_3 + H_2O$;
   $2Fe(OH)_3 + 3N_2O_5 = 2Fe(NO_3)_3 + 3H_2O$;
7. Interaction between acids and bases:

$HNO_3 + NaOH = NaNO_3 + H_2O$;
$H_3PO_4 + 3KOH = K_3PO_4 + 3H_2O$;

8. Interaction between stronger acids and salts of weaker acids:
   $H_2SO_4 + K_2SiO_3 = K_2SO_4 + H_2SiO_3$;
   $HBr + AgNO_3 = AgBr + HNO_3$;
9. Interaction between alkalis and salts:
   $2LiOH + CuCl_2 = Cu(OH)_2 + 2LiCl$;
   $Ca(OH)_2 + NiSO_4 = CaSO_4 + Ni(OH)_2$;
10. Interaction between two different salts (metathesis reaction):
    $2AgNO_3 + CaI_2 = 2AgI + Ca(NO_3)_2$;
    $Cr_2(SO_4)_3 + 3BaCl_2 = 2CrCl_3 + 3BaSO_4$.

Chemical properties

1. Interaction with some of the acids with the formation of other salt and acid:
   $BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl$;
   $Na_2S + H_2SO_4 = Na_2SO_4 + H_2S$;
2. Interaction with alkalis with the formation of other salt and base:
   $NiSO_4 + 2KOH = Ni(OH)_2 + K_2SO_4$;
   $2FeCl_3 + 3Ba(OH)_2 = 2Fe(OH)_3 + 3BaCl_2$;
3. Interaction with more active metals:
   $Zn + CuSO_4 = ZnSO_4 + Cu$;
   $Cu + Hg(NO_3)_2 = Cu(NO_3)_2 + Hg$;
4. **Some** salts may react with each other forming two new salts:
   $Ba(NO_3)_2 + K_2CO_3 = BaCO_3 + 2KNO_3$;$AlCl_3 + 3AgNO_3 = Al(NO_3)_3 + 3AgCl$.

Basic salts

Basic salts may form only such bases that have two and more groups OH-. They are products of incomplete substitution of OH--groups of corresponding bases to acid residues.

Preparation

1. Hydrolysis of neutral salts formed by weak base and strong acid:

$ZnCl_2 + HOH \leftrightarrow ZnOHCl + HCl$;
$2 CuSO_4 + 2 HOH \leftrightarrow (CuOH)_2SO_4 + H_2SO_4$.

2. By addition (by drops) of small quantities of alkalis to solutions of neutral salts of metals:

$AlCl_3 + 2NaOH = Al(OH)_2Cl + 2NaCl$;
$Ca(NO_3)_2 + NaOH = CaOHNO_3 + NaNO_3$.

3. Interaction with salts formed weak acids with medium salts:

$2MgCl_2 + 2Na_2CO_3 + H_2O = (MgOH)_2CO_3\downarrow + CO_2\uparrow + 4NaCl$;

$2CuSO_4 + 2(NH_4)_2SO_3 + H_2O = CuOH)_2SO_3\downarrow + SO_2\uparrow + (NH_4)_2SO_4$.

4. In a few cases by interaction of neutral salts with bases of the same name:

$CaCl_2 + Ca(OH)_2 = 2Ca(OH)Cl$;

$Ba(NO_3)_2 + Ba(OH)_2 = 2BaOHNO_3$.

Chemical properties

1. Interaction with acids or acidic oxides forming neutral salts and water (likewise bases):

$2Mg(OH)NO_3 + N_2O_5 = 2Mg(NO_3)_2 + H_2O$;

$Mg(OH)NO_3 + HNO_3 = Mg(NO_3)_2 + H_2O$.

2. Thermal decomposition:

$(CuOH)_2CO_3 \xrightarrow{t} 2\,CuO + CO_2 + H_2O$;

$2\,CaOHCl \xrightarrow{t} CaCl_2 + H_2O + CaO$.

3. Some salts may (weaken) loose water with the formation of so-called oxysalts with time or on heating:

$Bi(OH)_2Br \rightarrow BiOBr + H_2O$.

Acidic salts

Acid salts are the products of partial replacement of Hydrogen in acids for atoms of metals or ionic groups. Acid salts may form only such acids that have two and more atoms of Hydrogen.

Preparation

1. Interaction of acid with the deficit of base:

$NaOH + H_2SO_4 = NaHSO_4 + H_2O$;

2. Interaction of bases with acid oxides in large excess:

$Ca(OH)_2 + 2\,CO_2 = Ca(HCO_3)_2$;

3. Interaction of medium salts with acid (more with the same anion):

$Ca_3(PO_4)_2 + 4H_3PO_4 = 3\,Ca(H_2PO_4)_2$.

Chemical properties

1. Interaction with basic oxides with forming of neutral salts and water:

2NaHSO4 + Na2O = 2Na2SO4 + H2O;

2. Interaction with amphoteric oxides with forming of neutral salts and water:

$Zn(HSO_4)_2 + ZnO = 2ZnSO_4 + H_2O$;

3. Interaction with bases with forming of neutral salts and water:

$NaHSO_4 + NaOH = Na_2SO_4 + H_2O$;

$Ca(H_2PO_4)_2 + 2\,Ca(OH)_2 = Ca_3(PO_4)_2\downarrow + 3\,H_2O$.

4. Interaction with amphoteric hydroxides with forming of salts and water:
$Zn(HSO_4)_2 + Zn(OH)_2 = 2ZnSO_4 + 2H_2O$;
5. Interaction with active metals with forming of neutral salts and free Hydrogen isolation:
$2NaHSO_4 + 2Na = Na_2SO_4 + H_2\uparrow$
6. Thermal decomposition with medium salts formation:
$Ca(HCO_3)_2 \rightarrow CaCO_3\downarrow + CO_2\uparrow + H_2O$.

Double and mixed salts may be considered as the sort of neutral salts. Double salts may be prepared by interaction between any multibasic acid and different bases:

$$H_2SO_4 + KOH + NaOH = NaKSO_4 + 2H_2O.$$

or during synchronous crystallization of different salts:

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O = 2KAl(SO_4)_2{\cdot}24H_2O.$$

Mixed salts may be prepared by interaction of multiacidic bases and different acids. For example, preparation of bleaching powder:

$$Ca(OH)_2 + HCl + HClO = CaCl(ClO) + H_2O.$$

6.8 Structural-graphic formulas of chemical compounds

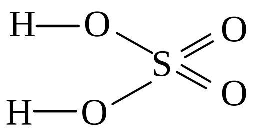
These schemes show the order of atom combination in molecules of substance.

The rules for graphic formula’s compilation are the following:

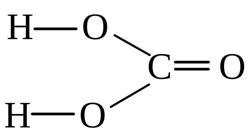
- It may directly connect ions to opposite charges only;
- Quantity of chemical bonds for each atom is equal to its charges (modulo) in most cases.

For example:

H_2SO_4; $H^{+}_{2}\,S^{6+}\,O^{2-}_{4}$

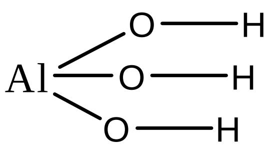


H_2SO_4

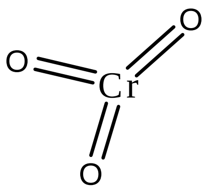


H_2CO_3

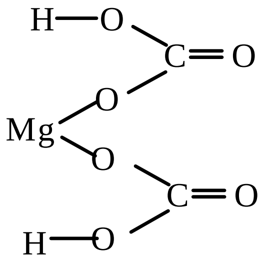
$Al(OH)_3$; $Al^{3+}(O^{2-}H^{+})_3$ or $H^{+}_{3}Al^{3+}O^{2-}_{3}$

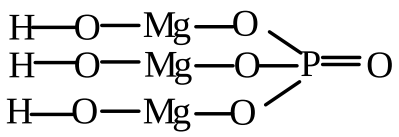


CrO_3; $Cr^{6+}O^{2-}_3$

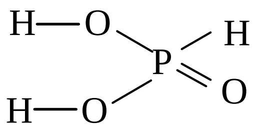


$Mg(HCO_3)_2$; $Mg^{2+}(H^{+}C^{4+}O^{2-}_3)_2$

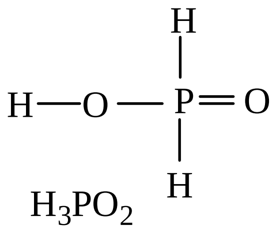




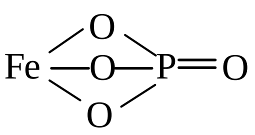
$(MgOH)_3PO_4$



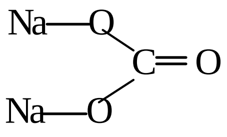
H_3PO_3



H_3PO_2



$FePO_4$



Na_2CO_3

PRACTICE PROBLEMS

1. To determine the oxidation numbers of elements in compounds: Fe_2O_3, H_2S, FeS, HNO_2, $H_4P_2O_7$, $Ca_3(PO_4)_2$, $Fe_2(SO_4)_3$, $Ni(NO_3)_3$, Na_3AlO_3, $KAlO_2$, $LiFe(SO_4)_2$, $CaHAsO_4$, Na_2O_2, $MnSO_3$, $(NH_4)H_2PO_4$.

2. Which oxides may react with water directly: BaO, Cu_2O, P_2O_5, SO_3, SO_2, K_2O, N_2O_3, CoO, Cl_2O_7, ZnO, NO_2, SiO_2, MnO_2, FeO, SrO? To write the corresponding equations of chemical reactions.

3. Which oxides do correspond to the next compounds: H_2SO_3, $Ca(OH)_2$, NaOH, $Fe(OH)_3$, HNO_3, $Co(OH)_3$, $H_4P_2O_7$, CuOH, NAOH, $CaBeO_2$, $HMnO_4$, H_2CrO_4, K_2MnO_4?

4. To compile equations for the transformations given below:

$Al \rightarrow Al_2O_3 \rightarrow Al(NO_3)_3 \rightarrow Al_2(SO_4)_3 \rightarrow Al(OH)_3$;

$Zn \rightarrow ZnO \rightarrow ZnSO_4 \rightarrow Zn(OH)_2 \rightarrow K_2ZnO_2 \rightarrow ZnCl_2 \rightarrow Zn_3(PO_4)_2 \rightarrow Na_2ZnO_2$.

5. To compile structural-graphic formulas of chemical compounds given below:

Cr_2O_3, $Ni(OH)_3$, H_3PO_4, $Al_2(SO_4)_3$, $Ca_3(PO_4)_2$.

1. What oxides may react with each other (by pairs): Na_2O, CaO, SO_2, H_2O, P_2O_3, ZnO?

2. To write reactions for conversing of Iron (III) Dihydroxychloride and Calcium Dihydrophosphate in neutral salts.

3. To write all possible reactions between: a) Aluminium Hydroxide and Orthophosphoric Acid; b) Barium Oxide and Sulfuric Acid (taking into account the possibility of neutral, acidic and basic salts forming).

EXAMPLE OF SOLUTION

1. To compile equations for the following transformations:

$Al \rightarrow AlCl_3 \rightarrow Al(OH)_3 \rightarrow Na_3AlO_3 \rightarrow Al_2(SO_4)_3 \rightarrow AlPO_4 \rightarrow Al_2O_3$.

An initial substance is Aluminium; each next substance is formed in the result of reaction and become itself the initial one for the next transformation. Therefore it will be at least six equations of reactions:

$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2$;

$AlCl_3 + 3NH_4OH \rightarrow Al(OH)_3 + 3NH_4Cl$;

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

$2Na_3AlO_3 + 6H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3Na_2SO_4 + 6H_2O$;

$Al_2(SO_4)_3 + 2K_3PO_4 \rightarrow 3K_2SO_4 + 2AlPO_4$;

$2AlPO_4 \xrightarrow{t} Al_2O_3 + P_2O_5$.

2. To compile equations of reactions for the next transformations:

$P \rightarrow P_2O_5 \rightarrow Ca_3(PO_4)_2 \rightarrow Ca(H_2PO_4)_2 \rightarrow H_3PO_4 \rightarrow (NH_4)_2HPO_4$.

$4P + 5O_2 \rightarrow 2P_2O_5$;

$P_2O_5 + 3CaO \rightarrow Ca_3(PO_4)_2$;

$Ca_3(PO_4)_2 + 4H_3PO_4 \rightarrow 3Ca(H_2PO_4)_2$;

$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4 + 2H_3PO_4$;

$H_3PO_4 + 2NH_3 \rightarrow (NH_4)_2HPO_4$.

3. To write all possible reactions between Calcium Hydroxide and Orthophosphoric Acid.

Since $Ca(OH)_2$ is a two-acidic base and H_3PO_4 – three-basic acid, it is possible to form one neutral salt, two acidic salts and one basic salt:

$3Ca(OH)_2 + 2H_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6H_2O$;

$Ca(OH)_2 + 2H_3PO_4 \rightarrow Ca(H_2PO_4)_2 + 2H_2O$;

$Ca(OH)_2 + H_3PO_4 \rightarrow CaHPO_4 + 2H_2O$;

$3Ca(OH)_2 + H_3PO_4 \rightarrow 3(CaOH)_3PO_4 + 3H_2O$.

LABORATORY TRAINING

Experiment 1. Interaction between oxides and water

To add a few grains of solid CaO, CuO, ZnO (total volume of each chemicals - near one match-head) into three tubes. To add 10-20 drops of distilled water into each tube. To mix a tube content. What oxides do directly react with water? To write a corresponding reaction.

Experiment 2. Preparation of insoluble hydroxides

To add separately 1-4 drops of each soluble Iron (III) salts ($FeCl_3$ or $Fe_2(SO_4)_3$), Copper ($CuSO_4$ or $CuCl_2$ or $Cu(NO_3)_2$), Manganese (II) ($MnSO_4$ or $MnCl_2$), and Nickel ($NiSO_4$), Cobalt (II) ($CoSO_4$ or $CoCl_2$) into tubes #1, 2, 3, 4, 5. To add 1-2 drops of any alkali into each tube. What do you observe? To write corresponding reactions. To point out color of precipitate in each tube. To explain why color of Manganese (II) Hydroxide is changed.

Experiment 3. Preparation of amphoteric hydroxides

To add 1 drop of any alkali (NaOH or KOH) into three tubes. To add by drops the solution of Aluminium salt (for example, $Al_2(SO_4)_3$) into tube # 1 up to the precipitate appearance; into tube # 2 - Zinc salt (for example, $ZnSO_4$) analogously to previous case; into tube # 3 - Chromium (III) salt (for example, $Cr_2(SO_4)_3$). To divide each prepared precipitate into two tubes. To add solution of any acid (for example, HNO_3) to the first part of precipitate, alkali solution up to the whole dissolving of precipitate - to the second one. What do you observe? To write corresponding reactions.

Experiment 4. Interaction of salts solution (metathesis)

To add 2-3 drops of $BaCl_2$ solution into tube # 1 and to drop the same quantity of Sodium Sulfate; 2-3 drops of Lead (II) Nitrate - into tube # 2 and to add 1-2 drops of Potassium Iodide; 2-3 drops of Cobalt (II)

Sulfate into tube # 3 and to add 1-2 drops of Sodium HydroPhosphate. What do you observe? To write corresponding reactions.

To prepare a report of laboratory work in the next form:

LABORATORY WORK #1.

Chapter. *Classification of inorganic substances*

Condition of experiment	Visual effect	Equation	Conclusions
Experiment 1. Interaction of oxides with water			
To add a few grains of solid CaO, CuO, ZnO into three tubes. To add 10-20 drops of distillated water into each tube. To mix a tube content.	Solid CuO and ZnO are not dissolved in water. CaO is dissolved in water; content of the first tube become clear.	$CaO + H_2O = Ca(OH)_2$	Only oxides of earth-alkaline metals may react with water directly forming the alkalis.

CHAPTER # 7. THEORY OF ELECTROLYTIC DISSOCIATION

Vocabulary

English	Українська назва	English	Українська назва
Hydration	*Гідратація*	*Degree of dissociation*	*Ступінь дисоціації*
Solvent	*Розчинник*	*Electrolyte*	*Електроліт*
Ionization	*Іонізація*	*Conductivity*	*Провідність*
Dissociation	*Дисоціація*	*Ion*	*Іон*
Doublet	*Диполь*		

7.1 Solutions

Suppose a lump of sugar is dropped into a glass of water. You know from experience that the sugar will dissolve. Sugar is described as “soluble in water”. By “soluble” we mean the capability of being dissolved. Examination of sugar-water mixture, even under a microscope, would not reveal any particles of sugar. Such a mixture is called **“solution”**. Solution is a homogenous mixture of two or more substances in a single phase. In solution, atoms, and molecules of charged particles - ions are thoroughly mixed, with the result that the mixture has the same composition and properties throughout.

In the simplest type of solution, such as sugar-water solution, the molecules of one substance are distributed around the molecules of another one. The dissolving medium in a solution is called **solvent**, and the substance dissolved in a solution is called **solute**. In general, the solute is the substance, which mass is less than 50% of total mass of solution.

Types of solutions. Solutions are formed in all three states - gaseous, liquid, and solid. Nine possible combinations of gases, liquids, and solids in solutions are summarized in Table 10.

Table 10. Types of solutions

Solute	Solvent	Example
Gas	Gas	Air
Gas	Liquid	Soda Water
Gas	Solid	Hydrogen in platinum
Liquid	Gas	Water vapor in air (mist, fog)
Liquid	Liquid	Alcohol in water
Liquid	Solid	Mercury in Copper (amalgam)
Solid	Gas	Sulfur vapor in air
Solid	Liquid	Sugar in water
Solid	Solid	Copper in nickel (different types of alloys)

7.2 Concentration of solutions

The concentration of solution is the measurement of the amount of solute in a given amount of solvent or solution. Some medications are solutions of drugs - one-teaspoonful dose at correct concentration might cure the condition; the same dose in the wrong concentration might kill the patient.

Sometimes solutions are referred as “concentrated” or “diluted”. These are relative terms. “Diluted” means that there is relatively small amount of solute in solvent. “Concentrated”, on the other hand, means that these terms are unrelated to the degree in which the solution is saturated. Saturated solution of substance that is not very soluble might be very diluted.

Percent by Mass (mass concentration, percent concentration)

Percent by Mass (P) of a solute in solution is the number of grams of solute dissolved in 100 g of solution. For example, the percent by mass of a solution made from 10 g of Sodium Hydroxide (NaOH) dissolved in 90 g of water is found as follows:

$$P = \frac{\text{Mass of solute } m_s}{\text{mass of solute } m_s + \text{mass of solvent } m_{solv}} \times 100\% =$$

$$= \frac{10\text{ g NaOH}}{10\text{ g NaOH} + 90\text{ g H}_2\text{O}} \times 100\% = 10\ \%\ \text{NaOH (by mass)}.$$

Note that the mass of solution is the sum of the masses of the solute and solvent. Percent concentration is common for solutions used for practical purposes - household or industrial cleaning, killing pests in the garden, medical applications. Percent-by-mass concentration is based only on the mass of solute and is unrelated to its chemical formula of molar mass.

$$P = \frac{m_{solute}}{m_{solution}} \times 100\% \tag{6}$$

Molarity (molar concentration)

Molarity (M) is the number of moles of solute in one litre of solution. To find the molarity of a solution one must know the molar mass of the solute. For example, “one-molar” solution of Sodium hydroxide (NaOH) contains one mole of NaOH in each litre of solution. The concentration of the proceeding solution is written as 1 M NaOH.

One mole of Sodium hydroxide (NaOH) has a mass of 40 g/mol (see Chapter 1.2). This quantity of NaOH dissolved in enough water to make exactly 1,00 L of solution gives a 1 M solution. If 20,0 g of NaOH, which is 0,500 mol, is dissolved in 1,00 L of solution, 0,500 M NaOH solution is produced:

$$\textbf{Molarity} = \frac{\text{Number of moles of solute}}{\text{Number of Litres of Solution}} = \frac{\nu}{V} = \frac{0{,}500\ \text{mol NaOH}}{1{,}00\ \text{L}} =$$

= 0,500 M NaOH.

Note that one molar solution is not made by adding 1 mol of solute to 1 L of solvent. In such case, the final total volume would be slightly different from 1 L. Instead of this 1 mol of salute is firstly dissolved in less than 1 L of solvent. Then, the resulting solution is carefully diluted with more solvent to bring the total volume to 1 L, using volumetric flask.

Molarity is useful when the quantity of solute participating in a chemical reaction taking place in solution is of interest. Any required molar quantity of the solute can be selected by measuring out the appropriate volume of the solution of known molarity.

$$\text{M} = \frac{\nu}{V} = \frac{\text{mass of solute}}{\text{Molar mass of solute} \times \text{Volume of solution in Litres}} \quad \text{or}$$

$$\boldsymbol{M = \frac{m_{solute}}{M_{solute} \times V}} \tag{7}$$

Normality (normal concentration)

The concentration of solutions can be expressed by stating the quantity of the solute in equivalents rather than in moles. This measurement of concentration is called Normality (N). The normality of solution is the number of equivalents (υ_E) of solute per litre (V) of solution:

$$\textbf{Normality} = \frac{\text{Number of equivalents of solute}}{\text{Number of Litres of Solution}} = \frac{\nu_E}{V}.$$

The normality of an acid or base solution is commonly expressed using the number of H^+ or OH^- ions available for a complete neutralization. Therefore:

$$E_{acid} = \frac{M_{acid}}{\text{number of hydrogen atoms in acid}},$$

$$E_{base} = \frac{M_{base}}{\text{number of OH groups in base}}.$$

For neutral salts equivalent mass may be expressed as:

$$E_{\text{neutral salt}} = \frac{M_{\text{neutral salt}}}{\text{number of atoms of metals in salt} \times \text{Valency of metals}},$$

where E_{acid}, E_{base}, $E_{\text{neutral salt}}$ - equivalent mass of acid, base or neutral salt respectively, g/g-eq;

M_{acid}, M_{base}, $M_{\text{neutral salt}}$ - molar mass of acid, base or neutral salt respectively, g/mol.

So, $\upsilon_E = \frac{m_{solute}}{E_{solute}}$ and

$$N = \frac{m_{solute}}{E_{solute} \times V} \tag{8}$$

Titre

Titre (T) is a special unit for measuring of concentration connected with chemical quantitative analysis. Titre is the number of grams of solute in 1 millilitre of solution. For example, the titre of a solution made from 0,3 g of Silver Nitrate ($AgNO_3$) dissolved in 150 mL of solution is found as follows:

$$T = \frac{\text{Mass of solute } m_s \text{ in grams}}{\text{Volume of solution in mililiters}} =$$

$$= \frac{0{,}3 \text{ g } AgNO_3}{1150 \text{ mL of soution}} = 0{,}002 \text{ g/mL}.$$

So,

$$T = \frac{m_{\text{solute in g}}}{V_{\text{solution in mL}}} \tag{9}$$

Table 11. Interconnection of concentration units

Measuring unit		Formulas for re-calculation			
Name	Symbol	**M**	**N**	**T**	**P**
Molarity (molar concentration)	**M**	-	$\frac{N \cdot E}{M_r}$	$\frac{T \cdot 1000}{M_r}$	$\frac{P \cdot 10d}{M_r}$
Normality (normal concentration)	**N**	$\frac{M \cdot M_r}{E}$	-	$\frac{T \cdot 1000}{E}$	$\frac{P \cdot 10d}{E}$
Titre	**T**	$\frac{M \cdot M_r}{1000}$	$\frac{N \cdot E}{1000}$	-	$\frac{P \cdot d}{100}$
Percent by Mass (mass concentration)	**P**	$\frac{M \cdot M_r}{10d}$	$\frac{N \cdot E}{10d}$	$\frac{T \cdot 100}{d}$	-

M_r - relative molar mass of solute, g/mol;

E - equivalent mass of solute, g/g-eq;

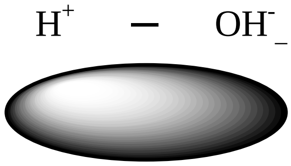
d - density of solution, g/L.

7.3 Theory of dissociation

It is experimentally established that solutions of certain substances in water may conduct an electric current (for example, solution of table salt in water) while the solution of sugar may not. The first group of substances was named **electrolytes**, the second one - **non-electrolytes**.

In order to understand the unique properties of electrolyte solutions, we will look briefly at the theory of Svante Arrhenius (1859-1927). His work forms the basis of the modern theory of ions in aqueous solutions, the solutions in which water is the solvent. Arrhenius considered the ions to be electrically charged. As a whole the solution contains equal numbers of positive and negative charges. He concluded that ions were produced by "ionization" of molecules in aqueous solution.

Water - solvent in aqueous solution - is not inert component. The polarity of water molecules plays an important role in the formation of solutions of ionic compounds in water. Molecule of H_2O is a polar particle called **"doublet":**



The charged ends of water molecules attract the ions in the ionic compounds and bring them into solution. The energy released when an ion is attracted to a water molecule also affects the heat of solution of the ionic compound in water.

The solution process for ionic compounds. Suppose we drop a few crystals of Sodium Chloride into a beaker of water. At the crystal surface, water molecules come into contact with Na^+ and Cl^- ions. The positive ends of the water molecules are attracted to Cl^- ions; the negative ends are attracted to Na^+ ions. The attraction between water molecules and the ions is strong enough to draw the ions away from the crystal surface and into solution, as illustrated in Fig. 15.

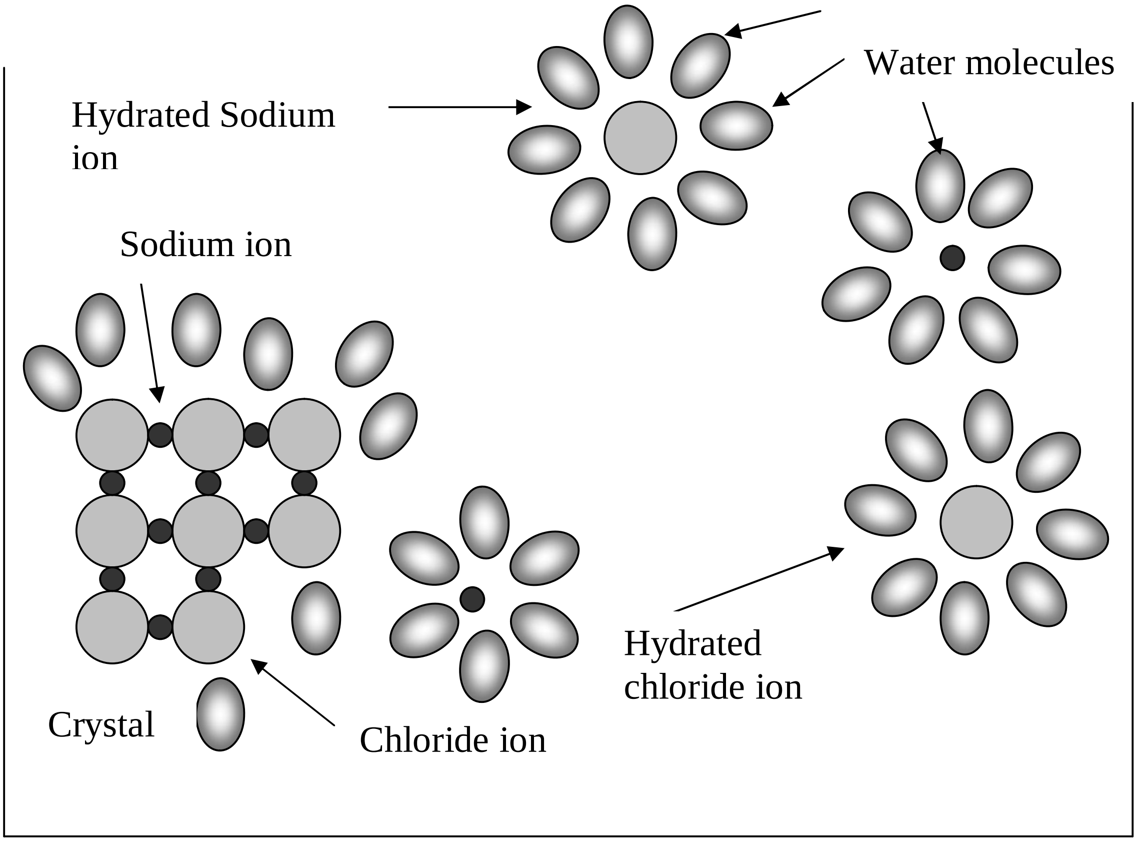


Figure 15. Table salt (Sodium Chloride) dissolves in water forming hydrated Sodium and Chloride ions

This solution process with water as the solvent is referred to as **hydration**. The ions are said to be **hydrated**. The attraction between ions and water molecules is strong enough that each ion in solution remains surrounded by water molecules.

The separation of ions that occurs when an ionic compound dissolves is called **dissociation** (means disintegration, decay, decomposition). The equations representing the dissociation of Sodium Chloride in water are:

$$\text{NaCl (s)} \xleftrightarrow{H_2O} \text{Na}^+ \text{ (aq)} + \text{Cl}^- \text{ (aq)}$$

where (s) - solid phase;

(aq) - aqueous solution

or in simplified form

$$\text{NaCl} \longleftrightarrow \text{Na}^+ + \text{Cl}^-.$$

7.4 Degree of dissociation

Degree of dissociation (α) of electrolyte is the ratio:

$$\alpha = \frac{\text{Number of dissociated molecules of electrolyte}}{\text{Total number of dissolved molecules of electrolyte in solution}}.$$

α measures in percents (0…100%) or per unit (0…1). Degree of dissociation depends on:

- nature of chemical bonds in solute and solvent;
- concentration of solute;
- Temperature of solution.

The main trends of these interdependences are:

1. Degree of dissociation is rising with decreasing of concentration of electrolyte;
2. Degree of dissociation is rising with rise in temperature.

Depending on degree of dissociation, all electrolytes are subdivided into three types: strong, medium and weak. This subdivision is relative, though.

Degree of dissociation of **strong electrolytes** is more than 30%, **medium** - from 3% till 30%, **weak** - less or equal than 3%. In **Appendix 9** it is presented the division of main classes of inorganic substances as electrolytes.

7.5 Main classes of inorganic substances from viewpoint of theory of electrolytic dissociation

Traditional definition of **an acid** according Arrhenius's theory: a chemical compound that contains Hydrogen and ionizes in aqueous solution to form Hydrogen ions:

$HCl \leftrightarrow H^+ + Cl^-$;

$HNO_3 \leftrightarrow H^+ + NO_3^-$.

An acid that can donate one proton (Hydrogen ion) per molecule is known as a monoprotic acid (like foregoing ones). Acids contained more than one proton per molecule are polyprotic and ionize in more than one stage. For example:

$H_2SO_4 \leftrightarrow H^+ + HSO_4^-$;	$H_3PO_4 \leftrightarrow H^+ + H_2PO_4^-$;
$HSO_4^- \leftrightarrow H^+ + SO_4^{2-}$;	$H_2PO_4^- \leftrightarrow H^+ + HPO_4^{2-}$;
	$HPO_4^{2-} \leftrightarrow H^+ + PO_4^{3-}$.

Traditional definition of **a base** according Arrhenius's theory: this is a substance that contains hydroxide ions (OH^-) and dissociates to give hydroxide ions in aqueous solutions:

$NaOH \leftrightarrow Na^+ + OH^-$;

$KOH \leftrightarrow K^+ + OH^-$.

A base that can donate one hydroxyl OH^- per molecule is known as a monohydroxyl base (alkalis) (like foregoing ones). Bases contained more than one OH^--group per molecule are polyhydroxyl and ionize in more than one stages. For example:

$Ca(OH)_2 \leftrightarrow CaOH^+ + OH^-$;

$CaOH^+ \leftrightarrow Ca^{2+} + OH^-$.

Neutral salts are dissociated with forming of metal cations (positive charged ions) and anions of acidic residues:

$CaCl_2 \leftrightarrow Ca^{2+} + 2Cl^-$;

$Fe_2(SO_4)_3 \leftrightarrow 2\,Fe^{3+} + 3SO_4^{2-}$;

$Ba(NO_2)_2 \leftrightarrow Ba^{2+} + 2NO_2^-$.

Acidic and basic salts are ionized in some steps as salts and corresponding acids or bases. For example:

Acidic salt NH_4HSO_4:

1 step - like neutral salt: $NH_4HSO_4 \leftrightarrow NH_4^+ + HSO_4^-$;

2 step - like acid: $HSO_4^- \leftrightarrow H^+ + SO_4^{2-}$.

Basic salt BaOHCl:

1 step - like neutral salt: $BaOHCl \leftrightarrow BaOH^+ + Cl^-$;

2 step - like base: $BaOH^+ \leftrightarrow Ba^{2+} + OH^-$.

All simple substances and oxides are weak electrolytes and do not dissociate in aqueous solutions.

7.6 Ionic equations

Double replacement reactions and other reactions of ions in aqueous solution are usually represented by that are known as “net ionic equations”. To write a net ionic equation, one firstly writes an equation in which all strong electrolytes are shown as dissociated ions in solution (without steps, of course). For example:

1. Formation of slightly soluble substance:

$CuSO_4 + 2NaOH = Cu(OH)_2\downarrow + Na_2SO_4$

$Cu^{2+} + \cancel{SO_4^{2-}} + \cancel{2Na^+} + 2OH^- = Cu(OH)_2\downarrow + \cancel{2Na^+} + \cancel{SO_4^{2-}}$ - this is a complete ionic equation.

$Cu^{2+} + 2OH^- = Cu(OH)_2\downarrow$ - this is net ionic equation.

2. Formation of weak electrolyte:

a) $HCl + KOH = KCl + H_2O$,

$H^+ + \cancel{Cl^-} + \cancel{K^+} + OH^- = \cancel{K^+} + \cancel{Cl^-} + H_2O$,

$H^+ + OH^- = H_2O$.

b) $CH_3COONa + HCl = CH_3COOH + NaCl$,

$CH_3COO^- + \cancel{Na^+} + H^+ + \cancel{Cl^-} = CH_3COOH + \cancel{Na^+} + \cancel{Cl^-}$,

$CH_3COO^- + H^+ = CH_3COOH$.

3. Formation of gas:

a) $K_2CO_3 + 2HNO_3 = 2KNO_3 + CO_2\uparrow + H_2O$,

$\cancel{2K^+} + CO_3^{2-} + 2H^+ + \cancel{2NO_3^-} = \cancel{2K^+} + \cancel{2NO_3^-} + CO_2\uparrow + H_2O$,

$CO_3^{2-} + 2H^+ = CO_2\uparrow + H_2O$.

b) $FeS + 2HCl = FeCl_2 + H_2S\uparrow$.

Iron (II) Sulfide is slightly soluble and Hydrogen Sulfide is a weak electrolyte (gas). Therefore:

$FeS + 2\cancel{H^+} + 2Cl^- = \cancel{Fe^{2+}} + 2Cl^- + H_2S\uparrow$,

$FeS + 2H^+ = Fe^{2+} + H_2S\uparrow$.

Interactions in the solutions of electrolytes are realized completely if in the result the following will be formed:

а) weak electrolyte;
б) sediments;
в) gases.

PRACTICE PROBLEMS

1. Write the dissociation equation for the ions of the following compounds:

H_2SO_4, $HClO_4$, $Ca(OH)_2$, $AlCl_3$, $Fe_2(SO_4)_3$, K_2CO_3, $Bi(NO_3)_3$, Na_2HPO_4, NH_4HCO_3, $Co(NO_3)_3$.

2. Write molecular, complete and net ionic equations:
   - $BaCl_2 + Fe_2(SO_4)_3 \rightarrow$
   - $Cu(NO_3)_2 + Na_2CO_3 \rightarrow$
   - $Na_2SiO_3 + H_2SO_4 \rightarrow$
   - $FeCl_3 + KOH \rightarrow$
   - $H_3PO_4 + Ba(OH)_2 \rightarrow$
   - $Cu(OH)_2 + HCl \rightarrow$
   - $Na_2HPO_4 + CaCl_2 \rightarrow$
3. Which of two reactions does proceed in the solution up to the end and why? Draw the corresponding molecular, complete and net ionic equations:
   - Calcium Chloride + Magnesium Nitrate →
   - Sodium Carbonate + Zinc Chloride →
   - Lithium Sulfate + Potassium hydroxide →
   - Iron (II) Sulfate + Sodium hydroxide →
   - Iron (III) hydroxide + Nitric Acid →
4. Draw molecular equations of the reactions between substances interacted in aqueous solution according to the following scheme:
   - $Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4$;
   - $Fe(OH)_3 + 3H^+ \rightarrow Fe^{3+} + 3H_2O$;

- $CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$;
- $3Mg^{2+} + 2PO_4^{3-} \rightarrow Mg_3(PO_4)_2$;
- $Ca^{2+} + 2\ F^- \rightarrow CaF_2$.

LABORATORY TRAINING

Experiment 1. Slightly soluble substances production

A) Put separately 5-6 drops of Na_2SO_4, $(NH_4)_2CO_3$, Na_3PO_4 solutions into three test-tubes and add 3-4 drops of $BaCl_2$ solution into each of them. What does happen? Draw molecular and net ionic equations.

B) Put 5-6 drops of $CuSO_4$ and $Cu(NO_3)_2$ solutions into two test-tubes. Add 4-5 drops of NaOH solution into one test-tube and 4-5 drops of $Ba(OH)_2$ into another. What does happen? Draw molecular and net ionic equations.

Experiment 2. Weak electrolytes production

Put 5-6 drops of CH_3COONa and $Pb(CH_3COO)_2$ solutions into two test-tubes, add 5-6 drops of 2 N HCl or 2 N H_2SO_4 into each of them. Heat the mixture and identify by odor the acetic acid vapor isolation. Draw molecular and net ionic equations.

Experiment 3. Gases production

A) Put 5-6 drops of NH_4Cl into the test-tube; add the same volume of NaOH. Heat the mixture on water bath. Identify by odor the kind of gas. Draw molecular and net ionic equations.

B) Put 0,01 - 0,02 g of $CaCO_3$ or $BaCO_3$ solid salt into the test-tube and add 4-5 drops of 2 N HCl solution. What does happen? Draw molecular and net ionic equations.

Experiment 4. Properties of amphoteric hydroxides and their production

Produce $Zn(OH)_2$ precipitation in two test-tubes by adding drops of $ZnSO_4$ solution to 1-2 drops of NaOH solution to forming of sediment. Add 5-6 drops of 2 N HCl into one test-tube and 5-6 drops of 2 N NaOH into another. What does happen with $Zn(OH)_2$ precipitation? Draw molecular and net ionic reactions of $Zn(OH)_2$ production and its dilution in acid and alkali.

CHAPTER # 8. IONIC PRODUCT OF WATER. HYDROLYSIS OF SALTS

Vocabulary

English	Українська назва	English	Українська назва
Ionic product	*Іонний добуток*	*Methyl orange*	*Метилоранж*
Acidity	*Кислотність*	*Phenolphthalein*	*Фенолфталеїн*
Alkalinity	*Лужність*	*Litmus*	*Лакмус*
Hydrolysis	*Гідроліз*	*Medium of solution*	*Середовище розчину*

8.1 Ionic product of water. Notion of pH

When the law of mass action is applied to the dissociation of water, we have:

$$\frac{[H^+]\cdot[OH^-]}{[H_2O]}=K \text{ or } [H^+]\cdot[OH^-] = K\cdot[H_2O].$$

Denoting $K\cdot[H_2O]$ by K_w, we obtain $[H^+]\cdot[OH^-] = K_w$. The quantity K_w is equal to product of concentration of the Hydrogen and hydroxyl ions in water, and, is, therefore, called the **ionic product of water**. Its numerical value can easily be found, since K and $[H_2O]$ are known: the dissociation constant of water, K, is equal to $1{,}8\cdot10^{-16}$, while the concentration of undissociated water molecules is, owing to insignificant dissociation, practically equal to the total number of moles of water per litre, i.e. 100/18=55,56 moles/L. Consequently, $K_w= 1{,}8\cdot10^{-16} \text{ x } 55{,}56 = 1\cdot10^{-14}$.

The ion product of water is an extremely important value, since it enables the concentration of OH^-ions to be found for any aqueous solution with a known concentration of H^+ ions and vice versa. For example, for pure water

$$[H^+] = [OH^-] = \sqrt{K_w} =10^{-7} \text{ g-ions/L}.$$

By using the ion product of water, the acidity or alkalinity of any solution can be expressed in terms of Hydrogen ion concentration (Fig. 16).

$[H^+]$	**10^{-2}**	**10^{-3}**	**10^{-4}**	**10^{-5}**	**10^{-6}**	**10^{-7}**	**10^{-8}**	**10^{-9}**	**10^{-10}**	**10^{-11}**	**10^{-12}**	**$[H^+]$**
← Increasing acidity							Increasing alkalinity →					
pH	2	3	4	5	6	7	8	9	10	11	12	pH

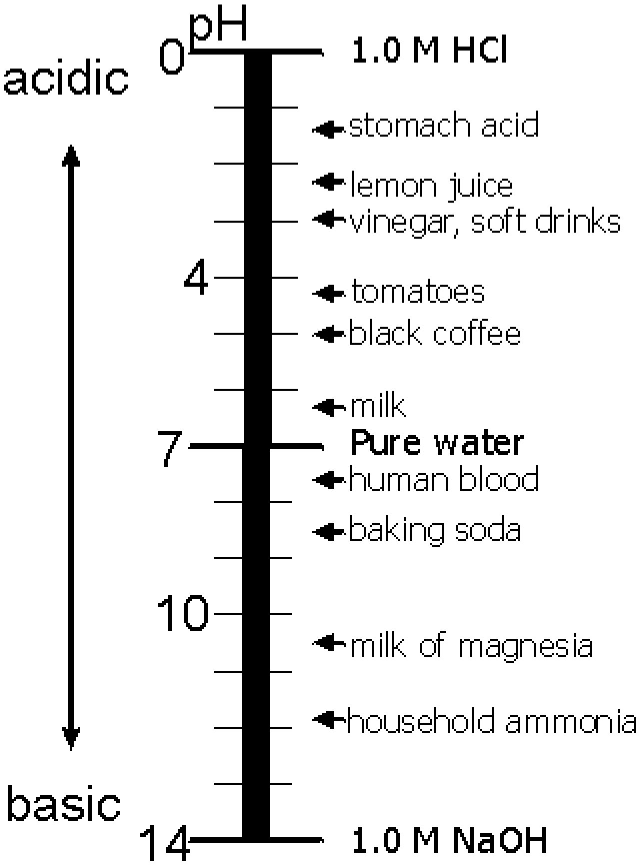


Figure 16. Acidity and alkalinity scale

In neutral solution, $[H^+]$ (often denoted by C_H) is, according to the foregoing, equal to 10^{-7}. Obviously, it is higher in an acid solution and lower in an alkaline. Thus, as the solution becomes more and more acid, C_H will pass through the values 10^{-6}, 10^{-5}, 10^{-4}, etc. And, conversely, as the solution becomes more and more alkaline, we shall have: 10^{-8}, 10^{-9}, 10^{-10}, etc.

The quantitative designation of the acidity or alkalinity of a solution may be still further simplified by using the **Hydrogen ion concentration index** (pH). The relation defines this index:

pH = - lg C_H^+ - negative common logarithm of H^+-ions concentration (more punctually - H^+-ions activity). Thus a neutral solution will have pH=7, an acid solution will have pH less than 7, and an alkaline solution will have pH more than 7.

In practice, the acidity or alkalinity of a solution is conveniently determined by means of **indicators –** substances that change color depending on the relative concentrations of H^+ and OH^- ions. The best-known indicator is **litmus**, which turns red when there is a surplus of H^+ ions, i.e., in acid solution, blue when there is a surplus of OH^- ions, i.e., in alkaline solution, and violet in neutral solution. If filter paper impregnated with litmus ("litmus paper") is immersed in the solution to be tested, its color shows at once whether the solution is acid, alkaline or neutral.

The color change of different indicators occurs at different Hydrogen ion concentrations, which is important for chemical analysis. For example, litmus changes its color (red to blue) at approximately pH=7, methyl orange (red to yellow) at pH=4, and phenolphthalein (colorless to pink) at pH=9.

For more precious measuring of pH it is widely used the special tools – pH-meters, which provides assurance of measuring within the limits of ± 0,01.

8.2 General notion of Hydrolysis

When various substances are dissolved in water, chemical reaction of an exchange nature often occurs. Such processes are grouped under the heading of **hydrolysis**. In general, hydrolysis is an exchange reaction of substances with water. The following discussion will be confined to the hydrolysis of salts, which, in practice, is by far the most common case of hydrolysis.

When a salt formed by a strong base and a strong acid, such as NaCl, dissolves, the water dissociation equilibrium does not shift, since the ions of such a salt do not form slightly dissociated products with H^+ and OH^- ions. Therefore, in the system

$$NaCl + HOH \leftrightarrow NaOH + HCl$$

the only remaining slightly dissociated compound is water itself. As a result, the equilibrium of the reaction is almost wholly shifted to the left, i.e., practically no hydrolysis of NaCl occurs, and there is no appreciable surplus of either H^+ or OH^- ions in the solution.

It is different when a salt of a strong base and a weak acid (CH_3COONa), or vice versa, (NH_4Cl) dissolves. In the former case, the H^+ will be partially bound, while in the latter, the OH^- ion will be partially bound due to the equations:

$$CH_3COO^- + HOH \leftrightarrow CH_3COOH + NaOH;$$

$$NH_4^+ + HOH \leftrightarrow NH_4OH + H^+.$$

Since both CH_3COOH and NH_4OH are much more dissociated than water, both these equilibria are greatly displaced to the left. Therefore, hydrolysis of the salts in accordance with the equations

$$CH_3COONa + HOH \leftrightarrow CH_3COOH + NaOH;$$

$$NH_4Cl + HOH \leftrightarrow NH_4OH + HCl$$

takes place only to an insignificant extent. Nevertheless, the first solution contains a certain surplus of OH^- ions, while the second solution contains a certain surplus of H^+ ions.

Since both CH_3COOH and NH_4OH are much more dissociated than water, both these equilibria are greatly displaced to the left. Therefore, hydrolysis of the salts in accordance with the equations

$CH_3COONH_4 + HOH \leftrightarrow CH_3COOH + NH_4OH$

should be shifted further to the right. In other words, the hydrolysis of a salt formed by a ***weak*** base and a ***weak*** acid will be, generally speaking, more complete than if only one of these substances is slightly dissociated.

The acidity or alkalinity of solutions of such salts depends on the relative strength of the acid and the base. If their strengths are equal, the solution may be neutral, which is the case, for example, in the hydrolysis, of CH_3COONH_4. Thus, neutrality of a solution does not, in itself, prove that the salt is not hydrolyzed.

In practice, one mostly has to deal with the hydrolysis of salts with multiply charged ions of the ***weak*** constituent (acid or base) and singly charged ions of the ***strong*** constituent. Hydrolysis of such compounds, e.g., $CuCl_2$ and Na_2CO_3 results, as a rule, in ***basic*** or ***acidic*** salts, respectively:

$CuCl_2 + HOH \leftrightarrow Cu(OH)Cl + HCl$

or $Cu^{2+} + HOH \leftrightarrow Cu(OH)^+ + H^+$

$Na_2CO_3 + HOH \leftrightarrow NaHCO_3 + NaOH$

or $CO_3^{2-} + HOH \leftrightarrow HCO_3^- + OH^-$.

Hydrolysis of such salts does not usually proceed any further, i.e., to formation of free weak base or acid, owing to the accumulation of H^+ or OH^- ions, respectively, in solution. Exceptions are those cases where the basic or acidic properties of the multivalent constituent are extremely weak. In such case hydrolysis often proceeds practically to completion.

8.3 Different types of Hydrolysis

Individual possible cases of hydrolysis of salts are compared below (from the point of view of the acidity or alkalinity of the solution and the nature of the product obtained). The basis for the comparison is, on one hand, the strength of the corresponding acids and bases, and, on the other hand, the type of salt with regard to valency of the cation and the anion.

I. Strong base, weak acid. The solution is **alkaline**. The following cases are possible, depending on the valency of the cation or the anion.

a) Cation and anion monovalent. The hydrolysis products are free acid and free base, e.g.:

$NaCN + HOH \leftrightarrow NaOH + HCN$

or, in net ionic form, $CN^- + HOH \leftrightarrow HCN + OH^-$ (pH>7).

b) Cation monovalent, anion multivalent. This is the most typical case. Hydrolysis gives acid salts and free alkali, e.g.:

$Na_3PO_4 + HOH \leftrightarrow Na_2HPO_4 + NaOH$

or, in net ionic form, $PO_4^{3-} + HOH \leftrightarrow HPO_4^{2-} + OH^-$ (pH>7).

In a large volume of water hydrolysis proceeds further:

$Na_2HPO_4 + HOH \leftrightarrow NaH_2PO_4 + NaOH$

or, in net ionic form, $HPO_4^{2-} + HOH \leftrightarrow H_2PO_4^- + OH^-$.

However, it does not reach the stage of formation of free weak acid owing to the accumulation of free alkali (OH^- ions) in the solution.

c) Cation multivalent, anion monovalent. This case is rather rare. Hydrolysis results in basic salt and free acid. But the solution is alkaline since it contains more OH^- ions from the basic salt (formed by the strong base) than H^+ ions from the weak acid, e.g.:

$Ba(CN)_2 + HOH \leftrightarrow BaOHCN + HCN$

or, in ionic form, $CN^- + HOH \leftrightarrow HCN + OH^-$.

d) Cation and anion multivalent. This case is never encountered in practice, as the compounds of this group are all insoluble in water.

II. Weak base, strong acid. The solution is **acid**. The following cases are possible, depending on the valency of the cation or the anion.

a) Cation and anion monovalent. The hydrolysis gives free acid and free base, e.g.:

$NH_4NO_3 + HOH \leftrightarrow NH_4OH + HNO_3$

or, in ionic form, $NH_4^+ + HOH \leftrightarrow NH_4OH + H^+$.

b) Cation multivalent, anion monovalent. This is the most typical case. Hydrolysis results in basic salts and free acid, e.g.:

$AlCl_3 + HOH \leftrightarrow Al(OH)Cl_2 + HCl$

or, in net ionic form, $Al^{3+} + HOH \leftrightarrow Al(OH)^{2+} + H^+$ (pH<7).

In a large volume of water hydrolysis proceeds further:

$Al(OH)Cl_2 + HOH \leftrightarrow Al(OH)_2Cl + HCl$

or, in ionic form, $Al(OH)^{2+} + HOH \leftrightarrow Al(OH)_2^+ + H^+$.

However, it does not reach the stage of formation of free weak base owing to the accumulation of free acid (H^+ ions) in the solution.

c) Cation monovalent, anion multivalent. This is very rare case. The result of hydrolysis is an acid salt and free base. In this case, the solution contains more H^+ ions from the acid salt (formed by the strong acid) than OH^- ions from the weak base, e.g.:

$(NH_4)_2SO_4 + HOH \leftrightarrow NH_4OH + NH_4HSO_4$

or, in net ionic form, $NH_4^+ + HOH \leftrightarrow NH_4OH + H^+$ (pH<7).

d) Cation and anion multivalent. Hydrolysis results in basic salt and free acid, e.g.:

$Fe_2(SO_4)_3 + 2\ HOH \leftrightarrow 2\ Fe(OH)SO_4 + H_2SO_4$

or in net ionic form, $Fe^{3+} + HOH \leftrightarrow Fe(OH)^{2+} + H^+ (pH<7)$.

III. Weak base, weak acid. In this case the alkalinity or acidity of the solution depends on the relative strengths of the acid and the base. The nature of the hydrolysis products depends on the strengths of the acid and the base as well as on the valences of the cation and the anion. For example, Aluminum Acetate hydrolyses bring to forming of basic salts, according to the equations:

$Al(CH_3COO)_3 + HOH \leftrightarrow Al(OH)(CH_3COO)_2 + CH_3COOH$

$Al(OH)(CH_3COO)_2 + HOH \leftrightarrow Al(OH)_2(CH_3COO) + CH_3COOH$ $(pH \approx 7)$.

While Aluminium Sulfide, a salt of a much weaker acid, is hydrolyzed to free base and the free acid:

$Al_2S_3 + 6HOH \leftrightarrow 2\ Al(OH)_3 + 3H_2S$.

The last case concerns to the salts marked as symbol - (dash) in Table of salts and bases Solubility in water **(Appendix 5).**

IV. Strong base, strong acid. Solutions of such salts have neutral medium, since they are practically unhydrolyzed. This group includes NaCl, Na_2SO_4, $BaCl_2$ etc.

PRACTICE PROBLEMS

1. What is the value of pH in solutions in which the concentration of Hydrogen ions is: $1 \cdot 10^{-7}$; $1 \cdot 10^{-5}$; $1 \cdot 10^{-10}$?

2. What is pH value of 0,1 M Nitric acid solution if its dissociation is complete?

3. Haw will the concentration of hydroxide ions change if pH of solution decreases from 10 to 4?

4. What aqueous solution of salt will have acidic medium? Write the corresponding equations:

a) Aluminium Nitrate, Potassium Sulfide, Potassium Chloride;
b) Potassium Carbonate, Iron (II) Sulfate, Lithium Chloride;
c) Copper (II) Chloride, Sodium Chloride, Lithium Carbonate.

5. What salt aqueous solution will have alkaline medium? Write the corresponding equations:

a) Calcium Chloride, Aluminium Chloride, Sodium Silicate;
b) Lithium Nitrate, Potassium Carbonate, Zinc Nitrate;
c) Potassium Chloride, Aluminium Chloride, Sodium Sulfide.

6. Give examples of salt hydrolysis in cation (singly-, doubly- and triple-charged).

7. Give examples of salt hydrolysis in anion (singly- and doubly-charged).

LABORATORY TRAINING

Experiment 1. Identification of reaction medium in solutions of salts

Draw the reactions of hydrolysis for salt solutions of Na_2CO_3, $(NH_4)_2SO_4$, $ZnSO_4$, $Cu(NO_3)_2$, $Al_2(SO_4)_3$, Na_3PO_4 and theoretically provide for pH of these salt solutions. Then identify reaction medium by putting the drop of solution on universal litmus paper. Draw molecular and ionic equations of hydrolysis in form of the next table:

Formula of salt	Color of indicator	Medium	Reaction of hydrolysis process

Experiment 2. Influence of temperature to hydrolysis

A) Fill each of two test tubes with 5-6 drops of 2N CH_3COONa solution and one drop of phenolphthalein solution. Leave one test-tube for comparison and heat another on water bath and note color change. Draw molecular and ionic hydrolysis equations.

B) Fill test-tube with 5-6 drops of $FeCl_3$ and 4-5 drops of CH_3COONa. Note solution color change as the result Iron (III) Acetate production. Add 10 - 20 mL of distilled water and heat the mixture on water bath up to brown precipitation formation. Draw molecular and ionic equations of hydrolysis (1^{st} and 2^{d} steps).

Experiment 3. Hydrolysis strengthening in case of solution dilution

Put 4-5 drops of Bithmus (III) Chloride $BiCl_3$ and by drops (15-20 drops) distilled water up to basic salt precipitation formation. Save the solution with precipitation for the next experiment. Draw hydrolysis equation taking into account that $Bi(OH)_2Cl$ is produced as the result of hydrolysis.

Experiment 4. Reversibility of hydrolysis process

Add by drops hydrochloric acid solution up to precipitation produced in previous experiment. Than add distilled water up to basic salt precipitation production. Explain the phenomenon, which occurs. Draw molecular and ionic equations.

CHAPTER # 9. OXIDATION-REDUCTION REACTIONS

Vocabulary

English	Українська назва	English	Українська назва
Oxidation number (or oxidation state)	*Ступінь окислення*	*Reducing agent*	*Відновник*
Oxidation-reduction (redox) reactions	*Окисно-відновні реакції*	*Intermolecular redox reactions*	*Міжмолекулярні окисно-відновні реакції*
Reduction process	*Процес відновлення*	*Intramolecular redox reactions*	*Внутрішньо-молекулярні окисно-відновні реакції*
Oxidation process	*Процес окислення*	*Disproportination redox reactions*	*Реакції самоокислення-самовідновлення (диспропорціонування)*
Oxidizing agent, oxidizing compound, oxidant, oxidizer	*Окисник*		

9.1 Oxidation of Elements

When element is in free state - forms an elementary substance - the motion of the electrons about all the atoms of this substance occurs identically. This holds for all elementary substances regardless of their structure. For example, in a Hydrogen molecule, the electrons travel about both atoms to an equal extent - the molecule H_2 is non-polar. For crystals with a covalent bond, the chemical bonds between the atoms are also symmetrical relative to the joined atoms. For metals, the distribution of both the bound and the free electrons is also uniform on an average.

Matters are different in compound substances. The chemical bonds between the atoms of different elements are not symmetrical; polar bonds are generally the rule in molecules of compounds. This nonuniformity in the distribution of the electrons is the greatest in ionic compounds - in the formation of substances with an ionic bond, the valence electrons pass virtually completely from the atom of one element to the atom of another one.

The element whose electrons pass to atoms of another element (completely with an ionic bond or partly with a polar one) is said to be **positively oxidized.** An element to whose atoms electrons from atoms of another element pass is **negatively oxidized** (or **reduced).**

The number of electrons that have passed from one atom of a given positively oxidized element or to one atom of a given negatively oxidized or reduced element is called the **oxidation number** (or **oxidation state**) of the element.

In elementary substances, the oxidation number of an element is always zero. In compounds, some elements always display the same oxidation number, but for most elements it differs in different compounds.

The elements having a constant oxidation number are the alkali metals (+1), the alkaline-earth metals (+2), and Fluorine (- 1). Hydrogen in most compounds is characterized by an oxidation number of +1, while in metal hydrides and in some other compounds it is - 1. The oxidation number of Oxygen, as a rule, is - 2. The most important exceptions here are the peroxide compounds, where it is - 1, and Oxygen Fluoride OF_2, in which the oxidation number of Oxygen is + 2. For elements with changing oxidation number, its value is always simple to find knowing the formula of a given compound and taking into consideration that the sum of the oxidation numbers of all the atoms in a molecule is zero.

Let us determine as an example the oxidation number of carbon in CO, CO_2, CH_4, C_2H_6, and C_2H_5OH. We shall denote it by *x*. Hence, remembering that the oxidation number of Hydrogen is +1 and that of Oxygen - 2, we get

CO	$x + (-2) = 0$	$x = +2$
CO_2	$x + 2\cdot(-2) = 0$	$x = +4$
CH_4	$x + 4\cdot(+1) = 0$	$x = -4$
C_2H_6	$2x + 6\cdot(+1) = 0$	$x = -3$
C_2H_5OH	$2x + 6\cdot(-1) + (-2) = 0$	$x = -2$

To find the oxidation number of elements in compounds, the table of electronegativity of elements (**Appendix 7**) can be used. It must be borne in mind here that when a chemical bond is formed, the electrons are displaced to the atom of the element with the higher electronegativity. For instance, the relative electronegativity of Phosphorus is 2,2, and that of Iodine 2,5. Consequently, in the compound PI_3, the shared electrons are displaced to the Iodine atoms, and the oxidation numbers of phosphorus and Iodine are +3 and - 1, respectively. In compound NI_3, however, the oxidation numbers of Nitrogen and Iodine are - 3 and +1 because the electronegativity of Nitrogen (3,0) is higher than that of Iodine.

9.2 Oxidation-Reduction Reactions

All chemical reactions can be divided into two groups. In those of the first group, the oxidation state of all the elements in the reactants remains constant, while in those of the second group, the oxidation state of one or several elements changes.

We can exemplify the reactions of the first group by the neutralization reaction:

$HCl + NaOH = NaCl + H_2O$

An example of a reaction of the second group **is** the reaction of metal with an acid:

$Zn + 2HC1 = ZnCl_2 + H_2\uparrow$.

If in the neutralization reaction no element changes its oxidation number, in the second example the oxidation number of the Zinc changes from 0 to +2, and of the Hydrogen from +1 to 0.

Reactions as a result of which the oxidation numbers of elements change are called oxidation-reduction (redox) reactions.

Oxidation-reduction reactions are of great importance in biological systems. Photosynthesis, breathing, digestion - all these are chains of oxidation-reduction reactions. In engineering, the significance of redox reactions is also great. For example, the entire metallurgical industry is based on oxidation-reduction processes during which metals are recovered from natural compounds.

Simple example of an oxidation-reduction reaction is the reaction of formation of an ionic compound from elementary substances, for example, the reaction of Sodium with Chlorine:

$2Na + Cl_2 = 2NaCl$.

This reaction, like any heterogeneous one, proceeds in several steps. In one of them, the Sodium atoms transform into positively charged ions; the oxidation number of Sodium changes from 0 to -1:

$Na = Na^+ + \bar{e}$.

Such a process - the losing of electrons attended by an increase in the oxidation number of element - is called **oxidation.**

The Chlorine atoms, which transform into negatively charged ions, gain the electrons lost by Sodium; the oxidation number of Chlorine changes from 0 to -1:

$Cl_2 + 2\bar{e} = 2C1^-$.

The gaining of electrons attended by a decrease in the oxidation number of an element is called **reduction.**

Hence, in the reaction considered above, Sodium is oxidized, and Chlorine is reduced.

Substance containing an element that is oxidized is called **reducing agent**, and substance containing an element that is reduced is called oxidizing **agent (oxidant).**

Consequently, in the above example, Sodium is a reducing agent, and Chlorine an oxidizing one.

Inspection of the oxidation-reduction equations shows that one molecule of Chlorine when reduced gains two electrons, while the oxidation of one Sodium atom is attended by the loss of one electron. The total number of electrons in the system in chemical reactions does not change: **the number of electrons lost by the molecules (atoms, ions) of the reducing agent is equal to the number of electrons gained by the molecules (atoms, ions) of the oxidizing agent**. Therefore, one molecule of Chlorine can oxidize two Sodium atoms.

9.3 Compiling Equations of Oxidation-Reduction Reactions

In previous section, we considered very simple example of redox reaction - the formation of a compound from two elementary substances. Usually, the equations of redox reactions are more complicated and it is often quite difficult task to balance them. We shall consider a few examples.

Example 1. The reaction between Hydrogen Iodide and concentrated Sulfuric acid. This reaction proceeds as follows:

$HI + H_2SO_4 \text{ (conc)} \rightarrow I_2 + H_2S + H_2O$.

If we calculate the oxidation number of each element in the reactants and in the products, we shall see that it changes both in Iodine and in Sulfur. In the Iodine of HI it is -1, and in free Iodine it is 0. The oxidation number of Sulfur, on the other hand, changes from +6 (in H_2SO_4) to -2 (in H_2S). Hence, the oxidation number of Iodine increases, and of Sulfur decreases. Consequently, Iodine is oxidized, and Sulfur is reduced.

The equation of Iodine oxidation has a simple form:

$2I^- = I_2 + 2\bar{e}$ (oxidation)

The equation of Sulfur reduction is more complicated because both the reactant (H_2SO_4 or SO_4^{2-}) and the product (H_2S) contain other elements in addition to Sulfur. In compiling this equation, we shall proceed from the fact that the reaction takes place in an acidic aqueous solution, and the ion SO_4^{2-} transforms into the molecule H_2S:

$SO_4^{2-} \rightarrow H_2S$.

The four Oxygen atoms liberated in this process should be combined with Hydrogen into four molecules of water. Eight Hydrogen ions are needed for this. In addition, two Hydrogen ions are needed to form a molecule of H_2S. Hence, ten Hydrogen ions should react with the SO_4^{2-} ion:

$SO_4^{2-} + 10\,H^+ \rightarrow H_2S + 4H_2O$.

The total charge on the ions in the left-hand side of this formula is eight elementary positive charges, while the right-hand side contains only uncharged particles. Since the total charge does not change in the course of the process, eight electrons also participate in the reduction process:

$SO_4^{2-} + 10H^+ + 8\bar{e} \rightarrow H_2S + 4H_2O$ (reduction).

In the above example, the ratio of the number of electrons participating in the reduction process to that liberated in oxidation is 4:1. To obtain the overall equation of the reaction, we have to take this ratio into account when summing the equations of the reduction and oxidation processes, i.e. multiply the reduction equation by four. It is customary practice to indicate the required multipliers to the right of a vertical line when writing the equations:

$$\begin{array}{l|l} \quad 2I^- = I_2 + 2\bar{e} & 4 \\ + & \\ \quad SO_4^{2-} + 10H^+ + 8\bar{e} \rightarrow H_2S + 4H_2O & 1 \\ \hline SO_4^{2-} + 8\,I^- + 10H^+ = 4\,I_2 + H_2S + 4H_2O & \end{array}$$

The reaction equation obtained can also be written in the molecular form:

$H_2SO_4 + 8HI = 4I_2 + H_2S + H_2O$.

Example 2. Reaction of Aluminium with Potassium Nitrate in a basic solution. The skeleton equation is:

$KNO_3 + Al + KOH + H_2O \rightarrow NH_3 + KAlO_2$.

Here the oxidation number changes in Nitrogen and Aluminium. Metallic Aluminium (its oxidation number is zero) transforms into the ion $A1O_2^-$, in which the oxidation number of the Aluminium is +3. To compile the oxidation equation, we shall proceed from the scheme:

$Al \rightarrow AlO_2^-$.

In a basic solution, the OH^- ion is the source of the Oxygen needed for this process to occur. Four hydroxide ions are required to combine one Aluminium atom into AlO_2^- ion:

$Al + 4\,OH^- \rightarrow AlO_2^- + 2H_2O$.

The left-hand side of the formula contains four negative charges, and the right-hand side only one. Hence, in the course of the process, three electrons are given up:

$Al + 4\,OH^- = AlO_2^- + 2H_2O + 3\bar{e}$ (oxidation).

To obtain the reduction equation, we shall proceed from the scheme:

$NO_3^- \rightarrow NH_3$.

Here in the course of the process, the Nitrogen atoms lose Oxygen atoms and is combined with Hydrogen atoms. In a basic solution, it is possible with the participation of water molecules. Three water molecules are needed to be combined with three Oxygen atoms, and three more water molecules to form a molecule of NH_3:

$NO_3^- + 6H_2O \to NH_3 + 9\ OH^-$.

The total charge of the right-hand side of the formula is nine negative charges, and of the left-hand side - one. Consequently, eight electrons participate in the process:

$NO_3^- + 6H_2O + 8\bar{e} = NH_3 + 9\ OH^-$ (reduction).

The ratio between the number of electrons liberated in oxidation and the number of electrons gained in reduction is 3:8 in the given example. Hence, to obtain the overall equation of the reaction, we must summate the equations of the oxidation and reduction processes, multiplying the first of them by 8 and the second by 3:

$$\begin{array}{cl|l} + & Al + 4\ OH^- = AlO_2^- + 2H_2O + 3\bar{e} & 8 \\ & NO_3^- + 6H_2O + 8\bar{e} = NH_3 + 9\ OH^- & 3 \\ \hline & 8\ Al + 3\ NO_3^- + 5\ OH^- = 8\ AlO_2^- + 3\ NH_3 & \end{array}$$

or in the molecular form:

$8\ Al + 3\ KNO_3 + 5\ KOH + 2\ H_2O = 8\ KAlO_2 + 3\ NH_3$.

Example 3. Catalytic oxidation of ammonia. This reaction is used in the production of Nitric acid. It is conducted at a temperature of about 750^0C. The skeleton equation is:

$NH_3 + O_2 \to NO + H_2O$.

The condensation of water vapor (steam) at 750^0C is impossible. We shall therefore not write the equations of the oxidation and reduction processes as we did for reactions proceeding in an aqueous solution - with the participation of water molecules, Hydrogen or hydroxide ions. We shall only count the number of electrons participating in the oxidation and reduction. We shall take into account that the increase in the oxidation number of an element is equal to the number of lost electrons, and the decrease equals the number of gained electrons.

According to the skeleton equation, the oxidation number changes both in the Nitrogen and in the Oxygen. In the former, it grows from - 3 to +2, and in the latter, it diminishes from 0 to -2. Let us write these changes as formulas, indicating the oxidation numbers of the relevant elements as superscripts. To avoid confusion with the charge of an ion, we shall use Roman numerals for this purpose:

$N^{-III} \to N^{+II} + 5\bar{e}$ (oxidation);

$O_2^0 + 4\ \bar{e} \to 2\ O^{-II}$ (reduction).

The ratio of the number of electrons gained in reduction to the number of electrons lost in oxidation is 4:5. Hence, five molecules of Oxygen can oxidize four molecules of Ammonia:

$4\ NH_3 + 5\ O_2 = 4\ NO + 6\ H_2O$.

The reaction equations in the above three examples were compiled in a definite sequence. It can also be adhered to in other cases when compiling the equations of redox reactions. The sequence of operations is as follows:

1. Draw up a skeleton equation indicating the reactants and products.
2. Determine the oxidation numbers of the elements in the substances of the right-hand and left-hand sides of the equation; indicate the elements whose oxidation number changes.
3. Draw up the reduction and oxidation equations; find the ratio of the number of electrons gained in reduction to that lost in oxidation.
4. Sum the oxidation and reduction equations with account taken of the ratio of the number of electrons found in point 3.

9.4 Most Important Oxidizing and Reducing Agents

What substances can display the properties of oxidizing agents, and what - of reducing agents? We have already mentioned that an oxidizing agent contains an element whose oxidation number decreases, while a reducing agent contains an element whose oxidation number grows in the course of a reaction. Consequently, oxidizing agents will include first of all compounds with the higher, and reducing agents will include compounds with the lower oxidation numbers featuring a given element.

Metals display only a positive oxidation state in their compounds, and their minimum oxidation number is zero. In other words, they have the minimum oxidation number only in the free state. Indeed, all free metals, although to a different extent, are capable of exhibiting only reducing properties. The reducing agents used in practice include Aluminium, Magnesium, Sodium, Potassium and Zinc. If a metal can have several oxidation numbers, those of its compounds in which it displays the lowest of them are also reducing agents, as a rule. Examples are the compounds of Iron (II), Tin (II), Chromium (II) and Copper (I).

Those compounds of metals can be oxidizing agents in which the oxidation number is high and either is equal to the number of the group, which the metal belongs to or is close to it. Practical use has been found, in particular, by an Ammonia solution of Silver oxide, an Ammonia solution of Copper (II) Sulfate, Mercury (II) Chloride, Lead (IV) Oxide, Iron (III)

Chloride, Potassium Chromate and Dichromate (K_2CrO_4 and $K_2Cr_2O_7$), Potassium Permanganate $KMnO_4$, and Manganese (IV) oxide MnO_2.

Non-metals exhibit both positive and negative oxidation states. It is natural that compounds containing non-metals in their higher positive oxidation states can be oxidizing agents, and compounds in which a non-metal displays a negative oxidation state can be reducing agents.

The most important reducing agents are Hydrogen H_2, Carbon C and Carbon (II) Oxide CO.

Non-metals of the upper part of groups VI and VII of the Periodic Table are strong oxidizing agents. The strong oxidizing properties of these substances are explained by the high electronegativity of their atoms. Fluorine F_2 has the strongest oxidizing properties, but in practice Oxygen O_2, Chlorine Cl_2 and Bromine Br_2 are used most frequently as oxidizing agents.

The compounds used as oxidizing agents also include acids. Hydrochloric HCl, Sulfuric H_2SO_4 and nitric HNO_3 acids have the greatest practical significance. The oxidizing element in Hydrochloric acid is Hydrogen H^+; in Nitric acid it is Nitrogen N^{5+}, in dilute Sulfuric acid - Hydrogen H^+, and in the concentrated acid - Sulfur S^{+6}. Hence, the equation of reduction with Hydrochloric and dilute Sulfuric and a few other acids (H_3PO_4, CH_3COOH, $HClO_4$) has the form:

$$2H^+ + 2\bar{e} \rightarrow H_2.$$

Nitric acid, depending on its concentration, temperature, and the nature of the reducing agent, can be reduced to different oxidation numbers of the Nitrogen. One of the usual products of its reduction is Nitrogen (II) Oxide NO:

$$NO_3^- + 4H^+ + 3\bar{e} = NO + 2H_2O.$$

Various products may also be formed in reduction with concentrated Sulfuric acid. One of them is Sulfur (IV) Oxide:

$$SO_4^{2-} + 4H^+ + 2\bar{e} = SO_2 + 2H_2O.$$

Other compounds of non-metals used as oxidizing agents are Hydrogen Peroxide H_2O_2, the salts of acids in which the acid-forming element exhibits a high oxidation number - Chlorates ($KClO_3$), Perchlorates ($KClO_4$).

Possible oxidation numbers of some chemical elements are presented in **Appendix 10**.

9.5 Types of Redox Reactions

In all reactions, presented in sub-chapter 3, **oxidizing and reducing atoms** are parts of different substances. Such type of redox reactions is the most extended and called **Intermolecular Oxidation-Reduction**.

Compounds with the maximum oxidation number of a given element can play the role of oxidizing agents in redox reactions. The oxidation number can only be lower in this case. Conversely, compounds with the minimum oxidation number can only be reducing' agents. Here the oxidation number of an element can only grow. If an element is in an intermediate oxidation state, however, its atoms can, depending on the conditions prevailing, either take on or give up electrons. In the first case, the oxidation number of the element will be lower, and in the second one it will grow. Consequently, compounds containing elements in intermediate oxidation states have **oxidation-reduction duality -** they are capable of entering into-reactions with either oxidizing or reducing agents.

For example, Nitrogen forms compounds in which its oxidation number changes from -3 (Ammonia and Ammonium salts) to +5 (Nitric acid and its salts). The Nitrogen in Ammonia can only be a reducing agent, and that in Nitric acid - only an oxidizing agent. Nitrous acid HNO_2 and its salts, in which the oxidation number of Nitrogen is +3 however, enter into reactions with both strong oxidizing and strong reducing agents. In the first case, it is oxidized to Nitric acid, and in the second, it is usually reduced to Nitrogen (II) Oxide NO. We can exemplify the oxidation-reduction duality of Nitrous acid and its salts by the reactions:

$5\ KNO_2 + 2\ KMnO_4 + 3\ H_2SO_4 = 5\ KNO_3 + 2\ MnSO_4 + K_2SO_3 + 3\ H_2O$ -

N^{+3} is a reducing agent;

$2\ HNO_2 + H_2S = 2\ NO + S + 2H_2O$ -

N^{+3} is an oxidizing agent.

In addition to Nitrous acid HNO_2, Sulfur S, Iodine I_2, Hydrogen Peroxide H_2O_2 and a number of other substances have **oxidation-reduction duality**.

Substances containing element in intermediate oxidation state often have another characteristic property. In definite conditions one part of the element is oxidized and the other part is reduced. This process is known as **autoxidation-autoreduction.** For instance, when Chlorine reacts with water, the mixture of Hydrochloric and Hypochlorous acids is produced:

$$Cl_2 + H_2O = HCl + HClO.$$

Here the Chlorine undergoes both oxidation and reduction:

$$\begin{array}{l|l} Cl_2 + 2\bar{e} = 2\ Cl^- & 1\ \text{(reduction);} \\ Cl_2 - 2\bar{e} = 2Cl^+ & 1\ \text{(oxidation).} \end{array}$$

Autoxidation-autoreduction is also called **disproportionation.**

Some compounds in definite conditions (usually when heated) experience **intramolecular oxidation-reduction.** In this process, one constituent part of the substance is an oxidizing agent, and the other is a reducing one. Examples of intramolecular oxidation-reduction are many processes of thermal dissociation. For instance, when Potassium Chlorate decomposes by heating:

$$2\ KClO_3 \xrightarrow{t} 2\ KCl + 3\ O_2$$

the Oxygen is oxidized (its oxidation number grows from -2 to 0), and the Chlorine is reduced (its oxidation number diminishes from +5 to -1).

Another example is the decomposition of Ammonium Nitrite employed in the laboratory to obtain pure Nitrogen:

$$NH_4NO_2 = N_2 + 2H_2O.$$

Here the ion NH_3 is oxidized and the ion NO_2^- is reduced to free Nitrogen.

9.6 Influence of Medium to Redox Reactions

Among Redox reactions it was marked out the group of processes where composition of oxidation and reduction processes products depend on medium (for example, reactions with Potassium Permanganate $KMnO_4$, Potassium Dichromate $K_2Cr_2O_7$ (Table 12).

Example 1. $KMnO_4 + NaI + H_2SO_4 \rightarrow$

or $K^{1+}Mn^{7+}O^{2-}_4 + Na^{1+}I^{1-} + H^{1+}_2S^{6+}O^{2-}_4 \rightarrow$

Presence of H_2SO_4 (diluted) determines an acidic medium. Oxidizing agent is Mn^{7+} in acidic medium gained 5 electrons (see Table 12). Reducing agent is I^-:

$$\begin{array}{l|l} Mn^{7+} + 5\bar{e} \rightarrow Mn^{2+} & 2 \text{ (reduction);} \\ 2I^- \ - 2\bar{e} \rightarrow I_2 & 5 \text{ (oxidation).} \end{array}$$

Products of reduction or oxidation and ions which do not change oxidation number in reaction are connected with ions of substance determined the medium of reaction:

$Mn^{2+} + SO_4^{2-} \rightarrow MnSO_4$; $2K^+ + SO_4^{2-} \rightarrow K_2SO_4$;

$2Na^+ + SO_4^{2-} \rightarrow Na_2SO_4$; $2H^+ + O^{2-} \rightarrow H_2O$.

So, in total:

$$2KMnO_4+10NaI+8H_2SO_4=2MnSO_4+5I_2+K_2SO_4+5Na_2SO_4+8H_2O.$$

Table 12. Influence of Medium to Composition of products of Redox reactions products

Compound and its function in redox reaction	Medium	Scheme of process	Typical products
Oxidizing agent $KMnO_4$	Acidic (H^+, pH<7)	$Mn^{7+}+5\bar{e}\rightarrow Mn^{2+}$	Salts of Mn^{2+} and residue of acid determined medium
	Alkaline (OH^-, pH>7)	$Mn^{7+}+1\bar{e}\rightarrow Mn^{6+}$	Salts of Manganic acid (H_2MnO_4) and alkali determined medium
	Neutral (H_2O)	$Mn^{7+}+3\bar{e}\rightarrow Mn^{4+}$	MnO_2
Oxidizing agent MnO_2	Acidic (H^+, pH<7)	$Mn^{4+}+2\bar{e}\rightarrow Mn^{2+}$	Salts of Mn^{2+} and residue of acid determined medium
Oxidizing agent $K_2Cr_2O_7$	Acidic (H^+, pH<7)	$Cr^{6+} + 3\bar{e}\rightarrow Cr^{3+}$	Salts of Cr^{3+} and residue of acid determined medium
Oxidizing agent H_2O_2	Acidic (H^+, pH<7)	$O^{1-}+1\bar{e}\rightarrow O^{2-}$	H_2O
Reducing agents - Compounds included Cr^{3+}	Alkaline (OH^-, pH>7)	$Cr^{3+}-3\bar{e}\rightarrow Cr^{6+}$	Salts of Chromic acid (H_2CrO_4) and alkali determined medium
Reducing agents - Amphoteric metals in free state (Zn, Al, Be)	Alkaline (OH^-, pH>7)	$Zn^0-2\bar{e}\rightarrow Zn^{2+}$ $Al^0 - 3\bar{e}\rightarrow Al^{3+}$ $Be^0 - 2\bar{e}\rightarrow Be^{2+}$	Salts included alkaline and anions $[Zn(OH)_4]^{2-}$, $[Al(OH)_6]^{3-}$, $[Be(OH)_4]^{2-}$ respectively

9.7 Electromotive Series of Metals

If from the entire series of standard electrode potentials (see **Appendix 11**) we separate only the electrode processes that correspond to the general equation:

$$M^{z+}+ ze^- = M^0$$

we get an electromotive (or activity) series of metals. In addition to metals, Hydrogen is included in this series, which permits us to see what metals are capable to displace Hydrogen from aqueous solutions of acids. The electromotive series for the most important metals are given in Table 13.

Table 13. Electromotive Series of Metals

Equation of electrode process	Standard potential at 25^0C, V	Equation of electrode process	Standard potential at 25^0C, V
$Li^+ + \bar{e} \rightarrow Li^0$	- 3,045	$Co^{2+} + 2\bar{e} \rightarrow Co^0$	- 0,277
$Rb^+ + \bar{e} \rightarrow Rb^0$	- 2,925	$Ni^{2+} + 2\bar{e} \rightarrow Ni^0$	- 0,250
$K^+ + \bar{e} \rightarrow K^0$	- 2,924	$Sn^{2+} + 2\bar{e} \rightarrow Sn^0$	- 0,136
$Cs^+ + \bar{e} \rightarrow Cs^0$	- 2,923	$Pb^{2+} + 2\bar{e} \rightarrow Pb^0$	- 0,126
$Ca^{2+} + 2\bar{e} \rightarrow Ca^0$	- 2,866	$Fe^{3+} + 3\bar{e} \rightarrow Fe^0$	- 0,037
$Na^+ + \bar{e} \rightarrow Na^0$	- 2,714	$\mathbf{2H^+ + 2\bar{e} \rightarrow H_2^0}$	**0,000**
$Mg^{2+} + 2\bar{e} \rightarrow Mg^0$	- 2,363	$Bi^{3+} + 3\bar{e} \rightarrow Bi^0$	0,215
$Al^{3+} + 3\bar{e} \rightarrow Al^0$	- 1,663	$Cu^{2+} + 2\bar{e} \rightarrow Cu^0$	0,337
$Ti^{2+} + 2\bar{e} \rightarrow Ti^0$	- 1,630	$Cu^+ + \bar{e} \rightarrow Cu^0$	0,520
$Mn^{2+} + 2\bar{e} \rightarrow Mn^0$	- 1,179	$Hg_2^{2+} + 2\bar{e} \rightarrow 2\,Hg^0$	0,788
$Cr^{2+} + 2\bar{e} \rightarrow Cr^0$	- 0,913	$Ag^+ + \bar{e} \rightarrow Ag^0$	0,799
$Zn^{2+} + 2\bar{e} \rightarrow Zn^0$	- 0,763	$Hg^{2+} + 2\bar{e} \rightarrow Hg^0$	0,850
$Cr^{3+} + 3\bar{e} \rightarrow Cr^0$	- 0,744	$Pt^{2+} + 2\bar{e} \rightarrow Pt^0$	1,188
$Fe^{2+} + 2\bar{e} \rightarrow Fe^0$	- 0,440	$Au^{3+} + 3\bar{e} \rightarrow Au^0$	1,498
$Cd^{2+} + 2\bar{e} \rightarrow Cd^0$	- 0,403	$Au^+ + \bar{e} \rightarrow Au^0$	1,692

The position of metal in the series characterizes its ability to participate in oxidation-reduction reactions in aqueous solutions in standard conditions. Ions of the metals are oxidizing agents, and the metals in the form of elementary substances are reducing agents. The farther a metal is in the electromotive series, the stronger an oxidizing agent in an aqueous solution is its ions. Conversely, the nearer a metal is to the top of the series the stronger as the reducing properties exhibited by the elementary substance - metal. The potential of the electrode process:

$$2H^+ + 2\bar{e} = H_2$$

in a neutral medium (pH = 7) is - 0,41 V. The active metals at the top of the series having a potential that is considerably more negative than - 0,41 V displace Hydrogen from water:

$2\,M + 2H_2O = 2\,MOH + H_2\uparrow$. Magnesium displaces Hydrogen only from hot water. The metals between Magnesium and Cadmium do not usually displace Hydrogen from water. The surfaces of these metals become covered with oxide films having a protective action.

The metals between Magnesium and Hydrogen displace Hydrogen from solutions of acids. The surfaces of some metals also become covered with protective films that inhibit the reaction. For example, the oxide film on Aluminium makes this metal stable not only in water, but also in solutions of some acids. Lead is not dissolved in Sulfuric acid when its concentration is below 80% because the salt of $PbSO_4$ is formed when lead reacts with Sulfuric acid is insoluble and produces a protective film on the surface of the metal. The phenomenon of the deep inhibition of the oxidation of the metal due to the presence of protective oxide or salt films on its surface is called passivation, and the state of the metal is called the passive state.

Metals are capable to displace one another from solutions of their salts. The direction of the reaction is determined by their relative position in the electromotive series. When considering specific cases of such reactions, one must remember that active metals displace Hydrogen not only from water, but also from any aqueous solution. Consequently, the mutual displacement of metals from solutions of their salts occurs in practice only with metals below Magnesium in the series. For example:

$Zn + CuSO_4 = ZnSO_4 + Cu$.

N. Beketov first studied the displacement of metals from their compounds by other metals in detail. As a result of his investigations, he arranged the metals in a "displacement series" according to their chemical activity. This series was the prototype of the electromotive series of metals.

PRACTICE PROBLEMS

1. Determine oxidation number of each element in compounds:
   a. CH_4, C_2H_6, C_2H_4, C_2H_2, CH_3OH, C_2H_5OH;
   b. CO_2, H_2CO_3, $HCOOH$, CH_3COOH, $H_2C_2O_4$;
   c. HNO_3, HNO_2, N_2O_4, NO_2, N_2O, Ca_3N_2;
   d. NH_3, N_2H_4, NH_2OH, N_2, HNO_2, K_3N;
   e. H_2S, H_2SO_3, H_2SO_4, FeS_2, $Na_2S_2O_3$, Al_2S_3;
   f. H_3PO_4, H_3PO_3, PCl_3, P_2O_5, $H_4P_2O_7$;
   g. $HClO_4$, $Ca(ClO)_2$, $KClO_3$, $NaClO_2$, KCl;
   h. CrO, K_3CrO_3, $NaCrO_2$, $BaCrO_4$, $K_2Cr_2O_7$.

2. Balance Redox reactions using method of electron balance. Point out oxidizing and reducing agents:
   a. $Ca + HNO_3 \rightarrow Ca(NO_3)_2 + N_2O + H_2O$;
   b. $K_2S + HNO_3 \rightarrow S + NO_2 + KNO_3 + H_2O$;
   b. $NaCrO_2 + Br_2 + NaOH \rightarrow Na_2CrO_4 + NaBr + H_2O$;

c. $HI + KMnO_4 + H_2SO_4 \rightarrow I_2 + MnSO_4 + K_2SO_4 + H_2O$;
d. $Au + HNO_3 + HCl \rightarrow AuCl_3 + NO + H_2O$;
e. $Ag + H_2S + O_2 \rightarrow Ag_2S + H_2O$.

3. To point out oxidizing and reducing agents and products of reactions. Balance equations:

a. $MnO_2 + O_2 + KOH \rightarrow$
b. $Na_2SO_3 + KMnO_4 + H_2SO_4 \rightarrow$
c. $Na_2SO_3 + KMnO_4 + H_2O \rightarrow$
d. $Na_2SO_3 + KMnO_4 + KOH \rightarrow$
e. $NaNO_2 + K_2Cr_2O_7 + H_2SO_4 \rightarrow$
f. $Mg + H_2SO_4$ (conc.) $\rightarrow$
g. $Fe + HNO_3$ (diluted) $\rightarrow$
h. $C + HNO_3$ (conc.) $\rightarrow$
i. $Zn + HNO_3$ (diluted) $\rightarrow$
j. $P + HNO_3$ (diluted) $\rightarrow$
k. $HBr + KMnO_4 \rightarrow$
l. $H_2S + HNO_3$ (diluted) $\rightarrow$
m. $SO_2 + Br_2 + H_2O \rightarrow$
n. $NaNO_2 + K_2Cr_2O_7 + H_2SO_4 \rightarrow$
o. $HBr + HNO_2 \rightarrow$
p. $H_2O_2 + K_2Cr_2O_7 + H_2SO_4 \rightarrow$
q. $SO_2 + Br_2 + H_2O \rightarrow$

4. Point out a type of redox reaction (Intermolecular, Intramolecular, Disproportionation). Determine chemical elements charged oxidation degree. To balance equations:

a. $Ca(OH)_2 + Cl_2 \rightarrow CaCl_2 + Ca(ClO)_2 + H_2O$;
b. $NO_2 + H_2O \rightarrow HNO_3 + NO$;
c. $KClO \rightarrow KClO_3 + KCl$;
d. $H_3PO_3 \rightarrow PH_3 + H_3PO_4$;
e. $HCl + KClO_3 \rightarrow Cl_2 + KCl + H_2O$;
f. $H_2S + H_2SO_4 \rightarrow SO_2 + H_2O$;
g. $KI + KIO_3 + H_2SO_4 \rightarrow I_2 + K_2SO_4 + H_2O$;
h. $KClO_3 + H_2SO_4 \rightarrow ClO_2 + O_2 + K_2SO_4 + H_2O$;
i. $HNO_3 \rightarrow NO_2 + O_2 + H_2O$;
j. $Pb(NO_3)_2 \rightarrow PbO + NO_2 + O_2$;
k. $(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + H_2O$;
l. $Au(NO_3)_3 \rightarrow Au + NO_2 + O_2$;

m. $H_2O_2 \rightarrow H_2O + O_2$.

LABORATORY TRAINING

Experiment 1. Reducing properties of metal ions of lower oxidation number

Add 1-2 drops of Iron (III) Sulfate $Fe_2(SO_4)_3$ to 2-3 drops of Ammonium Thiocyanate NH_4SCN. Register color of solution. Further add to the same tube the solution of Tin (II) Chloride $SnCl_2$ (by drops) up to whole decoloration of mixture. Draw up equations of reactions. For Redox reaction write the scheme of electron balance, and mark oxidizing and reducing agents.

Experiment 2. Influence of medium to redox reactions

Put 2-3 drops of Potassium Permanganate solution $KMnO_4$ in the 3 tubes. Add 1-2 drops of diluted Sulfuric acid to the first tube; - 5-10 drops of distillated water to the second one; 2-3 drops of alkali solution (NaOH or KOH) in the third one. Is the color of $KMnO_4$ solution changed? Then add in each tube few crystals of Sodium Sulfite or Potassium Sulfite. What do you observe? Draw up equations of reactions, write the scheme of electron balance, mark oxidizing and reducing agents.

Experiment 3. Redox properties of Chromium compounds

A) Put 2-3 drops of Potassium Dichromate $K_2Cr_2O_7$ solution in to the tube, add 2-3 drops of diluted Sulfuric acid and few crystals of solid Sodium Sulfite or Potassium Sulfite. What do you observe? Draw up equations of reactions, write the scheme of electron balance, mark oxidizing and reducing agents.

B) Put 1-2 drops of alkali solution (NaOH or KOH), add by drops the solution of Chromium (III) Sulfate $Cr_2(SO_4)_3$ up to the formation of precipitate. Register the color of mixture. Further add alkali solution (NaOH or KOH) to the same tube up to the dissolving of precipitate (register the color of solution), then - 3-4 drops of 10% solution of Hydrogen Peroxide H_2O_2. Heat a content of tube during 2-3 minutes in water bath. How is the a color of solution changed? Draw up equations of reactions of corresponded transformations: $Cr^{3+} \rightarrow Cr(OH)_3\downarrow \rightarrow CrO_2^- \rightarrow CrO_4^{2-}$. For Redox reaction write the scheme of electron balance, mark oxidizing and reducing agents.

CHAPTER # 10. COMPLEX (COORDINATION) COMPOUNDS

Vocabulary

English	Українська назва	English	Українська назва
Chelation, complexing agent	*Комплексоутворювач, центральний атом*	*Ligand, addend*	*Ліганд, аденд*
Internal (inner) sphere	*Внутрішня сфера*	*Complex ion, polyatomic ion*	*Комплексний іон*
Outer sphere	*Зовнішня сфера*	*Coordination number*	*Координаційне число*

10.1 General characteristics

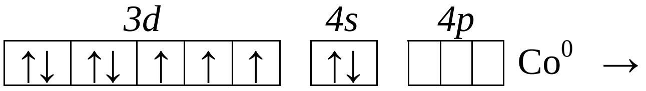
All the variety of inorganic compounds can be divided into two groups: 1) second order compounds or simple; 2) the highest order compounds.

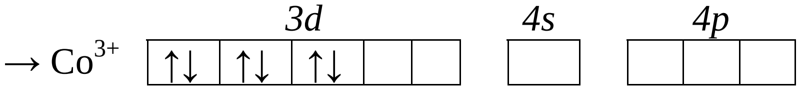
The substances whose value of element oxidation number coincides with presented valency or with quantity of chemical bonds in molecule (NH_3, H_2O, SO_3, AgCl, etc.) are called simple compounds but the substances in which additional valence bonds occur are considered as compounds of the highest order and are called coordinate or complex.

The simple compounds are structured at the account of ionic, covalent polar or covalent non-polar bond. In contrast to this the additional covalent bond is formed in complex compounds on the basis of donor-acceptor interaction. Owing to this bond the complex bond is formed. Donor-acceptor interaction between central ion-complexing agent and ligands takes place. At the same time ion-complexing agent takes part in formation of the bonds, giving free orbitals of their external and pre-external energy levels but ligands - giving electron pairs of one of the atoms. For example, the following stages can be presented in case of $[Co(NH_3)_6]^{3+}$ complex ion formation:

1) Co^{3+} ion formation from cobalt atom:

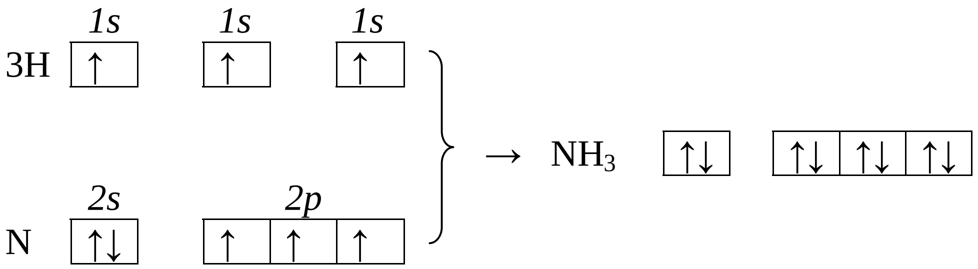
$$_{27}Co^0\ 1s^22s^22p^63s^23p^63d^74s^24p^0 \xrightarrow{-3\bar{e}} Co^{3+}\ 1s^22s^22p^63s^23p^63d^64s^04p^0$$



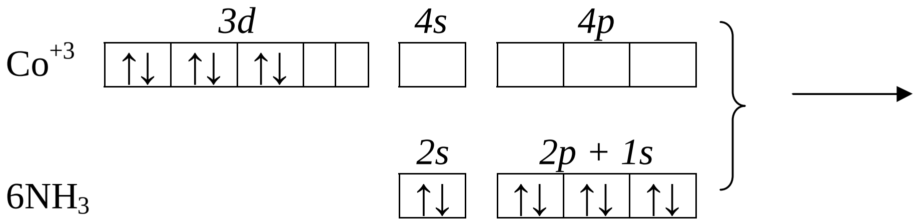


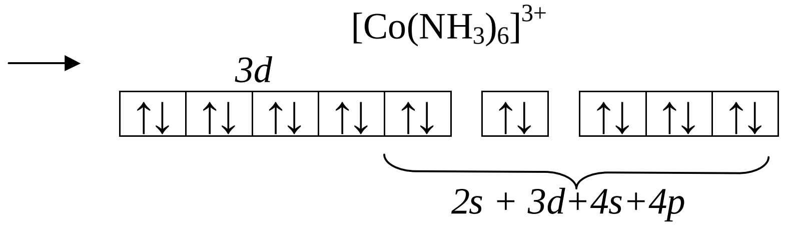
2) ammonia molecule formation:

$$_7N^0\ 1s^22s^22p^3 \xrightarrow{+3\bar{e}} N^{3-}\ 1s^22s^22p^6;\quad {}_1H^0\ 1s^1 \xrightarrow{-1\bar{e}} H^{1+}\ 1s^0$$ or



3) formation of $[Co(NH_3)_6]^{+3}$ complex ion at the account of six free orbitals 3d, 4s and 4p of Co^{+3} sublevels and paired Nitrogen 2s electrons which is the part of ammonia six molecules:





The main principles of complex compound formation were presented in 1893 by Swiss chemist Alfred Werner as **coordination theory**:

1. In the molecule of any complex compound one of the ions takes the central place and is called complexing agent or central ion;

2. Some quantity of ions or neutral molecules with opposite charges is placed close enough around the central ion and is called ligands.

Central ion with ligands placed around it forms so-called inner coordination sphere of compound (complex ion);

3. Ions, which are located far from central ion, make outer coordination sphere of complex compound;

4. Number, which shows how many ligands are located around complexing agent in the inner sphere, is called coordinating.

Structure of complex compound may be presented as:

$$\overset{\substack{\text{Complexing agent}\\ \downarrow}}{[Cu}(\underset{\substack{\uparrow\\ \text{Ligands, addends}}}{NH_3})_{\underset{\uparrow}{4}}]SO_4 \quad \text{Coordination number}$$

$$\underbrace{[Cu(NH_3)_4]}_{\text{Inner sphere}}\overbrace{SO_4}^{\text{Outer sphere}}$$

10.2 Nomenclature

Because of the large number of complicated coordination compounds, it has been necessary to develop a systematic method for naming them. Complex species may be a *cation* such as $[Cu(H_2O)_4]^{2+}$, an anion such as $[Fe(CN)_6]^{4-}$, or a *neutral* molecule such as $[Cr(NH_3)_3Cl_3]$. Many different electronically satisfied entities may act as electron-pair donor ligands. The names of some common ligands are given in the margin. It may be seen that the names of negatively-charged ligands end in *o*. The name of the molecule is generally used for neutral ligands. Water and ammonia are the two important exceptions. The rules listed below enable you to name a large number of common complex substances. The rules for naming chemical compounds are established by nomenclature committees of the International Union of Pure and Applied Chemistry (IUPAC).

10.3 Rules for naming of coordination compounds

The following rules should be taken into account while drawing the formulas of complex compounds:

1. Complex ion charge is numerically equal to algebraic sum of ion-complexing agent and ligands charges;

2. Total ion charges, located in outer sphere, are numerically equal and opposite in sign to the charge of inner coordinating sphere. For example, for $K_4[Fe(CN)_6]$ inner sphere charge is (2+) + (6-) = 4-, outer sphere charge is 4 · (1+) = 4+, complex compound charge is (4-) + (4+) = 0.

Multicharged ions of heavy metals, which have 18-electronic or transient from 8- to 18-electrinic outer configuration and have free orbitals show the ability to complex formation. Ions of some non-metals may be complexing agents. Generally the charge of complexing agent corresponds to the charge of given atom in simple compound composition. Therefore the process of complex compound may be easily presented as the composition of simple substance molecules:

$4KCN + Fe(CN)_2 = K_4[Fe(CN)_6]$;

$NiSO_4 + 6NH_3 = [Ni(NH_3)_6]SO_4$;

$2NaOH + Zn(OH)_2 = Na_2[Zn(OH)_4]$.

The prevailing coordination numbers are 2, 4, and 6. It can be pointed out that coordination number mostly is equal to doubled or triple charge of ion-complexing agent (see Table 14).

The ability of ligands to coordination depends on atoms presented in them or groups with undivided electron pairs owing to which the link with the central atom takes place. The prevalent electron donors are the atoms of N, O, C, Cl, Br, I.

The name of the positive ion is written before the name of the negative ion.

The name of the ligands is written before the name of the metal to which it is coordinated.

The Greek prefixes *mono-*, *di-*, *tri-*, *tetra-*, *penta-*, *hexa-*, and so on are used to indicate the number of ligands when these ligands are relatively simple. The Greek prefixes *bis-*, *tris-*, and *tetrakis-* are used with more complicated ligands.

The names of negative ligands always end in *o*, as in *fluoro* (F^-), *chloro* (Cl^-), *bromo* (Br^-), *iodo* (I^-), *oxo* (O^{2-}), *hydroxo* (OH^-), and *cyano* (CN^-). A handful of neutral ligands are given common names, such as *aquo* (H_2O), *ammine* (NH_3), and *carbonyl* (CO).

Ligands are listed in the following order: negative ions, neutral molecules, and positive ions. Ligands with the same charge are listed in alphabetical order.

A Roman numeral in parentheses indicates the oxidation number of the metal atom after the name of the metal atom.

The names of complexes with a net negative charge end in *-ate*. $Co(SCN)_4^{2-}$, for example, is the Tetrathiocyanatocobaltate (II) ion. When the symbol for the metal is derived from its Latin name, *-ate* is added to the Latin name of the metal. Thus, negatively charged Iron complexes are ferrates and negatively charged Copper complexes are cuprates (see examples in Table 14).

Table 14. Characteristics of some complex compounds

Complexing agent	Coordination number	Formula	Name
Ag^{+}	2	$[Ag(NH_3)_2]Cl$	Diaminesilver (I) Chloride
Cu^{2+}	4	$[Cu(NH_3)_4](OH)_2$	TetramineCopper (II) Hydroxide
Hg^{2+}	4	$K_2[HgI_4]$	Potassium Tetraiodomercurate (II)
Zn^{2+}	4	$Na_2[Zn(OH)_4]$	Sodium Tetra-hydroxozincate
Co^{2+}	4	$(NH_4)_2[Co(SCN)_4]$	Ammonium Tetra-thiocyanocobaltate (II)
B^{3+}	4	$Na[BF_4]$	Sodium Tetrafluoroborate
Co^{3+}	6	$[Co(H_2O)_6]Cl_3$	Hexaquocobalt (III) Chloride
Al^{3+}	6	$Na_3[Al(OH)_6]$	Sodium Hexa-hydroxoaluminate

PRACTICE PROBLEMS

1. Define oxidation number, coordination number of complexing agent and charge of complex ion in the following compounds: $[Cd(NH_3)_4](OH)_2$, $Cu_2[Fe(CN)_6]$, $[Cr(H_2O)_6]Br_3$, $K_3[FeF_6]$, $Na_3[Cr(OH)_6]$, $[Ni(CO)_4]$, $[Cu(NH_3)_4]_3(PO_4)_2$, $K_3[Co(CN)_6]$.

2. Which salts are used for $K_4[Fe(CN)_6]$ production? Equate the reactions.

3. Write given formulas as complex compounds: $2HF{\cdot}SiF_2$; $2KCl{\cdot}PbCl_2$; $NiCl_2{\cdot}6NH_3$; $CuSO_4{\cdot}4NH_3$; $Zn(OH)_2{\cdot}Ca(OH)_2$; $3KNO_2{\cdot}Co(NO_2)_3$; $4KCN{\cdot}Fe(CN)_2$, $CoSO_4{\cdot}6H_2O$.

4. Write molecular and ionic reactions between the following substances: $ZnSO_4$ and $K_3[Fe(CN)_6]$; $FeCl_3$ and $K_3[Fe(CN)_6]$; KCl and $Na_3[Co(NO_2)_6]$; $K_2[HgI_4]$ and $AgNO_3$; $FeCl_3$ and KSCN (surplus); NaCl and $K[Sb(OH)_6]$; $CuSO_4$ and NH_3; $ZnCl_2$ and KOH (surplus).

LABORATORY TRAINING

Experiment 1. Compound formation with complex cation

Add by drops ammonia solution firstly up to the formation of HydroxoSulfate and then up to its complete dilution and formation of complex compound $[Cu(NH_3)_4]SO_4$ into the test-tube with 4-5 drops of cuprous Sulfate or Chloride (II). How does the initial color of the solution change? Equate the reaction according to the process stages of reagent interactions.

Experiment 2. Compound formation with complex anion

A) Put 4-5 drops of $Hg(NO_3)_2$ solution into the test-tube and add by one drop of KI solution up to the formation of red precipitate of Mercury (II) iodide. Continue to add KI solution up to complete dilution of precipitate and formation of soluble complex compound - Potassium Tetraiodomercurate (II). Equate the reaction taking into account the stages.

B) Put 5-7 drops of Cobalt (II) Sulfate or Chloride solution into the test-tube. Add little by little the granules of KNO_2 up to solution saturation (there are some undissolved salt at the bottom of test-tube). Add by drops concentrated acetic acid to the mixture up to the formation of yellow precipitate of $K_3[Co(NO_2)_6]$. Equate the reaction according to stages taking into account that nitrous acid, which is isolated under acidation, oxidizes Co^{2+} to Co^{3+}:

$CoCl_2 + KNO_2 \rightarrow$

$KNO_2 + CH_3COOH \rightarrow HNO_2 +\dots$

$Co(NO_2)_2 + HNO_2 \rightarrow NO +\dots$

$Co(NO_2)_3 + KNO_2 \rightarrow$

Experiment 3. Complex compounds in metathesis

A) Add 2-3 drops of $K_3[Fe(CN)_6]$ solution to 4-5 drops of any Iron (II) salt solution. What is the color of precipitate? Equate molecular and ionic reactions.

B) Add 2-3 drops of $K_4[Fe(CN)_6]$ solution to 4-5 drops of any Cooper (II) salt solution. Identify the color of precipitate and equate molecular and ionic reactions.

C) Add 2-3 drops of $K_4[Fe(CN)_6]$ solution to 4-5 drops of Iron (III) salt solution. Identify the color of precipitate and equate molecular and ionic reactions.

D) Add 2-3 drops of KSCN or NH_4SCN solution to 4-5 drops of Iron (III) salt solution. Identify the color of precipitate and equate molecular and ionic reactions.

CHAPTER # 11. THE HALOGENS

Vocabulary

English	Українська назва	English	Українська назва
Halogen	*Галоген*	*Bleaching agent*	*Відбілювач*
Poisonous	*Отруйний*	*Bleaching powder*	*Хлорне вапно*
Halide	*Галогенід*	*Herbicide*	*Гербіцид*

11.1 General characteristics

The elements of Group 7A (or the main sub-group of VII group), the Halogens, are:

Symbol	Electron configuration
Fluorine F	$[He]2s^2 2p^5$
Chlorine Cl	$[Ne]3s^2 3p^5$
Bromine Br	$[Ar]4s^2 4p^5$
Iodine I	$[Kr]5s^2 5p^5$
Astatine As	$[Xe]6s^2\ 6p^5$

All the isotopes of astatine are radioactive, and so this element will not be considered further here. The similarity of their properties is conditioned by similar electronic structure of the atoms where the external energy level is expressed by the electronic formula $ns^2\ np^5$. Moreover only F has no *d*-sublevel and as the result it is exclusively one-valent. Taking into account that F is the most electronegative element it is characterized by two levels of oxidation in compounds (0 and 1-).

Appearance

Fluorine is a poisonous pale yellow gas, Chlorine is a poisonous pale green gas, Bromine is a toxic and caustic brown volatile liquid, and Iodine is a shiny black solid, which easily sublimes to form a violet vapor on heating.

General Reactivity

The elements of Group 17, the Halogens, are very similar set of non-metals. They all exist as diatomic molecules, X_2, and oxidize metals to form halides. The halogen oxides are acidic, and the hydrides HX are covalent. Fluorine is the most electronegative element of all. Generally, electronegativity and oxidizing ability decrease on descending the Group. The result of this decreasing electronegativity is increased covalent character in the compounds, so that AlF_3 is ionic whereas $AlCl_3$ is covalent.

Fluorine shows some anomalies because of the small size of its atom and ion. This allows several F atoms to pack around a different central atom, as in $[AlF_6]^{3-}$ compared with $[AlCl_4]^-$. The F-F bond is also unexpectedly weak because the small size of the F atom brings the lone pairs closer together than in other halogens, and repulsion weakens the bond.

Occurrence and Extraction

The Halogens are too reactive to occur free in nature. Fluorine is mined as fluorspar, calcium fluoride and cryolite. It is extracted by electrolysis as no oxidant will oxidize fluorides to Fluorine. Chlorine is also found in minerals such as rock salt, and huge quantities of Chloride ions occur in seawater, inland lakes and subterranean brine wells. It is obtained by the electrolysis of molten Sodium Chloride or brine. Bromine is also found as the bromide ion in seawater, and in larger quantities in brine wells, from which it is extracted. Iodine is mined as Sodium Iodate (V) $NaIO_3$, which is present in Chile saltpetre. It is obtained by reaction with Sodium Hydrogen Sulfite.

Physical Properties

At room temperature all the Halogens exist as diatomic molecules. The melting points, boiling points, atomic radii and ionic radii all increase on descending the Group. More than 8 electrons never surround Fluorine, whereas the other halogens may be surrounded by up to 14 electrons.

Chemical Properties

The most characteristic chemical feature of the Halogens is their ability to oxidize. Fluorine has the strongest oxidizing ability, so other elements, which are combined with Fluorine, have their highest possible oxidation number:

$$2F_2 + H_2O = 2HF + OF_2$$

$$\begin{array}{l|l} F_2^0 + 2\bar{e} \rightarrow 2F^- & 2 \text{ (reduction);} \\ O^{2-} - 4\bar{e} \rightarrow O^{2+} & 1 \text{ (oxidation).} \end{array}$$

$$2F_2 + 2NaOH \rightarrow 2NaF + OF_2 + H_2O.$$

Fluorine is such a strong oxidizing agent that it must be prepared by electrolysis of solid salts:

$$2NaF_{solid} \xrightarrow{\text{electrolysis}} 2Na + F_2\uparrow.$$

Chlorine is the next strongest oxidizing agent, but it can be prepared by chemical oxidation. Most elements react directly with Chlorine, Bromine and Iodine, with decreasing reactivity going down the Group, but often the reaction must be activated by heat or UV light. The oxidation of Thiosulfate ions, $S_2O_3^{2-}$, by the Halogens is quantitative.

This means that oxidizing agents can be estimated accurately; the oxidizing agent is reacted with excess I^- ions, and the liberated I_2 titrated with standard Thiosulfate solution. The end point is detected with starch as indicator, which forms a dark blue complex with Iodine.

Chlorine, Bromine and Iodine disproportionate in the presence of water and alkalis.

Oxides and Oxoacids

There are no Fluorine oxides as F is more electronegative than O. Chlorine, Bromine and Iodine each form several oxides, which are thermally unstable, such as Chlorine dioxide ClO_2. The only Fluorine oxoacid, HOF, is unstable at room temperature, but there are many oxoacids of the other Halogens. The best-known salts of these are: Hypochlorite, Chlorate (I) CIO^-, Chlorite, Chlorate (III) ClO_2^-, Hypochlorate, Chlorate (V) CIO_3^-, and Perchlorate, Chlorate (VII) ClO_4^-. These are all powerful oxidizing agents.

Halides

The Halogens can be combined with each other to form interhalogens and polyhalide ions. Olyhalide ions have the general formula [Y-X-Y]-. It is not possible for F to represent X in a polyhalide ion, as it cannot expand its octet.

Hydrides

Hydrogen halides have the general formula HX. HF is a colorless liquid, which boils at $19{,}5^0C$, and all the other Hydrogen halides are colorless gases. HF is a liquid due to the extensive Hydrogen bonding which occurs between molecules. All the Hydrogen halides are easily dissolved to give acidic solutions, the most widely used being hydrochloric acid, HCl. All except HF are typical acids; they liberate carbon dioxide from Carbonates and form salts with basic oxides. HF is a weak acid because the H-F bond is very strong, and because Hydrogen-bonding occurs between F- and HF in solution.

Oxidation States

Fluorine in all its compounds has an assigned oxidation number of -1, as it is the most electronegative of all the elements. The other halogens show a wide range of oxidation numbers, and the redox chemistry of these halogens is important. The oxidation numbers most commonly shown are odd; there are few compounds with even oxidation numbers and they are often thermally unstable. Chlorine is the third most electronegative element after F and O. The halide ions are readily formed by accepting one electron, as this completes an octet of valence electrons. The electron affinity decreases on descending the Group.

Industrial information

The Halogens are probably the most important Group of the Periodic Table used in industry. Fluorine is widely used as an oxidizing agent. HF is used to etch glass. Chlorine is used for chlorinating of drinking water, and in many organochlorine compounds. Some of these, such as the insecticide DDT, are effective but environmentally damaging, and much controversy surrounds their use. Chlorine dioxide ClO_2 is used to bleach wood pulp for paper making, as it gives a good whiteness without degrading the paper. Hypochlorites are used in domestic bleaches. Potassium chlorate (V) $KClO_3$ is used as an oxidant in fireworks and matches. The properties of the Halogens on the example of Chlorine will be presented below.

11.2 Chlorine

Being the third period element, Chlorine has the following electronic structure: $1s^2 2s^2 2p^6 3s^2 3p^5$. The following oxidation numbers are possible for Chlorine in the compounds on the basis of external energy level structure ($3s^2 3p^5$) (see Chapter 2.2-2.3):

Ground (nonexcited) state (1-, 0, 1+ oxidation number, for example, in HCl, Cl_2, HClO compounds):

3s	*3p*			*3d*				
↑↓	↑↓	↑↓	↑					

The first excited state (3+ oxidation number, for example, in $HClO_2$ compound);

3s	*3p*			*3d*				
↑↓	↑↓	↑	↑	↑				

The second excited state (5+ oxidation number, for example, in $HClO_3$ compound);

3s	*3p*			*3d*				
↑↓	↑	↑	↑	↑	↑			

The third excited state (7+ oxidation number, for example, in $HClO_4$ compound).

3s	*3p*			*3d*				
↑	↑	↑	↑	↑	↑	↑		

The general characteristics of the most important Chlorine compounds are shown in Table 15.

Table 15. General characteristics of Chlorine compounds

Oxidation number	-1	0	+1	+3	+5	+7
Compounds	HCl, NaCl	Cl_2	Cl_2O, HClO, KClO	Cl_2O_3, $HClO_2$, $NaClO_2$	Cl_2O_5 $HClO_3$ $KClO_3$	Cl_2O_7 $HClO_4$ $NaClO_4$
Names of acids and salts	Hydrochloric, Chlorides	-	Hypochlorous, Hypochlorites, Chlorates (I)	Chlorous, Chlorites, Chlorates (III)	Chloric, Chlorates, Chlorates (V)	Perchloric, Perchlorates, Chlorates (VII)
Redox properties	Only reducing agent	Properties of oxidizing and reducing agent; oxidizing properties prevail	Properties of oxidizing and reducing agent; oxidizing properties prevail	Properties of oxidizing and reducing agent	Reducing properties surpasses oxidizing ones	Only oxidizing agent
Acid-Base properties	HCl - strong acid	-	HClO - weak acid; unstable in free state	$HClO_2$ - acid of medium strength; unstable in free state	$HClO_3$ - strong acid; unstable in free state	$HClO_4$ - extrastrong acid; stable in free state

Strengthening of acid properties

Chlorine (Cl_2) is the typical non-metal with brightly expressed features of oxidant. Due to high activity Chlorine in nature occurs only in bound state as Chlorides: NaCl - halite or rock salt, NaCl · KCl - sylvinite, $KCl \cdot MgCl_2 \cdot 6H_2O$ - carnallite, $MgCl_2 \cdot 5H_2O$ - bischofite, etc. Chlorides are abundant in sea water.

In industry Chlorine is prepared by the electrolysis of concentrated solution of NaCl:

$$2NaCl + 2H_2O \leftrightarrow 2NaOH + Cl_2\uparrow + H_2\uparrow$$

and in the laboratory - by influence of HCl on MnO_2 or $KMnO_4$:

$$2KMnO_4 + 16HCl = 5Cl_2 + 2MnCl_2 + 2KCl + 8H_2O$$

$$\begin{array}{l|l} Mn^{7+} + 5\bar{e} \rightarrow Mn^{2+} & 2\ \text{(reduction);} \\ 2Cl^{-}\ - 2\bar{e} \rightarrow Cl_2 & 5\ \text{(oxidation).} \end{array}$$

Chlorine actively reacts almost with all periodic system elements. With the metals it forms the salts and with non-metals - halogenous anhydrides:

$$Mg + Cl_2 = MgCl_2;$$

$$2P + 3Cl_2 = 2PCl_3.$$

Halogenous anhydrides are hydrolyzed forming both nonmetal acids with the relevant oxidation numbers:

$$PCl_5 + 4H_2O = H_3PO_4 + 5HCl.$$

Chlorine does not react directly with Oxygen, Carbon and Nitrogen.

HCl (Hydrochloric aqua solution) is of practical value. In the reaction of the Halogens and Hydrogen composition there is the tendency of oxidative activity weakening from Fluorine and Iodine: Fluorine reacts with Hydrogen generating the explosion in the dark; Chlorine - in air or while heating with the explosion, Bromine and Iodine - in case of extensive heating, for example,

$$Cl_2 + H_2 = 2HCl.$$

The intensity of HF, HCl, HBr, HI acids increases. It is characterized by number of reaction typical for acids:

$$2HCl + 2Na = 2NaCl + H_2\uparrow;$$

$$2HCl + SrO = SrCl_2 + H_2O;$$

$$2HCl + Ca(OH)_2 = CaCl_2 + 2H_2O.$$

Halogens form Oxygen compounds as well, mainly: oxides, acids and salts.

The basis for preparation of halogens oxygen-contained compounds is their interaction with water and alkalis. In cold the reaction is carried out in case of dynamic balance:

$Cl_2 + H_2O \leftrightarrow HCl + HClO$

$Cl_2^0 + 2\bar{e} \rightarrow 2Cl^-$ | 1 (reduction);

$Cl_2^0 - 2\bar{e} \rightarrow 2Cl^+$ | 1 (oxidation).

$2Cl_2 + 2Ca(OH)_2 = CaCl_2 + Ca(ClO)_2 + 2H_2O.$

On heating such mixture reacts with the formation of Chlorates:

$3Cl_2 + 3H_2O \xleftrightarrow{t} 5HCl + HClO_3;$

$Cl_2^0 + 2\bar{e} \rightarrow 2Cl^-$ | 5 (reduction);

$Cl_2^0 - 10\bar{e} \rightarrow 2Cl^{+5}$ | 1 (oxidation).

$3Cl_2 + 6NaOH = 5NaCl + NaClO_3 + 3H_2O.$

HClO, HBrO, HIO electrolytes are the less stable and the weakest among Chlorine oxyacids and other halogens.

Thus in air HClO is decayed with active (atomic) Oxygen:

$HClO = HCl + \overset{\bullet}{O}.$

Active Oxygen discolors many colorants and that is why Chlorine (1+) oxyacid salts are called bleaching: NaClO are used for bleach and wash; the mixture of $Ca(ClO)_2$ and $CaCl_2$ which is known as bleaching powder, is used in agriculture for disinfections of the facilities, warehouses, and animal corpses.

Sodium, Magnesium and Calcium chlorates are of great value for the agriculture. They are used as herbicides for wild grass control. In Redox reactions Cl^- is exclusively reducing agent, but Cl^{7+} - only the oxidizing one. Halogens with the medium oxidation numbers (Cl^0, Cl^+, Cl^{3+}, Cl^{5+}) may be mainly as the reducing agents, but also the oxidizing ones. Oxidative activity of the compounds is increased from Cl^{7+} to Cl^{1+}.

For example,

$2KI + NaClO + H_2SO_4 = I_2 + NaCl + K_2SO_4 + H_2O$

$Cl^+ + 2\bar{e} \rightarrow Cl^-$ | 1 (reduction);

$2I^- - 2\bar{e} \rightarrow I_2$ | 1 (oxidation).

PRACTICE PROBLEMS

1. How oxidative and reducing activity of the Halogens is changed in the group?

2. Which oxidative levels are typical for Fluorine and what is the difference between Fluorine and other halogens?

3. Write the formulas of four oxidative Chlorine acids and indicate the strongest acid and oxidizing agent.

4. Which chemical reactions should be carried out in order to receive bleaching powder, having $KMnO_4$, HCl, CaO and H_2O?

5. Write the equations according to the transformation series:

$KCl \rightarrow Cl_2 \rightarrow KClO \rightarrow KClO_3 \rightarrow KCl$;

$NaF \rightarrow CaF_2 \rightarrow F_2 \rightarrow HF \rightarrow H_2[SiF_6]$.

6. Complete the equations and put the coefficients according to the schemes of electron redistribution:

1) $Ni(OH)_2 + NaClO + H_2O \rightarrow Ni(OH)_3 + \ldots$
2) $KI + KIO_3 + H_2SO_4 \rightarrow$
3) $Zn + KClO_3 + H_2SO_4 \rightarrow$
4) $KMnO_4 + NaI + H_2O \rightarrow$

LABORATORY TRAINING

Experiment 1. Interaction between metals and halogenhydrides

Put Zinc granule into the first test-tube, small amount of Iron chips into the second and some Copper chips into the third. Add 5-7 drops of hydrochloric acid solution into each of them. Determine in which cases the reactions take place and the gas is evolved. Write the reactions.

Experiment 2. Halogens oxidative activity in free state

Put 3-4 drops of KBr or NaBr solution into the test-tube, add 5-6 drops of chloric water (Chlorine solution in H2O, which includes free Chlorine in the form of Cl2). Free evolved Bromine is extracted by shaking the mixture with 3-4 drops of benzol. Determine the color of the Bromine and write the reaction. Carry out similar test with KI and Bromine water in another test-tube.

Experiment 3. Reducing properties of I^- ions

Put 4-5 drops of H_2SO_4 into 2-3 drops of KI and add by dropping the solution of Sodium or Potassium Nitrite (KNO_2, $NaNO_2$) up to the change of mixture color. Prove the presence of free Iodine in the mixture adding some drops of starch. Write the equation.

Experiment 4. Chlorates as oxidazing agents

Add 2-3 drops of $KClO_3$ solution to the same volume of Iron (II) Sulfate solution and add 1-2 drops diluted sulfuric acid. Check the mixture for the presence of Fe^{3+} adding Potassium or Ammonium thiocyanate.

Experiment 5. The salts of hydrohalogen acids insoluble in water

Put 3-5 drops of solutions hydrochloric and hydroiodic acids salts (for example, NaCl and KI) into the test-tubes and add into each several drops of $Pb(NO_3)_2$. Determine the color of occurred precipitates, write the equations.

CHAPTER # 12. THE CHALCOGENS

Vocabulary

English	Українська назва	English	Українська назва
Chalcogen	*Халькоген*	*Perhydrol*	*Пергідроль*
Ozone	*Озон*	*Rare element*	*Розсіяний елемент*
Hydrogen Peroxide	*Пероксид водню*	*“Bad egg gas”*	*Сірководень*

12.1 General characteristics

The elements of Group 6A (or the main sub-group of VI group) are:

Symbol	Electron configuration
Oxygen O	[He]$2s^2 2p^4$
Sulfur S	[Ne]$3s^2 3p^4$
Selenium Se	[Ar]$3d^{10} 4s^2 4p^4$
Tellurium Te	[Kr]$4d^{10} 5s^2 5p^4$
Polonium Po	[Xe]$4f^{14} 5d^{10} 6s^2\ 6p^4$

Often this group of chemical elements (except the last Po) is named **the Chalcogens.**

Appearance

The first element of this sub-group, Oxygen, is the only gas, and is colorless and odorless. Sulfur is a pale yellow, brittle solid. Selenium can have either an amorphous or a crystalline structure; the amorphous form can be red or black, and the crystalline form can be red or gray. Tellurium is a silvery-white color with a metallic luster. Polonium is a naturally radioactive element.

Selenium and Tellurium are rare elements with few uses, and along with Polonium will not be considered further here.

General Reactivity

Oxygen and Sulfur are highly electronegative elements - the electronegativity of Oxygen is second only to that of Fluorine. Their general reactivity is therefore dominated by their ability to gain electrons.

There is a transition down the sub-group from non-metallic to more metallic properties, so that Oxygen is a non-metal and Tellurium a metalloid. All the elements except Polonium form M^{2-} ions.

There is a marked difference between Oxygen and the other members of the Group. This arises from:

- the small size of the O atom which enables it to form double bonds;
- its inability to expand its valence shell like the other elements as it has no accessible d-orbitals;
- its high electronegativity, which enables it to participate in Hydrogen-bonding.

Occurrence and Extraction

Oxygen occurs widely as the free element in the form of O_2, comprising 21% of the air by volume. It also occurs as O_3, ozone, at high altitudes in the ozone layer. In the combined form it is found in very many minerals, and also in water. Oxygen is obtained industrially by the fractional distillation of liquid air. It is stored under pressure in cylinders.

Sulfur is found as the free element and also as metal Sulfide ores and a number of Sulfates. Native sulfur is brought to the surface from underground deposits by the Frasch Process, which uses superheated water to melt the Sulfur and force it upwards.

Physical Properties

The covalent and ionic radii increase going down the sub-group, as electrons occupy shells with higher quantum numbers.

Oxygen occurs as two gaseous allotropes, O_2 (dioxygen or more commonly Oxygen) and O_3 (trioxygen or ozone). Oxygen is more common. It condenses to a pale blue paramagnetic liquid at -183^0C. Ozone is a pale blue, pungent gas, which condenses to an inky-blue liquid at -112^0C. The ozone layer in the upper atmosphere is an important shield against harmful UV radiation from the Sun.

Sulfur has several allotropes, the two main ones being rhombic and monoclinic sulfur. These both consist of S_8 molecules.

Industrial Information

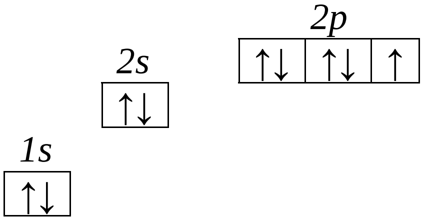
Sulfuric acid is of immense industrial importance. Because it has three chemical functions and is very cheap to produce, Sulfuric acid is used at some stage of the manufacture of most products. It is said that the economic prosperity of a country can be assessed by its consumption of sulfuric acid. It is manufactured by the Contact Process.

Hydrogen peroxide H_2O_2 is used to bleach hair and textiles, as a mild disinfectant and in pollution control.

Sulfur hexafluoride SF_6 cannot be ionized by electric fields and so is widely used as a gaseous insulator in transformers and electrical switchgear.

12.2 Oxygen

Oxygen is the element of the second period, its formula is $1s^2 2s^2 2p^4$.



On the assumption of external electron shell structure (graphic presentation) and electronegativity of Oxygen, it is characterized by oxidation number equal to 2-, moreover, in composition with Fluorine the oxidation number of Oxygen will be 2+ (for example, OF_2) but in peroxides it will be 1- (for example, H_2O_2) or, sometimes, -½ (for example, superoxide KO_2).

Oxygen, like Fluorine, forms compounds with all elements except Helium, Neon and Argon. Atomic Oxygen is extremely active.

In elemental state Oxygen is mostly characterized as the oxidizing agent in the reactions:

1) $4FeS + 7O_2 = 2Fe_2O_3 + 4SO_2$

$O_2^0 + 4\bar{e} \rightarrow 2O^{2-}$ | 7 (reduction);
$S^{2-} - 6\bar{e} \rightarrow S^{+4}$ | 4 (oxidation).
$Fe^{2+} - 1\bar{e} \rightarrow Fe^{3+}$ |

2) $2KI + O_3 + H_2O = I_2 + 2KOH + O_2$

$O^0 + 2\bar{e} \rightarrow O^{2-}$ | 1 (reduction);
$2I^- - 2\bar{e} \rightarrow I_2^0$ | 1 (oxidation).

Oxygen compounds in which the oxidation number is equal to 1- are called **peroxides.** For example, Hydrogen peroxide H_2O_2, where covalent and non-polar bonds in molecule connect two atoms of Oxygen.

Water solution of Hydrogen peroxide (perhydrol) presents weak dibasic acid:

$H_2O_2 \leftrightarrow H^+ + HO_2^-$;
$HO_2^- \leftrightarrow H^+ + O_2^{2-}$.

Medium of oxidation number of Oxygen in peroxides causes its oxidation-reduction duality in the reactions. H_2O_2 is the reducing agent:

$H_2O_2 + 2KMnO_4 + 2KOH = 2K_2MnO_4 + 2H_2O + O_2$

$Mn^{7+} + \bar{e} \rightarrow Mn^{6+}$ | 2 (reduction);

$$\begin{array}{l|l} 2O^{-} - 2\,\bar{e} \rightarrow O_2^{0} & 1\text{ (oxidation).} \end{array}$$

but in presence of strong reducing agent it is oxidizing agent:

$H_2O_2 + 2KI + H_2SO_4 = I_2 + K_2SO_4 + 2H_2O$

$$\begin{array}{l|l} 2O^{-} + 2\,\bar{e} \rightarrow 2O^{2-} & 1\text{ (reduction);} \\ 2I^{-} - 2\,\bar{e} \rightarrow I_2^{0} & 1\text{ (oxidation).} \end{array}$$

Ozone is also a highly reactive and powerful oxidizing agent which can cleave the C=C double bond.

12.3 Sulfur

In contrast to Oxygen, Sulfur atom has free *d*-sublevel in the external electronic shell: $1s^2 2s^2 2p^6 3s^2 3p^4 3d^0$.

Accordingly, Sulfur can form the compounds due to two, four and six unpaired electrons, showing such oxidation levels: 2-, 0, 2+, 4+, 6+:

Ground (nonexcited) state (2-, 0, 2+ oxidation number, for example, in H_2S, S, SO compounds):

3s	*3p*			*3d*				
↑↓	↑↓	↑	↑					

The first excited state (4+ oxidation number, for example, in SO_2 compound):

3s	*3p*			*3d*				
↑↓	↑	↑	↑	↑				

The second excited state (6+ oxidation number, for example, in H_2SO_4 compound):

3s	*3p*			*3d*				
↑	↑	↑	↑	↑	↑			

Characteristic of the most important sulfur compounds is shown in Table 16.

Table 16. Characteristic of the most important Sulfur compounds

Oxidation numbers	2-	1-	0	2+	4+	6+
Compounds	H_2S, CuS	H_2S_2; FeS_2 (pyrite)	S	SO	SO_2, H_2SO_3	SO_3, H_2SO_4
Name of corresponding acids and salts	Hydrosulfuric acid, sulfides	Persulfides	Free Sulfur	Sulfur (II) Oxide	Sulfur acid, sulphites	Sulfuric acid, sulphates
Redox properties	Only reducing agent	Properties of oxidizing and reducing agent	Properties of oxidizing and reducing agent	-	Reducing properties surpasses oxidizing ones	Only oxidizing agent
Acid-base properties	H_2S - weak acid	-	-	Unstable non-Salifiable Oxide	H_2SO_3 - acid of medium strength, unstable in water solutions	H_2SO_4 - strong acid, stable in water solutions

Strengthening of acid properties

Sulfur is the typical non-metal, which is inferior to Halogens, Oxygen and Nitrogen in electroactivity and thus is oxidized by them:

$S + O_2 = SO_2$;

$S + 2Cl_2 = SCl_4$.

As oxidizing agent, Sulfur reacts with the metals and Hydrogen at high temperature. For example,

$Zn + S = ZnS$;

$S + H_2 = H_2S$.

Hydrogen sulphide (H_2S) is the gas and occurs in nature as the result of putrescent bacteria action to proteins containing sulfur so it can be detected by its characteristic odor ("bad eggs gas"). Inhalation of pure Hydrogen sulphide can bring about to immediate death; even 0,01% of its concentration in the air is extremely dangerous for human being.

Aqueous solution of H_2S is the weak dibasic acid; therefore there are acid and neutral salts (sulphides and hydrosulphides):

$H_2S \leftrightarrow H^+ + HS^-$;

$HS^- \leftrightarrow H^+ + S^{2-}$.

H_2S is strong reducing agent. In air it burns with the generation of SO_2 or S (in case of Oxygen deficit):

$2\ H_2S + 3\ O_2 = 2\ H_2O + 2\ SO_3$

$O_2^0 + 4\bar{e} \rightarrow 2O^{2-}$ | 3 (reduction);

$S^{2-} - 6\ \bar{e} \rightarrow S^{4+}$ | 2 (oxidation).

or $2\ H_2S + O_2$ (in deficit) $= 2\ H_2O + 2\ S$

$O_2^0 + 4\bar{e} \rightarrow 2O^{2-}$ | 1 (reduction);

$S^{2-} - 2\ \bar{e} \rightarrow S^0$ | 2 (oxidation).

Sulfur dioxide (SO_2) is **sulfurous gas** (pungent, choking gas) formed when Sulfur or Sulfides are burnt in air or Oxygen, and as all fossil fuels contain Sulfur it is formed when they burn and contributes to the problem of "*acid rain*" :

$S + O_2 \xrightarrow{t} SO_2 \uparrow$;

$2CuS + 3O_2 \xrightarrow{t} 2\ CuO + 2\ SO_2 \uparrow$;

$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2\uparrow$.

SO_2 may be prepared by Sulfuric acid reduction:

$2H_2SO_4$ (conc) $+ Cu = CuSO_4 + SO_2 \uparrow + 2H_2O$.

Aqueous solution of SO_2 is called Sulfurous acid, which is unknown in free state. H_2SO_3 is of medium strength and can produce acid and neutral salts. Sulfurous acid salts decay in case of strong acids action with SO_2

isolation. This is the base for getting of Sulfur dioxide in laboratory conditions:

$Na_2SO_3 + 2HCl = 2NaCl + SO_2\uparrow + H_2O$.

The medium of oxidation number in Sulfur (IV) compounds causes their oxidation-reduction duality:

$Na_2SO_3 + Cl_2 + H_2O = NaHSO_4 + HCl + NaCl$

$$\begin{array}{l|l} Cl_2^0 \ + \ 2\,\bar{e} \rightarrow \ 2Cl^- & 1 \ \text{(reduction);} \\ S^{4+} \ - \ 2\,\bar{e} \rightarrow S^{6+} & 1 \ \text{(oxidation).} \end{array}$$

$SO_2 + 2\,H_2S = 3\,S + 2H_2O$

$$\begin{array}{l|l} S^{4+} + 4\,\bar{e} \rightarrow S^0 & 1 \ \text{(reduction);} \\ S^{2-} \ - 2\,\bar{e} \rightarrow S^0 & 2 \ \text{(oxidation).} \end{array}$$

SO_2 is used for fumigation of basements, cellars in order to avoid funguses. Calcium hydroSulfite $Ca(HSO_3)_2$ with sulfurous acid is used for sulfitation - one of the methods for preserving of tender fruits and vegetables.

Sulfur trioxide (SO_3) or Sulfur (VI) oxide is the Sulfur acid anhydride. In industry it is produced by SO_2 oxidation in presence of catalyst (Pt) (in so-called Contact Process):

$2\,SO_2 + O_2 = 2\,SO_3$.

Sulfuric acid is manufactured as the result of SO_2 interaction with water or dilute sulfuric acid:

$SO_3 + H_2O = H_2SO_4$.

Strong acidic properties of H_2SO_4 solutions are the basis for their use in fertilizer production or mineral premixes for animals (simple and triple superphosphates, Ammonium Sulfate):

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 5H_2O = \underbrace{Ca(H_2PO_4)_2\cdot H_2O + 2[CaSO_4\cdot 2H_2O]}_{\text{Simple superphosphate}};$$

$Ca_3(PO_4)_2 + 3H_2SO_4 = 2H_3PO_4 + 3CaSO_4$;

$$Ca_3(PO_4)_2 + 4H_3PO_4 + 3H_2O = \underbrace{3\,Ca(H_2PO_4)_2\cdot H_2O}_{\text{Triple superphosphate}}.$$

$H_2SO_4 + 2NH_3 = (NH_4)_2SO_4$.

Concentrated H_2SO_4 is a fairly strong oxidizing agent. Non-metals are oxidized by it up to oxides and H_2SO_4 itself reduces to SO_2:

$C + 2\ H_2SO_4\ (conc) = CO_2 + SO_2 + 2\ H_2O$

$$\left.\begin{array}{l} S^{6+} + 2\ \bar{e} \rightarrow S^{4+} \\ C^0\ - 4\ \bar{e} \rightarrow C^{4+} \end{array}\right| \begin{array}{l} 2\ \text{(reduction);} \\ 1\ \text{(oxidation).} \end{array}$$

PRACTICE PROBLEMS

1. Detect Oxygen and Sulfur oxidation numbers in the following compounds: O_2, O_3, CaO, BaO, OF_2, S_8, FeS, S_2, K_2SO_4, Na_2SO_3, SO_3, $Al_2(SO_4)_3$.

2. At which numbers of oxidation does Sulfur present oxidation-reduction duality?

3. In which cases does Oxygen present the properties of reducing agent?

4. Why Hydrogen Sulfide cannot act as the oxidizing agent?

5. Set up the reaction of Sulfuric acid getting taking into account the following series of conversions:

$FeS_2 \rightarrow SO_2 \rightarrow H_2SO_3 \rightarrow H_2SO_4$.

6. Set up the reaction according to series of conversions:

$SO_3 \rightarrow H_2SO_4 \rightarrow (NH_4)_2SO_4 \rightarrow CaSO_4$.

7. Complete the equations of redox reactions:

$H_2S + H_2O_2 \rightarrow$

$HClO + H_2O_2 \rightarrow$

$KMnO_4 \xrightarrow{t} K_2MnO_4 + MnO_2 + O_2$

$S + NaOH \rightarrow Na_2S + Na_2SO_3 + \ldots$

$NaHSO_3 + Cl_2 + H_2O \rightarrow NaHSO_4 + \ldots$

LABORATORY TRAINING

Experiment 1. Oxidizing properties of H_2O_2

Add 2-3 drops of H_2SO_4 and 3-4 drops of Hydrogen Peroxide to 2-3 drops of Potassium or Sodium iodide. Prove free Iodine release in given reaction by adding starch solution. Set up the reaction.

Experiment 2. Reducing properties of H_2O_2

Drop H_2O_2 up to discoloration of the mixture to the test-tube to 2-3 drops of $KMnO_4$, acidified by 1-2 drops of dilute H_2SO_4. What gas is released? Set up the reaction.

Experiment 3. Reducing properties of S^{2-}

Fill test-tube with 5-7 drops of hydroSulfide water and add some drops of chloric water up to mixture turbidity.

Fill another test-tube with 5-7 drops of Sodium or Ammonium Sulfide. Add 3-4 drops of concentrated nitric acid and watch solution turbidity as the result of sulfur generation. Set up the reactions.

Experiment 4. Reducing properties of S^{4+}

Fill test-tube with 5-7 drops of Na_2SO_3, acidify by 3-4 drops of H_2SO_4 and add 3-5 drops of iodic water (acting component I_2). Why does the color of I_2 disappear? Write the reaction.

Experiment 5. Oxidizing properties of S^{4+}

Acidify 5-6 drops of Na_2SO_3 by 2-3 drops of diluted H_2SO_4 and add some drops of hydrosulfuric water up to mixture turbidity. Write the reaction.

Experiment 6. Dilution of concentrated Sulfuric acid

Carefully add 2-3 drops of concentrated H2SO4 to 3-4 drops of distilled water (but not conversely). Pay attention to the heating of the mixture in test-tube. Why is it necessary to add concentrated H2SO4 into water and is it wrong to add water into the acid?

Experiment 7. Oxidizing properties of H2SO4

A) Put Zinc granule into test-tube and add 15-20 drops of dilute sulfuric acid. What gas is released? Write the reaction.

B) Put Zinc granule into test-tube and add 7-8 drops of concentrated sulfuric acid. Heat the mixture in water bath. Detect the presence of Hydrogen Sulfide by odor (carefully direct gas by the movement of palm). Write the reaction. What is the ion-oxidizing agent in first reaction and what is in the second one?

Experiment 8. Qualitative reaction of SO_4^{2-} ion

Fill test-tube with 8-9 drops of Potassium or Sodium Sulfate solution and add 5-6 drops of $BaCl_2$. Test the solubility of received precipitate in HNO_3 or HCl, as well as in NaOH and KOH. Write the reactions of precipitate formation.

Experiment 9. Instability of thiosulfuric acid

Dissolve some grains of Potassium Thiosulfate ($Na_2S_2O_3$) in 15-20 drops of distilled water and add 8-10 drops of Sulfuric acid. Observe turbidity of solution in 5-10 min. What is the reason? Write the reaction.

CHAPTER # 13. NITROGEN, PHOSPHORUS

Vocabulary

English	Українська назва	English	Українська назва
Laughing gas	*Веселящий газ*	*Caliche*	*чілійська селітра*
Ammophos	*Амофос*	*Nitre, saltpetre, saltpeter, niter*	*Селітра (як добриво)*
Diammophos	*Дифмофос*		

13.1 General characteristics

The elements of Group 5A (or the main sub-group of V group) are:

Symbol	Electron configuration
Nitrogen N	[He]$2s^2 2p^3$
Phosphorus P	[Ne]$3s^2 3p^3$
Arsenic As	[Ar]$3d^{10} 4s^2 4p^3$
Antimony Sb	[Kr]$4d^{10} 5s^2 5p^3$
Bismuth Bi	[Xe]$4f^{14} 5d^{10} 6s^2\ 6p^3$

The most important members of this sub-group are Nitrogen and Phosphorus. The other elements will mostly not be considered here.

Appearance

The appearance of the Group 5A elements varies widely. Nitrogen is a colorless, odorless gas; Phosphorus exists in white, red and black solid forms (allotropic modifications); Arsenic is found in yellow and gray solid forms; Antimony is found in a metallic or amorphous gray form; and finally Bismuth is a white, crystalline, brittle metal. These appearances reflect the changing nature of the elements as the sub-Group is descended, from non-metal to metal.

General Reactivity

The elements of Group 5A show a marked trend towards metallic character on descending the Group. This trend is reflected both in their structures and in their chemical properties, as for example in the oxides, which become increasingly basic.

Occurrence

Nitrogen is found in the atmosphere, and makes up 78% of the air by volume. Phosphorus is not found free in nature, but occurs in several minerals and ores such as Phosphate rock (see **Appendix 12**). The other elements are all found in the elemental form in the Earth crust, but more frequently as minerals.

Physical Properties

The physical properties of this Group vary widely as Nitrogen is a gas, and the other elements are solids of increasingly metallic character.

Nitrogen exists as the diatomic molecule N_2. It is a colorless, odorless gas, which condenses to a colorless liquid at -196^0C. The strength of the bond and the short bond length provide evidence for the bond between the N atoms being a triple bond: $N \equiv N$.

Phosphorus has at least two allotropes, red and white one. White phosphorus is a solid composed of covalent tetrahedral P_4 molecules, and red phosphorus is an amorphous solid, which has an extended covalent structure.

The covalent radii of the atoms increase on descending the sub-Group. However, the N atom is anomalously small and so it can multiple-bond to other N, C and O atoms.

Chemical Properties

Both Nitrogen and phosphorus exist in oxidation states +3 and +5 in their compounds. Nitrogen is very unreactive. The only element to react with Nitrogen at room temperature is Lithium, to form the nitride Li_3N. Magnesium also reacts directly, but only when ignited. Some microorganisms, however, have developed a mechanism for reacting directly with Nitrogen gas and building it into protein - this is called Nitrogen fixation, and is an important early step in the food chain.

Phosphorus is more reactive than Nitrogen. It reacts with metals to form phosphides, with Sulfur to form Sulfides, with halogens to form halides, and ignites in air to form oxides. It also reacts with both alkalis and concentrated nitric acid.

Industrial Information

For industrial use Nitrogen is obtained by fractional distillation of the air. It is used for the manufacture of ammonia by the Haber-Bosch Process:

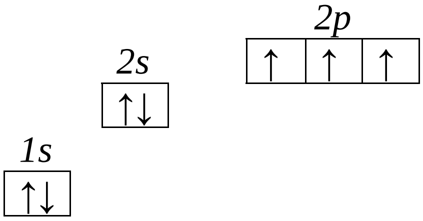
$N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$

A catalyst of finely-divided Iron is required for this equilibrium reaction. The mixture is heated to 450°C at 250 atm of pressure. Working at high pressure increases the yield of ammonia, but this adds to the cost of the plant, and a compromise between cost and yield is needed. The reaction is exothermic so low temperatures increase the yield of ammonia, but this slows up the reaction so again a compromise is needed. At the temperatures and pressures used in practice about 15% conversion is attained. The ammonia is condensed and removed from the plant and the unreacted gases are recycled.

Ammonia has numerous uses - approximately 100 megatonnes are produced worldwide each year. It is used as a fertilizer both directly and after conversion to other fertilizers such as Ammonium Nitrate. It is also a raw material for nitric acid manufacture and for the production of nylon. Gaseous Nitrogen is used to provide an inert atmosphere for reactions, which cannot be carried out in Oxygen. It is also used as a carrier gas in liquid-gas chromatography. Phosphorus is used in match-heads and on safety.

13.1 Nitrogen

Its electronic formula is $1s^2 2s^2 2p^3$. On the basis of graphic drawing of the external energy level ($2s^2 2p^3$) the following valency state and oxidation numbers are possible for Nitrogen:



Valency is III (owing to three unpaired electrons of *2p*-sublevel). Valency is IV (three - owing to unpaired *2p*-electrons, the forth bond - after donor-acceptor mechanism using *2s*-electrons). Oxidation numbers are 3-, 2-, 1-, 0, 1+, 2+, 3+, 4+, 5+.

Nitrogen is the typical non-metal, only Fluorine and Oxygen have stronger electronegativity (3,0). The most widespread Nitrogen compounds of different oxidation levels (from 3- to 5+) are shown in Table 17.

Ammonia (NH_3) is colorless gas with purgen odor. In the laboratory heating of NH_4Cl with Calcium hydroxide or any strong alkalis can produce it:

$2\ NH_4Cl + Ca(OH)_2 \xrightarrow{t} 2\ NH_3\uparrow + CaCl_2 + 2\ H_2O.$

Ammonia can react with water and acids, showing the main properties in the reactions. Practically it does not make NH_4OH hydroxide well dissolved in water (31% at 20^0C), but reacts with H_2O by means of Hydrogen bond:

Table 17. General characteristic of Nitrogen compounds

Oxidation numbers	3-	2-	1-	0	1+	2+	3+	4+	5+
Nitrogen compounds	NH_3 (NH_4^+)	N_2H_4 - hydrazine	NH_2OH - hydroxylamine	N_2	N_2O - laughing gas	NO (N_2O_2)	N_2O_3	NO_2 (N_2O_4)	N_2O_5
Properties in reactions without oxidation number	Weak basic properties; Proton acceptor	Basic properties; Proton acceptor	Weak base	Low chemical activity	Indifferent oxides		Acid oxides		
							HNO_2	HNO_2 + HNO_3	HNO_3
Properties in reactions with oxidation number change	Reducing agent only	Reduction properties prevail over oxidation ones		Oxidizing agent; reducing agent relative to F_2 and O_2	Oxidizing and reducing agents (depending on reaction conditions)				Oxidizing agent only

$NH_3 + H_2O \leftrightarrow NH_3{\cdot}H_2O$;

$NH_3{\cdot}H_2O \leftrightarrow NH_4OH$.

The following important fertilizers are produced by ammonia interaction with acids:

$NH_3 + HNO_3 = NH_4NO_3$ - Ammonia Nitrate;

$2NH_3 + H_2SO_4 = (NH_4)_2SO_4$ - Ammonia Sulfate;

$NH_3 + H_3PO_4 = NH_4H_2PO_4$ - Ammonia dihydrophosphate (**ammophos**);

$2NH_3 + H_3PO_4 = (NH_4)_2HPO_4$ - Ammonia hydrophosphate (**diammophos**).

Nitric oxide (NO) is get by oxidation of Ammonia and it is used as the intermediate product in HNO_3 production:

$4\,NH_3 + 5\,O_2 \xrightarrow{Kt} 4\,NO + 6\,H_2O$

$$\begin{array}{l|l} O_2^0 + 4\,\bar{e} \rightarrow 2\,O^{2-} & 5 \text{ (reduction);} \\ N^{3-} - 5\,\bar{e} \rightarrow N^{2+} & 4 \text{ (oxidation).} \end{array}$$

Nitrogen oxide (III) and nitrous acid

Nitrogen oxide (III) is nitrous acid anhydride:

$N_2O_3 + H_2O \leftrightarrow 2HNO_2$.

As acid oxide it reacts with alkalis:

$N_2O_3 + 2NaOH = 2NaNO_2 + H_2O$.

Nitrous acid (HNO_2) dissociates with Hydrogen ions formation:

$HNO_2 \leftrightarrow H^+ + NO_2^-$.

At it’s heating and under the influence of strong acids the process of disproportion takes place:

$3HNO_2 \leftrightarrow HNO_3 + 2NO + H_2O$

$$\begin{array}{l|l} N^{3+} + \bar{e} \rightarrow N^{2+} & 2 \text{ (reduction);} \\ N^{3+} - 2\,\bar{e} \rightarrow N^{5+} & 1 \text{ (oxidation).} \end{array}$$

Nitrous acid and its salts can be both reducing and oxidizing agents:

$2NaNO_2 + 2KI + 2H_2SO_4 = I_2 + 2NO + K_2SO_4 + Na_2SO_4 + 2H_2O$

$$\begin{array}{l|l} N^{3+} + 1\,\bar{e} \rightarrow N^{2+} & 2 \text{ (reduction);} \\ 2I^- - 2\,\bar{e} \rightarrow I_2^0 & 1 \text{ (oxidation).} \end{array}$$

$5KNO_2 + 2KMnO_4 + 3H_2SO_4 = 5KNO_3 + 2MnSO_4 + K_2SO_4 + 3H_2O$

$$\begin{array}{l|l} Mn^{7+} + 5\,\bar{e} \rightarrow Mn^{2+} & 2 \text{ (reduction);} \\ N^{3+-} - 2\,\bar{e} \rightarrow N^{5+} & 5 \text{ (oxidation).} \end{array}$$

Nitric oxide (V) and nitric acid

Nitric acid and its salts (Nitrates) have the oxidizing properties:

$3KNO_3 + 8Al + 5KOH + 2H_2O = 3NH_3 + 8KAlO_2$

$N^{5+} + 8\bar{e} \rightarrow N^{3-}$ | 3 (reduction);

$Al^{0} - 3\bar{e} \rightarrow Al^{3+}$ | 8 (oxidation).

Particular feature of nitric acid is in interaction almost with all metals and non-metals, at the same time it oxidizes them. The reduction of N(5+) but not H(1+) as with acids-oxidizing agents always takes place. Generally NO and NO_2 prevail among reduction products. Active metals (Mg, Zn, Ca and others) reduce diluted HNO_3 up to N_2 and NH_4NO_3.

At the same time some N(5+) reduction products can be isolated. However, the equations of such reactions are relative and only one compound (NO_2, NO or N_2, NH_3), formed in quantity, is indicated in the products:

$4\,Mg + 10HNO_3$ (diluted) $= 4Mg(NO_3)_2 + NH_4NO_3 + 3H_2O$;

$Cu + 4HNO_3$ (conc) $= Cu(NO_3)_2 + 2NO_2 + 2H_2O$;

$S + 6HNO_3$ (conc) $= H_2SO_4 + 6NO_2 + 2H_2O$;

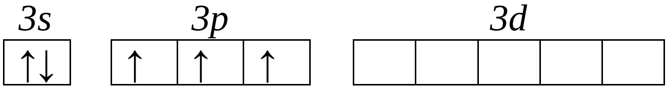
$3P + 5HNO_3$ (diluted) $+ 2H_2O = 3H_3PO_4 + 5NO$.

Nitric acid salts - Sodium, Potassium, ammonia, and calcium Nitrates are of great practical value. They are called saltpeters and are used in great quantity as fertililizers.

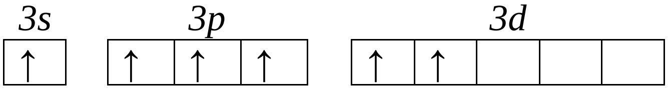
13.2 Phosphorus

The electronic formula of phosphorus is $1s^2 2s^2 2p^6 3s^2 3p^3 3d^0$. $3s^2 3p^3 3d^0$ is the configuration of external electronic shell of phosphorus atom. In contrast to Nitrogen atom the phosphorus atom has unoccupied d-orbitals, thus gives the possibility to pass into excited state at "pair break" of *3s*-electrons. According to current concept the following oxidation numbers are typical for phosphorus atom: 3-, 0, 3+, 5+:

Ground (nonexcited) state (3-, 0, 3+ oxidation number, for example, in PH_3, P, P_2O_3 compounds):



The excited state (5+ oxidation number, for example, in P_2O_5 compound):



The most typical phosphorus compounds are given in Table 18.

Table 18. Compounds of Phosphorus

Oxidation numbers	3-	0	1+	3+	5+
Compound	PH_3	P (P_2, P_4, P_n)	H_3PO_2	P_2O_3, H_3PO_3	P_2O_5, H_3PO_4, HPO_3, $H_4P_2O_7$
Chemical properties	Reducing agent only	Oxidizing and reducing agents	Hypophosphorous acid, strong reducing agent	Phosphorus acid, reducing agent	Phosphoric anhydride and phosphoric acids, oxidizing agent only

Phosphorus is produced from natural Phosphates of P_2O_5 vapors reduction by coal, which is isolated from melt (at 1500^0C) according to the reaction:

$Ca_3(PO_4)_2 + 3SiO_2 \xrightarrow{t} 3CaSiO_3 + P_2O_5$;

$P_2O_5 + 5C \xrightarrow{t} 5CO + 2P$

$$\begin{array}{l|l} P^{5+} + 5\bar{e} \rightarrow P^0 & 2 \text{ (reduction);} \\ C^0 - 2\bar{e} \rightarrow C^{2+} & 5 \text{ (oxidation).} \end{array}$$

Phosphorus behaves as the typical non-metal. It reacts with Oxygen, formed acid oxides:

$4P + 3O_2 = 2P_2O_3$;

$4P + 5O_2 = 2P_2O_5$.

Phosphorus oxides (V), phosphoric acid, Phosphates

P_2O_5 (P_4O_{10}) is very hygroscopic white powder and the most effective agent for drying. Interacting with water it forms phosphoric (monophosphoric) acid:

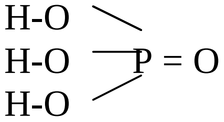
$P_4O_{10} + 6H_2O \xrightarrow{t} 4H_3PO_4$.

Acid properties of P_2O_5 are shown in its interaction with hydroxides and basic oxides:

$6KOH + P_2O_5 = 2K_3PO_4 + 3H_2O$;

$3CaO + P_2O_5 = Ca_3(PO_4)_2$.

Orthophosphoric acid H_3PO_4 is threebasic acid:

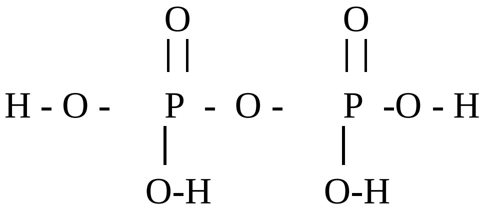


At heating monophosphoric acid dehydration and formation of cyclic or linear polyphosphoric acids take place and among them diphosphoric and metaphosphoric acids are of great value:

$2H_3PO_4 = H_2O + H_4P_2O_7$ (diphosphoric acid);

$H_4P_2O_7 = H_2O + 2HPO_3$ (metaphosphoric acid).

In fact, metaphosphoric acid is inorganic polymer of cyclic structure mostly with three and four chain rings: $(HPO_3)_3$ and $(HPO_3)_4$. Diphosphoric acid and other condensed phosphoric acids with the same structure are inorganic polymers:



$$H-O-\overset{\overset{\displaystyle O}{||}}{\underset{\underset{\displaystyle O-H}{|}}{P}}-O-\overset{\overset{\displaystyle O}{||}}{\underset{\underset{\displaystyle O-H}{|}}{P}}-O-H$$

In Phosphate fertilizer production the extraction phosphoric acid is received by sulfuric acid action to $Ca_3(PO_4)_2$, which is the part of natural phosphorites and apatites:

$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$.

Phosphoric acid forms mono- , di- and triple-substituted salts. For example, NaH_2PO_4 - Sodium dihydroPhosphate, Na_2HPO_4 - Sodium hydroPhosphate, Na_3PO_4 - Sodium Phosphate.

The ability of phosphoric acid to react with metals, basic oxides, hydroxides and weak acid salts are used in industry for production of mineral fertilizers:

$CaHPO_4 \cdot 2H_2O$ (precipitate);

$Ca_3(PO_4)_2 + 4H_3PO_4 = 3Ca(H_2PO_4)_2$;

in fact $Ca(H_2PO_4)_2 \cdot H_2O$ - triple superphosphate is produced.

$Ca_3(PO_4)_2 + 2H_2SO_4 = Ca(H_2PO_4)_2 + 2CaSO_4$ - is the receipt of simple superPhosphate. The real composition of simple superphosphate is $Ca(H_2PO_4)_2 \cdot H_2O + 2[CaSO_4 \cdot 2H_2O]$.

PRACTICE PROBLEMS

1. In which compounds and at which oxidation numbers can Nitrogen and phosphorus show only reducing or only oxidizing properties in the reactions and why?

2. Draw structural-graphic formulas of N_2O_3, N_2O_5, P_4O_{10}, HNO_2, HNO_3, H_3PO_4, H_3PO_3.

3. Estimate Nitrogen and Phosphorus oxidation numbers in the compounds:
$NH_3 \cdot H_2O$, PH_4I, $Ca(H_2PO_4)_2$, $NH_4H_2PO_4$, $Fe(NO_3)_3$, $Na_4P_2O_7$, NH_2OH, NH_4Cl.

4. Draw the reaction equations according to transformation series:

$N_2 \rightarrow NH_3 \rightarrow NO \rightarrow NO_2 \rightarrow HNO_3 \rightarrow NH_4NO_3$;

$Ca_3(PO_4)_2 \rightarrow P \rightarrow P_2O_5 \rightarrow H_3PO_4 \rightarrow Ca(H_2PO_4)_2 \rightarrow CaHPO_4$;

$Ca_3(PO_4)_2 \rightarrow H_3PO_4 \rightarrow NH_4H_2PO_4 \rightarrow (NH_4)_2HPO_4$.

5. Draw the diagrams of electron redistribution and put the coefficients in the equations of the following reactions:

$NaNO_2 + FeCl_2 + HCl \rightarrow FeCl_3 + NO + NaCl + H_2O$;

$NO_2 + H_2O + O_2 \rightarrow$

$NH_4NO_3 \rightarrow N_2O + H_2O \rightarrow$

$P + HNO_3 + H_2O \rightarrow$

LABORATORY TRAINING

Experiment 1. Study the ammonia solution properties

A) Put 5-6 drops of Iron Chloride (III) into test-tube, add 4-5 drops of ammonia solution. Describe the color of precipitation and write the reaction.

B) Put 5-6 drops of ammonia Chloride into test-tube, add 5-7 drops of alkali solution (KOH or NaOH) and heat the mixture in water bath. Identify the isolated gas taking into account the odor and color change of pink litmus paper wetted by water, putting it into the vapor under test-tube. Draw the reaction.

Experiment 2. Oxidation and reducing power of nitrous acid and Nitrites

A) Put 3-5 drops of $KMnO_4$ solution into the test-tube, acidify it by 2-3 drops of H_2SO_4 and add 5-7 drops of solution or 1-2 granules of $NaNO_2$. What properties does Sodium Nitrite show in this reaction? Write the reaction.

B) Fill the test-tube with 3-5 drops of $NaNO_2$, acidify it by 2-3 drops of H_2SO_4 solution and then add 3-4 drops of KI solution. Why does the color of solution change? Draw the reaction and determine the properties of $NaNO_2$ in this case.

Experiment 3. Oxidizing properties of nitric acid

Fill the test-tube with 3-5 drops of concentrated HNO_3, add piece of Copper. Make sure of gassing presence. Dilute the mixture by 20-30 drops of distilled water. How does the color of the gas change? Write the equation of oxidation-reduction reaction of cooper and concentrated and diluted HNO_3 interaction.

Experiment 4. Low soluble Phosphate formation

A) Add 1-2 drops of Potassium or ammonia thiocyanate solution to 3-4 drops of $FeCl_3$. The solution is colored in red. Draw the reaction equation.

Add some drops of Sodium or ammonia hydroPhosphate up to red color disappearance of Iron thiocyanate (III) and $FePO_4$ precipitation formation. Draw the equation of the reaction.

B) Put 4-5 drops of Na_3PO_4, Na_2HPO_4, NaH_2PO_4 solutions into three test tubes and adds the same volume of $CaCl_2$. Note the order of precipitation formation and draw the equation of the reactions.

Experiment 5. Representative reaction to phosphoric acid ions.

Add 5-6 drops of H_3PO_4 solution or its salt to 5-6 drops of molybdenum solution. Heat the mixture on water bath. The yellow precipitation of mixture $(NH_4)_3H_4[P(Mo_2O_7)_6]$ is formed. Draw the equation of the reaction.

CHAPTER # 14. CHEMISTRY OF MAIN BIOMETALS

Vocabulary

English	Українська назва	English	Українська назва
Macronutrient (macroelement)	*Макроелемент*	*Heavy metal*	*Важкий метал*
Micronutrient (microelement)	*Мікроелемент*	*Pollutant*	*Забруднювач*

14.1 The Alkali Metals

The elements of Group 1, the Alkali metals, are:

Symbol	Electron configuration
Lithium Li	[He]$2s^1$
Sodium Na	[Ne]$3s^1$
Potassium K	[Ar]$4s^1$
Rubidium Rb	[Kr]$5s^1$
Cesium Cs	[Xe]$6s^1$
Francium Fr	[Rn]$7s^1$

In each element the valency electron configuration is ns^1, where n is the period number. The last element, Francium, is radioactive and will not be considered here.

Appearance

All the Group 1A elements are silvery-colored metals. They are soft, and can be easily cut with a knife to expose a shiny surface, which dulls on oxidation.

General Reactivity

These elements are highly reactive metals. The reactivity increases on descending the Group from Lithium to Cesium. There is a closer similarity between the elements of this sub-Group than in any other Group of the Periodic Table.

Occurrence and Extraction

These elements are too reactive to be found free in nature. Sodium occurs mainly as NaCl (salt) in seawater and dried-up seabeds. Potassium is more widely distributed in minerals such as sylvite, KCl, but is also extracted from seawater. The alkali metals are so reactive that they cannot be displaced by another element, so are isolated by electrolysis of their molten salts.

Physical Properties

The alkali metals differ from other metals in several ways. They are soft, with low melting and boiling temperatures. They have low densities -

Li, Na and K are less dense than water. They show relatively weak metallic bonding, as only one electron is available from each atom.

Alkali metals color flames. When the element is placed in a flame the heat provides sufficient energy to promote the outermost electron to a higher energy level. On returning to ground level, energy is emitted and this energy has a wavelength in the visible region: Li - red; Na - yellow; K - lilac; Rb - red; Cs - blue.

The ionic radii of the alkali metals are all much smaller than the corresponding atomic radii. This is because the atom contains one electron in an *s*-level relatively far from the nucleus in a new quantum shell, and when it is removed to form the ion the remaining electrons are in levels closer to the nucleus. In addition, the increased effective nuclear charge attracts the electrons towards the nucleus and decreases the size of the ion.

Chemical Properties

The alkali metals are strong reducing agents. The standard electrode potentials all lie between -2,7V and -3,0V, indicating a strong tendency to form cations in solution. They can reduce Oxygen, Chlorine, Ammonia and Hydrogen. The reaction with Oxygen tarnishes the metals in air, so they are stored under oil. They cannot be stored under water because they react with it to produce Hydrogen and alkali hydroxides:

$2M + 2H_2O = 2MOH + H_2$.

This reaction illustrates the increasing reactivity on descending the Group. Li reacts steadily with water, with effervescence; Sodium reacts more violently and can burn with an orange flame; K ignites on contact with water and burns with a lilac flame; Cs sinks in water, and the rapid generation of Hydrogen gas under water produces a shock wave that can shatter a glass container. Na dissolves in liquid Ammonia to give a deep blue solution of Sodium cations and solvated electrons. This solution is used as a reducing agent.

At higher concentrations the color of the solution changes to bronze and it conducts electricity like a metal.

The chemistry of Li shows some anomalies, as the cation Li^+ is so small it polarizes anions and so introduces a covalent character to its compounds. Li has a diagonal relationship with Magnesium.

Oxides

The Alkali metals form ionic solid oxides of composition M_2O when burnt in air. However, Na also forms the peroxide Na_2O_2 as the main product, and K forms the superoxide KO_2, also as the main product:

$4Li + O_2 \xrightarrow{t} 2Li_2O$;

$2Na + O_2 \xrightarrow{t} Na_2O_2$;

$K + O_2 \xrightarrow{t} KO_2$.

Hydroxides

Alkali metal hydroxides are white ionic crystalline solids of formula MOH, and are soluble in water. They are all deliquescent except LiOH. The aqueous solutions are all strongly alkaline (hence the name of this Group) and therefore dangerous to handle. They neutralize acids to form salts, eg: $NaOH + HCl = NaCl + H_2O$.

Halides

Alkali metal halides are white ionic crystalline solids. They are all soluble in water except LiF.

Oxidation States

Alkali metals have oxidation states of 0 and +1. All the common compounds are based on the M^+ ion. This is because the first ionization energy of these elements is low, and the second ionization energy is much higher. The outermost electron is well shielded from the attraction of the nucleus by filled inner electron levels and so is relatively easy to remove. The next electron is much more difficult to remove as it is part of a full level and is also closer to the nucleus.

Industrial Information

Sodium hydroxide, Chloride and Carbonate are among the most important industrial chemicals associated with this Group. Sodium hydroxide is produced by the electrolysis of saturated brine in a cell with steel cathodes and titanium anodes. Sodium Carbonateis made by the Solvay Process, in which soluble Sodium Chloride is converted into insoluble Sodium Hydrogen Carbonate and filtered off, then heated to produce the Carbonate. However, the principal by-product of this process is calcium Chloride, and its deposition in rivers causes environmental concern. The Solvay Process is therefore gradually being replaced by the purification of Sodium Carbonate from minerals.

14.2 Other bioactive metals

Near 75% of all known chemical elements are metals. Among them there is a series of biologically active macro- and micronutrients (see Table 19).

Table 19. Characteristics of main bioactive metals

Element	Period	Group	Possible Oxidation numbers	Chemical properties
Mg	3	2A	0, +2	Weak amphoteric metal
K	4	1A	0, +1	Typical alkali metal
Ca	4	2A	0, +2	Alkali-Earth Metal
Mn	4	7B	0, +2, +3, +4, +5, +7	Transition metal

Fe	4	8B	0, +2, +3, +6	Transition metal
Co	4	8B	0, +2, +3, +6	Transition metal
Cu	4	1B	0, +1, +2	Transition metal
Zn	4	2B	0, +2	Transition metal
Al	3	3A	0, +1, +3	Amphoteric metal

All bioactive metals depending on its function for plant, animals or human body may be divided into macro-, micronutrients and toxicants (see Table 20).

Table 20. Characteristic of biological function

Element	Biological function
Mg	Included in Chlorophilium
K	Macronutrient for plant nutrition, needed for cell water balance and transparency of membranes
Ca	Macronutrient for plant and human nutrition, takes part in synthesis of proteins
Mn	Micronutrient, takes part in Redox processes. In excess - toxicant
Fe	Micronutrient, needed for processes of breathing and photosynthesis; includes in hemoglobin
Co	Micronutrient, included coferments (for example Vitamin B_{12} - cobalt ammine). In excess - toxicant
Cu	Irreplaceable micronutrient. In excess - toxicant
Zn	Micronutrient. In excess - toxicant

It is important to know the principles of interaction of metals with different types of acids (see Table 21).

Table 21. Interaction acids-oxidizing agents with metals

Formula of acid	Metals		Notes
	Active: The Alkali, The Alkali-Earth, Mg, Zn	Heavy with low activity	
	Scheme of products		
H_2SO_4 (conc.)	Sulfate + S + H_2O or Sulfate + H_2S + H_2O	Sulfate + SO_2 + H_2O	Fe is immunized by acid
HNO_3 (conc.)	Nitrate + N_2O + H_2O	Nitrate + NO_2 + H_2O	Not reacts with Au, Pt, Rh, Ir, Ti, Ta;

			Al, Fe, Co, Ni, Cr are immunized by acid
HNO_3 (diluted)	Nitrate + N_2 + H_2O or Nitrate + NH_4NO_3+ H_2O	Nitrate + NO + H_2O	Fe and Sn forms NH_4NO_3

PRACTICE PROBLEMS

1. Characterize general features of metals atoms.

2. Draw the diagrams of electron redistribution and put the coefficients in the equations of the following reactions and characterize metal properties in these reactions:

$Ca + H_2O \rightarrow$

$Mn + H_2SO_4$ (conc.) $\rightarrow$

$Zn + CuSO_4 \rightarrow$

$Al + Fe_2O_3 \rightarrow$

LABORATORY TRAINING

Experiment 1. Replacing of metals

Put into two test tubes 5-6 drops of $CuSO_4$ and Pb $(CH_3COO)_2$ solutions and add in each tube one granule of free Zinc. 5-10 min. later register how color of Zinc granule is changed. Write the reactions.

Experiment 2. Qualitative test of K^+ in salts or fertilizers

Fill test-tube with 3-4 drops of Potassium salt solution and add 2-3 drops of $Na_3[Co(NO_2)_6]$. Form yellow precipitate $NaK_2[Co(NO_2)_6]$. Write the reactions of precipitate formation.

Experiment 3.Change of Calcium Phosphates solubility

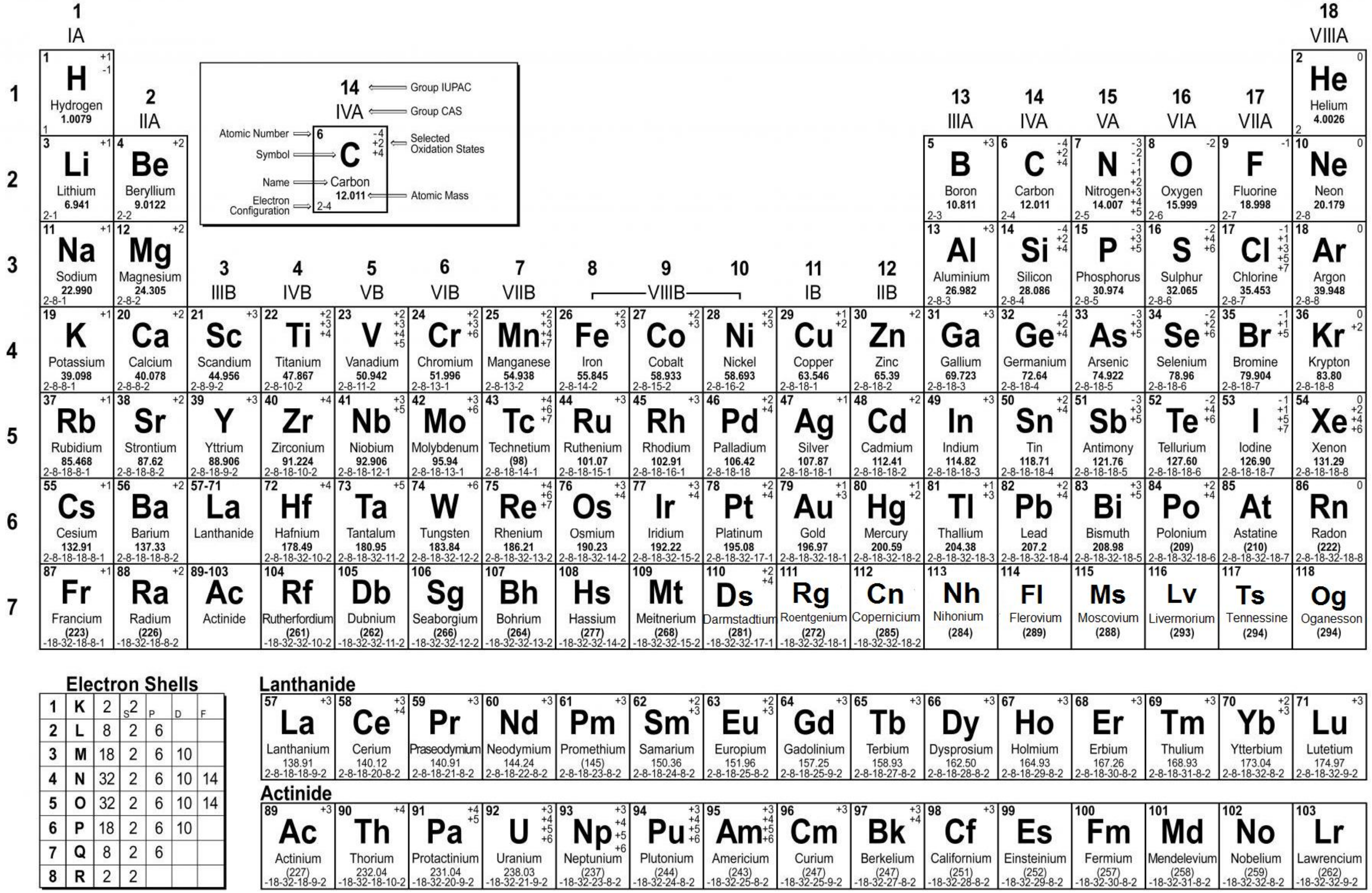
Add 2-3 drops of Na_2HPO_4 solution to 1-2 drops of $CaCl_2$ Solution. Why was precipitate formed?

Add by drops Solution of Phosphorus acid to precipitate until to total dissolving. Write the reactions of precipitate formation and dissolving.

Experiment 4. Oxidizing property of Cu^{+2} ions

Add 2-3 drops of KI solution to 3-4 drops of $CuSO_4$ solution. Observe formation of CuI precipitate and Iodine I_2 isolation. Write the reaction.

APPENDIX 1 Mendeleev's Periodical table of the Chemical Elements



	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 +1 -1 H Hydrogen 1.0079 1																	2 0 He Helium 4.0026 2
2	3 +1 Li Lithium 6.941 2-1	4 +2 Be Beryllium 9.0122 2-2											5 +3 B Boron 10.811 2-3	6 -4 +2 +4 C Carbon 12.011 2-4	7 -3 -2 -1 +1 +2 +3 +4 +5 N Nitrogen 14.007 2-5	8 -2 O Oxygen 15.999 2-6	9 -1 F Fluorine 18.998 2-7	10 0 Ne Neon 20.179 2-8
3	11 +1 Na Sodium 22.990 2-8-1	12 +2 Mg Magnesium 24.305 2-8-2											13 +3 Al Aluminium 26.982 2-8-3	14 -4 +2 +4 Si Silicon 28.086 2-8-4	15 -3 +3 +5 P Phosphorus 30.974 2-8-5	16 -2 +4 +6 S Sulphur 32.065 2-8-6	17 -1 +1 +3 +5 +7 Cl Chlorine 35.453 2-8-7	18 0 Ar Argon 39.948 2-8-8
4	19 +1 K Potassium 39.098 2-8-8-1	20 +2 Ca Calcium 40.078 2-8-8-2	21 +3 Sc Scandium 44.956 2-8-9-2	22 +2 +3 +4 Ti Titanium 47.867 2-8-10-2	23 +2 +3 +4 +5 V Vanadium 50.942 2-8-11-2	24 +2 +3 +6 Cr Chromium 51.996 2-8-13-1	25 +2 +3 +4 +7 Mn Manganese 54.938 2-8-13-2	26 +2 +3 Fe Iron 55.845 2-8-14-2	27 +2 +3 Co Cobalt 58.933 2-8-15-2	28 +2 +3 Ni Nickel 58.693 2-8-16-2	29 +1 +2 Cu Copper 63.546 2-8-18-1	30 +2 Zn Zinc 65.39 2-8-18-2	31 +3 Ga Gallium 69.723 2-8-18-3	32 -4 +2 +4 Ge Germanium 72.64 2-8-18-4	33 -3 +3 +5 As Arsenic 74.922 2-8-18-5	34 -2 +2 +6 Se Selenium 78.96 2-8-18-6	35 -1 +1 +5 Br Bromine 79.904 2-8-18-7	36 0 +2 Kr Krypton 83.80 2-8-18-8
5	37 +1 Rb Rubidium 85.468 2-8-18-8-1	38 +2 Sr Strontium 87.62 2-8-18-8-2	39 +3 Y Yttrium 88.906 2-8-18-9-2	40 +4 Zr Zirconium 91.224 2-8-18-10-2	41 +3 +5 Nb Niobium 92.906 2-8-18-12-1	42 +3 +6 Mo Molybdenum 95.94 2-8-18-13-1	43 +4 +6 +7 Tc Technetium (98) 2-8-18-14-1	44 +3 Ru Ruthenium 101.07 2-8-18-15-1	45 +3 Rh Rhodium 102.91 2-8-18-16-1	46 +2 +4 Pd Palladium 106.42 2-8-18-18	47 +1 Ag Silver 107.87 2-8-18-18-1	48 +2 Cd Cadmium 112.41 2-8-18-18-2	49 +3 In Indium 114.82 2-8-18-18-3	50 +2 +4 Sn Tin 118.71 2-8-18-18-4	51 -3 +3 +5 Sb Antimony 121.76 2-8-18-18-5	52 -2 +4 +6 Te Tellurium 127.60 2-8-18-18-6	53 -1 +1 +5 +7 I Iodine 126.90 2-8-18-18-7	54 0 +2 +4 +6 Xe Xenon 131.29 2-8-18-18-8
6	55 +1 Cs Cesium 132.91 2-8-18-18-8-1	56 +2 Ba Barium 137.33 2-8-18-18-8-2	57-71 La Lanthanide	72 +4 Hf Hafnium 178.49 2-8-18-32-10-2	73 +5 Ta Tantalum 180.95 2-8-18-32-11-2	74 +6 W Tungsten 183.84 2-8-18-32-12-2	75 +4 +6 +7 Re Rhenium 186.21 2-8-18-32-13-2	76 +3 +4 Os Osmium 190.23 2-8-18-32-14-2	77 +3 +4 Ir Iridium 192.22 2-8-18-32-15-2	78 +2 +4 Pt Platinum 195.08 2-8-18-32-17-1	79 +1 +3 Au Gold 196.97 2-8-18-32-18-1	80 +1 +2 Hg Mercury 200.59 2-8-18-32-18-2	81 +1 +3 Tl Thallium 204.38 2-8-18-32-18-3	82 +2 +4 Pb Lead 207.2 2-8-18-32-18-4	83 +3 +5 Bi Bismuth 208.98 2-8-18-32-18-5	84 +2 +4 Po Polonium (209) 2-8-18-32-18-6	85 At Astatine (210) 2-8-18-32-18-7	86 0 Rn Radon (222) 2-8-18-32-18-8
7	87 +1 Fr Francium (223) -18-32-18-8-1	88 +2 Ra Radium (226) -18-32-18-8-2	89-103 Ac Actinide	104 Rf Rutherfordium (261) -18-32-32-10-2	105 Db Dubnium (262) -18-32-32-11-2	106 Sg Seaborgium (266) -18-32-32-12-2	107 Bh Bohrium (264) -18-32-32-13-2	108 Hs Hassium (277) -18-32-32-14-2	109 Mt Meitnerium (268) -18-32-32-15-2	110 +2 +4 Ds Darmstadtium (281) -18-32-32-17-1	111 Rg Roentgenium (272) -18-32-32-18-1	112 Cn Copernicium (285) -18-32-32-18-2	113 Nh Nihonium (284)	114 Fl Flerovium (289)	115 Ms Moscovium (288)	116 Lv Livermorium (293)	117 Ts Tennessine (294)	118 Og Oganesson (294)

14 ⟸ Group IUPAC
IVA ⟸ Group CAS
Atomic Number ⟹ 6
Symbol ⟹ C
Name ⟹ Carbon
Electron Configuration ⟹ 2-4
-4 +2 +4 ⟸ Selected Oxidation States
12.011 ⟸ Atomic Mass

Electron Shells

1	K	2	S 2	P	D	F
2	L	8	2	6		
3	M	18	2	6	10	
4	N	32	2	6	10	14
5	O	32	2	6	10	14
6	P	18	2	6	10	
7	Q	8	2	6		
8	R	2	2			

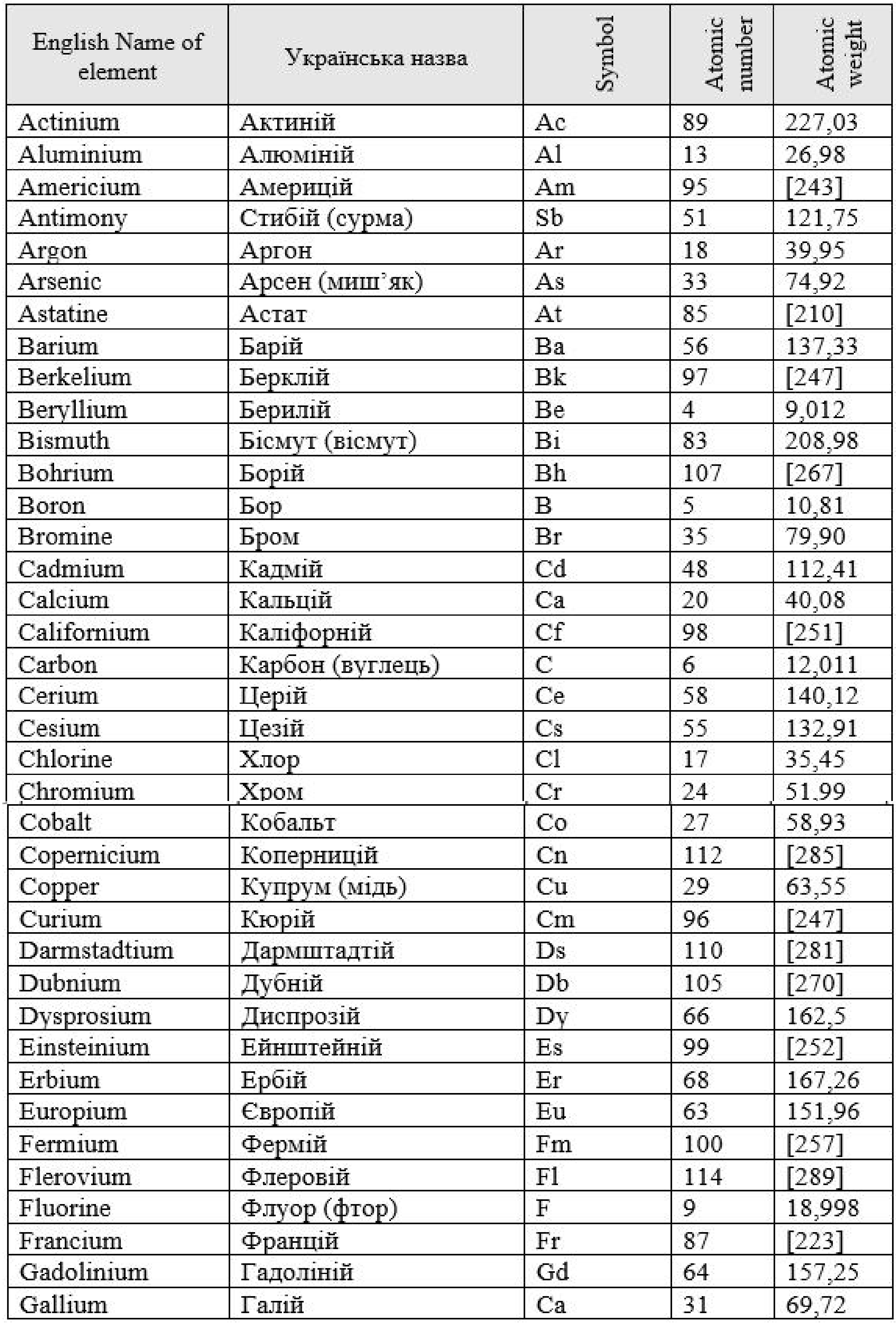
Lanthanide

57 +3 La Lanthanium 138.91 2-8-18-18-9-2	58 +3 +4 Ce Cerium 140.12 2-8-18-20-8-2	59 +3 Pr Praseodymium 140.91 2-8-18-21-8-2	60 +3 Nd Neodymium 144.24 2-8-18-22-8-2	61 +3 Pm Promethium (145) 2-8-18-23-8-2	62 +2 +3 Sm Samarium 150.36 2-8-18-24-8-2	63 +2 +3 Eu Europium 151.96 2-8-18-25-8-2	64 +3 Gd Gadolinium 157.25 2-8-18-25-9-2	65 +3 Tb Terbium 158.93 2-8-18-27-8-2	66 +3 Dy Dysprosium 162.50 2-8-18-28-8-2	67 +3 Ho Holmium 164.93 2-8-18-29-8-2	68 +3 Er Erbium 167.26 2-8-18-30-8-2	69 +3 Tm Thulium 168.93 2-8-18-31-8-2	70 +2 +3 Yb Ytterbium 173.04 2-8-18-32-8-2	71 +3 Lu Lutetium 174.97 2-8-18-32-9-2

Actinide

89 +3 Ac Actinium (227) -18-32-18-9-2	90 +4 Th Thorium 232.04 -18-32-18-10-2	91 +4 +5 Pa Protactinium 231.04 -18-32-20-9-2	92 +3 +4 +5 +6 U Uranium 238.03 -18-32-21-9-2	93 +3 +4 +5 +6 Np Neptunium (237) -18-32-23-8-2	94 +3 +4 +5 +6 Pu Plutonium (244) -18-32-24-8-2	95 +3 +4 +5 +6 Am Americium (243) -18-32-25-8-2	96 +3 Cm Curium (247) -18-32-25-9-2	97 +3 +4 Bk Berkelium (247) -18-32-27-8-2	98 +3 Cf Californium (251) -18-32-28-8-2	99 Es Einsteinium (252) -18-32-29-8-2	100 Fm Fermium (257) -18-32-30-8-2	101 Md Mendelevium (258) -18-32-31-8-2	102 No Nobelium (259) -18-32-32-8-2	103 Lr Lawrencium (262) -18-32-32-9-2

APPENDIX 2 The chemical elements - their symbols, atomic numbers and atomic weights

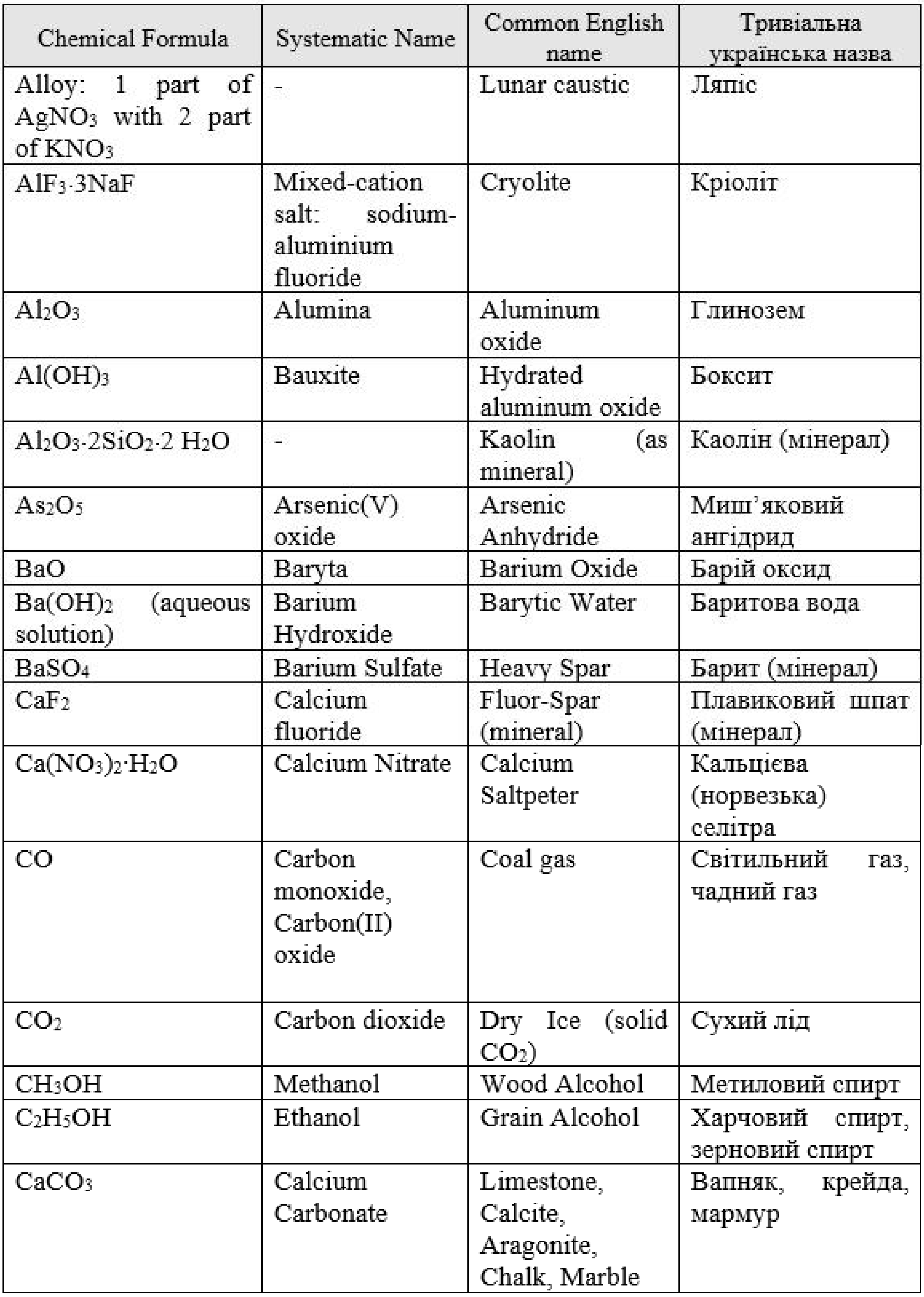


English Name of element	Українська назва	Symbol	Atomic number	Atomic weight
Actinium	Актиній	Ac	89	227,03
Aluminium	Алюміній	Al	13	26,98
Americium	Америцій	Am	95	[243]
Antimony	Стибій (сурма)	Sb	51	121,75
Argon	Аргон	Ar	18	39,95
Arsenic	Арсен (миш’як)	As	33	74,92
Astatine	Астат	At	85	[210]
Barium	Барій	Ba	56	137,33
Berkelium	Берклій	Bk	97	[247]
Beryllium	Берилій	Be	4	9,012
Bismuth	Бісмут (вісмут)	Bi	83	208,98
Bohrium	Борій	Bh	107	[267]
Boron	Бор	B	5	10,81
Bromine	Бром	Br	35	79,90
Cadmium	Кадмій	Cd	48	112,41
Calcium	Кальцій	Ca	20	40,08
Californium	Каліфорній	Cf	98	[251]
Carbon	Карбон (вуглець)	C	6	12,011
Cerium	Церій	Ce	58	140,12
Cesium	Цезій	Cs	55	132,91
Chlorine	Хлор	Cl	17	35,45
Chromium	Хром	Cr	24	51,99
Cobalt	Кобальт	Co	27	58,93
Copernicium	Коперницій	Cn	112	[285]
Copper	Купрум (мідь)	Cu	29	63,55
Curium	Кюрій	Cm	96	[247]
Darmstadtium	Дармштадтій	Ds	110	[281]
Dubnium	Дубній	Db	105	[270]
Dysprosium	Диспрозій	Dy	66	162,5
Einsteinium	Ейнштейній	Es	99	[252]
Erbium	Ербій	Er	68	167,26
Europium	Європій	Eu	63	151,96
Fermium	Фермій	Fm	100	[257]
Flerovium	Флеровій	Fl	114	[289]
Fluorine	Флуор (фтор)	F	9	18,998
Francium	Францій	Fr	87	[223]
Gadolinium	Гадоліній	Gd	64	157,25
Gallium	Галій	Ca	31	69,72

Germanium	Германій	Ce	32	72,59
Gold	Аурум (золото)	Au	79	196,97
Hafnium	Гафній	Hf	72	178,49
Hassium	Гассій	Hs	108	[265]
Helium	Гелій	He	2	4,00
Holmium	Гольмій	Ho	67	164,93
Hydrogen	Гідроген (водень)	H	1	1,01
Indium	Індій	In	49	114,82
Iodine	Йод	I	53	126,91
Iridium	Іридій	Ir	77	192,22
Iron	Ферум (залізо)	Fe	26	55,85
Krypton	Криптон	Kr	36	83,80
Lanthanum	Лантан	La	57	138,92
Lawrencium	Лоуренсій	Lr	103	[266]
Lead	Плюмбум (свинець)	Pb	82	207,2
Lithium	Літій	Li	3	6,94
Livermorium	Ліверморій	Lv	116	[293]
Lutetium	Лютецій	Lu	71	174,97
Magnesium	Магній	Mg	12	24,31
Manganese	Манган (марганець)	Mn	25	54,94
Meitnerium	Мейтнерій	Mt	109	[278]
Mendelevium	Менделевій	Md	101	[258]
Mercury	Меркурій (ртуть)	Hg	80	200,59
Molybdenum	Молібден	Mo	42	95,94
Moscovium	Московій	Ms	115	[288]
Nickel	Нікол (нікель)	Ni	28	58,69
Nihonium	Ніхоній	Nh	113	[284]
Niobium	Ніобій	Nd	41	92,91
Nitrogen	Нітроген (азот)	N	7	14,01
Neodymium	Неодим	Nd	60	144,24
Neon	Неон	Ne	10	20,18
Neptunium	Нептуній	Np	93	237,05
Nobelium	Нобелій	No	102	[259]
Oganesson	Оганесон	Og	118	[294]
Osmium	Осмій	Os	76	190,2
Oxygen	Оксиген (кисень)	O	8	16,00
Palladium	Палладій	Pd	46	106,42
Phosphorus	Фосфор	P	15	30,97
Platinum	Платина	Pt	78	195,08
Plutonium	Плутоній	Pu	94	[244]
Polonium	Полоній	Po	84	[209]
Potassium	Калій	K	19	39,10
Praseodymium	Празеодим	Pr	59	140,91

Promethium	Прометій	Pm	61	[145]
Protactinium	Протактиній	Pa	91	231,04
Radium	Радій	Ra	88	226,03
Radon	Радон	Rn	86	[222]
Rhenium	Реній	Re	75	186,21
Rhodium	Родій	Rh	45	102,906
Roentgenium	Рентгеній	Rg	111	[281]
Rubidium	Рубідій	Rb	37	85,47
Ruthenium	Рутеній	Ru	44	101,07
Rutherfordium	Резерфордій	Rf	104	[267]
Samarium	Самарій	Sm	62	150,36
Seaborgium	Сиборгій	Sg	106	[269]
Scandium	Скандій	Sc	21	44,96
Selenium	Селен	Se	34	78,97
Silicon	Силіцій (кремній)	Si	14	28,09
Silver	Срібло	Ag	47	107,87
Sodium	Натрій	Na	11	22,989
Strontium	Стронцій	Sr	38	87,62
Sulfur	Сульфур (сірка)	S	16	32,06
Tantalum	Тантал	Ta	73	180,95
Technetium	Технецій	Tc	43	[99]
Tellurium	Телур	Te	52	127,60
Tennessine	Теннессин	Ts	117	[294]
Terbium	Тербій	Tb	65	158,93
Thallium	Талій	Tl	81	204,38
Thorium	Торій	Th	90	232,04
Thulium	Тулій	Tm	69	168,93
Tin	Станум (олово)	Sn	50	118,71
Titanium	Титан	Ti	22	47,88
Tungsten	Вольфрам	W	74	183,85
Uranium	Уран	U	92	238,03
Vanadium	Ванадій	V	23	50,94
Xenon	Ксенон	Xe	54	131,29
Ytterbium	Ітербій	Yb	70	173,04
Yttrium	Ітрій	Y	39	88,91
Zinc	Цинк	Zn	30	65,38
Zirconium	Цирконій	Zr	40	91,22

APPENDIX 3 Some familiar substances with their systematic and common names



Chemical Formula	Systematic Name	Common English name	Тривіальна українська назва
Alloy: 1 part of $AgNO_3$ with 2 part of KNO_3	-	Lunar caustic	Ляпіс
$AlF_3 \cdot 3NaF$	Mixed-cation salt: sodium-aluminium fluoride	Cryolite	Кріоліт
Al_2O_3	Alumina	Aluminum oxide	Глинозем
$Al(OH)_3$	Bauxite	Hydrated aluminum oxide	Боксит
$Al_2O_3 \cdot 2SiO_2 \cdot 2\ H_2O$	-	Kaolin (as mineral)	Каолін (мінерал)
As_2O_5	Arsenic(V) oxide	Arsenic Anhydride	Миш'яковий ангідрид
BaO	Baryta	Barium Oxide	Барій оксид
$Ba(OH)_2$ (aqueous solution)	Barium Hydroxide	Barytic Water	Баритова вода
$BaSO_4$	Barium Sulfate	Heavy Spar	Барит (мінерал)
CaF_2	Calcium fluoride	Fluor-Spar (mineral)	Плавиковий шпат (мінерал)
$Ca(NO_3)_2 \cdot H_2O$	Calcium Nitrate	Calcium Saltpeter	Кальцієва (норвезька) селітра
CO	Carbon monoxide, Carbon(II) oxide	Coal gas	Світильний газ, чадний газ
CO_2	Carbon dioxide	Dry Ice (solid CO_2)	Сухий лід
CH_3OH	Methanol	Wood Alcohol	Метиловий спирт
C_2H_5OH	Ethanol	Grain Alcohol	Харчовий спирт, зерновий спирт
$CaCO_3$	Calcium Carbonate	Limestone, Calcite, Aragonite, Chalk, Marble	Вапняк, крейда, мармур

$Ca(NO_3)_2 \cdot H_2O$	Calcium Nitrate	Calcium Saltpeter	Кальцієва (норвезька) селітра
CO	Carbon monoxide, Carbon(II) oxide	Coal gas	Світильний газ, чадний газ
CO_2	Carbon dioxide	Dry Ice (solid CO_2)	Сухий лід
CH_3OH	Methanol	Wood Alcohol	Метиловий спирт
C_2H_5OH	Ethanol	Grain Alcohol	Харчовий спирт, зерновий спирт
$CaCO_3$	Calcium Carbonate	Limestone, Calcite, Aragonite, Chalk, Marble	Вапняк, крейда, мармур
$CaSO_4$	Anhydrous Calcium Sulfate	Anhydrite	Ангідрит
$CaSO_4 \cdot 0{,}5\ H_2O$	Calcium sulfate hemihydrate	Plaster of Paris	Гіпс
$Ca(H_2PO_4)_2 \cdot H_2O$	Calcium Dihydrophosphate Hydrate	Triple Superphosphate	Подвійний суперфосфат
$Ca(H_2PO_4)_2 \cdot H_2O + 2[CaSO_4 \cdot 2H_2O]$	Calcium Dihydrophosphate Hydrate + Calcium Sulfate Dihydrate	Simple Super-Phosphate	Простий суперфосфат
$CaHPO_4 \cdot 2H_2O$	Calcium Hydrophospate Dihydrate	Precipitate	Преципітат
CaO	Calcium Oxide	Quicklime or burnt lime	Вапно (негашене)
$Ca(OH)_2$	Calcium Hydroxide	Slaked/slack Lime	Вапно (гашене)
$Ca(OH)_2$ (aq)	Calcium Hydroxide (suspension)	Limewater, Lime Milk	Вапняна вода, вапняне молоко
2CaO + NaOH	Mixture of Calcium Oxide and Sodium Hydroxide	Soda Lime	Натронне вапно

$CaOCl_2$	Calcium Hypochlorite-Chloride	Chloride of Lime, Bleaching Powder	Хлорне (білильне) вапно
$3Ca_3(PO_4)_2x\ x\cdot Ca(F, Cl)_2$	-	Apatite (mineral)	Апатит (мінерал)
$Ca_3P_6O_{18}$	Calcium Hexametaphosphate	Calgon	Калгон
$CaSO_4\cdot 1/2\ H_2O$	Calcium Sulfate Hemihydrate	Plaster of Paris, alabaster	Гіпс (обпалений), алебастр
$CaSO_4\cdot 2H_2O$	Alcium Sulfate Dihydrate	Gypsum	Гіпс
$Cu(CH_3COO)_2x\ 3\ Cu(AsO_2)_2$	Mixed salt - Copper Acetate-arsenite	Paris Green	Паризька зелень
$2\ CuCO_3\cdot Cu(OH)_2$ $CuCO_3\cdot Cu(OH)_2$	Mixed Copper Hydroxide-Carbonate	Azurite (mineral) Malachite (mineral)	Лазурит (мінерал) Малахіт (мінерал)
$CuSO_4\cdot 5\ H_2O$	Copper(II) Sulfate Pentahydrate	Blue Vitriol	Мідний купорос
$Fe_3[Fe(CN)_6]_2$	Iron(II) Hexacianoferrate(III)	Turnbull’s Blue	Турнбулева синь
$Fe_4[Fe(CN)_6]_3$	Iron(III) Hexacianoferrate(II)	Prussian Blue	Берлінська лазур
Fe_2O_3	Iron(III) Oxide	Mummy (mineral colour)	Мумія (коричневий пігмент, мінеральна фарба)
Fe_3O_4 or $FeO\cdot Fe_2O_3$	Mixed Iron(II) and Iron(III) Oxide	Loadstone, Magnetite (mineral)	Магнітний залізняк, магнетит (мінерал)
FeS_2	Iron(II) Persulfide	Pyrite, Brazil; Fool's Gold, Sulfur-Ore (mineral)	Пірит, залізний колчедан, залізна обманка
$FeSO_4\cdot 7H_2O$	Iron(II) Sulfate Heptahydrate	Green Vitriol	Залізний купорос
HCl	Hydrochloric acid	Muriatic Acid	Соляна кислота

HF	Hydrofluoric acid	Etching Acid	Плавикова (травильна) кислота
H_2O_2 (27-31% solution)	Hydrogen Peroxide	Perhydrol	Пергідроль
H_2SO_4 (90,5-92,5% solution)	Concentrated Sulfuric Acid	Vitriolic Oil	Купоросне масло
Hg	Mercury	Quicksilver	Ртуть
Hg_2Cl_2	Mercury(I) Chloride	Calomel	Каломель
HgS	Mercury(II) Sulfide	Cinnabar, Vermilion (mineral)	Кіновар, вермільйон (штучна кіновар)
Hg_2Cl_2	Mercury(I) Chloride	Calomel	Каломель
$HgCl_2$	Mercury(II) Chloride	(Corrosive) Sublimate	Сулема
$KAl(SO_4)_2 \cdot 12\ H_2O$	Potassium-Aluminium Sulfate	Potash Alum	Алюмокалієві галуни
$KCl \cdot MgCl_2 \cdot 6H_2O$	Potassium-Magnesium hexahydrate	Carnallite (mineral)	Карналіт (мінерал)
KNO_3	Potassium Nitrate	Potassium (Indian) Saltpetre	Натрієва (індійська) селітра
KOH	Potassium Hydroxide	Caustic Potash, Potassa	Їдке калі, каустичний поташ
$K_4[Fe(CN)_6]$	Potassium Hexacyano-ferrate(II)	Yellow blood salt, Yellow Prussiate of Potash	Жовта кров᾽яна сіль
$K_3[Fe(CN)_6]$	Potassium Hexacyano-ferrate(III)	Red blood salt, Red prussiate of Potash, Prussian red	Червона кров᾽яна сіль
K_2CO_3	Potassium Carbonate	Potash	Поташ
$KNaC_4H_4O_6$	Potassium-Sodium Tartrate	Seignette᾽s salt, Rochelle salt	Калій-натрій виннокислий, сегнетова сіль
$MgCO_3$	Magnesium Carbonate	Magnesite (mineral)	Магнезит (мінерал)

MgO	Magnesium Oxide	Magnesia Alba	Біла магнезія, палена магнезія
$3MgO\cdot 4SiO_2\cdot H_2O$	-	Talc (mineral)	Тальк, жировик (мінерал)
$Mg(OH)_2$	Magnesium Hydroxide	Milk of Magnesia	Магнезіальне молоко
$MgSO_4\cdot 7H_2O$	Magnesium Sulfate Heptahydrate	Epsom Salt	Англійська сіль, гірка сіль, магнезія, епсомська сіль
Mixture of concentrated HNO_3 (1 volume) and concentrated HCl (2-4 volumes)	-	Aqua-regia, aqua-regis, A.R.	Царська вода (водка)
Mixture of solutions $CuSO_4$ and $Ca(OH)_2$	-	Bordeaux Mixture, Bordo Mix	Бордоська суміш
$MnO_2\cdot nH_2O$	Manganese (IV) Oxide Hydrate	Pyrolusite Black (mineral)	Піролюзитова чернь (мінерал)
NH_4Cl	Ammonia Chloride (solution)	Sal Ammoniac, Salmiac, Nushadir salt, Sal armagnac, Salt armoniack	Нашатир
NH_4NO_3	Ammonium Nitrate	Ammonium Nitram, Ammonium nitricum, Ammonium saltpeter	Аміачна селітра
NH_4OH $(NH_3\cdot H_2O)$ (aq)	Ammonium Hydroxide	Ammonia Water, Aqueous/ liquid Ammonia	Аміачна вода, водний аміак
N_2O	Nitrogen(I) oxide	Laughing Gas, Sweet air, Protoxide of nitrogen, Hyponitrous oxide	Звеселяючий газ
$Na_2CO_3\cdot 10H_2O$	Sodium Carbonate Decahydrate	Washing Soda	Сода кристалічна, важка, побутова, для прання

$NaCl$	Sodium Chloride	Table salt, common salt, halite (mine-ral), rock salt, Saline (medicine), regular salt	Столова сіль, харчова сіль
$NaHCO_3$	Sodium Hydrocarbonate	Baking Soda	Харчова сода, бікарбонат, питна сода
$NaNO_3$	Sodium Nitrate	Chile Saltpeter	Натрієва (чилійська самородна) селітра
$NaOH$	Sodium Hydroxide	Lye, Caustic Soda, White caustic	Їдкий натрій, луг
$Na_3PO_4 \cdot 12H_2O$	Sodium Phosphate Dodecahydrate	TSP, Sodium Phosphate tribasic	Тринатрій фосфат (компонент пральних засобів)
$Na_2S_2O_3$ or $Na_2S_2O_3 \cdot 5H_2O$	Sodium Thiosulfate or Sodium Thiosulfate Pentahydrate	Antichlor	Антихлор, тіосульфат натрію, натрій гіпосульфіт
$Na_2B_4O_7 \cdot 10\ H_2O$	Sodium Tetraborate Decahydrate	Borax	Бура
$Na_2SO_4 \cdot 10\ H_2O$	Sodium Sulfate Decahydrate	Glauber's Salt	Глауберова сіль
P_2O_5 or P_4O_{10}	Phosphorus(V) Oxide	Phosphoric Anhydride	Фосфорний ангідрид
$2PbCO_3 \cdot Pb(OH)_2$	Lead(II) Carbonate-Hydroxide	White Lead	Свинцеві білила (художня фарба)
$Pb(CH_3COO)_2x$ $x3H_2O$	Lead(II) Acetate Trihydrate	Lead Sugar	Свинцевий цукор
PbO	Lead(II) Oxide	Litharge (mineral)	Свинцевий глет
PbS	Lead(II) Sulphide	Galena, Lead Glance (mineral)	Галеніт, свинцевий блиск

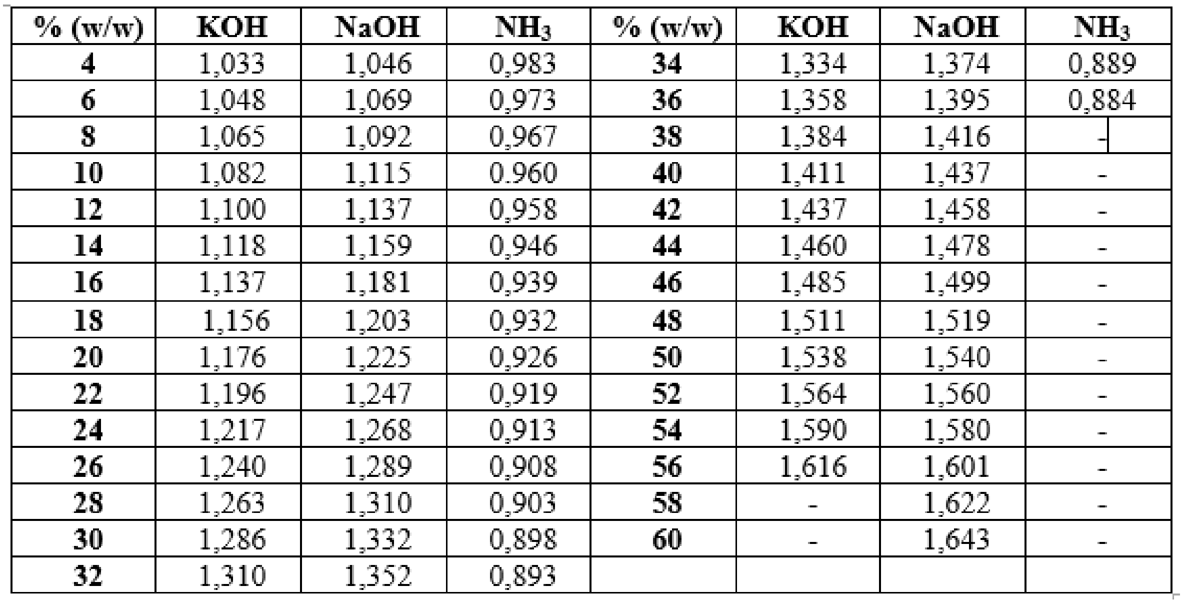
S	Sulfur (Sulphur)	Brimstone	Самородна (у вигляді грудочок) сірка
SO_3	Sulfur(VI) Oxide	Sulfuric Anhydride	Сірчаний ангідрид
SiO_2	Silicon(IV) Oxide	Silica, Quartz, Sand (As minerals)	Кварц, пісок, біла сажа
Solution of (15,5-60%) SO_3 in H_2SO_4	Fuming sulfuric acid	Oleum	Олеум
TiO_2	Titanium(IV) Oxide	Titanium White	Титанові білила (художня фарба)
$ZnSO_4 \cdot 7\ H_2O$	Zinc Sulfate Heptahydrate	White Vitriol	Цинковий купорос
ZnO	Zinc Oxide	Zinc White	Цинкові білила
$ZnCO_3$	Zinc Carbonate	Calamine	Каламін
ZrO_2	Zirconium dioxide	Zirconia	Цирконієві білила

APPENDIX 4 Electronegativity values of the elements (Pauling's scale)

H 2,1																	**He**
Li 1,0	**Be** 1,5											**B** 2,0	**C** 2,5	**N** 3,0	**O** 3,5	**F** 4,0	**Ne**
Na 0,9	**Mg** 1,2											**Al** 1,5	**Si** 1,8	**P** 2,1	**S** 2,5	**Cl** 3,0	**Ar**
K 0,8	**Ca** 1,0	**Sc** 1,3	**Ti** 1,5	**V** 1,6	**Cr** 1,6	**Mn** 1,5	**Fe** 1,8	**Co** 1,8	**Ni** 1,8	**Cu** 1,9	**Zn** 1,6	**Ga** 1,6	**Ge** 1,8	**As** 2,0	**Se** 2,4	**Br** 2,8	**Kr** 3,0
Rb 0,8	**Sr** 1,0	**Y** 1,2	**Zr** 1,4	**Nb** 1,6	**Mo** 1,8	**Tc** 1,9	**Ru** 2,2	**Rh** 2,2	**Pd** 2,2	**Ag** 1,9	**Cd** 1,7	**In** 1,7	**Sn** 1,8	**Sb** 1,9	**Te** 2,1	**I** 2,5	**Xe** 2,6
Cs 0,7	**Ba** 0,9	**La** 1,1	**Hf** 1,3	**Ta** 1,5	**W** 1,7	**Re** 1,9	**Os** 2,2	**Ir** 2,2	**Pt** 2,2	**Au** 2,4	**Hg** 1,9	**Tl** 1,8	**Pb** 1,8	**Bi** 1,9	**Po** 2,0	**At** 2,2	**Rn** 2,4
Fr 0,7	**Ra** 0,7	**Ac** 1,1															

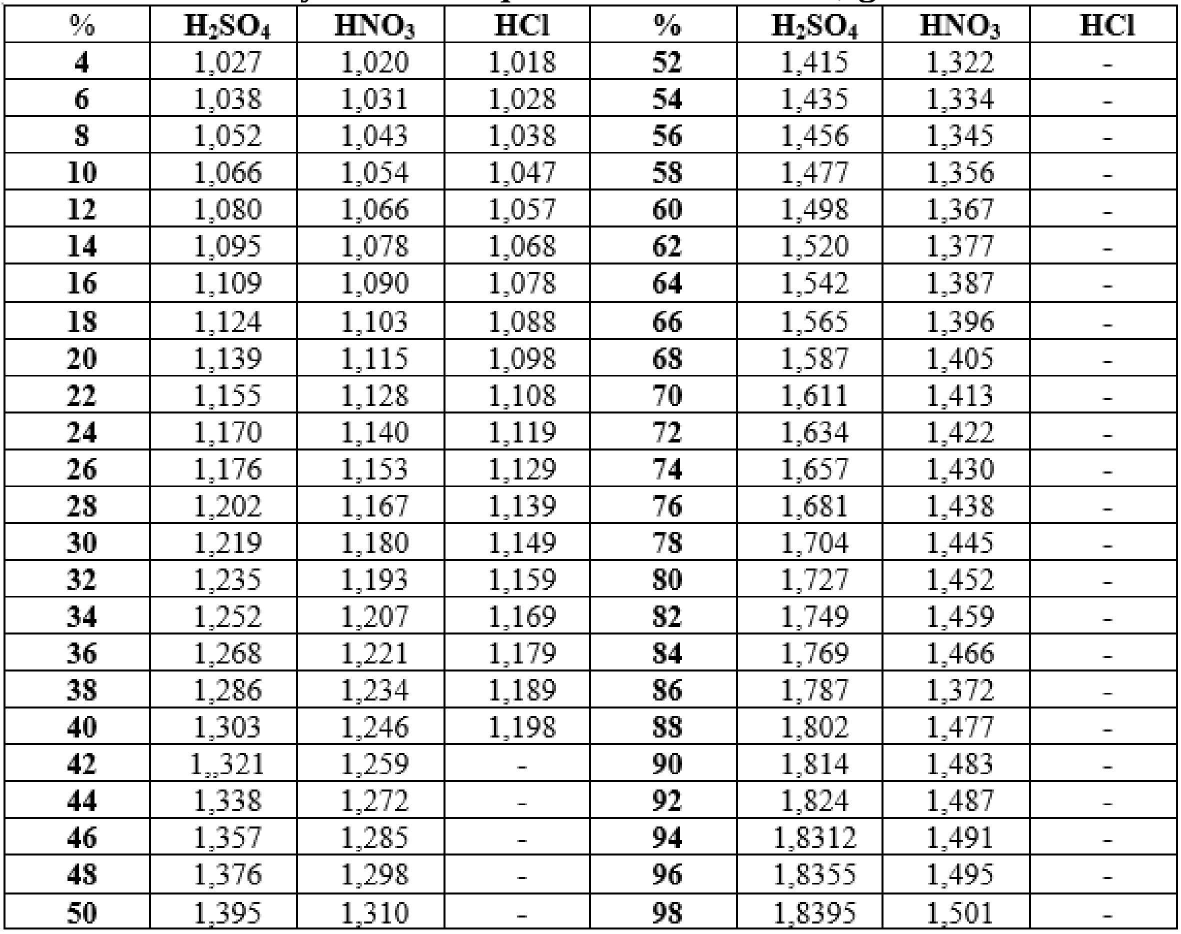
Ce 1,1	**Pr** 1,1	**Nd** 1,1	**Pm** 1,1	**Sm** 1,1	**Eu** 1,1	**Gd** 1,1	**Tb** 1,1	**Dy** 1,1	**Ho** 1,1	**Er** 1,1	**Tm** 1,1	**Yb** 1,1	**Lu** 1,1
Th 1,3	**Pa** 1,5	**U** 1,7	**Np** 1,3	**Pu** 1,3	**Am** 1,3	**Cm** 1,3	**Bk** 1,3	**Cf** 1,3	**Es** 1,3	**Fm** 1,3	**Md** 1,3	**No** 1,3	**Lr** 1,3

APPENDIX 5 Density of alkali aqua solutions at 18 °C, g/cm^3



% (w/w)	KOH	NaOH	NH_3	% (w/w)	KOH	NaOH	NH_3
4	1,033	1,046	0,983	**34**	1,334	1,374	0,889
6	1,048	1,069	0,973	**36**	1,358	1,395	0,884
8	1,065	1,092	0,967	**38**	1,384	1,416	-
10	1,082	1,115	0.960	**40**	1,411	1,437	-
12	1,100	1,137	0,958	**42**	1,437	1,458	-
14	1,118	1,159	0,946	**44**	1,460	1,478	-
16	1,137	1,181	0,939	**46**	1,485	1,499	-
18	1,156	1,203	0,932	**48**	1,511	1,519	-
20	1,176	1,225	0,926	**50**	1,538	1,540	-
22	1,196	1,247	0,919	**52**	1,564	1,560	-
24	1,217	1,268	0,913	**54**	1,590	1,580	-
26	1,240	1,289	0,908	**56**	1,616	1,601	-
28	1,263	1,310	0,903	**58**	-	1,622	-
30	1,286	1,332	0,898	**60**	-	1,643	-
32	1,310	1,352	0,893				

Density of acidic aqua solutions at 18 °C, g/cm^3



%	H_2SO_4	HNO_3	HCl	%	H_2SO_4	HNO_3	HCl
4	1,027	1,020	1,018	**52**	1,415	1,322	-
6	1,038	1,031	1,028	**54**	1,435	1,334	-
8	1,052	1,043	1,038	**56**	1,456	1,345	-
10	1,066	1,054	1,047	**58**	1,477	1,356	-
12	1,080	1,066	1,057	**60**	1,498	1,367	-
14	1,095	1,078	1,068	**62**	1,520	1,377	-
16	1,109	1,090	1,078	**64**	1,542	1,387	-
18	1,124	1,103	1,088	**66**	1,565	1,396	-
20	1,139	1,115	1,098	**68**	1,587	1,405	-
22	1,155	1,128	1,108	**70**	1,611	1,413	-
24	1,170	1,140	1,119	**72**	1,634	1,422	-
26	1,176	1,153	1,129	**74**	1,657	1,430	-
28	1,202	1,167	1,139	**76**	1,681	1,438	-
30	1,219	1,180	1,149	**78**	1,704	1,445	-
32	1,235	1,193	1,159	**80**	1,727	1,452	-
34	1,252	1,207	1,169	**82**	1,749	1,459	-
36	1,268	1,221	1,179	**84**	1,769	1,466	-
38	1,286	1,234	1,189	**86**	1,787	1,372	-
40	1,303	1,246	1,198	**88**	1,802	1,477	-
42	1,,321	1,259	-	**90**	1,814	1,483	-
44	1,338	1,272	-	**92**	1,824	1,487	-
46	1,357	1,285	-	**94**	1,8312	1,491	-
48	1,376	1,298	-	**96**	1,8355	1,495	-
50	1,395	1,310	-	**98**	1,8395	1,501	-

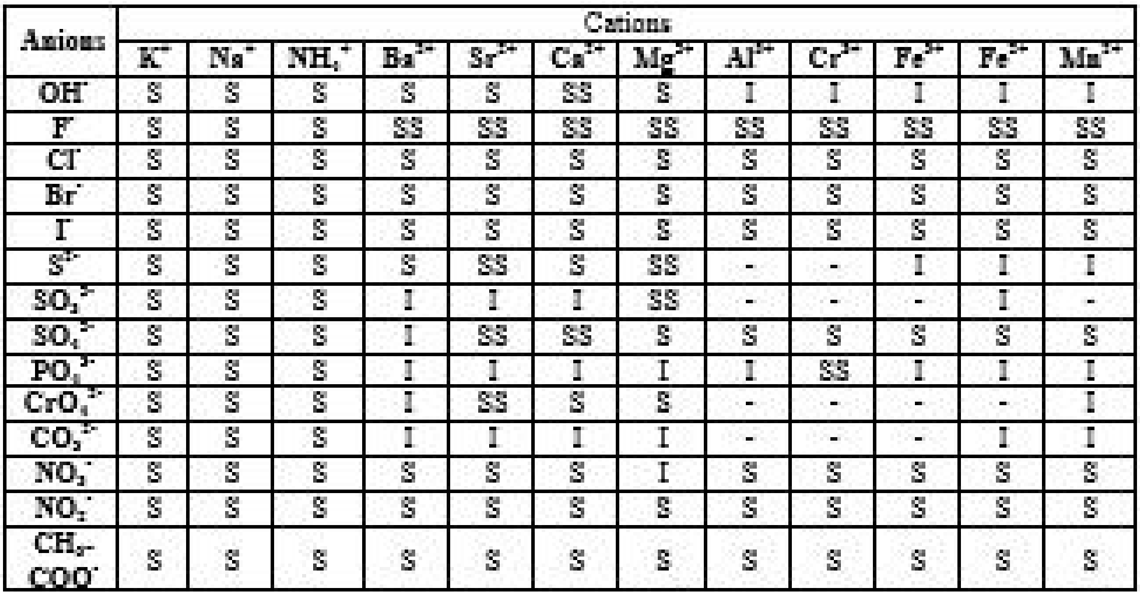
APPENDIX 6 Formulas of the some acids and names of their anions

Formula	English	Українська назва кислоти	Anion	Name of anion
Oxygen-free acids				
HF	Hydrofluoric	Гідроген-фторидна	F^-	Fluoride
HCl	Hydrochloric	Гідроген-хлоридна (соляна)	Cl^-	Chloride
HBr	Hydrobromic	Гідроген-бромідна	Br^-	Bromide
HI	Hydriodic	Гідроген-йодидна	I^-	Iodide
HCN	Hydrocyanic (prussic)	Ціановоднева (синильна)	CN^-	Cyanide
HCNS	Thiocyanic	Тіоціановоднева (роданиста)	SCN^-	Thiocyanate
H_2S	Hydro-Sulfuric	Гідроген-сульфідна	S^{2-} HS-	Sulphide Hydrosulphide
H_2Se	Hydroselenic	Гідроген-селенідна	Se^{2-} HSe^-	Selenide Hydroselenide
Oxygen-containing acids (oxyacids)				
CH_3COOH	Acetic	Етанова (оцтова)	CH_3COO^-	Acetate
HBO_2	Metaboric	Метаборна	BO_2^-	Metaborate
H_3BO_3	Orthoboric	Ортоборна	$[B(OH)_4]^-$	Borate
H_2CO_3	Carbonic	Карбонатна (вугільна)	CO_3^{2-} HCO_3^-	Carbonate Hydrocarbonate
H_2SiO_3	Silicic	Силікатна (кремнієва)	SiO_3^{2-} $HSiO_3^-$	Silicate Hydrosilicate
H_2SO_3	Sulfurous	Сульфітна (сірчиста)	SO_3^{2-} HSO_3^-	Sulfite Hydrosulfite
H_2SO_4	Sulfuric	Сульфатна (сірчана)	SO_4^{2-} HSO_4^-	Sulfate Hydrosulfate
HNO_2	Nitrous	Нітритна (азотиста)	NO_2^-	Nitrite

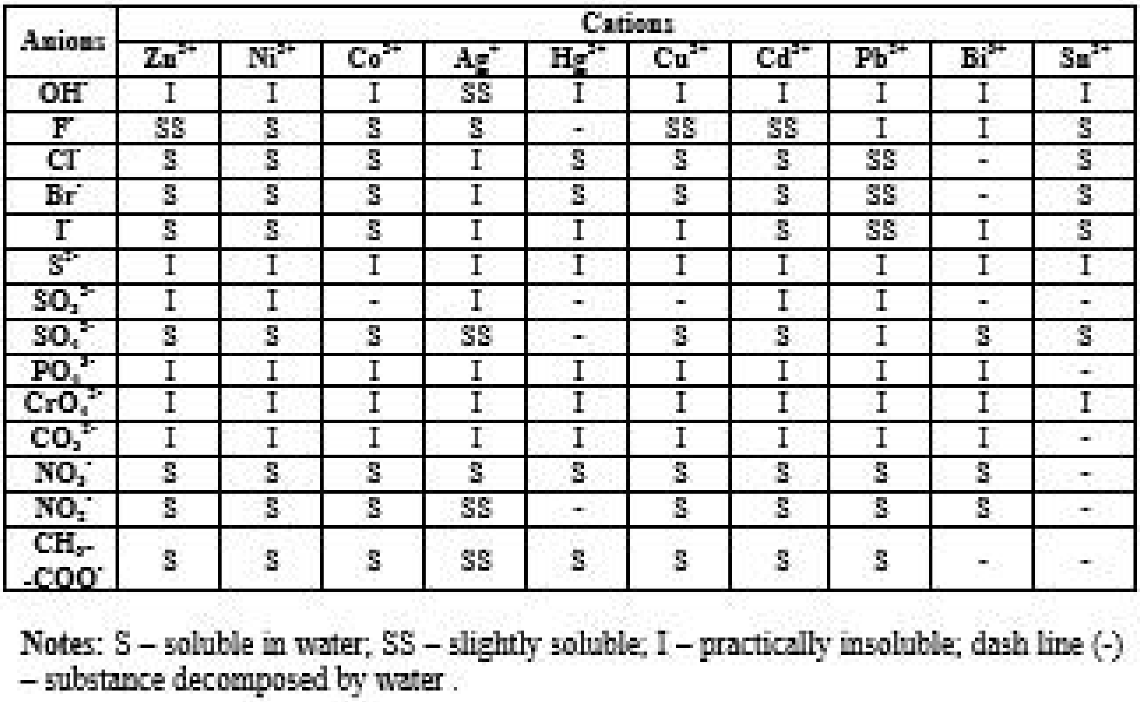
HNO_3	Nitric	Нітратна (азотна)	NO_3^-	Nitrate
HPO_3	Metaphosphoric	Метафосфатна	PO_3^-	Metaphosphate
H_3PO_4	Orthophosphoric (phosphoric)	Ортофосфатна (фосфорна)	PO_4^{3-} HPO_4^{2-} $H_2PO_4^-$	Orthophospate Hydroorthophospate Dihydroorthophospate
$H_4P_2O_7$	Diphosphoric (pyrophosphoric)	Дифосфорна (пірофосфорна)	$P_2O_7^{4-}$ $HP_2O_7^{3-}$ $H_2P_2O_7^{2-}$ $H_3P_2O_7^-$	Diphosphate Hydrodiphosphate Dihydrodiphosphate Trihydrodiphosphate
HPO_2	Metaphosphorous	Метафосфітна	PO_2^-	Metaphosphite
H_3PO_3	Orthophosphorous	Ортофосфітна	HPO_3^{2-} $H_2PO_3^-$	Orthophosphite Hydroorthophosphite
H_3AsO_4	Orthoarsenic	Ортоарсенатна	AsO_4^{3-} $HAsO_4^{2-}$ $H_2AsO_4^-$	Orthoarsenate Hydroarsenate Dihydroorthoarsenate
H_3AsO_3	Orthoarsenous	Ортоарсенітна	AsO_3^{3-} $HAsO_3^{2-}$ $H_2AsO_3^-$	Orthoarsenite Hydroorthoarsenite Dihydroorthoarsenite
$HAsO_2$	Metaarsenous	Метаарсенітна	AsO_2^-	Metaarsenite
$HClO$	Hypochlorous	Хлоратна (I) (хлорнуватиста)	ClO^-	Hypochlorite
$HClO_2$	Chlorous	Хлоратна(III) (хлориста)	ClO_2^-	Chlorite
$HClO_3$	Chloric	Хлоратна (V) (хлорнувата)	ClO_3^-	Chlorate
$HClO_4$	Perchloric	Хлоратна (VII) (хлорна)	ClO_4^-	Perchlorate

$HMnO_4$	Permanganic	Манганатна (VII) (марганцева)	MnO_4^-	Permanganate
H_2MnO_4	Manganic	Манганатна (VI) (марганцевиста)	MnO_4^{2-} $HMnO_4^-$	Manganate Hydromanganate
HVO_3	Vanadic	Ванадатна	VO_3^-	Vanadate
H_2MoO_4	Molybdenic	Молібдатна	MoO_4^{2-} $HMoO_4^-$	Molybdate Hydromolybdate
H_2CrO_4	Chromic	Хроматна	CrO_4^{2-} $HCrO_4^-$	Chromate Hydrochromate
$H_2Cr_2O_7$	Dichromic	Дихроматна	$Cr_2O_7^{2-}$ $HCr_2O_7^-$	Dichromate Hydrodichromate
Acids responded to amphoteric hydroxides in reactions with basic substances				
$HAlO_2$	Metaaluminic	Метаалюмінатна	AlO_2^-	Metaaluminate
H_3AlO_3	Orthoaluminic	Ортоалюмінатна	AlO_3^{3-} $HAlO_3^{2-}$ $H_2AlO_3^-$	Orthoaluminate Hydroaluminate Dihydroaluminate
H_2PbO_2	Leadic	Плюмбатна (свинцева)	PbO_2^{2-} $HPbO_2^-$	Leadcate Hydroleadcate
H_2ZnO_2	Zinc	Цинкатна	ZnO_2^{2-} $HZnO_2^-$	Zincate Hydrozincate
$HCrO_2$	Metachromous	Метахромітна	CrO_2^-	Metachromite
H_3CrO_3	Orthochromous	Ортохромітна	CrO_3^{3-} $HCrO_3^{2-}$ $H_2CrO_3^-$	Orthochromite Hydroorthochromite Dihydroorthochromite

APPENDIX 8 Solubility of salts and bases in water



Anions	Cations											
	K^+	Na^+	NH_4^+	Ba^{2+}	Sr^{2+}	Ca^{2+}	Mg^{2+}	Al^{3+}	Cr^{3+}	Fe^{3+}	Fe^{2+}	Mn^{2+}
OH^-	S	S	S	S	S	SS	S	I	I	I	I	I
F^-	S	S	S	SS	SS	SS	SS	SS	SS	SS	SS	SS
Cl^-	S	S	S	S	S	S	S	S	S	S	S	S
Br^-	S	S	S	S	S	S	S	S	S	S	S	S
I^-	S	S	S	S	S	S	S	S	S	S	S	S
S^{2-}	S	S	S	S	SS	S	SS	-	-	I	I	I
SO_3^{2-}	S	S	S	I	I	I	SS	-	-	-	I	-
SO_4^{2-}	S	S	S	I	SS	SS	S	S	S	S	S	S
PO_4^{3-}	S	S	S	I	I	I	I	I	SS	I	I	I
CrO_4^{2-}	S	S	S	I	SS	S	S	-	-	-	-	I
CO_3^{2-}	S	S	S	I	I	I	I	-	-	-	I	I
NO_3^-	S	S	S	S	S	S	I	S	S	S	S	S
NO_2^-	S	S	S	S	S	S	S	S	S	S	S	S
CH_3-COO^-	S	S	S	S	S	S	S	S	S	S	S	S



Anions	Cations									
	Zn^{2+}	Ni^{2+}	Co^{2+}	Ag^+	Hg^{2+}	Cu^{2+}	Cd^{2+}	Pb^{2+}	Bi^{3+}	Sn^{2+}
OH^-	I	I	I	SS	I	I	I	I	I	I
F^-	SS	S	S	S	-	SS	SS	I	I	S
Cl^-	S	S	S	I	S	S	S	SS	-	S
Br^-	S	S	S	I	S	S	S	SS	-	S
I^-	S	S	S	I	I	I	S	SS	I	S
S^{2-}	I	I	I	I	I	I	I	I	I	I
SO_3^{2-}	I	I	-	I	-	-	I	I	-	-
SO_4^{2-}	S	S	S	SS	-	S	S	I	S	S
PO_4^{3-}	I	I	I	I	I	I	I	I	I	-
CrO_4^{2-}	I	I	I	I	I	I	I	I	I	I
CO_3^{2-}	I	I	I	I	I	I	I	I	I	-
NO_3^-	S	S	S	S	S	S	S	S	S	-
NO_2^-	S	S	S	SS	-	S	S	S	S	-
CH_3--COO^-	S	S	S	SS	S	S	S	S	-	-

Notes: S – soluble in water; SS – slightly soluble; I – practically insoluble; dash line (-) – substance decomposed by water .