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MEDICAL CHEMISTRY

STUDY GUIDE

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Рекомендовано Державною установою
“Центральний методичний кабінет з вищої медичної освіти МОЗ України”
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“Центральний методичний кабінет з вищої медичної освіти МОЗ України”
як навчальний посібник для англомовних студентів
вищих навчальних закладів МОЗ України

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В перших розділах посібника представлено матеріал: загальної хімії і хімії елементів, де розглядаються основні поняття і якісні уявлення хімії: енергетика хімічних реакцій, будова речовини, вчення про розчини, окисно-відновні системи, роль і хімічні властивості s-, p- та d-елементів, та комплексоутворюючі властивості комплексних сполук, їх вміст в живому організмі та біологічна роль. Підкреслюється токсична дія деяких елементів, їх сполук та шляхи їх знешкодження. Даються способи розрахунку розчинів лікарських засобів та їх аналізу.

В другій частині посібника надається теоретичні і практичні основи термодинаміки, кінетики, каталізу, хімічної рівноваги, добутку розчинності, потенціометричних методів аналізу, хроматографії, процесів сорбції, фізико-хімії поверхневих явищ і перебігу їх в організмі.

В викладанні матеріалу підсилюється роль лабораторних і практичних робіт, які сприяють не тільки підвищенню якості знань, формуванню практичних навичок, розвитку самостійності навчаючихся, але й методам експерименту (макро-, полу- і мікрометодам).

Основна мета цього посібника ― допомогти самостійно навчитися розв’язувати розрахункові задачі, а також самостійно наблизити студента до проводження малого лабораторного практикуму.

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Plan of Practical lessons, the I th Semester
For the I-st Year Foreign Students of the Medical Faculty
(Medical Chemistry)

№	*Content of the practical lessons*	*Hours*
	Module 1. Acid-base equilibrium and formation of complexes in biological liquids.	
1	Introduction. Safety in the chemical laboratory. Periodical system by D.I. Mendeleev. Electronic structure of elements and ions. Control test of initial knowledge.	2
2	Biogenic s,p - elements: chemical properties, biological role, used in medicine.	2
3	Biogenic d - elements: chemical properties, biological role, used in medicine.	2
4	Formation of complexes in biological systems.	2
5	Methods of expressing concentration of solution.	2
6	Acid-base equilibrium in the organism. pH scale of biological liquids.	2
7	Volumetric analysis. Neutralization method. Alkalimetry. Acidimetry.	2
8	Buffer systems: classification, mechanism of the action.	2
9	Buffer capacity. The Role of Buffers in Biological Systems	2
10	Colligative properties of solutions. Osmosis.	2
	Module 2. Equilibriums in biologocal systems on the boder of the phases.	
11	Thermal effects of the chemical direction of the processes.	2
12	Kinetics of biochemical reactions. Chemical equilibrium. Solubility equilibrium.	2
13	Potentiometric method of analysis.	2
14	Determination of oxidation-reduction (redox) potential.	2
15	Sorbtion of biological active compounds on the layer liquid - gas.	2
16	Sorbtion of biological active compounds on the layer solid compound - solution.	2
	Ion exchange. Chromatography.	
17	Preparation, purification and properties of colloidal solutions.	2
18	Coagulation of colloidal solutions. Colloidal stability.	2
19	Properties of biopolymers. Isoelectric point of proteins.	2
20	***Differential test from medical chemistry***	2

Plan of Practical lessons, the I th Semester
For the I-st Year Foreign Students of the Dental Faculty
(Medical Chemistry)

№	*Content of the practical lessons*	*Hours*
	Homogenous equilibrium in biological liquids	
1	Introduction. Safety in the chemical laboratory. Periodical system by D.I. Mendeleev. Electronic structure of elements and ions. Control test of initial knowledge.	2
2	Biogenic s - elements: chemical properties, biological role, used in medicine.	2
3	Biogenic p - elements: chemical properties, biological role, used in medicine.	2
4	Biogenic d - elements: chemical properties, biological role, used in medicine.	2
5	Formation of complexes in biological systems.	2
6	Methods of expressing concentration of solution.	2
7	Acid-base equilibrium in the organism. pH scale of biological liquids.	2
8	Volumetric analysis. Neutralization method. Alkalimetry. Acidimetry.	2
9	Buffer systems: classification, mechanism of the action.	2
10	Buffer capacity. The Role of Buffers in Biological Systems	2
11	Colligative properties of solutions. Osmosis.	2
	Heterogeneous equilibrium in biological liquids.	
12	Thermal effects of the chemical direction of the processes.	2
13	Kinetics of biochemical reactions.	2
14	Potentiometric method of analysis.	2
15	Determination of oxidation-reduction (redox) potential.	2
16	Adsorption and ion exchange processes in biological systems. Chromatography.	2
17	Preparation, purification and properties of colloidal solutions.	2
18	Coagulation of colloidal solutions. Colloidal stability.	2
19	Physicochemical properties of biopolymers solutions.	2
20	***Practical skills examination. Differentiated-credit of Medical Chemistry***	2

Preface

With chemical appearances, man encounters for centuries and learned to use them in his life. But the processes occurring in living organisms can be explained using the basic theoretical concepts of inorganic, physical, and colloid chemistry. The human body is a complex chemical laboratory. For understanding how going chemical reactions in biological systems, it is necessary to study their mechanism in vitro.

It is known that the human body contains nearly all the elements of the periodic table, many of which go into the body from the environment and can participate in biochemical processes in health and disease. The relationship of the chemical composition of the Earth's crust, oceans and living organisms indicated in the writings by Academician Vernadsky. Significant contribution to the development of these ideas has been made by a number of scientists — A.I.Vinogradov, V.V.Kovalsky etc.

In human body, the chemical elements are in ionic form or bound with proteins in the form of complex compounds. Theory of complex compounds created by A.Verner which subsequently was developed by L.Chugaevym, N.Kurnakov, I.Tananaevym, K.Yatsimirskim and others has been used to explain the behavior of complex compounds in vivo.

Studying the role of chemical elementsis impossible without their qualitative and quantitative analysis. Analysis of drugs requires knowledge of methods for determining the purity and hence their suitability for therapeutic purposes. These issues are solved by analytical chemistry. The founder of qualitative analysis is considered to be the English scientist R. Boyle, the founder of quantitative analysis — russian scientist Mikhail Lomonosov. A number of foreign and Ukrainian scientists developed theoretical concepts and practical analysis methods that are used in medicine — A.Lavuaze, I.Bertselius, J. L. Gay-Lussac, N.Tananaev, I.Alimarin, A.Babko etc.

Processes that occurs in vivo, are not just a chemical reaction, it is a complex of physical and chemical processes which subjects to the laws of physical chemistry. The founder of physical chemistry is the great Russian scientist Mikhail Lomonosov. He first began to lecture on physical chemistry and organized the laboratory for the practical classes with students. In the future, a great contribution to the development of physical chemistry was made by many scientists in different sections: J.H.Van't Hoff, V.Ostvald, V.Nernst, S.Arrenius, K.Scheele, J.Gibbs, I.Langmuir, G. Freundlich, M.Tsvet, M. Dubinin, N.Zelinskii, P.Rebinder, N.Semenov etc.

Living organisms are highly dispersed systems that are studed by colloid chemistry. Since the XVIII century has been conducted research T.Lovits, F.Reyss in the future — I.Borschov, A.Dumanskiy, N.Peskov, P.Rebinder, B.Deryagin, L.Landau and other. Various processes in cells, tissues and organs come with colloidal substances.

To sum up, knowledge of the laws of all sections of chemistry helps to understand how the flow in vivo processes in health and disease, gives the opportunity to influence the changes occurring in the body and, ultimately, improves the quality of life.

Training of future medical specialists begins with learning the basic sciences — biology, physics, chemistry, biochemistry, physiology and others. From 2005 - 2006 academic year under the terms of the Bologna, process entered a course of medical chemistry, which could be used to study many medical disciplines.

In Ukraine there are many foreign students including those who are studying in English, but the textbooks on medical chemistry for those students (English language students) are insufficient.

Moreover chemistry is not studied in secondary schools.

Therefore, it becomes necessary to have a textbook, which would have covered the most important theoretical questions of chemistry that will allow students to understand the essence of physicochemical processes that occur in living organisms. The textbook is prepared under the experimental curriculum, developed on the basis of the European Credit Transfer System (ECTS).

The textbook contains two sections, corresponding to two modules of medical chemistry.

This chapter deals with the questions relating to the equilibrium processes in homogeneous systems.

The first chapter is the theoretical material, which covers issues of structure and properties of chemical elements and their compounds, properties of electrolyte and nonelectrolyte solutions, elements of quantitative analysis.

In order to check the compression of the material, students are given a set of exercises to each topic, for example, problem solving, test questions.

The second part of the textbook deals with the questions of processes that occur at the interface of phases: the elements of thermodynamics, kinetics, chemical equilibrium, potentiometry and surface phenomena.

Each section explains many examples of physicochemical processes, foundations of which occur in living organisms that help future doctors understand their progress in the human body.

The authors greatly appreciate all that who express their comments and suggestions towards improving the quality of the textbook.

TOPIC 1: Periodic system of D.I. Mendeleev. Electron-atomic structure of elements and ions.

1. Actuality of the topic: The laboratory safety information allows to avoid undesirable incidents during practical chemical experiments. The students are offered a refresher course on the structure of chemical compounds to study inorganic chemistry deeply.

2. General aim:
- mastering the rules of the laboratory safety;
- to be capable of explaining the dependence of location and properties of chemical elements in Periodic Table.

3. Actual aims and abilities:
- to know electronic structure of atoms;
- to master the Periodic Law and to be orientated in Periodic Table of D.I.Mendeleev;
- to be capable of writing the various types of chemical reactions.

4. Literature:
4.1. Lecture materials;
4.2. "Chemistry"3th ed. 2001. J. Mc Murry and R. Fay; Prentice Hall, Upper Saddle River, New Jersey 07458, ISBN 0-13-087205-9;
4.3. Ebbing, D.D. and S.D. Gammon. 2002. General Chemistry. Seventh Edition.Houghton Mifflin Co., Boston, MA.

Subject and tasks of chemistry:

Chemistry is a natural science that studies the composition of (qualitative and quantitative) structure, chemical properties and reactivity of chemical compounds.

According to Lomonosov "chemistry is the science of chemical elements and their compounds".

The main tasks of chemistry and the chemical industry:

1) Synthesis of compounds with known properties.
2) Intensification of chemical plants
3) Obtain chemical current sources
4) Receiving of waste product

Phenomena — any change in the animate and inanimate nature, and in the human society.
Physical phenomenon is a phenomenon in which molecules of a substance are not destroyed and therefore new substances are not formed, but changes occur:
1. Changing the aggregate state of matter (ice, steam, H_2O)
2. Changing m, V, body size.
Crushing chalk $CaCO_3$, melt sugar, stirring sugar and sand, nuclear transformation.

That is:
In the physical phenomenon, that change only the physical properties of matter (physical state, size, m, V, S , and so on), but a new substance is not formed.

Chemical phenomenon is a phenomenon in which molecules dissolved into atoms (decay), which regroup, the formation of new substances with new chemical properties (in contrast with physical manifested).
An example of chemical manifested chemical reaction: $4Al + 3O_2 \rightarrow 2Al_2O_3$

The main features of chemical reactions:	
1. The sediment:	$BaCl_2 + K_2SO_4 \rightarrow BaSO_4\downarrow + 2KCl$ White curd-like precipitate ($BaSO_4$ - heavy dose used in X-ray)
2. The formation of gas:	$Na_2S + 2HCl \rightarrow 2NaCl + H_2S\uparrow$ (H_2S – hydrogen sulphide)
3. The formation of weak electrolyte: (H_2O, NH_4OH)	$NaOH + HNO_3 \rightarrow NaNO_3 + H_2O$ weak electrolyte
4. The change of colour:	$t°$ $4CuO \rightarrow 2Cu_2O + O_2$ black compound red compound
5. Formation of complex compound:	in solution $3NaOH + Al(OH)_3 \rightarrow Na_3[Al(OH)_6]$
6. The release or absorption of energy:	a) exothermic reaction (heat emission) $N_2 + 3H_2 \rightarrow 2NH_3 + Q$ heat energy b) endothermic reaction (heat absorption) $N_2 + O_2 \rightarrow 2NO - Q$ c) $2Mg + O_2 = 2MgO$ + E of light

Basic concepts and laws of chemistry:

Atomic and molecular doctrine (M. V. Lomonosov 1741):

1) All substances consist of molecules

2) Molecules consist of atoms

3) Particles of matter (atoms, molecules) are in constant motion, which determines the thermal state of the body.

4) The molecules of simple substances consist of the same atoms and molecules of complex substances from different atoms: H_2,O_2, N_2, F_2, Cl_2, Br_2, I_2, P_4, S_8, H_2O, H_2SO_4.

In 1860 at the international Congress of chemists in Carneros, Germany were given the basic concepts of chemistry.

Molecule is the smallest particle of matter that retains its chemical properties, the latter depend on the composition and the structure of molecules.

Atom is the smallest particle of a chemical element that retains its chemical properties, the latter depending on the structure of the atom.

Atom is an electro-neutral particle, consisting of a positively charged nucleus and the negatively charged electrons forms the electronic shell of the atom.

The sequence number of the elements in the periodic system coincides with the charge on the nucleus of an element which is numerically equal to the number of protons in the nucleus of an atom and the number of electrons in its electron shell.

Characteristics of elementary particles:

Proton($^1_1$p) — is an elementary particle that has a charge of +1 and a mass of approximately 1 atomic mass units.

In chemistry per unit of mass adopted the mass of $\frac{1}{12}$ of the mass of the atom of Carbon is ^{12}C.

1 a.m. = $\frac{1{,}993\cdot10^{-23}\text{г}}{12} = \underbrace{1{,}667\cdot10^{-23}}_{1\text{ a. m.}}$

Neutron ($^1_0$n) — is an electrically neutral elementary particle with a mass approximately equal to 1 a.m.

Electron ($^1_0$e) — is an elementary particle a charge 1 and a mass approximately equal to 0.

The electron mass is so small that is neglected in chemistry:

$m_e = \underbrace{9{,}1\cdot10^{-28}\text{g}}_{\approx 0}$

In chemistry per unit charge passed charge of the electron.

$q_e = \underbrace{1{,}6 \cdot 10^{-19}\ К}_{-1}$

According to the proton-neutron theory of the structure of an atomic nucleus the nucleus of an atom consists of protons and neutrons. The entire mass of the atom is concentrated in the nucleus, because the mass of electrons is neglected:

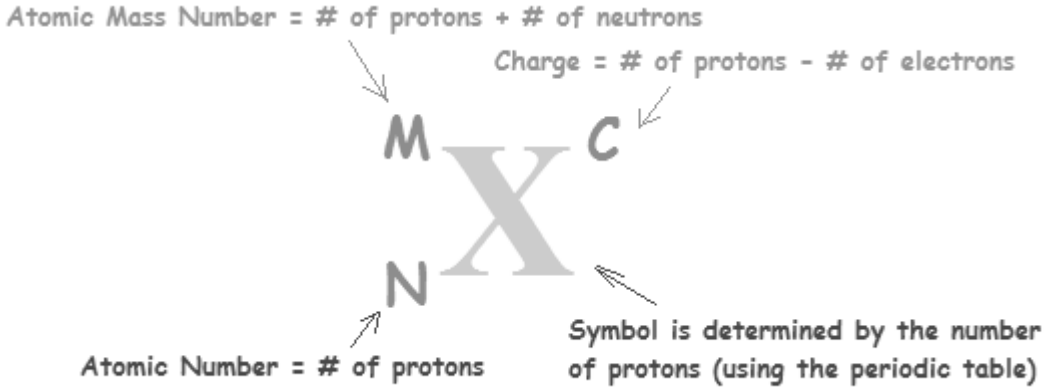
$$A = Z + N$$

A — mass (nucleon) number
Z — is the number of protons (p)
N — is the number of neutrons (n)

(Subatomic Particles)

Subatomic Particle	***Mass***	***Charge***
Proton	~ 1 a.m.u.	+1
Electron	~ 0 a.m.u.	-1
Neutron	~ 1 a.m.u.	0

Table 1.1



Picture 1.

Chemical element is a certain type of atoms with the same positive charge on the nucleus (Z). Chemical elements consist of isotopes.

Isotopes are atoms of the same element with the same positive charge of the nucleus, but with different acidity of neutrons in the nucleus. And as a result, with different mass numbers.

$^{1}_{1}H$ protium (1p) — $^{2}_{1}H(^{2}_{1}D)$ deuterium (1p + 1n) — natural isotopes of hydrogen

$^{3}_{1}H(^{3}_{1}T)$ tritium (1p + 2n) — artificial

It ıts and simple matter.

$^{16}_{8}O$; $^{17}_{8}O$; $^{18}_{8}O$; $^{35}_{17}Cl$; ^{37}Cl;

A simple substance is characterized by:

$t_{melting}$; $t_{boil.}$;

$\rho_{density}$; t°; p(solubility) ;

These characteristics are referred to collectively molecules
Characteristics of chemical elements (related to one atom of the element):
nuclear charge (z)
relative atomic mass (Ar)
valence

oxidation
radius (r)
ionization energy (I)
energy of the electron affinity (E)
electronegativity (X)
mass fraction (w)
molar fraction (χ)

Mass fraction characterizes the prevalence element in the earth's crust.
Well–known geochemist academician Vinogradov create the table called "the average prevalence" of elements in the earth's crust. Under the earth's crust we understand;
(6 km zone of the solid shell of the Earth).

$$w(x)_{element} = \frac{m(x)_{element}}{m_{crust}} \cdot 100\%$$

w (O) = 47,2% from mass of crust
w(Si) = 27,6%
To characterize the isotopic composition of an element using the mole fraction (χ).

$$\chi\,(X_{isotope}) = \frac{\upsilon\,(X_{isotope})}{\upsilon(element)}$$

$^{35}_{17}Cl$; $^{37}_{17}Cl$;
χ: ≈75% ≈25%

$$Ar_{\,average}\,(element) = \frac{A_1 \cdot \chi_1 + A_2 \cdot \chi_2 + A_n \cdot \chi_n}{100\%}$$

The relative atomic mass of an element is calculated as the average of the mass numbers (A) and its isotopes, taking into account their isotopic composition, that is, their molar fractions (χ).

$$Ar\,(Cl) = \frac{35 \cdot 75 + 37 \cdot 25}{100\%} \approx 35{,}5 \text{ a.m.}$$

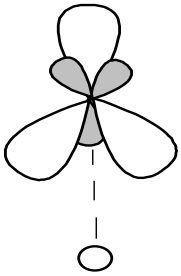
Chlorine is the only element that does not conduct rounding, but take Ar ≈ 35,5 a.m.
For other elements Ar is rounded off well-known rules. Due to rounding it is possible to receive the mass number of the most common isotope of this element.
Relative atomic mass (Ar) is the ratio of the average mass of an atom of natural isotopic composition element $\frac{1}{12}$ of the mass of the ^{12}C atom of Carbon.
Relative molecular mass (Mr) is the ratio of the average mass of a molecule of natural isotopic composition of a substance to $\frac{1}{12}$ of the mass of the ^{12}C atom of Carbon.
Relative molecular mass is the sum of the relative atomic masses of elements based on their quantities.
$Mr(H_2SO_4) = 2Ar(H) + Ar(S) + 4Ar(O) = 2 \cdot 1 + 32 + 4 \cdot 16 = 98$ a.m.
The phenomenon allotrope is the existence of several simple atom substances of the same element.
Allotrope causes:
Different acidity of the atoms in the molecule.

O_2 O_3
oxygen ozone

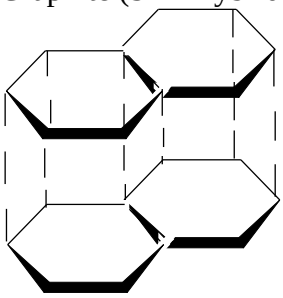
Simple substances that consist of atoms of the same element are called ultraprime modifications, which differ in both physical and chemical properties.

Different crystalline structure (grid)
Different crystalline structure (grid) of C:

- Diamond (SP^3- hybridization, <109◦28', forms - tetrahedral)



- Graphite (SP^2- hybridization, <120°, forms - plane)



- Carbin (SP- hybridization, <180°, forms - linear)

$(-C \equiv C-)_n$

Mole is a measure of the amount of substance.
Mole is the amount of substance that contains as many structural units (atoms, molecules, ions, electrons, etc) and atoms as contained in 12g isotopes of carbon ^{12}C.

$$N_A = \frac{12g}{1{,}993 \cdot 10^{-23} g} = 6{,}02 \cdot 10^{23} \frac{g}{mol}$$

constant Avagadro

$$\upsilon(x) = \frac{N(X)}{N_A}$$

1 mol C — $6{,}02 \cdot 10^{23}$ at. C
1 mol H_2O — $6{,}02 \cdot 10^{23}$ molecule H_2O
1 mol Fe — $6{,}02 \cdot 10^{23}$ atoms Fe
1 mol H_2SO_4 — $6{,}02 \cdot 10^{23}$ molecule H_2SO_4
1 mol H_2SO_4 — $2 \cdot 6{,}02 \cdot 10^{23}$ atoms H
1 mol H_2SO_4 — $6{,}02 \cdot 10^{23}$ atoms S
1 mol H_2SO_4 — $4 \cdot 6{,}02 \cdot 10^{23}$ atoms O

Molar mass is the mass of one mole of a substance.
It is calculated as the ratio of the mass of the substance to the acidity of a substance.

$$M(\chi) = \frac{m(\chi)\ g}{\upsilon(X)\ mol}$$

g/mol
[g/mol] ≡ [kg/kmol] ≡ [T/mmol]
10^3 10^6

$$\upsilon(x) = \frac{m(\chi)}{M(X)}$$

$$m(\chi) = \upsilon(X) \cdot M(X)$$

Molar mass is measured in grams per mole and it is always numerically equals to the relative molecular mass, measured in a.m.

$$M(X) = M(X)$$
g/mol a.m.

This is for complex substances, as well as for simple molecules which consist of 2 or more atoms.

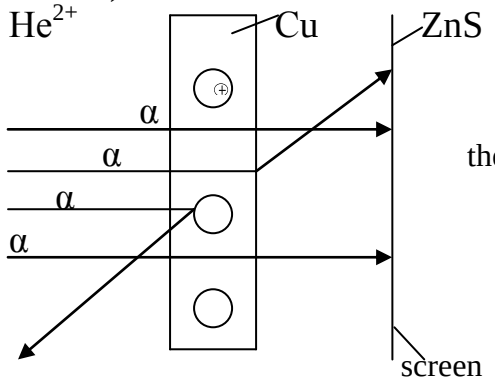
$M(X) = Ar$ (g/mol, a.m.) } for simple substances whose molecules are monatomic (for all Me, for such non Me: C; Si, molecules monatomic noble gases: He, Ne, Ar)

The structure of the atom

Physical experiments and facts, pointing to the complexity of the structure of the atom:

1) Cathode rays (electron flow)
2) Radioactivity (spontaneous decay of certain elements with the selection of elementary particles: beta- flow of electrons, α-positively charged nucleus ($_2^4He$,), γ-electro-magnetic oscillations with very small wave lengths).
3) The phenomenon of electrolysis
4) The periodic law

The first model of the atom (1903) - Thompson: (Atom was considered as a positively charged sphere in which layers of disseminated electrons, do not move, and only fluctuate. This model is called static. This model could not explain the phenomenon of "scattering of α-particles" (1911, Ernest Rutherford.)



the scattering of "α - particles "

The essence of the experience lies in the following:

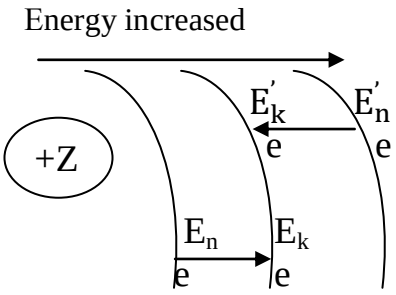
Rutherford took the metal plates and sent them to an α-particle. He saw that most of the α-particles passed through the record straight. Behind the plate there was a screen coated with zinc sulphide which gave the opportunity to positron outbreaks, to record the passage of α-particles. Hower part of the α-particles changed their direction from straight (deviated, dissipated), only 1 of 10 thousand α-particles was thrown back. To explain this phenomenon Rutherford proposed his model of atomic structure the dynamic planetary model of the Rutherford atom: the atom consists of a positively charged nucleus of a very small size $r_{core} = 10^{-13}$cm; $r_{atom} = 10^{-8}$cm;
that is the core that is 100,000 times smaller than the atom. Around the nucleus in circular orbtal spin electrons.

Short comings of the Rutherford's model:

1) Could not explain the stability of atoms.
2) Could not explain linear atomic spectra.

To overcome these disadvantages and develop Rutherford's model, Niels Bohr put forward postulate 3:

I. The electrons in an atom move in a stationary orbital called allowed.
II. Moving on permitted orbital electrons neither emix nor absorb energy.
III. During the transition from one stationary orbit to another electron absorbs or emits energy.



$\Delta E = E_k - E_n = h\upsilon$ — this energy absorption, which is calculated according to the Planck equation, as the product of h and υ, where h – Plank constant, υ – the frequency of the electromagnetic waves $\Delta E = E_n' - E_k' = h\upsilon$ — the radiation energy
That is, the Plank and Bohr energy of the electrons in the atom is changing constantly, and portions of the quantity.

The modern theory of atomic structure

— this theory is described by quantum mechanics.

The energy state of an electron in an atom is described by 4 quantum numbers.
n — is the main quantum number
l — is the side (orbital) quantum number
m_l — is the magnetic quantum number
S — is the spin quantum number

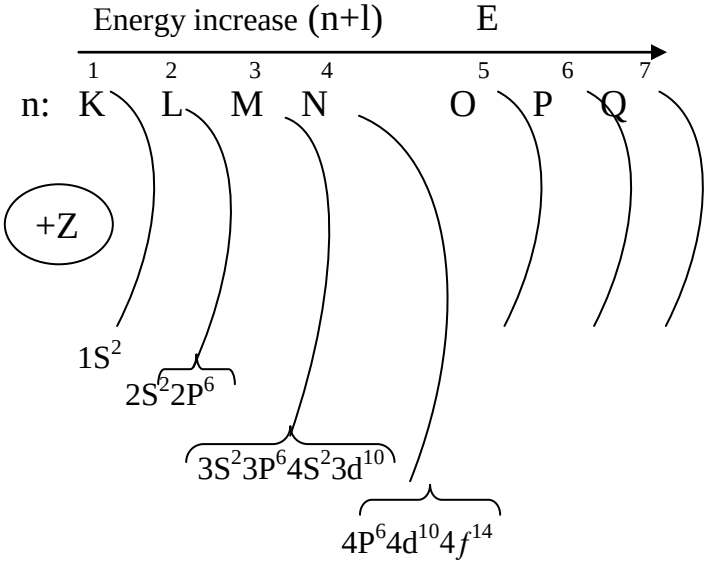
Schrodinger equation relates the energy of the electron in the atom with the 4 quantum numbers.

$E_e = \int_{function} (n, l, m_l, S)$

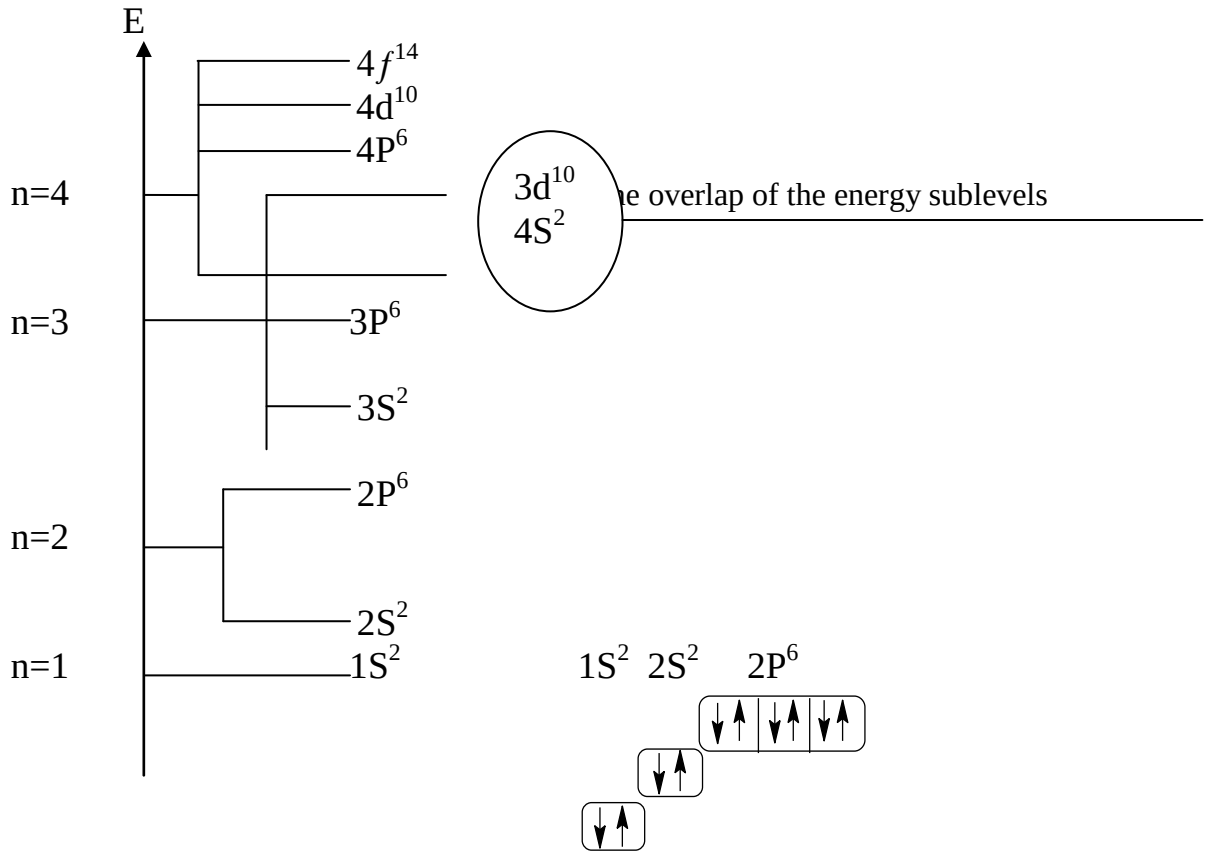
That is, the energy of the electron in the atom is a function of 4 quantum numbers.

The electrons in the atoms on the energy levels are divided into sublevels, and orbitals.

The main quantum number n — characterizes the energy of the electron at the energy level, as well as the size of the level. n numerically acquires the value of the natural numbers from 1 to ∞. $n_{max} = 7$ (really), because the physical meaning of n is the number of the period in which there is the unit of the particular item.



Σ2p = 2 + 1 =3 Σ3S = 3 + 0 =3
Σ3p = 3 + 1 =4 Σ3d = 3 + 2 =5 Σ4S = 4 + 0 =4



Side (orbital) quantum number - e — characterizes the energy of an electron at the energy sublevels, and the form of the sublevels.
l always takes the value 1 less than n.
l: 0,1,2 … (n-1)
The number of sublevels level = the main number

n	l	The main number	The number of sublevels level
1	0	S	1
2	0	S	2
	1	P	
3	0	S	3
	1	P	
	2	d	
4	0	S	4
	1	P	
	2	d	
	3	*f*	

In the modern view, the electron has a corpuscular-wave duality, i.e. the electron is both a particle and a wave.
In quantum mechanics for finding the electron, the atom uses a concept such as orbital.
Orbital is around nuclear space where you are likely to find the electron.
The probability is 90% of the time the electron is in this space.

Coulomb's Law:

The force of interaction 2 charges is directly proportional to the product of these charges and inversely proportional to the square of the distance between them.

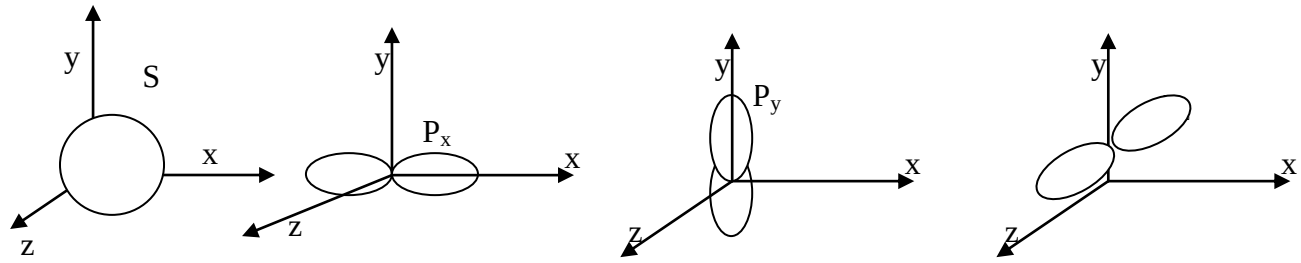
$$F_{\text{Coulomb's}} = k\frac{\overset{(+Z)}{q_1} \times \overset{(-1)}{q_2}}{E\,r^2}$$

E — the dielectric constant of the environment = (81)

Magnetic quantum number m_l - characterizes the energy of the electron orbitals, and also the orientation of the orbitals, as well as the orientation of the orbit in space.

Takes the value: m_l: –l … 0 …+l

	l	m_l	*The number of orbitals in a sublevel*
□	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



Spin quantum number is s — characterizes the rotation of the electron around its own axis

S: $+\frac{1}{2}$; $-\frac{1}{2}$.

Graphically depict electron arrow, and the direction of the arrow is the direction of spin. Graphic orbit - cell (quantum cell).

- □ - free orbital
- ↑ - not coupled electron
- ↑↓ - paired electron

1932y. scientists Ivanenko and Gapon proposed proton-neutron theory of the structure of the atomic nucleus.

$$A = Z + N$$

mass number number **p** number **n**

The nucleus of an atom consists of protons, the number of protons determines the charge on the nucleus,numerically is equal to the ordinal number of the element in the periodic system. The entire mass of the atom is concentrated in the nucleus, the mass of the electrons is neglected.

Rules and principles, which are filled with electrons energy levels, sublevels, orbitals in real atoms.

1. The Pauli Principle:

"In the atom there may not even be two electrons with the same four quantum numbers."

A consequence of the Pauli principle:

"Orbital can contain only two electrons, but with the opposite (antiparallel) spin."

The graphical representation of the Pauli exclusion principle:

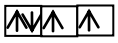
s^2; p^6; d^{10}; f^{14} - max e capacity of orbitals

2. Hund's rules:

"Within one sublevel (with the same l) electrons fill orbitals in such a way that the sum of their spins was max"

Example:

p^4



$$\sum S: +\frac{1}{2} - \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = 1$$

$$\sum S: +\frac{1}{2} - \frac{1}{2} + \frac{1}{2} - \frac{1}{2} = 0$$

The corollary from Hund's rules:

"Within one sublevel electrons fill orbitals one at a time, and then when all the orbitals are occupied, it fills in the second electron, but with opposite spin.

3. The rule of least energy (Kleczkowsky rules):

Electrons in an atom sublevels in the sequence of increasing energy, which is characterized by the sum (n+l), i.e. in the sequence of growth of this amount; if the sum (n+l) for the two sublevels is equal, preference is given to sublevel with a large l or less n".

n	l	The number of orbitals		The number of electrons	
		on the sub-level	on the level	on the sub-level	on the level
1	0 (s)	1	1	2	2
2	0 (s)	1	4	2	8
	1 (p)	3		6	
3	0 (s)	1	9	2	18
	1 (p)	3		6	
	2 (d)	5		10	
4	0 (s)	1	16	2	32
	1 (p)	3		6	
	2 (d)	5		10	
	3 (f)	7		14	

$N_{orbitals\ on\ the\ level} = n^2$

$N_{electrons\ at\ the\ level} = 2n^2$

The distribution of electrons in energy sublevel, as well as items in the periods of the periodic system.

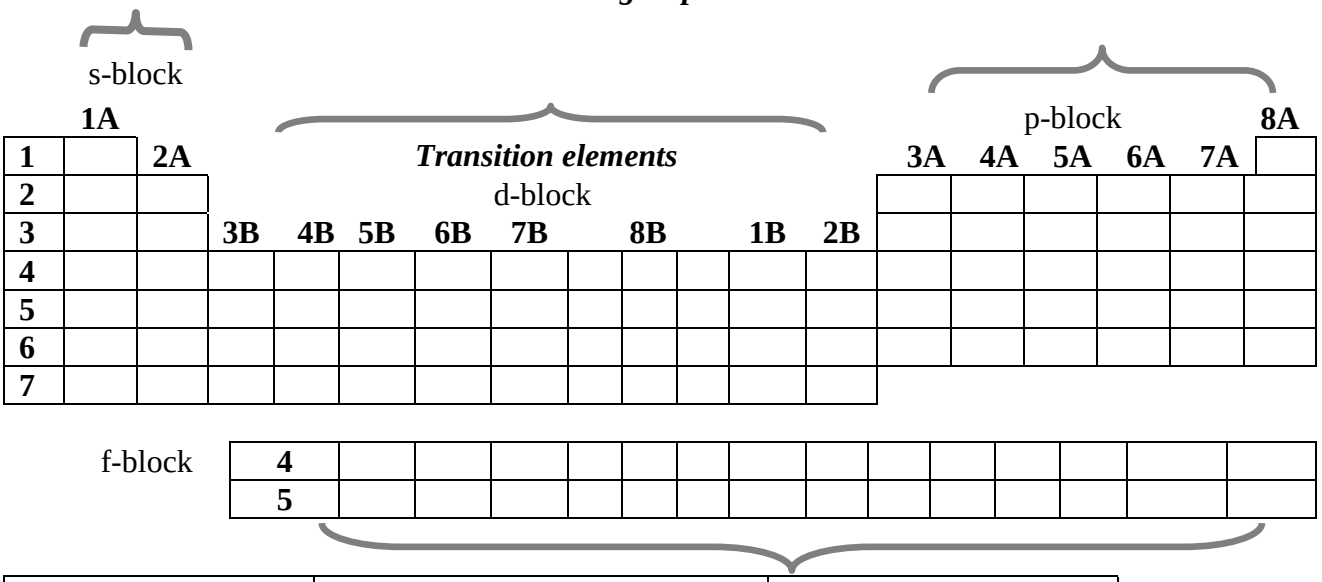
$N_{periods}$	I	II	III	IV	V	VI	VII
Electronic formula	$1s^2$	$2S^22p^6$	$3s^23p^6$	$4s^23d^{10}4p^6$	$5s^24d^{10}5p^6$	$6s^24f^{14}5d^{10}6p^6$	$7s^25f^{14}6d^8$…
The number of elements	2	8	8	18	18	32	24

All elements of the periodic system are divided into 4 families. Depending on which of sublevel (s,p,d,f) for a given item gets his last valence electron.

s – 14 elements
p – 30 elements
d – 38 elements
f – 28 elements

$\sum = 110$

Main-group elements



Quantum numbers n, l	***Spectroscopic notation or subshell (n, l)***	***Maximum number of electrons allowed in the subshell = 2 (2l + 1)***
6,2	6d	10
5,3	5f	14
7,0	7s	2
6,1	6p	6
5,2	5d	10
4,3	4f	14
6,0	6s	2
5,1	5p	6
4,2	4d	10
5,0	5s	2
4,1	4p	6
3,2	3d	10
4,0	4s	2
3,1	3p	6
3,0	3s	2
2,1	2p	6
2,0	2s	2
1,0	1s	2

Table 1.2

For members of these families valence electrons are:
1) For s and p elements - the last electrons energy level;
2) For d-elements - electrons of the d-sublevel;

3) For f-elements — electrons the last and third from the end of the f-sublevel.
For some d-elements, the phenomenon of "leakage (failure) electrons with external s-sublevel in the previous d-sublevel.
This phenomenon occurs in: Cr, Cu, Nb, Mo, Ru, Rh, Au, Pt.
Pd (palladium) - a double breakthrough.

The plan of the characteristic chemical properties of elements based on its electronic structure.

1. And out the charge on the nucleus of the element (Z) (serial number) e-member formula.
2. Establish a family.
3. Show the valence electrons.
4. Only valence electrons draw electron-graphic formulas (orbital patterns in normal and excited states).
5. In the corresponding orbital structures, the number of unpaired electrons establishes spin-valence (V), which is numerically coincides with the degree of oxidation.
6. Give the possible oxidation States

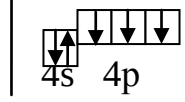
Example:
In accordance with the Arsenic set properties scheme.
Electronic formula:

$_{33}As \quad 1s^2 2s^2 2_P{}^6 3s^2 3p^6 \underline{4s^2} 3d^{10} \underline{4p^3}$

p – family valence electron

Electronic graphic formula (orbital patterns)
By Pauli's

E I (not excited normal state)



4s 4p V = III

Degree oxidation ± 3

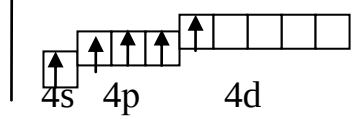
$^{+3}HAsO_2$ meta acid

$^{+3}_{+3\ -2}As_2O_3 \rightarrow H_3AsO_3$ orto acid

$^{-3\ +1}AsH_3$ – arsine

As* (excited state)

E



4s 4p 4d V = V

Degree oxidation +5

$^{+5}HAsO_3$ meta acid

$^{+5\ -2}As_2O_5 \rightarrow H_3AsO_3$ orto acid

Dmitri Ivanovich Mendeleev established the periodic law and the creation of the periodic system of elements.

On March 1, 1869 year, at the Congress of chemists Dmitri Ivanovich Mendeleev proposed his periodic law and the periodic system of the elements, which was a graphical representation of the periodic law. At that time periodic system contains 64 elements.

The main criterion for location of elements in the system Dmitri Ivanovich Mendeleev took the atomic weight and chemical properties of elements.

This meant that each successive element is larger than 1e at the last energy level than the previous one:

Na^{+11} Mg^{+12} Al^{+13} Si^{+14} P^{+15} S^{+16} Cl^{+17} Ar^{+18}

On this basis of the periodic law in the formulation of Dmitri Ivanovich Mendeleev was:

(Mosley - charges of the atomic nuclei of the last increase by 1 e)

Property of simple bodies, as well as the forms and properties of the compounds of the elements are in periodic dependence on atomic weights.

Thus, in the periodic system of the elements are located in order to increas atomic mass.

Hower it should be remembered that Dmitri Ivanovich Mendeleev at the location of the elements takes into account not only the atomic mass, but chemical properties.

But with the development of chemistry have opened new elements, the location of which has not always followed this criterion, the atomic mass

$18Ar - {}^{39.9}$	$19K - {}^{39.0}$
$27Co - {}^{58.9}$	$28Ni - {}^{58.7}$
$52Te - {}^{127.6}$	$53I - {}^{126.9}$

1. The number of the element = the charge and number of electrons.
2. The number of the period = number of levels.
3. The group number = maximum positive oxidation state (the number of valence electrons)
4. Metallic properties increase from top to bottom and from right to left.
5. Metal properties have elements with a small number of valence electrons.
6. The periodicity is due to a specific frequency in completing the electronic levels (shells) - moves to the next period, period to another electronic level, located further from the nucleus, therefore drastically reducing the attraction of the electron - reduction of the metal properties

$$F = \frac{Z_{core} \cdot e}{r^2 \cdot 1}$$

If these elements are strictly the largest atomic mass: Ar falls within the subgroup of active alkali metals, and K — active alkali metal in the subgroup of inert gases.

If this is violated, the so-called frequency at which the properties of the elements recur periodically at a fixed interval.

And so with the development of chemistry (opening the complexity of the structure of the atom) there is a need in the modern formulation of the periodic law:

Properties of simple substances, as well as the forms and properties of the connection element are in periodic dependence of the charge on the nucleus of the atom.

BUT: the current wording was not a contradiction with the periodic law Dmitri Ivanovich Mendeleev, it is only by the periodic law, in the light of the new presents on the complexity of the structure of the atom.

Periodic system as a graphical image of the periodic law.

1. All the elements are situated in ascending order of the charges of the nuclei (the number of the element).
2. Periodic system consists of:
   7 periods
   10 rows
   8 groups

Period is a horizontal row of elements which begins with metals and ends with inert gases, in addition to the 7th last.

Periods are:

1. Small — 1, 2, 3 — they contain the same number of elements
2. Large — 4, 5, 6, 7 — they contain 2 numers of elements

a) top row — even (they are all metals)
b) bottom row — odd

The number of horizontal sequence of elements is arranged in order of increasing charge of the nucleus (sequence number), series: even, odd.

Group — a vertical row of elements with similar atomic structure, similar chemical properties, as well as the same high valence for the absorption of oxygen.

The group consists of two subgroups:
a) the main subgroup — subgroup A (it contains elements of both large and small periods (metals and nonmetals, S and P elements)
b) side subgroup — subgroup, it contains elements of only large periods — metals — d elements.

In the main subgroups metallic properties increase from top to bottom, and non-metallic weaken.
The reason: Increasing atomic R (radius)

N)2e)5e
P)))5e
As)))18e)5e
Sb))))18e)5e
Bi)))))18e)6e

V – A
because R

According to the theory of atomic structure, it is easily explained that with increasing Z kernel, metallic properties of elements in each subset are not reinforced and non-metallic weaken.

The similarity and difference of the elements of the main and auxiliary groups.

Similarity:

Elements of the main groups (A) and side (B) subgroups in the higher oxidation state to form the oxides, the nature of which is acidic.

$Cl_2O_7 \rightarrow HClO_4$ | $SO_3 – H_2SO_4$
$Mn_2O_7 \rightarrow HMnO_4$ | $CrO_3 – H_2CrO_4$

Difference:

1) In the subgroup A — from top-down enhanced metal properties and the basic characteristics of oxides, in the subgroup B — not.
2) The elements group B — all metals, and subgroups A and the metals and the nonmetals.
3) In the main subgroups stability of oxides decreases from top to bottom and side increases.

$$\overset{t^\circ}{CO_2 \not\rightarrow} \qquad \overset{t^\circ \text{ - very high}}{CrO_3 \rightarrow Cr_2O_3}$$

$$\overset{t^\circ}{PbO_2 \rightarrow PbO + O_2} \qquad \overset{t^\circ}{MoO_3 \not\rightarrow} \uparrow \text{difficult}$$

easy

$$\overset{t^\circ}{WO_3 \not\rightarrow}$$

1) In the main subgroups of the filling of the electron, is the outer level (the last level), and the second — last and before last, so the elements of auxiliary groups often have variable valency.

The value of the periodic law

1. Due to the discovery of the periodic law in chemistry from a descriptive, science has become more exact.
2. Were refined the atomic mass of already known elements.
3. Were described chemical properties of atomic mass are yet undiscovered elements.

Ecabor — Sc (eca — like, similar)
Ecaaluminium — Ga
Ecasilicium — Ge

4. On the periodic law and the periodic table of elements was confirmed the validity of such philosophical laws:
a) the transition of quantity into quality (Proust law $2H_2 + O_2 \rightarrow 2H_2O$)
b) the fighting unity and struggle of opposites
c) the law of negation.
5. It was designated the relationship between the position of the element, its properties from the structure of the atom.

The history of the discovery of the periodic law Dmitri Ivanovich Mendeleev.

Prerequisites of opening
1) French Somcuta in the 1862 year, established items in ascending order of their atomic masses in spirals, around the cylinder, each layer contained 16 items.
2) John Newlands: placed in a table: notice that the properties of substances are similar. For example: Cl is similar to F; K is similar to Na. S — called natural "law of octaves"; Octave — frequency properties after 7 elements.
3) Meyer — graph V octaves from m the periodic dependence of the periodic variable (combining elements in accordance with the chemical properties)
4) Triad of Dobereiner (nominated triad of elements. Average properties).

$$A(Na) = \frac{A(Li) \bullet A(K)}{2} = 23$$

Ar(Na) = 23

5) Every eighth repeated properties to the first towards him, against: Co, Ni, I.

Chemistry biogenic elements and the basics of qualitative analysis

The abundance of chemical elements in the earth's crust is not uniform. Most abundant element is oxygen — 47.2%, followed by silicon — 27.6% of the metals, it is aluminium — 8.8%.

Interrelation of chemical composition of crustal oceans and the chemical composition of living organisms showed in his writings "academician Vernadsky", who believed that living organisms and the Earth's crust make a single whole — the biosphere.

Biosphere is a certain environment that transformed human and cosmic radiation and adapted to life.

Basics of Vernadsky's theory:

1. Created by science ***biogeochemistry*** — the role of living matter in the migration and concentration of chemical elements in the earth's crust (circuit), as well as the value of the chemical elements in the life and evolution of living organisms.

2. Living organisms and the crust are unified systems. Living organisms are actively involved in the geochemical processes of chemical elements.

3. Chemical composition of the crust and the living organism are similar.

4. Organisms assimilate from the environment necessary components, concentrating them in specific and functional organs and tissues.

5. Biogeochemical provinces (endemic gout, tooth decay, etc.).

The lack or excess of certain elements in the crust can cause various endemic diseases. Such territory is called biogeochemical provinces.

Biogeochemical provinces in Ukraine:

1) Western region of Ukraine, some areas of the Crimea, Kryzhopolsky district in Vinnytsia region **—** lack of iodine;

2) Woodlands **—** lack of Co, Zn, Mn, Mo, and B - cause of multiple sclerosis;

3) Donbass **—** mercury mining **—** frequent infections, tooth decay, diseases of the bones and joints.

A lot of toxic substances get into the environment: CO, CO_2, SO_2, H_2S, compound Pb, Hg, etc. The task of chemists, ecologists, physicians is to proactively lead work that prevents contamination of the population.

In living organisms detected around 80 chemical elements. They play a role in the body and are called *biogenic elements.*

The human body gets chemical elements with food, water. Of these isolated organogenic elements **—** C, H, O, N, P, S, in which the percentage content 97.4% of the human body and which current amount is vital.

Depending on the percentage of the elements in the human body they are divided into:

a) Macroelements 10^{-2} % and more **—** C, H, O, N, P, S, Na, Ca, K, Mg, Cl;

b) Microelements 10^{-3} - 10^{-12} % **—** Mn, Cu, Fe, Zn, Co, I, Mo.

5. The main questions of the seminar:

5.1. The introduction to the laboratory safety.

5.2. Mendeleev Periodic Law as a background of inorganic chemistry.

5.3. Electronic structure of atoms and ions.

5.4. The groups of inorganic compounds.

6. The control test estimates the initial level of knowledge.

Sample 1

1.Write the chemical reaction.

$Na_2O + SiO_2 \rightarrow$

$Ca(OH_2) + Cr_2O_3 \rightarrow$

$Ba(H_2PO_4) + Al_2(SO_4)_3 \rightarrow$

2.Write the dissociation equation of given electrolytes:

$H_2SO_4 \rightarrow$

$BaCl_2 \rightarrow$

$Cr(OH)Br_2 \rightarrow$

3.Depict the electronic structure of sodium atom and ion.

Sample 2

1.Write the chemical reaction.

$CaO + CO_2 \rightarrow$

$Ba(OH)_2 + SO_3 \rightarrow$

$Al(HSO_4)_3 + Na_3PO_4 \rightarrow$

2.Write the dissociation equation of given electrolytes:

$Ca(OH)_2 \rightarrow$

$Al_2(SO_4)_3 \rightarrow$

$KH_2PO_4 \rightarrow$

3.Depict the electronic structure of potassium atom and ion.

TOPIC 2: Biogenic s,p-elements, chemical properties, biological role and application in medicine.

2.1 Biogenic s-elements, chemical properties, biological role and application in medicine.

1. ***Actuality of the topic*:** humans and the environment consist of chemical compounds which have properties that influence the mechanism of biological activities. The medicines and drugs are synthesized from them, overcoming the complex chemical ways.

2. ***General aim:*** To study the properties of s-elements and their influence on the human organism.

3. ***Actual aims and abilities:***
   - to understand the characteristics of energetic states of the given elements;
   - to know the compounds of elements and their properties;
   - to be able to write the electronic configuration of atoms and ions;
   - to carry out the quantitative analysis.

4. ***Literature:***

4.1. Lecture materials;

4.2. "Chemistry" 3th ed. 2001. J. Mc Murry and R. Fay; Prentice Hall, Upper Saddle River, New Jersey 07458, ISBN 0-13-087205-9;

4.3. Ebbing, D.D. and S.D. Gammon. 2002. General Chemistry. Seventh Edition. Houghton Mifflin Co., Boston, MA.

S-elements and their compounds

S-elements are chemical elements in which the s-sublevel filled outer energy level. These are the elements I-A and II-A of the Periodic system of Mendeleev. Electronic configuration, namely distribution of the electron energy levels and sublevels for atoms and ions s-elements can be illustrated by Na and Ca:

Na $1s^2 2s^2 2p^6 3s^1$ Na^+ $1S^2 2S^2 2p^6 3s^0$

Ca $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ Ca^{+2} $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0$

Metal properties are enhanced in the band.

Valence electron number of Alkali Metals

Hydrogen	Lithium	Sodium	Potassium	Rubidium	Cesium	Francium
1	1	1	1	1	1	1

Table 2.1

The electronic configurations of alkali metals

Z	*Element*	*Nom. of electrons*
1	Hydrogen	1
3	Lithium	2, 1
11	Sodium	2, 8, 1
19	Potassium	2, 8, 8, 1
37	Rubidium	2, 8, 18, 8, 1
55	Caesium	2, 8, 18, 18, 8, 1
87	Francium	2, 8, 18, 32, 18, 8, 1

Table 2.2

Alkali metals

General characteristics.
I_A; ns^1; S – family.
Me° -1e ⇒ Me^{+1}

$Me_2O + H_2O \Rightarrow 2MeOH$
$2Me + H_2 \Rightarrow 2MeH$ – hydride Me
$MeH + H_2O \Rightarrow MeOH + H_2\uparrow$

Chemistry of Na & K

1) The prevalence in nature:
ω(Na)=2,64% by weight of the earth's crust
ω(K)=2,6% by weight of the earth's crust

Natural compounds:
NaCl – Rock salt or halite;
$NaCl \cdot KCl$ – Silvinit;
$KCl \cdot MgCl_2 \cdot 6H_2O$ – Carnallite;
$KCl \cdot MgSO_4 \cdot 3H_2O$ – Kainite;

2) Extraction of Na

2.1) By electrolysis of molten NaCl (or KCl)
$2NaCl \leftrightarrow 2Na + Cl_2^\circ \uparrow$
2.2) By electrolysis of molten NaOH:
$4NaOH \rightarrow 4Na + O_2\uparrow + 2H_2O$
Scheme: $NaOH \rightleftarrows Na^+ + OH^-$
$K^{(-)}$: $Na^+ + 1e \Rightarrow Na^\circ$ | 4
$A^{(+)}$: $4OH^- - 4e \Rightarrow O_2^\circ + 2H_2O$ | 1
This is an expensive method.

3) Production of K:

3.1) $KCl + Na \rightarrow NaCl + K$
Through the melting of KCl, passing couples of Na at t°≈800℃. When this is displaced in the form of vapors.
3.2) $KOH + Na \rightarrow NaOH + K$
KOH melts with liquid Na, which is directed counter-current at t°=440℃
Alloy of Na & K, which is obtained, is used as a coolant in nuclear reactors and as a reducing agent in the production of Ti.

$TiCl_4 + 4Na \Rightarrow Ti + 4NaCl$

3) Physical properties:

Silver-white Me, ϱ(Na) = 0,97g/cm^3 ;

ϱ(K)=0,86 g/cm^3. Very soft, easy to cut with a knife.

4) Chemical properties:

They are strong reducing agents.

4.1) On air Na and K are rapidly oxidized, so they are stored under a layer of kerosene.

$4Na + O_2 \rightarrow 2Na_2O$

4.2) They are actively responding to simple substances, which are nonmetals and take the role of oxidants.

$2Na + Cl_2 \Rightarrow 2NaCl$	Chloride
$2Na + S \Rightarrow Na_2S$	Sulfide
$6Na + N_2 \Rightarrow 2Na_3N$	Nitride
$3Na + P \Rightarrow Na_3P$	Phosphide
$4Na + C \Rightarrow Na_4C$	Carbide
$4Na + Si \Rightarrow Na_4Si$	Silicate
$3Na + B \Rightarrow Na_3B$	Boron

3) $Na + 2H_2O \rightarrow 2NaOH + H_2\uparrow + Q$

4) Na & K when heated, react with hydrogen.

$2Na + H_2 \rightarrow 2NaH$ – hydride Na

The hydrides are subjected to irreversible hydrolysis.

$NaH + H_2O \rightarrow NaOH + H_2\uparrow$

5) When Na is heated in excess of O_2, a peroxide of Na is formed

$2Na + O_2 \Rightarrow Na_2O_2$ Na-O-O-Na

<u>*Bases of NaOH & KOH*</u>

1) Physical properties:

White, opaque, hard crystalline substance. Dissolve well in water. When dissolved in water generates, heat because the hydrate is formed of non-permanent staff.

$NaOH \cdot nH_2O$

In the solid state, in air they absorb moisture, so they are used for drying gas. Used for drying gases of the main character (NH_3 & PH_3).

Solid NaOH and KOH and aqueous solutions absorb CO_2.

$$NaOH \rightarrow \begin{cases} NaHCO_3(KHCO_3) \\ Na_2CO_3(K_2CO_3) \end{cases} + H_2O$$

If the air leaves a pellet of NaOH, it is first transformed into the solution (soluble meadow). Over time, this substance interacts with CO_2 (air) and forms ash (Na_2CO_3) is a white powder

NaOH & KOH meet all the properties of an alkali. They react:

1)$NaOH + HCl \rightarrow NaCl + H_2O$

2) $NaOH + SO_2 \rightarrow Na_2SO_3$ ($NaHSO_3$)

$NaOH + CO_2 \rightarrow Na_2CO_3$

3) With nonmetals:

$2NaOH + Cl_2 \rightarrow NaCl + NaClO + H_2O$

$4NaOH + 2Cl_2 \rightarrow 3NaCl + NaClO_2 + 2H_2O$

$6NaOH + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$

$8NaOH + 6Cl_2 \rightarrow 7NaCl + NaClO_4 + 4H_2O$

4) NaOH & KOH not subjected to decay, melt without decomposing:
$Al_2O_3 + 2NaOH \Rightarrow 2NaAlO_2 + H_2O$
$Al_2O_3 + 6NaOH \rightarrow 2Na_3AlO_3 + 3H_2O$
5) $CuSO_4 + 2NaOH \Rightarrow Cu(OH)_2\downarrow + Na_2SO_4$
6)$KHSO_4 + KOH \rightarrow K_2SO_4 + H_2O$
7) With acidic gases.

2) Formation:
The electrolysis of aqueous solutions NaCl or KCl.
$NaCl + H_2O \rightarrow$
Scheme:
$NaCl \rightleftarrows Na^+ + Cl^-$
$K^{(+)}: 2H_2O + 2e \Rightarrow H_2 + 2OH^-$ 1
$A^{(-)}: 2Cl - 2e \Rightarrow Cl_2^\circ$ 1
$2H_2O + 2Cl \rightarrow H_2 + Cl_2 + 2OH$
$2H_2O + 2NaCl \rightarrow H_2 + Cl_2 + 2NaOH$
The solution is evaporated, which produces a precipitate of NaCl, which is not reacted. It is used for further electrolysis and the solution which is granulated.

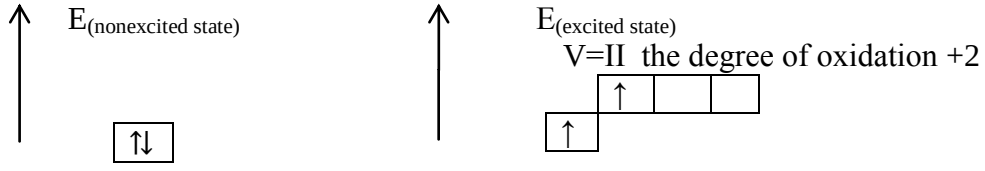
3) The use of NaOH:
To clean oil products, the production of artificial silk, paper, textile and chemical industry, at home used to clean surfaces.
NaOH – caustic soda;
KOH – expensive, rarely used, for the production of liquid soap.

<u>Salt of Na & K</u>
NaCl – seasoning for food, for canning, raw materials for NaOH, HCl, Cl_2.
Na_2CO_3 – soda.
Na_2SO_4 – in the manufacture of glass and soda(like form of Glauber's salt – $Na_2SO_4 \cdot 10H_2O$).
Still used in medicine as a laxative.

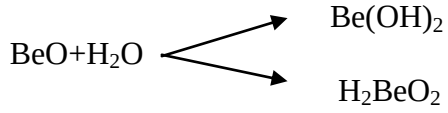
Qualitative reaction:
Sodium salt stained flame burns from yellow to purple (it is necessary to look through the glass).

<u>Alkaline earth metals</u>

II_A: ns^2
Be – amphoteric Me
Mg – $Mg(OH)_2\downarrow$
Alkaline earth – Ca, Sr, Ba.
Me° $-2e \rightarrow Me^{+2}$; $MeO \rightarrow Me(OH)_2$



Be does not react with water, Mg interacts when heated:
$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2\uparrow$
$Me(Ca, Sn, Ba) + H_2O \rightarrow Me(OH)_2 + H_2\uparrow$
Alkaline earth Me form hydrides, when is heated with hydrogen,:
$Me + H_2 \rightarrow MeH_2$



Chemistry of Ca

1)The prevalence in nature:
(Ca) =3,6% from the mass of the earth's crust
$CaCO_3$ – Calcite, Chalk, Limestone, Marble;
$CaSO_4 \cdot 2H_2O$ – Gypsum;
$CaSO_4$ – Anhydrite;
$Ca_3(SO_4)_2$ – Apatite and phosphate;
$CaCO_3 \cdot MgCO_3$ – Dolomite;

2) Production of Ca:
The electrolysis of a mixture of molten salts: 6 parts $CaCl_2$ and 1 part CaF_2 (to reduce the melting temperature)
$CaCl_2 \rightarrow Ca + Cl_2$

3) Physical properties of Ca:
Silvery-white, solid Me. Refers to a light Me (ϱ=1,55g/cm^3), heavier than water. Stored under a layer of kerosene.

4) Chemical properties:
Under normal conditions Ca, is oxidized by oxygen in air.
$2Ca + O_2 \rightarrow 2CaO$
$Ca + Cl_2 \rightarrow CaCl_2$
With other nonmetals-oxidants is reacts when is heated.

$Ca + S \rightarrow CaS$	Sulfide
$3Ca + N_2 \rightarrow Ca_3N_2$	Nitride
$3Ca + 2P \rightarrow Ca_3P_2$	Phosphide
$Ca + 2C \rightarrow CaC_2$	Carbide
$2Ca + Si \rightarrow Ca_2Si$	Silicate

Complex substances oxidizers
1) $Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2\uparrow$
2) $Ca + 2HCl \rightarrow CaCl_2 + H_2\uparrow$
3) $4Ca + 10HNO_3 \rightarrow 4Ca(NO_3)_2 + NH_4NO_3 + 3H_2O$

Oxide of Ca

1) Physical properties:
CaO – burnt lime (quicklime), a white powder. By burned limestone or chalk.
$CaCO_3 \xrightarrow{t°1000℃} CaO + CO_2\uparrow$ ΔH° =178 kJ/mol
To prevent the reverse process, the guardianship process is carried out at t°=1000-1200℃ with the release of CO_2 from the sphere of reaction.
2) The chemical properties:
$CaO + H_2O \rightarrow Ca(OH)_2$; ΔH° = -65 kJ/mol
The process of slaking quicklime.

Hydroxide of Ca

1) General characteristics:
$Ca(OH)_2$ – slaked lime
Held in the hydrated form
$2Ca(OH)_2 + 2Cl_2 \rightarrow CaCl_2 + Ca(ClO)_2 + 2H_2O$
A mixture of $Ca(OH)_2$, sand and water is called lime mortar. Used for plaster, to bond the bricks.
Hardening lime mortar is due to 2 processes:
1) Precipitation from a supersaturated solution crystals $Ca(OH)_2$

2) Formation of $CaCO_3$:
$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

2) The physical properties:
A white solid, soluble in water. At 20℃. 1.5g of $Ca(OH)_2$ dissolved in 1 liter of H_2O.
$Ca(OH)_2$ as a suspension in water is called limestone milk and the solution of $Ca(OH)_2$ in water is called limestone water. It is transparent, is used as a reagent for CO_2.
$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$
$CaCO_3 + CO_2 + H_2O \Rightarrow Ca(HCO_3)_2$
$Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2\uparrow + H_2O$

Salt of Ca

$CaCO_3$ is used as building material for lime production, glass, cement, metallurgy. For wapenamanda soil (to reduce acidity).
$2H^+ + CaCO_3 \rightarrow CO_2 + H_2O + Ca^{2+}$
$CaSO_4 \cdot 2H_2O$ – gypsum
$CaSO_4 \cdot 2H_2O \Rightarrow CaSO_4 \cdot 0{,}5H_2O + 1{,}5H_2O$
Alabaster by stirring in water, hardens, forming gypsum
$CaSO_4 \cdot 0{,}5H_2O + 1{,}5H_2O \Rightarrow CaSO_4 \cdot 2H_2O$
Gypsum is used for the manufacture of building boards, panels, moulds, masks, plaster bandages in medicine (lime-gypsum mortars for plastering).
$CaSO_4$ is gypsum(water attaches).

Water hardness and how to rectify it:
Water hardness is a set of properties of water due to the presence of salts of Ca & Mg. Hard water has the following disadvantages:
1) Degrades the quality of the fabrics in the water.
2) Requires high costs of soap, because it produces precipitation.
$C_{17}H_{35}COONa + Ca^{2+} \rightarrow (C_{17}H_{35}COO)_2Ca\downarrow + 2Na^+$
3) Bad mushy foods, it is impossible to brew tea.
4) Mg ions in large quantities impart a bitter taste to it, perform a laxative effect on the human stomach.
5) In steam boilers form a scum.

Hardness is:
1) Carbonate (temporary):
Due to the presence of $Ca(HCO_3)_2$ & $Mg(HCO_3)_2$ water can be prevented by boiling
$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2\uparrow$
When boiling $Mg(HCO_3)_2$ it can turn into precipitate of basic salt $MgCO_3 + CO_2 + H_2O$
$Mg(HCO_3)_2 = MgCO_3 + CO_2 + H_2O$ or in the form of $Mg(OH)_2$ when pH>10,3
$Mg^{+2} + 2OH^- \rightarrow Mg(OH)_2$
The hydroxide ions are formed as a result of hydrolysis:
$HCO_3^- + H_2O \rightleftarrows H_2CO_3 + OH^-$

2) No carbonate hardness (permanent):
Due to the presence of water in salts of Ca & Mg, with strong acids (chlorides, sulfates). It does not disappear when boiling.
The amount of temporary and permanent hardness is called total.
$T = \frac{[Ca2+]}{20{,}04} + \frac{[Mg2+]}{12{,}16}$
$[Ca^{+2}]$; $[Mg^{+2}]$ – this is the equilibrium ion concentration.
Ca^{+2} & Mg^{+2} measured in mg per 1 l H_2O(mg/l)
Hardness is normal water for ions Ca & Mg.

$[Ca^{+2}][Mg^{+2}]$ – [mol/l]
Depending on T of water is:
1)When T to 1.5 mmol/l is very soft water.
2) From 1.5 to mmol/l is soft water.
3) From 4 to 8 is medium hardness.
4) From 8 to 12 is hard water.
5) More than 12 is very hard water.
The hardness of water for domestic purposes (sanitary standards) should not be more than 7mmol/l.

Ways to soften water:

1) Boiling.
2) Chemical methods:

a) The Limestone way: (To prevent carbonate hardness.)

$Ca^{+2} + 2HCO_3^- + Ca^{+2} + 2OH^- \rightarrow 2CaCO_3 + 2H_2O$

$Mg^{+2} + 2HCO_3^- + 2Ca^{+2} + 4OH^- \rightarrow Mg(OH)_2\downarrow + 2CaCO_3 + 2H_2O$

b) The Lime soda: (To prevent carbonate hardness.)

$Ca^{+2} + CO_3^{-2} \rightarrow CaCO_3$

$Mg^{+2} + CO_3^{-2} \rightarrow MgCO_3$

$MgCO_3 + Ca^{+2} + 2OH^- \rightarrow Mg(OH)_2 + CaCO_3$

c) The Phosphate method:

Take as reagent of Na_3PO_4

$3Ca^{+2} + 2PO_4^{-3} \rightarrow Ca_3(PO_4)_2$

$3Mg^{+2} + 2PO_4^{-3} \rightarrow Mg_3(PO_4)_2$

d) Control:

*(*Cations can be synthetic permanent “CC-1”, “CP-2” or natural alumosilicate of Na.)

Na_2R – cation

$Na_2R + Ca^{+2} \Rightarrow CaR + 2Na^+$

$Na_2R + Mg^{+2} \Rightarrow MgR + 2Na^+$

Over time, the cation exchanger is regenerated by soaking it in a solution NaCl

$CaR + 2NaCl \rightarrow Na_2R + CaCl_2$

$MgR + 2NaCl \rightarrow Na_2R + MgCl_2$

Characteristic of flame coloration

Physical property	Li	Na	K	Rb	Cs
Flame colour	crimson red	Yellow	pale violet	violet	bluish

Table 2.3

Characteristics of some s-elements

Element, degree of oxidation	***Oxides***	***Peroxides***	***Hydrooxides***	***Salt***
H_2, +1, -1	H_2O	H_2O_2		
Na, +1	Na_2O	Na_2O_2	NaOH	NaCl, Na_2CO_3, $NaNO_3$, Na_2SO_4, $NaHSO_4$, Na_3PO_4, NaH_2PO_4, Na_2HPO_4
Ca, +2	CaO	CaO_2	$Ca(OH)_2$	$CaCl_2$, $CaCO_3$, $Ca(NO_3)_2$, $CaSO_4$, $CaHSO_4$, $Ca_3(PO_4)_2$, $Ca(H_2PO_4)_2$, $CaHPO_4$

Table 2.4

Electronic Configuration:

Element	***Symbol***	***Electronic configuration:***
Beryllium	Be	$1s^2 2s^2$
Magnesium	Mg	$1s^2 2s^2 2p^6 3s^2$
Calcium	Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
Strontium	Sr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$
Barium	Ba	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$
Radium	Ra	$[Rn]7s^2$

Table 2.5

The biological role of s - elements, i.e. their presence in the human body, drugs and toxic effects shown in Table

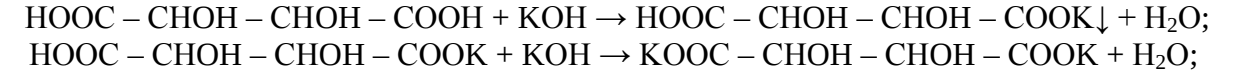
The biological role of S – elements

Element	***Location and role in the body***	***Herbal drugs***	***Toxic effect, antidotes***
H	Element organogen	H_2O_2– 3%–antiseptic; a local haemostatic; HCl– 8,2-8,3% – with reduced gastric acidity.	-
Na	Extracellular cation. Buffer systems, osmosis, K, Na - pump	NaCl – 0,9% – saline (isotonic solution) – a simple blood substitution; for the preparation of medicinal substances; NaCl – 4-10% – hypertonic solution; $NaHCO_3$– baking soda, antacid; Na_2SO_4–lenitive;	-
Ca	Bone and dental tissue in the form of compounds:$Ca_5(OH)(PO_4)_3$or $CaCO_3 \cdot 3Ca_3(PO_4)_2 \cdot H_2O$	$CaCl_2$– antiallergic, anti-inflammatory drug, increases blood clotting. Ca–gluconate– anti-inflammatory effect; $2CaSO_4 \cdot 2H_2O$– burnt plaster casts;	-
Mg	Intracellular ion; action against the spasm	$MgSO_4$– 25%–solution, a strong purgative; MgO– magnesia, the antacid effect; $MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$– white magnesia, the antacid effect; $3MgO \cdot 4SiO_2 \cdot H_2O$– talcum powder, adsorbing agent for powders;	-
Ba	Retina	$Ba(SO_4)_2$ — contrast agent in X-ray	Soluble saltsBa^{2+} are toxic; antidotes – Na_2SO_4, $MgSO_4$

Table 2.6

Qualitative reaction on the S-elements

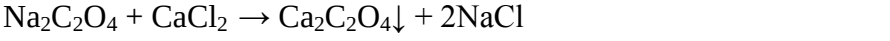
1. <u>The qualitative reaction on potassium ion:</u>
   In a test tube put 5 drops of tartaric acid (tatrant), add 2 drops of KOH solution and rub with a glass rod to form a precipitate. Then add 2 to 3 drops of KOH



$$HOOC - CHOH - CHOH - COOH + KOH \rightarrow HOOC - CHOH - CHOH - COOK\downarrow + H_2O;$$

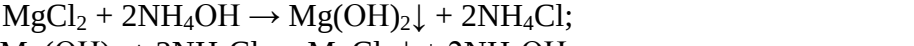
$$HOOC - CHOH - CHOH - COOK + KOH \rightarrow KOOC - CHOH - CHOH - COOK + H_2O;$$

2. <u>The qualitative reaction on calcium ion:</u>
   In a test tube put 2 drops of solution $Na_2C_2O_4$, add 1 drop of $CaCl_2$.

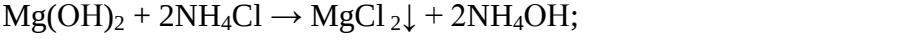


$$Na_2C_2O_4 + CaCl_2 \rightarrow Ca_2C_2O_4\downarrow + 2NaCl$$

3. <u>The qualitative reaction on magnesium ion:</u>
   In a test tube put 2 drops of solution of $MgCl_2$ and add drops of ammonia solution before precipitation. Then add NH_4Cl solution until complete dissolution of sediment.



$$MgCl_2 + 2NH_4OH \rightarrow Mg(OH)_2\downarrow + 2NH_4Cl;$$



$$Mg(OH)_2 + 2NH_4Cl \rightarrow MgCl_2\downarrow + 2NH_4OH;$$

5. ***The main questions of the seminar:***

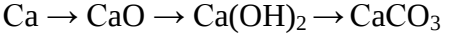
5.1. s-elements:
- electronic structure,
- oxides, hydroxides,
- peroxides, superperoxides,
- biological meaning of sodium, potassium, calcium, magnesium, strontium.

6.The questions for individual learning:

6.1. The role of biogenic elements in human organism.
6.2. The scientific study of V. I. Vernadskiy about biosphere.
6.3. The medicines containing of sodium, potassium, calcium, magnesium.

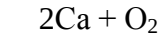
7. The examples of the task:

7.1. The chemical conversion of calcium is given. Write the chemical reaction of the scheme:

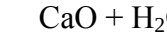


$$Ca \rightarrow CaO \rightarrow Ca(OH)_2 \rightarrow CaCO_3$$

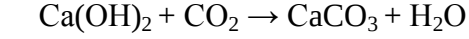
The answer:



$$2Ca + O_2 \rightarrow 2CaO$$



$$CaO + H_2O \rightarrow Ca(OH)_2$$



$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

8. Homework (must be performed in the laboratory notebook):

8.1. Hydrogen (H_2) acts as the oxidizing agent as well as the reducing agent. How do you explain the redox properties of it?
8.2. The chemical conversion of sodium is given. Write the reaction of the given scheme:

$$Na_2CO_3 \rightarrow NaHCO_3 \rightarrow Na_2CO_3 \rightarrow BaCO_3$$

9. The control test **contains 3 tasks:**

9.1. Write the electronic configuration of the sodium atom and ion.
The electronic formula of Na atom is $1s^2 2s^2 2p^6 3s^1$ and Na^+ is $1s^2 2s^2 2p^6 3s^0$
9.2. Write the electronic configuration of the beryllium atom and ion.
The electronic formula of Be atom is $1s^2 2s^2$ and Be^{+2} is $1s^2 2s^0$
9.3. Write the chemical equations of the given chain:
a) $BeCl_2 \rightarrow Be(OH)_2 \rightarrow BeSO_4$

The answer:
$BeCl_2 + 2NaOH \rightarrow Be(OH)_2 + NaCl$
$Be(OH)_2 + H_2SO_4 \rightarrow BeSO_4 + 2H_2O$

10. The algorithm of the experiments:
10.1. The quantitative reaction on the potassium ions.
10.2. The quantitative reaction on the calcium ions.
10.3. The quantitative reaction on the magnesium ions.

11. The detailed explanation of the following experiments:
11.1. The qualitative reaction on the potassium ions.
Put 5 drops of tartric in a test-tube then add 5 drops of KOH and the resulting solution must be mixed by a glass rod to form a precipitate.
Note the effect of the reaction, write the chemical equation, and make a conclusion.

11.2. The qualitative reaction on the calcium ions.
In a test-tube put 2 drops of $Na_2C_2O_4$ solution and add 1 drop of $CaCl_2$ solution. Note the effect of the reaction, write the chemical equation, and make a conclusion.

11.3. The qualitative reaction on the magnesium ions.
In a test-tube put 2 drops of magnum chloride solution and add the ammonia solution until precipitation occurs. Then add certain amounts of ammonium chloride solution for complete disappearance of the precipitation. Write the chemical equation, and make a conclusion.

2.2 Biogenic p-elements, chemical properties, biological role, application in medicine.

***1. Actuality of the topic*:** the chemical compounds of p-elements play an important role in human activity. Some of them are used as medicals but others pollute the nature and are toxic for humans.

***2.General aim*:** is to study the properties of p-elements and biomedical influence on the human organism.

3. Actual aims and abilities:
- to understand the character of energetic states of given elements;
- to know the compounds of elements and their properties;
- to be able to write the electronic configuration of atoms and ions;
- to carry out the quantitative analysis.

4. Literature:
4.1. Lecture materials;
4.2. "Chemistry" 3th ed. 2001. J. Mc Murry and R. Fay; Prentice Hall, Upper Saddle River, New Jersey 07458, ISBN 0-13-087205-9;
4.3. Ebbing, D.D. and S.D. Gammon. 2002. General Chemistry. Seventh Edition. Houghton Mifflin Co., Boston, MA.

p-Elements are called chemical elements, in which the p-sublevel filled outer energy level.
These elements III-A, IV-A, V-A, VI-A and VII-A of the Periodic Mendeleyev system.

Electronic configuration, i.e. distribution of the electron energy levels and sublevels for atoms and ions of p-elements can be illustrated by P and Br:

P $1s^2 2s^2 2p^6 3s^2 3p^3$ P^{+3} $1s^2 2s^2 2p^6 3s^2 3p^0$

Br $1s^2 2s^2 2p^6 3s^2 3p^6\ 3d^{10} 4s^2 4p^5$ Br^{-1} $1s^2 2s^2 2p^6 3s^2 3p^6\ 3d^{10} 4s^2 4p^6$.

In a system period non-metallic properties are increased.

III$_A$ subgroup

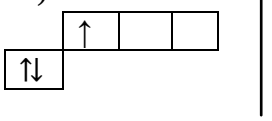
1) General characteristics:

III_A: ns^2np^1 p-family

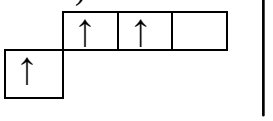
B
Al
Ga
In
Tl

R of the atom increases, E decreases, I/n decreases,
non-metallic properties (oxidation) loosen, prevail metals (recovery).

E E(nonexcited state)



E E(excited state)



V = I the degree of oxidation. +1 V = II the degree of oxidation +3

Chemistry of Al

1) The prevalence in nature:

ω(Al) = 8.8% of the mass of the earth's crust.

Natural compounds:

$K_2O \cdot Al_2O_3 \cdot 6SiO_2$ – Muscovite (also known as common mica, isinglass, or potash mica).

$AlO_3 \cdot 2SiO_2 \cdot 2H_2O$ – White clay(Kaolinite)

Mica $\frac{Na[Al2Si2O8 \cdot nH2O]}{K2[Al2Si2O8 \cdot nH2O]}$

Bauxite is hydrated $Al_2O_3 \bullet nH_2O$, which contains 30-60% Al_2O_3, Fe_2O_3 impurity, which provide bauxite red.

Al_2O_3 – corundum, very firm.

$\frac{3NaF \cdot AlFe}{Na3[AlF4]}$ – Sodiumtetrafluoroaluminate (III), cryolite.

2) Formation:

In the industry it is produced by electrolysis of molten Al_2O_3 in molten cryolite with additions of CaF_2.

The electrolysis is carried out at t°=950-980℃ raw materials must be clean. Pure Al_2O_3 is produced from bauxite and nepheline.

$Al_2O_3 \rightleftarrows 2Al + 3O^{-2}$

$K^{(-)}$: $2Al + 6e \rightarrow 2Al^0$ |6|2

$A^{(+)}$: $3O^{-2} - 6e \rightarrow 3O^0$ |6|2

$4Al + 6O^{-2} \rightarrow 4Al^0 + 3O_2{}^0\uparrow$

$2Al_2O_3 \rightarrow 4Al^0 + 3O^0{}_2\uparrow$

The anode is coal, it is oxidized and the oxide ions form gaseous oxygen. The anode is oxidized with 12-14 coal bricks, which are dipped into the melt from above. O_2, which is allocated coal oxidizes the anode to CO or CO_2

$C + O_2 - \frac{CO}{CO2}$

The cathode is the bottom of the electrolysis and metal Al is deposited on the bottom.

3) Physical properties:

Al — silver-white light Me (ϱ=,7g/cm^3). *Mechanical strong,* t°$_{boil}$ *=660℃.*

Al has good electrical and thermal conductivity. At t° =600℃ Al becomes brittle and can pulverize.

4) Chemical properties:

All compounds of Al has the oxidation state +3. He is a strong reducing agent. Al is easily oxidized under normal temperature, its surface is covered with an oxide film. Saves Me from further oxidation.

1) $4Al + 3O_2 \rightarrow 2Al_2O_3$

The thickness of the oxide film — 0,00001 mm., It is flexible, firm, durable, not far behind tensile, twisting, electrically conductive, melts at t°=20-50c. Al oxide film does not corrode due to moisture in the air.

How the oxide film is destroyed:

a) mechanical (rubbing with emery);

b) chemically (dipped in hot alkaline solution), Al reacts with water:

$2Al + 6H_2O \rightarrow 2Al(OH)_{3\downarrow} + 3H_2\uparrow$

2) In normal t°Al has almost no interaction with conc. HNO_3 and is highly diluted, due to the formation of an oxide film, so HNO_3 is stored and transported in Al containers.

3) Al dissolve in H_2SO_4 & HCl (s).

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

$2Al + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2\uparrow$

4) Al is amphoteric Me, and different from other Me interacts with alkaline solutions.

$2Al + 2NaOH + 10H_2O \rightarrow 2Na[Al(OH)_4(H_2O)_2] + 3H_2\uparrow$

5) When heated Al reacts with Halogens

$2Al + 3Cl_2 \rightarrow 2AlCl_3$

6) By heating(melting) Al interacts with sulfur, carbone and nitrogen.

$2Al + 3S \rightarrow Al_2S_3$

$4Al + 3C \rightarrow Al_4C_3 + 12H_2O \rightarrow 3CH_4\uparrow + 4Al(OH)_3\downarrow$

$2Al + N_2 \Rightarrow 2AlN^{-3}$

Aluminium oxide Al_2O_3

1) The prevalence in nature:

In nature it occurs in the form of the mineral corundum and its variants:

Sapphire is if colorless crystals of corundum colored blue;

Amethyst is if colorless crystals of corundum colored in purple color;

Ruby is if colorless crystals of corundum colored red.

Al_2O_3 is aluminum oxide (alumina).

2) Physical properties:

The substance of white color, very refractory t°=20-50c, has a greater hardness.

3)Formation:

$4Al + 3O_2 \rightarrow 2Al_2O_3$

$2Al(OH)_3 \Rightarrow Al_2O_3 + 3H_2O$

In industry Al_2O_3 is produced from bauxite and nepheline.

4) Chemical properties:

1. Al_2O_3 is insoluble in water and does not interact with it:

Aluminum exhibits amphoteric properties, i.e. self aluminum Al, Al_2O_3 and its oxide hydroxide $Al(OH)_3$ and can be reacted with acids and alkalis:

$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$$

In this reaction, the aluminum oxide exhibits basical properties.

2. He is amphoteric, reacting with it and alkalis:

When aluminum oxide fuse with an alkali, sodium aluminate is formed:

$$Al_2O_3 + 2NaOH \xrightarrow{t} 2\,NaAlO_2 + H_2O \quad (1)$$

$$Al_2O_3 + 6NaOH \Rightarrow 2Na_3AlO_3 + 3H_2O$$

(To derive sodium aluminate should be assumed that if the aluminum oxide can react with water, then it would be consistent with acid $HAlO_2$

$$Al_2O_3 + H_2O \rightarrow H_2Al_2O_4 \rightarrow 2\,HAlO_2 \quad (1)$$

In the water solution the complex compound is formed:

$$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na\,[Al(OH)_4] \quad (2)$$

In the reactions 1 and 2 of aluminum oxide exhibits amphoteric properties.

$$Al_2O_3 + 2NaOH + 7H_2O \rightarrow 2Na[Al(OH)_4(H_2O)_2]$$

Aluminum hydroxide $Al(OH)_3$

$Al(OH)_3$ — is a white solid that is practically insoluble in water.

Receive an indirect way of Al salts by the action of alkaline solutions.

$AlCl_3 + 3NaOH \Rightarrow Al(OH)_3 + 3NaCl$

$Al^{3+} + 3OH^- \rightarrow Al(OH)_3$

$Al(OH)_3$ – typical amphoteric hydrolysis reacts with acids and alkalis

$Al(OH)_3 + NaOH + 2H_2O \Rightarrow Na[Al(OH)_4(H_2O)_2]$

Dissociation of Al $(OH)_3$ connected with oxidation and addition of reducing agent.

$Al^{+3} + 3OH^- \leftrightarrow Al\,(OH)_3 \Rightarrow H_3AlO_3 \leftrightarrow [Al(OH)_4(H_2O)_2]$

When you add acid, the equilibrium changes to left with formation of the corresponding salts of Al.

When you add the lye, the equilibrium will change to the right to the corresponding aluminates.

The use of Al:

1) In the aviation industry in 2/3 years consists of dural mine.
2) Cables, electricity cables,(2 times less than copper).
3) The packaging for nitric acid.
4) Case of buses, cars.
5) Food packaging.
6) Dishes.
7) Paint (protection against corrosion).
8) Aluminothermic

$3Fe_3O_4 + 8Al = 4Al_2O_3 + 9Fe \quad \Delta H° = -3300\text{кJ}$

A mixture of equivalent amounts of powders of Al and iron oxides is called - termite.

$Fe_3O_4 = FeO \cdot Fe_2O_3$

For welding of steel products: in the military.

Many p-elements show redox properties:

$5KN^{+3}O_2 + 2KMn^{+7}O_4 + 3H_2SO_4 \rightarrow 5KN^{+5}O_3 + 2Mn^{+2}SO_4 + K_2SO_4 + 3H_2O.$

$$\begin{array}{lcll} N^{+3} & -2e & \rightarrow N^{+5} & 5 \\ Mn^{+7} & +5e & \rightarrow Mn^{+2} & 2 \end{array} \quad 10$$

$KI^{-1} + K_2Cr_2^{+6}O_7 + H_2SO_4 \rightarrow I_2^0 + Cr_2^{+3}(SO_4)_3 + K_2SO_4 + H_2O$

$$\begin{array}{lcll} 2I^{-1} & -2e & \rightarrow I_2^0 & 3 \\ 2Cr^{+6} & +6e & \rightarrow 2Cr^{+3} & 2 \end{array} \quad 6$$

Oxidation degree and some basic compounds p-elements are shown in Table 2.7

Oxidation and basic compounds of p-elements

Element	Degree of oxidation	Oxygen and hydrogen compounds	Acid, bases	Salt
Al	+3	Al_2O_3	$Al(OH)_3$	$AlCl_3$, $Al(NO_3)_3$, $Al_2(SO_4)_3$, $AlPO_4$, $NaAlO_2$
C	+2 +4	CO CO_2	H_2CO_3	carbonates – Na_2CO_3 hydrogencarbonate – $NaHCO_3$
N	-3 +1 +2 +3 +4 +5	NH_3 N_2O NO N_2O_3 NO_2 N_2O_5	NH_4OH HNO_2 HNO_2+HNO_3 HNO_3	NH_4Cl, $(NH_4)_2SO_4$, NH_4NO_3 non salifiable nitrites – $NaNO_2$, $Ca(NO_2)_2$ nitrate + nitrite – $NaNO_2$ + $NaNO_3$ nitrates – $NaNO_3$, $Ca(NO_3)_2$
P	-3 +3 +5	PH_3 P_2O_3 P_2O_5	 H_3PO_3 H_3PO_4	 phosphites – Na_3PO_3 phosphates – Na_3PO_4 hydrogenphosphate – Na_2HPO_4
S	-2 +4 +6	H_2S SO_2 SO_3	H_2S H_2SO_3 H_2SO_4	sulphides – Na_2S, CaS hydrosulphides –NaHS,$Ca(HS)_2$ sulphites – Na_2SO_3, $CaSO_3$ hydrogensulphites – $NaHSO_3$, $Ca(HSO_3)_2$ sulphates – Na_2SO_4, $CaSO_4$ hydrogen sulphates – $NaHSO_4$, $Ca(HSO_4)_2$
Cl, Br, I	-1 +1 +3 +5 +7	HX X — Cl, Br, I 	HX – HCl HXO – HClO HXO_2 – $HClO_2$ HXO_3 – $HClO_3$ HXO_4 – $HClO_4$	chlorides – NaCl, $CaCl_2$ sodium hypochlorite – NaClO sodium chlorite – $NaClO_2$ sodium chlorate – $NaClO_3$ sodium perchlorate – $NaClO_4$

Table 2.7

Colour

Halogen	Fluorine	Chlorine	Bromine	Iodine
Colour	Pale Yellow	Greenish Yellow	Reddish brown	Dark violet

Table 2.8

The biological role of p — elements, ie their presence in the human body, drugs and toxic effects shown in Table 2.9.

The biological role of P– elements

Element	***Location and role in the body***	***Herbal drugs***	***Toxic effect, antidotes***
B	Carbohydrate-phosphorus metabolism	H_3BO_3 – disinfectant properties (eye and ear drops); $Na_2B_4O_7$(bur) – antiseptic	–
Al	blood, nerve cells in the brain; involved in the construction of the epithelial and connective tissue	$Al(OH)_3$ – absorbent and antacid properties; almagel - water suspension; $Al_2O_3•2SiO_2•2H_2O$ – kaolin, adsorbing action; $Al_2(SO_4)_3$ – hemostatic, antimicrobial action and for water purification. $KAl(SO_4)_2•12H_2O$ (alum) – hemostatic, antimicrobial action;	–
C	Organogen, 21,15%	C (carbol, activated charcoal) –flatulence adsorb gases, toxic substances; CO_2 – stimulatory effect on respiratory centers, inhalations, baths; $NaHCO_3$ – baking soda, antacid.	Coal dust– anthracosis; CO_2– carbon monoxide; antidote - oxygen
Si	Lens of the eye, hair; gives strength, elastic fabric.	Silicon carbide and oxide used in dentistry.	SiO_2–dust causes silicosis.
Pb	The biological role has not been studied	$(CH_3COO)(OH)Pb$ – lead water, anti-inflammatory, antimicrobial action.	Pb^{2+} – toxic, binds SH-groups of proteins, enzymes;
N	Organogen; 3,1%; proteins, nucleic acids.	NH_4OH – 9,5-10,5% solution, irritating effect on the CNS; NH_4Cl – diuretic; $NaNO_2$ – vasodilator; N_2O – inhaled anesthetics.	–
P	Organogen; 0,95% nucleic acids, ATP,bone and dental tissue in the form of compounds:$Ca_5(OH)(PO_4)_3$or $CaCO_3• 3Ca_3(PO_4)_2•H_2O$	Calcium glycerophosphate – a means of fortifying; ATP – the energy product.	P–honky poison; antidote – 0,5% solution $CuSO_4$
As	Brain tissue, muscle, involved in the synthesis of hemoglobin.	As –organic compounds – for the treatment of sexually transmitted diseases; As_2O_3 – necrotising tissue (used in dentistry)	As_2O_3 – white arsenic, a powerful poison antidotes – Na_2S, MgS, $Na_2S_2O_3$

O	Organogen; 62,4%;	O_2 + CO_2 – stimulates the respiratory center;	–
S	Organogen; 0,16%; proteins, amino acids - cysteine, methionine;	S – (cleaned) – antimicrobial action ; SO_2 – disinfectant ; Na_2SO_4 – weakpurgative; S – organic compounds - sulfa drugs – antimicrobialaction ; H_3C-SO-CH_3– dimixed; well penetrates through biological membranes, anti-inflammatory effect.	SO_2 – irritating to mucous membranes of the respiratory tract and eyes.
F	Bone and dental tissue $Ca_5(PO_4)_3F$	NaF, KF – sedatives	Excess fluoride causes *fluorosis* or speckled enamel
Cl	Gastric juice, extracellular anion	HCl – 8,2-8,3% – at low acidity of gastric juice; NaCl – 0,9% solution, the simplest blood substitution; $CaCl_2$+$Ca(OCl)_2$ – chloride of lime, chloramine – disinfectants;	Cl_2 – gas, irritating to the mucous
Br	Pituitary gland, kidney, strengthens the processes of inhibition of the CNS	NaBr, KBr, NH_4Br–sedatives	–
I	Thyroid gland (a hormone thyroxine)	I_2 alcohol solution – 5%, 10% - disinfectant; I_2+ aqueous solution KI – Lugol's solution – disinfectant with angina	–

Table 2.9

Chemical properties and biological role of the p-elements and their compounds

Qualitative reaction on the P-elements

1. <u>The qualitative determination of carbonate-anion:</u>
   In a test tube put 2 drops of solution of Na_2CO_3 and add 2 drops of $BaCl_2$. Specify the external effect of the reaction. To precipitate add a solution of acetic (acetate) acid.

$$Na_2CO_3 + BaCl_2 \rightarrow 2NaCl + BaCO_3\downarrow$$
$$BaCO_3 + CH_3COOH \rightarrow \text{ insoluble}$$

2. <u>The qualitative determination of sulphate anion:</u>
   In a test tube put 2 drops of H_2SO_4 solution and add 2 drops of $BaCl_2$. To the residue add 5 drops of HCl.

$$H_2SO_4 + BaCl_2 \rightarrow BaSO_4\downarrow + 2HCl$$
$$BaSO_4 + 2HCl \rightarrow \text{ insoluble}$$

3. <u>The qualitative determination of nitrite anion:</u>
   In a test tube put 2 drops of solution of $NaNO_2$, add 2 drops of acetic (acetate), acid

CH_3COOH and add 2 drops of KI.

$2NaN^{+3}O_2 + 2KI^{-1} + 4CH_3COOH \rightarrow N^{+2}O + I_2^0 + 2CH_3COOK + 2CH_3COONa + 2H_2O;$

$N^{+3} + 1e \rightarrow N^{+2} \quad | 2$

$2I^- - 2e \rightarrow I_2^0 \quad | 1$

4. <u>The qualitative determination of thiosulphate anion:</u>
   In a test tube put 3 drops of solution $Na_2S_2O_3$ and add 2 drops of HCl.

$Na_2S_2^{+2}O_3 + HCl \rightarrow NaCl + S^0\downarrow + S^{+4}O_2 + H_2O;$

5. <u>The qualitative determination of manganate anion:</u>
   In a test tube put 2 drops of solution of $KMnO_4$, add 2 drops of H_2SO_4 and dropwise H_2O_2.

$2KMn^{+7}O_4 + 5H_2O_2^{-1} + 3H_2SO_4 \rightarrow 2Mn^{+2}SO_4 + 5O_2^0 + K_2SO_4 + 8H_2O$

$Mn^{+7} + 5e \rightarrow Mn^{+2} \quad | 2$

$2O^{-1} - 2e \rightarrow O_2 \quad | 5$

5. ***The main questions of the seminar:***

5.1. p-elements:
- electronic structure, valancy, the oxidation stage;
- acid-base properties,
- redox properties,
- biological meaning of nitrogen oxide (II), nitrites, phosphorus, arsenic, oxygen, sulphur, halogens.

6.The questions for individual learning:

6.1. The biological role and medicals of phosphorus, arsenic, oxygen, sulfur, halogens.

7. The examples of the task:

7.1. Write the chemical reaction of the presented chemical conversion:

$P_2O_5 \rightarrow H_3PO_4 \rightarrow Ca_3(PO_4)_2 \rightarrow CaHPO_4$

The answer:

$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$

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

$Ca_3(PO_4)_2 + H_3PO_4 \rightarrow 3CaHPO_4$

8. Homework (must be performed in the laboratory notebook):

8.1. White the electronic configuration of S in the oxidation stage +4.

8.2. Write the chemical reaction of the scheme: $S \rightarrow SO_2 \rightarrow SO_3 \rightarrow Na_2SO_4$.

8.3. What are the products of the reaction: $NaI + KMnO_4 + H_2SO_4 \rightarrow$

9. The control test **contains 3 tasks:**

for instance:

9.1. Write the electronic configuration of nitrogen atom and ion in the oxidative stage +4.
The electronic formula of N atom is $1s^22s^22p^3$ and N^{+4} is $1s^22s^1$

9.2. Write the chemical equations of given chain:
$SO_2 \rightarrow SO_3 \rightarrow H_2SO_4$

The answer:

$SO_2 + O_2 \rightarrow SO_3$

$SO_3 + H_2O \rightarrow H_2SO_4$

9.3. Complete the redox reaction and fix the coefficients using the method of electronic balance:
$H_2S + KMnO_4 + HNO_3 \rightarrow$

The answer:

$5H_2S + 2KMnO_4 + 6HNO_3 \rightarrow 2Mn(NO_3)_2 + 5S + 2KNO_3 + 8H_2O$

$S^0 + 2e^- \rightarrow S^{2-}$ | 5
$Mn^{7+} + 5e^- \rightarrow Mn^{2+}$ | 2

10. The algorithm of the experiments:

10.1. The quantitative reaction on the carbonate ions.
10.2. The quantitative reaction on the sulphate ions.
10.3. The quantitative reaction on the nitrite ions.
10.4. The quantitative reaction on the tiosulphate ions.

11. The detailed explanation of the following experiments:

11.1. The qualitative reaction on the carbonate ions

In a test-tube put 2 drops of Na_2CO_3 solution and add 2 drops of $BaCl_2$ solution. After the appearance of the precipitation acetic acid must be added. Note the effect of the reaction and write the equations. Make a conclusion.

11.2. The qualitative reaction on the sulfate ions

In a test-tube put 2 drops of H_2SO_4 solution and add 2 drops of $BaCl_2$ solution. Then add 5 drops of hydrochloric acid must be added to the formed precipitation. Note the effect of the reaction and write the equations. Make a conclusion.

11.3. The qualitative reaction on the nitrite ions

In a test-tube put 2 drops of $NaNO_2$ solution and add 2 drops of acetic acid and 2 drops of KI. Note the effect of the reaction. Write the equations. Make a conclusion.

11.4. The qualitative reaction on the tiosulfate ions.

In a test-tube put 3 drops of $Na_2S_2O_3$ solution and add 2 drops of hydrochloric acid. Note the effect of the reaction. Write the equations. Make a conclusion.

12. Control test:

Sample 1

1.Write the electronic structure of sodium atom and ion.
2. Write the electronic structure of boron atom and B^{3+} ion.
3.Write the equations of the chain given below.

$$SO_2 \rightarrow SO_3 \rightarrow H_2SO_4 \rightarrow SO_2$$

4. Write the products and give the oxidation and reduction half-reactions for the following redox reactions. $H_2S + KMnO_4 + HNO_3 \rightarrow$

Sample 2

1.Write the electronic structure of lithium atom and ion.
2. Write the electronic structure of carbon atom and C^{4+} ion.
3. Write the equations of the chain given below.

$$Cl_2 \rightarrow NaClO \rightarrow NaCl \rightarrow AgCl$$

4. Write the products and give the oxidation and reduction half-reactions for the following redox reactions. $Cl_2 + Ca(OH)_2 \rightarrow$

TOPIC 3: Biogenic d- elements, chemical properties, biological role, application in medicine.

1. ***Actuality of the topic*:** tiny amount of d-elements are contained in human organism. However the role of these micro elements is significant in physiologic and patalogic processes. The nature of micro elements influences the structure and properties of enzymes. The disfunction of metabolism causes a various type of diseases.

2.General aim: is to study the properties of d-elements and its biological meaning.

3. Actual aims and abilities:

- to understand the character of energetic states of given elements;
- to be capable explaining the acid-base properties of d-elements;
- to understand the main concept of the complexes;
- to know the medicals and drugs containing d-elements.

4. Literature:

4.1. Lecture materials;

4.2. "Chemistry" 3th ed. 2001. J. Mc Murry and R. Fay; Prentice Hall, Upper Saddle River, New Jersey 07458, ISBN 0-13-087205-9;

4.3. Ebbing, D.D. and S.D. Gammon. 2002. General Chemistry. Seventh Edition. Houghton Mifflin Co., Boston, MA.

d-Elements is called the chemical elements in which the filled d-sublevel penultimate energy level. These elements I-B, II-B, III-B, IV-B, V-B, VI-B, VII-B and VIII-B groups of the Periodic Mendeleyev System.

Electronic configuration, ie distribution of the electron energy levels and sublevels for atoms and ions of d-elements can be illustrated by V and Cu:

V $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$ V^{+3} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^0$

Cu $1s^2 2s^2 2p^6 3s^2 3p^6\ 3d^{10} 4s^1$ Cu^{+2} $1s^2 2s^2 2p^6 3s^2 3p^6\ 3d^9 4s^0$

d - elements are metals. But some of them show amphoteric properties.

General characteristics of d-block elements

For first series (Sc z = 21) to (Zn z = 30)								
Sc	(z = 21)	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$4s^2$	$3d^1$
Ti	(z = 22)	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$4s^2$	$3d^2$
V	(z = 23)	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$4s^2$	$3d^3$
Cr	(z = 24)	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$4s^1$	$3d^5$
Mn	(z = 25)	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$4s^2$	$3d^5$
Fe	(z = 26)	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$4s^2$	$3d^6$
Co	(z = 27)	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$4s^2$	$3d^7$
Ni	(z = 28)	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$4s^2$	$3d^8$
Cu	(z = 29)	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$4s^1$	$3d^{10}$
Zn	(z = 30)	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$4s^2$	$3d^{10}$

Table 3.1

Variable oxidation state

Sc	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
								+1	
+2	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3		
	+4	+4	+4	+4	+4	+4	+4		
		+5		+5					
			+6	+6	+6				
				+7					

Table 3.2

Since Zn, Cr and less Fe, and their oxides and hydroxides can be reacted with acids as well as with bases.

For example: $ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2\uparrow$

In this reaction, ZnO exhibits basical properties.

When fused with sodium hydroxide ZnO appear acidic properties of zinc oxide :

$$ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O \quad (1)$$

Sodium zincate

(To derive salt sodium zincate must assume that if the zinc oxide can react with water, then it would be consistent with acid H_2ZnO_2: $ZnO + H_2O \rightarrow H_2ZnO_2$).

In aqueous solution, the complex compound is formed :

$$ZnO + 2NaOH + H_2O \rightarrow Na_2[Zn(OH)_4].$$

In Reactions 1 and 2, ZnO show amphoteric properties .

Many d-variable valency elements have, however, they form multiple oxides with different properties that correspond to a base or an acid (Table 3.3):

Degree of oxidation and connections of d-elements

Element	The degree of oxidation	Properties	Oxide	Acid	Base	Salts
Mn	+2 +4 +7	Basical Amphoteric Acidic	MnO MnO_2 Mn_2O_7	– – $HMnO_4$	$Mn(OH)_2$ $Mn(OH)_4$ –	$MnCl_2$ K_2MnO_3 $KMnO_4$
Fe	+2 +3 +6	Basical Amphoteric Acidic	FeO Fe_2O_3 –	– – –	$Fe(OH)_2$ $Fe(OH)_3$	$FeCl_2$, $FeSO_4$ $FeCl_3$, $Fe_2(SO_4)_3$ $NaFeO_2$, K_2FeO_4
Zn	+2	Amphoteric	ZnO	–	$Zn(OH)_2$	$ZnCl_2$, Na_2ZnO_2

Table 3.3

Sign " – " means that the compound does not exist or unstable. Many d-elements show redox properties, which vary depending on the degree of oxidation (Table 3.4):

Redox properties of d-elements

Element	The degree of oxidation	Oxidant or reductant
Fe	+ 2 +3 +6	reductant oxidant and reductant oxidant
Cr	+2 +3 +6	reductant reductant and oxidant strong oxidant

Mn	+2 +4 +6 +7	reductant oxidant and reductant oxidant and reductant strong oxidant

Table 3.4

Redox properties of d-elements show an example:

$$10Fe^{+2}SO_4 + 2KMn^{+7}O_4 + 8H_2SO_4 \rightarrow 2Mn^{+2}SO_4 + 5Fe_2^{+3}(SO_4)_3 + K_2SO_4 + 8H_2O$$

$$Mn^{+7} + 5e \rightarrow Mn^{+2} \quad | \; 10 \; | \; 2$$
$$2Fe^{+2} - 2e \rightarrow 2Fe^{+3} \quad | \quad | \; 5$$

$$3K_2Cr_2^{+6}O_7 + 10H_3P^{+3}O_3 \rightarrow 6Cr^{+3}PO_4 + 2H_3P^{+5}O_4 + 2K_3PO_4 + 11H_2O$$

$$2Cr^{+6} + 6e \rightarrow 2Cr^{+3} \quad | \quad | \; 1$$
$$P^{+3} - 2e \rightarrow P^{+5} \quad | \quad | \; 3$$

$$4Fe^{+2}SO_4 + O_2^0 + 8NaOH + 2H_2O \rightarrow 4Fe^{+3}(O^{-2}H)_3 + 4Na_2SO_4$$

$$Fe^{+2} - 1e \rightarrow Fe^{+3} \quad | \; 4 \; | \; 4$$
$$O_2^0 + 4e \rightarrow 2O^{-2} \quad | \quad | \; 1$$

Degree of oxidation and the basic compounds of some d-elements shown in Table 3.5

Element, degree of oxidation	Oxygen and hydrogen compounds	Acid, bases	Salt
Cr, +3 +6	Cr_2O_3 CrO_3	$Cr(OH)_3$ H_2CrO_4, $H_2Cr_2O_7$	$CrCl_3$, $Cr_2(SO_4)_3$, $NaCrO_2$ K_2CrO_4, $K_2Cr_2O_7$
Mn, +2 +7	MnO Mn_2O_7	$Mn(OH)_2$ $HMnO_4$	$MnCl_2$, $MnSO_4$ $KMnO_4$
Fe, +2 +3	FeO Fe_2O_3	$Fe(OH)_2$ $Fe(OH)_3$	$FeCl_2$, $FeSO_4$ $FeCl_3$, $Fe_2(SO_4)_3$, $NaFeO_2$
Cu, +2	CuO	$Cu(OH)_2$	$CuCl_2$, $CuSO_4$
Zn, +2	ZnO	$Zn(OH)_2$	$ZnCl_2$, $ZnSO_4$, Na_2ZnO_2

Table 3.5

Redox reactions are reactions that occur with a change in the oxidation state of the atoms making up the molecules of the reactants

The degree of oxidation is conditioned charge has atom, which is calculated on the assumption that the molecule consists of ions and the total charge of the molecule is zero.

When calculating the degree of oxidation based on the fact that the degree of oxidation of the hydrogen is always 1 (except hydrides), oxygen -2 (except peroxide), one alkali metal, alkaline earth metal +2

For example, oxidation of nitrogen in the nitrate HNO_3 acid calculated from the fact that the degree of oxidation of hydrogen +1, oxygen - 2, three oxygen atoms give -6, then:

$$X\ 1 + (-6) = 0,\ X = 5.$$

A. Basics of the theory oxidation-reduction reactions:

1) *Reduction agents* are molecules, atoms or ions that donate electrons. At the same time they are oxidized:

$$H_2^0 - 2e \rightarrow 2H^+$$
$$Al^0 - 3e \rightarrow Al^{+3}$$
$$2Cl - 2e \rightarrow Cl_2^0$$

The most common reducing agents: molecules: CO, H_2, formic aldehyde; atoms: metals, non-metals (C, S, P); negatively charged ions of non-metals: Cl^-, Br^-, I^-, S^{-2}, N^{-3}, P^{-3}, the metal ions in the lower oxidation state: Fe^{+2}, Cr^{+3}, Mn^{+2}; electric current on the cathode.

2) *Oxidizing agents* are molecules, atoms or ions, which accept electrons. At the same time they are restored:

$$Cl_2^0 + 2e \rightarrow 2Cl^-$$
$$S + 2e \rightarrow S^{-2}$$
$$Fe^{+3} + 1e \rightarrow Fe^{+2}$$

The most common oxidants molecules: O_2, O_3, $KMnO_4$, MnO_2, $K_2Cr_2O_7$, PbO_2, CrO_3, HNO_3, halogens; nonmetals in a positive oxidation state: N^{+5}, S^{+6}, Cl^+, Cl^{+3},Cl^{+5}, Cl^{+7}; metal ions in a higher oxidation state: Fe^{+3}, Cr^{+6}, Mn^{+7}, Pb^{+4}; electrical current at the anode.

3) *Oxidation* is the process of return E molecule, atom or ion. That is, when the oxidation degree of oxidation increases:

4) *Reduction* is the process of joining the electron molecule, atom or ion. I.e. when restoring the degree of oxidation degrees. Oxidation always accompanied by reduction and vice versa. The number of electrons, which gives a reducing agent, equals the number of electrons, which takes oxidant

5) Compounds which contain a degree of oxidation of the intermediate may be either oxidizing or reducing agents:

+3	+4	+3	+6
HNO_3	H_2SO_3	H_3AsO_3	K_2MnO_4

Table 3.6

B. Redox processes and periodic system.

In periods with increasing atomic number of the element, reducing properties decrease and increase oxidation, because it is easier to accept electrons to complete the energy level. For example, alkaline metals — strong reducing agents, halogens — strong oxidizing agents. In major subgroups recovery properties increase as it increases the radius of the atom and the electrons easier to split off. In the sub-group metals are only so they restorers.

Redox properties associated with the electronegativity: the more electronegative element, the stronger it's oxidizing properties (F - the most electronegative element). On the contrary, metals having a low electronegativity are reduced. Redox properties depend on the degree of oxidation: the more positive charge of the same element, the more pronounced oxidative properties:

+7	+4	+2
$KMnO_4$	MnO_2	$MnSO_4$
oxidant	oxidant and reducing agent	reducing agent

Table 3.7

C. Influence of the medium on the stroke of the redox reaction.

In general to create an acidic environment using H_2SO_4, HCl. Hydrochloric acid may not be only a conduit state but also a reducing agent. Nitric acid HNO_3, can not be only medium but also the oxidant.

2) To create an alkaline environment using alkali NaOH, KOH and Na_2CO_3.

Environmental influence on the course of the redox reaction can be illustrated by the recovery $KMnO_4$.

+7 $HMnO_4$	H^+ (+5e)	Mn^{+2} ($MnSO_4$, $MnCl_2$)	colorless solution
	H_2O (+3e)	Mn^{+4} (MnO_2)	brown
	OH^- (+1e)	Mn^{+6} (K_2MnO_4)	green solution

Table 3.8

D. Change of oxidants and reducing agents in the reaction.

1) In an acidic medium the H^+ ions and OH^- form water.

2) With an acidic medium that has metal cations (+1, +2, +3) to form salts with acidic residues.

3) Metal ions, which give the water-insoluble base in alkaline and neutral environments, corresponding to provide base ($Fe(OH)_3$, $Cu(OH)_2$).

4) The metal ions which give amphoteric hydroxides in alkaline medium yield the corresponding salts ($Na_3[Cr(OH)_6]$, $Na_2[Pb(OH)_4]$).

E. Preparation of redox equations.

1) Record the starting materials of the formula:

$FeSO_4 + KMnO_4 + H_2SO_4 \rightarrow$

2) Find an oxidant and a reducing agent, depending on the degree of oxidation:

$Fe^{+2}SO_4 + KMn^{+7}O_4 + H_2SO_4 \rightarrow$

Reducing agent oxidant

3) Write down the formula of the reaction products in accordance with the change of initial oxidant and reducing agent:

$$\overset{+2}{FeSO_4} + \overset{+7}{KMnO_4} + H_2SO_4 \rightarrow \overset{+2}{MnSO_4} + \overset{+3}{Fe_2(SO_4)_3} + K_2SO_4 + H_2O$$

4) Make up an electronic balance and pick up additional factors so that the number of electrons that gives reducing agent equal to the number of electrons that takes oxidant:

$$\begin{array}{lcll} Mn^{+7} + 5e & \rightarrow & Mn^{+2} & 2 \\ 2Fe^{+2} - 2e & \rightarrow & 2Fe^{+3} & 5 \end{array} \quad 10$$

5) Puts the coefficients in accordance with the law of conservation of mass. First (usually) give the coefficients to the elements that alter the degree of oxidation, after the reaction:

$$FeSO_4 + KMnO_4 + H_2SO_4 \rightarrow 2MnSO_4 + 5Fe_2(SO_4)_3 + K_2SO_4 + H_2O$$

Then to the reaction:

$$10FeSO_4 + 2KMnO_4 + H_2SO_4 \rightarrow 2MnSO_4 + 5Fe_2(SO_4)_3 + K_2SO_4 + H_2O$$

Further, the number of atoms counted satellites these elements.

Further, the number of hydrogen atoms:

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow 2MnSO_4 + 5Fe_2(SO_4)_3 + K_2SO_4 + H_2O$$

Correct placement of check on the number of coefficients of oxygen atoms:

O atoms 80 to 80 atoms of reaction = O after the reaction.

The final form of the equation of a redox reaction is as follows:

$$\overset{+2}{10FeSO_4} + \overset{+7}{2KMnO_4} + 8H_2SO_4 \rightarrow \overset{+2}{2MnSO_4} + \overset{+3}{5Fe_2(SO_4)_3} + K_2SO_4 + 8H_2O$$

$$\begin{array}{lcll} Mn^{+7} + 5e & \rightarrow & Mn^{+2} & 2 \\ 2Fe^{+2} - 2e & \rightarrow & 2Fe^{+3} & 5 \end{array} \quad 10$$

Coordination Complexes

Complex	Shape	Ligands	Coordination number	Name
$[Fe(H_2O)_6]^{3+}$	octahedral	water	6	hexa-aqua iron III ion
$[Fe(CN)_6]^{3-}$	octahedral	cyanide CN^-	6	hexacyano ferrate III ion
$[CuCl_4]^{3-}$	tetrahedral	chloride Cl^-	4	tetrachloro cuprate I ion
$[Cu(NH_3)_4]^{2+}$	square planar	ammonia	4	tetra-ammine copper II ion

$[Ag(NH_3)_2]^+$	linear	ammonia	2	diammine silver I ion
$Ni(CO)_4$	tetrahedral	carbon monoxide	4	tetracarbonyl nickel 0 molecule

Table 3.9

Coloured compounds

Complex ion	Oxidation state of metal	Colour	Ligand
$[Fe(H_2O)_6]^{3+}$	III	pale green	Water
$[Fe(H_2O)_6]^{2+}$	II	yellow	Water
$[Cu(H_2O)_6]^{2+}$	II	blue	Water
$[Cu(NH_3)_4]^{2+}$	II	deep blue	ammonia
$[CuCl_4]^2$	II	green	chloride ion

Table 3.10

Crystal field theory

Complex ion	Electronic configuration	No of unpaired electrons	Magnetism
$[Fe(H_2O)_6]^{3+}$	$[Ar]4s^0\ 3d^5$	5	paramagnetic
$[Cr(H_2O)_6]^{3+}$	$[Ar]4s^0\ 3d^3$	3	paramagnetic
$[Cu(H_2O)_6]^{2+}$	$[Ar]4s^0\ 3d^9$	1	paramagnetic
$[Ni(NH_3)_6]^{2+}$	$[Ar]4s^0\ 3d^9$	2	paramagnetic
$[CoCl_4]^{2-}$	$[Ar]4s^0\ 3d^7$	3	paramagnetic

Table 3.11

The biological role of D– elements

Element	***Location and role in the body***	***Herbal drugs***	***Toxic effect, antidotes***
Fe	Hemoglobin (Fe^{2+}); catalase and peroxidase ($Fe^{2+} \rightarrow Fe^{3+}$); cytochrome c ($Fe^{2+} \rightarrow Fe^{3+}$) hematopoietic processes and electron transfer	$FeCl_3 \cdot 6H_2O$ — hemostatic; iron supplements to treat iron deficiency anemia	—
Cr	Enzymes pepsin, trypsin, exchange of glucose	Chromium picolinate for diabetes	Compounds Cr^{+6} cause skin and mucous membranes
Mn	Lungs, muscles, an activator of enzymes	$KMnO_4$ — antiseptic	—

Co	Processes of hematopoiesis	Vitamin B_{12}(cyanocobalamin)	—
Ni	Pancreas; effect on carbohydrate metabolism	—	Carcinogen
Mo	Enzyme xanthine oxidase, purine metabolism	—	Excess disturbes purine metabolism — endemic gout
Cu	Liver; processes of hematopoiesis	—	Excess of copper — Wilson's disease; $CuSO_4$ — an antidote for poisoning by white phosphorus
Zn	The enzyme carbonic anhydrase, endocrine glands, the processes of reproduction.	$ZnSO_4$ (0,1-0,25%) — astringent, anti-inflammatory effects (eye drops); ZnO — antibacterial astringent (in dermatology)	—
Ag	Kidney, endocrine glands	$AgNO_3$ (lapis) — bactericidal, astringent, protargol, colloidal silver — bactericidal action	—
Hg	Kidney	$HgCl_2$ (sulema)) (1:1000) — antiseptic; Hg_2Cl_2 ((calomel) – laxative HgO(ointment) — in dermatology Hg — in thermometers	A pair of Hg and $HgCl_2$ affect the central nervous system; spilled mercury bind $FeCl_3$, S, $KMnO_4$

Table 3.12

Qualitative reaction on the D-elements

1. The qualitative detection of Iron (II) ions.
   In a test tube put 2 drops of $FeSO_4$ and add 2 drops of solution of $K_3Fe(CN)_6$
   $3FeSO_4 + 2\ K_3[Fe(CN)_6] \rightarrow Fe_3[Fe(CN)_6]_2\downarrow + 3K_2SO_4$ (turbulent blue)

2. The qualitative detection of Iron (III) ions.
   a) In a test tube put 2 drops of solution $FeCl_3$ and add 2 drops of solution of $K_4Fe(CN)_6$

   $4FeCl_3 + 3K_4[Fe(CN)_6] \rightarrow Fe_4[Fe(CN)_6]_3\downarrow + 12KCl$ (prussian blue)

   b) In a test tube add to 2 drops of solution $FeCl_3$ and add 2 drops of solution of KSCN.
   $FeCl_3 + KSCN \rightarrow Fe(SCN)_3 + 3KCl$
   blood-red

3. The qualitative detection of Copper (II) ions.
In a test tube put 2 drops of solution $CuSO_4$ and add dropwise, a solution of ammonia.

$$CuSO_4 + 4NH_4OH \rightarrow [Cu(NH_3)_4]SO_4 + 4H_2O \quad \text{(purple)}$$

4. The qualitative detection of MnO_4^- ions.
In a test tube put 2 drops of solution of $KMnO_4$, add 2 drops of solution of H_2SO_4 and dropwise of H_2O_2.

$$2KMn^{+7}O_4 + 5H_2O_2^{-1} + 3H_2SO_4 \rightarrow 2Mn^{+2}SO_4 + 5O_2^0 + K_2SO_4 + 8H_2O$$

$$Mn^{+7} + 5e \rightarrow Mn^{+2} \mid 2$$
$$2O^{-1} - 2e \rightarrow O_2 \mid 5$$

5. The main questions of the seminar:

Chromium as an example of d-elements: electronic structure, oxidation stage, acid-base properties, redox properties.

6. The questions for individual learning:

6.1. The biological role and medicals of iron, zinc, manganese, molybdenum compounds.

7. The examples of the task:

7.1.Write the equations of the given chemical conversion:

$Fe \rightarrow FeO \rightarrow FeSO_4 \rightarrow Fe(OH)_2$

Answer:

$2Fe + O_2 \rightarrow 2FeO$

$FeO + H_2SO_4 \rightarrow FeSO_4 + H_2O$

$FeSO_4 + 2NaOH \rightarrow Fe(OH)_2 + Na_2SO_4$

8. Homework (must be performed in the laboratory notebook):

8.1. Write the chemical reaction of the scheme:

$Fe_2O_3 \rightarrow Fe_2(SO_4)_3 \rightarrow NaFeO_2 \rightarrow FeCl_3$

8.2. Finish the redox reaction: $K_2Cr_2O_7 + NaCl + H_2SO_4 \rightarrow$

***9. The control test* contains 3 tests:**

for instance:

9.1. The electronic configuration of iron (II)

9.2. Write the equations of the chemical conversion:

$Cr_2O_3 \rightarrow Cr_2(SO_4)_3 \rightarrow Cr(OH)_3$

The answer: $Cr_2O_3 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + H_2O$

$Cr_2(SO_4)_3 + 6NaOH \rightarrow 2Cr(OH)_3 + 3Na_2SO_4$

9.3. Write the reaction products and the equation coefficients using the electronic balance of the reaction:

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O$$

$$Fe^{3+} + 1e^- \rightarrow Fe^{2+} \mid 5$$
$$Mn^{7+} + 5e^- \rightarrow Mn^{2+} \mid 1$$

10. The algorithm of the experiments:

10.1. The quantitative reaction on the manganate- ions.

10.2. The quantitative reaction on the iron (II) ions.

10.3. The quantitative reaction on the iron (III) ions.

10.4. The quantitative reaction on the copper (II) ions.

11. The detailed explanation of the following experiments:

11.1. The qualitative reaction on the manganate ions

In a test-tube put 2 drops of $KMnO_4$ solution, then add 2 drops of H_2SO_4 solution with the following dropwise adding of H_2O_2. Note the effect of the reaction and write the equations. Make a conclusion.

11.2. The qualitative reaction on the iron (II) ions

In a test-tube put 2 drops of $FeSO_4$ solution and 2 drops of $K_3[Fe(CN)_6]$. Note the effect of the reaction and write the equations. Make a conclusion.

11.3. The qualitative reaction on the iron (III) ions

a) In a test-tube put 2 drops of $FeCl_3$ solution and 2 drops of $K_4[Fe(CN)_6]$. Note the effect of the reaction and write the equations. Make a conclusion.

b) In the test-tube put 2 drops of $FeCl_3$ solution and 2 drops of KSCN. Note the effect of the reaction and write the equations. Make a conclusion.

11.4. The qualitative reaction on the copper (II) ions

a) In a test-tube put 2 drops of $CuSO_4$ solution and 2 drops of ammonia. Note the effect of the reaction and write the equations.

12. Control test:

Sample 1

1. Write the electronic structure of zinc atom and Zn^{2+}ion.
2. Write the equations of the chain given below:

$$Fe\ Cl_3 \rightarrow Fe\ (OH)_3 \rightarrow KFeO_2 \rightarrow Fe_2\ (SO_4)_3$$

3. Write the products and give the oxidation and reduction half-reactions for the following redox reactions: $Cr_2(SO_4)_3 + KMnO_4 + KOH \rightarrow$

Sample 2

1. Write the electronic structure of copper atom and Cu^{2+}ion.
2. Write the equations of the chain given below:

$$Cr \rightarrow Cr\ (NO_3)_3 \rightarrow Na_2CrO_4 \rightarrow \rightarrow BaCrO_4$$

3. Write the products and give the oxidation and reduction half-reactions for the following redox reactions: $FeSO_4 + KMnO_4 + H_2SO_4 \rightarrow$

TOPIC 4 : The formation of complexes in biological systems.

***1. Actuality of the topic*:** many chemical substances are identified in quantitive and qualitative analysis conversting to the complexes. The complexes have physiological significance in the processes of breathing, photosynthesis, biological oxidation, and enzymatic catalysis.

2. General aim: to explain the physiological action of the complexes and their application as medicals.

3. Actual aims and abilities:

- to know the structure and nomenclature of complexes;
- to be able to write the instability constant of complexes.

4. Literature:

4.1. Lecture materials;

4.2. “Chemistry” 3th ed. 2001. J. Mc Murry and R. Fay; Prentice Hall, Upper Saddle River, New Jersey 07458, ISBN 0-13-087205-9;
4.3. Ebbing, D.D. and S.D. Gammon. 2002. General Chemistry. Seventh Edition. Houghton Mifflin Co., Boston, MA.

Complex called the compound in the crystal lattice which are complicated and complex ions which pass into solution as a result of dissociation.

Swiss chemist Alfred Werner developed a theory in 1883 that explains the structure of complex compounds.

Werner’s coordination theory

a) *the central atom* or complexing agent it is positively charged metal ion (less nonmetal);

b*) the ligand*. It is electrically neutral or negatively infected ions and are located (coordinated) around the central atom .

Central atom and ligands comprise the *inner coordination sphere*;

c) *an outer coordination sphere* constitute a positive or negatively charged ions that are on more distance from the central ion or associated therewith;

d) *the coordination number* indicates the number of ligands. As a rule a coordination number equal to twice the valence of the metal.

Table 4.1 shows examples of the structure of complex compounds.

The composition and structure of complex compounds

Component parts	Cationic complex $[Cu(NH_3)_4]SO_3$	Anionic complex $Na_2[Pt(Br)_6]$
Complexing agent	Cu^{2+}	Pt^{4+}
Ligand	NH_3	Br^-
The inner coordination sphere	$Cu(NH_3)_4$	$Pt(Br)_6$
An outer coordination sphere	SO_3^{-2}	Na^+
Coordination number	4	6
Charge of the complex ion	$[Cu(NH_3)_4]^{2+}$	$[Pt(Br)_6]^{2-}$

Table 4.1

Preparation of complex compounds

Complex compounds prepared by such reactions:

1) Connection reactions:

$$HgI_2 + 2KI \rightarrow K_2[HgI_4]$$

2) Substitution reactions:

$$[Cu(H_2O)_4]\,SO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]\,SO_4 + 4H_2O$$

3) Exchange reactions:

$$2\,ZnCl_2 + K_4[Fe(CN)_6] \rightarrow Zn_2[Fe(CN)_6] + 4KCl$$

4) Redox reactions:

$$2Al + 6KOH + 6H_2O \rightarrow K_3[Al(OH)_6] + 3H_2\uparrow$$

Classification of complex compounds

1) By the charge of the complex ion:

Cationic	Anionic	Neutral
$[Ag(NH_3)_2]^+Cl$	$Na[Al(OH)_4]^-$	$Fe(CO)_5$
$[Cu(NH_3)_4]^{2+}SO_4$	$H_2[Pt(Cl)_6]^{2-}$	$[Pt(NH_3)_2Cl_2]$
$[Co(NH_3)_4]^{3+}Cl^3$	$K_3[Fe(CN)_6]^{3-}$	$[Cr(H_2O)_3F_3]$

Table 4.2

2) By the nature of the ligand:

Complex name	Ligand, its name	Example of connection
Ammines	NH_3 — ammine	$[Zn(NH_3)_4]SO_4$
Aquacomplexes	H_2O — aqua	$[Al(H_2O)_6]Cl_3$
Hydroxocomplexes	OH — hydroxo	$Na_2[Zn(OH)_4]$
Acidocomplexes	Cl^- — chlorine CN^- — cyanide NO_2^- — nitrite CO_3^{2-} — carbonate SCN^- — thiocyanide SO_4^{2-} — sulphate	$K_3[AlCl_6]$ $K_4[Fe(CN)_6]$ $Na_3[Co(NO_2)_6]$ $[Co(NH_3)_4CO_3]$ $(NH_4)_2[Hg(SCN)_4]$ $K_2[Be(SO_4)_2]$

Table 4.3

There are also *intracomplex* compounds — chelates polynuclear complexes, clathrates, fullerenes.

Complex compounds denticity

One characteristic is their denticity ligands.

Denticity — is the number of seats occupied by ligands in the inner coordination sphere of the complex.

Complex compounds denticity

Denticity	Ligands
monodentate	NH_3, H_2O, OH^-, Cl^-, Br^-, F^-, NO_2^-, SCN^-, CN^-
bidentate	CO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$, $C_2O_4^{2-}$
polydentate	Aminopolycarboxylic acid (complexones), proteins

Table 4.4

Nomenclature of complex compounds:

Complex compounds are reffered by these rules:

1) the number of ligands is called a mono, di, three, tetra, penta, hexa,
2) ligands are referred to by their nomenclature;
3) the charge of the central atom is determined by the formula:

$\overset{x}{[Cu}\overset{0}{(NH_3)_4]}SO_4$ $\quad$ $\overset{+1}{K_4}\overset{x}{[Fe}\overset{-}{(CN)_6]}$

$X + 4 \cdot 0 + (-2) = 0;\ X = +2;$ $\quad$ $1 \cdot 4 + X + 6 \cdot (-1) = 0;\ X = 6;$

4) cation referred to in the nominative case;
5) in the anionic complex central atom has the ending — am;
6) the name of complex ion is start since the coordination number.

Examples of the nomenclature are complex compounds in ***Table 4.5***

Nomenclature of complex compounds		
Cationic complexes	***Anionic complexes***	***Neutral complexes***
$[Zn(NH_3)_4]SO_4$ tetraaminezinc (II) sulfate	$K_4[Fe(CN)_6]$ potassiumhexacyanoferrate (II)	$[Pt(NH_3)_2Cl_2]$ diamminedichloroplatinum (II)
$[Cr(H_2O)_6]Cl_3$ hexaaquachromium (III) chloride	$Na_2[Zn(OH)_4]$ sodiumtetrahydroxozincate (II)	$[Co(NH_3)_3(NO_2)_3]$ triamminetrinitritocobalt (III)
$[Pt(NH_3)_4Cl_2]Cl_2$ tetraaminedichloroplatinum (IV) chloride	$K_2[CoCl_4]$ potassiumtetrachlorocobaltate (II)	$[Cr(H_2O)_3F_3]$ triaquatrifluorochromium (III)

Table 4.5

Nature of chemical bonding in complex compounds

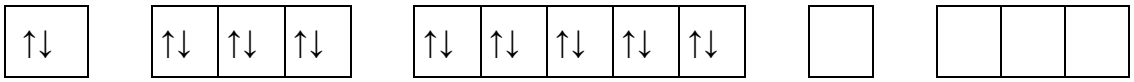
Structure physico-chemical and biological properties of complex compounds depend on the nature of chemical bonds in them. Currently, the nature of chemical bonds in complex compounds such theories explain:

1) the method of valence bonds;
2) the crystal field theory;
3) the method of molecular orbitals.

Let us consider the simpler *method of valence bonds*.

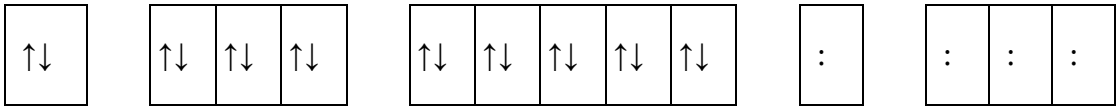
Under this method, the connection between the central atom and the ligand is formed by the donor–acceptor mechanism. The donor is a ligand that donates a lone electron pair, acceptor is central atom, which has free orbitals.

For example, during the formation of the ion $[Zn(NH_3)_4]^{2+}$ is a donor molecule of ammonia, in which the nitrogen atom has an unshared electron pair. Acceptor is a zinc atom, which has free d - orbitals. Electron-graphic formula of the third and fourth energy levels of zinc ions Zn^{+2} has the form:



3s 3p 3d 4s 4p

Lone pairs of the nitrogen atoms of four ammonia molecules located on the ligand-free 4s-and 4p-orbitals of the zinc ion:



3s 3p 3d 4s 4p

Spatial structure of complex compounds

Identical Ligands symmetrically arranged in the space around the central atom.

The spatial configuration of complex compounds

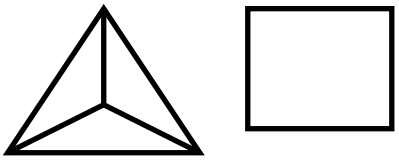
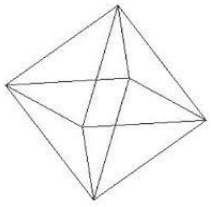
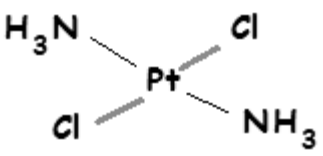
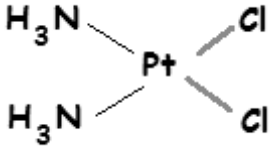
Complex compound	Coordination number	Configuration
$[Ag(NH_3)_2]Cl$	2	line
$[Cu(NH_3)_4]SO_4$	4	tetrahedral 
$H_2[Pt(Cl)_6]$	6	octahedron 

Table 4.6

Isomerism of complex compounds

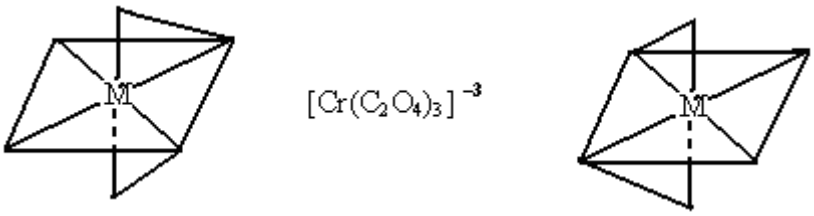
Geometrical isomers due to different placement of dissimilar ligands in the inner sphere:





cys-isomer ***trans-isomer***

Optical isomers due to the presence of incompatible mirror images:



Hydrate isomerism due to different arrangement of water molecules in the inner and outer areas:

$$[Cr(H_2O)_6]Cl_3 \leftrightarrow [CrCl_2(H_2O)_4]Cl \cdot 2H_2O \leftrightarrow [Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$$

Ionization isomerism due to different distribution of acidic residues between the inner and outer spheres:

$$[CoBr(NH_3)_5]SO_4 \leftrightarrow [CoSO_4(NH_3)_5]Br$$

Structural isomerism or communication due to different method of connecting atoms in the ligand:

$$[Co(NH_3)_5NO_2]^{2+} \leftrightarrow [Co(NH_3)_5ONO]^{2+}$$

Properties of complex compounds

1) *Dissociation* of complex compounds.

Complex compounds are strong electrolytes. In aqueous solution, they readily dissociate to a complex ion and the outer sphere. This is called the primary dissociation. Examples of primary dissociation of complexes are given in ***Table 4.7***

Dissociation of the complex compounds

Types of complex connections	Dissociation equation
Cationic complex	$[Ag(NH_3)_2]Cl \leftrightarrow [Ag(NH_3)_2]^+ + Cl^-$ $[Cr(H_2O)_6]Cl_3 \leftrightarrow [Cr(H_2O)_6]^{3+} + 3Cl^-$
Anionic complex	$K_4[Fe(CN)_6] \leftrightarrow 4K^+ + [Fe(CN)_6]^{4-}$ $Na_2[Zn(OH)_4] \leftrightarrow 2Na^+ + [Zn(OH)_4]^{2+}$

Table 4.7

The formed complex ion may also dissociate, albeit weaker. This *secondary* dissociation, which is stepwise:

$$[Ag(NH_3)_2]^+ \leftrightarrow Ag(NH_3)^+ + NH_3 \quad \text{I step}$$
$$Ag(NH_3)^+ \leftrightarrow Ag^+ + NH_3 \quad \text{II step}$$

We can write the equation in a secondary dissociation step of:

$$[Ag(NH_3)_2]^+ \leftrightarrow Ag^+ + 2NH_3.$$

2) *Stability* of complex compounds.

Each stage is characterized by the dissociation of the complex ion *dissociation constant.*

Overall dissociation constant of the complex ion can be written as:

$$Cd = \frac{[Ag^+] \bullet [NH_3]^2}{[Ag(NH_3)_2]^+}$$

Complex ion is the more stable, less than its Ci or *instability constant*: Cd = Ci.

The reciprocal value is called *resistance constant* Cr = 1 / Ci. The more constant resistance, the more stable complex.

The biological significance of complex compounds

In humans, drugs of many d-elements form complex compounds. Examples of such compounds are shown in ***Table 4.8***

Biologically active complexes

Metal	Biological system
Fe	hemoglobin; cytochromes; catalase; peroxidase
Zn	carbonic anhydrase
Cu	cytochrome
Mn	carboxylase
Mg	chlorophyll
Hg	$K_2[HgI_4]$ — Lugol's solution
Co	Vitamin B12 (cyanocobalamine)

Table 4.8

Metabolism in the human body supported the complexation process, metal-ligand homeostasis violation, that over can bring to the different diseases, for example, iron-deficient anemia. Many complex connections are used as medicinal substances. Connections of iron are used for treatment of iron — deficient anemia's, preparations of zinc — in dermatology, platinum — like antitumor preparations, chelating (complexion agents) are used as antioxidants and for fastening of heavy metals at poisoning (lead, mercury, cadmium of and other).

The biological significance of complex compounds

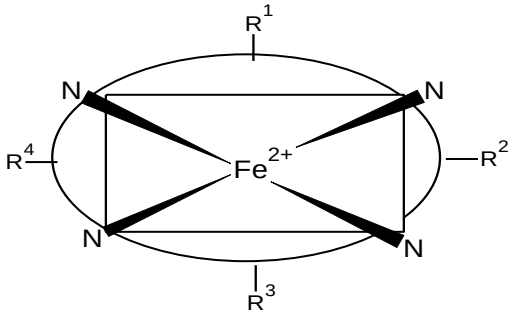
In humans, drugs of many d- elements form complex compounds:

Metabolism in the human body supported the complication process, namely metal-ligand homeostasis, the violation of which can lead to various diseases, such as iron deficiency anemia.

Many complex compounds are used as therapeutic agents. Iron compounds used for the treatment of iron deficiency anemia, zinc supplements in dermatology, platinum like anticancer drugs, chelating (complexion agents) are used as antioxidants and to bind poisoning with heavy metals (lead, mercury, cadmium, etc.).

Most of the chemical elements contained in the organs and tissues have complex compound with proteins and other biopolymers. This proteins, amino acids, nucleic acids, peptides, fatty acids, carbohydrates, vitamins, hormones, enzymes.

Complexing ability of bioligands can be explained by the presence in their molecules of several functional groups -COOH, NH_2 — primary amines, secondary, tertiary are able to coordinate metal ions. Examples are porfinic system. This tetradentate macromolecules. Schematically looks like this: (***Picture 4.1***)



Nitrogen donor atoms are located on square corners, tightly coordinated in space. Therefore porfinic form stable complex compounds with the metal. Thus, as the central atom can act Mg^{2+}, Fe^{2+} forms an active center of hemoglobin. Protein molecule of 400 polypeptide chains forms globin. Each connected globin a gem.

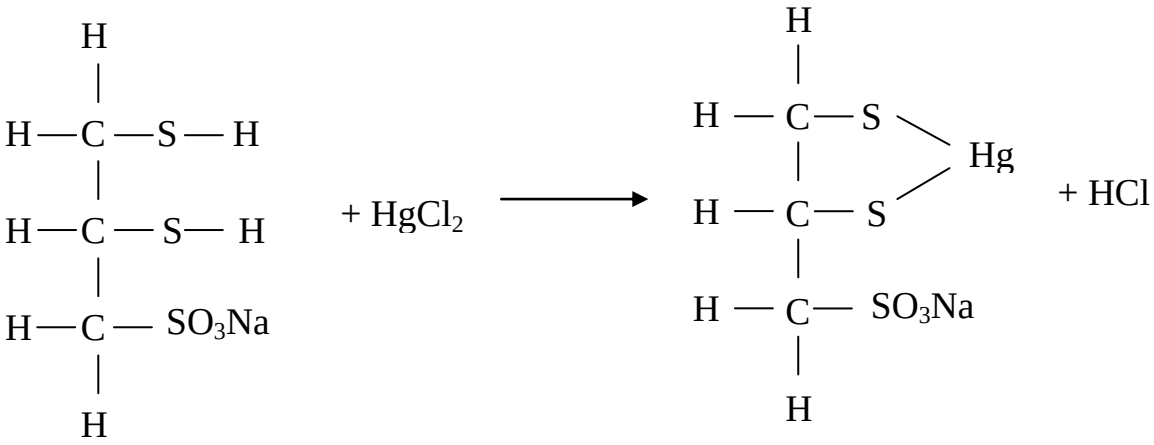
In six iron atoms coordinating ties. 4 keeps it in plane porfinic nucleus, and 2 are directed perpendicular to this plane. One of them is communicat with oxygen. 10 000 atoms form a hemoglobin $C_{3082}O_{870}N_{760}S_8Fe_4$ which means several similar carbon chains connect to donor atoms

of nitrogen in a closed cycle. Different R radicals known as BIOCOMPLEXES of other metals (Cu, Al, Si, Mn)

We can use some of them in the medical practice as drugs.

Feramid **—** a complex of iron chloride with nicotinic acid amides $[Fe(C_6H_5CONH_2)Cl_2]$

Cobalt porfin complex is part of B_{12}, which plays an important role in the development and formation of red blood cells, its deficiency leads to pernicious anemia. Metal-gem properties depend on the occurance of toxic substances such as CO (carbon monoxide) and HCN - cyanides, salts of strong acids, when inhaled CO forms. Metal complex compounds are carbonyl hemoglobin HbCO, stability constants are 200 times more than HbO_2. So even a small amount of CO & quot; significantly share deoxyhemoglobin. As a result, access of oxygen to organs decreases, manifesting signs of hypoxia. A similar mechanism of action of cyanide, but their toxic effect is more higher. High toxicity attributed high resistance connection Fe = CN^-, which causes higher resistance cyanide hemoglobin. Toxic effects of copper compounds from the fact that copper ions interact with tiols -SH groups and amino $–NH_2$ (blocking) proteins. This can be caused by bioclastic chelate type, resulting in proteins becoming insoluble, losing enzymatic activity, disrupting vital functions. Toxic effects of silver compounds from the fact that silver ions interact with toxic sulphur and nitrogen-containing proteins (nucleic acids). Similarly, there are compounds of gold. Toxicity increases with atomic number in series. Property Metal ions form strong ties with sulphurligands used in the selection of proteins, which are used in poisoning. Such drugs are called **—** antidote.



Chelating agent used as antidotes. Hg, Cd which are complex toxines in the body and are destroyed easily. Metalic-ligands homeostasis is a form of general homeostatic system.

The body has a clear self-regulatory systems homeostasis (elements in compounds with biooligands). Their level in the blood, tissue homeostasis is supported by regulatory mechanisms: absorption processes, separation of water, electrolytes and non-electrolytes, constant stability of chelates. Poor absorption of heavy metals is a consequence of the formation of slightly soluble complexes. Often abnormal digestive processes or change causes a violation of homeostasis.

There are many ways of metaloligands regulation of homeostasis. So for Cu, Co, Fe, Zn the basic way is to change the level of absorption of cadmium and iodine – a selection from the urine of metal complexes. Harmful substances excreted from the body through bioligand that connects, tie them into complexes (helatotherapia). Many chemical elements with bioligand positively affect immunogenesis (protective reaction), increases the formation of antitoxins.

According to Yatsymirskiy's quote; complexing agents are an organism's life.

Complexation in biological systems

The electronic configuration of the complexes gives them some important properties:

Colour

	Fe(II)	**Fe(III)**	**Co(II)**	**Cu(II)**	**Al(III)**	**Cr(III)**
Hydrated ion	$[Fe(H_2O)_6]^{2+}$ pale green soln	$[Fe(H_2O)_6]^{3+}$ yellow/brown soln	$[Co(H_2O)_6]^{2+}$ pink soln	$[Cu(H_2O)_6]^{2+}$ blue soln	$[Al(H_2O)_6]^{3+}$ colourless soln	$[Cr(H_2O)_6]^{3+}$ green soln
OH^- little	$[Fe(H_2O)_4(OH)_2]$ dark green ppt	$[Fe(H_2O)_3(OH)_3]$ brown ppt	$[Co(H_2O)_4(OH)_2]$ blue/green ppt	$[Cu(H_2O)_4(OH)_2]$ blue ppt	$[Al(H_2O)_3(OH)_3]$ white ppt	$[Cr(H_2O)_3(OH)_3]$ green ppt
OH^- excess	$[Fe(H_2O)_4(OH)_2]$ dark green ppt	$[Fe(H_2O)_3(OH)_3]$ brown ppt	$[Co(H_2O)_4(OH)_2]$ blue/green ppt	$[Cu(H_2O)_4(OH)_2]$ blue ppt	$[Al(OH)_4]^-$ colourless soln	$[Cr(OH)_3]^{3-}$ green soln
NH_3 little	$[Fe(H_2O)_4(OH)_2]$ dark green ppt	$[Fe(H_2O)_3(OH)_3]$ brown ppt	$[Co(H_2O)_4(OH)_2]$ blue/green ppt	$[Cu(H_2O)_4(OH)_2]$ blue ppt	$[Al(H_2O)_3(OH)_3]$ white ppt	$[Cr(H_2O)_3(OH)_3]$ green ppt
NH_3 excess	$[Fe(H_2O)_4(OH)_2]$ dark green ppt	$[Fe(H_2O)_3(OH)_3]$ brown ppt	$[Co(NH_3)_6]^{2+}$ straw coloured soln	$[Cu(NH_3)_4(H_2O)_2]^{2+}$ deep blue soln	$[Al(H_2O)_3(OH)_3]$ white ppt	$[Cr(NH_3]_6]^{3+}$ green soln
CO_3^{2-}	$FeCO_3$ dark green ppt	$[Fe(H_2O)_3(OH)_3]$ brown ppt + bubbles	$CoCO_3$ blue/green ppt	$CuCO_3$ turquoise ppt	$[Al(H_2O)_3(OH)_3]$ white ppt + bubbles	$[Cr(H_2O)_3(OH)_3]$ green ppt + bubbles

Table 4.9

Task for individual learning:

1. Write electronic structure:
   s-elements: Na, K, Ca, Mg, and their ions Na^{+1}, K^{+1}, Ca^{+2}, Mg^{+2}.
2. Write electronic Structure:
   p-elements: Al, N, O, S, F, Cl, Br and their ions Al^{+3}, N^{+3}, O^{-2}, S^{+4}, F^{-1}, Cl^{-1}, Br^{-1}.
3. Write electronic Structure:
   d-elements: Cr, Mn, Fe, Cu, Zn ions and their ions Cr^{+3}, Mn^{+2}, Fe^{+3}, Cu^{+2}, Zn^{+2}.
4. Write amphoteric properties of oxides and hydroxides of Al^{+3}, Pb^{+2}, Sn^{+2}, As^{+3}, Zn^{+2}, Cr^{+3}, Fe^{+3}, Co^{+3}.
5. Write a few examples equations of their interaction with acids and bases.
6. Write a few examples of oxidation-reduction properties of elements.
7. Complete the reactions and find the coefficients by using the electronical balance method:
   $KMnO_4 + H_2S + H_2SO_4 \rightarrow MnSO_4 + S + \ldots...$
   $KMnO_4 + CaS + H_2SO_4 \rightarrow MnSO_4 + S + \ldots...$
   $KMnO_4 + KNO_2 + H_2SO_4 \rightarrow MnSO_4 + KNO_3 + \ldots..$
   $KMnO_4 + KNO_2 + KOH \rightarrow K_2MnO_4 + KNO_3 + \ldots..$
   $KMnO_4 + FeSO_4 + H_2SO_4 \rightarrow MnSO_4 + Fe_2(SO_4)_3 + \ldots...$
   $KMnO_4 + HCl \rightarrow MnCl_2 + Cl_2 + \ldots...$
   $KMnO_4 + Na_2SO_3 + H_2SO_4 \rightarrow MnSO_4 + Na_2SO_4 + \ldots..$
   $KMnO_4 + H_3AsO_3 + H_2SO_4 \rightarrow MnSO_4 + H_3AsO_4 + \ldots...$
   $K_2Cr_2O_7 + KI + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + I_2 + \ldots....$
   $K_2Cr_2O_7 + HCl \rightarrow CrCl_3 + Cl_2 + \ldots....$
   $K_2Cr_2O_7 + FeSO_4 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + Fe_2(SO_4)_3 + \ldots...$
   $K_2Cr_2O_7 + H_3PO_3 \rightarrow CrPO_4 + H_3PO_4 + ...$
   $K_2Cr_2O_7 + H_2S + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + S + \ldots....$
   $K_2Cr_2O_7 + Na_2SO_3 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + Na_2SO_4 + \ldots...$
   $K_2Cr_2O_7 + NaNO_2 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + NaNO_3 + \ldots..$
   $KI + PbO_2 + HNO_3 \rightarrow Pb(NO_3)_2 + I_2 + \ldots..$
8. The biological role of elements and their compounds (as found in the human body, an example of their function and use in biochemical processes, drugs, toxicity, disposal): Na, K, Ca, Ba, Al, N,

P, As, Fe, Co, Pb, Hg, I_2, F_2.

9. S-element are:
   a) elements filled at the outer s-sublevel
   b) main groups
   c) small periods.
10. Which of the groups below contains just s-elements:
   a) Li, Be, B, C;
   b) H, P, O, Al;
   c) Na, Ca, Rb, Sr.
11. P-elements could be described as elements with:
   a) sub-side
   b) long periods
   c) which is filled at the outer p-sublevel
12. Which of the groups below contain just p-elements:
   a) Li, Fe, B, C;
   b) N, P, O, Al;
   c) K, N, Rb, Sr.
13. D-elements are elements:
   a) which are filled with penultimate d-sub;
   b) main groups
   c) small periods
14. Which of the groups below have only d-elements:
   a) Cr, Fe, B, C;
   b) N, P, Cl, Co;
   c) Fe, Mn, Ni, Cr.
15. Complex compounds. Werner Coordination Theory: the central atom (complexing), ligand, coordination number, the inner sphere, outer sphere, nomenclature, classification by natural ligands. Examples of complex compounds of Fe, Co, Zn, Mg in biological systems.

5. The main questions of the practical lesson:

5.1. What are the complexes?

5.2. The basic rules of Werner theory (central atom, ligands, coordination number exterior sphere).

5.3. Classification of the complexes:
- by charge of complex ion;
- by nature of ligands;
- by chelates;

5.4. Dissociation of complexes,the constant instability of complexes.

5.5. Biological meaning of complex irons-, cobalt-, zinc- containing biocomplexes; complexions.

6. The questions for individual learning:

6.1. Isomerization of complexes (geometric, hydrated).

7. The examples of the task:

7.1. How can the compound $[Ag(NH_3)_2]OH$ be named?

The answer: diamminesilver (I) hydroxide

7.2. What is the charge of the central ion in the molecule $Na[Al(OH)_4]$?

The answer:

The charge of sodium is +1, the charge of hydroxide groups is -1, the charge of aluminum ion is X (unknown).

$(+1) + 4(-1) + X = 0$

$X = +3$

7.3. What is the charge of complex ion in the molecule $[Co(NH_3)_5CI]CI_2$:
The answer:
The charge of chloride ion in the exterior sphere is -1, the charge of complex ion is +2.

7.4. Write the dissociation of complex compound $[Co(NH_3)_5CI]CI_2$:
The answer:
$[Co(NH_3)_5CI]CI_2 \leftrightarrow [Co(NH_3)_5CI]^{2+} + 2CI^-$

7.5. Write the instability constant of $[Co(NH_3)_5Br]SO_4$:
The answer:
$[Co(NH_3)_5Br]SO_4 \leftrightarrow [Co(NH_3)_5Br]^{2+} + SO_4^{2-}$

$$K_{instab} = \frac{[Co(NH_3)_5Br] \cdot [SO_4]}{[Co(NH_3)_5Br]SO_4}$$

8. Homework (must be done performed in the laboratory notebook):
8.1. How do you call the substances?
$[AI(H_2O)_6]CI_3$;
$Na_3[Co(NO_2)_6]$;
$K_2[HgI_4]$.

8.2 What is the charge of complex ion and central ion in given compounds?
$Na_3[Cr(OH)_4SO_4]$;
$[Pt(NH_3)_4CI_2]CI_2$.

8.3. Write the equation of K_{instab} of complex ion $[Fe(CN)_6]^{4-}$

***9. The control test* contains 5 tests:**
for instance:
9.1. If given the complex of copper $[Cu(NH_3)_4]SO_4$:
How is it named?
What is the charge of complex ion?
What is the oxidation stage of metal ion?
What is the coordination number?
How does the dissociation equation look like? (write it)

9.2. If given the complex of $Fe_4[Fe(CN)_6]_3$:
How is it named?
What is the charge of complex ion?
What is the charge of central ion?
What is coordination number?
How does the dissociation equation look like? (write it)

10. The algorithm of the experiments:
10.1. Formation of sodiumaluminate.
10.2. Instability of complex ions.
10.3. Formation of potassiumtriiodide.

11. The detailed explanation of the following experiments:
<u>11.1. Formation of sodiumaluminate.</u>
Put 1 drop of $AlCl_3$ solution in a test-tube, then add 1 drop of NaOH solution until precipitation

occurs. Then the excess of NaOH must be added to dissolve the precipitation. Note the effect of the reaction and write the equations. Make a conclusion.

11.2. Instability of complex ions.
Put 2 drops of $CoCl_2$ solution in the test-tube and 3 drops of concentrated NH_4SCN solution until the blue color appears. Then add water and the color is changed. Note the effect of the reaction and write the equations. Make a conclusion.

11.3. Formation of potassiumtriiodide
In a test-tube put 1-2 crystals of I_2 and add 3 ml of H_2O. Then add the concentrated solution of KI until dissolving of the crystals(by drops). Note the effect of the reaction and write the equations. Make a conclusion.

12. Control test:

Sample 1

I) How can the compound $K_4[Fe(CN)_6]$ be called?
What is the charge of the central ion?
What is the charge of complex ion?
What is the coordination number?
Write the dissociation of the given complex.
II) How can the compound $[Cu(NH_3)_4]SO_4$ be called?
What is the charge of the central ion?
What is the charge of complex ion?
What is the coordination number?
Write the dissociation of the given complex.

Sample 2

I) How can the compound $K_2[CoCl_4]$ be called?
What is the charge of the central ion?
What is the charge of complex ion?
What is the coordination number?
Write the dissociation of the given complex.
II) How can the compound $[Ni(NH_3)_6]SO_4$ can be called?
What is the charge of the central ion?
What is the charge of complex ion?
What is the coordination number?
Write the dissociation of the given complex.

TOPIC 5: Preparation of the solutions and calculation of their concentrations.

1. Actuality of the topic: Preparation of the solution with certain concentration is necessary for following studying of biochemistry, pharmacy, hygiene and for interpretation of laboratory analysis data as well as for calculation of the medical dose.

2. General aim: *is* to learn the different ways of concentration expression and relationship between them.

3. Actual aims and abilities:
- to be capable of calculating the mass of the solid substance for preparing the solution;

- to have information about using chemical apparatus for soluted preparation.

4. Literature:

4.1. Lecture materials;

4.2. “Chemistry” 3th ed. 2001. J. Mc Murry and R. Fay; Prentice Hall, Upper Saddle River, New Jersey 07458, ISBN 0-13-087205-9;

4.3. Ebbing, D.D. and S.D. Gammon. 2002. General Chemistry. Seventh Edition. Houghton Mifflin Co., Boston, MA.

Solutions play an important role in living organisms and inanimate nature.

Mortar is homogeneous system consisting of two or more components and products of their interaction.

One component of the solution is a solvent, the amount of which in solution is greater than the solute. The most common and universal solvent is water, so we will consider only aqueous solutions.

The role of water in the human body:

Water plays an important role in living organisms. The human body contains in average up to 70 % water.

The role of water in the human body:

1) inorganic solvent (ions and molecules), organic compounds (low-molecular substances - carboxylic acids and their salts, amino acids, monosaccharides, etc., proteins, polysaccharides, nucleic acids), it is a medium for the colloidal particles and coarse particles;

2) as a highly polar substance causes the dissociation of electrolytes;

3) in an aqueous medium are the hydrolysis reaction, hydration, redox reaction;

4) participates in the biosynthesis, catalysis, osmosis, swelling;

5) carries nutrients and displays products of metabolism;

6) participate in thermoregulation (in the synthesis of 1 mol of water allocated 57 kcal);

a) high specific heat capacity (the amount of heat required to raise the temperature of the body from about 14.5 to about 15.5) prevents overheating of the body;

b) high specific heat of evaporation (the amount of heat required to evaporate water 1ml) provides a constant body temperature through evaporation from the surface of its body;

c) high thermal conductivity (after metals) provides heat removal from the deep parts of the body;

7) daily water demand of 2.5 – 3l;

8) without water person can live 5-6 days;

9) loss of 1-1.5 liters of water causes thirst; the loss of 6-8 % of water disturbes metabolism; slows redox processes, increases blood viscosity, increases body temperature, breathing quickens; the loss of 10 % water is an irreversible processes that lead to the death of the organism.

Water is distributed unevenly in organs and tissues of the human body that can be seen from Table 5.1.

The water content in specific organs of a living body. **Table 5.1**

Organs and tissues	Water content %
cerebral cortex	83,3
connective tissue	80
kidneys	82-83
leather	72
blood	79,3
spinal cord	69,7
fatty tissue	29
skeleton	22
tooth tissue	0,2

An important indicator is the *inflexibility* of water, which is caused by the presence of hydrocarbons, sulphates and chlorides of calcium and magnesium. Hard water slows the digestive process by reducing the production of gastric juice, by drinking hard water calcium salts are deposited in the blood vessels and joints. When sterilizing medical instruments salt is deposited on them. Hard water is incompatible with certain drugs, such as sulphonamides.

Classification of solutions:

1) the state of aggregation: gaseous (air), liquid (solutions gases, liquids, and solids in a liquid medium), solid (alloys);

2) concentration of the solute (dilute and concentrated);

3) ability to dissolve substances (unsaturated, saturated, supersaturated);

4) size of particles of the solute (true — the particle size $10^{-10} – 10^{-11}$ m colloid — particle size of $10^{-7} – 10^{-9}$m, coarse - particle size of $10^{-4} – 10^{-6}$m).

The mechanism of the dissolution process:

Dissolution is the physico- chemical process, and explained by the interaction of the molecules of the solute and solvent.

Dissolution occurs in two stages:

a) at the first stage water dipoles suitable polar groups substance to crystal lattice, the process of hydration of ions. Hydration energy of the ions is greater than the energy of the crystal lattice, so the intermolecular bonds weakens the substance, and then broken and hydrated molecules or ions pass into the solvent. This step is an exothermic process.

b) in the second step there is diffusion of the particles in the volume of the hydrated solvent.

The general rule ability to dissolve substances can be formulated as follows: *a like dissolves in similar* (polar substances are soluble in polar solvents and nonpolar — nonpolar).

Education solutions is a spontaneous process that goes with increasing molecular motion not ordered substance, ie with an increase in entropy — $\Delta S>0$ and a decrease in the Gibbs energy $\Delta G <0$.

The solubility of gases, liquids and solids.

A. Solubility of gases occurs as a result of van der Waals forces (nitrogen, oxygen in water) or chemical interaction (HCl, CO_2, NH_3 in water). Solubility depends on the nature of the gas and the solvent gas, pressure, temperature, presence of electrolytes.

Influence of the *nature* of the solvent gas and subject to the general rule: polar gases dissolve in polar solvents (HCl, NH_3 in water, which also interact with it); non-polar solvents in non-polar gases (N_2 hexane, acetone O_2).

Henry Dalton's rule describes the dependence of the solubility of gas pressure:

at a constant temperature the solubility of gas is directly proportional to the partial pressure of the gas:

$$N = kP$$

where N — the molar fraction of the gas;

P — partial pressure of the gas;

k — coefficient of Henry.

Partial pressure is a part of the total pressure, which is accounted for by each gas in the mixture.

The total pressure of the gas mixture equals the sum of the partial pressures of the gases of the mixture.

When dissolved, gases decrease entropy: $\Delta S < 0$.

The dependence of the solubility of the gas pressure is of great biological importance, for example: gas exchange in the lungs. O_2 partial pressure in the inhaled air is more than the blood, so the oxygen dissolves in the lung capillaries. A partial pressure of CO_2 in the blood is greater than CO_2 in air, so it is removed from the blood.

Saturation of oxygen is used for treating certain diseases, such as anemia, gas gangrene, decompression sickness, placing the patient in a hyperbaric chamber.

With decreasing pressure the solubility of gases decreases. This can be observed by opening the bottles with carbonated water in which gas is dissolved under the pressure.

With increasing temperature the solubility of gases decreases. Since the process is exothermic dissolution, according to the Le Chatelier's principle increase in temperature leads to the decrease in solubility of gases.

In the presence of electrolytes in solution, the solubility of gases decreases, since part of the water is on the hydration of the electrolyte ions, reducing the total number of water molecules. Russian scientist I.M.Sechenov established relationship between the solubility of gases and the electrolyte concentration

$$C = C_0 \cdot e^{-kc}$$

where C — solubility of the gas in the electrolyte solution,

C_0 — solubility of the gas in the pure solvent,

c — concentration of the electrolyte,

k — constant depending on the nature of the gas, electrolyte temperature.

According to this law dissolves in the blood and other less oxygen gas than in water, because the blood contains much electrolyte.

B. Solubility of liquid in another liquid is dependent on its nature.

Table 5.2 shows examples of liquids that are mixed in different ways with each other.

Solubility of liquids

Solubility of liquids	Practically insoluble fat - water; petrol - water
The limited solubility of benzene - water; aniline - water	Unlimited solubility of ethanol - water; toluene - benzene
Solubility of liquids	Practically insoluble fat - water; petrol - water
The limited solubility of benzene - water; aniline - water	Unlimited solubility of ethanol - water; toluene - benzene

Table 5.2

If it limited to two soluble liquids, such as carbon tetrachloride CCl_4 and add water I_2, which is soluble in both liquids and shake, then I_2 distributed among them according to the rule *of the Nernst distribution*:

$$K_{dis} = \frac{C(CCl_4)}{C(H_2O)}$$

It is based on this *extraction*, (extraction of substances from mixtures. For example, the extraction of proteins from blood serum, drugs from plants.)

Nernst distribution rule explains the penetration of substances through the cell membrane. Thus, water-insoluble compound — fats, cholesterol is penetrating into the cell through the membrane lipid bilayer, in which they are dissolved. Their accumulation in the lipid layer obeys the distribution.

B. Solubility of solids depends on the nature of the substance and solvent and temperature.

Polar solvents are well dissolved polar substances (salts, acids, water), non-polar solvents dissolve by polar substance (naphthalen alcohol).

The solubility of most of the solids increases with increasing temperature. But the solubility of $Ca(OH)_2$ decreases with increasing temperature as the process is exothermic.

Ways of expressing the concentration of solutions

An important characteristic of the solution is its quantitative composition.

Consider the most important and common ways of expressing the concentration of solutions.

The most commonly used ways of expressing such solution concentration.

1. ***Mass fraction*** ϖ is a ratio of the mass of the solute m_x (g) solution to the mass $m_{solution}$:

$$\bar{\omega}\frac{m_x}{m_{sol.}} \times 100\%$$

Units of mass fraction percentage or in parts.

Mass of the solution related to the volume and density:

$$m_{solution} = V\rho$$

where $m_{solution}$ — mass of the solution in g;

V — volume of solution in ml;

ρ — density of the solution in g/ml.

Mass of the solution can be termed as the sum of the masses of water and solute mass:

$$m_{solution} = m_{water} + m_x$$

2. ***Molar concentration of*** C_X is the amount of solute ν per unit volume of solution:

$$C_x = \frac{\upsilon}{V}$$

express

$$\upsilon = \frac{m_x}{M_x}$$

then

$$C_x = \frac{m_X}{M_X \cdot V}$$

where, m_x — weight of the substance in g

V — volume of solution in liters.

The units — mol/l or mmol/l.

From the formula of the molar concentration can find a lot of dissolved substances or hitch:

$$m_X = C_X \cdot M_X \cdot V$$

3. But the substance does not react in a molar ratio, and the equivalent.

Equivalent is particle of a substance X, which is equivalent to one proton and one electron. To find the equivalent it is necessary to know the ***equivalence factor*** $f_{eqv.}$ — a number that indicates how the particle substance X is equivalent to one proton and one electron.

Equivalence factor is given by:

$$f_{eqv.} = \frac{1}{z}$$

where z is found for each class of compounds:

a) z for acid is the number of protons, which is replaced by a metal:

For example, $f_{eqv.}(HCl) = \frac{1}{1}$; $f_{eqv.}(H_2SO_4) = \frac{1}{2}$ or 0,5, if replaced only by one proton.

b) z for a reason is this number oxygroup:

For example, $f_{eqv.}(NaOH) = \frac{1}{1}$; $f_{eqv.}(Ca(OH)_2) = \frac{1}{2}$;

c) z for salt is the total valence of the metal (the product valence of the metal to its number):

For example, $f_{eqv.}(Na_2SO_4) = \frac{1}{2}$; $f_{eqv.}(Al_2(SO_4)_3) = \frac{1}{6}$;

d) z for the oxidation is reduction reactions this is the number of electrons, which gives a

reducing or oxidizing agent accepts:

For example, for the reaction $Fe^{+2} - 1e \rightarrow Fe^{+3}$ $f_{eqv}(Fe^{+2}) = \frac{1}{1}$;

for the reaction of $Mn^{+7} + 5e = Mn^{+2}$ $f_{eqv}(Mn^{+7}) = \frac{1}{5}$.

Using an equivalence factor, molar mass equivalent can be calculated:

$$M_{f\,eqv.\,X} = f_{eqv.} \cdot M_X$$

Knowing the molar mass equivalent, we can calculate the molar concentration equivalent $Cf_{eqv}.x$ (form the normal concentration of C_N) — is the equivalent amount of a substance per unit volume

of solution:

$$C_N = \frac{m_X}{M_X \cdot f_{eqv.} \cdot V}$$

where m_x — mass of the substance in g

V — volume of solution in liters.

The units mol/l or mmol/l.

From the formula of the molar concentration equivalent we can find a lot of dissolved substances or

hitch:

$$m_X = C_X \cdot M_X \cdot f_{eqv.} \cdot V$$

4.***Molarity concentration*** b_X is number of substances in ν_x 1kg solvent:

$$b_X = \frac{V_X}{m_{solvent}} = \frac{m_X}{M_X \cdot m_{solvent}}$$ Units mol/kg solvent.

5. ***The titer of the solutiont*** is a mass of solute in 1 ml of solution:

$$t = \frac{m_X}{V}$$ Units g/ml.

6. To calculate the concentration of the solutions according to titration use ***the rule of equivalents the product of molar solution concentration on the volume of the solution is of constant:***

$$C_{N_1} \cdot V_1 = C_{N_2} \cdot V_2$$

7. To calculate the concentration of solutions using the formula that binds different ways of expressing concentration:

$$C_X = \frac{\omega\% \cdot \rho \cdot 10}{M_X}\ ; \qquad C_N = \frac{\omega\% \cdot \rho \cdot 10}{M_X \cdot f_{eqv.}}$$

<u>Examples</u>

A. Preparation of solutions with mass fractions.

If the problem is given by the mass fraction, a solution must be found with the formula of mass fraction.

1) Calculate a sample of preparation 5l of physiological solution (ρ = 1,03).

$V_{sol-n} = 5$ l $\rho_{sol-n} = 1{,}03$ ϖ (NaCl) = 0.9% m(x) =?	Physiological solution – it is 0,9% NaCl. Use the formula to calculate the mass fraction: $\overline{w} = \frac{m_x}{m\,(sol.)}$ $m(sol - n) = V\rho;$

1) Find the mass of the solution:

$$m\,(sol - n) = 1.03 \cdot 5000 = 5150\ (g);$$

2) Find the mass of the solute:

$$m(x) = \frac{\overline{w} \cdot m\,(sol.)}{100\%} = \frac{0.9 \cdot 5150}{100} = 46.35\ (g)$$

The answer: 46.35 g NaCl is needed for adding 5 liters of water.

2) How much ml of 37% solution of HCl (ρ = 1,18) should be taken to prepare 2 l pharmacopic drug HCl with mass fraction of 8,2% (ρ = 1,04).

ϖ_1 (HCl) = 37%	Problem can be solved in two ways.
ρ_1 = 1,18	I method.
ϖ_2 (HCl) = 8,2%	Denote the parameters of the original 37% solution ρ_2 = 1,04;
V_2 = 2 l	numeral 1, and the solution which we must prepare the numeral 2.
V_1 =?	Use the formula for calculating the mass fraction:

$$\overline{w} = \frac{m_x}{m\,(sol.)}$$

$$m(sol.) = V\rho;$$

1) Data for first solution is not enough for the calculation of formula mass fraction, so we use the formula for finding the mass of the second solution:

$$m_2\,(sol-n) = 1.04 \cdot 2000 = 2080\ (g);$$

2) Find the mass of the solute in this solution:

$$m_{x_2} = \frac{\varpi_2 \cdot m_2\,(sol-n)}{100} \frac{8.2 \cdot 2080}{100} = 170.56\ (g)\ \text{of HCl}$$

3) The mass of the solute is the same in both races solid solution,

$$m_{x_1} = m_{x_2}$$

4) Find the mass of the first solution:

$$m_1\,(sol-n) = \frac{m_{x_1}}{\varpi_1} \cdot 100\% = \frac{170.56 \cdot 100}{37} = 460.97g$$

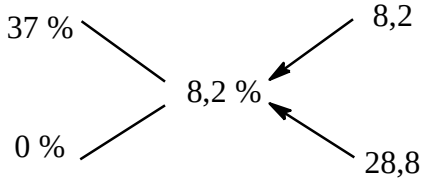
5) Find the volume of the first solution:

$$V_1 = \frac{m_1\,(sol-n)}{\rho_1} = \frac{460.97}{1.18} = 390.65\ ml$$

The answer: You should take a 390.65 ml of 37% for the first solution of HCI and add water up to 2l.

II method.

1) Settled under the Rules of the cross:



2) Total units: 8.2 + 28.8 = 37 units;

3) Find $m_{sol\text{-}n2}$ = 2000 · 1,04 = 2080g;

4) Find the mass of the solution, which falls to 1 part solution:

$$2080 : 37 = 56.22\ g;$$

5) Find the mass of the first solution:

$$m_1\,(sol-n) = 56.22 \cdot 8{,}2 = 460{,}97\ g;$$

6) Find the volume of the first solution:

$$V_1 = \frac{m_1\,(sol-n)}{\rho_1} = \frac{460.97}{1.18} = 390.65\ ml$$

The answer: You should take 390.65 ml of 37% for the first solution of HCl and add water up to 2L.

3) What is the volume of water necessary to dissolve 1 mol of KOH to prepare 5% solution.

$\nu = 1$ mol of KOH $\overline{w} = 5\%$ V (H_2O) =?	1) Find the mass of the solute: $\nu = m / M;\ m = \nu \cdot M = 1 \cdot 56 = 56$ g; 2) Write the formula for the mass fraction: $\overline{w} = \frac{m_x}{m\ (sol.)} \cdot 100\%$

hence the mass of the solution:

$$m\ (sol.) = \frac{m_x}{\overline{w}} \cdot 100\% = 1120\ g$$

3) We expect a lot of water:

$$m_{water} = m_{water} - m_{substanse} = 1120 - 56 = 1064g.$$

The answer: You should take 1064g of water.

4) The patient must enter the 100mg of bemegride. How many ml of 0.5% -of the solution is necessary to take?

$m_x = 100$ mg $\overline{w} = 0.5\%$ V (bemegride) =?	Use the formula to calculate the mass fraction: $m(sol.) = V\rho$ 1) Set turn the substance in g: $m_x = 100$ mg $= 0.1$ g;

2) Find the mass of the solution bemegride:

$$m\ (sol.) = \frac{m_x}{\overline{w}} \cdot 100\% = \frac{0.1 \cdot 100}{0.5} = 20\ g$$

3) Find the volume of the solution bemegride:

$$V = \frac{m\ (sol.)}{\rho} = \frac{20}{1} = 20\ ml$$

The answer: 20ml

5) A child who was born in asphyxia was injected etimizol 1mg per for 1 kg of body weight. How many ml of 1.5% of solution of this preparation is necessary for a child weighing 2800g.

$m_{child} = 2800$ mg $\overline{w} = 1.5\%$ V (sol.) =?	Use a formula to calculate the mass fraction: dose = 1mg/kg weight $\overline{w} = \frac{m_x}{m\ (sol.)} \cdot 100\%$ $m(sol.) = V\rho$

1) Find the mass of etimizol, which must be used

1mg etimizol – to 1kg of body weight

X mg – at 2.8 kg

$X = 2.8$ mg $= 0.0028$ g;

2) Find the mass of the solution etimizol:

$$m(sol.) = \frac{m_x}{\overline{w}} \cdot 100\% = \frac{0.0028}{1.5} \cdot 100 = 0.19\ g$$

3) Since the density of the solution is not given, then take it to 1:
Then, the volume of solution etimizol equal to its mass, ie 0.19 ml.
The answer: you must enter 0, 19ml of solution etimizol.

6) How many grams of oxalate (oxalic acid) must be dissolved in 200ml water to get 10% solution?

$V_{water} = 200$ m	I method.
$\bar{w} = 10\%$	1) If we put a lot of substance m_x, then the mass solution
m_x =?	$m(sol.) = 200 + m_x$
	(200ml H_2O = 200g H_2O);

2) Using a formula mass fraction:

$$\bar{w} = \frac{m_x}{m\ (sol.)} \cdot 100\%$$

$$10 = \frac{m_x}{200 + m_x} \cdot 100\%$$

The calculation results, the $m_x = 22.2$ g

The answer: You should get 22.2 g of oxalic acid.

II method

1) What is the mass fraction of water in the solution?

$$\bar{w}(H_2O) = 100\% - 10\% = 90\%$$

2) Find the mass of the solution:

$$m\ (sol.) = \frac{m(H_2O)}{\bar{w}} \cdot 100\% = \frac{200}{90} \cdot 100 = 222.2\ g$$

3) Find the mass of oxalic acid:

$$222.2 - 200 = 22.2\ g$$

The answer: You should get 22.2 g of oxalic acid.

B. Preparation of solutions with a molar concentration of C_X.

If a molar concentration is given in the task, find the solution mass.

1) Calculate the weight of the NaOH for the preparation of 2l 0.3 M solution of it.

$C_x(NaOH) = 0.3mo;/l$	1) Write the formula of molar concentration:
$V = 2$ l	$C_x = \frac{m_x}{M_x \cdot V}$
m_x =?	2) From this formula we find m_X:
	$m_x = C_x \cdot M_x \cdot V = 0.3 \cdot 40 \cdot 2 = 24$ g

The answer: You should take 24 g NaOH.

2) Calculate the molar concentration of KOH solution, if 3l solution contains 10 g of the substance.

$m_x(KOH) = 10$ g	1) Write the formula of molar concentration:
$V = 3$ l	$C_x = \frac{m_x}{M_x \cdot V}$
C_x =?	2) Calculate the C_X:
	$C_x = \frac{100}{56 \cdot 3 = 0{,}59\ mol/l}$

The answer: the molar concentration of – 0.59 mol / liter.

3) What is the molar concentration that corresponds to a solution of hydrochloric acid in gastric juice if the mass fraction of HCl it 0,5-0,54%?

$\bar{w}(HCl) = 0.5 - 0.54\%$	I method
C_x =?	1) Find the average content of hydrochloric acid in gastric juice:
	$\bar{w}_{arithmetic\ mean} = \frac{0.5 + 0.54}{2} = 0.52\%$

2) Suppose we have 100g of gastric juice. It contains 0.52 g of HCl. Molar concentration is calculated on 1000 ml of solution. Taking density of the gastric juice of 1, we find a lot of hydrochloric acid in 1000 ml of solution:

$$\text{in 100g of solution} - 0.52 \text{ g HCl}$$
$$\text{at 1000g (ml)} - X$$
$$X = 5.2 \text{ g of HCl};$$

3) Find the molar concentration of C_X:

$$C_x = \frac{5.2}{3.65 \cdot 1} = 0.142 \text{ mol/l}$$

The answer: the molar concentration of hydrochloric acid in gastric juice is 0.142 moles per liter.

II method

1) Find the average content of hydrochloric acid in gastric juice:

$$C_x = \frac{5.2}{3.65 \cdot 1} = 0.142 \text{ mol/l}$$

2) Using formula that relates two ways of expressing solution concentration C_X and ω:

$$C_x = \frac{\overline{w}\% \cdot \rho \cdot \omega}{M_X} = \frac{0.52 \cdot 1 \cdot 10}{36.5} = 0.142 \text{ mol/l}$$

The answer: the molar concentration of hydrochloric acid in gastric juice is 0.142 moles per liter.

B. Preparation of solutions with a molar concentration equivalent C_N.

If the problem is given by the molar concentration equivalent, to find a solution start with the formula of the molar concentration equivalent.

1) In 250 ml of solution contains 26.5 g of Na_2SO_3. Calculate C_N.

$V = 250$ ml $m_x = 26.5$ g $C_N = ?$	1) Write the formula of molar concentration equivalent and calculate it (the volume of solution express in l): $$C_N = \frac{m_x}{M_x \cdot f_{eqv.} \cdot V} = \frac{26.5}{106 \cdot 1/2 \cdot 0.25} - 2 \text{ mol/l}$$

The answer: the molar concentration equivalent solution of baking soda - 2 mol / liter.

2) How much $KMnO_4$ is necessary for the preparation of 2l solution with C_N = 0.1 mol/l, if $f_{eqv.}$ $KMnO_4$ = 1/5?

$V = 2$ l $C_N = 0.1$ mol/l $f_{eqv.}(KMnO_4) = 1/5$ $m(KMnO_4) = ?$	1) Write the formula of molar concentration equivalent: $$C_N = \frac{m_x}{M_x \cdot f_{eqv.} \cdot V}$$ hence: $$m_x = C_N \cdot M_x \cdot f_{eqv.} \cdot V = 0.1 \cdot 158 \cdot \frac{1}{5} \cdot 2 = 31.6 \text{ g}$$

The answer: Mass $KMnO_4$ is 31.6g

3) Compute the C_N solution H_2SO_4 with w = 30% (ρ = 1,22, $f_{eqv.}$ = 1/2).

$\omega = 30\%$ $\rho = 1.22$ $f_{eqv.} = 1/2$ $C_N = ?$	1) Using a formula that relates the C_N and ω: $$C_N = \frac{\omega\% \cdot \rho \cdot 10}{M_x \cdot f_{eqv.}} = \frac{30 \cdot 1.22 \cdot 10}{98 \cdot 1/2} = 7.47 \text{ mol/l}$$

The answer: 30%-th solution corresponds to a solution with C_N = 7.47 mol/litre.

4) What volume of 30% solution of H_3PO_4 (ρ = 1,18) is necessary for cooking 5 l solution with C_N = 2 mol / l phosphate acid if it reacts completely?

$\omega_1 = 30\%$
$\rho_1 = 1.18$
$V_2 = 5\,l$
$C_N = 2\ mol/l$
$V_1 = ?$

Denote the parameters of the original 30% solution numeral 1, and the solution which we must prepare, 2H-th - the number 2

1) data from the first solution is insufficient to calculate the formula of mass fraction, so using the formula of the molar concentration equivalent to find the mass of C_N substance in the second solution

$$C_N = \frac{m_x}{M_x \cdot f_{eqv.} \cdot V}$$

hence

$$m_{x_2} = C_N \cdot M_x \cdot f_{eqv.} \cdot V = 0.2 \cdot 98 \cdot \frac{1}{3} \cdot 5 = 326.6\ g$$

the (as phosphate acid reacts completely, all three hydrogen atoms are replaced by metal, then the equivalence factor equal to 1/3).

2) The mass of the solute is the same in both solutions

$$m_{x_1} = m_{x_2}$$

3) Using the mass fraction, we find the mass of the first solution:

$$\overline{w} = \frac{m_x}{m\ (sol.)} \cdot 100\%$$

hence

$$m\ (sol.) = \frac{m_x}{\overline{w}} \cdot 100\% = \frac{326.6}{30} \cdot 100 = 1088\ g$$

4) Find the volume of the 30 th solution:

$$V = \frac{m\ (sol.)}{\rho} = \frac{1088}{1.18} = 922\ ml$$

The answer: You should take 30 % of 922ml of mud and water to dolt 5L.

5) How will the concentration of the solution with HCl C_N = 0.2 mol / l, change if up to 50ml to 100ml refill of water is added?

$V\ (sol.) = 50\ ml$
$V_{water} = 100\ ml$
$C_{N_1}(HCl) = 0.2\ mol/l$
$C_{N_2}(HCl) == ?$

1) Volume of the solution after adding water:

$$50 + 100 = 150\ ml;$$

2) According to the law of equivalents:

$$C_{N_1} \cdot V_1 = C_{N_2} \cdot V_2$$

3) Find the concentration after the addition of water:

$$C_{N_2} = \frac{C_{N_1} \cdot V_1}{V_2} = \frac{0.2 \cdot 50}{150} = 0.067\ mol/l$$

The answer: 0.067 mol / liter.

16. Mass fraction of substances in solution is:
   a) the ratio of substance weight to the mass of the solution
   b) the ratio of solution weight to the mass of the substance
   c) the difference between the mass of solution and mass of the substance
17. Mass fraction of a substance in solution is:
   a) ratio of solution weight to the mass of the substance
   b) ratio of substance weight to the mass of the substance
   c) the difference between the mass of solution and mass of matter
18. The formula for mass fraction:
   a) b) c)

$\omega = \frac{m_{sol-n}}{m_{solvent}} \cdot 100\%$ $\omega = \frac{m_{sol-n}}{m_{solvent}} + 100\%$ $\omega = \frac{m_{solvent}}{m_{solution}} \cdot 100\%$

19. Molar concentration is:
    a) the amount of substance per volume of solution
    b) the quantity in mass units of solution
    c) the amount of substance per volume of solvent
20. Molar concentration is:
    a) weight ratio of substance weight to the volume of solution
    b) the amount of substance per volume of solution
    c) the amount of substance in 1 g solution
21. Molar concentration is:
    a) the quantity in units of weight solvent
    b) the amount of substance per volume of solvent
    c) the amount of substance per volume of solution
22. The formula for molar concentration:
    a) b) c)

$Cx = \frac{m_X}{M_X V}$ $Cx = \frac{m_X}{M_X + V}$ $Cx = \frac{M_X}{m_X V}$

23. Factor equivalence of acids is this unit is divided into:
    a) the valence acid residues;
    b) the number of hydrogen atoms, which replaced the metal;
    c) the number of atoms of hydrogen, which is an acid.
24. Factor equivalence of base is this unit is divided into:
    a) the valency of oxygroup
    b) the number of metal atoms
    c) the number of oxygroup
25. Factor equivalence of salt is this unit is divided into:
    a) the valence of metal
    b) the oxidation of metal
    c) the total valence of the metal
26. Factor equivalence in redox reactions is a unit divided into:
    a) the number of electrons that takes oxidants, or gives reductant
    b) the number of electrons involved in the reaction
    c) change in the degree of oxidation
27. Molar mass equivalent is:
    a) the product of molar mass of substance by a factor of equivalence
    b) the product of the mass of matter on the equivalence factor
    c) the ratio of the molar mass of substance to the equivalence factor
28. Molar concentration equivalent is:
    a) the equivalent weight ratio of substance to the volume of a solution
    b) the amount of substance per volume of solution
    c) the number of mole equivalents of substance per volume of solution
29. The formula for molar concentration of equivalent:
    a) b) c)

$Cx = \frac{m_{\tilde{O}}}{M_X f_{eqv}.V}$ $Cx = \frac{m_{\tilde{O}} \cdot f_{eqv}}{M_X.V}$ $C_N = \frac{m_X}{M_X \cdot f_{\text{eqv.}} \cdot V}$

30. Molar concentration is
    a) the amount of substance in 1 kg of solvent
    b) the mass of substance in 1 liter of solvent
    c) the amount of substance in 1 liter of solvent

31. Titre of a solution is the
    a) the mass of 1 kg of the substance in solution
    b) the mass of substance in 1 ml
    c) the mass of substance in 1 g solution
32. By rule of equivalents:

a) $C_{N_1} - V_{N_1} = C_{N_2} - V_{N_2}$ b) $C_{N_1} + V_{N_1} = C_{N_2} + V_{N_2}$ c) $C_{N_1} \cdot V_{N_1} = C_{N_2} \cdot V_{N_2}$

5. The main questions of the seminar:

5.1. What is the mass fraction?
5.2. What is the molar concentration?
5.3. Factor of equivalency (acids, bases, salts, oxidizing agents, reducing agents)
5.4. Molar mass of equivalent;
5.5. Relationship of various concentration expressions;
5.6. The law of equivalent.

6. The questions for individual learning:

6.1. Molality;
6.2. Laboratory apparatus for the solution preparation (the volumetric flasks, the calibration pipets, burets and others)

7. The examples of the task:

7.1. How many grammes of boric acid and water do you need for preparation of 250 g of solution with the mass fraction of boric acid equal 3%?
The answer: mass percentage is calculated using the equation 5.1

$$\omega = \frac{m_x}{m_p} \cdot 100\% \omega \qquad 5.1$$

thus, $m_x = \frac{\omega \cdot m_p}{100}$ 5.2

$$m_{H_3BO_3} = \frac{3 \cdot 250}{100} = 7.5\,\text{g}$$

weight of water is 242,5 g: 250-7,5 = 242,5 g

7.2. How many grammes of sodium chloride must be taken for preparation of 1 l of solution withC_X =2 mol/l?
The answer: molar concentration is calculated using the equation 5.3

$$C_x = \frac{m_x}{M_x \cdot V_p} \qquad 5.3$$

thus, $m_x = C_x M_x V_p = 2 \cdot 58.5 \cdot 1 = 117$ g

7.3. What weigh of $KMnO_4$ have to be taken for preparation of 2 l of the solution with C_N=0.5 mol/l analyzing in the acid medium?
The answer: molar concentration is calculated using the equation 5.4

$$C_m = \frac{m_x}{M_x \cdot feqv \cdot V_p} \qquad 5.4$$

thus, $m_x = C_m M_x feqv V_p = 0.5 \cdot 158 \cdot 1/5 \cdot 2 = 31.6$

7.4. What is the molar concentration of equivalent of sulfuric acid if the weight fraction is 10 % (density is 1.22, f_{eqv} = 1/2).
The answer: molar concentration of equivalent is

$$C_n = \frac{\omega \cdot \rho \cdot 10}{M_x \cdot f eqv x} = \frac{10 \cdot 1.22 \cdot 10}{98 \cdot 0.5} = 2.38 \text{ mol/l}$$

7.5. A patient must be injected by 100 g bemegrid. How many milliliters of the solution with the weight fraction of 0.5 % must be injected?
The answer: m_x = 100 mg = 0,1 g

$$\omega = \frac{m_x}{m_p} \cdot 100\%; \quad p = 1; \quad m_p = V_p \cdot \rho; \quad \omega = \frac{m_x}{V_p \cdot \rho} \cdot 100\%$$

$$V_p = \frac{m_x}{\omega \cdot \rho} \cdot 100\% = \frac{0.1}{0.5 \cdot 1} \cdot 100\% = 20 \text{ml}$$

8. Homework (must be performed in the laboratory notebook):
8.1. What weight of NaCl and H_2O must be taken for preparation of 2 L isotonic solution (the weight fraction is 0.9 %, density is 1.02)
8.2. Calculate the molar equivalent concentration of sulfuric acid if density is 1.04 and weight fraction is 3.2 %.
8.3. A patient (the weight is 76 kg) must be injected the solution of $NaHCO_3$ in the concentration of 0.66 mol/kg. How many milliliters of this solution with the weight fraction of 4.2 % must be taken?

***9. The control test*:**
for instance:

9.1. Mass fraction of a substance in solution is
a) the mass of a substance multiples to the mass of solutions;
b) the ratio of them as of substance to the mass of the solvent;
c) the ratio of them as of substance to the mass of the solution.
The answer: c
9.2. What is the weight of KOH must be taken for preparation of 2 kg of the solution with the mass percentage equal 2 %?
a) 40 g
b) 20 g
c) 60 g
The answer: a

***10. Control test*:**

Sample 1

1.What is the mass fraction of a solute in a solution?
2.How is the equivalent factor of a salt calculated?
3.How many grams of NaOH must be taken for preparation of 0.3 M solution in the volume of 2 L?
4.Calculate the mass fraction of a solute in a solution containing 4.5 g of the solute dissolved in 200 ml of water (ρ = 1.07).

Sample 2

1.What is the molar concentration?
2.What is the molality?
3. The concentration of $KMnO_4$ is 0.25 M. How many grams of it must be taken to prepare 3 L of the solution?

4. How many grams of oxalate $H_2C_2O_4$ must be taken to prepare 300 ml of the solution containing 5 % by mass of the solute ($\rho = 1.05$)?

TOPIC 6: Acid-base equilibrium in human body. pH scale of biological liquids.

1. ***Actuality of the topic:*** the role of biological catalysts and the unique behaviour of the biochemical processes is absolutely connected to the presence of hydrogen ions. To predict the processes in living things, to have a better understanding of the physiological processes and biochemical reactions, the establishing of the hydrogen ion concentrations is important.

2.General aim: is to estimate and predict the phisiological processes that are depended on pH values.

3. Actual aims and abilities:

- to be able to estimate the solution properties and the direction of chemical reaction depending on pH;
- to calculate the pH values of the solutions of strong and weak electrolytes;
- to determine pH using indicators.

4. Literature:

4.1. Lecture materials;

Hydrogen index of biological fluids.

When dissolved in water, some substances interact with the polar water molecules dissociate into ions. Such substances, in solution or melt conduct electric current are called *electrolytes*. These include acids, bases and salts.

Electrolytes play an important role in the human body. Biological fluids such as blood, gastric juice, urine, intracellular and extracellular fluid are electrolytes. Thus, blood containing cations Na^+, K^+, Ca^{2+}, Mg^{2+} and others as well as anions Cl^-, HCO_3^-, $H_2PO_4^-$, HPO_4^{2-}, SO_4^{2-}. Electrolytes are involved in maintaining the osmotic pressure of the reaction environment to influence the solubility of proteins and low molecular weight compounds are known to catalyze metabolic processes involved in blood clotting.

Electrolytic dissociation

Disintegration agents ions under the influence of the polar water molecules, called *electrolytic dissociation*. Electrolytes which completely dissociate into ions, called *strong* (acid — chloride, sulphate, nitrate; base (alkali) — sodium hydroxide, potassium hydroxide, calcium hydroxide and all soluble salt). Electrolytes that dissociate partially, called *weak* (acid — sulfite, nitrite, hydrogen sulfide, acetic; foundation — ammonium hydroxide and water).

Quantitatively characterized by electrolytic dissociation *degree of dissociation.*

The degree of dissociation α — is the ratio of the dissociated molecules to the total number of dissolved molecules.

$$\alpha = \frac{Cdis}{C_X}$$

Where C_{dis}. — the number of dissociated molecules;

C_X — the total number of molecules or the total concentration of the electrolyte.

For the degree of dissociation of the strong electrolyte is close to 1 (or 100%).

To characterize the concentration of strong electrolytes instead use the concept of *activity* — this is the actual number of ions in solution, which is less than the total concentration, as part of the ions interact with each other, and again formed molecule.

Activity and concentration related in the equation:

$$\alpha_X = f \cdot C_X$$

where α_X — activity;

f — *the activity coefficient*, which shows how much of dissociated molecules.

For dilute solutions of strong electrolytes f = 1, then αH = CX, so calculations for the most commonly used value of CX.

Quantitative characteristic of the interaction of ions in solution is the *ionic strength of the solution*, which is equal to half the sum of the product of concentration of each ion by the square of its charge:

$$\mu = 1/2 \cdot (C_{X1} \cdot z_1^2 + C_{X2} \cdot z_2^2 + \ldots\ldots\ldots + C_{Xn} \cdot z_n^2),$$

where μ — ionic strength of the solution;

z — ion charge;

C_X — ion concentration.

The ionic strength of biological fluids which are electrolytes, as well as saline (0.9 % solution of NaCl), the average is 0.15 mol. Therefore it is necessary to calculate the *ionic strength solutions substitutes that it approaches the value of the ionic strength of biological fluids.*

Weak electrolytes dissociate reversibly in solution equilibrium is established, which is characterized by *the dissociation constant KD* .

For substances A_XB_Y dissociation equation has the form :

$$A_XB_Y \leftrightarrow xA + yB$$

and the expression of the dissociation constant:

$$K_D = \frac{[A]^X \bullet [B]^y}{[A_X B_Y]}$$

where $[A]^X$ — ion concentration A;

$[B]^y$ — ion concentration in;

$[A_XB_Y]$ — concentration of undissociated molecules of the substance.

For example, in acetic acid, which dissociates according to the equation:

$$\underbrace{\underbrace{CH_3COOH}_{\text{potential acidity}} \leftrightarrow \underbrace{H^+ + CH_3COO^-}_{\text{active acidity}}}_{\text{total acidity}}$$

dissociation constant expression has the form:

$$K_D = \frac{[H^+] \bullet [CH_3COO^-]}{[CH_3COOH]}$$

The dissociation constant and the degree of dissociation are related by:

$$K_D = \frac{\alpha^2 \bullet C}{1 - \alpha}$$

called **Ostwald dilution rule.**

In the solution of a weak acid distinguished general, active and potential acidity.

Total acidity is the total concentration of acid in mole eq. It is determined by titration.

Active acidity is the concentration of protons. It is determined by colorimetric or potentiometric methods.

Potential acidity is the concentration of undissociated acid molecules. It defined as the difference between total and active acidity.The concentration of protons in the acid solution is calculated by the formula

$$[H^+] = \alpha \cdot [acid]$$

strong acid	strong acid
$\alpha = 1$	$\alpha = 1$
$[H^+] = \alpha \cdot [acid]$	$[H^+] = \sqrt{Cd \cdot [acid]}$

α – acid degree of dissociation

The dissociation of the base form of hydroxide anions, whose concentration is calculated as follows:

$$[OH^-] = \alpha \cdot [base]$$

strong base	strong base
$\alpha = 1$	$\alpha = 1$
$[OH^-] = \alpha \cdot [base]$	$[OH^-] = \sqrt{Cd \cdot [base]}$

α – base degree of dissociation

Thus, a solution of strong acid equals the total acidity of the active.

Similarly, in solutions of weak bases distinguished general, active and potential alkalinity.

$$\underbrace{\underset{\text{potential alkalinity}}{NH_4OH} \leftrightarrow \underset{\text{active alkalinity}}{NH_4^+ + OH^-}}_{\text{total alkalinity}}$$

Total alkalinity is the total concentration of base in mole eq. It is determined by titration.

Active alkalinity is the concentration of hydroxide anions.

Potential alkalinity is the concentration of undissociated molecules base. It defined as the difference between total and active alkalinity.

The concentration of hydroxide ions is calculated according to the formula:

Thus, the strong base in solution equal to the total active alkalinity.

Ionic product of water. pH.

Water is a weak electrolyte. The degree of dissociation of water — $1{,}8 \cdot 10^{-9}$.

It dissociates into ions:

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

Dissociation constant of water is expressed by the equation:

$$K_D = \frac{[H^+] \bullet [OH^-]}{[H_2O]} = 1{,}8 \cdot 10^{-16}.$$

where $[H_2O]$ is concentration of undissociated molecules of water.

Since water is slightly dissociates, the concentration of undissociated molecules may be taken as equal to the concentration of water, 1000/18 = 55.56 (where the weight is 1000g 1 liter of water, and 18 is the molar mass of water).

then:

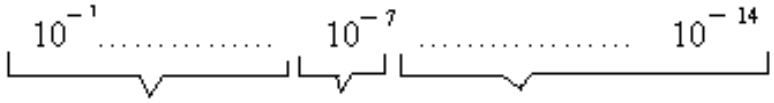
$$K_d \bullet [H_2O] = [H^+] \bullet [OH^-] = K_w$$

K_w is the ionic product of water, i.e. the product of concentration of hydrogen ions (protons) by the concentration of hydroxide ions (anions) in water at a particular temperature.

It is constant and equal to:

$1{,}8 \cdot 10^{-16} \cdot 55{,}56 = 1{,}008 \cdot 10^{-14} \approx 10^{-14}$ ($t=25^0C$).

Since water is dissociated into a hydrogen ion (proton) and a hydroxide ion(anion), the concentration of each of them in water at 10^{-7} constant g-ion/l. This is neutral environment. If the hydrogen ion concentration is greater than 10^{-7} g- ion/l, this is acidic environment. If the hydroxide ions predominant concentration is alkaline environment. I.e. by increasing the concentration of hydrogen ions in the same time decreasing the concentration of hydroxide ions, and vice versa, but their product is constant.



acidic medium | neutrons medium | alkaline medium

Thus, the reaction medium solution may be expressed in terms of hydrogen ion concentration.

In practice, use value **pH.**

pH is the negative logarithm proton concentration.

$$pH = -\lg [H^+]$$

For example, if $[H^+] = 10^{-3}$, $pH = -\lg 10^{-3} = 3$.

If $[H^+] = 10^{-11}$, $pH = -\lg 10^{-11} = 11$.

Similarly, we can find the pOH:

$$pOH = -\lg [OH^-]$$

For example, if $[OH^-] = 10^{-2}$, $pOH = -\lg 10^{-2} = 2$.

If $[OH^-] = 10^{-9}$, $pOH = -\lg 10^{-9} = 9$.

Taking the logarithm of the ion product of water we get:

$$-\lg 10^{-14} = -\lg[H^+] + (-\lg [OH^-]) = pH + pOH = 14.$$

In a neutral medium pH = 7; in an acidic medium pH < 7; in an alkaline medium pH > 7.

pH 1 ……. 7 ……14

acidic medium | neutrons medium | alkaline medium

The simple way to determine the pH of the solutions is the use of indicators.

Thus, the pink color of methyl orange indicates an acidic environment. Crimson color of phenolphthalein or methyl orange yellow color indicates an alkaline environment.

The universal indicator (this indicator mixture with different color change interval, which overlap) can be determined from the reaction medium a solution of pH 1 to pH 14.

Biological pH

The pH is an important characteristic of biological fluids and the whole organism.

The pH of some biological fluids given in Table 6.1

pH of biological fluids

biological fluid	pH
blood serum	7,36 ($[H^+]=4{,}36\cdot10^{-8}$)
gastric juice	0,9 – 1,5 ([HCl]=0,047 or 0,5-0,54%)
urine	4,8 – 7,5
saliva	6,35 – 6,85
intestinal juice	9 – 10
bile	6,5 – 7,3
spinal fluid	7,35 – 7,8

Table 6.1

The pH of body fluids is constant and can vary within very narrow ranges:

a) For example, by lowering the pH of blood is increased by 0.1 ventilation twice. Decrease in blood pH of 0.2 - 0.3 units for a long time can lead to loss of life. Recent incompatible with life outside the blood pH of 7.1 - 7.8. Venous blood is saturated with carbon dioxide, so it is pH = 7.35. Arterial blood oxygenated and pH = 7.45.

pH of the cell is less than the blood cells so as to accumulate carbon dioxide.

Displacement of blood pH to the acid side is called **acidosis**.

Displacement of blood pH to the alkaline side is called **alkalosis**.

b) the pH of the urine depends on the food the person takes. At the use of animal food urine is more acidic, as in the hydrolysis of proteins, amino acids are formed. When used vegetable food urine pH shifts in the alkaline region, as salts of weak organic acids which are vegetable juices, hydrolysis give an alkaline reaction.

pH affects the enzymes:

a) as active gastric pepsin at pH 1.5-2.0 until the food lump not impregnated gastric juice with a lower pH;

b) saliva of amylase activity at pH = 6.7;

c) fabric cathepsins at pH close to neutral catalyze synthesis protein at acidic pH and its splitting;

d) phosphatase cleaves proteins in the gut at a pH of 9-10.

The pH also affects the microorganisms. For example, Vibrio cholerae develops at pH = 7,6-9,2. Therefore, people with acidity of gastric juice did not infected with cholera.

Theory of acids and bases. Hydrolysis of salts

Basic acid properties of inorganic compounds explain the different theories.

One of them is *Protolytic Bronsted Lowry theory*, according to which:

acids are proton donors

bases are proton acceptors

For example, the acid chloride dissociates according to the equation:

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

In this case the HCl gives proton (proton donor) and an acid.

Chloride anion Cl^- can accept a proton (a proton acceptor) and is the basis.

Ammonia is a base, as it is a proton acceptor:

$$NH_3 + H^+ \leftrightarrow NH_4^+$$

According to the theory of Bronsted and Lowry, reactions that are called proton transfer *protolytic*. These include the *hydrolysis* and *neutralization* reactions.

a) *Reactions generally occur as neutralization between acids and bases to form a salt and water:*

$$HCl + NaOH \rightarrow NaCl + H_2O$$

When interacting with ammonia water is formed:

$$HCl + NH_3 \leftrightarrow NH_4Cl$$

b) *Hydrolysis of salts is an exchange reaction of salt ions with water to form weak electrolytes.*

Salts formed with a strong acid and a strong base is not hydrolyzed.

Salts formed with a weak base and strong acid to hydrolyze the weak base and strong acid, which gives as a result of dissociation of acid medium:

$$NH_4Cl + H_2O \leftrightarrow NH_4OH + \mathbf{H^+} + Cl^-$$

Salts derived from a weak acid and a strong base, hydrolysed to the weak acid and strong base, which gives as a result of dissociation of the alkaline medium:

$$Na_2CO_3 + H_2O \leftrightarrow CO_2 + 2Na^+ + \mathbf{2OH^-}$$

Salts derived from a weak acid and a weak base to hydrolyze the weak acid and weak base. Reaction medium will depend on the strength of the acid or base:

$$CH_3COONH_4 + H_2O \leftrightarrow NH_4OH + CH_3COOH.$$

Quantitatively characterized by a degree of hydrolysis of salts hydrolysis.

Degree of hydrolysis is the ratio of hydrolyse to the total number of molecules of the dissolved molecules.

$$\alpha_g = \frac{n(hydr.)}{n(tot.)}$$

The degree of hydrolysis depends on temperature and concentration.

The smaller the concentration of the solution, the more dilute the solution, the greater the degree of hydrolysis.

The higher the temperature, the greater the degree of hydrolysis, since the hydrolysis process is endothermic.

Dissociation constant associated with the constant hydrolysis K_g.

The salt formed with a weak base and strong acid K_g expression has the formula:

$$K_g = \frac{K_w}{K_b}$$

where K_w — ionic product of water;

K_b — dissociation constant of the weak base.

The salt formed of a weak acid and a strong base CG expression has the formula:

$$K_g = \frac{K_b}{K_a}$$

where HF — ionic product of water;

K_a — dissociation constant of the weak acid.

Hydrolysis role in the biochemical processes

Among inorganic substances in the human body hydrolyzes sodium carbonate:

$$Na_2CO_3 + H_2O \rightarrow NaHCO_3 + NaOH$$

But mostly the human body subjected to hydrolysis in the presence of organic compounds enzymes. Fats are hydrolyzed in an alkaline medium into glycerol and salts of higher carboxylic acids (soap). Proteins are hydrolyzed to amino acids. Complex carbohydrates — to monosaccharides. That low-molecular substances — amino acid, monosaccharides, etc. — are absorbed in human body.

33. Ionic products of water is:
    a) the sum of the concentrations of protons and hydroxide ions
    b) the product of the concentrations of protons and hydroxide ions
    c) the ratio of the concentrations of protons and hydroxide ions
34. Equations of ionic product of water:
    a) $H^+ + OH^- = 10^{-14}$ b) $H^+ \cdot OH^- = 10^{-16}$ c) $[H^+] \cdot [OH^-] = 10^{-14}$
35. For pH = 2 ion product of water is equal to:
    a) 10^{-2}mol/l b) 10^{-14} mol/l c) 10^{-12}mol/ l
36. For pH = 11 ion product of water is equal to:
    a) 10^{-2}mol/l b) 10^{-11} mol/l c) 10^{-14}mol/ l
37. Active acidity is:
    a) the acid concentration
    b) the concentration of acid balance
    c) the concentration of protons
38. Potential acidity is:
    a) the concentration of non-dissociatiable acid molecules
    b) the concentration of acid
    c) the concentration of hydrogen ions
39. Total acidity is:
    a) the concentration of non-dissociatiable acid molecules;
    b) the total concentration of acid
    c) the concentration of protons
40. Titration determines:
    a) the active acidity
    b) the potential acidity

c) the total acidity

41. The formula for active acidity of acid solution:
    a) $[H^+]=\alpha$ [acid]
    b) $[H^+]=\alpha$ + [acid]
    c) $[H^+]=\alpha$ - [acid]
42. The formula for the active solvent of strong acid:
    a) $[H^+]=\alpha$
    b) $[H^+]$= [acid]
    c) $[H^+]=\alpha$ [base]
43. Formula for active acidity of weak acid solution:
    a) $[H^+]=\sqrt{\hat{E}d \cdot [acid]}$
    b) $[H^+]$= [acid]
    c) $[H^+]$= Kd • [acid]
44. Total acidity is practically defined by:
    a) titration
    b) cryometry
    c) osmometry
45. Active alkalinity is:
    a) the concentration of alkali
    b) the concentration of hydroxide ions
    c) the concentration of protons
46. Potential alkalinity is:
    a) the concentration of non-dissociable molecular basis
    b) the concentration of the base
    c) the concentration of hydrogen ions
47. Total alkalinity is:
    a) the concentration of non-dissociable molecular basis
    b) the total concentration of bases
    c) OH concentration
48. Formula for the active alkalinity of a solution of strong base:
    a) $[OH^-] = \alpha$ [base]
    b) $[OH^-] = \alpha$ + [base]
    c) $[OH^-] = \alpha$ – [base]
49. Formula for the active alkalinity of a solution of weak base:
    a) $[OH^-]=\sqrt{Kd \cdot [base]}$
    b) [OH-] = [base]
    c) $[OH^-]$ = Kd • [base]
50. pH is:
    a) the natural logarithm of the concentration of protons
    b) the negative logarithm of proton concentration
    c) the negative logarithm of the concentration of acid
51. Formula for pH of strong acid solution:
    a) pH = - lg Kd [acid]
    b) pH = - lg [acid]
    c) pH = - lg α - [acid]
52. Formula for solution pH of weak acids:
    a) $pH = -\lg\sqrt{\hat{E}d \cdot [acid]}$
    b) pH = - lg [acid]
    c) pH = - lg Kd • [acid]
53. pOH is:

a) the natural logarithm of the concentration of alkali
b) the negative logarithm of the concentration of hydroxide ions
c) the negative logarithm of the concentration of base

54. Formula for pH solution base:
a) pOH = - lg α [base]
b) pOH = - lg α + [base]
c) pOH = - lg α - [base]

55. Formula for the solution pOH of strong base:
a) pOH = - lg [base]
b) pOH = - lg α + [base]
c) pOH = - lg α - [base]

56. Formula for pOH solution of weak base:
a) $pOH = -\lg\sqrt{Kd \cdot [base]}$
b) pOH = - lg [base]
c) pOH = - lg K • [base]

57. pH + pOH =
a) 7
b) 14
c) 1

58. pH of blood is:
a) 7.36
b) 1.86
c) 6.02

59. pH of gastric juice is:
a) 7
b) 0,9-1,5
c) 3,1-4,4

60. pH of urine is:
a) 4,8-7,5
b) 8-10,5
c) 3,1-4,4

61. Pepsin in gastric juice acts as:
a) acidic medium
b) an alkaline medium
c) an neutral environment

62. Venous blood pH is:
a) greater than arterial blood pH
b) lesser than the pH of arterial blood
c) equal to the pH of arterial blood

63. pH in the cell:
a) lesser than the pH of the blood
b) blood pH greater than
c) the same as pH levels.

64. Acidosis — a shift in blood pH:
a) in the alkaline side
b) in the acid side
c) to pH 7

65. Alkalosis — a shift in blood pH:
a) in the acid side
b) in the alkaline side

c) to pH 7

66. pH of 0.0001 M sulphate solution is:
    a) 1
    b) 4
    c) 10
67. pH of 0.001 M solution NNO_3 is:
    a) 4
    b) 3
    c) 11
68. pOH of 0.1 M HCl solution is:
    a) 1
    b) 12
    c) 13
69. pH of 0.001 M NaOH is:
    a) 3
    b) 11
    c) 6
70. pOH 0.01 M KOH solution is:
    a)12
    b) 2
    c) 7
71. If the pOH alkali solution is 4, the concentration of H^+ is:
    a) 10^{-4}
    b) 10^{-7}
    c) 10^{-10}
72. If the acid solution pH is 8, the concentration of OH^- is:
    a) 10^{-4}
    b) 10^{-7}
    c) 10^{-6}

5. The main questions of the seminar:

5.1. Brensted and Loury theory of acids and bases.
5.2 Dissociation constant and ion product of water
5.3. Total, active and potential acidity and basecity and their calculations.
5.4. Oswald's law of dilution.
5.5. Calculation of the strong and weak electrolyte of pH.
5.6. Biological meaning of pH (the value of blood, stomach liquid, urine, intestinal liquid, acidosis and alkalosis, the influence of pH values on the activity of enzymes).
5.7. Indicators: the points of inflection; methyl orange and phenolphthalein, the standard indicator.

6. The question for individual learning:

6.1. What is an indicator?
6.2. Determination of pH using indicators.

7. The examples of the task:

7.1. What is pH of solution knowing that the concentration of H^+-ions is $4.2\ 10^{-5}$•mol/l)
The answer:
$[H^+] = 4{,}2 \cdot 10^{-5}$ mol/l.
$pH = -\log [H^+] = \lg 4.2 \cdot 10^{-5} = -\lg 462 - \lg 10^{-5} = 5 - 0.62 = 4.8$

7.2. What is the pH value of HCl solution knowing that HCl concentration is 0.15 mol/l and

NaOH is 0.2 mol/l?
The answer:
HCl solution pH = - lg[H^+]; [H^+] = α·[acid] = 1· 0.15 = 0,15 mol/l
pH = -lg 0.15 = -lg 1.5· 10^{-1} = - lg 1.5 – lg 10^{-1} = 1 – 0.18 = 0.82
NaOH solution pH + pOH = 14; pH = 14 – pOH; pOH = - lg [OH^-]
[OH^-] = α·[base] =1 · 0,2 = 0,2 mol/l
pOH = -lg 0.2 = -lg 2 · 10^{-1} = - lg 2 –lg 10^{-1}= 1 – 0.3 = 0,7
pH = 14 – 0,7 = 13,3.

7.3. Calculate the pH values of HCOOH solution with C_N= 0.1 mol/l (K_d= 1.8·10^{-5}) and NH_4OH solution with Cn=0.2 mol/l (K_d = 1.85 · 10^{-5}).
The answer:
HCOOH solution of pH = -lg[H^+]

$$[H^+] = \sqrt{K_D \cdot [acid]} = \sqrt{1.8 \cdot 10^{-1} \cdot 0.1} = 4.24 \cdot 10^{-3}$$

pH = - lg 4.24 ·10^{-3} = -lg 4.24 – lg 10^{-3} = 3 - 0.63 = 2.37 .

NH_4OH solution of pH = 14 – pOH
pOH = - lg[OH^-]

$$[OH^-] = \sqrt{K_D \cdot [base]} = \sqrt{1.8 \cdot 10^{-5} \cdot 0.2} = 1.92 \cdot 10^{-3}$$

pOH = -lg 1.92 · 10^{-3} = -lg 1.92 - lg 10^{-3} = 3 – 0.28= 2.72
pH = 14 – 2.72 = 11.28.

7.4. What is the pH of the solution knowing that 80 ml of water and 20 ml of 0.1 M (α = 1) sodium
hydroxide were mixed?
The answer: since after mixing the base solution was obtained, equivalent law is used to find
The pH $V_1 \cdot C_1 = V_2 \cdot C_2$;
V_2 = 80 ml + 20 ml = 100 ml

$$C_2 = \frac{V_1 \cdot C_1}{V_2} = \frac{20 \cdot 0{,}1}{100} = 0{,}02 = 2 \cdot 10^{-2}$$ (the concentration of resulting solution)

[OH^-] = α· C_{base} =1 · 2·10^{-2}.
pOH = -lg[OH^-] = - lg 2·10^{-2} = - lg 2 – lg 10^{-2} = 2 -0.3 = 1.7
pH = 14 – 1.7 = 12.3
ΔpH = 12.3 – 7 = 5.3.

7.5. What is the pH of the solution after mixing the equal volumes of 0.2 M (α =1) HCl and of 0.1 M(α = 1) NaOH?
The answer: HC1 + NaOH = NaC1 + H_2O
Acid interacts with base in ratio 1:1. Thus, 0.1 mol of HCl is in excess in solution (0.2 – 0.1 = = 0.1M). The volume of the mixture was doubled twice resulting the final concentration of HCl is equal of 0.05 M.
[H^+] = α·[acid] = 1 · 0.05 = 5 · 10^{-2}.
pH = - lg [H^+] = - lg 5·10^{-2} = 2 – 0,7 = 1.3 .

7.6. What are the concentration of hydrogen ions in blood at pH = 7.36?

8. Control test:

Sample 1

- What is the ionic product of water?

- What is the pH of 0.001 M NaOH?
- What is the equation of pH calculation of the weak acids?
- What is the pH of the solution if the equal volumes of 0.25 M HNO_3 and of 0.1 M of NaOH were mixed?
- Calculate $[OH^-]$ if pH=3.24.

Sample 2

- What is the pH of 0.0001 M sulfuric acid?
- What is the ionic product of water if pH=2?
- What is the active acidity?
- What is the pH of NaOH (ρ=1, α=1) if 10 ml of it was added to 40 ml of water?
- What is the concentration of HCl if pH=0.7?

TOPIC 7: Volumetric analysis. Neutralization method. Alkalimetry. Acidimetry.

1. Actuality of the topic: neutralization method is a part of volumetric analysis in acids, bases and salts. This method is widely used for the quantitative analysis of medical composites in clinical and biological investigations.

2. General aim:is to interpret the results of the analysis in medical practice.

3. Actual aims and abilities:

- to prepare the working solutions;
- to be able to establish the molar equivalent concentration of the working solutions.
- to be capable of detecting the percent containing hydrochloric acid in pharm drugs.

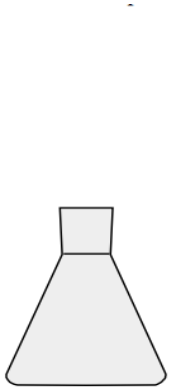
4. Literature:

4.1. Lecture materials;

Titration or volumetric analysis is the part of the quantitative analyzing substances.
Titration — is a procedure of careful addition of one solution to another.
Measuring utensils and its application.
Titrimetric analysis uses different measuring chemical vessels.
1) Conical flasks used for titration.
2) Volumetric flasks used for the preparation of solutions exact concentration.
4) Burette — for titration.
3) Pipettes — to transfer a certain amount of liquid.
4) Funnels — to filter sediments.
5) Glass measuring — to measure the approximate volume of fluid.

Titrimetric analysis is based on an accurate measurement solution value titrate spent on interaction with a certain amount of test substance.

Titrated solution is solution called with exactly known concentration.

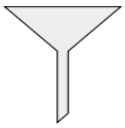


Conical flask

Volumetric flask

Burette

Pipette



Funnel

Glass measuring

Methods of preparation of titrant:

1) Fiksanal: ampoule accurately weighed, weight substance which is dissolved in a given volume of solvent;

2) For accurately weight, which was dissolved in a defined volume of solvent;

3) Estimate by rigging, and then installing the exact concentration (titer) in the starting material.

Not all substance can be prepared by volumetric solution, accurately weighed. For example: NaOH is absorbs moisture from the air and carbon (IV) oxide (carbon dioxide); as well H_2SO_4 is highly hygroscopic (absorbs water). Therefore, taking the approximate weight, dissolved in the water and then mainting on the titer of the starting material. Sources of substances which are prepared by titrant are accurately weighed.

Such substances must meet a certain requirements:

a) Must be chemically pure, i.e. not containing the impurities;

b) The composition must be conform to the formula. For example, $H_2C_2O_4 \cdot 2H_2O$;

c) Should not be changed during storage;

d) Must be well soluble in water.

End of the reaction between the test of solution and titrated to establish the change in color of the indicator.

Indicators — these are a weak organic acids or bases that change their color depending on pH. pH range where the indicator changes its color is called a color change interval.

Indicators change their color as molecules and ions have different color bar graph, and the presence of molecules or ions depends on the reaction of medium solution.

Depending on the type of chemical reaction, in the titrimetric analysis is divided into different methods: neutralization, precipitation chelatometry, oximetry.

We examine a method of neutralizing or method of acid-base titration.

Neutralization method — a method of volumetric analysis in which titrant uses acids and bases. Method is based on the neutralization reaction. For example:

$$HCl + NaOH \rightarrow NaCl + H_2O.$$

In ionic form, the equation can be written as:

$$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O.$$

Short ionic equation:

$$H^+ + OH^- \rightarrow + H_2O$$

This is the basic equation of the method of neutralization.

pH REACTION MEDIUM WATER SOLUTIONS

The method of neutralization

Neutralization method — a method of volumetric analysis, which uses volumetric solution of acids and alkalis. The method is based on neutralization reaction: $H^+ + OH^- \rightleftarrows H_2O$.

Depending on the method of neutralization of the titrant, it is divided into alkalimetry and acidimetry.

Water — a weak electrolyte that dissociates by the equation:

$$H_2O \rightleftarrows H^+ + OH^-$$

Ionic product of water — a product of the concentration of hydrogen ions (protons) on the concentration of hydroxide ions:

$$[H^+] + [OH^-] = 10^{-14}$$

It is a constant at a given temperature.

↑ ACID ↑	***Strength***	***Hydroxyl ions***	***pH***	***Hydrogen ions***	***Common Substances***	↓ ALKALINE ↓
	Strong Acid	10^{-14}	0	10^{0}	Sulphuric Acid	
		10^{-13}	1	10^{-1}	Hydrochloric Acid	
		10^{-12}	2	10^{-2}		
		10^{-11}	3	10^{-3}	Lemon Juice/vinegar	
	Weak Acid	10^{-10}	4	10^{-4}	Wine of beer	
		10^{-9}	5	10^{-5}	Human Scin	
		10^{-8}	6	10^{-6}	Rain water	
	Neutral	10^{-7}	7	10^{-7}	Distilled water	
	Weak Alkali	10^{-6}	8	10^{-8}	Ethanol/blood	
		10^{-5}	9	10^{-9}	Sea water	
		10^{-4}	10	10^{-10}	Milk of magnesia	
	Strong Alkali	10^{-3}	11	10^{-11}	Lime water	
		10^{-2}	12	10^{-12}	Ammonia	
		10^{-1}	13	10^{-13}		
		10^{0}	14	10^{-14}	Lye	

Table 8.1

Dissociation of acids follows of the scheme:

$$CH_3COOH \rightleftarrows H^+ + CH_3COO^-$$

Active acidity is a concentration drowned.

Potential acidity is a concentration dissociating acid of molecules.

Total acidity is the total concentration of acid in the mole eq.

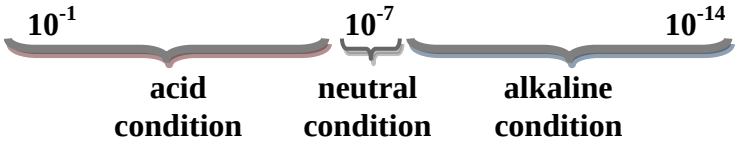
The amount of active and potential acidity equal to the total acidity.

When the titration is determined by the total acidity.

Total alkalinity is the concentration of anions hydroxide.

Potential alkalinity is the concentration of undissociated molecules of the base.

Total alkalinity is the total concentration of alkali in the mole eq.
The amount of active and potential alkalinity equals to total alkalinity.
When the titration is determined by the total alkalinity.
The reaction of medium is determined by the concentration of protons.



Concentration of protons in an acid solution is calculated by the formula:

$$[H^+] = \alpha \bullet [acid] \qquad [OH^-] = \alpha \bullet [base]$$

strong acid, $\alpha = 1$

$$[H^+] = \alpha \bullet [acid] \qquad [H^+] = \sqrt{Cd \bullet [acid]}$$

α — acid degree of dissociation

The dissociation of the base form of hydroxide anions, whose concentration is calculated as follows:

strong base, $\alpha = 1$

$$[OH^-] = \alpha \bullet [base] \qquad [OH^-] = \sqrt{Cd \bullet [base]}$$

α — base degree of dissociation

The reaction of medium is more convenient to express the solution via the pH.
pH is the negative logarithm of hydrogen ion concentration:

$$pH = -\lg[H^+]$$

Similarly, we can calculate the pOH:

$$pOH = -\lg[OH^-]$$

Based on the negative logarithm of the ion product of water is:

$$pOH + pH = 14$$

blood pH = 7.36;
gastric juice pH = 0,9 – 1,5.

Examples

A. Calculating the pH of solutions of strong and weak acids and bases.

1) Calculate the pH, if $[H^+] = 10^{-2}$.

$$pH = -\lg[H^+] = -\lg 10^{-2} = 2.$$

2) Calculate the pOH if $[OH^-] = 10^{-5}$.

$$pOH = -\lg[OH^-] = -\lg 10^{-5} = 5.$$

3) Calculate the pH if $[OH^-] = 10^{-4}$.

$$pOH = -\lg[OH^-] = -\lg 10^{-4} = 4.$$
$$pH = 14 - pOH = 14 - 4 = 10.5$$

4) Calculate the pH of the solution with the concentration of H^+ -ion $3{,}7 \cdot 10^{-5}$ mol / liter.

$[H^+] = 3{,}7 \cdot 10^{-5}$	$pH = -\lg[H^+] = -\lg 3{,}7 \cdot 10^{-5} = -\lg 3{,}7 - \lg 10 - 5 = 5 - 0.57 = 4.43.$
pH =?	

The answer: pH = 4.43.

5) Calculate the pH of HCl C_N = 0.1 mol/liter.

C_N (HCl) = 0,1 mol/l pH -?	1)To calculate the pH of the solution, one must know $[H^+]$. Since the strong acid is HCl. Then $[H^+] = [\text{acid}] = 0.1\ \text{mol/l} = 10^{-1}$;

2) Find the pH of the solution:

$$pH = -\lg[H^+] = -\lg 10^{-1} = 1.$$

The answer: pH = 1.

6) Calculate the pH of 0.0001 N HCl solution.

$$pH = -\lg[\text{HCl}] - \lg[H^+] = -\lg \cdot 10^{-4} = 4.$$

7) Calculate the pH of the NaOH with CH = 0.2 mol/liter.

C_N (NaOH) = 0.2 mol/l pH =?	1) Because of the condition given by the foundation, then first we will find $[OH^-]$. In a solution of strong base $[OH^-] = [\text{base}] = 0{,}2 = 2 \cdot 10^{-1}$;

2) Find the pOH: $pOH = -\lg[OH^-] = -\lg 2 \cdot 10^{-1} = -\lg 2 - \lg 10^{-1} = 1 - 0.3 = 0.7.$
3) Find the pH: $pH = 14 - pOH = 14 - 0{,}7 = 13{,}3.$
The answer: pH = 13.3.

8) Calculate the pH of 0.001 N solution of NaOH.

$$pOH = -\lg[\text{NaOH}] = -\lg[OH^-] = -\lg 10^{-3} = 3.$$
$$pH = 14 - pOH = 14 - 3 = 11.$$

9) Calculate the pH of the solution of HCOOH with C_N = 0.1 mol/l (Kd = 1,8 · 10^{-5})

C_N (HCOOH) = 0.1 mol/l Cd = $1{,}8 \cdot 10^{-5}$ pH =?	1) To calculate the pH of the solution, one must know $[H^+]$. Since HCOOH is a weak acid, then use the formula: $[H^+] = \sqrt{\text{Cd} \cdot [\text{acid}]} = \sqrt{1.8 \cdot 10^{-4} \cdot 0.1 = 4.24 \cdot 10^{-3}}$

2) Find the pH: $pH = -\lg 4{,}24 \cdot 10^{-3} = -\lg 4{,}24 - \lg 10^{-3} = 3 - 0.63 = 2.37.$
The answer: pH = 2,37.10

10) Calculate the pH of the solution of NH_4OH with C_N = 0.15 mol/l (Kd = 1,85 · 10^{-5}).

C_N (NH_4OH) = 015 mol/l Cd = $1{,}8 \cdot 10^{-5}$ pH -?	1) Because of the condition given by the foundation, then first find $[OH^-]$. In the solution of a weak base: $[OH^-] = \sqrt{\text{Cd} \cdot [\text{base}]} = \sqrt{1.8 \cdot 10^{-5} \cdot 0.15 = 1.64 \cdot 10^{-3}}$

2) Find the pOH

$$pOH = -\lg 1{,}64 \cdot 10^{-3} = -\lg 1.64 - \lg 10 \cdot 10^{-3} = 3 - 0.21 = 2.79.$$

3) Find the pH: $pH = 14 - pOH = 14 - 2.79 = 11.21.$
The answer: pH = 11.21.

11) Calculate the pH of the solution of H_2SO_4 w = 3% (ρ = 1,1; $F_{eqv.}$ = 1/2).

ω = 3% ρ = 1,1 $f_{eqv.}$ = 1/2 pH -?	1) Transfer IARF share in the normal concentration equivalents using a formula which connects the C_N and ω: $C_N = \frac{\omega\% \cdot \rho \cdot 10}{M_X \cdot f_{eqv.}} = \frac{3 \cdot 1.22 \cdot 10}{98 \cdot 1/2} = 0.73\ \text{mol/l}$

2) Find the $[H^+]$ and the pH:

$$[H^+] = [acid] = 0{,}73 = 7{,}3 \cdot 10^{-1};$$

$$pH = -\lg[H^+] = -\lg 7{,}3 \cdot 10^{-1} = -\lg 7{,}3 - \lg 10^{-1} = 1 - 0{,}86 = 0{,}14$$

The answer: 0,14.

B. Determination of pH solutions after dilution with water.

12) How to change the pH of the solution HNO_3, if a 40ml solution of 0.1N are added to 20ml of water?

$V_1(HNO_3) = 40$ ml $C_{N1} = 0{,}1$ mol/l $V(H_2O) = 20$ ml --- Δ pH (HNO_3) -?	1) Δ pH = pH_1 - pH_2, where pH_1 - pH in solution of HNO_3 before adding water pH_2 is the pH of the solution after the addition of HNO_3 water; 2) Find the pH_1: to calculate the pH of the solution you need to know$[H^+]$. Since the strong acid of HNO_3, then $[H^+] = [acid] = 0.1\ mol/l = 10^{-1}$

3) Find the solution pH_1: pH_1 = - lg $[H^+]$ = -lg 10^{-1} = 1;

4) Upon dilution with water the acid of concentration decreases. Find it by using the law of equivalents: $C_{N_1} \cdot V_1 = C_{N_2} \cdot V_2$; where V_2 - volume of the solution after adding water,

$$V_2 = 40 + 20 = 60\text{ml};$$

hence:

$$C_{N_2} = \frac{C_{N_1} \cdot V_1}{V_2} = \frac{0.1 \cdot 40}{60} = 0.067 = 6.7 \cdot 10^{-2}$$

5) Find pH_2: $[H^+]_2$ = [acid] = 6.7 · 10^{-2};

$$pH_2 = -\lg[H^+] = -\lg 6{,}7 \cdot 10^{-2} = -\lg 6{,}7 - \lg 10^{-2} = 2 - 0{,}83 = 1.17;$$

6) Δ pH = 1.17 - 1 = 0.17.

The answer: 0.83.

13) How to change the pH of the solution of NH_4OH, if a 50 ml 0.1 N solution of its add 30ml of water? (Kd = 1,85·10^{-5}).

$V(NH_4OH) = 50$ml $C_N(NH_4OH) = 0.1$mol/l $Cd = 1{,}8 \cdot 10^{-5}$ $V(H_2O) = 30$ ml --- Δ pH =?	1) Δ pH = pH_1 - pH_2, where pH_1 - is the solution pH before adding NH_4OH water; is the pH of the solution after the addition of NH_4OH water; Since by the condition given by the foundation, then first find $[OH^-]$ In the solution of a weak base

$$[OH^-] = \sqrt{Cd \cdot [base]} = \sqrt{1.8 \cdot 10^{-5} \cdot 10^{-1} = 1.64 \cdot 10^{-3}}$$

2) Find the $pOH_1 = -\lg 1{,}34 \cdot 10^{-3} = -\lg 1{,}34 - \lg 10^{-3} = 3 - 0.127 = 2.87;$

$$pH_1 = 14 - 2.87 = 11.13.$$

3) Upon dilution with water the concentration of base decreases. Find it using the law of equivalents: $C_{N_1} \cdot V_1 = C_{N_2} \cdot V_2$; where V_2 - volume of the solution after adding water,

$$V_2 = 50 + 30 = 80\text{ ml};$$

$$C_{N_2} = \frac{C_{N_1} \cdot V_{N_1}}{V_2} = \frac{0.1 \cdot 50}{80} = 0.0625 = 6.25 \cdot 10^{-2}$$

4) Find the pOH_2: $[OH^-] = \sqrt{Cd \cdot [base]} = \sqrt{1.8 \cdot 10^{-5} \cdot 6.25 \cdot 10^{-2} = 1.06 \cdot 10^{-3}}$

$$pOH_2 = -\lg 1{,}06 \cdot 10^{-3} = -\lg 1{,}06 - \lg 10^{-3} = 3 - 0.025 = 2.975$$

$$pH_2 = 14 - 2.975 = 11.025.$$

5) Find the Δ pH: $\Delta pH = 11.13 - 11.025 = 0.105$.

The answer: 0.105.

14) How to change the pH of water if the 80 ml are added to 20 ml of solution NaOH with C_N = 0.1 mol/l, (α = 1)

$V\,(NaOH) = 20ml$ $C_N\,(NaOH) = 0.1mol/l$ $Cd = 1{,}8 \cdot 10^{-5}$ $V(H_2O) = 80\ ml$	1) H_2O – pH = 7; 2) After you have added solution of NaOH to the water obtained by solution of the base, the concentration which we find in law of equivalents:
$\Delta\ pH = ?$	$$C_{N_1} \cdot V_1 = C_{N_2} \cdot V_2$$ $$V_2 = 80\ ml + 20\ ml = 100\ ml.$$

3) Find the concentration of alkali solution, C_{N2}, $[OH^-]$, pOH and pH:

$C_{N_2} = \frac{C_{N_1} \cdot V_{N_1}}{V_2} = \frac{0.1 \cdot 20}{100} = 0.02 = 2 \cdot 10^{-2}$ – concentration of NaOH in the solution.

$$[OH^-] = [base] = 2 \cdot 10^{-2}.$$
$$pOH = -\lg 2 \cdot 10^{-2} = -\lg 2 - \lg 10^{-2} = 2 - 0.3 = 1.7$$
$$pH = 14 - 1.7 = 12.3$$

4) Find the change in the pH of water: $\Delta\ pH = 12.3 - 7 = 5{,}3$.

The answer: 5.3.

B) Determination of the pH after pouring acid solutions and base.

15) Determine the pH of the solution obtained after mixing the equal volumes of HCl and C_N = 0.3 mol/l NaOH

$C_N = 0.1mol/l$ $C_N\,(HCl) = 0.3mol/l$ $C_N\,(NaOH) = 0.1mol/l$ $V(HCl) = V(NaOH)$	1) When mixing acid and alkali reactents according to the equation:
$pH = ?$	$$HCl + NaOH \rightarrow NaCl + H_2O;$$

From the equation it is clear that the acid and alkali react in a ratio of 1:1. Since the acid was taken 0.3 mol after reaction in solution remained acid: $0{,}3 - 0{,}1 = 0{,}2$ mol. Since the volume of the mixture increased 2 times, the concentration of acid in solution: $0{,}2/2 = 0.1$ mol/l;

2) Find the pH of the resulting solution:

$$[H^+] = [acid] = 0{,}1 = 10.^{-1}$$
$$pH = -\lg [H^+] = -\lg 10^{-1} = 1.$$

The answer: pH = 1.

16) Determine the pH of the solution obtained after mixing equal volumes of solutions of H_2SO_4 and C_N = 0.2 mol/l NaOH with C_N = 0.6 mol/liter.

$C_N\,(H_2SO_4) = 0.2mol/l$ $C_N\,(NaOH) = 0.6mol/l$ $V(H_2SO_4) = V(NaOH)$	1) When mixing acid and alkali reactens according to the equation:
$pH = ?$	$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O;$$

From the equation it is clear that the acid and alkali react in the ratio 1:2. The acid was taken 0.2 mole, then:

1 mol H_2SO_4 — 2 mol NaOH

0.2 mol H_2SO_4 — x mol NaOH

x = 0.4 mol NaOH.

By the condition of the problem given 0.6 mol NaOH, then left after the reaction $0.6 - 0.4 =$ 0.2 mol NaOH. Since the volume of the mixture was increased 2 times, the concentration of NaOH solution: $0{,}2/2 = 0.1$ mol/l;

2) Find the $[OH^-]$, pOH, pH, the resulting solution:

$$[OH^-] = [\,base\,] = 0{,}1 = 10^{-1}.$$
$$pOH = -\lg [OH^-] = -\lg 10^{-1} = 1.$$
$$pH = 14 - pOH = 14 - 1 = 13.$$

The answer: pH = 13.

G. Calculation of $[H^+]$ for a given value of pH and pOH.

17) Calculate the $[H^+]$ in the blood if the pH = 7.36.

$pH = 7.36$
$[H^+] = ?$

$$[H^+] = \text{ant lg}\, pH = \text{ant lg}\, 7{,}36 = \text{ant lg}\,[\,8 - 0.64\,] = 4{,}36 \cdot 10^{-8}\text{mol/l}$$

The answer: $4{,}36 \cdot 10^{-8}$ mol/l

18) Calculate the $[H^+]$ solution if pOH = 4.29.

$pOH = 4.29$
$[H^+] = ?$

1) Find the pH:

$$pH = 14 - pOH = 14 - 4{,}29 = 9.71;$$

$$[H^+] = \text{ant lg}\, pH = \text{ant lg}\, 9{,}71 = \text{ant lg}\,[\,10 - 0.29\,] = 1{,}95 \cdot 10^{-10}\text{mol/l}.$$

The answer: $1{,}95 \cdot 10^{-10}$mol/l

Depending on the method of titration neutralization method is divided into Alkalimetry and acidimetry.

Alkalimetry

Alkalimetry — a method of determining the acids and salts giving acidic reaction in the hydrolysis using an alkali titrant.

Titrated solutions — are solutions of NaOH or KOH. Their composition is unstable (they absorb H_2O and CO_2 from the air), the first solution is prepared by estimated rigging, and then establish a titer of Exodus substances. The starting materials are in alkalimetry oxalic acid $H_2C_2O_4 \cdot 2H_2O$ (HOOC-COOH) or succinic acid, HOOC-CH_2- CH_2-COOH which react with the working solution as the alkali:

$$H_2C_2O_4 + NaOH \rightarrow Na_2C_2O_4 + H_2O$$

$$HOOC\text{-}CH_2\text{-}CH_2\text{-}COOH + NaOH \rightarrow NaOOC\text{-}CH_2\text{-}CH_2\text{-}COONa + H_2O$$

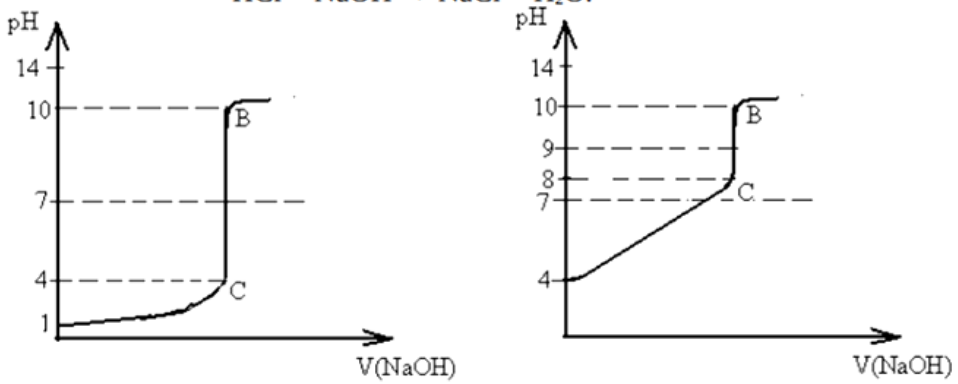
Stroke is characteriz by titration curve.

The titration curve shows the change in pH of the solution titration according to the amount that is titrated.

There are two cases in alkalimetry titration.

A) Strong acid is titrated with a strong base (alkali)

$$HCl + NaOH \rightarrow NaCl + H_2O.$$



А Б

Consider the curve A:

The initial pH of the strong acid may be equal to 1. When you titrate this solution with an alkali solution pH gradually increases — stage 1 - C. At point C the acid is very little, and when you add a drop of discharged standard solution of alkali there is a sharp change in pH— segment C - B. This changes of the color, of the indicator and finishes titration.

Such an abrupt change in pH when adding one extra drop of titrant is called jump titration. In the titration of the strong acid the alkali titration jump within a pH of 4-10.

Titration jumps in the middle point with pH = 7. This equivalence point, i.e. the pH at which the substance reacts in equivalent amounts. The end-point is determined by the change in color of the indicator. The principle of selection of the indicator is as follows: the transition interval indicator should coincide with a jump of the titration. For this case we take phenolphthalein indicator, as its color transition interval of pH = 8,2-10,0. In the beginning the acid in the test solution changes phenolphthalein colorless and at the end of the titration appears crimson color.

B) Weak acid is titrated with a strong base. For example:

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O \quad (1)$$

$$CH_3COOH + H_2O \rightarrow CH_3COOH + Na^+ + OH^- \quad (2)$$

Consider the curve B:

The initial pH of the weak acid may be equal to 4. When you added to this solution was titrated with an alkali solution pH gradually increases - section 4 - C. At point C is very little acid, and adding a drop of titrant discharge alkali is a sharp change in pH - C- section B. This changes the color of the indicator and titration finishes.

In the titration of a weak acids with alkali titration jump within pH = 8-10 equivalence point and pH = 9.

Phenolphthalein indicator also changes.

That is, when titrating with an alkali, it is preferable to use the phenolphthalein indicator.

In the titration of a weak acid and alkali, why is the jump equivalence point in an alkaline environment? This is due to the fact that the interaction of the weak acid and the alkali salt is formed (rection 1), which is hydrolyzed and provides an alkaline environment (reaction 2)

Alkalimetry application in medicine

Currently, there are many methods for determining the concentration of substances, but alkalimetry is used for preliminary analysis or in cases when there is no possibility to apply other methods.

For example, using alkalimetry can define:

Acid: HCl — 8,2-8,3%-solution is used as a pharmaceutical grade formulation at low pH; H_2SO_4, H_3PO_4, H_3BO_3, CH_3COOH, citric acid, etc. are used in pharmacy for analysis of biological fluids and can determine acidity of the gastric juice, urine.

Acidimetric

Acidimetric — a method of determining bases and salts giving at alkaline hydrolysis using acid titrant.

Titrated solutions working method — are solutions of HCl or H_2SO_4.

Since their composition are unstable (HCl evaporates, namely "smoke" and H_2SO_4 absorb water from the air), the first solution is prepared by estimated rigging, and then a titer of Exodus substances.

The starting materials are in the acidimetric:

Washing soda Na_2CO_3;

Borax (sodium tetra borate) $Na_2B_4O_7 \cdot 10H_2O$;

Sodium oxalate $Na_2C_2O_4$.

They react with acids working solution as follows:

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2\uparrow + H_2O$$

$$Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 4H_3BO_3 + 2NaCl$$

$$Na_2C_2O_4 + 2HCl \rightarrow H_2C_2O_4 + 2NaCl$$

These salts can be used as starting materials, since they provide for an alkaline hydrolysis reaction, and can be titrated with acid.

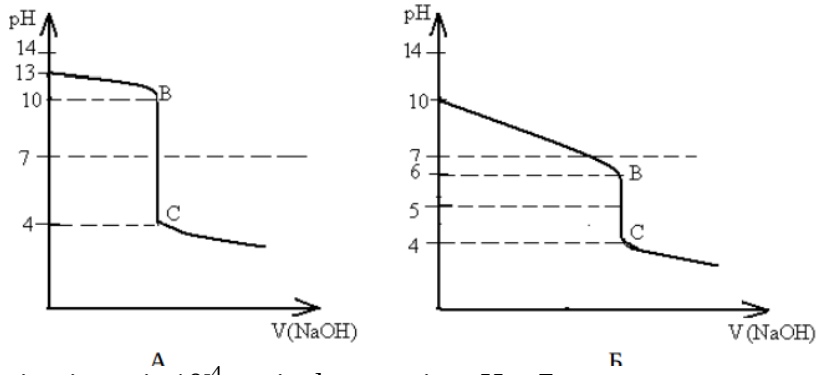
Stroke is characterized by a titration curve.

A) The strong base is titrated with a strong acid:

$$NaOH + HCl \rightarrow NaCl + H_2O$$

Consider the curve A:

The initial pH of the strong base can be equal to 13. When you added to this solution a titrant acid pH decreases gradually — segment 13 - B. At point B, the base is very small, and when you add one drop of titrant acid there is a sharp change in pH — section B - C. It changes the color of the indicator and titration is finished.



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Thus, the pH titration jump is 10^{-4} equivalence point pH = 7.

Methyl orange indicator is chosen as its transition interval, pH = 3,1-4,4 coincides with a jump in the titration. That is, in the test solution, methyl orange is yellow in base, and at the end of the titration changes color to pink.

The weak base titrated with a strong acid. For example:

$$NH_4OH + HCl \rightarrow NH_4Cl + H_2O$$

$$NH_4Cl + H_2O \rightarrow NH_4OH + H^+ + Cl^-$$

Consider the curve B:

The initial pH of the weak base can be equal to 10. When you add to this solution a titrant acid pH decreases gradually — segment 10 - B. At point B, the base is very small, and when you add one drop of titrant acid there is a sharp change in pH - segment BC. This changes the color of the indicator and complete the titration.

In the titration of a weak base with a strong acid titration jump lies within a pH = 6-4, and the equivalence point of pH = 5.

It is used methyl orange indicator.

That is, when a strong acid titration is used it is preferable to use methyl orange indicator.

In the titration of a weak base with a strong acid titration jump and the equivalence point are in an acidic environment. This is explained with the fact that the interaction of a weak base and a strong acid, a salt (reaction 1), which is hydrolyzes and provides an acidic environment (reaction 2).

Acidimetry application in medicine

Currently, there are many methods for determining the concentration of substances, but it is used in pre acidimetric analysis or in cases where there is no possibility to apply other methods.

For example, using for acidimetry can define:

- NaOH, KOH used in pharmacy for the analysis;
- NH_4OH measured in drinking water, as its excess adversely affects the central nervous system;
- $NaHCO_3$ antacid is necessary to know its purity;
- Define the temporary hardness of water;
- Determine the pH of the intestinal juice.

VOLUMETRIC ANALYSIS

Volumetric or titrimetric analysis is based on an accurate measurement of the volume of titrant spent in the reaction with the substance under investigation.

Titrated solution is a solution with exactly known concentration.

The initial call substances that can prepare a solution of accurate weight.

Indicators — are weak organic acids or bases that change their color depending on the pH of the solution.

The interval transition color indicator — this pH range in which the indicator changes its color.***(Table 6.1)***

Main article: Acid-base titration			
Indicator	***Color on Acidic Side***	***Range of Color Change***	***Color on Basic Side***
Methyl Violet	Yellow	0.0 - 1.6	Violet
Bromophenol Blue	Yellow	3.0 - 4.6	Blue
Methyl Orange	Pink	3.1 - 4.4	Yellow
Methyl Red	Red	4.4 - 6.2	Yellow
Litmus	Red	5.0 - 8.0	Blue
Bromothymol Blue	Yellow	6.0 - 7.6	Blue
Phenolphthalein	Colorless	8.3 - 10.5	raspberry
Alizarin Yellow	Yellow	10.1 - 12.0	Red

Table 7.1

Challenges for the preparation of solutions in alkalimetry

19) Calculate the sample of the solution for preparation of 2 l NaOH, if the title will be set to 0.1 N solution of oxalate (oxalic acid).

$V = 2\,l$
$C_N(H_2SO_4) = 0.1\ mol/l$
$m(NaOH) = ?$

1) As the titre of alkali will establish by 0.1 N solution of $H_2C_2O_4$, the alkaline solution should be also 0.1N.

2) To calculate the mass of alkali, use the formula C_N:

$$C_N = \frac{m_x}{M_x \cdot f_{eqv.} \cdot V}$$

hence

$$m_x = C_N \cdot M_x \cdot f_{eqv.} \cdot V = 0.1 \cdot 40 \cdot 1 \cdot 2 = 8\ g$$

The answer: The weight of alkali 8g.

20) Calculate the weight for the preparation of 1 liter of 0.15 N KOH solution.

$V = 1\,l$
$C_N = 0.15\ mol/l$
$m(KOH) = ?$

1) For the calculation we write the formula, C_N

$$C_N = \frac{m_x}{M_x \cdot f_{eqv.} \cdot V}$$

hence

$$m_x = C_N \cdot M_x \cdot f_{eqv.} \cdot V = 0.15 \cdot 56 \cdot 1 \cdot 1 = 8.4\ g$$

The answer: The weight of 8.4g, the alkali

21) Calculate the sample of the solution for preparation 2 l KOH, if the initial will be set at 0.1 N solution of succinic acid.

$V = 2\,l$
$C_N(S_4N_2O_7) = 0.1\ mol/l$
$m(KOH) = ?$

1) As the initial of alkali is established by 0.1 N solution $S_4N_6O_4$, the solution by 0.1 N solution of $S_4N_6O_4$, the solution should also be 0.1 N

2) To calculate the mass use of alkali formula C_N:

$$C_N = \frac{m_x}{M_x \cdot f_{eqv.} \cdot V}$$

hence

$$m_x = C_N \cdot M_x \cdot f_{eqv.} \cdot V = 0.1 \cdot 56 \cdot 1 \cdot 2 = 11.2 \text{ g}$$

The answer: The weight of alkali is 11.2 g

22) What volume of 30% solution H_2SO_4 (ρ = 1,18) is necessary for preparation of 2 l working solution with C_N = 0.1 mol/l, if acid reacts completely?

$\omega_1 = 30\%$
$V_2 = 2$ l
$\rho = 1.18$
$C_{N_2} = 0.1$ mol/l
$V_1 = ?$

Denote the parameters of the original 30% solution ; numeral 1, and the solution which we must prepare –0,1 N - the numeral 2.

1) data from the first solution is insufficient to calculate formula of mass fraction, so use the formula for molar concentration C_N equivalent to finding the mass of material in the second solution:

$$C_N = \frac{m_x}{M_x \cdot f_{eqv.} \cdot V}$$

hence

$$m_x = C_N \cdot M_x \cdot f_{eqv.} \cdot V = 0.1 \cdot 98 \cdot 1/2 \cdot 2 = 9.8 \text{ g}$$

(As sulphuric acid reacts completely, two hydrogen atoms are replaced by metal, then the equivalence factor is 1/2).

2) The mass of the solute is the same in both solutions

$$m_{x_1} = m_{x_2}$$

3) Using the mass fraction, we find the mass of the first solution:

$$\omega = \frac{m(x)}{m(sol.)} \cdot 100\%$$

hence

$$m(sol.) = \frac{m(x)}{\omega} \cdot 100\% = 32.7 \text{ g}$$

4) Find the volume of the 30% solution:

$$V = \frac{m(sol.)}{\rho} = \frac{32.7}{1.18} = 27.68 \text{ ml}$$

The answer: We need to take 27.68 ml 30% of the solution and pour water to 2 l.

Acidimetry — a method of determining the bases and salts, which give the hydrolysis of alkaline reaction, with the help of titrant acid.

Titrant acid HCI and H_2SO_4 are prepared for a rough trial, and then they establish their titre, the exact concentration of precursor – sodium carbonate Na_2CO_3, sodium tetra borate (borax)$Na_2B_4O_7 \cdot 10H_2O$ and sodium oxalate $Na_2C_2O_4$. Acid solutions are prepared with the same concentration as the starting material, sample of the acid is calculated knowing the concentration of the substance.

Challenges for the preparation of solutions in acidimetric

23) Calculate the mass of hydrochloric acid is necessary for the preparation of 3 l of the solution, if the titre will be installed on the 0.1 N solution of sodium carbonate.

$V = 3$ l
$C_N(Na_2SO_3) = 0.1$ mol/l
$m(HCl) = ?$

1) As the titre of hydrochloric acid will set to 0.1 N solution of Na_2SO_3, then the acid solution should be 0.1 N too

2) To calculate the mass of the acid we use the formula C_N:

$$C_N = \frac{m_x}{M_x \cdot f_{eqv.} \cdot V}$$

hence

$$m_x = C_N \cdot M_x \cdot f_{eqv.} \cdot V = 0.1 \cdot 36.5 \cdot 1 \cdot 3 = 10.5 \text{ g}$$

The answer: The mass of acid was 10.5g

24) Calculate the molar concentration of H_2SO_4, if in 400 ml of solution containing 49g acid.

$V = 400$ ml $m(H_2SO_4) = 49$ g $C_x = ?$	1) Write the formula for molar concentration: $$C_x = \frac{m_x}{M_x \cdot f_{eqv.} \cdot V} = \frac{49}{98 \cdot 0.4} = 1.25 \text{ mol/l}$$

T he answer: C_X (H_2SO_4) = 1,25 mol/liter.

25) Calculate the mass of Na_2SO_3 to prepare 1 l titrated of solution with C_N = 0.1 mol/liter.

$V = 1$ l $C_N(Na_2SO_3) = 0.1$ mol/l $m(Na_2SO_3) = ?$	1) To calculate the mass of Na_2SO_3 use the formula C_N: $$C_N = \frac{m_x}{M_x \cdot f_{eqv.} \cdot V}$$ hence $$m_x = C_N \cdot M_x \cdot f_{eqv.} \cdot V = 0.1 \cdot 106 \cdot 1/2 \cdot 1 = 5.3 \text{ g}$$

The answer: The mass of carbonate 5.3 g

26) Calculate the mass of a phosphate acid necessary for the preparation of 2 l of the solution, if the titre will be installed on the 0.1 N solution of borax.

$V = 2$ l $C_N(Na_2V_4O_7) = 0.1$ mol/l $m(Na_2V_4O_7) = ?$	1) Since the titer of the phosphate acid will set to 0.1 N solution of borax, then the acid solution should be 0.1 N too. 2) To calculate the mass of the acid we use the formula C_N: $$C_N = \frac{m_x}{M_x \cdot f_{eqv.} \cdot V}$$ hence $$m_x = C_N \cdot M_x \cdot f_{eqv.} \cdot V = 0.1 \cdot 202 \cdot 1/2 \cdot 2 = 20.2 \text{ g}$$

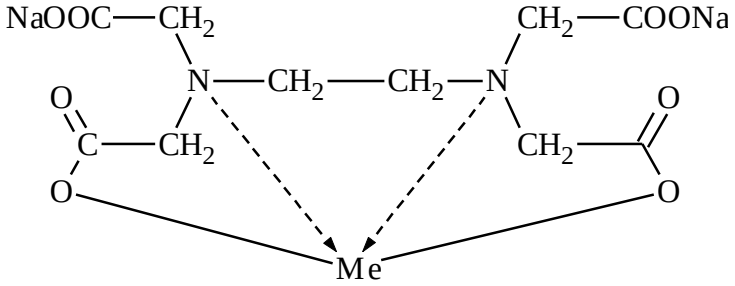
The answer: The mass of acid was 20.2g

CHELATOMETRY

Chelatometry is a method of volumetric analysis, which uses titrant complexing.

Complexones — amino polycarbonic acids and their derivatives.

Increasingly using ethylenediaminetetraacetic acid (**Trilon B)**, which is to give chelates metal cations:



Picture 7.1

To determine the end of the titration using indicators — Black T, blue chromogen, murexid.

The chemistry of the method:

$$Ind + Me \rightarrow Me\text{-}Ind;$$

blue cherry

$$Me\text{-}Ind + TrB \rightarrow Me\text{-}TrB + Ind$$

cherry red

The starting materials of the method: MgO; $CaCO_3$, Zn.

Examples

27) How many grams of Trilon B is necessary for the preparation of 250ml solution with C_N = 0.05 mol / l ?

$V = 250$ ml $C_N = 0.05$ mol/l $m_x = ?$	1) Since the problem is given by the molar concentration equivalent of C_N, the solution begins with the formula C_N: $$C_N = \frac{m_x}{M_x \cdot f_{eqv.} \cdot V}$$

hence

$$m_x = C_N \cdot M_x \cdot f_{eqv.} \cdot V = 0.05 \cdot 372 \cdot 1/2 \cdot 0.25 = 2.3 \text{ g}$$

The answer: The weight of TrB was 2.3 g

28) On titration of 10ml $MgCl_2$ solution with C_N = 0.1 mol/l spent 11.9 ml of working solution of Trilon B. Calculate the concentration of solution to Trilon B.

$V(MgCl_2) = 10$ ml $C_N(MgCl_2) = 0.1$ mol/l $V(Tr.B) = 10$ ml $C_N(Tr.B) = ?$	1) Solve by using the law equivalence: $$C_N(MgCl_2) \cdot V(MgCl_2) = C_N(Tr.B) \cdot V(Tr.B)$$ hence $$C_N(Tr.B) = \frac{C_N(MgCl_2) \cdot V(MgCl_2)}{V(Tr.B)} = \frac{0.1 \cdot 10}{11.9} = 0.084 \text{ mol/l}$$

The answer: C_N (Tr B) = 0.084 mol/liter.

29) Calculate the total hardness of water, if the titration of 30ml of it spent 2.7 ml of 0.1 N Trilon B.

$V(H_2O) = 30$ ml $C_N(Tr.B) = 0.1$ mol/l $V(Tr.B) = 2.7$ ml $C_N(H_2O) = ?$	1) Solve by using the law equivalence: $C_N(H_2O) \cdot V(H_2O) = C_N(v) \cdot V(Tr\ B)$ hence $$C_N(H_2O) = \frac{C_N(Tr.B) \cdot V(Tr.B)}{V(H_2O)} = \frac{0.1 \cdot 2.7}{30} = 9 \text{ mol/l}$$

The answer: The total water hardness 9mol/liter.

30) Calculate the mass of Trilon B to prepare 1 liter of solution if the titer (the exact concentration) will be set as 0.1 N solution of the starting material MgO.

$C(MgO) = 0.1$ mol/l $V(Tr.B) = 1$ ml $m(MgO) = ?$	1) Since the titre will set by Tr B0.1 N solution of starting material MgO, a sample of the Tr B is also counting on the basis of concentration of 0.1 mol / litre. The problem gives molar concentration equivalent C_N, the solution begins with the formula C_N: $$C_N = \frac{m_x}{M_x \cdot f_{eqv.} \cdot V}$$

hence

$$m_x = C_N \cdot M_x \cdot f_{eqv.} \cdot V = 0.1 \cdot 372 \cdot 1/2 \cdot 1 = 18.6 \text{ g}$$

The answer: The weight of Tr B was 18.6 g

31) Calculate the mass of zinc sulphate for the preparation of 200g of a solution with mass fraction of salt 1,5%.

$m_{sol-n} = 200$g $\omega(ZnSO_4) = 1.5\%$

$m(ZnSO_4) = ?$

1) The problem is given by the mass fraction, then use the formula:

$$\omega = \frac{m(x)}{m(sol.)} \cdot 100\%$$

hence

$$m_x = \frac{\omega \cdot m_{sol-n}}{100\%} = 3\ g$$

The answer: Response; linkage $ZnSO_4$ – 3g.

METHOD OF PERMAGANATION

Permanganation — a method of volumetric analysis, which uses potassium permanganate titrant $KMnO_4$. The main reaction is:

$$MnO_4^- + 8H^+ + 5\bar{e} \rightarrow Mn^{+2} + 4H_2O$$

$KMnO_4$ titrant is prepared for a rough hitch, and then set the title of the original substance - $H_2C_2O_4$ or $Na_2C_2O_4$.

Titration is carried out in an acidic medium. End of titration set for the appearance of pink color when adding one extra drop of solution $KMnO_4$.

Examples

32) Compute the mass of 400 ml to prepare $KMnO_4$ solution. If the title will be set to 0.1 N solution of starting material $H_2C_2O_4$

$V(sol-n) = 400ml$
$C(H_2C_2O_4) = 0.1\ mol/l$
$m(KMnO_4) = ?$

1) Since the titer of $KMnO_4$ solution will set on 0.1 N solution $H_2C_2O_4$, then $KMnO_4$ solution concentration must also be 0.1 mol/liter. Use the formula of the molar concentration of equivalent:

$$C_N = \frac{m_x}{M_x \cdot f_{eqv.} \cdot V}$$

hence

$$m_x = C_N \cdot M_x \cdot f_{eqv.} \cdot V = 0.1 \cdot 158 \cdot 1/5 \cdot 0.4 = 12.64\ g$$

The answer: The mass of $KMnO_4$ is 12.64g

33)The laboratory solution has 10% of $KMnO_4$ (ρ = 1,4). Calculate C_N.

$\omega(KMnO_4) = 10\%$
$\rho = 1.4$
$C_N = ?$

1) Using a formula that relates the C_N and ω:

$$C_N = \frac{\omega\% \cdot \rho \cdot 10}{M_x \cdot f_{eqv.}} = \frac{10\% \cdot 1.4 \cdot 10}{158 \cdot 1/5} = 4.43\ mol/l$$

Answer:C_N ($KMnO_4$) = 4.43 mol/liter.

34) Compute the mass of $Na_2C_2O_4$ for the preparation of 500 ml 0.1 N solution.

$V(sol-n) = 500\ ml$
$C_N = 0.1\ mol/l$
$m(Na_2C_2O_4) = ?$

1) Use the formula of the molar concentration equivalent:

$$C_N = \frac{m_x}{M_x \cdot f_{eqv.} \cdot V}$$

hence

$$m_x = C_N \cdot M_x \cdot f_{eqv.} \cdot V = 0.1 \cdot 134 \cdot 1/2 \cdot 0.5 = 3.35\ g$$

The answer: The mass was $Na_2C_2O_4$ 3.35 g

35) How many grams of iron (II) sulphate is necessary for the preparation of 100ml to solution, if there is a volumetric solution $KMnO_4$ with C_N = 0.08 mol/litre.

$V(sol-n) = 100$ ml
$C_N(KMnO_4) = 0.08$ mol/l
Use the $(FeSO_4) = ?$

1) Since titration carried 0.08 N $KMnO_4$ solution, the solution of $FeSO_4$ is necessary to prepare with the same concentration.

Formula of molar concentration equivalent of C_N

$$C_N = \frac{m_x}{M_x \cdot f_{eqv.} \cdot V}$$

hence

$$m_x = C_N \cdot M_x \cdot f_{eqv.} \cdot V = 0.08 \cdot 152 \cdot 1 \cdot 0.1 = 1.216 \text{ g}$$

The answer: The mass of $FeSO_4$ 1,216g

36) Calculate the volume of 30% solution of H_2O_2 (ρ = 1,27) for the preparation of 2 l of the solution, if the titration is carried out to 0.09 N $KMnO_4$ solution in acidic medium.

$V_2(sol - n\ H_2O_2) = 2$ l
$C_N(KMnO_4) = 0.09$ mol/l
$\omega_1(H_2O_2) = 30\%$
$\rho_1 = 1.27$
$V_1(sol - n\ H_2O_2) = ?$

1) Since the titration is carried of 0.09N $KMnO_4$ solution, the solution of H_2O_2 is necessary to prepare with the same concentration.

Using the formula of molar concentration equivalent C_N find the mass of H_2O_2 in 200 ml of 0.09 N solution:

$$C_N = \frac{m_x}{M_x \cdot f_{eqv.} \cdot V}$$

hence

$$m_x = C_N \cdot M_x \cdot f_{eqv.} \cdot V = 0.09 \cdot 34 \cdot 1/2 \cdot 2 = 3.06 \text{ g}$$

2) The mass of hydrogen peroxide is the same in solutions 1 and 2:

$$m_{x_1} = m_{x_2}$$

3) Using the mass fraction, we find the mass of a 1:

$$\omega = \frac{m(x)}{m(sol.)} \cdot 100\%$$

hence

$$m_1(sol - n) = \frac{m_{x_1}}{\omega_1} \cdot 100\% = \frac{3.06 \cdot 100}{30} = 10.2 \text{ g}$$

4) Find the volume of solution 1:

$$V = \frac{m(sol-n)}{\rho} = 8.03 \text{ ml}$$

The answer: The volume of 30% solution of hydrogen peroxide is 8.03 ml.

METHOD OF IODOMETRY

Iodometry — a method of volume analysis, which uses titrant I or $^{-}I_2$.

The basic equation of the method:

$$I_2 + 2\bar{e} \rightarrow 2I^{-}$$

Since the titration of iodine is slow, then to test the solution we add an excess of iodine, and the residue titrated of sodium thiosulphate $Na_2S_2O_3$:

$$2\ Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6.$$

The precursor method — I_2.

Titration is carried out in acidic or neutral media. Indicator is starch. End of titration is set by the disappearance of blue color or iodine with starch.

Examples

37) Compute the mass of iodine for the preparation of 500 ml 0.1 N solution.

$V(solution) = 500$ ml
$C_N = 0.1$ mol/l

$m(I_2) = ?$

1) As the problem is given by the molar concentration equivalent of C_N, then use the formula:

$$C_N = \frac{m_x}{M_x \cdot f_{eqv.} \cdot V}$$

hence

$$m_x = C_N \cdot M_x \cdot f_{eqv.} \cdot V = 0.1 \cdot 254 \cdot 1/2 \cdot 0.5 = 6.35 \text{ g}$$

The answer: The linkage of iodine was 6.35 g

38) Compute the mass of $Na_2S_2O_3 \cdot 5H_2O$ for preparing of 200ml solution, if the titre is set at 0.1 N solution of I_2.

$V(sol - n) = 200 \text{ ml}$
$C_N = 0.2 \text{ mol/l}$
$m(Na_2S_2O_3 \cdot 5H_2O) = ?$

1) Since the titre is set to $Na_2S_2O_3$ of 0.1 N iodine solution, the concentration thiosulphate should be with the same concentration Since the problem is given by thiosulphate should be with the same concentration. Since the problem is given by the molar concentration equivalent to C_N, then use the formula:

$$C_N = \frac{m_x}{M_x \cdot f_{eqv.} \cdot V}$$

hence

$$m_x = C_N \cdot M_x \cdot f_{eqv.} \cdot V = 0.1 \cdot 248 \cdot 1 \cdot 0.2 = 4.96 \text{ g}$$

The answer: The linkage $Na_2S_2O_3 \cdot 5H_2O$ 4,96 g

39) To determine of the titer to the solution of $Na_2S_2O_3 \cdot 5H_2O$ use as potassium dichromate to $K_2Cr_2O_7$. Calculate the C_N solution if it took titration of 5ml 4.8 ml of 0,1 N solution potassium dichromate.

$V(sol - n\ Na_2S_2O_3) = 5 \text{ ml}$
$C_N(K_2Cr_2O_7) = 0.1 \text{ mol/l}$
$V(sol - n\ K_2Cr_2O_7) = 4.8 \text{ ml}$
$C_N(Na_2S_2O_3) = ?$

1) Using the equation of the law equivalence:
$C_N(Na_2S_2O_3) \cdot V(Na_2S_2O_3) = C_N(K_2Cr_2O_7) \cdot V(K_2Cr_2O_7)$
hence

$$C_N(Na_2S_2O_3) = \frac{C_N(K_2Cr_2O_7) \cdot V(K_2Cr_2O_7)}{V(Na_2S_2O_3)} = \frac{0.1 \cdot 4.8}{5} = 0.096 \text{ mol/l}$$

The answer: $C_N(Na_2S_2O_3)$ = 0,096 mol/liter.

40) In the laboratory, there is a 5% solution of iodine (ρ = 1,15). How many ml of this solution is necessary for the preparation of 1 liter of 0.1 N iodine solution?

$V_2 = 1 \text{ l}$
$C_N = 0.1 \text{ mol/l}$
$\omega_1 = 5\%$
$\rho_1 = 1.15$
$V_1 = ?$

1) Data for the calculation of V_1 on the mass fraction is not enough, so we use the formula of molar concentration equivalent to C_N, to finding the mass of the substance in solution:

$$C_N = \frac{m_x}{M_x \cdot f_{eqv.} \cdot V}$$

hence

$$m_x = C_N \cdot M_x \cdot f_{eqv.} \cdot V = 0.1 \cdot 254 \cdot 1/2 \cdot 1 = 12.7 \text{ g}$$

2) The mass of iodine in both solutions is the same:

$$m_{x_1} = m_{x_2}$$

3) Using the mass fraction, we find the mass of a 1:

$$\omega = \frac{m(x)}{m(sol.)} \cdot 100\%$$

hence

$$m_1(sol-n) = \frac{m_{x_1}}{\omega_1} \cdot 100\% = \frac{12.7 \cdot 100}{5} = 254 \text{ g}$$

4) Find the volume of solution 1:

$$V = \frac{m(sol-n)}{\rho} = \frac{254}{1.15} = 220.87 \text{ ml}$$

Answer: The amount of 5% iodine solution was 220.87 ml.

73. Titrimetric analysis method — this method is:
    a) quantitative analysis of acids, bases, salts
    b) quantitative analysis of the investigated solution during titration
    c) qualitative analysis of acids, bases, salts in the process of titration
74. Titration process is:
    a) slowly adding one solution to another
    b) slowly adding one solution to another until the equivalent point
    c) slowly adding a solution to water
75. The requirements for reactions in titrametric analysis:
    a) must to take place quickly, quantitatively, not be reversed, to set of equivalent points
    b) must to take place quickly, quantitatively, be reversed
    c) have to go slowly, quantitatively, not be reversed, the possibility installation of the equivalent amount
76. The exact concentration by titration data is calculated by the formula:
    a)
    $$C_{N_2} = \frac{C_{N_1} \cdot V_1}{V_2}$$
    b)
    $$C_{N_2} = \frac{C_{N_1} \cdot V_1}{V_1}$$
    c)
    $$C_{N_1} = \frac{C_{N_2} \cdot V_1}{V_2}$$
77. Titrated solution is a solution that:
    a) the titer is not known
    b) the accurately known concentration
    c) which are prepared for a rough weight
78. Which of these is being used for preparing solutions during titration:
    a) the graduated cylinder
    b) the volumetric flask
    c) the measuring beaker
79. What dishes are used for chemical sampling during titration:
    a) the volumetric flask
    b) the drops
    c) the burette
80. Weak substances — are substances which are prepared with titrated solution of:
    a) the accurate weight
    b) the approximate weight
    c) titration data
81. One of the properties of the initial substances is:
    a) they change their composition during storage

b) chemically pure substances
c) substances of low molar mass

82. One of the properties of the initial substances is:
a) the chemical composition shall conform to the formula
b) can absorb carbon dioxide from the air
c) dissolve poorly

83. Solutions initial substances can be prepared by:
a) the approximate weight
b) the accurate weight
c) the following approximate weight titer determination

84. Acid-base indicators is:
a) substances that do not change color with the change of pH
b) substances that change color with the change of pH
c) substances that change color depending on the method of titration

85. Acid-base indicators is:
a) weak inorganic acid or base
b) weak inorganic and organic salts

86. Theory of indicators is:
a) only the chromophore
b) only ion
c) ion-chromophore

87. Methyl orange coloration in acid medium is:
a) pink
b) yellow
c) colorless

88. Methyl orange coloration in alkaline medium is:
a) pink
b) yellow
c) colorless

89. Transition interval coloring of methyl orange is:
a) 3,1-4,4
b) 8,2-10,0
c) 4,0-10,0

90. Phenolphthalein in acid medium is:
a) pink
b) raspberry
c) colorless

91. Phenolphthalein in alkaline environment has color:
a) pink
b) raspberry
c) colorless

92. Transition interval indicator phenolphthalein color:
a) 3,1-4,4
b) 3,1-8,2
c) 8,2-10,0

93. The principle of selecting indicator for the titration:
a) to jump in the titration color to transition interval indicator
b) the transition to color interval indicator jump in the titration

94. The principle of selecting indicator for the titration:
a) color transition of interval indicator jump in the titration
b) to the equivalence point titration
c) to titrations jump in color transition interval indicator

95. Which reaction is the basis of acid-base titration:
a) oxidation
b) precipitation
c) neutralization
96. The basic equation of the method of neutralization:
a) $[H^+] + [OH^-] = H_2O$
b) $H^+ + OH^- = H_2O$
c) $[H^+] + [OH^-] = 10^{-14}$
97. Working solution of the method of neutralization:
a) $H_2C_2O_4 \cdot 2H_2O$, H_2SO_4, NaOH, KOH
b) H_2SO_4, HCl, Na_2CO_3, NaOH
c) NaOH, KOH, H_2SO_4, HCl
98. The method of neutralization can be determined by:
a) acids, reductants
b) acids, bases, salts that are not subject to hydrolysis
c) acids, bases, salts, which are hydrolysis
99. Classes of compounds that are determined by acid-base titration are:
a) acids, bases, oxidants
b) acids, bases, salts that are not subject to hydrolysis
c) acids, bases, salts, which are hydrolysis
100 . Titration curves are:
a) staining solution during the titration
b) a graphic representation of the reaction environment changes during titration
c) change in volume during the titration solutions
101. Titration curves show:
a) changing in volume of titration solution
b) pH dependence of the volume change of titrated solution
c) a graphic indicator of change
102. Titration jump is:
a) the sudden change in pH during titration
b) the sudden change in pH near the equivalent point
c) the end point reaction
103. Focal point is:
a) the end point of reaction
b) pH at which the compounds are reacted in equal amounts
c) pH at which compounds reactes in equivalent amounts
104. Basic equation method alcalimetriy:
a) $[H^+] / [OH^-] = H_2O$
b) $H^+ + OH^- = H_2O$
c) $[H^+] + [OH^-] = 10^{-14}$
105. Original material alkalimetry method is:
a) $H_2C_2O_4 \cdot 2H_2O$, $H_2C_4H_4O_4$
b) $Na_2B_4O_7 \cdot 10H_2O$, Na_2CO_3
c) $H_2C_4H_4O_4$, $Na_2B_4O_7 \cdot 10H_2O$
106. Original material alkalimetry method is:
a) $Na_2B_4O_7 \cdot 10H_2O$, $H_2C_2O_4 \cdot 2H_2O$
b) $H_2C_2O_4$, Na_2CO_3
c) $H_2C_2O_4 \cdot 2H_2O$, $H_2C_4H_4O_4$
107. Titrated solutions in alkalimetry:
a) H_2SO_4, HCl
b) NaOH, KOH

c) $H_2C_2O_4 \cdot 2H_2O$

108. Titrated alkalimetry solutions to prepare:
    a) the accurate weight followed by titration
    b) the approximate weight
    c) the approximate weight followed by determining the concentration of initial substances
109. Titrated solutions can be prepared in alkalimetry:
    a) with fixanal
    b) for accurate weight
    c) for the precise volume
110. The exact concentration of working solution of KOH can be set:
    a) H_2SO_4
    b) $H_2C_2O_4 \cdot 2H_2O$
    c) $Na_2B_4O_7 \cdot 10H_2O$
111. The formula for the concentration of initial substance for $H_2C_2O_4$ (acid oxalate):
    a) $C_{N_{NaOH}} = \frac{C_{N_{oxalats}} \cdot V_{oxalats}}{V_{NaOH}}$
    b) $C_{N_{NaOH}} = \frac{C_{N_{oxalats}} + V_{oxalats}}{V_{NaOH}}$
    c) $C_{N_{NaOH}} = \frac{C_{N_{oxalats}} - V_{oxalats}}{V_{NaOH}}$
112. In what environment is the equivalent point in titration of strong acid and strong base:
    a) the acid
    b) the alkaline
    c) the neutral
113. Jump titration during the titration of strong acid and strong base lies within the pH:
    a) 4,0-10,0
    b) 3,1-4,1
    c) 8,1-10,0
114. Focal point during the titration of strong acid and strong base pH is:
    a) 6.5
    b) 7
    c) 9
115. Which is indicator is being used during the titration of strong acid and strong base is:
    a) phenolphthalein
    b) methyl orange
    c) universal
116. In what environment is a jump titration weak acid and strong base:
    a) neutral
    b) in acid
    c) in alkaline
117. Jump titration during titration of weak acid and strong base:
    a) 3,3-4,4
    b) 3,1-10,0
    c) 8-10,0
118. Lines within the pH is:
    a) 3,3-4,4
    b) 3,1-10,0
    c) 8-10,0
119. Which environment is a jump sodium hydroxide titration CH_3COOH:
    a) neutral
    b) in acid

c) in alkaline

120. Which environment is the equivalent point during the titration of weak acid and strong base:
    a) neutral
    b) in alkaline
    c) in acid
121. Which indicator used during the titration of weak acid and strong base:
    a) phenolphthalein
    b) metylorange
    c) universal
122. Alkalimetric method can determine in:
    a) acid
    b) base
    c) salts, are not amenable to hydrolysis
123. Alkalimetric method can be used to determine:
    a) the volume of biological fluids
    b) the acidity of gastric juice
    c) the volume of urine
124. Alkalimetric method can be use to determine:
    a) the volume of biological fluids
    b) the volume of gastric juice
    c) the acidity of urine
125. In alkalimetry the following type of titration is applied:
    a) the reverse titration
    b) the direct titration
    c) the substitution method
126. Basic equation inacidimetry:
    a) $[H^+] / [OH^-] = H_2O$
    b) $H^+ + OH^- = H_2O$
    c) $[H^+] + [OH^-] = 10^{-14}$
127. Acidimetry method can be used to determine:
    a) the acid salts, bases
    b) the acids, bases, salts that are not subject to hydrolysis
    c) the bases, salts, which are hydrolysis
128. In acidimetry we apply:
    a) the reverse titration
    b) the direct
    c) the method of substitution
129. Original material in acidimetry:
    a) $H_2C_4H_4O_4 \cdot 2H_2O$, $Na_2 B_4O_7 \cdot 10H_2O$
    b) $Na_2B_4O_7 \cdot 10H_2O$, Na_2CO_3
    c) $H_2C_2O_4 \cdot 2H_2O$, $H_2C_4H_4O_4$
130. Titrated solutions in acidimetry:
    a) H_2SO_4, HCl, Na_2CO_3
    b) H_2SO_4, HCl
    c) H_2SO_4, NaOH, HCl
131. Storm can be used to establish the titer acid that:
    a) it is a working solution
    b) it is the original substance
    c) it is changes color during the titration
132. Formula drills:
    a) $Na_2B_4O_7 \cdot 2H_2O$

b) $Na_2B_4O_7 \cdot 10H_2O$
c) $Na_3BO_3 \cdot 10H_2O$

133. Brown works with hydrochloric acid from the equation:
a) $Na_2B_4O_7 + HCl \rightarrow Na_3BO_3 + HClO + H_2O$
b) $Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 4H_3BO_3 + 2NaCl$;
c) $Na_2B_4O_7 + 2HCl \rightarrow 4H_3BO_3 + 2NaCl$.

134. Titrated H_2SO_4 solution can be prepared by:
a) the accurate weight
b) the approximate weight
c) of the fixanal

135. Titrated HCl solution can be prepared by:
a) the approximate weight
b) for accurate weight
c) the approximate weight following definition titer

136. Output substance which established titer sulfated acid is:
a) $H_2C_2O_4 \cdot 2H_2O$
b) Na_2CO_3
c) $H_2C_4H_4O_4$

137. Output substance which established titer sulfated acid is:
a) $H_2C_2O_4 \cdot 2H_2O$
b) $Na_2B_4O_7 \cdot 10H_2O$
c) $H_2C_4H_4O_4$

138. Output substance which established titer hydrochloric acid is:
a) $H_2C_2O_4 \cdot 2H_2O$
b) Na_2CO_3
c) $H_2C_4H_4O_4$

139. Output substance which established titer hydrochloric acid:
a) $Na_2B_4O_7 \cdot 2H_2O$
b) $H_2C_2O_4 \cdot 2H_2O$
c) $H_2C_4H_4O_4$

140. What is pH of the jump titration, during titration of strong acid and strong base is:
a) 4-7
b) 4-10
c) 8-10

141. In which environment is the equivalent point during the titration of strong base and strong acids:
a) acid
b) alkaline
c) neutral

142. Focal point during the titration of strong base and strong acids. The pH is:
a) 5
b) 10
c) 7

143. In which indicator is bring used in the titration of strong base and strong acids:
a) any indicator
b) methyl orange
c) phenolphthalein

144. In which environment is a weak base titration jump strong acid:
a) neutral
b) in acid

c) in alkaline

145. What is the pH of the jump titration, during titration of strong acid and strong base:
a) 4.6
b) 4.10
c) 8-10

146. In which environment is a jump NH_4OH hydrochloric acid titration:
a) neutral
b) in acid
c) in alkaline

147. In which environment is the equivalent point during the titration of weak acid and strong base:
a) acid
b) alkaline
c) neutral

148. Focal point during the titration of weak base and strong acids. The pH is:
a) 7
b) 5
c) 9

149. Which indicator is being used in titration of weak acid and strong base:
a) methyl orange
b) phenolphthalein
c) any indicator

150. Formulary drug is the concentration of hydrochloric acid is:
a) 36%
b) 1%
c) 8,2%

151. Which method of analysis can be used to determine the percentage of $NaHCO_3$ in pharmacological drugs is:
a) acidimetry
b) alkalimetry
c) oxidimetry

5. The main questions of the seminar:

5.1. What is the basic concepts of neutralization method, the main equation.

5.2. *Base standardization:*
- reparation of working titrated solutions;
- initial compounds;
- titration curves;the point of inflection, the equivalence point;
- indicators: the points of inflection; methyl orange and phenolphthalein, the colors in the acid and base mediums; the correct selection of the indicators.

Acid standardization:
- the working solutions, their preparations;
- the initial substances;
- the titration curves, the equivalence point
- indicators: the points of inflection; methyl orange and phenolphthalein, the colors in
- the acid and base medium; the correct selection of the indicators.

5.3. Application of acid standardization in the clinical analysis. Application of base standardization in the clinical analysis.

6. The questions for individual learning:

6.1. *The theory of indicators:*

What are the indicators?

Why does an indicator change the color?

The standard indicators.
Describe the determination method of ammonia in baking soda.

7. The examples of the task:

7.1. What is the concentration (C_N) of base taking into account that 5.3 ml of base were titrated by 5 ml of oxalate withC_N=0.10 mol/l.

The answer:

$$C_N(NaOH) \cdot V(NaOH) = C_N(H_2C_2O_4) \cdot V(H_2C_2O_4)$$

$$C_N(NaOH) = C_N(H_2C_2O_4) \cdot V(H_2C_2O_4)/ V(NaOH) = 0.1 \cdot 0.005/0.0053 = 0.094 \text{ mol/l}$$

7.2. How many grams of H_3PO_4 must be taken for preparation of 2 l solution with C_H 0.1 mol/l?

The answer:

$$C_N = \frac{m_x}{M_x \cdot f_{eqv.} \cdot V}$$

$$m_x = C_N \cdot M_x \cdot f_{eqv.} \cdot V = 0.1 \cdot 98 \cdot 1/3 \cdot 2 = 6.53 \text{ g}$$

7.3. Calculate the weight Na_2CO_3 to prepare 400 ml of aqueous solution with C_N = 0.05 mol/l.

The answer:

$$C_N = \frac{m_x}{M_x \cdot f_{eqv.} \cdot V}$$

$$m_x = C_N \cdot M_x \cdot f_{eqv.} \cdot V = 0.05 \cdot 106 \cdot 0.2 \cdot 0.4 = 1.06 \text{ g}$$

8. Homework (must be performed in the laboratory notebook):

8.1. What weight of NaOH must be taken for preparation of 1.5 l solution withCn=0.2 mol/l.
8.2. Calculate the molar equivalent concentration of KOH knowing that 5 ml of it was consumed for titration of 2 ml 0.1 N acetic acid solution.
8.3. What is the weight of H_2SO_4 must be taken for preparation of 1.5 l aqueous solution with C_N=0.2 mol/l.
8.4. Calculate the molar equivalent concentration of HCl knowing that 5 ml of the last was consumed for titration of 5 ml of 0.1 M sodium carbonate.

***9. The control test*:**

for instance:

9.1. The working solution is called:
a) the solution with known concentration;
b) the solution with unknown concentration;
c) the prepared solution from known weight.
The answer: a
9.2. Calculate the molar equivalent concentration of KOH if 3 ml of the last was consumed for titration of 3.2 ml 0.1N oxalate acid solution.
9.3. How is the indicator methyl orange coloured?
a) pink color;
b) yellow color;
c) violet color
The answer: a
9.4. Calculate the molar concentration of Na_2CO_3 if 3 ml of 2.6 g was dissolved in 100 ml calibrated flask.

10. The algorithm of the experiments:

10.1. Determination of NaOH concentration.
10.1. Determination of hydrochloric acid of weight fraction in pharmsolution

(Acidum hydrochloridum dilutum).

11. The detailed of explanation to the following experiment:

11.1. Determination of NaOH concentration.

In a flask for titration 5 ml of oxalate acid solution is put adding 2-3 drops of phenolphthalein. The mixture is heated to 50-60 C^o and the hot solution is titrated by NaOH solution. Fill the below to given table by received data.

11.2. Determination of hydrochloric acid weight fraction in pharmsolution (Acidum hydrochloridum dilutum).

5 ml of HCl pharm solution (ρ=1,04 g/ml) is put in the 100 ml flask and H_2O is added to the total volume.

5 ml of the obtained solution are put in the flask for titration with the following adding 1-2 drops of methyl orange. The mixture is titrated by 0.1 N NaOH solution

№	***V (HC1) / l***	***V (NaOH) / l***	***The average volume of NaOH / l***	***ω% HCl***
1				
2				

12. Control test:

Sample 1

1.White the equation of the neutralization methods. What are the compounds can be determined using this method?
2.What is a titrant?
3.What is the medium (pH) of the equivalent point at titration the strong acid by the strong base?
4.What is a titration curve?
5.What is an initial substance?
6.How many grams of oxalic acid must be dissolved in 100 grams of water to get 5 % solution?

Sample 2

1.What is the color of methyl orange in the basic medium?
2. What is the pH range of the point inflection titrating for the strong base by strong acid and why?
3.What are the initial substances can be used for titration of sulfuric acid?
4.What is the mass fraction of boric acid in the solution if 10 g of it is dissolved in 1 L volumetric flask (ρ=1.12 g/ml)?
5.What is an analyte?
6.Preparation of an analyte?

TOPIC 8: Buffer systems, classification and mechanism.

1. Actuality of the topic*:* Biochemical processes take place in organism at a specific pH that is supported by buffer systems. The latter is also used for creating of biological mediums. For biochemical investigations in *vitro,* the solutions are prepared using the buffer systems to establish pH of the corresponding biological liquids. Knowledge of the topic is useful for studying biochemistry, microbiology, physiology, pharmacy.

2.General aim*:* is to understand the action of buffer systems in maintaining of pH values and to calculate pH of buffer systems.

3. Actual aims and abilities:

- to be able to prepare the buffer systems with given pH.

4. Literature:

4.1. Lecture materials;

pH constancy of the internal environment of the human body is maintained by *buffer systems* (solutions).

Referred to as buffer systems which maintain a constant pH by adding a small amount of a strong acid or a strong base (alkali), as well as in dilution.

Ability to steadfastly maintain the pH is called buffering.

Types of buffer systems

There are two types of buffer systems:

a) an *acid* type of buffering system which consists of the weak acid and its salt formed with a strong base. For example, an acetate buffer:

$$CH_3COOH + CH_3COONa$$

b) buffering system *alkali* type consists of a weak base and its salt formed with a strong acid. For example, ammonium buffer:

$$NH_4OH + NH_4Cl$$

Composition of buffer systems may be different.

Table 9.1 shows examples of system that the most used buffers.

Name buffer system	Composition
Acetate	Acetate Acetic acid (acetate CH_3COOH and sodium acetate CH_3COONa
Formate	formate acid (formic) HCOOH and sodium formate HCOONa
Hydro carbonate	Hydro carbonate acid H_2CO_3 And sodium hydro carbonate $NaHCO_3$
Phosphate	Sodium dihydrogen phosphate NaH_2PO_4 and sodium hydro phosphate Na_2HPO_4
Citrate	Citric acid (citrate) $C_5H_7O_5COOH$ and sodium citrate $C_5H_7O_5COOK$
Oxalate	Oxalic Acid (oxalate) $H_2C_2O_4$ and sodium oxalate $Na_2C_2O_4$
Borate	Boric acid H_3BO_3 and sodium tetraborate $Na_2B_4O_7$
Ammonium	Ammonium hydroxide NH_4OH and ammonium chloride NH_4Cl

Table 9.1

Calculation of the hydrogen ion concentration and pH of the buffer systems

To calculate the $[H^+]$ and $[OH^-]$ in a buffer system use the *basic equation of buffer systems*.

For *acidic* buffer systems such as:

$$\left[H^+\right] = C_D \frac{\left[acid\right]}{\left[salt\right]}$$

where C_D – dissociation constant of a weak acid ;

[acid] — concentration of the acid in the buffer system;

[salt] — the salt concentration of the buffer system.

For buffer systems alkali type:

$$\left[OH^-\right] = C_D \frac{[base]}{[salt]}$$

where K_D — dissociation constant of a weak base;

[base] — concentration of base in the buffer system;

[salt] — the salt concentration of the buffer system.

To calculate the pH and pOH of the buffer systems, use Henderson- Hasselbach equation .

If you take the negative logarithm of the left and right side in the basic equation of the buffer systems to acid type, we obtain :

$$-\lg\left[H^+\right] = -\lg C_D \frac{[Acid]}{[Salt]}$$

$$pH = -\lg C_D + (-\lg \frac{[Acid]}{[Salt]})$$

$$pH = pC_D - \lg \frac{[Acid]}{[Salt]}$$

Thus $[H^+]$ (and thus pH) buffering system is dependent on the value of K_D weak electrolyte concentrations and ratios of components.

If you take the negative logarithm of the left and right sides in the basic equation of the buffer systems basical type, we obtain:

$$-\lg\left[OH^-\right] = -\lg C_D \frac{[base]}{[salt]}$$

$$pOH = -\lg C_D + (-\lg \frac{[base]}{[salt]})$$

$$pOH = pC_D - \lg \frac{[base]}{[salt]}$$

The mechanism of action in the buffer systems

Constancy of pH buffer systems can be explained as follows.

If to an acidic buffer system such as for example the *acetate*, with composition CH_3COOH + CH_3COONa, is added a small amount of a strong base (alkaline), it will react with acetic acid :

$$CH_3COOH + Na^+ + OH^- \rightarrow CH_3COONa + \mathbf{H_2O}$$

Thus the strong base is replaced with an equivalent amount of a weak electrolyte H_2O and the pH does not change.

To an acetate buffer system was added a small amount of a strong acid, it reacted with sodium acetate:

$$CH_3COONa + H^+ + Cl^- \rightarrow \mathbf{CH_3COOH} + NaCl$$

Thus, the strong acid is replaced by an equivalent amount of a weak acid CH_3COON and pH change.

Similarly, we can explain the mechanism of action of the buffer systems basic type, for example, *ammonia*, consisting of NH_4OH and NH_4Cl.

When adding a strong base (alkali) to react :

$$NH_4Cl + Na^+ + OH^- \rightarrow \mathbf{NH_4OH} + NaCl$$

Strong base is replaced by equivalent amount of weak base NH_4OH, and pH change.

When you add a strong acid to react :

$$NH_4OH + H^+ + Cl^- \rightarrow NH_4Cl + \mathbf{H_2O}$$

Strong acid is replaced by equivalent amount of weak electrolyte H_2O and pH does not change.

Show the mechanism of action for some buffer systems.

Phosphate buffer: $NaH_2PO_4 + Na_2HPO_4$
addition of acid: $Na_2HPO_4 + H^+ + Cl^- \rightarrow NaH_2PO_4 + NaCl$
addition of alkali: $NaH_2PO_4 + Na^+ + OH^- \rightarrow Na_2HPO_4 + H_2O$

Boron phosphate buffer : $Na_2B_4O_7 + KH_2PO_4$
addition of acid: $Na_2B_4O_7 + H^+ + Cl^- \rightarrow NaCl + H_3BO_3$
addition of alkali: $KH_2PO_4 + K^+ + OH^- \rightarrow K_2HPO_4 + H_2O$

Oxalate buffer: $KHC_2O_4 + H_2C_2O_4$
addition of acid: $KHC_2O_4 + H^+ + Cl^- \rightarrow KCl + H_2C_2O_4$
addition of alkali: $H_2C_2O_4 + K^+ + OH^- \rightarrow KHC_2O_4 + H_2O$

Citrate phosphate buffer: $C_5H_7O_5COOH + Na_2HPO_4$
addition of acid: $Na_2HPO_4 + H^+ + Cl^- \rightarrow NaH_2PO_4 + H_2O$
addition of alkali: $C_5H_7O_5COOH + Na^+ + OH^- \rightarrow C_5H_7O_5COONa + H_2O$

If the buffer system is to add slightly strong acid more than a certain amount, then the pH may change slightly concentration of the one component.

For example, if an acetate buffer to a concentration add V ml CH acid, the strong acid will react with the salt, and the salt concentration decreases, and increase the concentration of weak acid.

Why the pH buffer system does not change at a dilution buffer system? This is based on the fundamental equation system with dilution buffer while its concentration decreases and weak electrolyte and its salts, and their ratio remains constant.

$$[H^+] = K\frac{0{,}1}{0{,}1} = K\frac{0{,}01}{0{,}01}$$

where 0.01 is the concentration of weak electrolyte, and a salt thereof, after dilution with 10 times.

Buffering system of the body

Biological fluid pH is kept constant or may vary within very narrow limits. This is due to various factors, and in particular, the presence of the buffer systems.

One of the main products of metabolism in the human body is carbon dioxide. When converting the total amount of CO_2 1N hydrochloric acid solution 20 exits ≈ 1 acid. All acidic metabolic products, gets into blood, primarily neutralized buffer systems. Consider the most important buffer systems and their presence in biological fluids.

Hydrogen carbonate $H_2CO_3 + NaHCO_3$ buffer has the greatest value in the blood. The ratio of components in the blood should be:

$$\frac{[NaH\ CO_3]}{[H_2CO_3]} = \frac{20}{1}$$

Plasma pH can be determined from the Henderson - Hasselbach, if you know the amount of dissolved CO_2 and bicarbonate in the blood:

$$pH = 6{,}11 + \lg\frac{[NaHCO_3]}{[CO_2]}$$

where 6,11 - constant rate close largest constant acid dissociation carbonate.

If acidic metabolic products of hydrochloric acid present, the mechanism of action hydrogen carbonate buffer can thus show:

$$NaHCO_3 + H^+ + Cl^- \rightarrow NaCl + CO_2 + H_2O$$

Carbon dioxide, which is formed, light output.

To neutralize excess alkali products , such as prolonged vomiting, it is the following reaction:

$$H_2CO_3 + Na^+ + OH^- \rightarrow NaHCO_3 + H_2O$$

Excess sodium bicarbonate in this case excreted by the kidneys .

Phosphate buffer NaH_2PO_4 + Na_2HPO_4 + (as an acid, sodium dihydrogen phosphate) has the greatest value in the urine and juices of digestive glands and partly in the blood. The ratio of components in the blood should be:

$$\frac{Na_2HPO_4}{NaH_2PO_4} = \frac{4}{1}$$

The mechanism of action of phosphate buffer can show such reaction equations :

with an excess of acid: $Na_2HPO_4 + H^+ + Cl^- \rightarrow NaH_2PO_4 + NaCl$

with an excess of alkali: $NaH_2PO_4 + Na^+ + OH^- \rightarrow Na_2HPO_4 + H_2O$

Hemoglobin buffer HHb + KHb and **oxyhemoglobin buffer**

$HHbO_2$ + $KHbO_2$ are blood (erythrocytes) and make up to 75% buffering.

Mechanism of action of hemoglobin buffer can show such reaction equations:

with an excess of acid : $KHb + H^+ + Cl^- \rightarrow HHb + KCl$

with an excess of alkali: $HHb + K^+ + OH^- \rightarrow KHb + H_2O$

A similar effect shows in oxyhemoglobin buffer.

Protein buffer Pt-H + Pt-K (the protein and the protein acid salt) is in the blood and various tissues.

The mechanism of action of the protein buffer can show such reaction equations:

with an excess of acid: $Pt\text{-}K + H^+ + Cl^- \rightarrow Pt\text{-}H + KCl$

with an excess of alkali $Pt\text{-}H + K^+ + OH^- \rightarrow Pt\text{-}K + H_2O$

A protein molecule as a buffer Pt - COOH is in the blood and various tissues.

$$\begin{array}{l} \\ | \\ NH_2 \end{array}$$

Amphoteric protein molecule, can neutralize acidic and basic metabolic products.

This can be shown schematically as follows:

$$\begin{array}{l} Pt-COOH \\ | \\ NH_2 \end{array} + H^+ + Cl^- \rightarrow \begin{array}{l} Pt-COOH \\ | \\ {}^+NH_3 \end{array} + Cl^-;$$

$$\begin{array}{l} Pt-COOH \\ | \\ NH_2 \end{array} + K^+ + OH^- \rightarrow \begin{array}{l} Pt-COOK \\ | \\ NH_2 \end{array} + H_2O.$$

Alkaline reserve of blood and acid-base balance

Based on the above we can conclude that in a living organism it is possible to maintain balance between the amount of acidic and basic products. Therefore, in the clinic of interest to determine the blood alkali reserve.

Alkaline reserve is the amount of blood in the form of bicarbonate associated carbon dioxide, which is contained 100 ml of blood.

Normally, blood alkaline reserve is 50.65 % of bound CO_2.

Balance between the amount of acidic and basic foods in the body is determined by the *acid-base balance.*

Acid-base balance of the constancy of pH internal environment in the human body .

Therefore shifts in the acid - alkaline balance to the acidic side is called **—** *acidosis*, alkaline side **—** *alkalosis*.

Acidosis can be observed:

a) of the lung disease, when removal of carbon dioxide is hampered;

b) of the cardiac ischemia, when it is poorly supplied with blood;

c) of the diabetes, when blood is saturated with unoxidized glucose cleavage products (organic acid);

d) in inflammatory sites, where they can accumulate acidic decomposition products proteins.

Alkalosis can be observed with uncontrollable vomiting .Acid-base balance in the body:

a) maintain's of the buffer systems;

b) makes it easy to remove excess carbon dioxide;

c) helps kidney that remove hydrocarbons and acid phosphates.

Thus, the acid-alkaline balance is an important part of homeostasis of the internal environment of the human body, which ensures the normal biochemical processes.

BUFFER SYSTEMS

State the **buffer systems**, which steadfastly maintain the pH by adding small amounts of strong acid or alkali, as well as dilution

There are two types of buffer systems:

a) Acid **—** consisting of a weak acid and its salts, form strong base. Example, acetate buffer: $CH_3COOH + CH_3COONa$.

b) Base **—** consisting of a weak base and its salts, form strong acid. For example, an ammonia buffer: $NH_4OH + NH_4Cl$.

Basic equations of the buffer systems

acid type

$$[H^+] = Cd \cdot \frac{[acid]}{[salt]}$$

basic type

$$[OH^-] = Cd \cdot \frac{[base]}{[salt]}$$

Henderson – Hasselbalch equation

acid type

$$pH = pCd - \lg\frac{[acid]}{[salt]}$$

basic type

$$pOH = pCd - \lg\frac{[base]}{[salt]}$$

where $pCd = -lgCd$

Buffering capacity — the number of mole equivalents of strong acid or strong base to be added to 1 liter buffer system to shift the pH to 1.

Buffer capacity is determined by titration.

Formulas for calculating of the buffer capacity:

by acid

$$B_{acid} = \frac{C}{pH_0 - pH_1}$$

$pH_1 = 4.4$

by alkaline

$$B_{alkaline} = \frac{C}{pH_1 - pH_0}$$

$pH_1 = 8.2$

Examples

A. Calculating pH of buffer systems

1) Calculate the pH of acetate buffer that consisting of 50 ml 0.1 N solution of CH_3COOH and 40 ml 0.15 N solution CH_3COONa (C_D (CH_3COOH) = 1,8 · 10^{-5}).

50 ml 0.1 N CH_3COOH 40ml 0.15 N CH_3COONa $Cd(CH_3COOH) = 1.8 \cdot 10^{-5}$	1) To determine the pH of the buffer systems rational first find N of concentration in the main equation of the buffer systems of acid type $[H^+] = Cd \cdot \frac{[acid]}{[salt]} = 1.8 \cdot 10^{-5} \cdot \frac{50 \cdot 0.1}{40 \cdot 0.15} = 1.13 \cdot 10^{-5}$
$pH = ?$	

2)$pH = -\lg[H^+] = -\lg 1{,}13 \cdot 10^{-5} = -\lg 1{,}13 - \lg 10^{-5} = 5 - 0.053 = 4.947$

The answer: pH = 4.947.

2) Calculate the pH of the ammonia buffer consisting of 60ml 0.1 N solution of NH_4Cl and 30ml of 0.2 N NH_4OH solution (Cd (NH_4OH) = 1,8 · 10^{-5}).

60 ml 0.1 N NH_4Cl 30ml 0.2 N NH_4OH $Cd(NH_4OH) = 1.8 \cdot 10^{-5}$	1) To find the pH of the buffer system of primary type, you must first find the pOH. To find pOH first find a rational concentration of Cd H^- to the basic equation buffer systems of general type:
$pH = ?$	$[OH^-] = Cd \cdot \frac{[base]}{[salt]} = 1.8 \cdot 10^{-5} \cdot \frac{30 \cdot 0.2}{60 \cdot 0.1} = 1.8 \cdot 10^{-5}$ $pOH = -lg1.8 \cdot 10^{-5} = -lg1.8 - lg10^{-5} = 5 - 0.25 = 4.75$ $pH = 14 - pOH = 14 - 4.75 = 9.25.$

The answer: pH = 9.25.

B. Calculation of the ratio of components of buffer systems

3) Compute the ratio of the components of buffer phosphate, pH 6.3, if the concentration of the components of 0,1 mol/l (Cd (NaH_2PO_4) = 1,6 · 10^{-7}).

$pH = 6.3$ $C_N = 0.1\ mol/l$ $Cd(NaH_2PO_4) = 1.6 \cdot 10^{-7}$	1) To calculate the ratio of the components use the equation Henderson- Hasselbach for buffer systems of acid type:
$\frac{V(NaH_2PO_4)}{V(Na_2HPO_4)} = ?$	$pH = pCd - lg\frac{[acid]}{[salt]} = -lgCd - lg\frac{[acid]}{[salt]}$ $= -lgCd - lg\frac{C_N(NaH_2PO_4) \cdot V(NaH_2PO_4)}{C_N(Na_2HPO_4) \cdot V(Na_2HPO_4)}$

$$pCd(NaH_2PO_4) = -lg1.6 \cdot 10^{-7} = -lg1.6 - lg10^{-7} = 7 - 0.2 = 6.8$$

3) Substitute the data into the equation of Henderson - Hasselbach and find value:

$$6.3 = 6.8 - lg\frac{V(NaH_2PO_4)}{V(Na_2HPO_4)}$$

$$lg\frac{V(NaH_2PO_4)}{V(Na_2HPO_4)} = 6.8 - 6.3 = 0.5$$

$$\frac{V(NaH_2PO_4)}{V(Na_2HPO_4)} = ant\ lg0.5 = 3$$

The answer: $\frac{V(NaH_2PO_4)}{V(Na_2HPO_4)} = 3$.

4) Calculate the ratio of the components of the ammonia buffer with, pH 8.6, if the concentration of the components of 0,1 mol/l (K_D (NH_4OH)) = 1,8 · 10^{-5}).

$pH = 8.6$ $C_N = 0.1\ mol/l$ $Cd(NH_4OH) = 1.8 \cdot 10^{-5}$	1) To calculate the ratio of the components it is better to use the Henderson – Hasselbalch equation for the main buffer systems type:
$\frac{V(NH_4Cl)}{V(NH_4OH)} = ?$	$pOH = pCd - lg\frac{[base]}{[salt]}$ 2) Find the pOH of the conditions of the problem: $pOH = 14 - pH = 14 - 8,6 = 5,4;$

3) Find the value of pCd:

$$pCd(NH_4OH) = -lg1.8 \cdot 10^{-5} = -lg1.8 - lg10^{-5} = 4.74 - 0.2 = 4.54$$

4) Substitute the data into the equation Henderson - Hasselbach and find the ratio of components:

$$5,4 - 4,75 = lg\frac{V(NH_4Cl)}{V(NH_4OH)};$$

$$\lg \frac{V(NH_4Cl)}{V(NH_4OH)} = 0.65;$$

$$\frac{V(NH_4Cl)}{V(NH_4OH)} = \text{ant}\lg 0.65 = 4.5$$

The answer: $\frac{V(NH_4Cl)}{V(NH_4OH)} = 4{,}5.$

— Buffer system: definition, types, composition, examples, the basic equation of buffer systems both types of pH dependence of buffer systems on various factors, the Henderson – Hasselbalch equation, mechanism action of acetate, hydrocarbonate, phosphate, protein, protein molecule, hemoglobin, oxyhemoglobin.

— Buffer capacity: definition, calculation by acid and alkali, the dependence of various factors, practical method of determining the value of the buffer capacity, of blood by acid, alkali, and compare them.

— Buffer system in humans: hydrocarbonate (ratio components in the blood), phosphate (ratio of components in the blood), protein, protein molecule, hemoglobin, oxyhemoglobin in which organs and tissues are contained, their role, mechanism of action. Acid - base balance, blood alkaline reserve.

152. Mention buffer systems that counterouct the pH changes as a result of adding to it:
    a) a small number of strong acid or alkali and during breeding
    b) a large number of strong acid or alkali and during breeding
    c) a strong acid or alkali, and when concentrating
153. Systems that do not change the pH by adding small amounts of strong acid or alkali, and during breeding are called:
    a) colloidal
    b) buffer
    c) real
154. Buffer action — the ability to buffer solution consistently keep a constant of:
    a) molar concentration of component
    b) pH
    c) the dissociation constants of weak electrolyte
155. Composition of acid buffer system type are:
    a) strong acids and bases
    b) a weak acid and its salt, which formed by strong base
    c) strong acid and its salt, which formed by strong base
156. Composition of acetate buffer:
    a) $CH_3COOH + CH_3COOC_2H_5$
    b) $CH_3COOH + NaOH$
    c) $CH_3COOH + CH_3COONa$
157. Composition of hydrocarbonate buffer:
    a) $H_2CO_3 + NaHCO_3$
    b) $H_2CO_3 + NaCl$
    c) $NaHCO_3 + NaCl$
158. Value of hydrocarbonate buffer components in plasma at pH = 7.36 should be:
    a) 15: 1
    b) 20: 1
    c) 7: 1
159. Composition of phosphate buffer:
    a) $Na_3PO_4 + NaH_2PO_4$
    b) $Na_2HPO_4 + NaH_2PO_4$

c) $H_3PO_4 + NaH_2PO_4$

160. The ratio of components in phosphate buffer in blood plasma the pH = 7.36 should be:
    a) 8: 1
    b) 10: 1
    c) 4: 1
161. Protein structure buffer:
    a) PtCOOH + PtCOOK
    b) PtCOOH + $PtCONH_2$
    c) PtCOOH +($PtCOO)_2Ca$
162. Formula of protein molecule as a buffer:

    a) Pt — COOH
       |
       NH_2

    b) Pt — COOK
       |
       NH_2

    c) Pt — COCl
       |
       NH_2

163. Composition of hemoglobin buffer:
    a) HHb + $KHbO_2$
    b) HHb + KHb
    c) HHb + $NaHbO_2$
164. Composition of oxyhemoglobin buffer:
    a) HHb + $Ca(HbO_2)_2$
    b) HHb + KHb
    c) $HhbO_2 + KHbO_2$
165. Composition of buffer systems of general type is:
    a) strong acid and weak base;
    b) a weak base and its salt, which formed a strong acid;
    c) strong acid and its salt, which formed a strong base.
166. Composition of ammonia buffer is:
    a) $NH_4OH + NH_4Cl$
    b) $NH_4OH + HCl$
    c) $NH_4NO_3 + HNO_3$
167. The basic equation of acid buffer system type is:
    a) $[H^+] = \hat{E}d \frac{[acid]}{[base]}$
    b) $[H^+] = \hat{E}d \frac{[acid]}{[salt]}$
    c) $[H^+] = \hat{E}d \frac{[salt]}{[acid]}$
168. Henderson's equation for Hasselbach-acid buffer system is:
    a) $pH = -\lg K_d - \lg \frac{[salt]}{[acid]}$
    b) $pH = -\lg K_d + \lg \frac{[salt]}{[acid]}$
    c) $pH = -\lg K_d - \lg \frac{[acid]}{[salt]}$
169. Formula Henderson - Hasselbach to determine the pH of blood plasma is:
    a) $pH = pK + \lg \frac{[acid]}{[salt]}$
    b) $pH = pK + \lg \frac{[NaHCO_3]}{CO_2}$;
    c) $pH = -pK - \lg \frac{[salt]}{[acid]}$

170. The equation calculating of the pH buffer hydrocarbonate is:

a) pH = pK + lg $\frac{[H_2CO_3]}{[NaHCO_3]}$

b) pH = pK– lg $\frac{[NaHCO_3]}{[H_2CO_3]}$

c) pH = pK– lg $\frac{[H_2CO_3]}{[NaHCO_3]}$

171. Calculation formula for pH phosphate buffer is:

a) pH = pK– lg $\frac{[NaH_2PO_4]}{[Na_2HPO_4]}$;

b) pH = pK + lg $\frac{[NaH_2PO_4]}{[Na_2HPO_4]}$;

c) pH = pK– lg $\frac{[Na_2HPO_4]}{[NaH_2PO_4]}$.

172. The basic equation of general type of buffer system is:

a) $[OH^-] = Kd\frac{[acid]}{[base]}$

b) $[H^+] = Kd\frac{[acid]}{[base]}$

c) $[H^+] = Kd\frac{[acid]}{[salt]}$

173. Henderson- Hasselbach equation of buffer system for basic types is:

a) $[H^+] = Kd\frac{[salt]}{[acid]}$

b) $ðÎÍ = ðÊ - \lg\frac{[base]}{[salt]}$

c) $ðÎÍ = ðÊ - \lg\frac{[salt]}{[base]}$

174. Henderson equation - calculating Hasselbach pH buffer systems of general type:

a) pH = 14 –(pK – lg $\frac{[acid]}{[salt]}$)

b) pH = 14 –(pK + lg $\frac{[base]}{[salt]}$

c) pH = 14 –(pK – lg $\frac{[salt]}{[acid]}$)

175. pH buffer system depends on:

a) Kd size and ratio of components

b) the amount of documentation and product components

c) the amount and size of the Kd components

176. Acid-alkaline balance — this is permanent in the human values:

a) osmotic pressure

b) blood pressure

c) pH

177. Which organs and tissues work in keeping acid-alkaline balance:

a) heart, skin, bone

b) lungs, kidneys, blood
c) lungs, tooth tissue, kidney

178. How does lungs maintain acid-alkaline balance in the body:
a) bringing water
b) bringing carbon dioxide
c) bringing salt

179. Which of these buffer systems is contained in the blood?
a) CH_3COOH CH_3COONa b) $R-\underset{\underset{NH_2}{|}}{CH}-COOH$ c) NH_4OH NH_4NO_3

180. The mechanism of phosphate buffer in the blood:
a) $NaH_2PO_4+HCl \rightarrow H_3PO_4+NaCl$
b) $Na_2HPO_4+NaOH \rightarrow Na_3PO_4+H_2O$
c) $Na_2HPO_4 + HCl \rightarrow NaH_2PO_4+NaCl$

181. Mechanism of action for hydrogencarbonate buffer in the blood:
a) $NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O$
b) $NaHCO_3 + HCl \rightarrow NaCl + H_2CO_3$
c) $NaHCO_3 + NaOH \rightarrow H_2CO_3 + H_2O$

5. The main questions of the seminar:

5.1.What is the buffer system?
5.2. The main phisiological buffer systems: their composition, the examples.
5.3. Mechanism of the buffer system.
5.4. Henderson-Hasselbach equation.
5.5. Buffer system in organism: an action, ratio of compounds in hydrocarbonate and phosphate buffer systems.
5.6. Significance of buffer systems.

6. The question for individual learning:

6.1. Give the example of two buffer systems, explain their mechanism;
6.2. What is the role of hemoglobin and oxyhemoglobin in maintaining of blood pH?

7. The examples of the task

7.1. What is pH of buffer systems containing 100 ml of 0.1 M acetic acid solution and 200 ml of 0.2 M sodium acetate with $K_D = 1.75\ 10^{-5}$?

The answer:

$$pH = pK + \lg\frac{[salt]}{[acid]} = -\lg 1.75 \cdot 10^{-5} - \lg\frac{100 \cdot 0.1}{200 \cdot 0.2} = 5 - 0.24 - 0.25 = 4.51$$

$$pH = -lgK - \lg\frac{[acid]}{[salt]} = -\lg 1.75 \cdot 10^{-5} - \lg\frac{100 \cdot 0.1}{200 \cdot 0.2} = 5 - 0.24 - 0.25 = 4.51$$

7.2. What are the volumes of sodium acetate and acetic acid must be taken for preparation of 3 l acetate buffer in volume and with pH = 5.24 ($K_D = 1.758 \cdot 10^{-5}$) knowing that the concentration both of them is equal 0.1 M.

The answer:

$$pH = pK - \lg\frac{[salt]}{[acid]}$$

$$\lg\frac{C_S V_S}{C_a V_a} = \lg\frac{0.1 \cdot V_S}{0.1 \cdot V_a} = \lg\frac{V_S}{V_a} = 5.24 - 4.76 = 0.48$$

$$\frac{V_S}{V_a} = \text{antlg}\ 0.48 = 3$$

$$\frac{V_S}{V_a} = \frac{3}{1}$$

Thus, 3 parts of the salt solution and 1 part of the acid solution must be taken for preparation of buffer systems with pH = 5.24. The volume of salt is calculated as:

$$\frac{3000}{4} \cdot 3 = 2250\text{ml}$$

and acid as:

$$\frac{3000}{4} \cdot 1 = 750\text{ml}$$

8. Homework (must be performed in the laboratory notebook):

8.1. What is pH of the buffer solution contain 3.6 ml of 0.2 M NH_4Cl and 2.6 ml of 0.1 M NH_4OH (K_D=1,8·10 $^{-5}$)?

8.2. What are the volumes of sodium acetate and acetic acid must be taken for preparation of the acetate buffer in volume of 150 ml and with pH = 4.94 (K_D (CH_3COOH)= $1.8 \cdot 10^{-5}$) knowing that the concentration both of them is equal 0.1 M.

***9. The control test*:**

for instance:

9.1. The acid buffer system contains

a) the weak acid and the conjugative salt formed by strong base;

b) the strong acid and the conjugative salt formed by strong base;

c) the weak acid and the conjugative salt formed by weak base.

The answer: a

9.2. What is the ratio of acetic acid and sodium acetate must be taken for preparation of the buffer system with pH = 4.05 ($K_D = 1.75 \cdot 10^{-5}$)?

10. The algorithm of the experiments:

10.1. Preparation of the buffer system and calculation of pH.

10.2. Influence of acid and base on pH of buffer system.

10.3. Influence of dilution on pH of buffer system.

11. The detailed explanation of the following experiment:

<u>11.1. Preparation of buffer system and calculation of pH.</u>

Prepare the buffer systems as reported in the next table.

№ the test-tube	***Buffer system (ml)***		***Color***	***Approximated pH***	***Calculated pH***
	CH_3COOH (0.1 M)	CH_3COONa (0.1 M)			
1	9.0	1.0			
2	1.0	9.0			

Add 2 drops of the standard indicator to solution №1 and №2. Determine the approximated pH, to corresponding using the colored scale and calculate pH using equations. How does ratio of components influence on pH of buffer system.

<u>11.2. Influence of acid and base on pH of buffer system</u>.

Fill a test-tube with 5 ml of 0.1 M CH_3COOH solution and 5 ml of 0.1 M CH_3COONa solutions. The resulting mixture must be divided in 3 parts. Add 3 drops of 0.1 M HCl solution to the first part, 3 drops of 0.1 M NaOH solution to the second part, (drop abit).

12. Control test:

Sample 1

1/ How do you calculate $[H^+]$ in the solutions?

a) of a strong acid;
b) of an acidic buffer system.

2/ Write the mechanism of the boric buffer action ($H_3BO_3 + Na_2B_4O_7$).

3/ Calculate the pH value of ammonium buffer containing 30 ml of 0.1 M NH_4OH and 70 ml of 0.1 M NH_4Cl ($K_D=1.8*10^{-5}$).

4/ What is the ratio of the acid and salt in phosphate buffer have to be taken to get pH=6.4 ($K_D=1.6*10^{-7}$)?

Sample 2

1/ How do you calculate $[H^+]$ in the solutions?

c) of a strong acid;
d) of an acidic buffer system.

2/ Write the mechanism of the protein buffer action (PtCOOH + PtCOOK).

3/ Calculate the pH value of hydrocarbonate buffer containing 30 ml of 0.15 M salt and 90 ml of 0.09 M acid ($K_D=3.3*10^{-7}$).

4/ What is the ratio of the acid and salt in phosphate buffer have to be taken to get pH=6.2 ($K_D=1.6*10^{-7}$)?

TOPIC 9: Buffer capacity. The role of buffer solutions in biological systems.

1. Actuality of the topic: the ability of buffer system to maintain pH after addition of acid or alcalic is limited. Buffer capacity is a qualitative limit of buffer system. In the case of distraction of buffer capacity in organism, denaturising of proteins take place. Therefore the determination of buffer capacity has a greater diagnostic meaning. Knowledge of the topic is useful for studying biochemistry, physiology and other subjects.

2.General aim: *is* to determine the limits of buffer system.

3. Actual aims and abilities:

- to determine the buffer capacity acetate buffer and blood plasma.

4. Literature:

4.1. Lecture materials;

The ability of the buffer system to maintain a constant pH is limited, since the addition of a large amount of strong electrolyte gradually consumes one of the components of the buffer system. In this case, the solution shows a buffer action and pH change.

Quantitative measure of the ability in the buffer systems to maintain constant pH *buffering capacity B.*

The buffer capacity is equivalent to the number of moles of strong acid or strong alcalic which must be added to 1 liter of the buffer system to alter the pH to 1.

A practical method for determining the buffer capacity is titrimetric method .

The general formula for calculating the buffer capacity is the next:

$$B_K = \frac{C(electrolyte)}{\Delta pH}$$

where C (electrolyte) - is equivalent to the number of moles of strong acid or strong alcalic;

ΔpH – change pH when a strong electrolyte is added.

Buffer capacity depends on the initial concentrations of components. The highest concentration of the components, the greater the buffer capacity. The buffer capacity is maximum when the ratio of concentrations components is 1.

The buffer capacity can be calculated by the *acid* :

$$B_K = \frac{C(acid)}{pH_0 - pH_1}$$

Where is C (acid), — is the number of moles of equivalents of strong acid, is added to 1 liter of a buffering system;

pH_0 — initial pH buffer system;

pH_1 — final pH at the end of the titration. During the titration acid $pH_1 = 4.4$ (this is the upper limit of the transition interval methyl orange coloring).

When calculating C (acid) is arrive at the following expression:

$$B_K = \frac{C_X(acid) \bullet V(acid)}{V_{(Buf,sustem)} \bullet (pH_0 - pH_1)}$$

where C_X (acid) — is the concentration of acid, while titrating;

V (acid) — is the amount of acid that went for titration;

V (BUF. systems.) — is the amount of the buffer system.

Buffering capacity is calculated as *in alkali* :

$$B_c = \frac{C(alcalical)}{pH_1 - pH_0}$$

where C (alcalical) — is equivalent number of moles of alkali, is added to 1 liter of a buffering system;

pH_0 — initial pH buffer system ;

pH_1 — final pH at the end of the titration. during the titration alkaline $pH_1 = 8.2$ (this is the lower bound of the transition interval phenolphthalein color) .

When calculating C (*alkali*) arrive at the following expression:

$$B_c = \frac{C_X(alcalical) \bullet V(alcalical)}{V_{(buf.system,)} \bullet (pH_1 - pH_0)}$$

where C_X (alkaline) — is the concentration of alkali, which titrating;

V (alkaline) — is the amount of alkali, which went for titration;

V buf.syst.) — is the volume of the buffer system.

The quantity of buffer capacity according to serum acid is 0.05 mol equivalents/liter. In alkali, this figure is much less, as blood pH is in an alkaline medium (7,36), and alkali consumed for the titration is less than the acid.

<u>A. Calculation of changes in pH (Δ pH) by adding a strong acid or alkali</u>

1) How to change the pH of acetate buffer consisting of 50 ml 0.1 N (CH_3COONa) solution and 80 ml 0.1 N CH_3COOH solution (C_D (CH_3COOH) = 1,8 ·10^{-5}), while adding there to 10 ml 0.1 N solution of NaOH.

80 ml 0.1 N CH_3COOH
50ml 0.15 N CH_3COONa
$Cd(CH_3COOH) = 1.8 \cdot 10^{-5}$
10ml of 0.1 N NaOH
Δ pH = ?

1) So adding alkali, the pH should move to the alkaline side, so Δ pH = pH_1 - pH_2 where pH_2 - is the pH of the solution after adding alkali and pH_1 - before adding the alkali, this initial pH buffer solution.

2) To determine the pH of the buffer systems for the management to find first concentration of H^+ in the basic equation of the buffer systems acid type:

$$[H^+] = Cd \cdot \frac{[acid]}{[salt]} = 1.8 \cdot 10^{-5} \cdot \frac{80 \cdot 0.1}{50 \cdot 0.1} = 2.8 \cdot 10^{-5}$$

$$pH_1 = -\lg [H^+]_1 = -\lg 2.8 \cdot 10^{-5} = -\lg 2.8 - \lg 10^{-5} = 5 - 0.45 = 4.55$$

3) The alkali that is added to the buffer system, reacts with acid by the equation: CH_3COOH

$CH_3COONa + NaOH = CH_3COONa + H_2O$.

Thus, the acid concentration decreases and the concentration of salt increases the number of added bases, $10 \cdot 0{,}1$.

4) From this we find $[H^+]$ and then pH_2:

$$[H^+]_2 = Cd \cdot \frac{[acid] - [base]}{[salt] + [base]} = 1.8 \cdot 10^{-5} \cdot \frac{80 \cdot 0.1 - 10 \cdot 0.1}{50 \cdot 0.1 + 10 \cdot 0.1} = 2.1 \cdot 10^{-5}$$

$$pH_2 = -\lg [H^+]_2 = -\lg 2.1 \cdot 10^{-5} = -\lg 2.1 - \lg 10^{-5} = 5 - 0.32 = 4.68$$

5) Find the ΔpH: $\Delta pH = 4{,}68 - 4{,}55 = 0{,}13$.

The answer: ΔpH = 0,13.

2) How to change the pH of the ammonia buffer that consisting of 30 ml 0.15 N solution NH_4OH ($K_D = 1{,}8 \cdot 10^{-5}$) and 40 ml 0.1 N solution of NH_4NO_3, when you add to it 5 ml of 0.1 N solution of HNO_3?

30 ml 0.15 N NH_4OH
40ml 0.1 N NH_4NO_3
$Cd(NH_4OH) = 1.8 \cdot 10^{-5}$
10ml of 0.1 N HNO_3
Δ pH = ?

1) You add the acid, the pH should move to the acid side,so Δ pH = pH_1 - pH_2 where pH_2 - this is the pH of the solution after adding acid, and pH_1 - before adding the acid, this initial pH buffer solution.

2) For the buffer system of the main type of rationality to first find concentration of OH^- to the basic equation of the buffer systems basic types:

$$[OH^-] = Cd \cdot \frac{[base]}{[salt]} = 1.8 \cdot 10^{-5} \cdot \frac{30 \cdot 0.15}{40 \cdot 0.1} = 2.02 \cdot 10^{-5}$$

$$pOH_1 = -\lg 2.02 \cdot 10^{-5} = -\lg 2.02 - \lg 10^{-5} = 5 - 0.3 = 4.7$$

$$pH_1 = 14 - pOH = 14 - 4.7 = 9.3$$

3) The acid added to the buffer system, reacts with base on the equation:

$HNO_3 + NH_4NO_3 = NN_4OH + H_2O$.

Thus, the concentration of the base decreases, while the concentration salt increases the amount of added acid, ie $5 \cdot 0{,}1$.

4) From this we find the $[OH^-]$, and then pH_2:

$$[OH^-]_2 = Cd \cdot \frac{[base] - [asid]}{[salt] + [acid]} = 1.8 \cdot 10^{-5} \cdot \frac{30 \cdot 0.51 - 5 \cdot 0.1}{40 \cdot 0.1 + 5 \cdot 0.1} = 1.6 \cdot 10^{-5}$$

$$pOH_2 = -\lg 1.6 \cdot 10^{-5} = -\lg 1.6 - \lg 10^{-5} = 5 - 0.2 = 4.8$$

$$pH_2 = 14 - pOH = 14 - 4.8 = 9.2$$

5) Find the Δ pH:

$$\Delta pH = 9{,}3 - 9{,}2 = 0{,}1.$$

Answer:Δ pH = 0,1.

B. Calculation of buffer capacity

3) Calculate the buffer capacity of bicarbonate buffer, which consists of 70ml 0.1 N solution H_2CO_3 ($C_D = 3{,}3 \cdot 10^{-7}$) and 50 ml 0.1 N solution of $NaHCO_3$, if titrated 5ml of the buffer took 4.8 ml of 0,1 N solution of NaOH.

70 ml 0.1 N NH_2CO_3
50ml 0.1 N $NaHCO_3$
$Cd = 3.3 \cdot 10^{-7}$
4.8ml of 0.1 N NaOH

$V_{buf.syst.} = 5$ ml

$B_a = ?$

1) In alkaline buffer capacity is calculate from the formula:

$$B_{alkaline} = \frac{C}{pH_1 - pH_0}$$

2) Calculate pH_0:

$$[H^+]_1 = Cd \cdot \frac{[acid]}{[salt]} = 3.3 \cdot 10^{-7} \cdot \frac{70 \cdot 0.1}{50 \cdot 0.1} = 4.62 \cdot 10^{-7}$$

$$pH_0 = -\lg [H^+]_1 = -\lg 4.62 \cdot 10^{-7} = -\lg 4.6 - \lg 10^{-7} = 7 - 0.66 = 6.34$$

3) $pH_1 = 8.2$, as the alkali titration end when a crimson color;

4) The buffer capacity is calculated at 1 liter buffer system, so find how many would go to the alkali titration of 1 liter or 1,000 ml buffer system:

for 5ml buffer system – 4,8 ml NaOH
to 1000ml – X ml
x = 960ml;

5) We calculate the number of mole equivalents of alkali, which would go on buffer titrate 1 liter of system:

in 1,000 ml NaOH – 0,1 mol NaOH
in 960ml NaOH – X
X = 0.096 mol equiv.

6) We calculate buffer capacity:

$$B_a = \frac{0.096}{8.2 - 6.34} = 0.05 \frac{mol \cdot eqv}{pH}$$

The answer: The buffer capacity of alkaline 0.05

4) Calculate the buffer capacity of phosphate buffer, which consists of 100 ml 0.1 N solution of Na_2HPO_4 and 80 ml 0.1 N solution NaH_2PO_4 ($K_D = 1,6 \cdot 10^{-7}$), if titrated 10ml of this buffer took 7.8 ml of 0,1 N solution of HCl.

100 ml 0.1 N Na_2HPO_4
80ml 0.1 N NaH_2PO_4
$Cd = 1.6 \cdot 10^{-7}$
7.8ml of 0.1 N HCl
$V_{buf.syst.} = 10$ ml

$B_a = ?$

1) Buffering capacity of acid calculated according to formula:

$$B_{acid} = \frac{C}{pH_0 - pH_1}$$

2) Calculate: pH_0:

$$[H^+]_0 = Cd \cdot \frac{[acid]}{[salt]} = 1.6 \cdot 10^{-7} \cdot \frac{80 \cdot 0.1}{100 \cdot 0.1} = 1.28 \cdot 10^{-7}$$

$$pH_0 = -\lg [H^+]_1 = -\lg 1.28 \cdot 10^{-7} = -\lg 1.28 - \lg 10^{-7} = 7 - 0.107 = 6.89$$

3) pH = 4,4, since titration with acid finish when you change the yellow color to pink;

4) The buffer capacity is calculated at 1 liter buffer system, so find how many would go to the acid titration of 1 liter or 1,000 ml buffer system:

in 10ml buffer system – 7,8 ml HCl
to 1000ml – X ml
X = 780ml;

5) We calculate the number of mole equivalents of acid, which would go to titrate 1 liter buffer system:

in 1000ml HCl – 0,1 mol HCl
in 780ml HCl – X
X = 0.078 mol equiv.

6) Calculate the buffer capacity:

$$B_k = \frac{0.078}{6.89 - 4.4} = 0.03 \frac{mol \cdot eqv}{pH}$$

The answer: The buffering capacity of acid 0,03.

5) Calculate the buffer capacity of the ammonia buffer, which consists of 40 ml 0.1 N solution NH_4OH ($K_D = 1{,}8 \cdot 10^{-5}$) and 30ml of 0,2 N solution NH_4Cl if titration 7ml it consumed 5.5 ml of 0.1 N HCl solution.

40 ml 0.1 N NH_4OH
30ml 0.2 N NH_4OH
$Cd = 1.8 \cdot 10^{-5}$
5.5ml of 0.1 N HCl
$V_{buf.syst.} = 7$ ml
$B_a = ?$

1) Buffering capacity of acid calculated according to the formula:

$$B_{acid} = \frac{C}{pH_0 - pH_1}$$

2) To find the pH of the buffer system of primary type, you first need find pOH. For finding the pOH rational first find the concentration of OH^- the core equation of the buffer systems of general type:

$$[OH^-] = Cd \cdot \frac{[base]}{[salt]} = 1.8 \cdot 10^{-5} \cdot \frac{40 \cdot 0.1}{30 \cdot 0.1} = 1.2 \cdot 10^{-5}$$

$$pOH = -\lg 1.2 \cdot 10^{-5} = -\lg 1.2 - \lg 10^{-5} = 5 - 0.08 = 4.92$$

$$pH_0 = 14 - pOH = 14 - 4.92 = 9.08$$

3) pH_1 = 4,4, since titration with acid finish when you change the yellow color to pink;

4) The buffer capacity is calculated at 1 liter buffer system, so find how many would go to the acid titration of 1 liter or 1,000 ml buffer system:

in 7ml buffer system – 5,5 ml HCl
to 1000ml – Xml
X = 785.7 ml;

5) We calculate the number of mole equivalents of acid, which would go to titrate 1 liter buffer system:

in 1000ml HCl – 0,1 mol HCl
in 785.7 ml HCl – X
x = 0.07857 mol • eqv.

6) Calculate the buffer capacity:

$$B_a = \frac{0.07857}{9.08 - 4.4} = 0.017 \frac{mol \cdot eqv}{pH}$$

The answer: The buffering capacity of acid 0.017

6) Calculate the buffer capacity of blood serum by acid, if titrated 5ml it took 7.5 ml of 0,1 N solution of HCl.

7.5ml of 0.1 N HCl
$V_{buf.syst.} = 5$ ml
$B_a = ?$

1) buffering capacity of acid calculated as follows:

$$B_{acid} = \frac{C}{pH_0 - pH_1}$$

2) pH_0 - a serum pH = 7.36; pH_1 - a pH of the solution after the titration, ie, 4.4, as in the serum methyl orange colour yellow, and the titration acid change color to pink at pH 4.4.

3) The buffer capacity is calculated at 1 liter buffer system, so find how many would go to the acid titration of 1 liter or 1,000 ml buffer system:

for 5ml buffer system – 7,5 ml HCl
to 1000ml – X ml
X = 1,500 ml;

4) We calculate the number of mole equivalents of acid, which would go to titrate of 1 liter buffer system:

in 1000ml HCl – 0,1 mol HCl
in 1,500 ml HCl – X
X = 0.15 mol equiv.

6) Calculate the buffer capacity:

$$B_k = \frac{0.15}{7.36 - 4.4} = 0.05 \frac{\text{mol} \cdot \text{eqv}}{\text{pH}}$$

The answer: The buffering capacity of acid $0.05 \frac{mol \cdot eqv}{pH}$

182. Buffer capacity — the number of mol eq. strong acid or alkali to be added to:
    a) 1 ml of buffer to change the pH to 1
    b) 10 l buffer system to change the pH to 1
    c) 1 liter of buffer system to change the pH to 1
183. Buffer capacity — the number of mol eq. acid strong alkali to be added to 1 liter of buffer system to change the pH to:
    a) 2
    b) 1
    c) 10
184. The method of analysis to determine the practical buffer capacity is:
    a) electrometric
    b) titrimetry
    c) osmometry
185. Formula for the buffer capacity in acid is:
    a) $B = \frac{C}{pH_0 - pH_1}$
    b) $B = \frac{C}{pH_1 - pH_0}$;
    c) $B = \frac{C}{pH}$
186. pH_1 in the formula for calculating the buffer capacity for acid:
    a) 3.1
    b) 8.2
    c) 4.4
187. Formula for the buffer capacity for alkali:
    a) $B = \frac{C}{pH_0 - pH_1}$
    b) $B = \frac{C}{pH_1 - pH_0}$
    c) $B = \frac{C}{pOH}$
188. Formula pH for calculating the buffer capacity of alkali:
    a) 3.1
    b) 8.2
    c) 4.4
189. Buffer capacity depends on:
    a) the nature and concentration of components
    b) the ratio and concentration of components
    c) the reaction of the environment and natural components
190. Buffer capacity of blood acid is:
    a) 0.02 mol/l
    b) 0.1 mol/l

c) 0.05 mol/liter

191. Buffer capacity of blood acid in comparison with alkali capacity by:
   a) lower
   b) higher
   c) same

5. The main questions of the seminar:

5.1.What is buffer capacity?
5.2. Factors that influence buffer capacity.
5.3. Determination of the buffer capacity in acid and base.
5.4. What are the buffer capacity values of blood plasma in acid and base.
5.5. What is the base supply of blood. Acid-base equilibrium.

6. The question for individual learning:

6.1. Organs and systems that are responsible for the acid-base equilibrium in human organism?

7. Examples of the task

7.1. How does pH of the buffer system change after adding for 30 ml of 0.2 M NaOH solution taking into account that before the buffer system contained 100 ml of 0.1 M acetic acid and 200 ml of 0.2 M of sodium hydroxide?
The answer: Firstly, calculate pH of the buffer system before adding of base:

$$\mathrm{pH}_1 = \mathrm{pK} - \lg\frac{[\mathrm{acid}]}{[\mathrm{salt}]} = -\lg 1.75 \cdot 10^{-1} - \lg\frac{100 \cdot 0.1}{200 \cdot 0.2} = 5.3$$

After adding NaOH the formation of sodium acetate takes place according to:

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

Thus, the acid amount decreases and the salt amount increases by equivalent base amount correspondently:

$$\mathrm{pH}_2 = -\lg 1.75 \cdot 10^{-1} - \lg\frac{100 \cdot 0.1 - 30 \cdot 0.2}{200 \cdot 0.2 + 30 \cdot 0.2} = 5.82$$

$$\Delta\mathrm{pH} = \mathrm{pH}_2 - \mathrm{pH}_1 = 5.82 - 5.3 = 0.49$$

7.2. Calculate the buffer capacity of solution containing of 7 ml of 0.1 M acetic acid and 3 ml of 0.1 M sodium hydroxide (K_D=1,8·10^{-5}) knowing that it was titrated by 4 ml of 0.1 M NaOH.
The answer: the buffer capacity is calculated as:

$$\mathrm{B}_{\mathrm{base}} = \frac{\mathrm{C}}{\mathrm{pH}_1 - \mathrm{pH}_0}$$

$$\mathrm{pH}_0 = \mathrm{pK} - \lg\frac{[\mathrm{acid}]}{[\mathrm{salt}]} = -\lg 1.8 \cdot 10^{-1} - \lg\frac{7 \cdot 0.1}{3 \cdot 0.1} = 4.38$$

$$\mathrm{pH}_1 = 8.2$$

Calculation of C:
4 ml of NaOH is used for titration of 10 ml of buffer solution
400 ml of NaOH is used for titration of 1000 ml of buffer solution
1000 ml of NaOH solution contain 0.1 mol-equivalent of NaOH
400 ml of NaOH solution contain 0.04 mol- equivalent of NaOH
Finally,

$$\mathrm{B} = \frac{0.04}{8.2 - 4.38} = 0.01\mathrm{mol} \cdot \mathrm{eqiv/value\ pH}$$

8. Homework (must be performed in the laboratory notebook):

8.1. How does the pH of phosphate buffer change which contains from 100 ml to 0,1 M potassium dihydrophosphate and 100 ml of 0.3 M potassium hydrophosphate after adding of 10 ml of 0.2 M NaOH ($K_D(NH_4OH) = 1{,}6 \cdot 10^{-7}$) ?

8.2. Calculate the buffer capacity of ammonium buffer containing 60 ml of 0.1 N NH_4OH and 40ml of 0.2 N NH_4Cl knowing that for titration of 10 ml solution, 5.5 ml of 0.1 N HCl was used ($K_D(NH_4OH) = 1{,}8 \cdot 10^{-5}$).

***9. The control test*:**

for instance:

9.1. The buffer capacity is dependent on:

a) the total amount of the components;

b) the ratio of components;

c) the product of components.

The answer: b

9.2. What is the buffer capacity of blood plasma taking into account that 36 ml of 0.05 N HCl solution was used for titration.

10. The algorithm of the experiments:

10.1. Determination of the buffer capacity in blood plasma by acid and base.

11. The detailed explanation of the following experiment:

11.1. Determination of the buffer capacity in blood plasma by acid and base.

Fill the first flask for titration by 5 ml of blood plasma (pH = 7.36) and add 2 drops of methyl orange and titrate by 0.1 M HCl solution.

Fill the second flask for titration by 5 ml of blood plasma (pH = 7.36) and add 2 drops of phenolphthalein and titrate by 0.1 M NaOH solution.

Calculate the buffer capacity of blood plasma by acid and base. Make a conclusion.

12. Control test:

Sample 1

1/What are the buffer systems?

2/What is the pH change of the phosphate buffer consisting of 100 ml of 0.1 M KH_2PO_4 and 100 ml of 0.3 M Na_2HPO_4 after adding 10 ml 0.2 M NaOH ($K_D=1.6*10^{-7}$)?

3/ 36 ml of 0.05 M HCl were spent for titration of 100 ml serum blood. pH of blood is changed to pH=7. Calculate the buffer capacity of the blood.

Sample 2

1/ What are the composition of bicarbonated buffer and the ratio of its components in the blood?

2/ What is the pH change of the bicarbonated buffer consisting of 7 ml to 0.1 M acid and 5 ml of 0.3 M salt after adding 2 ml 0.1 M NaOH ($K_D=4.4*10^{-7}$)?

3/ Calculate the buffer capacity of the ammonia buffer containing 60 ml of 0.15 M base and 40 ml 0.2 M salt. Taking into account that 10 ml of the given buffer solution were titrated by 5.5 ml 0.1 M HCl ($K_D=1.8*10^{-5}$)

TOPIC 10: Colligative properties. Osmosis.

1. Actuality of the topic: osmosis and osmotic pressure play a significant role in the processes of biological equilibrium. Calculation of osmotic pressure is used for preparation of the medical

liquids for intraveined injection and for eye drops. Knowledge of the topic is important for understanding of many biological processes.

2.General aim: is to apply the theoretical information about osmosis for understanding the processes in humans.

3. Actual aims and abilities:

- to calculate osmotic pressure, osmotic concentration and isotonic coefficient.

4. Literature:

4.1. Lecture materials;

Some properties of the dilute solution depends on the number of solute particles and do not depend on their nature. Such properties are called *colligative.*

Colligative properties of solutions are called that due to thermal motion and the amount of kinetic particles in solution (but not the nature of the components)

These include diffusion, osmosis, reduction of elasticity (pressure) of the solvent vapor above the solution, lowering the freezing point and raising the boiling point of solutions.

Diffusion

Diffusion is a spontaneous proccess of alignment of the solute concentration due to thermal motion of the particles of the solution.

When diffusion U = const, $\Delta S > 0$, $\Delta G < 0$.

The speed of many biochemical processes depends on the diffusion rate, delivery rate of the substances for biochemical reactions. Diffusion in the course of the transfer of substances through the cell membrane is a passive transport of substances.

Osmosis

Some have the ability to pass the membrane, for example, only the water molecules pass and the solute molecule remain.

Membrane, which allows only the solvent molecules to pass through it and do not permit the solute molecule, called semipermeable.

They can be:

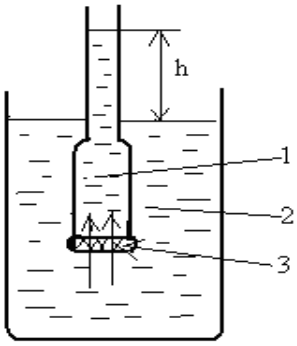
a) natural — plants and animals (cell membrane wall of intestine, blood vessels, the bladder wall, protoplasm);

b) artificial — collodion film, cellophane, gelatin;

c) inorganic — ferrocyanide copper silicates.

If a solution or a solvent and two solutions of differentconcentrations divided by a semipermeable membrane that will diffuse therethrough only water molecules.

Simplex and spontaneous diffusion of molecules of solvent through a semipermeable membrane in the direction of a more concentrated solution is called osmosis.



Osmosis is observed in the device, which is called the *osmometer* (***Picture 10.1)***.

Picture 10.1 The Simplest osmometer

1 - osmotic cell;

2 - vessel with the solvent;

3 - semi-permeable membrane;

h - the height of lifting solution in the osmometer.

When submerged in the osmotic cell vessel filled with water, the water molecules penetrate the semipermeable membrane into the cell and the volume of the liquid increases. When the liquid rises to a height of the osmometer h, an

equilibrium is established which the rate of diffusion of water molecules into the cell and out is the same. In this case, the hydrostatic pressure equals the osmotic pressure.

Excess hydrostatic pressure,which is installed in the system, and stops osmosis,is called osmotic pressure.

Method of measurement of osmotic pressure is called *osmometry*.

Osmotic pressure depends on primarily concentration of the solution.

It was experimentally proved that dilute solutions of non-electrolytes is similar to ideal gases (gases sparse). Therefore, the gas laws can be applied to such solutions.

Van't Hoff formulated the following law :

Osmotic pressure of a dilute solution of non-electrolyte gas pressure is equal to that which would produce solute being in the gaseous state at same temperature and occupying the same volume as the solution.

Mathematical expression of the law of van't Hoff for non-electrolytes has the form :

$$P_{Osm.\ Non\text{-}el.} = C_X R T,$$

where $P_{osm.\ non\text{-}el.}$ — Non-electrolyte osmotic pressure;

C_X — the molar concentration of the solution (for accurate measurements use the molal concentration);

R — universal gas constant (0.082 l0atm /degree 0mol);

T — absolute temperature (Kelvin).

The osmotic pressure of a molar solution of non-electrolyte is:

$P_{Osm.\ Non\text{-}el} = 0.082\ 10\ 0273 = 22.4$ bar .

In the electrolytic solution, particles are greater than in non-electrolyte solution at the same molar concentration. This is because electrolytes dissociate. For example, if the molecules are to dissolve 100 NaCl, then the solution is 200 particles, as one molecule in the dissociation gives two ions:

$$NaCl \leftrightarrow Na^{+} + Cl^{-}$$

Total number of dissolved particles in solution is called osmolarity

For solutions of non-electrolytes:

$$C_{osm.\ non\text{-}el.} = C_X.$$

Electrolyte solutions for osmotic concentration of the electrolyte is greater than the osmotic concentration of non-electrolyte at the same molar concentration of times :

$$C_{osm.\ non\text{-}el.} = I \bullet C_{osm.\ non\text{-}el.} = i \cdot C_X$$

where i — isotonic van't Hoff factor.

Then the equation of the osmotic pressure of the electrolyte solution has the form:

$$P_{Osm.\ Non\text{-}el..} = i\ C_X R T$$

Van't Hoff factor i shows how many times osmotic pressure and the osmotic concentration solution of electrolyte is greater than the osmotic pressure and osmolarity nonelectrolyte at the same molar concentration.

$$i = \frac{P_{Osm/El.}}{P_{Osm/Non-El.}} = \frac{C_{Osm.El.}}{C_{Osm.Non-El.}}$$

Van't Hoff factor is related to the degree of dissociation of dependence by the formula:

$$i = 1 + \alpha\ (n- 1)$$

where α — degree of dissociation;

n — number of ions per molecule which is dissociated electrolyte.

For example: $CaCl_2 \leftrightarrow Ca^{+2} + 2Cl^{-}$

$CaCl_2$ — strong electrolyte, so that the degree of dissociation = 1. Number of particles in solution at dissociation of one molecule is 3 ion.

Then: $i = 1 + 1(3-1) = 3$

For the degree of dissociation of weak electrolytes are conductometric method.

Solutions with the same osmotic pressure is called isotonic **osmolality.**

The solution whose osmolality is greater than the osmotic pressure of the solution or another standard, called **hypertensive solution**.

A solution which is less than the osmotic pressure than the osmotic pressure of the solution or other standard called **hypotonic solution.**

The biological significance of osmosis and osmotic pressure

Osmotic phenomena play an important role in animal and plant organisms.

1) The osmotic pressure of 7.7 atm blood = 770 kPa. It is created with inorganic and organic substances, colloidal particles, the total concentration of which is called osmolarity or osmolality (osmolality). Osmotic pressure fluctuations are possible within 1%. In humans, lowering P_{osm}. 1-2% with the introduction of a large amount of water, or a loss of salts (with strong sweating) causes vomiting, cramps, dizziness. Increasing $P_{osm.}$ and the introduction of large amounts of salts leads to the feeling of thirst, dehydration due to mucosal edema.

2) Osmotic blood concentration is 0.303 mol / l.

3) Some of the osmotic pressure of the blood due to macromolecular substances (proteins) is called oncotic and a pressure of 0,03 - 0,04 atm = 3,04-3,05 kPa.

4) Osmotic pressure of the liquid in the kidney of 25-30 times greater than the pressure in blood.

5) How to use a simple blood substitute 0.9 % solution of NaCl called or isotonic saline, as it osmotic pressure of the osmotic pressure of blood. For the same purpose, use 4-5% glucose solution.

6) The concentrated solutions of NaCl (10%) was used for rinsing purulent wounds (hypertensive dressings).

7) Hypertonic solution administered intravenously to relieve glaucoma intraocular pressure.

8) 35 % solution of CH_3COOK used as an osmotic diuretic.

9) 25 % solution of $MgSO_4$ used as a strong laxative.

10) Increase in blood glucose in diabetes is hyperosmolar coma.

11) The constant of osmotic pressure in the human body called isoosmia.

It is supported by:

a) The liver, which holds water and salt subcutaneous fat, which keeps the water in the human body;

b) The kidneys and the skin, which remove water and salt and light to remove water from the body.

12) *Hemolysis* — destruction of cell membranes to break them, placed in a hypotonic solution.Haemolysis occurs as a result of the fact that the cell concentration in the above than in a hypotonic solution and the water through the semipermeable the membrane is in a cell, towards a higher concentration in thereby increasing the volume of the cells and the membrane is broken.Hemolysis may proceed with the introduction of a hypotonic solution. Hemolysis starts at the value of the osmotic pressure of the blood 3,6-4,0 kPa.Complete hemolysis is observed at 2.6-3.0 kPa.1

13) *Plasmolysis* — cell shrinkage, placed in hypertonic solution. Plasmolysis occurs due to the fact that the concentration in the cell less than a hypertonic solution and water through the semipermeable membrane of the cells goes over the side a concentrated solution and its volume decreases .

14) Tension — this is due to the elasticity of the cell membrane high osmotic pressure inside the cell, as compared the extracellular fluid. Turgor explained some form organs and tissues in the body man.

15) In the plant cells an osmotic pressure reaches from to 5-20 atm and plants of deserts and salt flats — up to 170 atm.

16) An analytical method based on the measurement of the osmotic pressure, is called osmometry. It is used to determine molar mass of high-molecular compounds :

$$M_X = \frac{m_X \bullet 1000}{m_{Water} \bullet P_{Osm.}} RT$$

Where M_X — molar mass of the substance X;
m_X — mass of the substance;
m_{water} — mass of water;
$P_{osm.}$ — osmotic pressure;
R — universal gas constant (0.082 l0 atm / degree 0 mol);
T — absolute temperature (Kelvin)

Saturated vapor pressure above the solution

Saturated vapor pressure of the pure solvent depends on only on temperature. At higher temperatures the vapor pressure is increased.

The saturated vapor pressure of the solvent solution containing nonvolatile matter is lower than the pressure on the solvent as the solvent (water) is used for hydration of the particles in the solution, resulting in reduced solvent concentration per unit volume and less water evaporates. The higher of the solution concentration, the greater of the pressure drop.

French scientist F. Raul installed such a relationship:

relative reduction in the saturated vapor pressure solvent power is over sodium molar fraction of the dissolved a substance in solution.

$$\frac{P_0 - P}{P_0} = \frac{n}{n + n_0}$$

where P_0 — vapor pressure over the pure solvent ;
P — vapor pressure above the solution ;
P_0 - P — relative lowering of vapor pressure above the solution ;
n — number of moles of the substance;
n_0 — number of moles of the solvent.
$\frac{n}{n + n_0}$ — mole fraction of substance.

The relative decrease in the steam pressure is not take part of the solution it depends on the nature of the solute and solvent and the temperature, and depending on the number of particles in solution.

Raoult's law applies only to ideal solutions, for very dilute solutions in which no chemical interaction between the solute and the solvent.

Lowering the vapor pressure of the solvent over a solution affects the freezing and boiling points of the solution.

1) When the freezing temperature of vapor pressure over the liquid is equal to the vapor pressure over the solid phase. For example, the vapor pressure at 0^0C of ice is equal to the vapor pressure of the liquid:

$$P_{vaporice} = P_{vapor\ liquid}$$

Since the vapor pressure above the solution below, it must be cool, so he froze. Therefore solutions freeze at temperatures below 0^0C.

The difference between the freezing point of the solvent and the solution is called lowering the freezing point of the solution Δt_{freez} or depression.

$$\Delta t_{freez.} = t_{freez.\ water} - t_{freez.\ solution}$$

It depends on the concentration of the solution :

$$\Delta t_{freez.} = E_{Cr.} \cdot C_X$$

where Δt — lowering the freezing point of the solution;

C_X — the molar concentration of the solution (for accurate measurements use molality);

$E_{Cr.}$ — cryoscopic constant — is depression of molar solution of nonelectrolyte. E_{Cr} depends on the nature of the solvent (Table 10.1)

Cryoscopic constant and ebulioscoptic of some solvents

Solvent	Cryoscopic constant	Ebulioskoptic constant
Water	1,86	0,52
Ethanol	1,21	-
Acetone	1,5	2,4
Benzene	2,57	5,10
Acetic acid	3,07	3,90

Table 10.1

Depression molar solution of non-electrolyte is 1.86 .Molar solution of non-electrolyte freezes at t = - 1,860.

Since the colligative properties of solutions depend on the total number of particles in solution, the electrolyte will freeze at a lower temperature than non-electrolytes, as a result of dissociation of the electrolyte solution will be more particles. I.e., Depression is more in non-electrolytes than electrolytes at the same molar concentration. This shows the van't Hoff factor.

$$i = \frac{\Delta t_{Freez.El.}}{\Delta t_{Freez/Non-El...}}$$

2) The boiling temperature the vapor pressure above the liquid must be equal to the external pressure:

$$P_{vapour\ liquid} = P_{atm.}$$

Since the vapor pressure over the solution below, it should be heated to a higher temperature to the steam pressure was atmospheric pressure. Therefore solutions (water) to boil at a temperature above 100^0C.

The difference between the boiling point of the solvent and the solution is said to increase the boiling point of the solution $\Delta t_{Boil.}$

$$\Delta t_{boil.} = t_{boil.\ solution} - t_{boil.\ water}.$$

It depends on the concentration of the solution :

$$\Delta t_{boil.} = E_{Eb.} \cdot C_X,$$

where Δt — increase the boiling point of the solution;

C_X — the molar concentration of the solution (for accurate measurements use molality);

E_{Eb}.— Ebulioskopitic constant - this rise in temperature boiling molar solution of non-electrolyte.

E_{Eb}. depends on the nature of the solvent (Table 12.1)

Raising the boiling point of a molar solution of non-electrolyte equals 0.52. Molar solution of non-electrolyte boils at t = + 100,520. Low boiling of electrolytes is higher than the boiling point of non-electrolytes due to their dissociation. This ratio shows the Van't Hoff :

$$i = \frac{\Delta t_{Boil.El.}}{\Delta t_{Boil/Non-El.}}$$

Cryometry and ebuliometry

Analysis method is based on measuring the freezing point depression called cryometry, and on increasing the boiling point — ebuliometry.

These methods (often cryometry) is used to determine the molar mass of substances and isotonic coefficient van't Hoff.

1) To determine the molar mass of the non-electrolyte formula is used for depression :

$$M_X = E_{Cr.} \frac{m_X \bullet 1000}{m_{Water} \bullet \Delta t_{Freez.}}$$

where M_X — molar mass of the substance X;

E_{Cr}. — cryoscopic constant;

m_X — mass of the substance;

m_{water} — mass of water;

$\Delta t_{freez.}$ — depression or lowering the freezing point.

To determine the molar mass of the electrolyte used for depression formula :

$$M_X = i \bullet E_{Cr.} \frac{m_X \bullet 1000}{m_{Water} \bullet \Delta t_{Freez.}}$$

where M_X — molar mass of the substance X;

i — isotonic coefficient van't Hoff ;

$E_{Cr.}$ — cryoscopic constant;

m_X — mass of the substance;

m_{water} — mass of water;

$\Delta t_{freez.}$ — depression or lowering the freezing point .

To determine the molar mass nonelectrolyte by using higher boiling formula:

$$M_X = E_{Eb.} \frac{m_{X_X} \bullet 1000}{m_{Water} \bullet \Delta t_{Boil.}}$$

where M_X — molar mass of the substance X;

$E_{Eb.}$ — ebulioskopy constant;

m_X — mass of the substance;

m_{water} — mass of water;

$\Delta t_{boil.}$ — boiling point elevation.

To determine the molar mass of the electrolyte to increase the boiling point using the formula:

$$M_X = i \bullet E_{eb.} \frac{m_{X_X} \bullet 1000}{m_{water} \bullet \Delta t_{boil.}}$$

where M_X — molar mass of the substance X;

i — isotonic coefficient van't Hoff;

$E_{eb.}$ — ebulioskoptic constant;

m_X — mass of the substance

m_{water} — mass of water;

Δt_{boil} — boiling point elevation

2) To determine the van't Hoff method used for cryometry. First, determine the practical value $\Delta t_{freez.}$ using a Beckman thermometer, $\Delta t_{freez.}$ electrolyte. Then calculate $\Delta t_{freez.}$ non-electrolyte with the same molar concentration. Substituting these values into the formula, calculate i:

$$i = \frac{\Delta t_{freez.el.}}{\Delta t_{freez.non\text{-}el..}}$$

The biological significance of freezing point depression

1) Biological fluids are solutions of inorganic and organic matter , so do not freeze in the cold skin cells of exposed parts of the body.

2) Hardiness because this cell sap solutions of inorganic and organic substances are therefore not freezing at temperature below 0^0.

3) This also explains the safety of fruits and vegetables at 1^0

4) To keep the cooling products use a mixture of water and salt.

5) Measurement of $\Delta t_{freez.}$ biological fluids is used for calculating the total concentration of particles, osmotic concentration, it is impossible to make by other methods.

6) Cryometry is used to compute the molar mass biopolymers, as the temperature is lowered, they do not alter its structure.

7) Cryometry is used to determine the purity of medicines substances and determination of their molar mass.

8) Cryometry is used to determine osmotic pressure of blood plasma.

COLLIGATIVE PROPERTIES OF SOLUTIONS. OSMOSIS. CRYOMETRY.

Colligation is known as properties of solutions arising from thermal motion and the amount of kinetic particle system.

Osmosis is a spontaneous one-sided diffusion of solvent through a semi permeable membrane toward a solution with higher concentration.

Semipermeable membrane, which passes only the solvent molecules. Examples: natural - animal and plant cell membranes, the intestinal wall; artificial – colloid ion, cellophane, gelatin, parchment, clay wall of the vessel filled with sediment membrane.

Osmotic pressure is the excess hydrostatic pressure, which stops osmosis.

Osmotic concentration is the concentration of all the transport of particles of solute in solution.

Law Van't Hoff — the osmotic pressure of a dilute electrolyte solution is equal to the gas pressure that would produce the solute, while in a gaseous state, occupying the volume of the solution at the same temperature.

The equation of osmotic pressure for non-electrolytes:

$$P_{OSM} = CRT$$

where C — concentration of solution in mol/l;

R — universal gas constant, 0.082 l· atm / g mol;

T — temperature in Kelvin.

Equation for osmotic pressure of electrolytes:

$$P_{OSM} = i\,CRT$$

where i- isotonic coefficient of van't Hoff.

Isotonic coefficientVan't Hoff shows how many times the osmotic pressure of the electrolyte, the osmotic concentration of the electrolyte is greater than the osmotic pressure and osmotic concentration of the non electrolyte, at the same molar concentration.

$$i = \frac{P_{OSM.EL}}{P_{OSM.UNEL}} = \frac{C_{OSM.EL}}{C_{OSM.UNEL}}$$

Isotonic coefficient Van't Hoff related to the degree of dissociation α equation:

$$i = 1 + \alpha(\nu - 1)$$

where ν - the number of ions in the electrolyte which dissociates.

State the **isotonic** solutions with the same osmotic pressure.

Hypotonic solution is solution with small osmotic pressure.

Hypertonic solution is solution with a large osmotic pressure.

Haemolysis is the destruction of the cell membrane by placing the cells in the hypotonic solution.

Plasmolysis is wrinkling cells by placing it in the hypertensive solution.

Turgor is the elastic state of the cell membrane.

Osmotic blood pressure = 7.7 atm.

Oncotic pressure of blood is part of the osmotic pressure caused by the HMC and is equal to 0.04 atm.

Osmotic pressure of 1M solution of nonelectrolyte = 22.4 atm.

Examples

1) Calculate the osmotic pressure of 0,1 M urea solution.

$C_X(\text{urea}) = 0.1$ mol/l

$P_{OSM.} = ?$

1) Urea is non electrolyte so P_{OSM} is given by:

$P_{OSM.UNEL.} = CRT = 0{,}1 \cdot 0.082 \cdot 273 = 2.24$ atm.

The answer: 2.24 atm.

2) Calculate the osmotic pressure of 0.2 M solution of potassium chloride.

$C_X(KCl) = 0.2$ mol/l
$P_{OSM.} = ?$

1) Since the KCl electrolyte is then P_{OSM} calculated as follows:

$$P_{OSM.UNEL.} = iCRT$$

2) To find i use the formula:

$$i = 1 + \alpha(\nu - 1)$$

where α = 1, as KCl is a strong electrolyte and dissociates into two ions, so ν = 2.
Hence: $i = 1 + 1(2 - 1) = 2$;
3) Calculate the osmotic pressure:

$$P_{OSM.UNEL.} = 2 \cdot 0.2\ 0.082 \cdot 273 = 8.95 \text{ atm.}$$

The answer: 8.95 atm.

3) Calculate the osmotic pressure of 4% glucose solution.

$\omega = 4\%$
$C_6H_{12}O_6$
$P_{OSM.} = ?$

1) Transfer the mass fraction in the molar concentration:

$$C_N = \frac{\omega\% \cdot \rho \cdot 10}{M_X} = \frac{4 \cdot 1.1 \cdot 10}{180} = 0.24 \text{ mol/l}$$

2) Find the P_{OSM} glucose as a nonelectrolyte:

$$P_{OSM.UNEL.} = CRT = 0.24 \cdot 0.082 \cdot 273 = 5.47 \text{ atm.}$$

The answer: 5.47 atm.

4) Calculate the osmotic pressure of 10% solution of sodium chloride ρ = 1,2.

$\omega = 10\%$
NaCl
$P_{OSM.} = ?$

1) Transfer the mass fraction in the molar concentration:

$$C_N = \frac{\omega\% \cdot \rho \cdot 10}{M_X} = \frac{10 \cdot 1.12 \cdot 10}{58.5} = 1.91 \text{ mol/l}$$

2) Since the KCl electrolyte is then $P_{OSM.}$ calculated as follows:

$$P_{OSM.EL.} = iCRT.$$

To find i use the formula:

$$i = 1 + \alpha(\nu - 1),$$

where α = 1, since NaCl is a strong electrolyte and dissociates into two ions, so ν = 2.
Hence: $i = 1 + 1(2 - 1) = 2$;
3) Calculate the osmotic pressure:

$$P_{OSM.EL.} = 2 \cdot 1.91 \cdot 0.082 \cdot 273 = 49.04 \text{ atm.}$$

The answer: 49.04 atm.

5) Calculate the molar concentration of glucose, which no isotonic with blood in the 37°C.

$C_6H_{12}O_6$
$t = 37°C$
$P_{OSM.} = ?$

1) Since glucose non isotonic with blood, his $P_{OSM.}$ equal P_{OSM} blood and is equal to 7.7 atm.
2) Glucose is non electrolyte, so

$$P_{OSM.UNEL.} = CRT$$

Hence:

$$C = \frac{P}{RT} = \frac{7.7}{0.082 \cdot (273 + 37)} = 0.303 \text{ mol/l}$$

The answer: 0.303 mol / litre.

6) Whether the isotonic 1% in soluble urea and sodium chloride?

$\omega((NH_2)_2CO) = 1\%$
$\omega(NaCl) = 1\ \%$

$\rho = 1.03$

$P_{OSM.}(NaCl) = ?$
$P_{OSM.}((NH_2)_2CO) = ?$

1) Since isotonic solutions should be the same osmotic pressure, necessary to calculate the osmotic pressure each solution and compare.

2) Urea is nonelectrolyte so $P_{OSM.}$ is given by: $P_{OSM.\ UNEL.} = CRT$, pre-translated ω in C:

$$C_N = \frac{\omega\% \cdot \rho \cdot 10}{M_X} = \frac{1 \cdot 1.03 \cdot 10}{60} = 0.17 \text{ mol/l}$$

$$P_{OSM.}((NH_2)_2CO) = CRT = 0{,}17 \cdot 0{,}082 \cdot 273 = 3{,}84 \text{ atm.}$$

3) Find the $P_{OSM.}$ (NaCl), given that this electrolyte: $P_{OSM.\ EL.} = iCRT$.

$$C_N = \frac{\omega\% \cdot \rho \cdot 10}{M_X} = \frac{1 \cdot 1.03 \cdot 10}{58.5} = 0.17 \text{ mol/l}$$

$$i = 1 + \alpha(\nu - 1) = 1 + 1(2 - 1) = 2$$

$$P_{OSM.}(NaCl) = 2 \cdot 0.17 \cdot 0.082 \cdot 273 = 7.6 \text{ atm.}$$

Since the osmotic pressure of other differents, these solutions non isotonic.

The answer: solutions is non isotonic.

CRYOMETRY. EBULIOMETRY.

Saturated vapour pressure of solvent over the solution is lower than that of the solvent, since the dissolution of the substance decreases the concentration of solvent per unit volume of solution and there by decreases the number of water molecules, which leaves the surface of the solution. The larger C, the greater the pressure drop ΔP.

I Raoult's law: the relative decrease in vapor pressure of solvent over the solution equals the mole fraction of solute in solution:

$$\frac{P_0 - P}{P_0} = \frac{n}{n + n_0}$$

where P_0 — vapor pressure above the pure solvent;

P — vapor pressure above the solution;
P_0 - P — lowering the vapor pressure;
n — number of moles of substance;
n_0 — number of moles of solvent.

Fluid freezes at a temperature at which the vapor pressure of the solid state is equal to the vapor pressure of the substance in the liquid state. For example: when a pair of ice-0°C P = P water vapor. If the substance is dissolved, then P vapor solution will be lower. Water vapor than P and P couple of ice, is frozen solution. Therefore it is necessary to decrease the temperature of the solution. P to a vapor of solution was equal P a couple of ice.

Act II Raoul: temperature decrease (depression) freezing of the solution is directly proportional to its molar (molarity) of concentration:

$$\Delta t_{UNEL} = E_{cr} \cdot C$$

where the E_{cr} — Cryoscopy constant, which shows the depression of 1M aqueous solution of nonelectrolyte.

Molar solution of non-electrolyte Δt = 1.86.

For electrolytes equation is:

$$\Delta t_{EL} = i\, E_{cr} \cdot C$$

where the coefficient i of Van't Hoff shows how many times depression of the electrolyte solution more depressed then non-electrolyte solution at the same molar (molarity) concentration:

$$i = \frac{\Delta t_{EL.}}{\Delta t_{UNEL.}}$$

The liquid boils temperature at which the pressure of saturated steam is equal to the atmospheric pressure. When dissolved in water the pressure of steam decreases, and the solution will boil only when it as equal to the atmospheric pressure. For this we need to raise the temperature. The aqueous solutions must be above 100^0C.

Raising the boiling point is calculated by the formula:

$$\Delta t_{UNEL} = E_{eb.} \cdot C \qquad \Delta t_{EL} = i\, E_{eb.} \cdot C$$

$$E_{eb.}(H_2O) = 0.56.$$

Examples

7. Calculate depression 3.6% solution of glucose (ρ = 1,014).

$\omega = 3.6\%$ $\omega(NaCl) = 1\ \%$ $\rho = 1.014$ $\Delta t = ?$	1) Since glucose non-electrolyte, to find depression using the formula: $\Delta t_{noneelectrolyte.} = E_{cr.} \cdot C$; 2) the mass fraction translate into C: $C_N = \frac{\omega\% \cdot \rho \cdot 10}{M_X} = \frac{3.6 \cdot 1.014 \cdot 10}{180} = 0.2\ mol/l$

3) Find the depression: $\Delta t = 1{,}86 \cdot 0{,}2 = 0{,}38$.

The answer: 0.38.

8. Calculate the freezing point of 2M solution of NaCl .

$C_X = 2\ mol/l$ NaCl $\rho = 1.014$ $t_{freezing} = ?$	1) To determine the freezing temperature,you need to know Δt, as $\Delta t = 0° - t_{freezing}$, hence: $t_{freezing} = 0° - \Delta t$; 2) Calculate the depression of the solution NaCl: $\Delta t_{el.} = i \cdot E_{cr} \cdot C$; $i = 1 + \alpha(\nu - 1) = 1 + 1(2 - 1) = 2$; $\Delta t_{el.} = 2 \cdot 1{,}86. \cdot 2 = 7{,}44.$

3) Calculate $t_{freezing} = 0° - \Delta t = 0° - 7{,}44 = -7{,}44°$.

The answer: - 7.440.

9. At what temperature is freezing a 3% solution of ethanol in water?

C_2H_5OH $\omega = 3\%$ $t_{freezing} = ?$	1) To determine the freezing temperature need to know Δt, as $\Delta t = 0° - t_{freezing}$, hence: $t_{freezing} = 0° - \Delta t$;

2) Calculate the depression of the solution C:

$$C_N = \frac{\omega\% \cdot \rho \cdot 10}{M_X} = \frac{3 \cdot 1.0 \cdot 10}{46} = 0.65\ mol/l$$

3) Compute the solution C_2H_5OH depression and $t_{freezing}$:

$$\Delta t_{noneletrolyte} = E_{cr} \cdot C = 1.86 \cdot 0{,}65 = 1{,}2;.$$

$$t_{freezing} = 0° - \Delta t = 0° - 1{,}2 = -1.20.$$

The answer: - 1,20.

10. Calculate the depression of blood at 37°C, when the osmotic blood pressure 7.65 atm.

$P_{OSM.} = 7.65$ atm. $T = 37°C$ $\Delta t = ?$	1) The problem refers to the two parameters of blood – depression and osmotic pressure, so write two formulas: $\Delta t = E_{cr.} \cdot C$ и $P_{OSM.} = CRT$. In these formulas, there is a general parameter C; express it from each equation: $C = \frac{\Delta t}{E_{cr.}}$ and $C \cdot \frac{P_{osm.}}{RT}$

hence

$$\frac{\Delta t}{E_{cr.}} = \frac{P_{osm.}}{RT} \quad \rightarrow \quad \Delta t = \frac{P_{osm.} \cdot E_{cr.}}{RT}$$

$$\Delta t = \frac{7.65 \cdot 1.86}{0.082 \cdot (273 + 37)} = 0.56$$

The answer: 0.56.

11. Calculate the molar concentration of solution NaCl, which freezes at - 0.56° C.

$t_{freezing} = -0.56℃$ $\Delta t = 0℃$ NaCl	1) $t_{freezing} = 0° - \Delta t$; 2) Δt find a solution NaCl: $t_{freezing} = -(-0{,}56) = 0{,}56.$
$C(NaCl) = ?$	3) Given that the NaCl electrolyte: $\Delta t_{el.} = i \cdot E_{cr} \cdot C$; $i = 1\,\alpha\,(\nu - 1) = 1\,1\,(2 - 1) = 2;$ $C = \frac{\Delta t_{el.}}{E_{cr} \cdot i} = 0.15\ mol/l$

The answer: 0.15 mol / liter.

192. Colligative properties are caused by:
    a) potential energy of all particles in the P_{osm}
    b) thermal motion and kinetics of particles in the solution
    c) the nature and kinetics of particles in solution
193. Osmosis is:
    a) one-way diffusion of solute molecules through semi-permeable membrane
    b) voluntary unilateral diffusion of molecules across semi-permeable membrane towards greater concentration
    c) voluntary unilateral diffusion of molecules across semi-permeable membrane toward a lower concentration
194. Which kind of molecules we penetrate through semi-permeable membrane:
    a) solution
    b) solvent
    c) solute
195. Examples of natural semi-permeable membrane:
    a) cellophane
    b) the polyethylene
    c) the membrane of plant cells
196. Examples of natural semi-permeable membrane:
    a) cellophane
    b) polypropylene
    c) membrane of animal cells
197. Examples of artificial semi-permeable membrane:
    a) cellophane
    b) the polyethylene
    c) paper
198. Osmotic pressure is:
    a) the excess air pressure that stops osmosis
    b) the excess hydrostatic pressure, which stops osmosis
    c) hydrostatic pressure, which directs osmosis in the opposite direction
199. Osmotic pressure is measured by:
    a) stalahmometers

b) osmometers
c) viscosimeters

200. By law of Van't - Hoff osmotic pressure of dilute solutions in electrolyte gas pressure is:
a) committed to the solution in the gas state and in the bulk solution
b) committed to solvent in the gas state in the bulk solution and at the same temperature
c) commited to solute in the gas state in the bulk solution and at the same temperature
201. Mathematical expression of the law Van't Hoff for electrolyte:
a) $P = i \cdot CRT$
b) $P = CRT$
c) $P = n\ CRT$
202. Mathematical expression of the law Van't - Hoff for electrolytes:
a) $P = i \cdot CRT$
b) $P = CRT$
c) $P = n \cdot CRT$
203. Osmotic pressure in electrolyte 1M solution is:
a) 22.4 atm
b) 7.36 atm
c) 0.56 atm
204. Osmotic pressure of electrolyte is bigger than the osmotic pressure at the same pressure in an electrolyte molar concentration because:
a) electrolytes do not dissociate
b) electrolytes dissociate
c) kinetic particles are equal
205. Osmotic concentration is:
a) the number of kinetic particles of matter in solution
b) the number of kinetic solvent particles in the solution
c) the molar concentration of substances in solution
206. Osmotic concentration of electrolyte in comparison with the osmotic concentration in electrone at the same molar concentrations as:
a) electrolytes do not dissociate
b) electrolytes dissociate
c) because of kinetic particles are equal
207. Isotonic coefficient i shows:
a) how many times Posm. is electrolyte greater than Posm. in electrolyte;
b) how many times Posm. is electrolyte greater than Posm. in electrolyte at the same molar concentration;
c) how many times Posm. electrolyte is less than Posm. in electrolyte whith same molar concentration.
208. Van't Hoff isotonic coefficient is shows:
a) how many times Cosm. is electrolyte greater than Cosm. in electrolyte at the same molar concentration
b) how many times Cosm. is electrolyte less than Cosm. in electrolyte at the same molar concentration
209. How does isotonic coefficient change with the degree of dissociation:
a) $i = 1 - \alpha\ (n - 1)$
b) $i = 1 + \alpha\ (n - 1)$
c) $i = 1 + \alpha\ (n + 1)$
210. Hypotonic solution, osmotic pressure is called:
a) less than Posm second solution
b) with the same Posm second solution
c) greater than Posm second solution

211. Solution is called isotonic, when osmotic pressure is:
a) less than Posm second solution
b) with the same Posm second solution
c) greater than Posm second solution
212. Osmotic pressure in hypertonic solution is:
a) less than Posm second solution
b) with the same Posm second solution
c) greater than Posm second solution
213. In medicine we use isotonic NaCl solution with mass fraction there of:
a) 1%
b) 0,5%
c) 0,9%
214. Physiological or isotonic solution is recalled:
a) 0.9% solution of Na_2SO_4
b) 0.9% solution of NaCl
c) 0.9% solution of $NaNO_3$
215. In medicine is used hypertonic NaCl solution with mass fraction:
a) 1%
b) 10%
c) 0,9%
216. Isotonicity is:
a) constancy of pH
b) the constancy of blood pressure
c) the constant of osmotic pressure
217. Size osmotic pressure:
a) 22.4 atm
b) 7.36 atm
c) 7.7 atm
218. Osmotic concentration of blood is:
a) 1 mol/l
b) 0.303 mol/l
c) 0.7 mol/liter
219. Isotonicity in humans is supported by:
a) kidneys
b) skin and bones
c) brain and liver
220. Isotonicity a in humans is supported by:
a) liver and subcutaneous tissue
b) skin and bones
c) brain and liver
221. Hemolysis is:
a) wrinkled cells in hypotonic solution;
b) destruction of cells in hypotonic solution;
c) steady state cells
222. Plasmolysis is:
a) increase in cell volume
b) wrinkling cells in hypertonic solution
c) destruction of cells in hypotonic solution
223. Turgor is:
a) The elasticity of the membrane
b) wrinkling of the membrane

c) destruction of cells

224. Cell turgor explains:
a) increased osmotic pressure within cells
b) reduction of osmotic pressure in the cell
c) high blood pressure

225. Cell turgor explains:
a) Van't Hoff equilibrium
b) balance of Donnana
c) Raul balance

226. During hemolysis osmosis sent:
a) cells
b) osmosis stops
c) in the cell

227. What is the derection of plasmolysis during osmosis
a) cells
b) osmosis stops
c) in the cell

228. Oncotic blood pressure is:
a) 1 atm
b) 4 atm
c) 0.04 atm

229. Oncotic blood pressure is caused by:
a) electrolytes
b) proteins
c) in electrolytes

230. Laxatives are 25% in solution $MgSO_4$ because it is:
a) isotonic solution
b) hypertonic solution
c) hypotonic solution

231. What happens when the river fish will be put in pH more than 6:
a) hemolysis
b) plasmolysis
c) nothing happens

232. Isotonic solution of urea and 1M acetic acid are:
a) isotonic
b) hypotonic solution of urea
c) hypertonic solution of urea

233. The need to restore the body's osmotic pressure to normal conditional sense is:
a) hunger
b) thirst
c) sleep

234. When injected into the body from eating much sugar or salts osmotic pressure:
a) falling
b) changes
c) increases

235. What happens if the fish that is put into the river?
a) turgor
b) plasmolysis phenomenon
c) hemolysis phenomenon

236. Plasmolysed cells have:
a) Posm. > Posm. outside in the middle
b) Posm. = Posm. outside in the middle

c) Posm. < Posm. outside in the middle

237. Saturated vapor pressure above the solution in comparison with the saturated vapor over clean solvent is:
a) more
b) less
c) the same

238. The first law of Raul: relative decrease of vapor pressure:
a) solution containing solute fixed directly proportional to the molar fraction of dissolved substance
b) solution containing solute fixed equal molar fraction of dissolved substance
c) prime propotional solvent molar fraction solute

239. The equation of the first law Raul:
a) $\frac{P_0 - P}{P_0} = \frac{n}{n + n_0}$
b) $\frac{P - P_0}{P_0} = \frac{n}{n + n_0}$
c) $\frac{P - P_0}{P_0} = \frac{n_0}{n + n_0}$

240. Solutions freeze at temperatures:
a) 0° C
b) above 0°C
c) below 0°C.

241. Lower temperature freezing solution Δt is the difference between the temperature of freezing water:
a) solute freezing point
b) freezing the solution
c) freezing point of water and cryoscopic constant

242. Δt in electrolyte freezing solution is:
a) K·C
b) $\frac{K}{C}$
c) $\frac{C}{K}$

243. Cryoscopic constant is:
a) lowering the temperature of freezing 1 molar electrolyte solution
b) increase the temperature of freezing 1 molar solution
c) lowering the temperature of freezing 1 molar in electrolyte solution

244. Cryoscopic constant depends on nature:
a) solution
b) solute
c) solvent

245. Δt freezing electrolyte solution is:
a) $i \cdot$ K·C
b) $\frac{K}{C}$
c) $\frac{C}{K}$

246. The freezing temperature of electrolytes compared with non electrolytes by the same molar concentration is:
a) higher
b) lower
c) are equal
247. Electrolytes freeze at a lower temperature compared with non electrolyte because electrolytes:
a) dissociate
b) does not dissociate
c) evaporate
248. Reduction of saturated vapor pressure of the more than:
a) the lower concentration
b) the higher the concentrate
c) is independent
249. Isotonic coefficient shows:
a) how much electrolyte Δt is greater than non electrolyte
b) how many times the electrolyte Δt is greater than non electrolyte at the same molar concentration
c) how many times the electrolyte Δt is less than non electrolyte at the same molar concentration
250. Freezing in electrolyte 1M solution is:
a) 1°C
b) 1,86°C
c) 0°C
251. Blood freezes at temperature:
a) 0°C
b) -7,7°C
c) 0,56°C
252. The freezing temperature saline is:
a) -1°C
b) -1,86°C
c) - 0,56°C
253. Saturated vapor pressure of water is equal to:
a) atmospheric pressure at 100°C
b) osmotic pressure of 100°C
c) oncotic pressure
254. Vegetables and fruit can be stored for t = -1°C because:
a) freezing the cell sap due to higher content of organic matter in it
b) freezing the cell sap due to lower content of organic matter in it
c) freezing the cell sap with the same freezing vegetables
255. Liquid boiling of its saturated vapor pressure is:
a) equal to atmospheric pressure
b) greater than atmospheric pressure
c) less than atmospheric pressure
256. Raising the boiling point of solutions depends on:
a) concentration
b) volume
c) temperature
257. Increasing t in electrolyte boiling solution described by:
a) $\Delta t_{boil.} = E \cdot C$
b) $\Delta t_{boil.} = K \cdot C$
c) $\Delta t_{boil.} = E/C$

258. Increasing t boiling electrolyte solutions described by:
   a) $\Delta t_{boil.} = i \cdot E \cdot C$
   b) $\Delta t_{boil.} = i \cdot K \cdot C$
   c) $\Delta t_{boil.} = E/C$
259. Ebulioscopic constant E depends on:
   a) the nature of solute
   b) the nature of the solvent
   c) temperature
260. The greater the concentration of solution:
   a) the lower the boiling point
   b) the higher the boiling point
   c) boiling temperature 100°C

5. The main questions of the seminar:

5.1.What is the coligative properties of solution?
5.2. What is osmosis?
5.3. Semipermeable membranes (the determination and the samples).
5.4. Osmotic pressure.
5.5. Van't Hoff's law. Osmotic concentration.
5.6. Isotonic coefficient of Van't Hoff and its relationship with the dissociation degree.
5.7. Hypotonic, isotonic, hypertonic solutions and their meaning in medicine.
5.8. Biological meaning of osmosis.
5.9. Donnan membrane equilibrium.

6. The question for individual learning:

6.1. The freezing point of solution.
6.2. Raul law.
6.3. Cryometry and ebuliometry, application in medicine.

7. The examples of the task

7.1. Calculate the osmotic pressure of 0.2 M diamide carbonic acid ($CO(NH_2)_2$ at t = 0 °C.
The answer: The osmotic pressure for non-electrolytes is calculated as:
$P_{OSM.} = CRT = 0.2 \bullet 0.082 \bullet 273 = 4.48$ atm

7.2. Calculate the osmotic pressure of glucose solution with the weight fraction of 5 %, ρ= 1 g/ml, t = 27 ^oC.
The answer: firstly, the molar concentration is calculated as:

$$C_x = \frac{\omega\% \cdot \rho \cdot 10}{M} = \frac{5 \cdot 1 \cdot 10}{180} = 0.28 \text{ mol/l}$$

The osmotic pressure for non-electrolytes is found to be:
$P_{OCM.} = CRT = 0.28 \bullet 0{,}082 \bullet (273+27) = 6.8$ atm
7.3. Calculate P_{OSM} of NaCl with of 5.85 %, ρ= 1.04 g/ml, t = 0 ^oC.
The answer:
a) the molar concentration is calculated as:

$$C_x = \frac{\omega\% \cdot \rho \cdot 10}{M} = \frac{5.85 \cdot 1.04 \cdot 10}{58.5} = 1 \text{ mol/l}$$

b) isotonic coefficient (*i*) is determined as:

$$i = 1 + \alpha (n - 1) = 1 + 0.96 (2 - 1) = 1.96$$

c) the osmotic pressure for electrolytes is found to be:

$$P_{OSM.} = iCRT = 1.96 \bullet 1 \bullet 0{,}082 \bullet 273 = 4.36 \text{ atm}$$

8. Homework (must be performed in the laboratory notebook):

8.1. Calculate the osmotic pressure for diamide of carbonic acid ($CO(NH_2)_2$ and acetic acid knowing thatboth of them have 0.6 % of weight fraction and dissociation degree of acetic acid equals 0.01, ρ= 1 g/ml. Are the solutions isotonic?

8.2. Determine molar concentration of sucrose solution that is isotonic to blood.

***9. The control test*:**

for instance:

9.1. Colligative properties of the solutions are depended on:

a) solution concentration;

b) the amount of the soluble particles;

c) the molar concentration.

The answer is b.

9.2. Calculate P_{OSM} of NaCl with of 5.85 %, ρ= 1.04 g/ml, t = 0 ^oC.

10. The algorithm of the experiments:

10.1. Osmosis observation.

10.2. Preparation of the inorganic semipermeable membrane.

10.3. The formation of tree likewise compounds.

10.4. Hemolysis and plasmolysis of red blood cell (erythrocyte).

11. The detailed explanation of the following experiment:

11.1. Osmosis observation.

Osmosis meter is filled by sucrose solution and immersed in a glass with water. Fix the initial level of the solution in the osmosis meter and the level of the solution 30 min later. Make a conclusion.

11.2. Preparation of the inorganic semipermeable membrane.

A test-tube is filled with 2 ml of $CuSO_4$ solution and potassium hexacyanoferrate (II). Do not mix. Observe the change 20 min later. Write the equations and explain which substance is the semipermiable membrane. Why does a cell grow?

11.3. Three like wise formation

A test-tube is filled with 5 ml of sodium silicate and the crystals of $MnCl_2$, $CoSO_4$, $NiCl_2$ are immersed. Do not mix the solutions. Write the equations and indicate the semipermiable membrane.

11.4. Hemolysis and plasmolysis red blood cell (erythrocyte).

Prepare three compositions as stated in the following table:

1 test-tube	***2 test-tube***	***3 test-tube***
3 ml of 0.2 % NaCl	3 ml of 0.9 % NaCl	3 ml of 4 % NaCl
3 drops of blood	3 drops of blood	3 drops of blood

Leave the test-tube for 15 min (do not mix). Make a conclusion.

12. Control test

Sample 1

1/What is the condition of the liquid freezing?

2/What is the freezing point of the solution containing 10 g of sodium chloride in 100 g of water knowing the dissociation degree of sodium chloride is 60 %?

3/What is the osmotic pressure of 18 % of sucrose at 20 °C when the solution density is 1,07 g/cm^3?

Sample 2

1/What is the osmotic pressure?
2/What is the boiling point of 5 % sucrose in water?
3/What is the osmotic pressure of 5 % $NaHCO_3$ solution that is used for the injection during acidosis (ρ=1.035, α=0.98)?

TOPIC 11: Thermal effects of the chemical direction of the processes.

1. Actuality of the topic: knowledge of chemical thermodynamics is necessary to understand the energetics of biochemical processes. Calculation of thermal effect is used in dietology for determination of food energy.

2.General aim: is to interpret the base thermodynamics laws for biological process characterization.

3. Actual aims and abilities:

- to know thermodynamics laws;
- to be able to calculate thermodynamic equations and to use them for determination of food energy.

4. Literature:

4.1. Lecture materials;

Thermodynamics - the science of energy transformations.

Chemical Thermodynamics studying the thermodynamic properties of substances, depending on their composition, structure, state.

Bioenergy — the science of the transformation of energy in living organisms.

Basic conceptions of the thermodynamics

Thermodynamic system — the body or group of bodies which are in communication, and mentally isolated from the environment.

There are such types of thermodynamic systems:

a) *isolated* — systems that do not communicate with the environment neither energy nor mass. For example, the spacecraft; chemical reactor with thermal insulation, Dewar vessel;

b) *closed* — systems which are not exchanged mass but only energy. For example, the dissolution process, which may go with the evolution or absorption of heat (but without the evolution of gas);

c) *open* — systems which exchanges with the environment the mass and the energy. For example, a living organism;

d) *homogeneous* — systems, which consist of a single phase, i.e. there is no surface ofphase division(the interface). For example, the alcohol solution in water; the air;

e) *heterogeneous* — systems which consist of two or more phases, separated by the interface. For example, the salt crystals in a saturated solution, water - benzene, a living organism.

Phase — a homogeneous part of the system with the same chemical and thermodynamic properties, separated from other parts of the interface.

Properties and state of the system is determined by its physico-chemical *parameters*.

State of the system — a combination of all the physical and chemical properties of the system.

System parameters are divided into:

a) *extensive* — depends on the size of the system. For example, the volume V, mass m, heat capacity c;

b) *intensive* — independent from the system size. For example, the pressure P, the temperature T, the potential E, the concentration C (can take 20ml 0.1N solution and 500ml of 0.1N solution, i.e. the concentration will be the same).

Changing any of the thermodynamic parameters is called the thermodynamic process.

Thermodynamic processes can be reversible or irreversible.

Thermodynamically reversible is the process in which reactions take place practically under equilibrium conditions, when the rates of the forward and reverse reactions differ by infinitesimal amount, i.e. reset does not require energy. For example, synthesis of ammonia:

$$3H_2 + N_2 \rightarrow 2NH_3.$$

Thermodynamically irreversible is the process in which reactions occurs spontaneously and are characterized by a finite velocity. Resetting requires energy.For example, the synthesis of the water according to the equation $2H_2 + O_2 \rightarrow 2H_2O$ at a temperature of 600^0C, and water decomposition $2H_2O \rightarrow 2H_2 + O_2$ at a temperature of 800^0C. Thermodynamically irreversible are also the diffusion of gases, heat transfer, vital processes, aging.

The basic thermodynamic parameters are the temperature T, the pressure P, the volume V. Therefore, the thermodynamic processes can be:

a) *isothermal*, i.e. flow at a constant temperature (change P and V);

b) *isobaric*, i.e. flow at constant pressure (change V and T);

c) *isochoric*, i.e. at a constant volume flow (T and P are changed);

d) adiabatic, i.e. flow without heat exchange with the environmens (changing at a time P, T,V).

First law of thermodynamics

Body around us have a certain energy.

The internal energy of the system U is the total of the energies of all kinds of movements (translational, rotational, vibrational) of the particles forming the system (molecules, atoms, ions, nuclei, electrons).

Reserve of the internal energy determined by the nature of substance, its weight and condition of the system. To determine the absolute value of it is impossible, because internal energy depends from the state of the system, but you can define ΔU:

$$\Delta U = U_2 - U_1$$

In thermodynamics use such thermodynamic function as the *enthalpy H or enthalpy of the system.*

Enthalpy is the sum of the internal energy and the work of expansion A:

$$H = U + PV$$

Work A - an ordered form of energy transfer:

$$A = PV$$

The first law of thermodynamics is the law of conservation of energy, formulated by M.Lomonosov in 1760.

There are several formulations of the first law:

a) energy is neither created not destroyed, possible only the transition from one type of energy to another in equivalent amounts (Lomonosov);

b) the internal energy of an isolated system is a constant value regardless of the processes taking place in it;

c) the heat supplied to the system or educed from it, spent on the changes in internal energy of the system and commission work;

d) the perpetual motion machine of the first kind is impossible.

The first law of thermodynamics establishes a relationship between the amount of heat Q, which is supplied to the system, the work of A, which operates the system, and the change in internal energy ΔU:

$$Q = \Delta U + A$$

This equation is an expression of the first law of thermodynamics. Chemical reaction does work when it occurs with a change in volume . If the reaction proceeds with an increase in volume (for example, evolution of gas) it does work against the forces of external pressure (+ A) If the response is a decrease in volume (e.g., dissolutionalcohol in the water or gas in the liquid) , the external pressure does work on the chemical reaction (A).

If the process is isobaric, the$\Delta H = \Delta U + P\Delta V$,

Where ΔH - enthalpy.

Enthalpy depends on the nature of the materials and their status.

Thermal effects of chemical reactions

Physical chemistry section, which is studying thermal changes in chemical reaction is called *thermochemistry*.

Thermal effect of the chemical reaction is the amount of heat which is evolved or absorbed at chemical reaction process.

In thermochemistry, chemical processes are usually written in the form of thermochemical equations, which indicate the enthalpy state of aggregation of the starting materials and reaction products (stoichiometric coefficients can be fractional).

The reactions which occurs with heat, called *exothermic*.

For example, $C_{(s)} + H_2O_{(g)} = CO_{(g)} + H_{2(s)}$; $\Delta H = 132.0$ kJ.

The reactions that take place with heat absorption, called *endothermic*.

For example: $C_{(s)} + 1/2O_{2(g)} = CO_{(g)}$; $\Delta H = -110.5$ kJ.

This is the thermodynamic way of writing thermochemical reactions.

The basic law of thermochemistry was formulated by Russian scientist G.I.Gess in 1836:

The heat effectof chemical reaction does not depend on the way of its passage, but only on its initial and final state.

For example:

$C_{(s)} + 1/2O_{2(g)} = CO_{(g)}$	$\Delta H = -10,5$kJ
$CO_{(g)} + 1/2O_{2(g)} = CO_{2(g)}$	$\Delta H = -83.2$kJ
$C_{(s)} + O_{2(g)} = CO_{2(g)}$	$\Delta H = -393,7$kJ

Thermochemistry allows to determine the effects of different thermal reactions - the heat of formation of the chemical compound out of simple substances, heat of combustion, dissolution, neutralization, melting etc.

Thermal effects related to 1 mol of a substance under standard conditions - temperature 298K and a pressure of 101.3 kPa — called *standard*.

Standard heat (enthalpy) of production ΔH_o — the heat of reaction the formation of 1 mole of substance from simple substances at a temperature of 298K and a pressure of 101.3 kPa.

In thermochemistry thermal effects (enthalpy) of simple substances (H_2, O_2, N_2, etc.) is taken as zero.

Values of the standard thermodynamic functions are given in ***Table 11.1.***

Standard thermodynamic functions of certain substances

Compound	$\Delta H^0_{ret.,}$ kJ/mole	ΔG, kJ/mole	S^0, J/K·mole
Alanine (s)	-562,75	-370,20	129,2
Acetylene	226,73	209,2	200,83
Acetone (l)	-246,81	-153,55	198.74
Glycerol (l)	-670,70	-479,49	204,60
Glucose (s)	-1274,45	-910,56	212,13
Saccharose (s)	-2221,70	-1544,31	360,24
Acetic acid (l)	-484,21	-389,45	159,83
Ethanol (l)	-276,98	-174,18	161,04
H_2O (g)	-241,83	-228,60	188,72
H_2O (l)	-285,84	-237,19	69,94

NH_3 (g)	-46,19	-16,64	192,51
CO_2 (g)	-393,	-394,38	213,64
H_2 (g)	0	0	130,5
HCl (g)	-92,3	-95,2	186,8
O_2 (g)	0	0	205,0
SO_2 (g)	-296,9	-300,2	248,1
SO_3 (g)	-395,8	-371,2	256,7

Table 11.1

Standard heat (enthalpy) of combustion ΔH_o — the heat of reaction the combustion (oxidation) of 1 mole of substance at a temperature of 298K and a pressure of 101.3 kPa.

The standard enthalpy of combustion of certain substances

Compound	Combustion products	$\Delta H^0_{heat.}$, kJ/mole
NH_3 (g)	N_2 & H_2O	-382,57
NH_3 (g)	NO & H_2O	-292,71
SO_2 (g)	SO_3	-98,28
C_2H_5OH (l)	CO_2 & H_2O	-1366,91
$C_6H_{12}O_6$ (s)	″	-2821,90
$C_{12}H_{22}O_{11}$ (s)	″	-5645,49
CH_4 (g)	″	-890,34
C_2H_6 (g)	″	-1559,87
C_6H_6 l)	″	-3267,61

Table 11.2

The heat of combustion is practically determined in bomb calorimeter.

In thermochemical calculations use consequences of the law of Hess.

a) The heat of reaction is the difference between the sum of the heats formation of reaction products and the sum of the heats of formations the raw materials taken from the corresponding stoichiometric coefficients.

$$\Delta H = \sum \Delta H \text{ prod.} - \sum \Delta H \text{ form}$$

Calculate the heat of reaction $COg.+H_2g. = CH_4g.+ H_2Og.$, when the heat of formation of CO = -110 kJ / mole CH_4 = -74.9 kJ / mole, H_2O = -241.8 kJ / mole.

Decision: $COg.+ 3H_2g. = CH_4g. + H_2Og.$,

$$\Delta H = \sum \Delta H \text{ prod.} - \sum \Delta H \text{ form}$$

$$\Delta H = (\Delta H(CH_4) + \Delta H (H_2O)) - \Delta H (CO) = -74,9 + (-241,8) - (-110,5) = -206,2 \text{ kJ/mole}$$

b) The heat of reaction of combustion (oxidation) of the substance is equal to the difference between the sum of the heats of combustion (oxidation) of the starting materials and the amount of the heats of combustion (oxidation) reaction products taken from corresponding stoichiometric coefficients.

$$\Delta H\text{comb.} = \sum \Delta H\text{comb.form.} - \sum \Delta H \text{ comb.prod.}$$

Calculate the heat of reaction: $CH_4 + CO_2 \rightarrow CO + H_2$, If $\Delta H\text{comb.}(CH_4) = -890,3$kJ/mole, $\Delta H\text{comb.}(CO) = -283,0$ kJ/mole, $\Delta H\text{comb.}(H_2) = -241,8$kJ/mole. ($CO_2$) (don't burn).

Decision: $CH_4 + CO_2 \rightarrow 2CO + 2H_2\uparrow$

$\Delta H = \Delta H\text{comb.}(CH_4) - (2\Delta H\text{comb.}(CO) + 2\Delta H\text{comb.}(H_2)) = -890,3 - (- 2 \cdot 283,0 - 2 \cdot 241,8) =$
$= 159,3$ kJ/mole.

Heats of combustion is often used to determine the effects of thermal reactions of organic substances, since in the combustion of organic materials are always produced CO_2 and H_2O.

Laws and methods used to study the thermochemistry of the thermal effects of various biochemical reactions in vitro. Energy comparison of healthy and diseased cells allows us to study various pathological appearances, develop diagnostics and treatments.

Application I law of thermodynamics to biological systems and energy characteristic biochemical processes.

A. *Heat of combustion (oxidation) of food in the live organism is a source of energy, which is carried out by its vital functions (table 11.3).*

Calorific value of nutrients in vivo

Substance	Heat of combustion, Kcal
Carbohydrates	4,1
Fats	9,3
Proteins	4,1

Table 11.3

On the basis of data about calorie content of food compose scientifically based standards needs in food, taking into account energy costs.

B. *A living organism is an open system, irreversible, nonequilibrium heterogeneous.*

C. *The first law of thermodynamics apply to living organisms, as the body is not a source of energy and all kinds of work in it (mechanical work muscles, heart, osmotic processes, intestinal absorption, ion pumps, electrical phenomena, etc.) are performed by energy released during the oxidation of nutrients. Energy is stored in materials with energy bond (anhydride) - ATP, acetylphosphate.*

Second law of thermodynamics

The second law of thermodynamics explains the possibility of the reaction and its direction.

Many processes in nature occur spontaneously without any external influences and in one direction only. For example, the transfer of heat from a warmer to a less heated body , dissolving the salts, evaporating the liquid, biochemical processes in the body, the aging organism. And these processes are irreversible. Therefore to convert heat from a cold body to a hot (as in refrigerators) must expend energy (electricity) .

Spontaneously occur only those processes that come with the release of energy.

In spontaneous irreversible processes is the transition of a thermodynamic system with a more ordered state in less orderly.

Spontaneous processes used to produce useful work, while there are losses in the form of heat. Therefore, to return to a state where more energy.

Along with the thermodynamics of irreversible processes considering reversible processes, which take place almost in equilibrium conditions, such as the synthesis of ammonia. Reset does not require energy input.

There are several formulations of the second law of thermodynamics

a) all the processes of energy transformation occur with a scattering part as heat energy;

b) process, the only result which is conversion of heat into work, is impossible;

c) a perpetual motion machine of type II is impossible.

To evaluate the degree of disorder exists thermodynamic function - entropy.

Entropy is a measure of disorder.

$$\Delta S = \Delta Q / T$$

This equation is the mathematical expression of the second law of thermodynamics.

Entropy is a state function, its variation depends on the initial and final states of the system.

Spontaneously occurring processes occur with an increase in entropy: $\Delta S > 0$, the system becomes disordered. For example, evaporation, dissolution, diffusion.

Calculation ΔS in chemical reactions:

$$\Delta S = \Sigma S_{prod.} - \Sigma S_{form.}$$

Entropy changes in chemical reactions when the reaction is the change in volume. If the volume of the reaction increases, ΔS increases (increases as the disorder), and conversely.

On the course of a chemical process depends on two factors entropy and enthalpy.

Action enthalpy H and entropy S opposite factors. If the enthalpy factor operates in the direction of the particle aggregation and reducing energy, the entropy factor - the disaggregation of the particles and increase energy.

The total effect of these factors is transmitted the Gibbs energy (or isobaric- isothermal potential):

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

If :

$\Delta G < 0$ — process is possible, there is spontaneous;

$\Delta G > 0$ — process is impossible;

$\Delta G = 0$ — the system is in a state of chemical equilibrium.

Change ΔG can be calculated by the law of Hess:

$$\Delta G = \Sigma\,\Delta G_{prod.} - \Sigma\,\Delta G_{form.}$$

Biochemical processes for which $\Delta G < 0$ are called exergonic: they come with heat. If $\Delta G > 0$ - is the processendergonical, i.e. comes with heat absorption. In humans endergonicaly involve exergonic reaction, i.e. energy is used for the second occurrence of the first .

For isochoric- isothermal process (T, V = const) Helmholtz energy use :

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

When $\Delta F = 0$, the system is in a state of chemical equilibrium.

Application II law of thermodynamics to biological systems

A. Although living organisms are open, nonequilibrium systems are applicable to them, and I and II of the laws of thermodynamics, as biochemical processes are irreversible, occur spontaneously. In other words living organisms is *stationary systems*. Part of the energy that is released during the oxidation of food, irreversibly converted into heat, which dissipates into the surrounding space.

B. In the body, all the processes are spontaneous and therefore the entropy S increases. But the body temperature does not rise and does not come "termal death" because body consumes a substance with low entropy (HMC), and highlights the decay products with high entropy (small molecules). As a result, the entropy of an open system is a constant value.

THERMAL EFECTS OF CHEMICAL REACTIONS. ORIENTATION PROCESS

Thermal effect of chemical reaction - is the amount of heat that is released or absorbed during the reaction.

Hess's Law: the thermal effect of chemical reaction does not depend on the path of its passage, but depends on its initial and final states.

The heat of formation (the first consequence of Hess's Law) - is the thermal effect of formation of 1 mol of substance from simple substances at 25^0C (298 K) and 101.3 kPa, is equal to the difference between the sum of the heats of formation of reaction products and the sum of heats of formation of the initial substances, taken in view of the stoichiometric coefficients reaction equation:

$$\Delta H_{formation} = \sum \Delta H_{prod} - \sum \Delta H_{source}$$

Heat of combustion (second consequence of Hess's Law) - is the thermal effect of combustion of 1 mol of substance to CO_2(g)and H_2O(l) and T is the difference between the sum of the heats of combustion of the starting materials and the amount of combustion heat of the reaction products, taken in view of the stoichiometric coefficients of reactions:

$$\Delta H_{burn} = \sum \Delta H_{source} - \sum \Delta H_{prod}$$

Orientation process, or the possibility of chemical reaction is determined by the Gibbs energy.

Gibbs energy or the isobaric - isothermal potential - a manifestation of the cumulative effect of the enthalpy H and entropy S factors.

$$\Delta G = \sum \Delta G_{prod} - \sum \Delta G_{source}$$

If $\Delta G < 0$, then the reaction is possible.

If $\Delta G > 0$, then the reaction is impossible (is the reverse reaction).

If $\Delta G = 0$, then the system is in balance.

Examples

1) Calculate the heat of reaction of glucose oxidation, when $\Delta H_{formation}$ glucose -1272.45 kJ / mol of carbon dioxide -393.6 kJ / mol, water -285.9 kJ / mol.

$\Delta H_{form}(C_6H_{12}O_6) = -1272.4$ kJ/mol
$\Delta H_{form}(CO_2) = -393.6$ kJ/mol
$\Delta H_{form}(H_2O) = -285.9$ kJ/mol
$\Delta H_{reaction} = ?$

1) Oxidation of glucose is over reaction:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6\ CO_2 + 6H_2O;$$

2) Using the equation of the first consequences of the law of Hess:

$$\Delta H_{formation} = \sum \Delta H_{prod} - \sum \Delta H_{source}$$

3) Substitute these $\Delta H_{formation}$ reaction products and initial substances, taking into account the stoichiometric coefficients:

$$\Delta H_{reaction} = [\,6 \cdot (-393{,}6) + 6 \cdot (-285{,}9)\,] - (-1272) = -2804{,}55 \text{ kJ / mol.}$$

The answer: $\Delta H_{reaction} = -2804{,}55$ kJ / mol. exothermic reaction.

2) Calculate the reaction $Hg_2Cl_2 \rightarrow HgCl_2 + Hg$, when the Gibbs energy Hg_2Cl_2 - 210,66 kJ/mol, and $HgCl_2$ -185,77 kJ/ mol?

$\Delta G(Hg_2Cl_2) = -210.66$ kJ/mol
$\Delta G(Hg_2Cl_2) = -185.77$ kJ/mol
$\Delta G_{reaction} = ?$

1) Write the energy equation of Gibbs reaction

$$\Delta G = \sum \Delta G_{prod} - \sum \Delta G_{source};$$

2) Substitute the data from the equation anode:

$$\Delta G = -185{,}77 - (-210{,}66) = 24{,}89 \text{ kJ/mol.}$$

The answer: ΔG = 24,89 kJ / mol. Reaction is impossible.

3) Calculate the heat of the reaction of acetylene from Benzene, when the values of the heats of combustion:

Benzene - 2364.5 kJ / mol, acetylene - 1299.6 kJ / mol.

$\Delta H_{burn}(C_6H_6) = -1272.4$ kJ/mol
$\Delta H_{burn}(C_2H_2) = -393.6$ kJ/mol
$\Delta H_{reaction} = ?$

1) Based on the second consequence of the Hess's Law:

$$\Delta H_{reaction} = \Delta H_{burn}(C_6H_6) - 3\Delta H_{burn}(C_2H_2);$$

2) Substitute the data from the equation anode:

$$\Delta H_{reaction} = -3264.5 - 3\,(-1299.6) = 634.3 \text{ kJ / mol.}$$

The answer: $\Delta H_{reaction}$ = 634.3 kJ / mol.

4) The evaporation of 1 mol of water is 40.7 kJ. How much heat is spent in a day in the allocation of the skin 800.0 g of water?

$n(H_2O) = 1$ mol
$\Delta H_{evaportation} = -40.7$ kJ/mol
$m(H_2O) = 800$ g
$\Delta H = ?$

1) Find the amount of substance in 800.0 grams of water:

$$\nu = 44{,}44 \text{ mol;}$$

2) To determine the use of heat proportion:

1 mol (H_2O) — 40,7 kJ
44.44 mol (H_2O) — X
X = 1808.9 kJ.

The answer: 1808.9 kJ.

5) Calculate the Gibbs energy change in the process of assimilation body of sucrose, which is reduced to its oxidation, if:

$\Delta G_{form}(CO_2) = -394.4$ kJ/mol
$\Delta G_{form}(H_2O) = -237$ kJ/mol

$\Delta G_{form}(C_6H_{12}O_6) = -1545$ kJ/mol

$\Delta G_{reaction} = ?$

1) Write the equation of oxidation saccharine:

$C_6H_{12}O_6 + 6O_2 \rightarrow 6\ CO_2 + 6H_2O$;

2) We write the energy equation Gibb's reaction:

$\Delta G = \sum \Delta G_{prod} - \sum \Delta G_{source}$;

3) Substitute the data from the equation of the problem, taking into account stereometric factors:

$\Delta G_{reaction} = [12 \cdot (-394{,}4)\ 11 \cdot (-237)] - (-1{,}545) = -5794$ kJ / mol.

The answer: ΔG reaction = — 5794 kJ/mol.

6) The heat of formation of carbohydrates in the human body is 4.1 kcal / g. Daily demand for carbohydrates for students women's 383g. Calculate the daily needs of carbohydrate the student needs for energy.

$\Delta H_{form}(carb) = -4.1$ kcal/g

$m(carb) = 383$g

$\Delta H(day) = ?$

1) To resolve this problem, we use direct proportion: 4.1 kcal per 1 g carbohydrate

X — to 383g of carbohydrates

$X = \frac{4{,}1 \cdot 383}{1} = 1570{,}3$ kcal.

The answer: 1570.3 kcal.

261. Chemical thermodynamics studies the thermodynamic properties of substances depending on:
    a) status, color, structure
    b) the composition, structure, energy
    c) the status, composition, structure
262. Thermodynamic system — a body or group of bodies that:
    a) mentally separated from the environment
    b) not separated from the environment
    c) connection associated with each other
263. What object can be considered as thermodynamic system:
    a) one molecule
    b) ten molecules
    c) one mole of substance
264. Isolated thermodynamic system communicates with the external environment by:
    a) mass and energy
    b) energy
    c) no exchange mass or energy
265. Closed thermodynamic system:
    a) exchange mass and energy exchanges
    b) exchange mass and energy only
    c) no exchange mass or energy
266. Open system:
    a) communicates only with the medium weight
    b) communicates with the medium mass and energy
    c) shared with medium or mass or energy
267. Systems that communicate with the medium weight and energy are called:
    a) closed
    b) open
    c) isolated
268. Systems that exchanges only energy with the environment are called:
    a) isolated
    b) open

c) closed

269. Systems that are not shared with the environment neither mass not energy are called:
a) open
b) isolated
c) closed

270. What type of system is a living organism:
a) open
b) closed
c) homogeneous

271. In homogeneous systems:
a) present the surface of phases
b) there is no interface phases
c) its properties at all points are different.

272. In homogeneous systems:
a) properties at all points the same
b) properties in all various locations
c) is an interface between the phases

273. In heterogeneous systems:
a) no interface phase
b) all parts of the uniform
c) is an interface between phases

274. Body rights system:
a) homogeneous
b) heterogeneous
c) single-phase.

275. Intensive parameters are:
a) pressure, concentration, temperature
b) concentration, weight
c) internal energy, volume, heat

276. Intensive factors:
a) do not depend on the size of the system
b) depend on the size of the system
c) do not depend on volume and pressure.

277. What parameter of the system is busy:
a) R
b) U
c) H

278. Extensive options of:
a) volume, mass, termal value
b) mass, pressure, temperature
c) concentration, volume, capacity

279. Extensive options depend on:
a) heat system
b) system size
c) the of the system.

280. What parameter of the system is extensive:
a) V
b) C
c) E

281. Under the first law of thermodynamics heat, which goes to system is spent on?
a) change of internal energy systems and implementation work
b) the change of heat effect of reaction

c) increase temperature system

282. Under the first law of thermodynamics the internal energy of isolated systems is:
a) the value of the variable and depends on the system
b) the value was not dependent processes occurring in the system
c) size and becomes dependent processes in the system

283. According to Lomonosov energy is not created, not destroyed, but only:
a) switch from one mode to another in the energy equivalent quantities
b) impossible transition from one kind of energy into another
c) the possible transformation of one species in several other species.

284. The internal energy of the system:
a) does not depend on the way which brought the system in certain state
b) depends on the way which brought the system in certain state
c) depends on the work performed by this system

285. The internal energy of the system depends on:
a) pressure, ways of its formation
b) the nature of matter, its mass and state of the system
c) intensive and extensive parameters

286. Stock internal energy system is defined as:
a) the nature of matter, pressure and by its formation
b) mass objects, capacity, energy of Gibbs
c) the nature of matter, its weight and condition of the system.

287. Mathematical expression of the I law of thermodynamics:
a) $\Delta G = \Delta H - T\Delta S$
b) $Q = \Delta U + A$
c) $\Delta F = \Delta G - T \cdot \Delta S$

288. What kinds of engines are there:
a) possible
b) impossible
c) working with intervals.

289. Heat effect of reactions the quantity of heat is:
a) transmitted during the reaction to the environment
b) released or absorbed during the reaction
c) is the work of the reaction

290. Units of heat effect of reaction are:
a) kcal or kj
b) kcal or W
c) J or Volts.

291. Hess Law states that the thermal effect of chemical reaction depends upon:
a) the number of stages of the process
b) the nature and substance of the initial and final state of the system
c) the nature and concentration of initial substances

292. Heat effect of reaction does not depend on its way of passage, and depends on:
a) initial and final concentration;
b) the initial pressure and end state;
c) initial and final states.

293. Standard heat of formation a heat effect of formation:
a) 1mol matter of simple substances
b) 1g matter of simple substances
c) 1 l of substance from simple materials.

294. Standard heat of combustion - is:
a) the thermal effect of combustion 1g substances;
b) thermal effect of combustion of 1 kg of matter to CO_2 and H_2O

c) the thermal effect of combustion of one mole of a substance to CO_2(g) and H_2O(l).

295. Endothermic processes occurs:
a) with the energy
b) with transfer of energy
c) with absorption of energy

296. Exothermic processes go to:
a) the energy in the form of useful work
b) the absorption of energy in the form of useful work
c) the allocation of energy during the synthesis of macromolecules

297. Endothermic processes occurring in the body of:
a) the energy
b) the absorption energy
c) the scattering work

298. In the thermochemical equation:
a) indicate the thermal effect of reaction
b) show pressure in the system
c) no indication of matter substances

299. The thermochemical equation indicates:
a) aggregate state compounds
b) enthalpy of the system
c) temperature

300. The thermochemical equation indicates:
a) the oxidation
b) the fractional coefficients
c) the change in volume.

301. Macroergic compounds in humans is:
a) glucose
b) ATP
c) glycogen

302. Macroergic system in humans is:
a) starch
b) AMP
c) acetyl fat

303. In the body the energy accumulated in the compounds is:
a) of the ester bonds
b) of a peptide ties
c) with macroergic ties

304. In the body of nutrients chemical energy is converted:
a) into mechanical work
b) into internal energy
c) in enthalpy

305. Specify endodermic process in humans:
a) hydrolysis of proteins
b) hydrolysis of polysaccharides
c) protein synthesis
d) oxidation of carbohydrates

306. The second law of thermodynamics states that all processes of energy conversion go to:
a) a complete makeover heat to work
b) scattering of energy as heat
c) transformation of work in entropy

307. The second law of thermodynamics, a process whose only effect is a complete transformation

of heat into the work:
a) possible
b) impossible
c) is possible under certain conditions.

308. The second law of thermodynamics, a process whose only effect is a complete transformation of heat into the work:
a) possible
b) impossible
c) is possible under certain conditions.

309. What is the type of system of human body:
a) current
b) irreversible
c) stationary

310. The human body:
a) is the energy source
b) do not develop new energy
c) obtain energy by oxidation of nutrients

311. The engine of the second kind is:
a) possible
b) perform mechanical work
c) impossible

312. Entropy — a measure of:
a) disordered systems
b) aggregation of particles
c) ordering system

313. Which reaction occurs with the increase of entropy:
a) $N_2 + 3H_2 \rightarrow 2NH_3$
b) $H_2 + Cl_2 \rightarrow 2HCl$
c) $CaCO_3 \rightarrow CaO + CO_2$

314. Which reaction occurs with the reduction of entropy:
a) $NH_3 + HCl \rightarrow NH_4Cl$
b) $H_2 + Cl_2 \rightarrow 2HCl$
c) $CaCO_3 \rightarrow CaO + CO_2$

315. What reaction occurs without a change in entropy:
a) $N_2 + 3H_2 \rightarrow 2NH_3$
b) $H_2 + F_2 \rightarrow 2HF$
c) $MgCO_3 \rightarrow MgO + CO_2$

316. How will the system entropy $2SO_2 + O_2 \rightarrow 2SO_3$:
a) decrease
b) increase
c) will not change

317. How will the entropy of $2S + 3O_2 \rightarrow 2SO_3$:
a) decrease
b) increase
c) will not change.

318. How will the entropy of $H_2 + Br_2 \rightarrow 2HBr$:
a) decrease
b) increase
c) will not change

319. Gibbs energy equation:
a) $\Delta G = \Delta H + T\Delta S$

b) $\Delta G = \Delta H + T\Delta Q$
c) $\Delta G = \Delta H - T\Delta S$

320. Equation isobar-isothermal potential:
a) $\Delta G = \Delta H + T\Delta S$
b) $\Delta T = \Delta H + P\Delta Q$
c) $\Delta G = \Delta H - T\Delta S$

321. Energy Helmholtz calculated by the formula:
a) $\Delta F = \Delta G - T \cdot \Delta S$
b) $\Delta F = \Delta G - T \cdot \Delta U$
c) $\Delta F = \Delta U - T \cdot \Delta S$

322. Equation isochoric-isothermal potential:
a) $\Delta F = \Delta G - T \cdot \Delta S$
b) $\Delta F = \Delta U - T \cdot \Delta S$
c) $\Delta F = \Delta G - T \cdot \Delta U$

323. Reversible in the thermodynamic sense is the process in which:
a) transition of the system to the final state does not require spending energy
b) transition of the system to its original state at a cost energy
c) conversion of the initial state does not require spending energy

324. Thermodynamic equilibrium conditions:
a) $\Delta G > 0$
b) $\Delta G < 0$
c) $\Delta G = 0$

325. Voluntary processes are:
a) irreversible processes
b) reversible processes
c) power

326. In vivo processes are:
a) willfully
b) equilibrium
c) without permission

327. Unwarranted posts possible if:
a) $\Delta G > 0$
b) $\Delta G < 0$
c) $\Delta G = 0$

328. Calorimetry method is based on:
a) measurement of heat liberation or absorption in different physical and chemical processes
b) measuring the work performed by physical or chemical system
c) measuring the internal energy that occurs in individuals and chemical processes

329. Calorimetrics methods of analysis are used for:
a) determining the thermal effect of reaction
b) determining the pressure in the system
c) determination of internal energy system

330. Calorimetry method is used to determine:
a) the heat of dilution
b) the caloric food product
c) the amount of the system

331. Calorimetry method used to determine:
a) the caloric content of food
b) the heat of dissolution of 1 kg solvent
c) the neutralization the reaction heat effect

5. The main questions of the seminar:

5.1. Chemical thermodynamics as a branch of the physical chemistry. Thermodynamic system, types and the examples of the thermodynamic systems, intensive and extensive parameters of the system.

5.2. The first law of thermodynamics. Internal energy of system. Enthalpy.

5.3. Thermochemical equations. The standard enthalpy of formation and combustion.

5.4. Hess's law. Calorimetry.

5.5. The energetic characteristics of biochemical processes. Thermochemical calculations for the estimation of the calorie content in foodstuff and the dietotherapy.

6.The questions for individual learning:

6.1. The second law of thermodynamics. Entropy. Gibbs free energy.

6.2. Thermodynamic processes (reversible and irreversible). Thermodynamic equilibrium. Irreversibility of the processes in vital activity.

6.3. ATP as the source of the biochemical processes. Exergonic and endergonic processes in the human organism.

7. The examples of the task:

7.1.Calculation of ΔH.

Calculate$\Delta H°$of the reactionCO_{gas}+ H_{2gas} = CH_{4gas} + H_2O_{gas} knowing that the standard enthalpy of formation for CO=-110 кJ/mol, CH_4=-74.9 кJ/mol, H_2O= -241.8 кJ/mol.

The answer:

$\Delta H°_f = \sum \Delta H°_{PRODUCTS.} - \sum \Delta H°_{REACTANTS}$

$\Delta H°_f = (\Delta H^0_f (CH_4) + \Delta H^0_f(H_2O)) - \Delta H^0_f (CO) = - 74,9 + (-241,8) – (-110,5)= -206,2$ кJ/mol.

7.2. Calculations for the estimation of the calorie content in foodstuff

100 g of cod (fish)contain 11.6 gof proteins. The calorie content of 1 g of proteinsis 4.1ккcal. Calculate the calorie content of cod.

The answer:

1 g of protein contains─4.1ккcal

11.6 g of protein contain ─X ккcal

X = 11.6 · 4.1 = 47.56 ккcal.

7.3.Detect the spontaneity of the process.

Can the following reaction

$SiO_{2(solid)}$+2NaOH $_{(solution)}$ = $Na_2SiO_{3(solid)}$+ H_2O $_{(solution)}$

Occurs spontaneously when Gibbs energy of $SiO_{2(solid)}$ = – 803,75кJ/mol,

$NaOH_{(sol)}$=– 419,5 кJ/mol,

$Na_2SiO_{3(solid.)}$ = – 1427,8 кJ/mol,

$H_2O_{(sol)}$ =– 237,5 кJ/mol?

The answer:

$\Delta G = \sum \Delta G^o_{PRODUCTS} - \sum \Delta G^o_{REACTANTS.}$ =(-1427,8 – 237,5) – (-803,75 - 2·419,5) = - 22,5 кJ/mol.

Since$\Delta G < 0$, it is spontaneous.

8. Homework (must be performed in the laboratory notebook):

8.1. Calculate ΔH of the reaction:

$H_2C_2O_4$ +2$CH_3OH \rightarrow H_3COOC – COOCH_3$ + 2H_2O.

$\Delta H^0_f (H_2C_2O_4)$= -60.10 кJ/mol;

$\Delta H^0_f (CH_3OH)$ =-173.65кJ/mol;

$\Delta H^0_f (H_3COOC – COOCH_3)$= -401,0 кJ/mol;

$\Delta H^0_f H_2O$= -241.8 кJ/mol.

8.2. Energy of the fat formation in human organism contains 9.3 kcal/g. Daily necessity of the male organism is 106 g of fat. Calculate the daily energy of fat for the male organism.
8.3. Can the reaction of glucose oxidation follow spontaneously at room temperature if the standard Gibbs energies of glucose, water, carbon oxide (IV) equal - 910 кJ/mol; -237кJ/mol; -394 кJ/mol.

9. The control test
for instance :
1. Choose the correct answer. The extensive parameters of the system are:
   a) volume, mass;
   b) pressue, temperature;
   c) concentration, potential.
2. Choose the correct answer. Exergonic systems in the human organism is
   a) glucose;
   b) ATP;
   c) glycogen.
3. Energy of the carbohydrates formation in human organism contains 4.1 kcal/g. Daily necessity of the female-student organism is 135 g of carbohydrates. Calculate the daily energy of carbohydrates for the female-student organism

10. The algorithm of the experiments:
10.1. Determination of thermal effect of neutralization reaction.

11. The detailed explanation of the following experiment:
11.1. Determination of thermal effect of neutralization reaction.
Thermal effect of a chemical reaction is determined in calorimeter. The calorimeter with known mass is filled by 150 mls of NaOH solution with Cn=1 mol/L. The temperature of the solution must be measured. Tn the glass put 150 mls of 1 M HCl solution and the temperature of the second solution must be measured too. The solution of HCl is added to the solution of the NaOH *constantly mixing*. The temperature of the final solution is measured.

The experimental date are filled in the table.

Mass of the calorimeter (m_1)/g	
Concentration of the acid and base (C)	1 M
Volume of the solutions (V)	150 ml
Temperature of NaOH solution (t_{NaOH})/℃	
Temperature of HCl solution (t_{HCl})/℃	
The initial temperature of the resulting solution t_1=1/2 (t_{NaOH}+t_{HCl})/℃	
The temperature of the resulting solution after neutralization t_2/℃	
The total mass of the solutions m_2=2 V ρ	

Calculate the heat of the neutralization reaction using :

$$C_X = \frac{\varpi\% \cdot \rho \cdot 10}{M_X} =$$_____,

where $\Delta t = t_2 - t_1$; $C = m_1c_1 + m_2c_2$;
c_1 (specific heat of the glass) =0,753 J/g°C,
c_2 (specific heat of the solution) = 4,184 J/g°C.
NaOH + HC1 = NaCl + H_2O; ΔH = - _____.

12. Control test:

Sample 1

1. What is isolated thermodynamic system?
2. What is the standard enthalpy formation?
3. Choose the correct answer. The extensive parameters of the system are
   a) the volume, mass; b) pressure, temperature; c)the concentration, potential.
4. Choose the correct answer. Exergonic systems in the human organism is
   a)glucose; b)ATP; c) glycogen.
5. Energy of the carbohydrates formation in human organism contains 4.1 kcal/g. Daily necessity of the female-student organism is 383 g of carbohydrates. Calculate the daily energy of carbohydrates for the female-student organism.

Sample 2

1. Write the I law of thermodynamics.
2. What is the exergonic reaction?
3. Choose the correct answer. The processes of vital functions are
   a) reversible; b) irreversible; c) in equilibrium.
4. Choose the correct answer. Chemical thermodynamics studies the thermodynamic properties of the substances depending on:
   a) state, color, structure; b) state, structure, energy; c) state, structure, compositions.
5. Standard enthalpy formation of HCl equals -92.05 kJ/mol, HI equals -25.1 kJ/mol. Calculate the standard enthalpy change for the reaction $2HI + Cl_2 \rightarrow 2HCl + I_2$.

TOPIC 12: Kinetics of biochemical reactions. Chemical equilibrium. Solubility product.

12.1 Kinetics of biochemical reactions.

1. Actuality of the topic: knowledge and understanding of the kinetic laws is essential to study the mechanism of the organic reactions, the enzymatic processes, the formation of metabolite, the suction and transmutation of the drugs.

2. General aim: is to interprete the base kinetics laws for biological process characterization.

3. Actual aims and abilities:
- to have an idea about the main meanings of the chemical kinetics;
- to know the laws and rules of kinetics;
- to be able to reveal and explain the influence of the various factors on the rate of the chemical reactions, to determine the order and molecularity of the chemical reaction as well as the biological one.

4. Literature:

4.1. Lecture materials;

Kinetics of the zymogenic reactions.

Chemical kinetics is the study of the mechanisms and rate of chemical reactions.

Promptitude of the chemical reactions

The rate chemical reaction is the change in concentration one of the reactants per unit of time.

$$\upsilon = -\frac{\Delta C}{\Delta \tau}$$

For homogeneous processes: $\upsilon = -\frac{\Delta n}{V \bullet \Delta \tau}$

Where Δn — change the amount of substance;

V — the volume of solution;

Δτ — time change.

For heterogeneous processes: $\upsilon = -\frac{\Delta n}{S \bullet \Delta \tau}$

Where Δn — change the amount of substance;

S — the surface area;

Δτ — time change.

Factors affecting the rate of reaction:

a) *the nature of the substances*: inorganic compounds react faster since it in most cases, compounds with ionic bond; organiccompounds covalent chemical bonds, for which the gap.

It takes energy, so they react more slowly and hardconditions (high temperature, pressure, catalyst);

b) *concentration* is according to the law of mass action:

the chemical reaction rate is directly proportional to product of the concentrations of reactants

For the reaction aA + bB → cC + dD the rate of chemical reactions:

$$\upsilon = k \cdot [A]^a \cdot [B]^b$$

where k is rate constant of the reaction.

The reaction rate constant is the rate of a chemical reaction of the reactants at a concentration of 1 mole / l.

The rate constant depends on the temperature and nature of the substances.

c) *temperature* is according to Van't Hoff rule:

when temperature rises by 10^0 increases the chemical reaction rate of 2-4 times.

$$\frac{\upsilon_{t2}}{\upsilon_{t1}} = \gamma^{\frac{t2-t1}{10}}$$

Where $\boldsymbol{\upsilon_{t_2}}$ — the reaction rate at t_2;

$\boldsymbol{\upsilon_{t_1}}$ — the reaction rate at the temperature t_1;

$\boldsymbol{\gamma}$ — temperature coefficient, which means *how many times the reaction rate increases with increasing temperature* $10\,^{o}c$.

For biological systems, γ should be a small value, i.e. body temperature increases the rate of biochemical processes should not increase significantly.

Temperature and biological processes

Biological life exists in the temperature range from -100^0 to $+100^0$. Some fish live in Ceylon at $+50^0$; many bacteria can withstand temperatures of $70\text{-}100^0$; avian influenza virus - 70^0 myokinase enzyme can withstand heat up to 100^0.

Temperature range of active life of most organisms from $+1^0$ to $+45^0$. But "stone fly" Alaska develops at 0^0C, and cod at temperatures below zero.

All biological processes occur at a certain temperature range. The body temperature of most animals $35\text{-}40^0$. Cause of death of the animals at high temperature is the denaturation of proteins.

Energy of activation. Arrhenius equation

Increasing the reaction rate with increasing temperature is not due simply increasing the number of collisions and increasing energy and reacting species. Particles should have the necessary excess energy - activation to start the reaction.

The activation energy E_a is the excess energy of the molecule, necessary for the entry of substances in a chemical reaction.

The energy that is necessary to inform the molecule to turn it into an active and capable of reacting in a collision.

The activation energy is measured in kJ / mole. The activation energy depends on the nature of the substances. E_a is less than the faster the reaction proceeds. Typically, the activation energy is 40 – 200 kJ/mole.

Arrhenius derived an equation which relates the reaction rate constant, the activation energy and the temperature:

$$k = A \cdot e - Ea / RT$$

where A — the number of collisions per unit time per unit volume,

e — base of natural logarithms.

To calculate the energy of activation and reaction rate constants are used :

a) the method of active collisions;

b) the method of the transition state.

According to the method of active collisions in the reaction come only those molecules that have the required minimum energy.

By the method of the transition state or condition of the active complex reaction is the formation of an intermediate complex, fragile.

For example, for the reaction A + BC → AB + C, the formation of the active complex can be shown as:

$$A + BC \rightarrow A \text{ ..... } B \text{ ..... } C \rightarrow AB + C$$

Active complex

I.e. actively complex begins to form a connection between A and B and weakens the link between B and C.

The activation energy can reduce temperature rise by the action of radiant energy catalysts.

The activation energy for the biochemical processes in 2 - 3 times lower than for a reaction in vitro. This is due to the action of enzymes.

Molecularity and reaction order

To characterize the mechanism of the reactions they are distinguished by the molecular order and reactions.

A. M*olecular reactions determined by the number of molecules participating in the elementary act of interaction.*

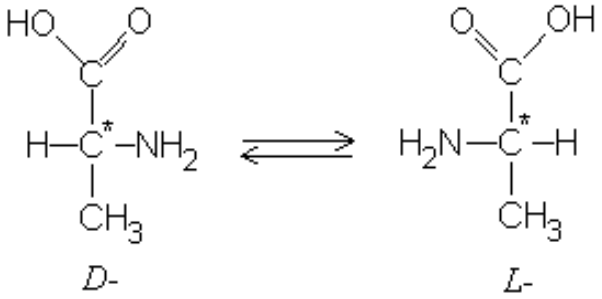
Distinguish the reaction of mono-, bi- and trimolecular.

a) *Monomolecular* called reaction in which the elementary event involves only one molecule. This thermal decomposition reaction, an isomerization dissociation.

For example:

$$CaCO_3 \rightarrow CaO + CO_2 \text{ - thermal decomposition;}$$

$$HCl \rightarrow H^+ + Cl^- \text{ - dissociation;}$$



Alanine - isomerization

In the body such a reaction is the dissociation of carbon (carbonate) acid:

$$H_2CO_3\ HCO_3^- + H^+$$

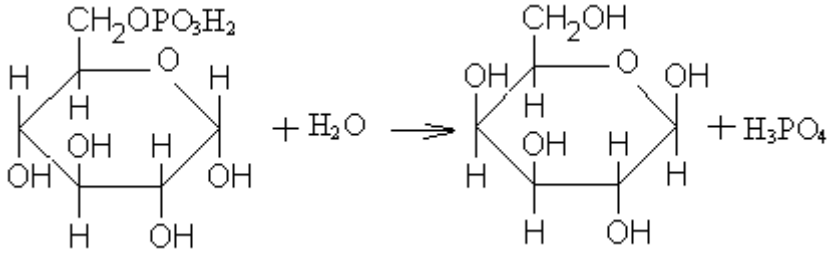
b) *Bimolecular* called reactions in which the elementary act involving two molecules (or atoms or ions).

For example, $H_2 + Cl_2 \rightarrow 2HCl$ — connection.

In humans, this reaction:

esterification: $CH_3COOH + C_2H_5OH \rightarrow C_2H_5 + H_2O\ CH_3COO$

hydrolysis:



glucose-6-phosphate glucose

c) *Trimolecular* reactions are rare, because interaction of a large number of particles is unlikely.

B. The reaction order n is the sum of the exponents in the equation for the reaction speed.

a) *A zero order*reaction, the rate of which is independent of the concentration substances:

$$\upsilon = k,\ n = 0$$

For example of such a reaction *in the human body* are enzymatic reactions in which the substrate is in excess, the enzyme and small, but it is released at the end of time, so the concentration of enzyme and substrate, and is constant.

b) *The first order* reaction rate which depends only on the concentration of one substance :

$$\upsilon = k \bullet c^i; \qquad n = 1.$$

For example: t

$$H_2 \rightarrow 2H$$

In humans examples of such reactions are:

1) hydrolysis, in which a large concentration of water in the reaction almost does not change, and the rate depends only on the concentration of substrate;

2) contacting the antigen with the antibody when the antibody concentration is constant in the body, and antigen concentration may be different;

3) the isomerization reaction is involved when only one substance.

c) The reactions of *the second order*, when the speed is dependent on the concentration of the two substances.

$$\upsilon = k \bullet c^1 \bullet c^1 \text{or} \quad \upsilon = k \bullet c^2; \qquad n = 2.$$

For example, the reaction:

connection: $H_2 + Cl_2 \rightarrow 2HCl$

exchange: $NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$, etc.

in humans, this reaction: $CO_2 + H_2O \rightarrow H_2CO_3$;

hydration of unsaturated compounds :

$$HOOC - CH = CH - COOH + HOH \rightarrow HOOC - \underset{\underset{OH}{|}}{CH} - \underset{\underset{H}{|}}{CH} - COOH$$

fumaric acid — malic acid

d) The third-order reactions are very rare.

Order of the reaction is used to elucidate *the mechanism* of the reaction.

For example, the decomposition reaction of Nitrogen (V) oxide follows the equation:

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

In fact, the reaction proceeds in two stages :

$$N_2O_5 \rightarrow N_2O_3 + O_2 \text{ — slow stage;}$$

$$N_2O_5 + N_2O_3 \rightarrow 4NO_2$$

The reaction rate is determined for the slow phase.

In kinetics often use the concept of half-life period $\boldsymbol{\tau_2^1}$, or half-reaction period .

The half -life period or half-reaction period - the time during which half the amount of reacted starting material.

Half-life is used to describe the process of radioactive decay.

For example, the half-life of **Th**^{232} – $1.39 \cdot 10^{i0}$ years; $\mathbf{Po^{210}}$ – 138.4 days; **Ro**^{212} – $3{,}04 \cdot 10^{-7}$ sec.

Complex reactions at chemistry and biochemistry

Most chemical and biochemical processes are particularly difficult to mechanisms.

Complex processes are parallel, serial, conjugated, cyclic, competing chain, photochemical.

A. *Concurrent* called reaction, which resulted from the raw materials produced several reaction products.

For example, the decomposition of potassium chlorate:

$$KClO_3 \begin{cases} \rightarrow KCl + O_2 \\ \rightarrow KClO_4 + KCl \end{cases}$$

In the body:

$$\text{glucose} \rightarrow PVA \begin{cases} \nearrow \text{Krebs cycle} \\ \searrow \text{Cyclohexosemonophosphate} \end{cases}$$

B. By following the call reactions that sequentially through the several stages.

For example, reaction with the alkali aluminum chloride:

$$AlCl_3 + NaOH \rightarrow Al(OH)_3\downarrow + NaCl \xrightarrow{NaOH_{form.},\ t} NaAlO_2$$

In humans — hydrolysis of starch:

$$(C_6H_{10}O_5)_n \rightarrow (C_6H_{10}O_5)_m \rightarrow C_{12}H_{22}O_{11} \rightarrow C_6H_{12}O_6$$

$m < n$

starch — dextrin — maltose — glucose

C. Conjugate call process in which a reaction can occur independently, and the other only with the first.

For example, the reaction of HI + H_2O_2 is only when simultaneous oxidation Fe^{2+} with hydrogen peroxide.

In humans, all endergonical reactions occur only in the presence of exergonic reactions , using their energy:

Glucose + ATP → Glucose- 6 -phosphate + ADP; ΔG = - 17.2kJ/mole.

This gives an exothermic reaction energy for the endothermic reaction :

Glucose + HPO_4^{2-} → Glucose-6 -phosphate + H_2O; ΔG = + 13.4kJ/mole.

D. Cyclic call processes in which some substances are transformed into reaction products and are removed from the loop and returned to the other loop.

In humans, it is the Krebs cycle, the urea cycle , the cycle of fatty acid oxidation (studied in the course of Biochemistry).

E. *Competing* called reactions, one of which may impede the flow of the other.

For example, in the organic chemistry reactions are competing substitution and elimination of alcohols.

$$CH_3\text{-}CH_2\text{-}OH + HCl \xrightarrow{H^+} CH_3\text{-}CH_2\text{—}Cl + HOH$$ - displacement

$$CH_3\text{—}CH_2\text{-}OH \xrightarrow{H^+} CH_2 = CH_2 + HOH$$ elimination

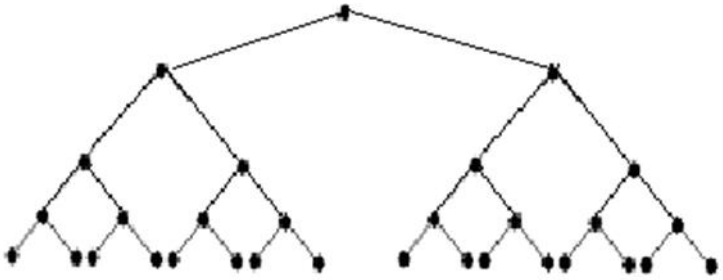
The second reaction may interfere with the flow of the first or walk along it.

F. *Chain* called processes that go through the course of repeating elementary reactions consecutive.

These reactions occur involving free radicals.

Free radicals are particles of one or more unpaired electrons.

The scheme chain process



One particle decays into two particles, each of which splits into two more, etc.

For example, bromination of methane

$$Br_2 \xrightarrow{h\nu} Br\cdot + Br\cdot$$ stage I

$$CH_4 + Br\cdot \rightarrow C\cdot H_3 + HBr$$ stage II

$$C\cdot H_3 + Br_2 \rightarrow CH_3Br + Br\cdot$$ stage III

In the human body by a chain mechanism occur radiation sicknes, malignant tumors, the effect of toxic substances, etc.

Free radicals are produced of the human body by radiation ray irradiation, ultraviolet radiation, ozone, nitrogen oxides, and as a result of certain biochemical reactions.

Free radicals are produced in the human body in large quantities, due to the high toxicity of the reaction ability, so they need to communicate.

Substances whichlink free radicals in the human body are called antioxidants.

Some antioxidants are enzymes — glyutationperoxyoxidase, superoxide dismutase, as well as vitamins retinol (vitamin A), ascorbic acid (vitamin C) and the most powerful antioxidant currently α- tocopherol (vitamin E).

G. P*hotochemically* referred reactions which occur under the influence of light.

Photochemical reactions proceed by a chain mechanism.

For example, the synthesis of hydrogen chloride is exposed to light :

$$H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$$

In nature, an example of the photochemical reaction is *photosynthesis*.

In the human body:

a) during the exposure to light of the isomerization is in the cis - retinal trans - retinal;

b) to prevent the accumulation of bilirubin in physiological jaundice in preterm infants, they are irradiated with light, under the action of which bilirubin is destroyed.

Catalysis and catalysts

The chemical reaction rate can be changed with the help of catalysts .

Catalysts are substances that change the rate of a chemical reaction, but at the end of the reaction remain chemically unchanged.

Catalysis is the phenomenon of the change rate of a chemical reaction by the action of catalysts.

Features of the catalysts:

a) catalysts after reaction remain unchanged and its composition quantity;

b) contacting the catalyst and the substance is not stoichiometric ratio;

c) catalysts do not affect the equilibrium constant;

d) catalysts are susceptible to the action of extraneous substances .

Substances that enhance the action of the catalyst, called *promoters*.

For example, in the process of ammonia synthesis catalyst promoters iron are oxides of potassium, calcium, etc.

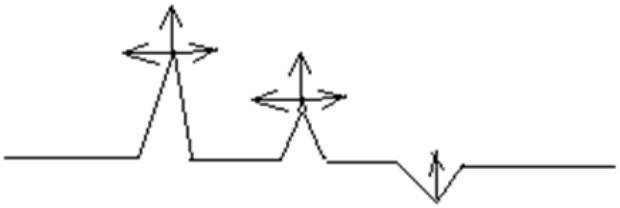
Substances that inhibit the activity of the catalyst, called *inhibitors or catalytic poisons*.

For example, the arsenic sulfide for platinum.

e) The majority of catalysts are selectively (selectively).

Ex.: V_2O_5 catalyzes the oxidation reaction of SO_2 to SO_3, but not reduction reaction.

f) Involved in the catalytic reactions are not the entire surface of the catalyst, and only active centers. This protrusions or depressions in the surface enzyme (Picture 12.1.1):



Pict. 12.1.1 The surface of the catalyst

Types of catalysis

A. *Homogeneous*, where in the catalyst and reactants are in the same state of aggregation:

$$SO_2 + O_2 \xrightarrow{NO} SO_3$$

In this reaction, the catalyst and gaseous substances.

B. *Heterogeneous*, where in the catalyst and reactants are in a different state of aggregation :

$$SO_2 + O_2 \xrightarrow{V_2O_5} SO_3$$

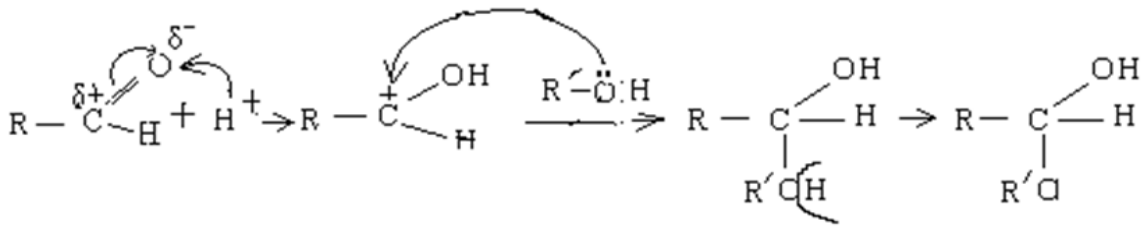
In this reaction, a catalyst in solid state, as reactants gaseous.

C. *Microheterogeneity* in which the catalyst material and are colloidally dispersed state. The particle size of the catalyst and reactant 10^{-7}- 10^{-9} m

In humans, this is the enzymatic catalysis.

D. *Acid - base*, the type where in the catalyst used proton H^+ or OH hydroxide anion.

Acid-base catalysis commonly used in organic chemistry reacting with alcohols, aldehydes, carboxylic acids and alcohols, hydrolysis of fats, etc.



In the body the hydrolysis of fats takes place in alkaline environment.

D. *Autocatalysis*, is the type where in the catalyst is one of the products reaction.

For example, oxidation of Fe^{+2} potassium permanganate in acidic environment is one of the products Mn^{+2}, which is the catalyst:

$$5Fe^{+2} + MnO_4^- + 8H^+ \rightarrow Mn^{+2} + 5Fe^{+3} + 4H_2O$$

In humans, the catalysis is observed in the decomposition of proteins to aminoacids:

trypsinogen → trypsin + hexapeptide

Trypsin generated during the reaction of a catalyst.

The mechanism of action of catalysts

The action of the catalysts due to the fact that the catalyst decreases the activation energy. On solid catalysts process begins with the adsorption of reactant molecules on the catalyst surface. Currently, the mechanism of action of catalysts such theories explain:

a) the theory of the formation of intermediates.

b) theory of active ensembles.

c) multiplet theory.

To explain the theory of *homogeneous catalysis* use the theory of the formation of intermediates.

For example, oxidation Sulphur (IV) oxide to Sulfur (VI) oxide in the presence of Nitrogen (II) oxide is according to the scheme:

$$2SO_2 + O_2 \xrightarrow{NO} 2SO_3$$

In the first stage, the catalyst reacts with NO one of the starting materials and the O_2 formed intermediate NO_2:

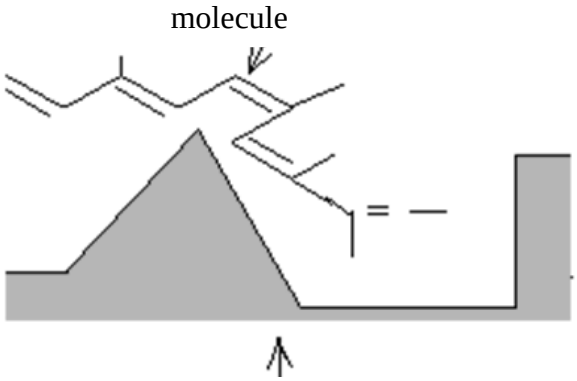
$$2NO + O_2 \rightarrow 2NO_2$$

In the second intermediate step NO_2 is reacted with the second precursor SO_2, NO is released as a catalyst:

$$NO_2 + SO_2 \rightarrow SO_3 + NO$$

To explain the use of heterogeneous catalysis use two theories:

a) multiplet theory, which is based on the principle of matching configuration of the molecule and the active site of the catalyst. A group of atoms of the catalyst, which comes into connection with a molecule called multiplet (Pict. 12.1.2). In this case, the deformation of bonds in the molecule, and they are broken.



Pict. 12.1.2. Multiplet structure

b) theory of active ensembles, according to which the catalytic

Activity shows a group of atoms of the catalyst on the surface inert carrier (carbon, asbestos, silica gel). For example, the ensemble of three iron atoms on the surface of a carbon catalyst at ammonia synthesis.

Enzymes like biological catalysts

Complex and diverse chemical reactions in living organisms are in the presence of biological catalysts **—** *ferments (enzymes).*

Enzymes are substances of protein nature, are produced in vivo and increases the rate of biochemical processes.

Enzymatic catalysis is significantly different from the chemical catalysis by the following factors:

a) a high reaction rate. For example, 1 mole of catalase decomposes 5million H_2O_2 molecules in 1min and 1 mole of platinum **—** 2000 molecules of H_2O_2;

b) high selectivity (specificity). For example, the enzyme lipase cleaves the ester bond only in fats; urease enzyme only catalyses the hydrolysis of urea;

c) the enzymes are sensitive to temperature. At a temperature above 40 – 50^0C enzyme activity decreases, and at t = 70 – 80^0C is an irreversible denaturation of proteins as enzymes;

d) enzymes act in a certain pH range (Table 12.1.1).

Optimal pH for the action of certain enzymes

Enzyme	Substrate	pH
β – fructofuranosidase	saccharose	4,5 – 6,5
urease	urea	6,7
pepsin	protein	1,5 – 2,0
arginase	arginine	9,5 – 9,9

Table 12.1.1

d) enzymes operate at a pressure of 1 atm. Inorganic catalyst can operate at very high pressures.

The mechanism of action of enzymes

High rate of enzymatic reactions due to the decrease of the activation energy of biochemical reactions.

The mechanism of enzyme catalysis consists of the steps:

a) the adsorption of the substrate S on the active centers of the enzyme to form F enzyme-substrate complex F-S, and the substrate and the active site enzyme must approach each other as the "lock and key" i.e. have the opposite configuration;

b) decomposition of the intermediate complex with F-S form the final product P and enzyme release F:

$$F + S \rightarrow F\text{-}S \rightarrow P + F$$

Formation of an enzyme — substrational complex has low activation energy and, therefore, increase the rate of enzymatic reaction.

Activation and inhibition of enzymes

The rate of enzymatic reaction may be accelerated or slowed by certain substances.

Substances with activating effect of biocatalysts called *activators*. Thus, the presence of NaCl facilitates more rapid hydrolysis of starch to glucose by saliva enzymes — amylase and maltase.

Substances that slow down the action of the catalyst are called *inhibitors*. For example, cyanide and carbon (II) oxide weaken the action of heme protein enzymes; tin- organic compounds — the enzyme ATPase; anions of carboxylic acids - carbonic anhydrase; sulfonamides inhibit the action of bacterial enzymes. The inhibitory effect is also increase in temperature, radiation, strong acids or alkalis, i.e. The factors that cause the denaturation of enzymes — proteins.

Metalloenzymes

Enzymes that contain a metal ion composition, called *metalloenzymes*.

Metal ions (usually transient, i.e. d- elements) transfer electrons between substances. For example, *carbonic anhydrase* contains Zn, *cytochrome* — Fe and Cu, *phosphohydrolaze* — Mg.

Enzymes as medicaments

Branch of medicine that studies the use of enzymes as drugs called enzyme therapy.

They are isolated from certain animal organs.

For example, in violation of the digestive functions using pepsin, pancreatin; decomposition of proteins in the festering wounds — *trypsin*, *lidaze*; for the treatment of vascular thrombosis - *streptokinase*, etc.

KINETICS OF BIOCHEMICAL PROCESSES

Chemical kinetics — the doctrine of the rate and mechanism of chemical reactions.

The chemical reaction rate — the change of substance concentration per unit time and per unit volume (for homogeneous reactions) or per unit area (for heterogeneous reactions).

$$V = -\frac{\Delta \nu}{\Delta \tau}$$

for homogeneous reactions: $V = -\frac{\Delta \nu}{\upsilon \cdot \Delta \tau}$; for heterogeneous reactions: $V = -\frac{\Delta \nu}{S \cdot \Delta \tau}$.

The chemical reaction rate depends on the nature of reactants, concentration, and temperature.

The law of mass action - **the chemical reaction rate** is directly proportional to the product of the concentrations of the reactants raised to a power equal to the stoichiometric coefficients.

For example, for the reaction $aA + bB \rightarrow cC$

where k — rate constant for chemical reaction, is equal to the rate of chemical reactions at the concentrations of substances 1 mol/l, depending on the nature of matter and temperature.

Vant - Hoff Rule — with increasing temperature at 10^0C the chemical reaction rate increases in 2 - 4 times.

$$\frac{Vt_2}{Vt_1} = \gamma^{\frac{t(2)-e(1)}{10}} \text{ or } \frac{k_2}{k_1} = \gamma^{\frac{t(2)-t(1)}{10}}$$

where γ - the temperature coefficient which shows how many times the speed of the chemical reaction changes when the temperature rises to 10^0C.

The activation energy Ea - is the smallest excess energy of the active molecule, by which chemical reactions are possible.

Arrhenius equation:

$$V = A \cdot e^{-Ea/RT}[A]^a \cdot [B]^b \text{ or } k = A \cdot e^{-Ea/RT}$$

Examples

1. ***How many times will the chemical reaction rate change $NO_{(g)} + Cl_{2(g)} \rightarrow NOCl_{(g)}$, if the concentration of NO increased in 2 times?***

$[NO]_2 = 2\,[NO]_1$
$\frac{V_2}{V_1} = ?$

1) We write the reaction equation:

$$NO_{(g)} + Cl_{2(g)} \rightarrow NOCl_{(g)}$$

2) The dependence of reaction rate on concentration expresses the law of mass action:

$$V_1 = k \cdot [NO]^2 \cdot [Cl_2]$$

3) After an increase of NO concentration equation is:

$$V_2 = k \cdot [2NO]^2 \cdot [Cl_2]$$

4) Find the change in velocity:

$$\frac{V_2}{V_1} = \frac{k \cdot [2NO]^2 \cdot [Cl_2]}{k \cdot [NO]^2 \cdot [Cl_2]} = \frac{2^2}{1} = 4$$

The answer: The rate will increase 4 times.

2. ***How will the rate of reaction $A + B_2 \rightarrow AB$, which flows in a closed vessel, if the system pressure is to increase by 5 times?***

$P_2 = 5\,P_1$
$\frac{V_2}{V_1} = ?$

1) The equation of the reaction:

$$2A + B_2 \rightarrow 2AB;$$

2) In a closed vessel, the pressure may increase by increasing the concentration. If pressure increases a factor of 5, then the concentration will increase a factor of 5.

3) Dependence of reaction rate on concentration is expressed in the law mass action. To increase pressure:

$$V_1 = k \cdot [A]^2 \cdot [B]$$

4) When the pressure increases and, consequently, increasing the concentration equation is:

$$V_2 = k \cdot [5A]^2 \cdot [5B]$$

5) Find the change in velocity:

$$\frac{V_2}{V_1} = \frac{k \cdot [5A]^2 \cdot [5B]}{k \cdot [A]^2 \cdot [B]} = \frac{5^2 \cdot 5^2}{1} = 125$$

The answer: The rate of increase in 125 times.

3. ***How many times will the rate of the reaction $NO_{(g)} + Cl_{2(g)} \longrightarrow NOCl_{(g)}$ change, if the system pressure is reduced to 4 times?***

$P_2 = 4\,P_1$
$\frac{V_2}{V_1} = ?$

1) The equation of the reaction:

$$NO_{(g)} + Cl_{2(g)} \longrightarrow NOCl_{(g)}$$

2) If the pressure reduces 4 times, then the concentration is also decreased by 4 times.

3) Dependence of reaction rate on concentration is expressed in the law of mass action. Before the increase in pressure:

$$V_1 = k \cdot [A]^2 \cdot [B]$$

4) When the pressure increases and, consequently, increasing the concentration equation is:

$$V_2 = k \cdot [1/4 \cdot A]^2 \cdot [1/4 \cdot B]$$

5) Find the change in velocity:

$$\frac{V_2}{V_1} = \frac{k \cdot [1/4 \cdot A]^2 \cdot [1/4 \cdot B]}{k \cdot [A]^2 \cdot [B]} = \frac{0.25^3}{1} = 0.0156$$

The answer: the rate of decline in 1/0.0156 time, 64 times

4. The reaction rate constant with C + 2D → K is 0,4 l/mol · sec. The concentration of C = 3mol/l, and the substance D = 4mol / litre. Calculate the rate of direct reaction.

$[C] = 3\,mol/l$ $[D] = 4\,mol/l$ $k = 0.4\ l/mol \cdot sec$ $V = ?$	1) Write the reaction equation: $C + 2D \rightarrow K;$ 2) Dependence of reaction rate on concentration expressed by the law of mass action: $V = k \cdot [C] \cdot [D]^2$

3) Substitute the data from the problem and calculate

$$V = 0{,}4 \cdot 3 \cdot 4 = 4.8\ mol / sec.$$

The answer: The reaction rate is 4.8 mol/sec.

5. Constant decay rate of penicillin at 36°C is $6 \cdot 10^{-6}$ sec^{-1}, and at 41°C – $1{,}2 \cdot 10^{-5}$ sec^{-1}. Calculate the temperature coefficient reaction.

$k\ (36℃) = 6 \cdot 10^{-6} sec^{-1}$ $k\ (41℃) = 1.2 \cdot 10^{-5} sec^{-1}$ $\gamma = ?$	1) Using the rule of Van't - Hoff: $\frac{k_2}{k_1} = \gamma^{\frac{t(2)-t(1)}{10}}$

hence

$$\gamma^{\frac{t(2)-t(1)}{10}} = \frac{1.2 \cdot 10^{-5}}{0.6 \cdot 10^{-5}} = 2$$

$$\gamma^{0.5} = 2$$

$$\gamma = 4$$

The answer: $\gamma = 4$.

6. How many times will rate of reaction increase, if the temperature increases to 30°C (γ = 3)?

$\Delta t = 30℃$ $\gamma = 3$ $\frac{V_2}{V_1} = ?$	1) Dependence of reaction rate on temperature expressed by the Vant Hoff rule: $\frac{V(t_2)}{V(t_1)} = \gamma^{\frac{t(2)-t(1)}{10}}$

2) Substitute the data from the equation anode:

$$\frac{V(t_2)}{V(t_1)} = \gamma^{\frac{30}{10}} = 3^3 = 27$$

The answer: 27 times

7. By increasing the temperature at 20°C the reaction rate increases by 16. Calculate the temperature coefficient of reaction.

$\Delta t = 20℃$ $V_2 = 16V_1$ $\gamma = ?$	1) Dependence of reaction rate on temperature expressed by the Van't Hoff rule: $\frac{V(t_2)}{V(t_1)} = \gamma^{\frac{t(2)-t(1)}{10}}$

2) Substitute the data from the equation anode:

$$\frac{V(t_2)}{V(t_1)} = \gamma^{\frac{20}{10}}$$

$$16 = \gamma^2$$

$$\gamma = 4$$

The answer: $\gamma = 4$

8. How many times will the rate of reaction change, if the temperature of the reaction changes from 18°C to 38°C, and the temperature coefficient is equal to 3?

$t_1 = 18°C$
$t_2 = 38°C$
$\gamma = 3$
$\frac{V_2}{V_1} = ? = ?$

1) Dependence of reaction rate on temperature expressed by the Van't Hoff rule:

$$\frac{V(t_2)}{V(t_1)} = \gamma^{\frac{t(2)-t(1)}{10}}$$

2) Substitute the data from the equation anode:

$$\frac{V(t_2)}{V(t_1)} = 3^{\frac{38-18}{10}} = 3^2 = 9$$

The answer: 9 times

332. Chemical kinetics is the study of:
   a) the effect of pressure on the rate of chemical reactions
   b) the rate and mechanisms of chemical reactions
   c) the catalysis
333. The speed of chemical reactions is the change of:
   a) the pressure per unit of time
   b) the concentration of one of the reactants per unit time
   c) a volume of reactants per unit time
334. The speed of chemical reactions in homogeneous system is:
   a) the number of grams of substance reacting per unit time in unit volume
   b) the amount of substance reacting per unit time in unit volume
   c) the number of milliliters, reacting per unit time in unit volume
335. The speed of the heterogeneous processes - is the number of substances that react:
   a) of 5 seconds per unit of interface phases
   b) of 18°C in the surface unit of phases
336. Chemical reaction rate equation for homogeneous processes:
   a) $V = -\Delta n / V \cdot \Delta\tau$
   b) $V = \Delta n / V \cdot \Delta\tau$
   c) $V = -\Delta n \cdot V \cdot \Delta\tau$
337. Rate equation for heterogeneous chemical reaction processes:
   a) $V = -\Delta n / S\,\Delta\tau$
   b) $V = -\Delta n \cdot S \cdot \Delta\tau$
   c) $V = \Delta n / S \cdot \Delta\tau$
338. The speed of the heterogeneous processes - is the number of substances that react:
   1) of 18°C in the surface unit of phases;
   2) of per unit time and per unit of interface.
339. Speed unit of a chemical reaction:
   a) l/mol • s
   b) mol / l • s
   c) l^2/s^{-1}.

340. The speed of chemical reactions is affected by the following factors:
a) the nature of substances, the potential temperature
b) the mass, concentration, temperature
c) the nature of substances, concentration, temperature
341. The speed of chemical reaction depends on:
a) substances volume
b) termal substances
c) concentration.
342. The speed of chemical reaction depends on:
a) volume
b) Gibbs energy
c) temperature
343. Which compounds react faster:
a) with ionic bonds
b) with covalently sphere mechanism
c) with hydrogen bonds
344. By law, the existing mass velosity of chemical reactions:
a) front off product concentration of reactants
b) front off relative concentration of reactants
c) front off logarithm of concentration of reactants.
345. The equation applicable law masses:
a) v = k [A][B]
b) v =k [A]^a[B]^b
c) v =k ⁄[A]^a[B]^b
346. The rate constant of reaction - is:
a) the rate of reaction if the concentration of reactants equal to 1 mol / l
b) the rate of reaction if the volume of reactants is 22.4 l
c) the rate of reaction if the pressure reaction course is 101.3 kPa.
347. The rate constant of chemical reaction depends on:
a) concentration and temperature
b) the nature of matter and temperature
c) the nature of the substances and pressure
348. Under the rule of Van't Hoff's temperature increases by 10°C, speed of chemical reactions:
a) decreases on average volume 3 times
b) increased on average 12 times
c) increased on average by 2-4 times Van't Hoff's formula is:
349. Van't Hoff's formula is:
a) $\frac{V_{t2}}{V_{t1}} = \gamma^{\frac{t2-t1}{2}}$; b) $\frac{V_{t2}}{V_{t1}} = \gamma^{\frac{t2+t1}{10}}$; c) $\frac{V_{t2}}{V_{t1}} = \gamma^{\frac{t2-t1}{10}}$;
350. Shows the temperature coefficient of times?
a) reaction rate increases with increasing temperature at 10°C
b) the reaction rate increases with increasing temperature by 1°C
c) the reaction rate decreases with increasing temperature at 10°C
351. Biological life exists within the temperature:
a) -100 -100°C
b) -50 -50 °C
c) -1 -40°C.
352. According to the theory of active collisions:
a) the molecule must have the necessary excess energy
b) the molecule must have a minimum of energy

c) shall have the necessary entropy

353. The activation energy is:
    a) the maximum energy of the active molecule which can react
    b) minimum energy active molecules that can react
    c) the average energy of active molecules that can react
354. The activation energy is energy that should be given to a molecule:
    a) that the reaction was reversible
    b) to make it active
    c) that the reaction proceeded slowly
355. The lower activation energy:
    a) the smaller molecules collide with each other
    b) the more the molecules collide with each other
    c) the greater the number of Avogadro
356. Transition state is characterized by:
    a) the destruction of bonds in reactants and the beginning form new links
    b) the weakening of bonds in reactants and the beginning form new links
    c) the cracking of reactants.
357. Arrhenius equation is:
    a) $k=E\cdot e^{-E/RT}$
    b) $k=A\cdot e^{-E/RT}$
    c) $k=A\cdot e^{-U/RT}$.
358. Arrhenius equation establishes the relationship between:
    a) the number of collisions between molecules and concentration
    b) the activation energy, reaction rate and pressure
    c) the constant speed, the activation energy and temperature
359. Enzymes:
    a) reduce the activation energy
    b) increase the activation energy
    c) do not affect the activation energy
360. The activation energy of oxidation of aldehydes to carboxylic acids in vivo:
    a) greater than the energy of activation in vitro
    b) less than the energy of activation in vitro
    c) the same for activation energy in vitro
361. Molecular reaction determined by the number of molecules:
    a) the initial substances does not depend on the number of reactive substances
    b) the catalyst depends on the number of reactants
    c) the reactants independent of the number of molecules of products
362. In the monomolecular reaction:
    a) in the elementary act of interaction is only one molecule
    b) in the elementary act of interaction occurs in a unit volume
    c) in the elementary act of interaction takes place at a pressure of 1 atm
363. Monomolecular reactions are reactions of:
    a) hydrolysis
    b) oxidation
    c) isomerization.
364. An example of monomolecular reactions in the body are:
    a) association of amino acids
    b) decomposition of carbonate acid
    c) hydrolysis of fats
365. In the bimolecular reaction between:
    a) two molecules
    b) two volumes

c) two mole molecules

366. An example of the bimolecular reaction:
a) dissociation
b) isomerization
c) hydrolysis

367. Bimolecular reactions in humans include:
a) synthesis of HMC
b) decomposition of glucose
c) esterification.

368. Trimolecular reaction belongs to:
a) $NH_3 \rightarrow N_2 + H_2$;
b) $NO + O_2 \rightarrow NO_2$;
c) $NaOH + HCl \rightarrow NaCl + H_2O$.

369. These reactions are:
a) the product of exponents in the equation for the reaction;
b) the sum of exponents in the equation for the reaction;
c) the ratio of exponents in the equation for the reaction.

370. The reaction rate of zero order:
a) does not depend on the concentration
b) depends on the square of the concentrations
c) depends on the ratio of the concentrations

371. Kinetic equation of zero order:
a) $v = k \bullet c^2$
b) $v = k$
c) $v = k \bullet c^{-1}$

372. An example of zero order reaction is:
a) enzyme reactions
b) calcium carbonate decomposition
c) hydrolysis

373. The reaction rate of the first order:
a) depends on the concentration of only one substance
b) depends on one mole of a substance
c) depends on the volume change

374. Kinetic equation of first order:
a) $v = k \bullet c$
b) $v = k$
c) $v = k \bullet c^{-2}$

375. An example of the first order reaction is:
a) hydrolysis
b) esterification
c) oxidation.

376. The reaction rate of the second order:
a) depends on the concentration of two substances
b) depends on the substance of 2 mol
c) depends on changes volume.

377. Kinetic equation of second order:
a) $v = k \bullet c$
b) $v = k \bullet c_1 \bullet c_2$
c) $v = k \bullet c^{-2}$

378. An example of second order reactions are:
a) esterification

b) fermentative
c) hydrolysis

379. Third reactions order depends on:
a) the concentration of third substance
b) the concentration of three substances
c) the concentration of substance in the third degree

380. An example of third order reactions are:
a) $2NO + O_2 \rightarrow 2NO_2$
b) $H_2 + I_2 \rightarrow 2HI$
c) $2CO + O_2 \rightarrow 2\ CO_2$

381. Consistent response in the human body are:
a) decomposition to pyruvic acid
b) decomposition of glycogen
c) schedule pies in the stomach.

382. In competing reactions:
a) one reaction accelerates the progress of the second reaction
b) one reaction prevents the flow of the second reaction
c) two reactions proceed in parallel

383. Parallel reactions are reaction that result in:
a) the initial substances produced several end products
b) the initial substances produced several similar products
c) the possible feedback

384. Chain reaction in the human body is:
a) the reaction of glucose
b) the radiation sickness
c) the diarrhea.

385. Chain mechanism in human body is:
a) the splitting of glycogen
b) synthesis of amino acid
c) cell growth

386. Period of half transformations in radionuclides - is:
a) of the time in which half the molecules displayed
b) volume, which laid out the half molecules
c) the limits of pH, which breaks half molecules

387. Antioxidants are substances that:
a) it linking free radicals in human body
b) it linking the products of metabolism in humans
c) it promote the development of redox reactions

388. Example of photochemical reactions in the body:
a) decomposition of chlorophyll under light
b) decomposition of melanin in action of light
c) schedule of bilirubin under light

389. Catalysis is:
1) increasing the rate of chemical reaction using catalysts
2) change the speed of chemical reaction using catalysts
3) decreasing the rate of chemical reaction using catalysts

390. Catalyst a substance that:
a) increase the speed of chemical reactions and late reactions remain chemically unchanged
b) substances that are involved in catalytic reactions
c) change the speed of chemical reactions and late reactions remain chemically unchanged

391. Catalysts:
a) do not affect the rate of equilibrium constants

b) increase the rate of equilibrium constants
c) reduce the rate of equilibrium constants

392. Promoter a compound that:
a) poison the catalyst
b) enhances the effect of catalysts
c) react with a catalyst

393. Features of catalytic reactions:
a) at the end of the reaction catalyst retains its qualitative and quantitative composition
b) the catalyst changes its number of members;
c) the catalyst at the end of the reaction is evaporated.

394. Heterogeneous catalysis is catalysis, in which reactants and catalysts:
a) stay in a state of aggregate
b) stay in a different state of aggregate
c) the reactants and catalysts are in constant temperature

395. Heterogeneous catalysis is due to:
a) the theory of intermediate compounds
b) the multiple theory
c) the theory of active collisions

396. Homogeneous catalysis is catalysis in which the reactants and catalyst
a) are in a different state of aggregate
b) are in the same condition in aggregate
c) are under different pressure.

397. In homogeneous catalysis:
1) catalysts create intermediates with one of the reacting substances on the surface
2) create an intermediate compound of reaction product catalyst forms an intermediate compound with one reactive substances are in one phase

398. Autocatalysis a phenomenon in which:
a) catalyst is one of the starting substance
b) catalyst is platinum
c) the catalyst is one of the reaction products

399. Enzymatic catalysis is:
a) termolability
b) little specificity
c) affects the constant equilibrium

400. Enzymatic catalysis is:
a) smooth
b) selective
c) resistant

401. For acid-base catalysis reaction is caused by acceleration availability of:
a) free radicals
b) protons
c) indicators

402. Catalytic poison a compound which:
a) enhances the action of catalysts
b) neutral to catalysts
c) reduce the effect of catalysts

403. Enzymatic catalysis:
a) increases the activation energy
b) reduces the activation energy
c) supports the activation energy

404. Enzymatic catalysis depends on:
a) reaction medium

b) pressure
c) the amount of protein consumed man.

5. The main questions of the seminar:

5.1. The rate of the homogeneous and heterogeneous reactions and its dependence on concentration. The law of mass action states. The rate constants.
5.2. The rate of the reaction. The kinetic equations of zero-, first- and second-orders.
5.3. Conception of the reaction mechanism. Molecularity of the reaction.
5.4. The dependence of the reaction rate on the temperature. Van't Hoff's rule. The characteristic properties of the temperature coefficient for the biological processes.
5.5. Collision theory. Activation energy. Arrhenius equation. Transition states.
5.6. Enzyme kinetics.

6.The questions for individual learning:

6.1. Half-life.
6.2. The parallel, consecutive, conjugate, reversible and chain reactions. Photochemical reactions.
6.3. Free radical reactions in the living organism. Antioxidants.
6.4. Catalysis and the catalysts. Homogeneous and heterogeneous catalysis. Acid-base catalysis. The mechanism action of the catalysts. Autocatalysis. The promoters and inhibitors.

7. The examples of the task:

7.1. The influence of the concentration on the reaction rate.

How does the reaction rate of the oxidation nitrogen (II) to nitrogen (IV) change if the system pressure is raised in 3 times?

The answer:

$$2NO + O_2 \longrightarrow 2NO_2;$$

$$V_1 = \kappa[NO]^2 \cdot [O_2];$$

When the pressure is increased in 3 times, the volume of the system is decreased in 3 times. Consequently the concentration of the components is increased in 3 times.

Then, $V_{2} = \kappa[3NO]^2 \cdot [3\ O_2] = 27\ \kappa[NO]^2 \cdot [O_2];$

$\frac{V_2}{V_1} = \frac{27\kappa[NO]^2 \cdot [O_2]}{\kappa[NO] \cdot [O_2]} = 27$ thus, the reaction rate is increased in 27 times.

7.2. The influence of the temperature on the reaction rate.

The reaction time is 2 min 15 sec at 50 °C.Calculate the reaction time at 70 °C knowing the temperature coefficient (γ)is 3.

The answer:

$$\frac{r_2}{r_1} = \gamma^{\frac{t_2 - t_1}{10}} = 3^{\frac{70-50}{10}} = 3^2 = 9$$

$$r_1 = \frac{\Delta C}{\Delta t_1}$$

$$r_2 = \frac{\Delta C}{\Delta t_2}$$

$$\frac{r_2}{r_1} = \frac{\Delta C \Delta t_1}{\Delta t_2 \Delta C}$$

Since ΔC is can celedit follows

$$\frac{r_2}{r_1} = \frac{\Delta t_1}{\Delta t_2} = \gamma^{\frac{t_2 - t_1}{10}}$$

Where,

$$\Delta t_2 = \frac{\Delta t_2}{\gamma^{\frac{t_2 - t_1}{10}}} = \frac{135}{9} = 15 \text{ sec}$$

7.3. Determination of the reaction order.
Determine the reaction order of the interaction of hydrogen with iodine.
The answer:

$$H_2 + I_2 \longrightarrow 2HI;$$

$$V = \kappa[H_2]\cdot[I_2];$$

The reaction rate depends on the concentration of two components and the sum of the exponents is 2. The reaction is the second order.

8. Homework (must be performed in the laboratory notebook):
8.1. How does the reaction rate of ammonia synthesis change if the volumes of molecular hydrogen and nitrogen are enlarged in 3 times?
8.2. The reaction time are 25 min at 30°C and 4 min at 50°C. Calculate the temperature coefficient (γ)of the reaction rate for the given temperature range.
8.3. Determine the reaction order of the hydrolysis.

***9. The control test*:**
for instance:
9.1. The reaction rate is affected by:
a) the volume
b) the concentration
c) the density
9.2. How does the reaction rate change if the temperature is increased by in 3 times at 30 ^{0}?

10. The algorithm of the experiments:
10.1. Dependence of the reaction rate on the concentration of the reactants.
10.2. Dependence of the reaction rate on the temperature.

11. The detailed explanation of the following experiment:
11.1. Dependence of the reaction rate on the concentration of the reactants.
Prepare the sodium thiosulphate solution of different concentrations.

	1 test-tube	*2 test-tube*	*3 test-tube*
$Na_2S_2O_3$	5 drops	10 drops	15 drops
H_2O	10 drops	5 drops	-

Add 1 drop of H_2SO_4 solution in the first test-tube and fix the end of the reaction (time when the dimness of the solution occurs). Analogous perform the same procedure for the last two test-tubes. Fill the table.

№ of the test-tube	Number of $Na_2S_2O_3$ drops	Number of H_2O drops	Reaction time / sec.	Relative rate, 1/sec
1				
2				
3				

Depict the graph of the reaction rate *vs* the concentration of the reactants where the abscise is the concentration data and the ordinate axis is the reaction rate. Write the reaction equation and make a conclusion.

11.2. Dependence of the reaction rate on the temperature.

In the first test-tube add 10 drops of $Na_2S_2O_3$ solution and measure the room temperature, then add 1 drop H_2SO_4 solution and fix time (sec) when the solution becomes to be muddy.

The second test-tube must be filled by 10 drops of $Na_2S_2O_3$ solution and heat the test-tube to a higher room temperature by 10 °C, add 1 drop of sulphuric acid and fix time (sec) when the solution becomes to be muddy.

The third test-tube must be filled by 10 drops of $Na_2S_2O_3$ solution and heat the test-tube to a higher room temperature by 20 °C, add 1 drop of sulphuric acid and fix time (sec) when the solution becomes to be muddy.

Fill the table. Is Van't Hoff rule valid for the given experiments?

№ of the test-tube	***$Na_2S_2O_3$***	***t***	***H_2SO_4***	***Time/sec***
1 test-tube	10 drops	room	1 drop	
2 test-tube	10 drops	room + 10 ^{0}C	1 drop	
3 test-tube	10 drops	room + 20 ^{0}C	1 drop	

12.2 Chemical equilibrium. Solubility equilibrium.

1. Actuality of the topic: the knowledge of the chemical equilibrium principles is necessary to study the direction of the chemical and enzymatic processes as a result of the action of the various factors.

2.General aim: is to interprete the basic chemical equilibrium for biological process characterization.

3. Actual aims and abilities:

- to have an idea about the main meanings of the chemical equilibrium;
- to know the Le Chatelier's principle;
- to be able to reveal and explain the influence of the various factors on the chemical equilibrium.

4. Literature:

4.1. Lecture materials;

Chemical reactions can take place through or to a state of equilibrium.

Reactions in which the starting material is completely converted to reaction products are called *irreversible*. I.e. such reactions go to the end.

State the **irreversible reactions** in which the starting materials are fully converted into reaction products, i.e. reaction goes to completion.

Signs of the irreversibility:

a) precipitation: $Na_2SO_4 + BaCl_2 \rightarrow 2NaCl + BaSO_4\downarrow$;
b) the allocation of gas: $Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + CO_2\uparrow$;
c) formation of a weak electrolyte: $2\ NaOH + H_2SO_4 \rightarrow Na_2SO_4 + H_2O$.

State the **reversible reactions** in which the final products interact to form the starting materials. Such reactions are not going to the end, to a state of equilibrium.

In irreversible reactions $\Delta G < 0$, $\Delta S > 0$, $\Delta H < 0$

Reactions in which the reaction products are reacted with each other to form precursors are called reversible.

In reversible reactions $\Delta G = 0$, $\Delta S = 0$, $\Delta H = 0$

Such reactions do not go to the end, to a state of equilibrium. The velocity of the forward reaction is reduced because there is a decrease in the concentration of the starting materials , and the velocity feedback - increases as the concentration of the reaction products increases. Eventually the speed will be equal and the system is set to equilibrium.

For example, synthesis of ammonia :

$$N_2 + 3H_2 \leftrightarrow 2NH_3$$

Chemical equilibrium is the state of the system, where the speed of the forward and reverse reactions are identical.

Thermodynamic equilibrium conditions according to II law of thermodynamics :

$$\Delta G = 0,\ \Delta S = 0,\ \Delta F = 0$$

Chemical equilibrium is characterized by the equilibrium constant.

A reversible reaction $aA + bB \leftrightarrow cC + dD$ equation equilibrium constant has the form :

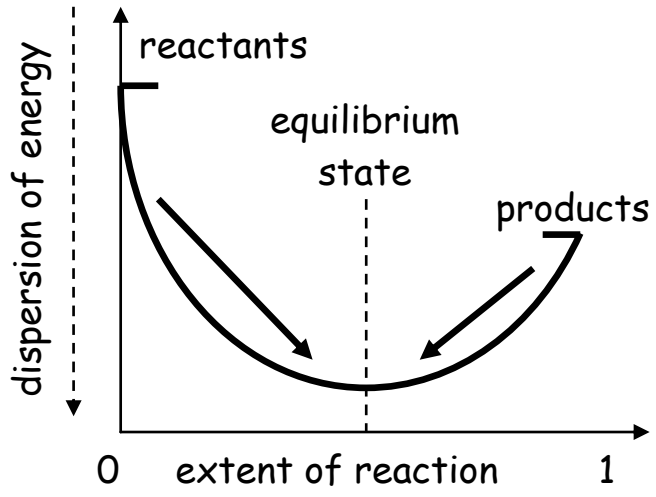
$$K_P = \frac{[C]^c \bullet [D]^d}{[A]^a \bullet [B]^b}$$

Chemical equilibrium constant is the ratio of the product of the equilibrium concentration of the reaction to the product of the equilibrium concentrations of the starting materials, combined to an extent equal to the stoichiometric coefficients.

For example, for the ammonia synthesis reaction $N_2 + 3H_2 \leftrightarrow 2NH_3$ equation Ce has the form:

$$C_e = \frac{[NH_3]^2}{[N_2] \bullet [H_2]^3}.$$

Chemical equilibrium



Picture 12.2.1

The equilibrium concentration is the concentration of the starting materials and reaction products which are currently established at equilibrium.

In such way, the Ce shows how many times the forward reaction is faster feedback .

If Ce > 1, the faster the direct reaction and $\Delta G < 0$.

If Ce < 1, the faster the reverse reaction and $\Delta G > 0$.

If Ce = 1, the system is in equilibrium and $\Delta G = 0$.

Is dynamic equilibrium, since the reaction does not stop and continues to move with the same speed and under the action of external factors, it may proceed to another state of equilibrium.

The equilibrium can be shifted under the influence of concentration, temperature, pressure.

The shift direction is determined by the equilibrium of Le Chatelier's principle:
if a system is in equilibrium, and is acted upon of external factor, the equilibrium is shifted in the direction of that reaction, which reduces this effect.

Thus:

a) when the concentration of the raw materials, the equilibrium shifts in the side of the forward reaction, i.e. in the direction of decreasing concentrations;

b) when the temperature rises, the equilibrium shifts to the side of the reactions which will absorb heat, i.e. toward the endothermic reaction;

With decreasing temperature, the equilibrium shifts to the side of the reaction that comes with increasing temperature, i.e., the side of the exothermic reaction .

c) increasing the pressure shifts the reaction equilibrium in the direction that goes with decreasing volume, and the pressure decrease - in the direction of the reaction, that comes with the increase in volume.

For example, during the reaction:

$$4NH_3 + 5O_2 \leftrightarrow 4NO + 6H_2O - \Delta H$$

a) with increasing NH_3 or O_2 concentrations, the equilibrium shifts in the side of the forward reaction;

b) when the pressure increases, the equilibrium shifts toward the backward reaction because it comes with a decrease in volume;

c) the temperature increases, the equilibrium shifts toward the backward reaction because it comes with the absorption of heat.

Chemical equilibrium a state of the system in which the speed of the forward and reverse reactions are equal.

Equilibrium is called concentration, which are installed on the equilibrium state (for the initial equilibrium concentration of the substance is the amount of material which remained at the time of equilibrium for the reaction products - is the amount of matter, which was formed at the time of equilibrium).

Chemical equilibrium is characterized by the equilibrium constant Ke, which is the ratio of product concentrations of the reaction products to the product of the concentrations of substances in the initial degrees are stoichiometric coefficients.

In accordance with the law of mass action for the reversible reaction:

$aA + bB \rightarrow cC + dD$ expression of the Ke can be written as follows:

$$K_p = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Thermodynamic equilibrium condition:

$$\Delta G = 0, \quad \Delta F = 0$$

K_P shows how many times the rate of direct reaction greater than the rate of reverse reaction.

If the Ke> 1, the faster the direct reaction; $\Delta G < 0$.

If the Ke<1, then quickly goes back reaction; $\Delta G > 0$.

If Ke = 1, then $\Delta G = 0$ (equilibrium state).

K_P depends on the nature of the reactants and temperature, and does not depend on the concentration of the catalyst.

Displacement of chemical equilibrium — is the transition system from one equilibrium state to another.

Le Chatelier's principle: if the system is in equilibrium, to produce effects (change the concentration, pressure, temperature), the equilibrium will shifted in the direction of the reaction, which weakens this effect.

Chemical equilibrium is established in a saturated solution of salt between the solid salt and converts to a solution of ions. For example, in a saturated solution of sulphide cuprum equilibrium is established:

$$CuS \rightleftarrows Cu^{2+} + S^{2-}$$

The equilibrium constant of this process is expressed by the equation:

$$K_d = \frac{[Ca^{2+}] \cdot [S^{2-}]}{[CuS]}$$

Concentration of CuS as a sparingly soluble substance constant, so

$$K_e\,[CuS] = SP$$

where SP - is the solubility product. Therefore:

$$S_P = [Cu^{2+}] \cdot [S^{2-}]$$

Thus, ***in a saturated solution of electrolyte product concentration of its ions is constant and is called the solubility product SP.*** This value quantifies the ability of the electrolyte to dissolve.

The numerical value of SP can be found, knowing its solubility. Example, the solubility of $CuSO_4$ at 20°C is equal to $1.5 \cdot 10^{-2}$. This means that in the saturated solution concentration of each of Ca^{2+} and SO_4^{2-} equal to $1.5 \cdot 10^{-2}$.

Consequently, the solubility product of this salt:

$$S_P = [Ca^{2+}] \cdot [SO4_4^{2-}] = 1.5 \cdot 10^{-2} \cdot 1.5 \cdot 10^{-2} = 2.25 \cdot 10^{-2}.$$

If the electrolyte contains two or more identical ions, the concentrations of these ions in the calculation of the SP should be elevated to the appropriate extent.

For example, the solubility of $Ca_3(PO_4)_2$ is equal to $7.14 \cdot 10^{-7}$.

Calcium phosphate dissociates from the equation:

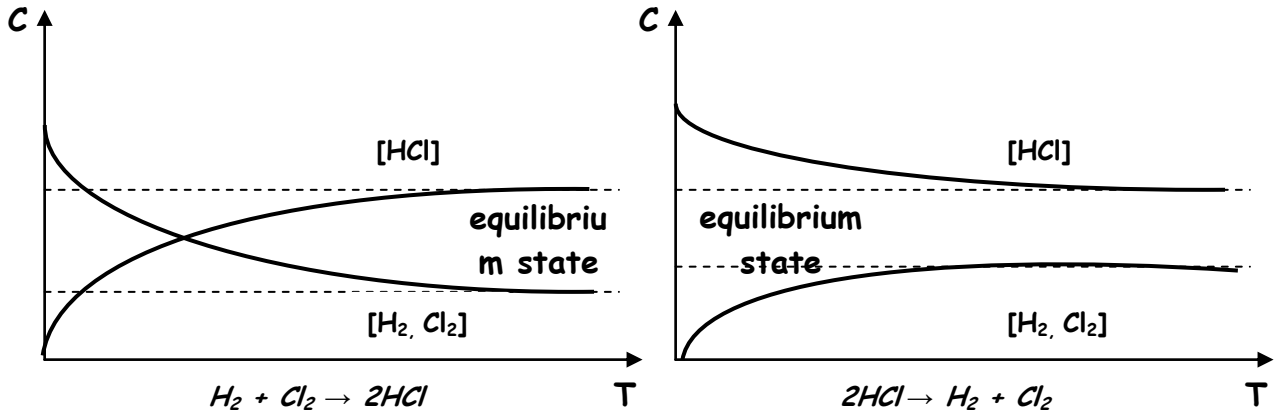
$$Ca_3(PO_4)_2 \rightleftarrows 2Ca^{+2} + 2PO_4^{3-}.$$

Then

$$[Ca^{2+}] = 3 \cdot 7{,}14 \cdot 10^{-7} = 21{,}42 \cdot 10^{-7};$$
$$[PO_4^{3-}] = 2 \cdot 7{,}14 \cdot 10^{-7} = 14{,}28 \cdot 10^{-7};$$
$$S_P = (21{,}42 \cdot 10^{-7})^3 \cdot (14{,}28 \cdot 10^{-7})^2 = 2{,}0 \cdot 10^{-29}.$$

If the product of ion concentrations less than SP, the residue does not fall out.
If the product of concentrations is more than SP, then precipitated.
If the product of ion concentrations equal to SP, then the equilibrium between saturated solution and precipitate.

It's the same both ways



Picture 12.2.2

Solubility equilibrium

Condition dissolve the precipitate: add a strong electrolyte, which has no common ion with the precipitate (and one of the ions precipitate yields a soluble compound).

For example, to dissolve the precipitate $Mg(OH)_2$ you need to add electrolyte NH_4Cl:

$$Mg(OH)_2\downarrow + NH_4Cl \longrightarrow MgCl_2 + NH_4OH$$

Balance in heterogeneous systems. Product solubility.

We have examined the equilibrium processes in reactions that go in homogeneous systems. But many reactions occur at the interface, ie heterogeneous systems . The simplest example is the formation and dissolution of poorly soluble substances precipitation . These are equilibrium processes, and since the concentration of the solids is constant, then it is not included in the equilibrium constant equation.

Upon dissolution of the poorly soluble substance in the system equilibrium is established between the sediment and brine above the sediment. For example, in a solution of $BaSO_4$ equilibrium is established :

$$BaSO_4 \leftrightarrow Ba^{2+} + SO_4^{2-}$$

Since the concentration of the solid phase is not included in the equation of the equilibrium constant, then $K_s = [Ba^{2+}] \cdot [SO_4^{2-}] = SP$.

SP is the solubility product.

The solubility product is the production ion concentration in a saturated solution.

SP constant and solubility of poorly soluble characterizes electrolytes.

Values ol certain electrolytes are given in Table 12.2.1.

SP certain electrolytes

Electrolyte	SP
Ag_2S	$6 \cdot 10^{-50}$
$AgCl$	$1{,}8 \cdot 10^{-10}$
Ag_2SO_4	$2 \cdot 10^{-5}$
$Ba_3(PO_4)_2$	$6 \cdot 10^{-39}$
$BaSO_4$	$1{,}1 \cdot 10^{-10}$
$Ca_3(PO_4)_2$	$2 \cdot 10^{-29}$
CaC_2O_3	$5{,}1 \cdot 10^{-9}$
CaC_2O_4	$2 \cdot 10^{-9}$
$Fe(OH)_3$	$3{,}7 \cdot 10^{-40}$
$Fe(OH)_2$	$1 \cdot 10^{-15}$

Table 12.2.1

For a saturated solution Ag_2CrO_4 SP expression has the form:

$SP(Ag_2CrO_4) = [Ag^+]^2 \cdot [CrO_4^{2-}]$.

To compute SP need to know solubility of the substance at a given temperature .

Conditions of formation and dissolution of precipitation

Equilibrium shift in heterogeneous systems based on the principle of Le Chatelier. If the electrolyte solution sparingly enter the titled ion, the dissociation equilibrium shifts to the left, i.e. the solubility of the substance decreases and the substance precipitates. Thus, *if the product of the concentration of ions exceeds SP, the substance precipitates.*

To dissolve the precipitate must enter a strong electrolyte which does not have common ions precipitate with one of ions provides a soluble compound .

For example:

a) dissolving the precipitate $Mg(OH)_2$, the electrolyte which should be added HCl, as a result it will form a solution of $MgCl_2$;

b) dissolving the precipitate $BaSO_4$ there is need to add electrolyte Na_2CO_3**,** as a result it will formed a soluble substance $BaCO_3$;

c) dissolving the precipitate AgCl, NH_3 must be added, as a result it will form insoluble complex compound $[Ag(NH_3)_2]Cl$.

The role of heterogeneous equilibrium in the general homeostasis of the organism

In humans violation of heterogeneous equilibrium leads to the formation of kidney stones in the gallbladder, salt deposits in the joints.

Especially most of these processes play a role in the formation of bone tissue. When the acidity of the main component of bone hydroxylapatite $Ca_5(OH)(PO_4)_3$, which will lead to the destruction of the bone.

A similar process occurs when the destruction of tooth tissue, where increased acidity in the mouth (under the influence microorganisms).

At lack of calcium ions and phosphate anions is in the blood as bone destruction.

When the concentration of uric acid and oxalic acid form kidney stones.

Examples

1. The equilibrium constant for the reaction $N_2O_4 \leftrightarrow NO_2$ is 0.26. Equilibrium concentration NO_2 is 0.28 moles per litre. Calculate the equilibrium and initial concentration of N_2O_4 ..

$S_p = 0.26$
$[NO_2]_{equally} = 0.28$ mol/l
$[N_2O_4]_{equally} = ?$
$[N_2O_4]_{source} = ?$

1) We write the reaction:

$$N_2O_4 \rightleftarrows 2\ NO_2;$$

2) Write the equation of the S_P for this reaction:

$$S_p = \frac{[NO_2]^2}{[N_2O_4]}$$

it follows:

$$[N_2O_4]_{\text{equally}} = \frac{[NO_2]^2}{S_p} = \frac{0{,}28^2}{0{,}26} = 0{,}3\ \text{mol/l}$$

it means $[N_2O_4]$, 3mol N_2O_4 remains at the moment of equilibrium.

3) From the reaction equation follows:

$$1\text{mol of } N_2O_4 - 2\text{ mol } NO_2$$
$$X = 0.14 \text{ moles per liter}$$
$$X \text{ mol} - 0.28 \text{ mol } NO_2$$
$$0.14 \text{ mol } N_2O_4 \text{ reacts;}$$

4) Total N_2O_4, its initial concentration is equal to:

$$[N_2O_4]_{\text{ex.}} = 0.14 \cdot 0.3 = 0.44 \text{ moles per liter}$$

The answer: $[N_2O_4]_{\text{eq.}} = 0.44$ mol/l.

2. The system $NO + O_2 \leftrightarrow NO_2$ equilibrium concentrations of substances: $[NO] = 0{,}2$ mol/l, $[O_2] = 0{,}3$ mol/l, $[NO_2] = 0{,}4$ mol/liter. Calculate the equilibrium constant.

$[NO] = 0{,}2$ mol/l
$[O_2] = 0{,}3$ mol/l
$[NO_2] = 0{,}4$ mol/l
$K_e = ?$

1) Write the reaction:

$$2NO + O_2 \rightarrow 2NO_2$$

2) Expression of the S_P for this reaction can be written as follows:

$$K_e = \frac{[NO_2]^2}{[NO]^2 \cdot [O_2]} = \frac{0.4^2}{0.2^2 \cdot 0.3} = 13.3$$

The answer: $K_e = 13.3$.

3. In what direction does the chemical equilibrium reaction shifts $N_2 + H_2 \leftrightarrow NH_3$, if the system pressure were to increase by 3 times?

$P_2 = 3P_1$ $\frac{K_{P_1}}{K_{P_2}} = ?$	1) Write the reaction: $N_2 + 3H_2 \rightarrow 2NH_3$ 2) Expression of the Ke for this reaction to improve Pressure: $K_{P_1} = \frac{[NH_3]^2}{[N_2] \cdot [H_2]^3}$

3) When the pressure is 3 times, the concentration increases, too, by 3 times. Expression of the Ke to the reaction after increasing pressure:

$$K_{P_1} = \frac{[3NH_3]^2}{[3N_2] \cdot [3H_2]^3} = \frac{1}{9}$$

4) Find the ratio of equilibrium constant:

$$\frac{K_{P_1}}{K_{P_2}} = \frac{1 \cdot 9}{1} = 9$$

K_{P_1} increases 9 times, then the balance shifts toward the direct reaction.

The answer: in the direction of the direct reaction.

4. In what direction will the equilibrium shift in the reaction $CO + H_2 \leftrightarrow CH_4 + CO_2$, if the concentrations of all substances is reduced to a factor of 2?

$C_1 = 2C_2$ $\frac{K_{P_1}}{K_{P_2}} = ?$	1) Write the reaction: $2CO + 2H_2 \rightarrow CH_4 + CO_2$ 2) Expression of the Ke for this reaction to reduce the concentration: $K_{P_1} = \frac{[CH_4] \cdot [CO_2]}{[CO]^2 \cdot [H_2]^2}$

3) The expression of the Ke to the reaction after reduction concentration:

$$K_{P_2} = \frac{[0.5CH_4] \cdot [0.5CO_2]}{[0.5CO]^2 \cdot [0.5H_2]^2} = \frac{1}{0.25} = 4$$

4) Find the ratio of equilibrium constants:

$$\frac{K_{P_1}}{K_{P_2}} = \frac{1}{4} = 0.25 \quad \text{or} \quad \frac{K_{P_2}}{K_{P_1}} = 4$$

Or in what direction is the balance shifted.

The answer: in the direction of the reverse reaction.

5. Calculate the solubility product of S_P lead phosphate $Pb_3(PO_4)_2$, if the solubility of this salt $1.5 \cdot 10^{-9}$ moles/litre.

$[Pb_3(PO_4)_2] = 1.5 \cdot 10^{-9}$ mol/l $S_p = ?$	1) Write the equation of the dissociation of salt $Pb_3(PO_4)_2 \rightarrow 3Pb^{+2} + 2PO_4^{-3}$ 2) S_p is calculated as: $S_p = [Pb^{+2}]^3 \cdot [PO_4^{-3}]^2$

3) Find the concentration of each ion in solution:

$$[Pb^{+2}] = 3 \cdot 1.5 \cdot 10^{-9} = 4.5 \cdot 10^{-9}$$
$$[PO_4^{-3}] = 2 \cdot 1.5 \cdot 10^{-9} = 3 \cdot 10^{-9}$$

Compute the S_p:

$$S_p = (4.5 \cdot 10^{-9})^3 \cdot (3 \cdot 10^{-9})^2 = 8.2 \cdot 10^{-43}$$

The answer: $S_p = 8.2 \cdot 10^{-43}$

5. The main questions of the seminar:

5.1. Reversible and irreversible chemical reactions.
5.2. Chemical equilibrium.
5.3. Thermodynamic conditions of equilibrium.
5.4. The constant of the chemical equilibrium and its expression.
5.5. The shift of chemical equilibrium changing temperature, pressure and concentration. Le Chatelier's principle.

6.The questions for individual learning:

6.1. Solubility and precipitation reactions.
6.2. The conditions of solubility and precipitation.
6.3. Solubility product.
6.4. The role of the heterogeneous equilibrium (in the presence of the salts) in the general homeostasis of human organism.

7. The examples of the task:

7.1. The shift of chemical equilibrium changing with the concentration.

What is the direction of the chemical reaction $HCl + O_2 \rightarrow H_2O + Cl_2$ if the concentration of all substances is accelerated in 2 times?

The answer:

I way

$$4HC1 + O_2 \rightarrow 2H_2O + 2C1_2$$

1) Accordingly the mass action law:

$$V_{forward} = K_1 \cdot [HCl]^4 \cdot [O_2]$$
$$V_{reverse} = K_2 \cdot [H_2O]^2 \cdot [Cl_2]^2$$

2) After the increase the concentrations twice:

$$V_{forward} = K_1 \cdot [2HCl]^4 \cdot [2O_2] = 32 \cdot K_1 \cdot [HCl]^4 \cdot [O_2]$$
$$V_{reverse} = K_2 \cdot [2H_2O]^2 \cdot [2Cl_2]^2 = 16 \cdot K_2 \cdot [H_2O]^2 \cdot [Cl_2]^2$$

3)

$$\frac{V_{forward}}{V_{reverse}} = \frac{32}{16} = 2$$

The chemical equilibrium is shifted in the side of the direct reaction.

II way

1) The equilibrium constant before the increase of concentrations.

$$K_{P_1} = \frac{[H_2O]^2 \cdot [Cl_2]^2}{[HCl]^4 \cdot [O_2]}$$

2) The equilibrium constant after the increase of concentrations.

$$K_{P_1} = \frac{[2H_2O]^2[2Cl_2]^2}{[2HCl]^4[2O_2]}$$

3)

$$\frac{K_{P_1}}{K_{P_2}} = 2$$

The chemical equilibrium is shifted in the side of the direct reaction.

7.2. The shift of chemical equilibrium changing the pressure.

The equilibrium of the reaction $NO + O_2 \rightarrow NO_2$ is stated at [NO] = 0.5 mol/l, $[NO_2]$ = 2.1mol/l, $[O_2]$ = 0.7mol/l. What is the direction of the reaction if the pressure in the system is lowered in 2 times?

The answer:

$$2\ NO + O_2 \rightarrow 2NO_2$$

I way.

$$K_{equil.} = \frac{[NO_2]^2}{[NO]^2 \cdot [O_2]}$$

1) $V_{forvard} = K_1 \cdot [NO]^2 \cdot [O_2] = K_1 \cdot (0.5)^2 \cdot (0.7) = K_1 \cdot 0.175$
2) $V_{reverse} = K_2 \cdot [NO_2]^2 = K_2 \cdot (2.1)^2 = K_2 \cdot 4.41$
3) After decreasing of the pressure in 2 times:

$$V_{forward} = K_1 \cdot (\frac{0.5}{2})^2 \cdot \frac{0.7}{2}$$

$$V_{reverse} = K_1 \cdot (\frac{2.1}{2})^2 = K_2 \cdot 1.101$$

4)

$$\frac{V_{forward}}{V_{forward'}} = \frac{K_1 \cdot 0.175}{K_1 \cdot 0.0219} = 8 \text{ times}$$

(it is decreased);

$$\frac{V_{reverse}}{V_{reverse}} = \frac{K_2 \cdot 4.41}{K_2 \cdot 1.101} = 4 \text{ times}$$

(it is decreased).
The chemical equilibrium is shifted in the indirect side.

II way

1) The equilibrium constant before the pressure changes:

$$K_{equil_1} = \frac{[2.1\ NO_2]^2}{[0.5\ NO]^2 \cdot [0.7\ O_2]} = \frac{4.41}{0.175} = 25.2$$

2) The equilibrium constant after the pressure changes:

$$K_{equil_2} = \frac{[2.1/2]^2}{[0.5/2]^2 \cdot [0.7/2]} = \frac{1.1025}{0.022} = 50.4$$

3)

$$\frac{K_{P_1}}{K_{P_2}} = \frac{50.4}{25.2} = 2$$

The chemical equilibrium is shifted in the indirect side.

7.3. Calculation of solubility product (SP) of the low soluble compounds.
Calculate SP of silver chromate if the solubility is $6{,}5 \cdot 10^{-5}$.
The answer:

1. Silver chromate is dissociated as

$$Ag_2CrO_4 \rightarrow 2Ag^+ + CrO_4^{2-}$$

2. The concentration is calculated as

$$[Ag^+] = 2 \cdot 6.5 \cdot 10^{-5} = 1.3 \cdot 10^{-4} \text{ mol/l}$$
$$[CrO_4^{2-}] = 6.5 \cdot 10^{-5} \text{ mol/l}$$

3. $Ag_2CrO_4 = [Ag^+]^2 \cdot [CrO_4^{2-}] = (1.3 \cdot 10^{-4}) \cdot 6.5 \cdot 10^{-5} = 1.1 \cdot 10^{-12}$

8. Homework (must be performed in the laboratory notebook):
8.1. The equilibrium constant of the thermal reaction $N_2O_4 \rightarrow 2NO_2$is 0.26. The equilibrium concentration of NO_2 is 0,28 mol/l. Calculate the equilibrium concentration of N_2O_4.
8.2. What is the equilibrium direction of the reaction $CH_4 + H_2O = CO + H_2$ if the volumes are lowered thrice?
8.3. Calculate SP of barium sulphate if solubility is $1.05 \cdot 10^{-5}$.

***9. The control test*:**

for instance:

9.1. The chemical equilibrium of the reaction $SO_3 \leftrightarrow SO_2 + O_2$ as the result of pressure decrease shifts in:

a) left side
b) right side
c) does not shift

9.2. Calculate SP of calcium oxalate if its solubility is $5.07 \cdot 10^{-5}$ mol/l.

10. The algorithm of the experiments:

10.1. Influence of the reactant concentration on the equilibrium shift.
10.2. Influence of temperature on the equilibrium shift.

11. The detailed explanation of the following experiment:

11.1. Influence of the reactant concentration on the equilibrium shift.

Add 1 drop of saturated $FeCl_3$ solution and 1 drop of NH_4SCN solution to 50 mls of water. The solution is mixed and divided in 4 test-tubes.

1) add 2 drops of saturated $FeCl_3$ solution;
2) add 2 drops of saturated NH_4SCN solution;
3) add some crystals of NH_4Cl;

Give data in table. Write the chemical equations, the equilibrium constants, make the conclusions.

№ test-tube	***Added component***	***Color change***	***Conclusion (equilibrium shift)***
1	$FeCl_3$		
2	NH_4SCN		
3	NH_4Cl		

11.2. Influence of temperature on the equilibrium shift.

In two test-tubes add 5 ml of starch solution and 1 drop of iodine solution. Heat one of them and then cool it. The second one is the blank test-tube. Make a conclusion.

***12. Control test*:**

Sample 1.

1. Chose the correct answer. Rate of the chemical reaction is the change:
   a) the pressure per unit of time;
   b) the concentration of the reactant per unit of time;
   c) the volume of the reactant per unit of time.
2. Chose the correct answer. In heterogeneous catalysis the reactants and the catalyst have:
   a) the same phase;
   b) the different phases;
   c) the interacted at different temperatures.
3. What is the reaction rate change of $NO_{(gas)} + Cl_{2(gas)} \rightarrow NOCl_{(gas)}$ if the concentration of NO is increased in 3 times?
4. Write the equilibrium constant for the reaction $CO + O_2 \leftrightarrow CO_2$.
5. The substance precipitates when the concentration of its ions is:
   a)equal or lower SP; b) higher or lower SP; c) higher SP.
6. The chemical equilibrium is reached during the synthesis of ammonia at the following concentrations: nitrogen – 2.5 mol/L, hydrogen – 1.8 mol/L and ammonia – 3.6 mol/L. Calculate the equilibrium constant of the reaction.

Sample 2.

1. Chose the correct answer. How many molecules participate in monomolecular interaction?

a) molecule;
b) two molecules;
c) three molecules.

2. Chose the correct answer. The enzymatic catalysis is
   a) homogeneous;
   b) selective;
   c) thermostable.
3. Chose the correct answer. Accordingly to the mass action law the reaction rate is directly proportional to:
   a) the concentration product of the reactants;
   b) the ratio of the reactant's product;
   c) lthe og of the reactant product.
4. Chose the correct answer. Accordingly to van't Hoff rule the increasing of temperature by 10 °C leads to the reaction rate
   a) decrease in 3-4 times;
   b) increase in 3-4 times;
   c) increase in 2-4 times.
5. The chemical equilibrium of the reaction $SO_3 \leftrightarrow SO_2 + O_2$ as the result of pressure decrease shifts in:
   a) left side;
   b) right side;
   c) does not shift.
6. Calculate SP of calcium oxalate if its solubility is $5.07 * 10^{-5}$ mol/L.

TOPIC 13: Potentiometric method of analysis.

1. Actuality of the topic: electrochemical phenomena are observed in human organism. The muscles movements, heartbeat, spreading of nerve impulses are accompanied by electrochemical phenomena. Electrochemical analysis is widely used in medicine for determination of pH, biological liquids, for determination of the concentration of acids and bases that can not be detected by visual titration.

2. General aim: is to detect the active and potential acidity of biological liquid and organs by potentiometry.

3. Actual aims and abilities:
- use the knowledge about the mechanism of creation of electrode potential to estimate the character of biochemical processes in wide pH range.
- to be able to measure the pH, the total acidity of biological liquids and organs for the diagnostic, prediction and medical treatment.

4. Literature:
4.1. Lecture materials;

Potentiometric methods of analysis or potentiometric electrochemical methods of analysis are widely used in medicine as for research purposes and for therapeutic purposes.

Potentiometric analysis method is based on measurement of the electromotive force cell.

Mechanism of potential. Nernst equation.

The cell is a system which the chemical energy of a redox reaction is converted into electrical energy.

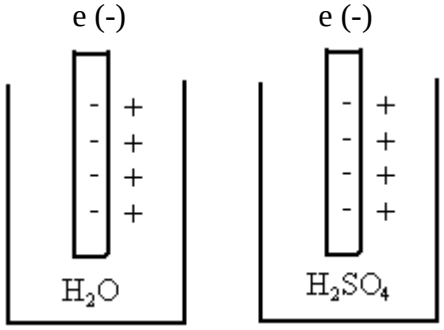
An example is the cell element Jacobi, consisting of zinc and copper electrodes immersed in solutions of their salts, in which the *potentials arise*.

The mechanism of building the next.

If a metal electrode is immersed in water, then under the action of the polar water molecules of a metal cations will break away from the metal surface and go into solution. At the surface of the electrode, positive ions are accumulated on the negative electrode (Picture. 13.1 A). I.e. at the interface between the electrode and the electrolyte occurs in electric double layer (as in a capacitor). When this solution is positively charged and the electrode negative. System consisting of an electrode immersed in the electrolyte is called half-cell, the scheme which can be written as:

Me │ electrolyte

Ease of cleavage of the ions depends on the lattice energy and hydration energy of the ions. The stronger the crystal lattice, the harder cleaved ions. The greater the energy of hydration, the easier cleaved ions.



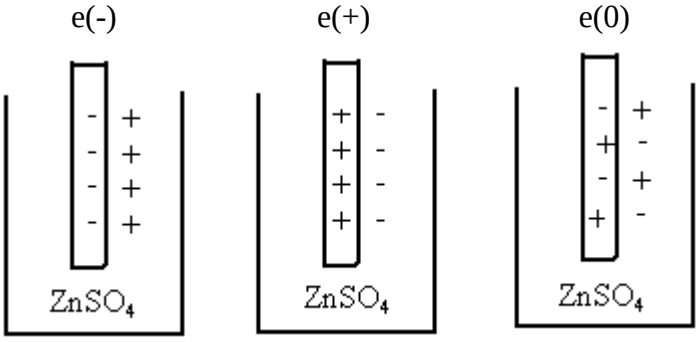
A and B

Picture. 13.1 Emergence of the electrode potential.

If the electrode is immersed in an acid solution (Picture. 13.2 B number) the same pattern, reconstituted charged positively and electrode negatively.

In practice, the electrode system is immersed in a solution of a metal salt, e.g., a zinc electrode is immersed in a solution of a zinc salt $ZnSO_4$. In this case, there are three different phenomena.

If the salt concentration is low (Picture. 13.1 A), the metal cations are transferred from the metal surface into the solution. Accumulated electrons on the metal and the adjacent layer of the solution is positively charged. Thus, again there is an electric double layer and the potential at the negative electrode.



C lower C highest C average

A B C

Picture. 13.2 B Influence of salt concentration on the sign of the potential

Scheme of such half-cell with a zinc electrode in a solution of zinc salts can be written as :

Zn │ $ZnSO_4$

Diagram of the process that goes on the electrode: $Zn \leftrightarrow Zn^{2+} + e$.

If the salt concentration is greater (Picture 16.2 B), the metal cations pass from the solution into the metal surface. Accumulates on the metal cations and the solution is charged negatively. I.e. there is an electric double layer and the potential at the positive electrode.

Diagram of the process that goes on the electrode: $Zn^{2+} + e \leftrightarrow Zn$.

If the salt concentration will be the average (Picture 13.2 - C), the amount of cations which are passed into the solution will be equal to the number of cations that are deposited on the metal surface. In this case, the potential of the electrode is zero.

Thus, the principle of operation of the electrode is that it should exchange its ions with the solution.

The potential appearing on the metal electrode, immersed in the metal salt solution, called electrode.

The magnitude of the electrode potential can be calculated by the Nernst equation :

$$e = e_0 + \frac{RT}{nF} \ln a(Me^{m+})$$

where e - electrode potential;

$e_0$normal (standard) electrode potential; the potential arising at the electrode immersed in the solution of its metal salt at a concentration of 1 mol / l;

R — universal gas constant, 8.313 J / mol • K ;

T — temperature in Kelvin;

n — is the ion charge;

F — Faraday number 96500 C / mol;

α — the activity of the metal ions.

To simplify the calculation instead of the ion activity concentration can be used .

$$e = e_0 + \frac{RT}{nF} \ln\left[Me^{n+}\right]$$

From the equation it is seen that the magnitude of electrode potential depends on the nature of the metal material of electrode (E_0) and the concentration of ions in solution (and the temperature).

At 18^0C equation is:

$$e = e_0 + \frac{8{,}313 \bullet 291 \bullet 2{,}3}{n \bullet 96500} \lg\left[Me^{n+}\right]$$

$$e = e_0 + \frac{0{,}058}{n} \lg\left[Me^{n+}\right]_e$$

At 25^0C equation is:

$$e = e_0 + \frac{0{,}059}{n} \lg\left[Me^{n+}\right]$$

For zinc electrode Nernst equation can be written as :

$$e_{Zn} = e_0(Zn) + \frac{RT}{nF} \ln\left[Zn^{2+}\right]$$

At 18^0C;

$$e_{Zn} = e_0(Zn) + \frac{0{,}058}{2} \lg\left[Zn^{2+}\right]$$

t 25^0C.

$$e_{Zn} = e_0(Zn) + \frac{0{,}059}{2} \lg\left[Zn^{2+}\right]$$

Values of the standard electrode potentials are shown in Table 13.1

Electrodes	Electrodes reaction	Potential of electrodes e_0
$Na^+ \mid Na$	$Na^+ + e \leftrightarrow Na$	-2,71
$Mg^{2+} \mid Mg$	$Mg^{2+} + 2e \leftrightarrow Mg$	-2,37
$Al^{3+} \mid Al$	$Al^{3+} + 3e \leftrightarrow Al$	-1,66
$Zn^{2+} \mid Zn$	$Zn^{2+} + 2e \leftrightarrow Zn$	-0,76
$Fe^{2+} \mid Fe$	$Fe^{2+} + 2e \leftrightarrow Fe$	-0,44
$Ni^{2+} \mid Ni$	$Ni^{2+} + 2e \leftrightarrow Ni$	-0,24
$2H^+ \mid H_2$	$2H^+ + 2e \leftrightarrow H_2$	0,00
$Cu^{2+} \mid Cu$	$Cu^{2+} + 2e \leftrightarrow Cu$	+0,34
$Ag^+ \mid Ag$	$Ag^+ + e \leftrightarrow Ag$	+0,80

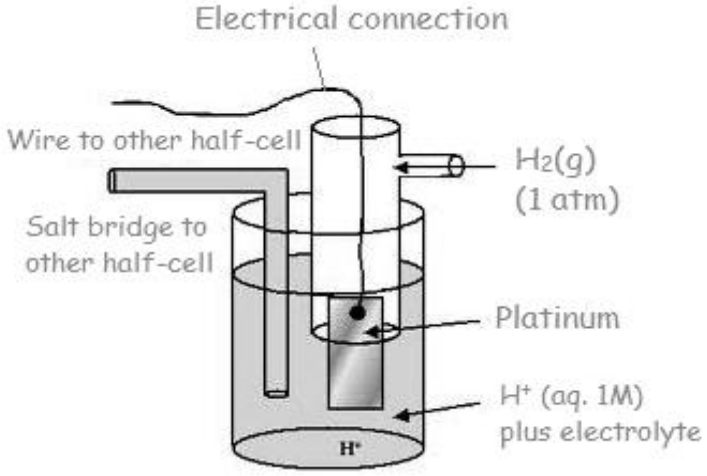
Table 13.1 Standard electrode potentials of some metals

Electrodes for measuring the pH of the solutions.

For clinical trials, it is important to know the concentration of hydrogen ions protons. It is therefore necessary to have an electrode which would be exchanged with H^+ ions, a solution containing protons.

1) Hydrogen Electrode.

Since hydrogen can not be made of a metal plate , then take the platinum coated platinum black (finely divided precipitate of platinum) and saturated with hydrogen gas (hydrogen dissolved in platinum) (13.3). This electrode was immersed in the acid solution. Now it can be exchanged with hydrogen ions, with a solution called by hydrogen electrode.



Picture 13.3 Hydrogen Electrode

Scheme hydrogen electrode:

$$Pt\ (H_2) \mid H^+$$

Process that goes on the hydrogen electrode is recorded as follows:

$$2H^+ + 2e \leftrightarrow H_2$$

Nernst equation for the hydrogen electrode at 25^0C:

$$e_H = e_0(H) + 0{,}059 \lg[H^+]$$

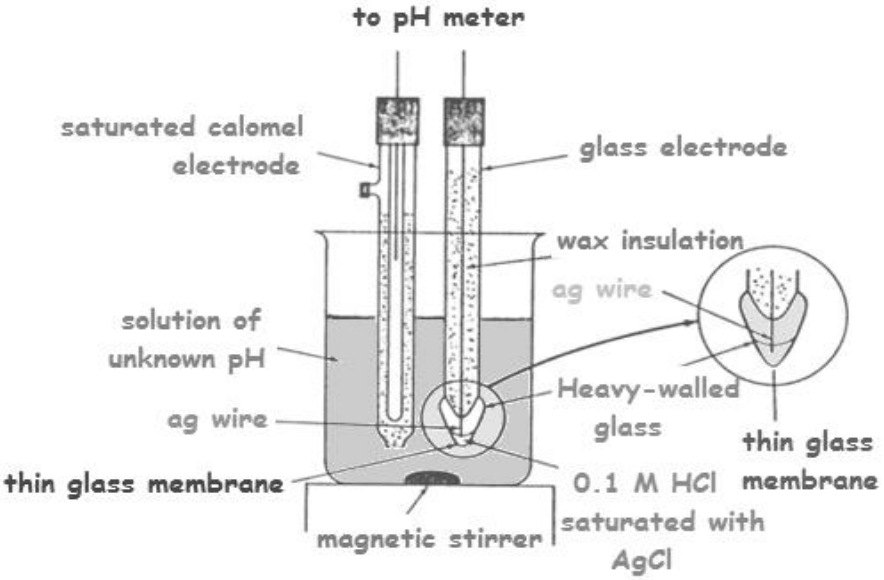
If hydrogen passed at a pressure of 101.3 kPa (1 atm.) A proton concentration equal to 1 mol/ l at a temperature of 298 K, *the potential of the electrode is taken as 0, is called the standard hydrogen electrode*

$$e_0(H) = 0$$

Standard hydrogen electrode was used to determine the electrode potentials of various metals. *Because it is called the reference electrode.*

2) The glass electrode.

Glass electrode is a glass tube with a ball on the end walls of which are saturated with hydrogen. Such an electrode can be exchanged with hydrogen ions, with a solution and its potential is dependent on the proton concentration (Picture 13.4).



Picture 13.4 The glass electrode

Scheme of a glass electrode:

$$\text{Glass} \mid H^+$$

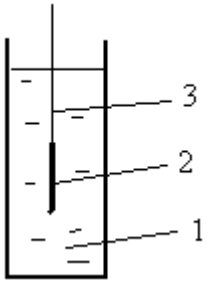
Process that goes on a glass electrode:

$$2H^+ + 2e \leftrightarrow H_2$$

Glass electrode which is used to measure the pH of biological fluids, since it does not contaminate the test solution with different impurities and does not adsorb the substance from the solution, which may influence the electrode potential.

3) Antimony electrode.

Antimony electrode consists of a metal plate covered with poorly soluble film of stibolyl oxide Sb_2O_3 (Picture 13.5).



Picture 13.5. Antimony electrode

1 — acid solution;
2 — layer Sb_2O_3;
3 — wire antimony.

Scheme of the electrode:

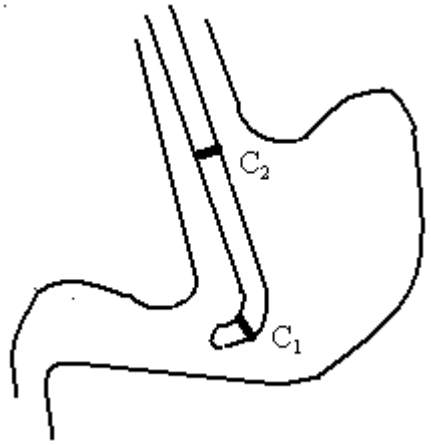
$$Sb, Sb_2O_3 \mid H^+$$

Process that goes on the electrode:

$$Sb + 3H_2O \leftrightarrow Sb_2O_3 + 6H^+ + 6e$$

Antimony electrode used for intragastric pH-metry.

To do this, take a pH sensor, which has two electrodes and antimony electrode. The probe is located in the stomach so that pH can be measured in two regions of the stomach (Picture 16.6). pH unit shows a pH meter.



Picture 13.6 pH probe location in the human stomach C_1 and C_2 - antimony electrodes.

Ion-selective electrodes

The term ion-selective electrodes are applied to the glass electrode, but most called electrodes, which measure concentration of various ions: Na^+ , K^+ , Li^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-} etc. I.e. if you want to measure the concentration of sodium ions, it is necessary to pre- saturate the glass with sodium ions. Then this electrode is a sodium ion exchange solution and its potential will depend on the concentration of sodium ions.

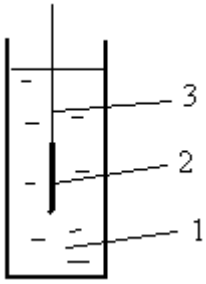
Ion-selective electrodes has recently been widely used in medicine and biology, as to determine the concentration of certain ions by which conventional chemical methods is not always possible.

Electrodes

To compile the cell need two electrodes. One electrode of the definition (see hydrogen, glass), the potential of which is dependent on the concentration of protons. Other — the reference electrode, the potential of which is constant.

To include silver chloride reference electrode and calomel electrodes .

a) *chloride electrode* consists of a silver plate coated with Silver chloride and immersed in a saturated solution of potassium chloride (Picture 13.7) .



Picture 13.7 Chloride electrode

1 — saturated solution of KCl;

2 — layer AgCl;

3 — wire of silver.

Silver chloride electrode scheme:

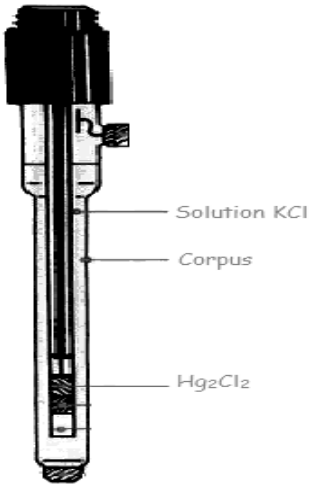
$$Ag \mid AgCl, KCl$$

Process that goes on the electrode:

$$Ag \leftrightarrow Ag^+ + e$$

Silver chloride electrode potential in a saturated solution of KCl is 0.228V at a temperature of 298K.

a) calomel electrode consists of mercury coated with calomel Hg_2Cl_2 and immersed in a saturated solution of KCl (Picture 13.8).



Picture 13.8 Calomel electrode

Calomel electrode scheme:

$Hg \mid Hg_2Cl_2, KCl$

Process that goes on the electrode:

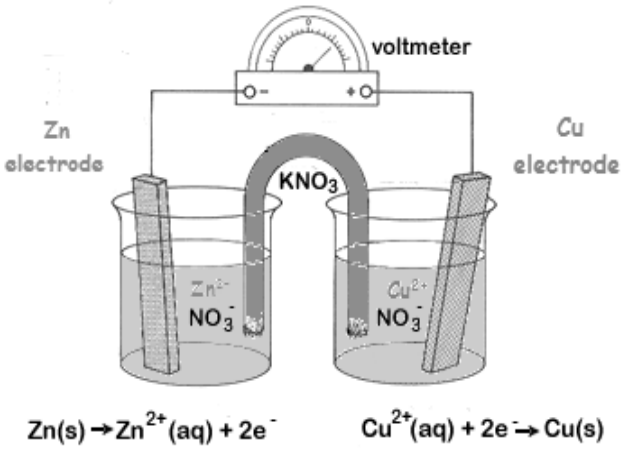
$$Hg \leftrightarrow Hg^{2+} + 2e$$

Calomel electrode potential of 0.25 V at a temperature of 298 K.

Galvanic Elements

Element of Daniel Jacobi

A classic example of the cell type is a general element of Daniel Jacobi. It consists of various metal electrodes immersed in solutions of salts of these metals.



Picture 13.9 Element of Daniel Jacobi

As can be seen from the figure element consists of zinc and copper electrodes immersed in solutions of their salts. Salt solutions are separated from each other, so they are not mixed up and do not affect the electrode potential electrolytic bridge filled with KCl solution must not be broken.

Element Jacobi written as follows:

$$(-)\ Zn \mid ZnSO_4 \parallel CuSO_4 \mid Cu\ (+)$$

In the element Jacobi electric energy comes from a chemical reactio:

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

Zinc as a more soluble active metal (oxidized), its ions into solution, while at the zinc electrode, a negative potential of e (-). Copper cations are restored, i.e. deposited on the copper electrode on which the positive potential occurs e (+).

Quantitative characteristic of the cell is its *electromotive force EMF*. *EMF* element equal to the difference of electrode potentials:

$$EMF = e_1 - e_2$$

Element of Daniel Jacobi:

$$EMF = e_{Cu} - e_{Zn}$$

EMF necessary for calculating the capacity of the positive electrode potential of the negative electrode is subtracted.

Write the Nernst equation for each electrode:

$$e_{Cu} = e_{0Cu} + \frac{RT}{nF}\ln[Cu^{2+}]; \quad e_{Zn} = e_{0Zn} + \frac{RT}{nF}\ln[Zn^{2+}]$$

Substitute into the equation EMF:

$$EMF = (e_{0Cu} + \frac{RT}{nF}\ln[Cu^{2+}]) - (e_{0Zn} + \frac{RT}{nF}\ln[Zn^{2+}])$$

$$EMF = e_{0Cu} - e_{0Zn} + \frac{RT}{nF}\ln\frac{[Cu^{2+}]}{[Zn^{2+}]}$$

At 18^0 C equation is:

$$EMF = e_{0Cu} - e_{0Zn} + \frac{0{,}058}{2}\lg\frac{[Cu^{2+}]}{[Zn^{2+}]}$$

At 25^0C equation is:

$$EMF = e_{0Cu} - e_{0Zn} + \frac{0{,}059}{2}\lg\frac{[Cu^{2+}]}{[Zn^{2+}]}$$

Equation EMF of the cell in the general form:

$$EMF = e_{01} - e_{02} + \frac{RT}{nF}\ln\frac{[Me_1^{n+}]}{[Me_2^{n+}]}$$

where e_{01} — the normal potential of the positive electrode;

e_{02} — the normal potential of the negative electrode;

$[Me_1^{n+}]$ — the concentration of metal ions in a half cell;

$[Me_2^{n+}]^{+}]$ — the concentration of metal ions in the other half-cell.

At 18^0C equation is:

$$EMF = e_{01} - e_{02} + \frac{0{,}058}{n}\lg\frac{[Me_1^{n+}]}{[Me_2^{n+}]}$$

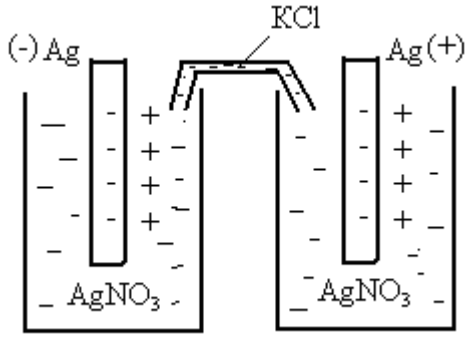
At 25^0C equation is:

$$EMF = e_{01} - e_{02} + \frac{0{,}059}{n}\lg\frac{[Me_1^{n+}]}{[Me_2^{n+}]}$$

Thus, the EMF of the cell depends upon the nature of the metal of which the electrodes (e_0) and the ratio of the half cell in the solution concentrations.

Element concentration

Can create a galvanic cell from two electrodes, one made of metal and immersed in solutions of their salts, but of different concentration.



$C_1 < C_2$

Picture 13.9 Concentration element

The electrochemical cell comprising two electrodes of one metalic immersed in solutions of varying salt concentration, the concentration is called

The electrode is immersed in a salt solution of lower concentration, is oxidized, metal cations will go into solution. In this case on the electrode, electrons are accumulated, and an electrode potential will be negative.

At the other electrode being restored ions from solution and the metal cations are deposited on the electrode, and the positive electrode potential will be.

The scheme of this element is as follows:

$$(-)Ag \mid AgNO_3 \parallel AgNO_3 \mid Ag(+).$$
$$C_1 < C_2$$

EMF equation of this element is written as follows:

$$EMF = \frac{RT}{nF} \ln \frac{C_1}{C_2}$$

Since the electrodes of a metal that $e_0 = 1$; $e_0 = 2$.

At 18^0C equation is:

$$EMF = \frac{0{,}058}{n} \lg \frac{C_1}{C_2}$$

At 25^0C equation is:

$$EMF = \frac{0{,}059}{n} \lg \frac{C_1}{C_2}$$

Thus, the EMF of the concentration cell depends only on the ratio of the half cell in the solution concentrations.

Electrochemical cells (circuits) to determine the pH

1) Hydrogen- hydrogen chain.

This circuit diagram:

$$(-)\ Pt(H_2) \mid H_X^+ \parallel H^+_{known.} \mid Pt(H_2)\ (+)$$
$$[H^+_X] < [H^+_{known.}]$$

This concentration of the element, so the EMF equation is:

$$EMF = e_{known.} - e_X$$

After we have of turning the Nernst equation:

$$EMF = \frac{RT}{nF} \ln \frac{[H^+_{known}]}{[H^+_X]}$$

At 18^0C and n = 1 equation is:

$$EMF = \frac{0,058}{1} \lg \frac{[H^+known]}{[H^+_X]}$$

Transform equation on:

$$\frac{EMF}{0,058} = \lg[H^+_{known}] - \lg[H^+_X]$$

The logarithm of the concentration of protons is pH. Then:

$$pH_X = \frac{EMF}{0,058} - \lg[H^+_{known}]$$

$$pH_X = pH_{known} + \frac{EMF}{0,058}$$

Provided $[H^+_{known}] < [H^+_X]$:

$$pH_X = pH_{known} - \frac{EMF}{0,058}$$

2) Hydrogen - silver chloride reference element:

$$pH = \frac{E - 0,228}{0,058}$$

(-) $Pt(H_2) \mid H^+ \parallel AgCl, KCl \mid Ag$ (+);

3) Hydrogen - calomel element:

$$pH = \frac{E - 0,25}{0,058}$$

(-) $Pt(H_2) \mid H^+ \parallel Hg_2Cl_2, KCl \mid Hg$ (+);

4) Calomel - glass element:

$$pH = \frac{E - 0,25}{0,058}$$

(-) Glass $\mid H^+ \parallel Hg_2Cl_2, KCl \mid Hg$ (+);

5) Glass - silver chloride reference element:

$$pH = \frac{E - 0,228}{0,058}$$

(-) Glass $\mid H^+ \parallel AgCl, KCl \mid Ag$ (+);

6) Antimony- silver chloride:

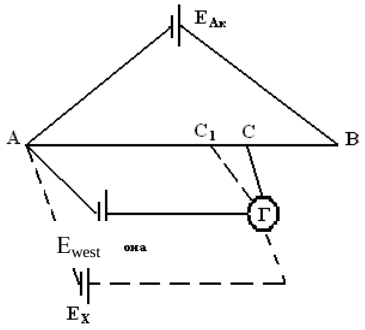
$$pH = \frac{E - 0,228}{0,058}$$

(-) Sb, $Sb_2O_3 \mid H^+ \parallel AgCl, KCl \mid Ag$ (+);

Currently, the industry produces devices for rapid and accurate measurement of the pH of solutions.

Opposition method for measuring EMF

EMF of the cell is measured by the compensation method , whose scheme is shown below (Picture 13.10) :



Picture 13.10 Scheme compensation method

Ak — battery;
AB — ilidewire;
E_{west}. — Weston element, which EMF = 1.018 V;
E_X — electrochemical cell with an unknown EMF;
AC — segment on which element is compensated Weston;
AC_1 — segment, which is compensated by a galvanic cell.
G — galvanometer.

Find rates Slidewire division:

$$R.D = \frac{E_{Weston}}{AC}$$

Find EMF of the cell

$$EMF = R.D \cdot AC_1$$

Oxidation-reduction or redox system

There are systems in which the inert electrodes are used ,those that are not exchanged with sodium ions.

Oxidation-reduction or redox systems are systems (chains), in which the electrodes are not exchanged with sodium ions, and only provide a supply or removal of electrons to the redox reaction occurring in the solution containing the reduced and oxidized forms of the same substance.

In redox systems using electrodes made of platinum, gold, etc.

Redox scheme — the system is recorded as follows:

$$Pt \mid FeCl_2, FeCl_3$$

If the solution is an oxidation reaction: $Fe^{2+} \leftrightarrow Fe^{3+} + e$, the electrons which are formed on the electrode, whereby it is negative there is a redox - potential.

If a reaction solution recovery $Fe^{3+} + e \leftrightarrow Fe^{2+}$, the electrons go from the electrode into the solution. In this case, the positive electrode redox - potential.

Redox potential is the reduction/oxidation potential of a compound measured under standard conditions against a standard reference half-cell.

Potential that arises on the indifferent an electrode immersed in a solution and oxidized reduced forms of the same substance, called are *redox - potential.*

Redox - potential can be calculated from equation Peters :

$$e_{red} = e_{0\ red} + \frac{RT}{nF}\ \ell n\ \frac{[oxidation]}{[reduction]}$$

where e_{red} — this redox - potential;

e_{0red} **— this is a normal redox potential; this potential, occurring at the electrode immersed in the solution at a ratio of the oxidized and its concentration reduced forms of 1;**

n — number of electrons, which sends or receives reductant or oxidant.

Values of the standard redox - potentials are given in Table 13.2.

Electrode solution		Electrode process	e^0, V
Pt	Cr^{2+}, Cr^{3+}	$Cr^{3+} + e \leftrightarrow Cr^{2+}$	−0,41
Pt	Sn^{2+}, Sn^{4+}	$Sn^{4+} + 2e \leftrightarrow Sn^{2+}$	+0,15
Pt	Cu^{+}, Cu^{2+}	$Cu^{2+} + e \leftrightarrow Cu^{+}$	+0, 17
Pt	Fe^{2+}, Fe^{3+}	$Fe^{3+} + e \leftrightarrow Fe^{2+}$	+0,77
Pt	Co^{2+}, Co^{3+}	$Co^{3+} + e \leftrightarrow Co^{2+}$	+1, 84

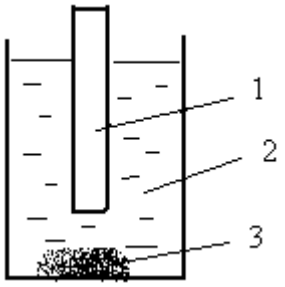
Table 13.2. Standard redox - electrode potentials of some

System $FeCl_2 + FeCl_3$ Peters equation has the form:

$$e\,(Fe^{2+}/\,Fe^{3+}) = e_0\,(Fe^{2+}/\,Fe^{3+}) + \frac{RT}{nF}\,\ell n\,\frac{[Fe^{3+}]}{[Fe^{2+}]}$$

Thus, the amount of redox - capacity depends on the nature of the substance in solution, and concentration ratio of the oxidized and reduced forms.

To measure the pH of the solutions used quinhydrone electrode, which is redox - electrode (Picture 13.11).



Picture 13.11 Quinhydrone electrode

1 — platinum electrode;
2 — acid solution;
3 — quinhydrone

Quinhydrone electrode consists of platinum immersed in a solution with protons, which added quinhydrone. Quinhydrone is an equimolar mixture of quinine $C_6H_4O_2$ and hydroquinone $C_6H_4(OH)_2$. In between them is the solution redox reaction :

$$C_6H_4(OH)_2 \leftrightarrow C_6H_4O_2 + 2H^+ + 2e$$

Redox equation - quinhydrone electrode potential has the form:

$$e_{XG} = e^0{}_{X\Gamma} + \frac{RT}{2F}\ln\frac{[quinine]\bullet[H^+]^2}{[hydroquinone]}$$

Redox-quinhydrone electrode potential will depend on the ratio of the concentrations of oxidized and reduced forms of quinhydrone and the concentration of protons.

Redox — the system can consist of two redox - electrodes. Diagram of such a system can be written as follows:

$$(-)\ Pt\ \big|\ Cr^{2+}, Cr^{3+}\ \big\|\ \big|\ Fe^{2+}, Fe^{3+}\ \big|\ Pt\ (+)$$

EMF equation of this system is :

$$EMF = e^0(Fe^{3+}/\,Fe^{2+}) - e^0\,(Cr^{2+}/\,Cr^{3+}) + \frac{RT}{nF}\lg\frac{[Fe^{3+}]\bullet[Cr^{2+}]}{[Fe^{2+}]\bullet[Cr^{3+}]}$$

Thus systems with a positive potential oxidant have are less positive potential .

The biological significance of redox systems

Oxidation - reduction or redox — potentials play an important role in the human body.

Biological oxidation is a chain of oxidation - reduction reactions that occur at a particular redox - potential. Changing the redox potential is gradual , and the energy is released in small portions, resulting in more efficient and full use of it. (If the potential changes directly from -0.42 V to 0.82V, it would be a blast in the body).

We give examples of redox - systems in the human body:

1) $CH_3{-}\underset{\underset{O}{\|}}{C}{-}COOH + 2H^+ + 2e \rightarrow CH_3{-}\underset{\underset{OH}{|}}{CH}{-}COOH$

Pyritic acid (oxidized form) — Lactic acid (reduced form)

e_{RED} = +0,185 V;

2) $HOOC{-}CH_2{-}CH_2{-}COOH \rightarrow HOOC{-}CH{=}CH{-}COOH + 2H^+ + 2e;$

Succinic acid (reduced form) — Fumaric acid (oxidized form)

e_{RED}= -0.031 V;

3) $HOOC{-}CH_2{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}COOH \rightarrow HOOC{-}CH_2{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}COOH + 2H^+ + 2e;$

Malic acid (reduced form) — Oxaloacetic acid (pike) (oxidized form)

e_{RED}= −0,102 V;

4) $CH_2{-}CH{-}COOH \rightarrow CH_2{-}CH{-}COOH + 2H^+ + 2e;$

SH NH_2 — S NH_2; $CH_2{-}CH{-}COOH$; NH_2

Cysteine (reduced form) — Cystine (oxidized form)

5) $NADH \leftrightarrow NAD^+ + H^+ + e$. NAD - is a coenzyme that transports hydrogen to a human body.

6) Ascorbic acid :

oxidized form + $2H^+ + 2e \rightarrow$ reduced form;

e_{RED} = + 0,06 V;

7) Cytochrome (Fe^{3+}) + e → cytochrome (Fe^{2+}) and others.

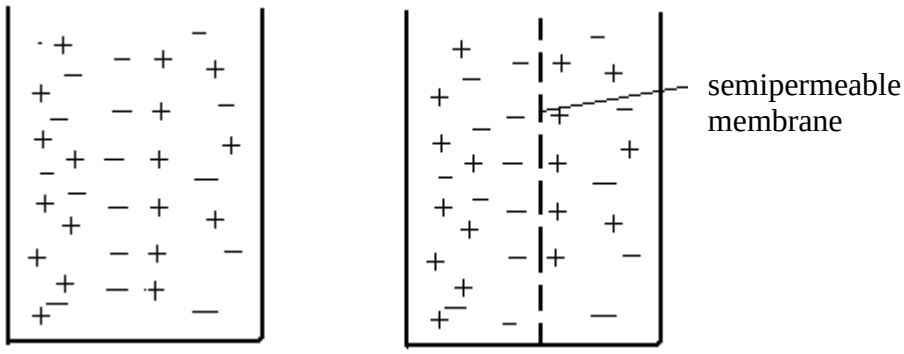
Diffuse and membrane potentials

As mentioned above in the half-cells are electrochemical cell to exclude the influence of the electrode potential.

If the electrolyte solutions are in a single vessel, as a result of ion diffusion can occur and diffuse membrane potentials .

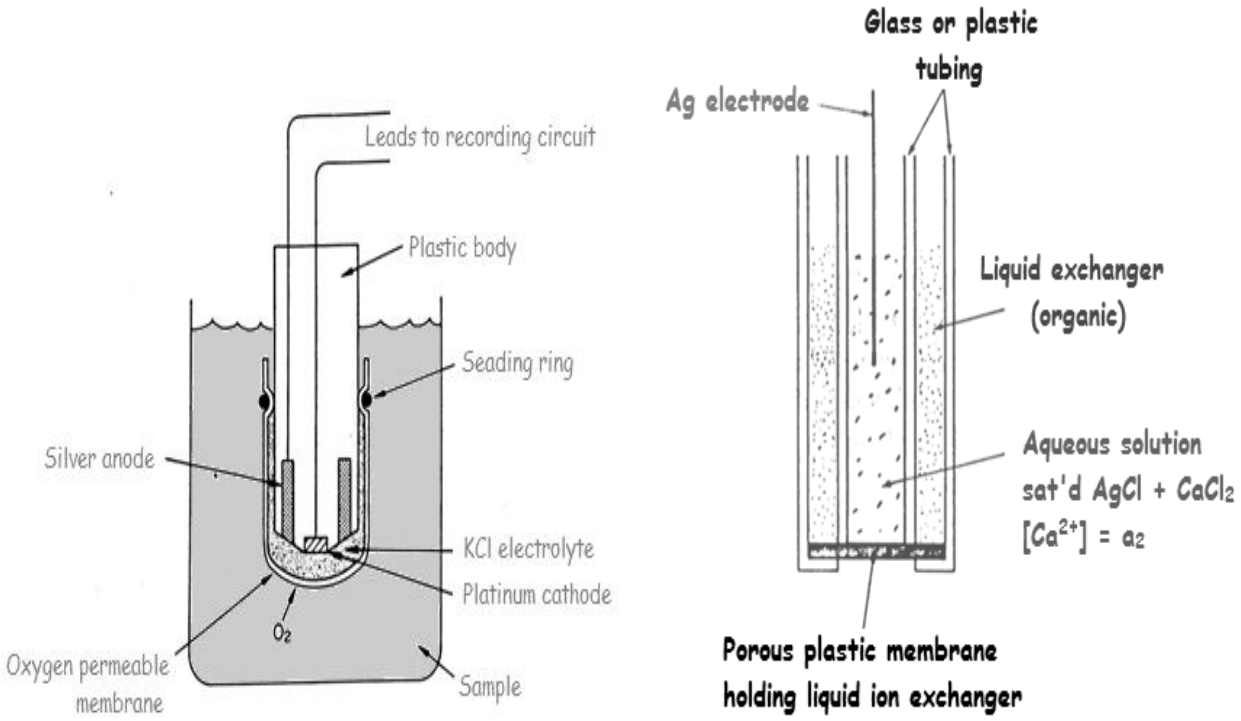
Potential mechanism of diffusion.

Through conventional boundary between two solutions of different concentrations of the diffusion of ions from a solution of higher concentration to lower concentration of the solution (Picture 13.12).



$C_1 > C_2$ $C_1 > C_2$

A B



Picture 13.12. The mechanism of diffusion (a) and membrane potential (b)

Consider Picture 13 - A

Assume that a solution of two different concentrations is poured into vessel of C_1 and C_2. Assume that the positively charged ions move faster. They accumulate on one side of the boundary between the conventional solutions, and negatively charged ions are behind and accumulate at the other side of the border. The border creates electric double layer and therefore the potential, which is formed called *diffuse*. This potential can change the EMF of the cell, if the half-cells do not divide.

The mechanism of membrane potential

Consider Picture 13 - B.

If two solutions of different concentrations are divided by a semipermeable membrane, which may allow only one type of ions, to pass throught it. One side of the membrane will accumulate, for example, positively charged ions, and on the other - negative ions.

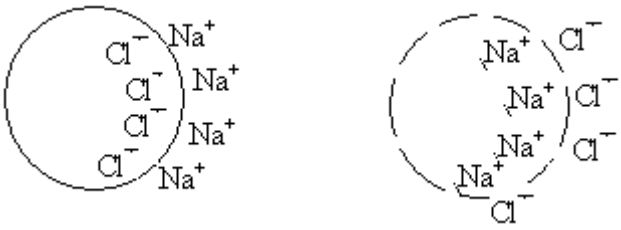
The membrane becomes an electric double layer, and consequently, the potential which is called membrane potential is created. This potential may also change the cell emf. Therefore, the solutions are placed in different vessels, and connect them to an electrolytic bridge, which is filled with agar dissolved therein KCl.

The biological significance of diffuse and membrane potentials

Diffuse and membrane potentials which occur in the human body and are called *biopotentials.*

Each cell of a living organism is surrounded by a membrane that separates intra-and extracellular fluid, the concentration of ions on each side of the membrane is different.

Consider the motion of ions for example, of the cations Na^+. In the extracellular fluid concentrations of Na^+ cation is greater than inside the cell. Therefore, Na^+ cations tend to pass into the cell. But if they don't pass the membrane. Cations Na^+ are accumulated on the outer side of the membrane and on the inner side they attract to anions Cl^- (Picture 16.13 A). An electric double layer, is the nature *of the membrane,* and in humans is called the *resting potential*. The magnitude of the resting potential is 50-100 mV.



Picture 13.13. Occurrence of resting and action potentials

Upon excitation of the cells under the action of electric field, temperature, mechanical impacts and other chemical mediators, the cell pores became permeable to sodium cations. They diffuse into cells and to accumulate on the inner side of the membrane (Picture 13.13 B) and the outer attract chlorine anions. Again there is an electric double layer, and consequently, the potential that is *diffused* in nature, as in the human body is called an *action potential*. The value of action potential is 100-130 mV.

After stopping movements, cells move into the rest condition. Cation sodium are carried to extracellular space (against their concentration) with the help of enzyme Na-ATPase. Similarly cations carry enzymes K + K-ATPase. So is working K, Na - pump.

It is possible to register biopotentials. This is underlies electrocardiography and diagnostic technique.

Electrometric methods of analysis

Electrometric methods of analysis are based on the measurment of EMF of galvanic elements. Earlier there were the examples of galvanic elements for the measurment of pH. Electrometric method is very exact, quick, it can measure colour and foggy span. It is important to use Electrometric methods for measuring pH of biological fluids, ingastric pH-measuring, to control pH during operations, to control medical preparates.

Electrometric titration is one of the directions of Electrometric method of analysis.

Electrometric titration is the method of determining the concentration of substances from the Electrometric measuring.

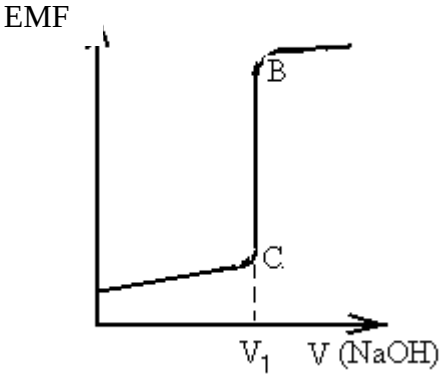
During the Electrometric titration the equivalent point is measured from EMF jumping.

Let's see the process of titration of strong acid by alkali. For this we make electric cell from definition electrode, for example, hydrogen electrode and comparison electrode, for example, chlorsilvery.

$$(-)\ Pt(H_2) \mid H^+ \parallel AgCl, KCl \mid Ag\ (+).$$

The element is connected to a pH meter. Further, we add a quantity of alkali solution from a burette, then EMF is measured.

EMF changes depending on the volume of titrant that shows the titration curve (Picture 13.14 B).



(Picture 13.14 B) Electrometric titration

First, EMF and pH change very slowly - segment 1-C, and at the equivalence point (V_1 - volume of alkali, which goes to the equivalence point titration) is a jump EMF - N_E section, which corresponds to the pH of the test solution . pH measured by pH - meter scale.

Potentiometric titration can also be used in non-aqueous media, which expands the possibilities of this method.

POTENTIOMETRIC METHOD OF ANALYSIS

Galvanic cell — a system in which chemical energy is converted into electrical energy.
Electrode is the potential arising at the metal electrode immersed in a salt solution of it self. The scheme of this half-cell: Me | Me^{n+}.
The magnitude of the electrode potential can be calculated by the **Nernst equation**:

$$e = e_0 + \frac{RT}{nF} \ln a_{Me^{n+}}$$

where e_0 — normal electrode potential, potential occurring at the electrode immersed in a salt solution of this metal with a concentration of 1 mol/L;
R — universal gas constant = 8.313 Dj/mol · K;
T — temperature in Kelvin;
n — ion is charge;
F — Faradays constant 96500 Cl/mol;
α — activity of metal ions (or concentration).
At 18°C equation is:

$$e = e_0 + \frac{0.058}{n} \ln a_{Me^{n+}}$$

At 25°C equation is:

$$e = e_0 + \frac{0.059}{n} \ln a_{Me^{n+}}$$

For example, the scheme and the equation for half-cell of silver electrodes at 18°C:

$$Ag \,|\, AgNO_3 \quad e = e^0_{Ag^+} + \frac{0.058}{n} \ln C_{Ag^+}$$

Determine the concentration of H using a hydrogen electrode, the circuit has the form: Pt (H_2) | H^+ (normal hydrogen electrode potential taken as 0) and the glass electrode: glass | H^+.
For intra gastric pH-metre using antimony electrode:

$$Sb \,|\, Sb_2O_3, \qquad H^+$$

Potentials of these electrodes depend on the concentration of H^+
Reference electrodes:
Silver chloride Ag | AgCl, KCl, whose potential is 0.238 V and calomel Hg | Hg_2Cl_2, KCl, whose potential is 0.25 V.

Scheme of galvanic element Jacobi:

$$^{(-)}\,Zn \;|\; ZnSO_4 \;||\; CuSO_4 \,|\, Cu\,^{(+)}$$

Equation emf of a galvanic cell Jacobi:

$$EMF = e^0_{Cu^{2+}} - e^0_{Zn^{2+}} + \frac{RT}{nF} \ln \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

Equation emf of a galvanic cell of the general type (the electrodes of different metals):

$$EMF = e^0_1 - e^0_2 + \frac{RT}{nF} \ln \frac{C_1}{C_2}$$

at 18°C:

$$EMF = e^0_1 - e^0_2 + \frac{0.058}{n} \lg \frac{C_1}{C_2}$$

at 25°C:

$$EMF = e^0_1 - e^0_2 + \frac{0.059}{n} \lg \frac{C_1}{C_2}$$

Concentration of an element in a galvanic cell consisting of one- metal electrodes immersed in solutions of different concentrations of salts. Scheme of the concentration of the element:

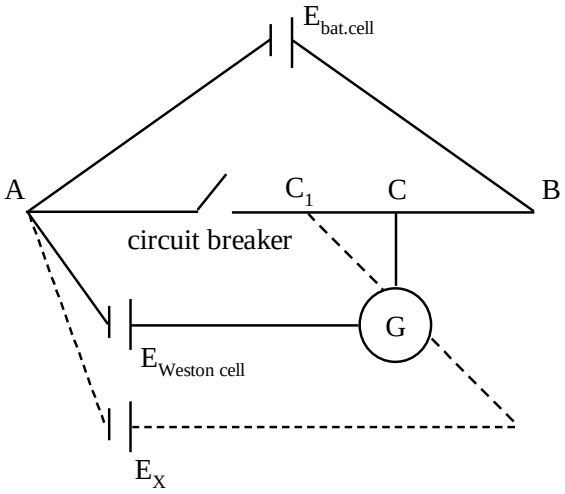
$$^{(-)}\,Ag\,|AgNO_3\,||\,AgNO_3\,|Ag\,^{(+)}$$

$$C_2 < C_1$$

EMF equation of the concentration of the element:

$$EMF = \frac{0.058}{n}\,\lg\frac{C_1}{C_2}$$

Almost EMF element determine the compensation method.



Find the length of division rheochord:

$$U_{min}\quad S.M. = \frac{E_{weston_{cell}}}{AC}$$

where

$$E_{weston_{cell}} A = 1.018\,V$$

AC — a segment that is off set by an element of Weston cell.

Find the emf of a galvanic cell

$$EMF = TS.D \cdot AC_1$$

where

AC_1 — a segment that is offset by a galvanic cell.

To determine the pH of the solutions of such cells and chains:

a) Hydrogen - hydrogen element:

$$^{(-)}\,Pt\,(H_2)\,|\,H^+\,||\,H^+\,|\,Pt(H_2)\,^{(+)}$$

$$C_X < C_{standard}$$

$$pH_X = pH_{standard} + \frac{EMF}{0.058}$$

$$^{(-)}\,Pt\,(H_2)\,|\,H^+\,||\,H^+\,|\,Pt(H_2)\,^{(+)}$$

$$C_{standard} < C_X$$

$$pH_X = pH_{standard} - \frac{EMF}{0.058}$$

b) Hydrogen-calomel cell:

$$^{(-)}\,Pt\,(H_2)\,|\,H^+\,||\,Hg_2Cl_2, KCl\,|\,Hg\,^{(+)}$$

$$pH = \frac{EMF - 0.25}{0.058}$$

c) Calomel-glasselement:

$$^{(-)}\,Slopes\,|\,H^+\,||\,Hg_2Cl_2, KCl\,|\,Hg\,^{(+)}$$

$$pH = \frac{EMF - 0.25}{0.058}$$

d) Hydrogen – an element of silver chloride:

$$^{(-)}\,Pt\,(H_2)\,|\,H^+\,||\,AgCl, KCl\,|\,Ag\,^{(+)}$$

$$pH = \frac{EMF - 0.238}{0.058}$$

Examples

1) An element consists of a hydrogen electrode immersed in the test solution and the normal hydrogen electrodes. Length division of rheochord 3.4 mV/mm, and analyzed element is compensated on a segment 40mm. Write down the scheme of this circuit and calculate the pH of test solution at 18°C.

$K_e = 3.4$ mV/mm $AC_1 = 40$ mm $t = 18°C$ $e°N = 0$ $pH = ?$	1) This element concentration, as if it is of identical electrodes: $^{(-)}\,Pt\,(H_2)\,|\,H^+\,||\,H^+\,|\,Pt(H_2)\,^{(+)}$ $C_{standard} < C_X$ 2) At 18°C:

$$pH_X = pH_{standard} + \frac{EMF}{0.058}$$

$$pH_{standard} = 0$$

then

$$pH_X = \frac{EMF}{0.058}$$

3) Find the emf:

$$EMF = K_e = U_{min} \cdot AC_1 = 3.4 \cdot 40 = 136\ mV = 0.136\ V$$

4) Find the pHx:

$$pH_X = \frac{0.136}{0.058} = 2.34$$

The answer: $pH = 2.34$

2) An element is composed of hydrogen electrodes immersed in a test solution and calomel electrode. Element Weston compensated on a segment of rheochord AC = 350mm. And analyzed element is compensated for by distance of 200mm. Write down the scheme of this circuit and calculate the pH of test solution at 25°C.

$AC = 350$ mm $AC_1 = 400$ mm $t = 25°C$ $pH = ?$	1) Scheme of calomel - hydrogen elements: $^{(-)}\,Pt\,(H_2)\,|\,H^+\,||\,Hg_2Cl_2, KCl\,|\,Hg\,^{(+)}$ 2) calculation formula for pH calomel-hydrogen element: $pH = \frac{E - 0.25}{0.059}$

3) Find the EMF:

$$EMF = \frac{E_{weston_{cell}}}{AC} \cdot AC_1 = \frac{1.1018}{350} \cdot 200 = 0.58\ V$$

4) Find the pH:

$$pH = \frac{E - 0.25}{0.058} = \frac{0.58 - 0.25}{0.059} = 5.59$$

The answer: $pH = 5.59$.

3) The element consists of two hydrogen electrodes. One of the electrodes immersed in a solution with a pH of 4, and the other in a solution with a pH of 1. Write down the scheme of this element and calculate the EMF at 18°C.

$pH = 4$ $pH = 1$ $t = 18°C$	1) It is an element concentration, as of identical electrodes: $^{(-)}\,Pt\,(H_2)\,\vert\,H^+\,\vert\,\vert\,H^+\,\vert\,Pt(H_2)\,^{(+)}$ $C_1 < C_2$
$EMF = ?$	2) If the $pH = 4$, then $[H^+] = 10^{-4}$. If the $pH = 1$, then $[H^+] = 10^{-1}$.

3) The equation of the EMF of the concentration of the element at 18°C:

$$EMF = 0.058 \cdot \lg\frac{C_2}{C_1} = 0.058 \cdot \lg\frac{10^{-1}}{10^{-4}} = 0.058 \cdot \lg 10^3 = 0.174\ V$$

The answer: $EMF = 0.174$ V.

4) The element is composed of hydrogen electrodes immersed in the test solution and silver chloride electrodes. Length division of rheochord is 5.6 mV / mm, and analyzed element is compensated on a segment 60mm. Write down the scheme of this circuit and calculate the pH of test solution at 18°C.

$K_e = 3.4\ mV/mm$ $AC_1 = 60\ mm$ $t = 18°C$ $e^0_{AgCl} = 0.238\ V$	1) Scheme of hydrogen - silver chloride elements: $^{(-)}\,Pt\,(H_2)\,\vert\,H^+\,\vert\,\vert\,AgCl, KCl\,\vert\,Ag\,^{(+)}$ 2) calculating the pH of the equation for this circuit: $pH = \frac{EMF - 0.238}{0.058}$
$EMF = ?$ $pH = ?$	3) Find the EMF: $EMF = K_e = U_{min} \cdot AC_1 = 5.6 \cdot 60 = 336\ mV = 0.336\ V$

4) Find the pH:

$$pH = \frac{0.336 - 0.238}{0.058} = 1.69$$

The answer: $pH = 1.69$.

5) The element is composed of hydrogen electrodes immersed in the blood and calomel electrodes. EMF of the element 698mV. Write down the scheme of the chain and calculate the pH of blood at 37°C.

$EMF = 698\ mV$ $t = 37°C$	1) Scheme of the hydrogen-calomel element: $^{(-)}\,Pt\,(H_2)\,\vert\,H^+\,\vert\,\vert\,Hg_2Cl_2, KCl\,\vert\,Hg\,^{(+)}$
$pH = ?$	2) The equation for calculating the pH of this circuit at 37°C: $pH = \frac{EMF - 0.25}{0.061}$

3) Find the pH of the blood:

$$pH = \frac{0.698 - 0.25}{0.061} = 7.36$$

The answer: $pH = 7.36$.

6) Calculate the EMF and then write scheme of copper - zinc element at 25°C, if the concentration of electrolytes in the half-cell: 1 M $CuSO_4$ and 0.01 M $ZnSO_4$. ($e°_{Zn}$ = - 0,76 V; $e°_{Cu}$ = 0.34 V).

$C(CuSO_4) = 1\ mol/l$ $C(ZnSO_4) = 0.01\ mol/l$

$e^0_{Zn} = -0.76$ V $e^0_{Cu} = +0.34$ V EMF = ?	1) Scheme of copper-zinc cell or element Jacobi: $^{(-)}\,Zn\,|\,ZnSO_4\,||\,CuSO_4\,|\,Cu\,^{(+)}$ 2) The equation of the EMF of this item: $EMF = e^0_{Cu} - e^0_{Zn} + \frac{RT}{nF}\ln\frac{[Cu^{2+}]}{[Zn^{2+}]}$

3) Substituting the data from the conditions of the problem, find the EMF at 25°C:

$$EMF = 0.34 - (-0.76) + \frac{0.059}{2}\lg\frac{1}{0.01} = 1.159\ V$$

The answer: EMF = 1.159 V.

7) EMF of hydrogen-hydrogen element at 25°C is 0.177 V. Proton concentration in a single half-cell is 10^{-4}. Write down the scheme of this element and calculate the concentration of proton in the other half-cell, which is smaller than the known.

EMF = 0.177 V $[H^+]_1 = 10^{-4}$ t = 25°C $e^0_{Cu} = +0.34$ V $[H^+]_2$ = ?	1) This element concentration, as a member of the identical electrodes: $^{(-)}\,Pt\,(H_2)\,|\,H^+\,||\,H^+\,|\,Pt(H_2)\,^{(+)}$ 2) The equation of the EMF at 25°C is as follows: $EMF = 0.059 \cdot \lg\frac{10^{-4}}{[H^+]_2}$

3) We transform this equation:

$$\frac{EMF}{0.059} = \lg 10^{-4} - \lg[H^+]_2$$

Hence:

$$-\lg[H^+]_2 = \frac{EMF}{0.059} = \lg 10^{-4} = \frac{0.177}{0.059} + 4 = 7$$

$$[H^+]_2 = \text{antlg}7 = 10^{-7}$$

The answer: $[H^+]_2 = 10^{-7}$.

8) Urine pH is measured by glass electrode. Electrode comparison — silver chloride. EMF of this element is compensated at 30cm interval, and the scale multiplier of division 0.02 V/cm. Write down the scheme of this element and calculate the pH at 37°C.

$AC_1 = 30$ cm $U_{min} = 0.02$ cm t = 37°C $e^0_{Cu} = +0.34$ V pH = ?	1) Scheme of glass - silver chloride elements: $^{(-)}\,glass\,|\,H^+\,|\,|\,AgCl, KCl\,|\,Ag\,^{(+)}$ 2) the calculation formula for pH glass - silver chloride elements: $pH = \frac{EMF - 0.238}{0.058}$

3) Find the EMF:

$$EMF = K_e = U_{min} = AC_1 = 0.02 \cdot 30 = 0.6\ V$$

4) Find the pH:

$$pH = \frac{0.6 - 0.238}{0.059} = 6.14$$

The answer: pH = 6.14.

5. The main questions of the seminar:

5.1. Galvanic cell. Determination, its structure, the schema.
5.2. Electrode potential. The half-cells.
5.3. Nernst equation, Standard electrode potential.
5.4. Reference electrodes: hydrogen electrode, saturated calomel electrode. Structure and their standard electrode potentials.Electrodes for pH measurements: hydrogen, glass electrodes,

their structure, scheme of the electrodes.
5.6. Electro motive force.
5.7. Concentrated galvanic cell, the principle, the schema, the equation.
5.8. Determination of pH using hydrogen-hydrogen, saturated calomel-hydrogen, saturated calomel-glass galvanic cells, the scheme, equation of pH calculation.
5.9. Measurement of pH using the pH meter.

6.The questions for individual learning:
6.1. Potentiometric titration.
6.2. Ion-selective electrodes.

7. The examples of the task:
7.1.pH calculation using emf.
The cell contains hydrogen electrode immersed in the solution with unknown concentration of H^+ and saturated calomel electrode. EMF equals 0.51 V. Write down the scheme of the given cell and calculate the pH at 18 °C.
The answer: $^{(-)}\ Pt\ (H_2)\ |\ H^+\ ||\ Hg_2Cl_2, KCl\ |\ Hg\ ^{(+)}$

$$pH = \frac{emf - e_{SCE}}{0{,}058} = \frac{0{,}51 - 0{,}25}{0{,}058} = 4$$

7.2. Calculation of pH according to the compensation method.
Objective 2. Element consists of a hydrogen electrode immersed in a solution of unknown concentration of $H^+$and calomel electrode.Weston element off set in the interval of rheochord AU=500mm, and a galvanic cell-in the interval reohord AC_1=250mm. Calculate the pH and the concentration of hydrogen ions.

8. Homework (must be performed in the laboratory notebook):
8.1. The cell contains the hydrogen electrode immersed in gastric juices and the saturated calomel electrode. Write scheme of the cell; calculate pH and Cn of gastric juices knowing that emf equals 0.33 at 18 °C.
8.2. The cell contains two hydrogen electrodes. One of them is immersed in the solution with pH= 4 and other in solution with pH = 1. Calculate emf at 25 °C.

***9. The control test*:**
for instance:
9.1. Choose the correct answer. Nernst equation is
а) $e = e_0 + \frac{0{,}058}{nF}\ln a_{Me^+}$ б) $e = e_0 + \frac{0{,}058}{n}\ln a_{Me^+}$ в) $e = e_0 + \frac{RT}{nF}\ln a_{Me^+}$
9.2. Immersing an electrode in the solution of its salt:
a) the electrode is positively charged;
b) the electrode is negatively charged;
c) the electrode does not charge.
9.3. The cell contains two electrodes. One of them is immersed in the solution with pH = 4 and an other in solution with pH = 2. Calculate emf at 18 °C.

10. The algorithm of the experiments:
10.1. Measurement of pH using pH meter.

11. The detailed explanation of the following experiment:
11.1. Measurement of pH using pH meter.
Detect pH of the solutions №1, №2, №3 using pH meter. Write the schema of the saturated calomel-glass cell, make a conclusion.

12. Control test:

Sample 1.

1. Write the cell reaction and the half-reactions for the galvanic cell
   $Tl(s)|Tl^{+}(aq)||Sn^{2+}(aq)|Sn(s)$
2. What is an electrochemical cell? Write an example.
3. Calculate the emf of the concentrated galvanic cell containing two copper electrodes where one is immersed in 0.001 M $CuSO_4$ solution and the other in 1 M $CuSO_4$ solution.

Sample 2.

1. Write the cell reaction and the half-reactions for the galvanic cell
   $Zn(s)|Zn^{2+}(aq)||Fe^{3+}(aq), Fe^{2+}(aq)|Pt$
2. What is the charge of the anode? Write the redox reaction occurring at the anode.
3. Calculate the emf of the galvanic cell containing the copper electrode and the zinc electrode where one is immersed in1.5 M $CuSO_4$ solution and the other in 0.01 M $ZnSO_4$ solution ($E°_{Zn}$=-0.76 V, $E°_{Cu}$=+0.34 V)

TOPIC 14: Determination of oxidation-reduction (redox) potential.

1. ***Actuality of the topic***: biological oxidation is a net reaction of the redox reactions. The particular redox system possessing the corresponding potential is in charge for every unit of biological net oxidation. Having knowledge of the topic is essential for studying biochemistry, physiology and other related subjects.

2. ***General aim:*** is to have an idea about the redox potentials for explanation of the biological oxidation in living organisms.

3. Actual aims and abilities:

- to use the physical and chemical characteristics of the redox systems to estimate and predict biological oxidation in tissues;
- to interpret the biological oxidation as a main source of energy in the organism;
- to use the redox elements for studying redox processes in living organisms with the aim of diagnostics, predictions and treatment.

4. Literature:

4.1. Lecture materials;

- **Oxidation** is the loss of electrons or an increase in oxidation state by a molecule, atom, or ion.
- **Reduction** is the gain of electrons or a decrease in oxidation state by a molecule, atom, or ion.

Reduction

$$Oxidant + e^{-} \rightarrow Product$$

(Electrons **gained**; oxidation number **decreases**)

Oxidation

$$Reductant \rightarrow Product + e^{-}$$

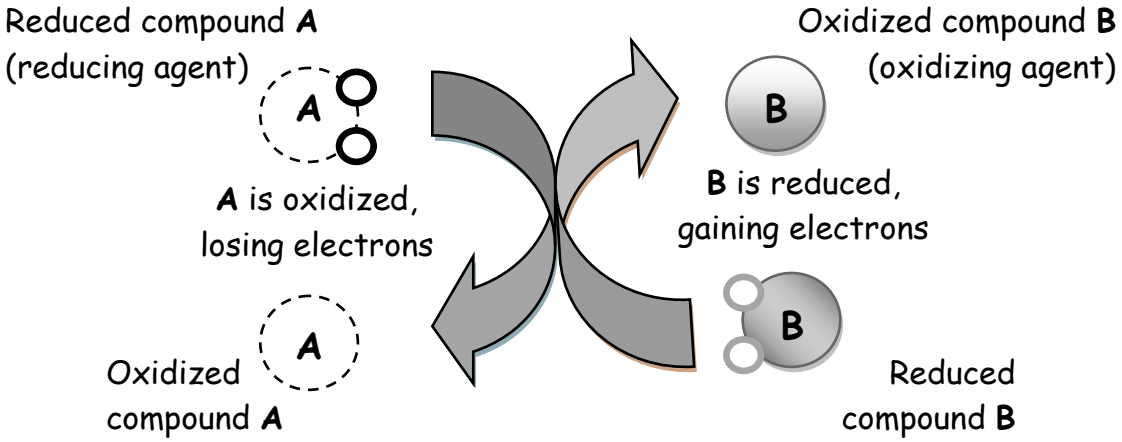
(Electrons **lost**; oxidation number **increases**)

Examples of redox reactions:

$$H_2 + Cl_2 \rightarrow 2\,HCl$$

the oxidation reaction: $H_2 \rightarrow 2H^+ + 2\,e^-$

the reduction reaction: $Cl_2 + 2\,e^- \rightarrow 2Cl^-$



Picture 14.1

The degree of oxidation — the charge is a conditioned atom which is calculated on the assumption that the molecule consists of ions and the total charge of the molecule is zero.

When calculating the degree of oxidation based on the fact that the degree of oxidation of the hydrogen is always 1 (except hydrides), oxygen - 2 (except peroxide), one alkali metal, alkaline - earth metals 2.

Theoretical Foundations of redox reactions:

1) *Reductants* — are molecules, atoms or ions that donate electrons. At the same time they are oxidized:

$$H_2^0 - 2e \rightarrow 2H^+;$$
$$Al^0 - 3e \rightarrow Al^{+3};$$
$$2Cl^- - 2e \rightarrow Cl_2^0.$$

The most common reducing agents: molecule: CO, H_2, formic aldehyde; atoms of metals, nonmetals (C, S, P);

Negatively charged ions nonmetals: Cl^-, Br^-, I^-, S^{-2}, N^{-3}, P^{-2}; metal ions in a lower degree of oxidation: Fe^{+2}, Cr^{+3}, Mn^{+2}; electrical current at the cathode.

2) *Oxidizing agents* — are molecules, atoms or ions, which accept electrons. At the same time they are restored:

$$Cl_2^0 + 2e \rightarrow 2Cl^-;$$
$$S + 2e \rightarrow S^{-2};$$
$$Fe^{+3} + 1e \rightarrow Fe^{+2}.$$

The most common oxidants molecule: O_2, O_3, $KMnO_4$, MnO_2, $K_2Cr_2O_7$, PbO_2, CrO_3, HNO_3, halogens;

- nonmetals in the positive degree of oxidation: N^{+5}, S^{+6}, Cl^+, Cl^{+3}, Cl^{+5}, Cl^{+7};
- metal ions in a higher oxidation: Fe^{+3}, Cr^{+6}, Mn^{+7}, Pb^{+4};
- electrical current at the anode.

3) *Oxidation* — a process recoil electrons of molecules, atoms or ion. I.e. oxidation by oxidation increases.

4) *Reduction* — is the process of joining the electron molecule, atom or ion. I.e. the reduction degree of oxidation is reduced.

Oxidation is always accompanied by reduction and vice versa. The number of electrons, which gives a reducing agent equals the number of electrons which takes oxidant.

5) Compounds which contain an oxidation degree of intermediate may be either oxidizing or reducing agents: $HN^{+3}O_2$, $H_2S^{+4}O_3$, $H_3As^{+3}O_3$, $K_2Mn^{+6}O_4$.

Redox processes and periodic system.

In *periods* with increasing atomic number of the element reducing properties decrease and increase oxidation, since it is easier to accept electrons to complete the energy level. For example, alkaline metals - strong reducing agents, halogens — strong oxidizing agents.

In *major subgroups* recovery properties increase as it increases the radius of the atom and the electrons easier to split off.

In *side subgroups* metals are alone so they restorer.

Redox properties are associated with the *electronegativity*: the more electronegative element, the stronger its oxidizing properties (F - the most electronegative element). On the contrary, metals having a low electronegativity and are reducing.

Redox properties depend on the degree of oxidation : the more positive charge of the same element, the more expressed oxidative properties are:

$KMn^{+7}O_4$	$Mn^{+4}O_2$	$Mn^{+2}SO_4$
oxidant	oxidant and	reductant

B) Influence of the medium on the stroke of the redox reaction.

1) Creating an acidic environment using H_2SO_4, HCl Hydrochloric acid may be not only medium but also a reducing agent. Nitric acid HNO_3, may be not only medium but also the oxidant.

2) Creating an alkaline environment using alkali NaOH, KOH, and Na_2CO_3.

Influence of the medium on the stroke of the redox reaction can be shown on the reduction reaction of $KMnO_4$.

$KMn^{+7}O_4$ + H^+ (+5e) → Mn^{+2} ($MnSO_4$, $MnCl_2$ – colorless solution);

$KMn^{+7}O_4$ + H_2O (+3e) → Mn^{+4} (MnO_2 – brown precipitate);

$KMn^{+7}O_4$ + OH^- (+1e) → Mn^{+6} (K_2MnO_4 – green solution).

Change of oxidants and reductants in the reaction.

1) In an acidic medium the H^+ ions and OH^- form water.

2) In an acidic medium with metal cations (+1, +2, +3) to form salts with acidic residues.

3) Metal ions, which give the water-insoluble base in alkaline and neutral environments, corresponding to provide base ($Fe(OH)_3$, $Cu(OH)_2$).

4) The metal ions which give amphoteric hydroxides in alkaline medium are allowed with the corresponding salts ($Na_3[Cr(OH)_6]$, $Na_2[Pb(OH)_4]$).

Writing equations of redox reactions

1) Write down starting materials of the formula:

$FeSO_4 + KMnO_4 + H_2SO_4 \rightarrow$

2) Find an oxidant and a reductant, depending on the degree of oxidation:

$\overset{+2}{FeSO_4}$ + $\overset{+7}{KMnO_4}$ + H_2SO_4 →

reductant oxidant

3) Write down formula of the reaction products in accordance with the change of initial oxidant and reductant:

$\overset{+2}{FeSO_4} + \overset{+7}{KMnO_4} + H_2SO_4 \rightarrow \overset{+2}{MnSO_4} + \overset{+3}{Fe_2(SO_4)_3} + K_2SO_4 + H_2O$

4) Make up an electronic balance and pick up additional factors so that the number of electrons that gives reductant equals to the number of electrons that takes oxidant:

$Mn^{+7} + 5e \rightarrow Mn^{+2}$	10	2
$2Fe^{+2} - 2e \rightarrow 2Fe^{+3}$		5

5) Put the coefficients in accordance with the law of conservation of mass. First (usually) give the coefficients to the elements that alter the degree of oxidation, after the reaction:

$FeSO_4 + KMnO_4 + H_2SO_4 \rightarrow 2MnSO_4 + 5Fe_2(SO_4)_3 + K_2SO_4 + H_2O$

then to the reaction:

$10FeSO_4 + 2KMnO_4 + H_2SO_4 \rightarrow 2MnSO_4 + 5Fe_2(SO_4)_3 + K_2SO_4 + H_2O$

Next the number of atoms of these elements.

Next the number of hydrogen atoms:

$10FeSO_4 + 2KMnO_4 + 8\,H_2SO_4 \rightarrow 2\,MnSO_4 + 5Fe_2(SO_4)_3 + K_2SO_4 + 8H_2O$

Check the correct placement on the number of coefficients of oxygen atoms:

80 atoms of O to reaction = 80 atoms of O after the reaction.

The final form of the equation of a redox reaction the following:

$$\overset{+2}{10FeSO_4} + \overset{+7}{2KMnO_4} + 8\,H_2SO_4 \rightarrow \overset{+2}{2\,MnSO_4} + \overset{+3}{5Fe_2(SO_4)_3} + K_2SO_4 + 8H_2O$$

$$\begin{array}{l|c|c|} Mn^{+7} + 5e \rightarrow Mn^{+2} & 10 & 2 \\ 2Fe^{+2} - 2e \rightarrow 2Fe^{+3} & & 5 \end{array}$$

The biological significance of redox reactions

Redox reactions occur in the body during metabolism. They are a source of energy in the process of cell respiration. Due to redox reactions in the human body is the synthesis of amino acids, carbohydrates, hormones and other biologically important substances. In humans, there exists a redox homeostasis.

Oxidation - reduction or redox — a system in which the indifferent electrodes do not exchange ions with a solution, but only provide a supply or removal of electrons for the oxidation - reduction reaction in a solution containing oxidized and reduced forms of the same substance.

Scheme of redox - system: Pt | $FeCl_2$, $FeCl_3$.

The potential Redox is calculated by the equation of Peters:

$$e_{red} = e^{\circ}_{red} + \frac{RT}{nF}\ln\frac{[\text{oxidized form}]}{[\text{reducting formt}]}$$

where $\mathbf{e^{\circ}_{red}}$ - normal redox potential and this potential occurrs at the electrode immersed in a solution at ratio in it oxidized and reduced forms equal to 1;

n - number of electrons, which gives or receives a reducing oxidant.

At 18 ° C:

$$e_{red} = e^{\circ}_{red} + \frac{0.058}{n}\lg\frac{[\text{oxidized form}]}{[\text{reducting form}]}$$

at 25 ° C:

$$e_{red} = e^{\circ}_{red} + \frac{0.059}{n}\lg\frac{[\text{oxidized form}]}{[\text{reducting form}]}$$

Examples

1. How many electrons are involved in oxidation - reduction reaction, if e_{red} = 0,121 V, e°_{red} = 0,18 V, the concentration of oxidized form of 1 mol/l, and reduced 10mol/l (t = 25°C)?

$e_{red} = 0.121$ V
$e^{\circ}_{red} = 0.18$ V
[Oxid.] = 1 mol/l
[Reduct.] = 10mol/l
t = 25℃
---
n = ?

1) Write the equation of Peters:

$$e_{red} = e^{\circ}_{red} + \frac{RT}{nF}\ln\frac{[\text{oxidized form}]}{[\text{reducing form}]}$$

2) At 25°C equation is:

$$e_{red} = e^{\circ}_{red} + \frac{0.059}{n}\lg\frac{[\text{oxidized form}]}{[\text{reducing form}]}$$

3) Substitute the data from the equation anode:

$$0.121 = 0.18 + \frac{0.059}{n}\lg\frac{1}{10}$$

$$0.121 - 0.18 = \frac{0.059}{n}\lg 10^{-1}$$
$$-0.059 = \frac{0.059 \cdot (-1)}{n} \cdot n = 1$$

The answer: 1 electron

2) Calculate the normal redox potential at 18℃, if e $_{red}$ = - 0,15 V, and in the 60% oxidized form and 30% reduced form. In oxidation - reduction reaction two electrons are involved.

$e_{red} = -0.15$ V [Oxid.] = 60% [Reduct.] = 30% t = 18℃	1) Write the equation of Peters: $e_{red} = e^{\circ}_{red} + \frac{RT}{nF}\ln\frac{[\text{oxidized form}]}{[\text{reducing form}]}$
$e^{\circ}_{red} = ?$	2) For 18°C equation is: $e_{red} = e^{\circ}_{red} + \frac{0.058}{n}\lg\frac{[\text{oxidized form}]}{[\text{reducing form}]}$

3) Substitute the data from the conditions of the problem:

$$-0.15 = e^{\circ}_{red} + \frac{0.058}{2}\lg\frac{60}{30}$$
$$-0.15 = e^{\circ}_{red} + 0.029 \cdot \lg 2$$
$$e^{\circ}_{red} = -0.15 - 0.0087 = 0.1587 \text{ V}$$

The answer: $e^{\circ}_{red} = 0.1587$ V

3) For the oxidation - reduction of pyruvate - lactate e$_{red}$ = 0,22 V, e°$_{red}$ = 0,180. In the reaction involves two electrons. Calculate the ratio of oxidized and reduced forms of matter at 18℃.

$e_{red} = 0.22$ V $e^{\circ}_{red} = 0.18$ V n = 2 t = 18℃	1) Write the equation of Peters: $e_{red} = e^{\circ}_{red} + \frac{RT}{nF}\ln\frac{[\text{oxidized form}]}{[\text{reducing form}]}$
$\frac{[\text{oxidized form}]}{[\text{reducing form}]} = ?$	2) At 180C equation is: $e_{red} = e^{\circ}_{red} + \frac{0.058}{n}\lg\frac{[\text{oxidized form}]}{[\text{reducing form}]}$

3) Substitute the

$$0{,}22 = 0{,}18 + \frac{0.058}{2}\lg\frac{[\text{oxidized form}]}{[\text{reducing form}]}$$
$$\lg\frac{[\text{oxidized form}]}{[\text{reducing form}]} = \frac{0.22 - 0.18}{0.029} = 1.4$$
$$\frac{[\text{oxidized form}]}{[\text{reducing form}]} = 25$$

The answer: 25.

4) The EMF of a galvanic cell (-) Pt (H_2) | [H^+] = 1 ‖ Mn $^{+2}$, MnO $^-$ | Pt (+) is 1.52 V. Calculate the redox - potential at 25°C.

EMF = 1.52 V t = 25℃	1) emf of a galvanic cell is equal to the difference electrode potentials: $EMF = e_{Mn^{+2}/MnO_4} - e_H$
$e_{red} = ?$	2) The potential of hydrogen electrode is equal to 0, since electrode immersed in a solution with [H^+] = 1, it normal hydrogen electrode;

3) Solve the equation for e_{red}:

$$e_{Mn^{+2}/MnO_4} = EMF - e_H = 1.52 - 0 = 1.52$$

The answer: 1,52 V.

5) The element consists of a calomel electrode and redox - a system Fe^{2+} - Fe^{3+}. EMF of this element is compensated on a segment of 20 cm, and element of Weston - at 60cm interval. Write down the scheme of this element and calculate e_{red} at 18°C.

$AC_1 = 60cm$ $AC_2 = 20cm$ $t = 18°C$	1) Write the scheme of element, suggesting that redox potential is negative with respect to calomel: $^{(-)}\,Pt \mid Fe^{+2}, Fe^{+3} \mid\mid Hg_2Cl_2, KCl \mid Hg\,^{(+)}$ 2) The equation of the EMF as the difference of electrodepotentials: $EMF = e_{KCl} - e_{red}$
$e_{red} = ?$	

3) Find the emf data:

$$EMF = \frac{1.018}{60} \cdot 20 = 0.339\ V$$

4) We find e_{red}:

$$e_{red} = 0.25 - 0.339 = -0.089\ V$$

The answer: $-$ 0,089 V

6) Are oxidized cytochromes restored in the redox - a system, if e_{red} flavin enzyme - 0,06 V and 0,5 V cytochromes?

Solution: as redox - potential flavin enzyme is negative, the enzyme will be the restorer of respect to the cytochrome. Consequently, the cytochromes recover.

7) What properties - of oxidizer and a reducing agent – does cytochrome have C (e_{red} = 0.26 V) relative to a system of pyruvate/lactate (e_{red} = 0,18 V)?

Solution: as redox - potential cytochrome with more positive, than redox - potential pyruvate / lactate, the cytochrome C is an oxidizer.

5. The main questions of the seminar:

5.1. Redox systems (determination, examples).
5.2. Mechanism of redox potential appearing.
5.3. Nernst equation, the depending factors of redox potential, the standard redox potential.
5.4. Biological importance of the redox system.
5.5. Diffusion and membrane potentials.

6.The questions for individual learning:

6.1. Explain the appearance of the redox potential during lactate acid oxidation to pyruvic acid. Write formula of electrode potential.

7. The examples of the task:

7.1.Calculation of the component ratio in the redox system.

The redox potential of $FeCl_3$/ $FeCl_2$ system is +0.888 V. The standard redox potential of the given system is +0.77 V. Calculate the ratio of oxidized and reduced forms at 25 °C.

The answer:

$$e_{red} = e^{\circ}_{red} + \frac{0.058}{n} \lg \frac{[\text{oxidized form}]}{[\text{reducting formt}]}$$

$$n = 1$$

$$0.888 = 0.77 + 0.059 \cdot \lg \frac{[Fe^{+3}]}{[Fe^{+2}]}$$

$$\lg\frac{[Fe^{+3}]}{[Fe^{+2}]} = \frac{0.888 - 0.77}{0.059} = 2$$

$$\frac{[Fe^{+3}]}{[Fe^{+2}]} = 100$$

8. Homework (must be performed in the laboratory notebook):

8.1. The redox potential and the standard redox potential of Cr^{3+}/ Cr^{2+} system are +0.468 V and +0.41 V correspondently. Calculate the ratio of oxidized and reduced form at 18 °C.

8.2. Calculate the standard redox potential of a system if redox potential is -0.15 V, the mass fractions of oxidized form is 20 % and reduced form is 80 % (n=1).

***9. The control test*:**

for instance:

9.1. Immersing the electrode in the redox system solution where the concentration of oxidized form is predominant, the electrode is charged:

a) negatively; b) positively; c) no change.

9.2. The transformation of $FeSO_4 \longrightarrow Fe_2(SO_4)_3$ is:

a)oxidation; b)reduction; c) no change.

9.3. How many electrons take place in the redox reaction if E_{red}=0.169 V, $E°_{red}$=0.110 V and the concentration of the oxidizing agent is lower in 10 times than the reducing agent?

10. The algorithm of the experiments:

10.1. Determination of the redox potential and its dependence on the ratio of oxidized and reduced forms.

11. The detailed explanation of the following experiment:

<u>11.1. Determination of the redox potential ant its dependence on the ratio of oxidized and reduced forms.</u>

<u>11.1. Make a galvanic cell.</u>

A half-cell - a platinum electrode immersed in a solution containing 1 ml of 0.01 M solution of $K_3[Fe (CN)_6]$ and 10 ml of 0.01 M solution of $K_4 [Fe (CN)_6]$;

II half-cell - hingidronic reference electrode whose potential is 0.669 V.

Element of Weston compensated on a segment 43 cm, and compiled a galvanic cell - the segment 12.7 cm.

Calculate the redox potential - e_{red}^1. Decision: EMF = e x-d - e red; e red = EMF - e-x g;

e red 1 = 0.669 - 0, 283 = 0.386 V.

<u>11.1.2. Make a galvanic cell.</u>

A half-cell - a platinum electrode immersed in a solution containing 10 mL of 0.01 M solution of $K_3[Fe (CN)_6]$ and 1 ml of 0.01 M solution $K_4 [Fe (CN)_6]$;

II half-cell - hingidronic reference electrode whose potential is 0.669 V.

Element of Weston compensated on a segment of 43 cm, and compiled a galvanic cell - to 9-cm segment.

Calculate the redox potential - e_{red}^2 (analogous to the experience 11.1.1.).

<u>11.1.3. Make a galvanic cell.</u>

A half-cell - a platinum electrode immersed in a solution containing 5 ml of 0.01 M solution of $K_3[Fe (CN)_6]$ and 5 ml of 0.01 M solution of $K_4 [Fe (CN)_6]$;

II half-cell - hingidronic reference electrode whose potential is 0.669 V.

Element of Weston compensated on a segment of 43 cm, and compiled a galvanic cell - on a segment of 11 cm

Calculate the normal redox potential – e_{red}^0 (similar to the experience in 11.1.1.).

12. Control test:

Sample 1.

1. Immersing the electrode in the redox system solution where the concentration of oxidized form is predominant, the electrode is charged:
   a) negatively
   b) positively
   c) no change
2. The transformation of $FeSO_4 \rightarrow Fe_2(SO_4)_3$ is:
   a)oxidation
   b)reduction
   c) no change
3. Write the Nernst equation for the Fe^{3+}/Fe^{2+} redox system.
4. The oxidation stage of the oxidazing agent in redox reactions:
   a)increase
   b)decrease
   c)no change
5. How many electrons take place in the redox reaction if E_{red}=0.169 V, $E°_{red}$=0.110 V and the concentration of the oxidizing agent is higher in 10 times than the reducing agent?

Sample 2.

1. Immersing the electrode in the redox system solution where the concentration of reduced form is predominant, the electrode is charged:
   a) negatively
   b) positively
   c) no change
2. The transformation of $Fe_2O_3 \rightarrow Fe$ is:
   a)oxidation
   b)reduction
   c) no change
3. Write the Nernst equation for the Mn^{7+}/Mn^{2+} redox system.
4. The oxidation stage of the reducing agent in redox reactions:
   a)increase
   b)decrease
   c)no change
5. Calculate the standard redox potential if E_{red}=-0.15 V and the percent ratio of oxidizing and reducing agents is 10%/90%. (n=1)

TOPIC 15: Sorbtion of biological active compounds on the layer liquid – gas

1. Actuality of the topic: The surface phenomena at the of solid-liquid and solid-gas interface are widely occurred in nature. The absorption process in human organism and the interaction of a substrate with an enzyme take place as a result of the adsorption processes. Adsorption therapy is used in the treatment process.

2.General aim: is to understand the sorption processes at the solid-liquid and solid-gas interface.

3. Actual aims and abilities:

- to have an idea about of the processes occurring at the interface solid-liquid;
- to characterize the adsorption processes using the isotherms of Langmur, BET, Freundlich;
- to explain the living processes on the basis of the adsorption phenomena.

4. Literature:

4.1. Lecture materials;

Physico - chemistry of surface appearances.

A living organism is a system of heterogeneous, there is the interface. This cell membranes, vessels and intestine wall, skin, etc. It is at the interface there are metabolism, respiration, enzymatic reactions, adsorption - desorption action of drugs, etc.

Processes that are at the interface in heterogeneous systems are called surface phenomena.

Surface phenomena are called *sorption.*

Sorption is the *absorptio*n of one substance for another.

If one material accumulates on the surface of another material it is *an adsorption process*. For example, the accumulation on the surface of activated carbon or starch.

If one substance accumulates inside (in volume) of the other substance it is an absorption process. For example, the uptake of hydrogen with platinum (see hydrogen electrode), or ammonia dissolves in water.

The reverse process is called adsorption desorption.

Since adsorption occurs more frequently than absorption, then in the future we will use the term "adsorption".

Depending on the state of aggregation of two contacting surfaces are two types of sorption processes, which occur most often:

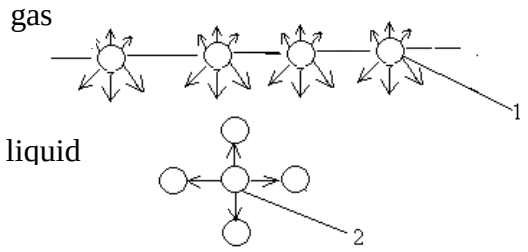
a) adsorption at the liquid - gas;

b) adsorption at the solid -liquid interface.

Sorption at the liquid - gas

We all have seen on the surface of water running insects which do not fall into it. This is explained by surface forces at the liquid - gas.

Properties of the liquid molecules at the interface and within the fluid are different. Molecules that are found inside fluid are drawn uniformly surrounding molecules , i.e. the resultant force is equal to zero (Picture. 15.1).



Picture 15.1. Intermolecular forces on the surface and in the bulk fluid.

1 — molecules on the surface of the gas- liquid;

2 — molecules within the liquid.

Molecules that are found on the surface (Picture 15.1) are attracted by the molecules of the liquid and gas phases. Moreover, the attraction of the molecules of liquid from the larger side than the gas molecules. Therefore, the surface of the molecule have excess energy, which is called the free surface energy SE. Thus, the surface of the molecule as drawn to the fluid inside. As a result, the magnitude of the surface layer decreases. For example, the mercury drops and water to form a ball which has the smallest surface. To increase the surface is necessary to spend a job that is related to the surface energy dependence:

$$G_S = \sigma \cdot S$$

where S — area of the interface;

σ — surface tension.

Surface tension is the work that is necessary expenditure to increase the surface of 1 m^2.

Surface tension is measured in N/m or J/m^2.

Each fluid has a constant net value of the surface tension at a constant temperature. The more polar liquid, the greater the surface tension. The higher the temperature, the lower the surface tension. Some of the surface tension of pure liquids are shown in Table 15.1

Liquid	Surface tension σ, N/m
Mercury	$471,6 \cdot 10^{-3}$
Water	$72,75 \cdot 10^{-3}$
Benzene	$28,9 \cdot 10^{-3}$
Acetic acid	$27,6 \cdot 10^{-3}$
Acetone	$23,7 \cdot 10^{-3}$
Ethanol	$22,3 \cdot 10^{-3}$
Diethyl ether	$17,0 \cdot 10^{-3}$

Table 15.1

Surface tension of liquids (298K)

There are various methods of determining the surface tension.

A) Stalagmometric method.

The measurement is performed by using stalagmometer (Picture 15.2).

Picture 15.2 Stalagmometer

This expansion of the glass tube with the capillary ends and out of which the fluid flows dropwise. Number of drops depends on the surface tension. The greater the surface tension is the greater the volume of the drop and less number of them are between the surface tension of the droplets and the inverse relationship:

$$\sigma_X \cdot n_X = \sigma_0 \cdot n_0$$

$$\text{hence} \quad \sigma_X = \frac{\sigma_0 \cdot n_0}{n_X}$$

where σ_X — surface tension of the test liquid;

n_X — the number of sample liquid droplet;

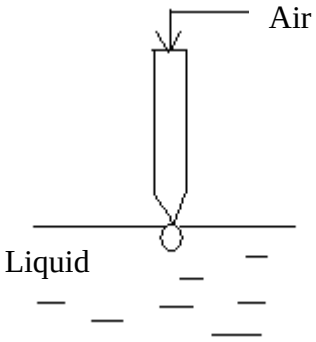
σ_0 — standard liquid surface tension;

n_0 — number of standard liquid droplets.

Accurate measurement is necessary to consider the density of the solutions.

B) Method of the greatest pressure of gas bubbles or method of Rebinder.

Measurement is carried out using capillary, which touches the surface of the liquid (Picture 15.3)



Picture 15.3 Rebinder method scheme

Through a capillary leaks the air at a certain pressure. The larger the surface tension, the more pressure must be applied to the gas bubble slipped through the phase interface. I.e. between the surface tension and the pressure of gas is directly in proportional relationship:

$$\frac{\sigma_X}{P_X} = \frac{\sigma_O}{P_O}$$

hence

$$\sigma_X = \frac{\sigma_0 \bullet P_X}{P_0}$$

where σ_X — surface tension of the test liquid;

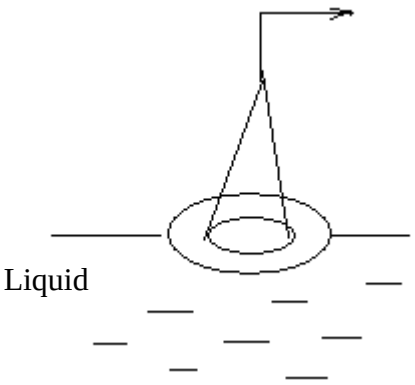
P_X — gas pressure above the liquid under study;

σ_0 — standard liquid surface tension;

P_0 — the pressure above the standard liquid.

C) Method of separation of the ring.

For this method we use a thin metal ring, which is applied to the surface of the liquid , and measure the force with which you can detach the ring from the liquid (Picture 15.4).



Picture 15.4 Scheme ring detachment method

The larger the surface tension, the greater the force must be applied to tear the ring. (It is also difficult to separate two glass wet plates).

Surface properties of solutions

The surface energy can be changed in two ways:

a) The change in the value of the interface;

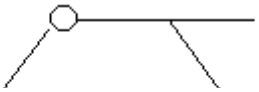
b) A change in the surface tension.

According to the second law of thermodynamics, any system tends to minimize energy. Reduction of surface energy may take place by reducing the interfacial surface tension or decrease. For a pure liquid reducing surface energy, and hence the surface tension occurs by reducing the surface. As a result, water droplet, for example, take the form of a ball. If some water dissolves the substance, the surface tension may be increased or decreased, depending on the nature of the substance.

Substances that lower the surface tension are called surface active (surfactant).

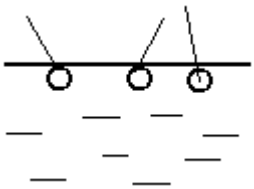
They include many organic compounds: such as fatty acids and their salts, alcohols, amines, proteins, fats, etc.

A characteristic feature is that they are amphiphilic surfactant, i.e. their molecules contain two parts polar (hydrophilic), e.g., COOH, OH, NH_2 and nonpolar (hydrophobic) hydrocarbyl group (Picture 15.4)



Polar Nonpolar

The polar portion has an affinity for water, soluble in water and hydrated. Nonpolar part is not soluble in water. Therefore, when the substance gets into the water, it is ejected from the water accumulates on the surface, orienting the hydrophilic portion for water and a hydrophobic air (Picture 15.5).



Picture 15.5 The arrangement of molecules in the surface layer.

Since the amphiphilic molecules themselves have a low surface tension, the liquid accumulating on the surface, they reduce the surface tension on it. Ie such substances are adsorbed positively.

The longer hydrocarbon radical, is the stronger the surface tension decreases.

Substances which increase the surface tension, are called surface inactive (SInC)

These include inorganic acids, alkalis, salts, formic acid, glycine.

These substances are highly soluble in water, hydrated, fluid accumulates inside and attract the surface molecules. As a result, the surface tension increases. Ie such substances are adsorbed negatively.

There are substances that do not alter the surface tension, for example, carbohydrates.

Measurement of adsorption is adsorption of T is the amount of substance, which accumulates on the surface of 1 cm^2. American scientist J.Gibbs derived an equation that relates the adsorption concentration of the substance and the surface tension:

$$G = -\frac{C}{RT} \bullet \frac{\Delta\sigma}{\Delta C}$$

where G — the adsorption;

C — the concentration of the substance;

R — universal gas constant, 8.313 J / degree • mol;

$\frac{\Delta\sigma}{\Delta C}$ — Surface activity , measured in N • m^2/mol or J • m / mole.

If $\frac{\Delta\sigma}{\Delta C} < 0$, G> 0 , then the adsorption of positive, solution is a surfactant.

If $\frac{\Delta\sigma}{\Delta C} > 0$, then G < 0 , then the adsorption is negative, solution is SAC.

Adsorption of the surfactant depends on the length of a hydrocarbon radical, hydrophobe . It is defined by the rule Duclos - Traube.

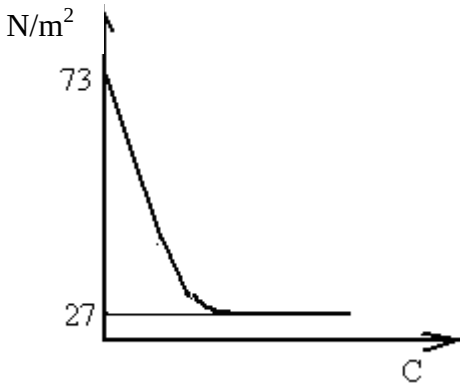
With increasing hydrocarbon radical a group - CH_2 surface activity increases of 3 - 3.5 times.

Duclo - Traubes Rule applies only to diluted solutions.

If the concentration of the substance is high enough, the entire surface is occupied by molecules of a substance and form a saturated monolayer, which is called the palisade Langmuir (Picture 15.6).

Picture 15.6 Langmuir Palisade

Dependence of the surface tension on the concentration shows adsorption isotherms (Picture 15.7).



Picture 15.7 Changing the surface tension concentration of butyric acid

Water has a surface tension of 72,75 N/m^2 and butyric acid - 27 N/m^2. By adding oleic acid to the water value of the surface tension of the water decreases. When the entire surface is occupied by water molecules butyric acid, i.e. palisade formed Langmuir, the value of the surface tension becomes equal to 27 N/m^2.

The biological significance of surface tension

Adsorption at the liquid-gas and the surface tension that are important for living organisms. The surface tension of biological fluids is less than water since they contain a surfactant such as fatty acids, bile acids, proteins, fats, etc. (Table 15.2).

The surface tension of biological fluids

Biological fluid surface tension	**Surface tension** σ, N/m
Water	$72{,}75 \cdot 10^{-3}$
Urine	$66{,}0 \cdot 10^{-3}$
Bile	$48{,}0 \cdot 10^{-3}$
Blood plasma	$45{,}4 \cdot 10^{-3}$
Tissue fluid	$60{,}0 \cdot 10^{-3}$

Table 15.2

Here are a few examples that show the role of surface tension in the human body.

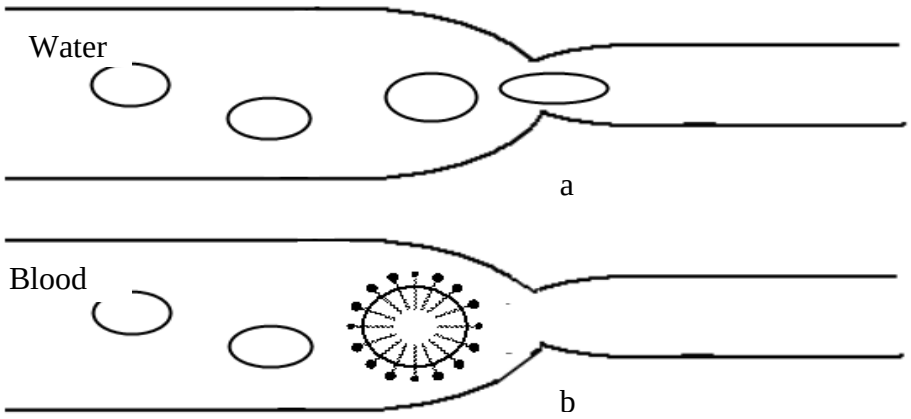
1) Surfactant such as proteins, lipids and others are adsorbed at the wall of the intestines, blood vessels, thus facilitating their absorption and promotes metabolism.

2) Emulsification of fats takes place under the action of bile acids, which are adsorbed onto the surface of fat droplets, they reduce the surface tension and thereby facilitate their crushing into minute particles.

3) The phenomenon of phagocytosis is based on reducing the surface tension of the cell membrane, through which the absorption of foreign body.

4) In the process of respiration surfactants play a major role. They consist of phosphoglycerides and protein and an inner surface lining the alveoli. When you exhale, they form a stockade Langmuir that gives light to subside.

5) The presence of a surfactant and the formation of surface films explained bends when every air bubble surrounded by a protein in the blood film and can not pass through small vessels (Picture 15.8 - b).



Picture 15.8

Flow in tubes of different diameters:

a) water and compressed gas bubble extends in the smaller-diameter pipe;

b) in the film of blood proteins (surfactants) does not deform the gas bubbles.

6) measurement of the surface tension is used for diagnostic purposes. So, in violation of the kidneys in urine appear proteins that reduce the surface tension. The appearance of bile acid in the urine and thus decrease the surface tension indicates hepatitis.

7) amphiphilic lipid molecules is important for the formation of the structure of biological membranes. The hydrophobic portion directed toward the center of the membrane, and hydrophilic - outward toward the aqueous environment.

5. The main questions of the seminar:

5.1. Basic aspects of adsorption. Determinations: sorption, physical and chemical adsorption, absorption, the adsorbentsand adsorbates.

5.2. Adsorption at the surface of the solid. Isotherms and equation of Langmur, BET, Freundlich. The value of sorption.

5.3. Hemosorption. Enterosorption.

5.4. Adsorption significance for the living organisms.

6.The questions for individual learning:

6.1. Immunosorbents. Plasmosorption. Application therapy.

7. The examples of the task:

7.1.What is the difference between adsorption and absorption.

The answer:

Adsorption is the process of adsorbate accumulation into the surface of the adsorbent and absorption is the distribution of the adsorbate in the bulk of the adsorbent.

8. Homework (must be performed in the laboratory notebook):

8.1. Write the example of the selective absorption.

8.2. Write the examples of the adsorption therapy application.

***9. The control test*:**

for instance:

9.1. How does the adsorption of gases change under temperature changing?

9.2. Adsorption theory of narcosis.

9.3. The basis of the ionic adsorption.

10. The algorithm of the experiments:

10.1. Adsorption of acetic acid by activated carbon.
10.2. Adsorption of the colored substances by activated carbon.
10.3. Dependence of the adsorption on the nature of the adsorbents.

11. The detailed explanation of the following experiment:

11.1.. Adsorption of acetic acid by activated carbon.

Prepare the solutions according to the table data.

№	*C_0 CH_3COOH*	*ml of 0.1N NaOH for 10 ml of acid*	*ml of 0.1N NaOH for 25 ml of acid V_0*	*ml of 0.1N NaOH for 10 ml of filtrate*	*ml of 0.1N NaOH for 25 ml of acid V_1*	*Relateve adsorption value $\Delta V=V_0-V_1$*
1	0.03 N					
2	0.07 N					
3	0.12 N					

In three test-tubes are put 1g of activated carbon and filled by 25 ml of acetic acid solution with C_N= 0.03, 0.07 and 0.12 mol/l. The test-tubes are closed and periodically stirred for 20 min.

During 20 min 10 ml of 0.03, 0.07 and 0.12 mol/l acetic acid are titrated –$V_{0.}$

The mixtures must be filtrated from the activated carbon 20 min later. 10 ml of the filtrate are titrated by 0.1 N NaOH in the presence of phenolphthalein -$V_{1.}$

Calculate the relative adsorption value: $\mathbf{\Delta V=V_0-V_1}$.The table is filled. Depict the graphical dependence of ΔVon $C_{0.}$Make a conclusion**.**

11.2. Adsorption of the colored substances by activated carbon.

In the test tube add 1 ml of mixture of fuchsin and fluorescein, nest add 0.2 g of activated carbon and stir it for 3 min. Filtrate the mixture. Write the observations and make the conclusions.

11.3. Dependence of the adsorption on the nature of the adsorbents.

Prepare three test-tubes:		
1 test-tube	***2 test-tube***	***3 test-tube***
5 ml $Pb(NO_3)_2$	5 ml $Pb(NO_3)_2$	5 ml $Pb(NO_3)_2$
0.2 g Al_2O_3	0.2 gactivated carbon	—

The test-tubes must be shaken for 2 min and filtrated in the clean test-tubes. In every filtrate add 2 drops of KI solution. Write the observations and make the conclusions.

12. Control test:

Sample 1.

1. Increasing the temperature, the surface tension at the interface liquid-gas is:
   a) lowered
   b) accelerated
   c) the surface tension does not depend on the temperature.
2. If $\frac{d\sigma}{dc} > 0$ the adsorption is
   a) negative
   b) positive

c) it does not influence on the adsorption
3. Depict the surface layer of a surfactant solution.
4. Write the surfactants containing in the body.

Sample 2.

1. Increasing the polarity, the surface tension at the interface liquid-gas is:
   a) lowered
   b) accelerated
   c) the surface tension does not depend on the polarity
2. The Gibbs equation for the adsorption is:
   a) $\Gamma = \frac{C}{RT} \cdot \frac{dC}{d\sigma}$
   b) $\Gamma = -\frac{C}{RT} \cdot \frac{d\sigma}{dC}$
   c) $\Gamma = -\frac{C}{RT} \cdot \frac{d\sigma}{dC}$
3. What is the surface tension?
4. What is the surfactant meaning in organism?

TOPIC 16: Ion exchange. Chromatography. Sorbtion of biological active compounds on the layer solid compound – solution.

1. Actuality of the topic: the selective absorption is largely extended in human beings. Chromatographic analysis, absorption therapy, the lowering of water hardness are all connected to the the absorption phenomenon. Ionic exchange plays the vital role in the transportation of the ions through the biological membrane.

2. General aim: is to formulate the theoretical knowledge of adsorption and ionic exchange for the following application in the medical practice.

3. Actual aims and abilities:
- to have an idea about of ionic exchange and its application in medical practice;
- to study the adsorption of the electrolytes (selective and ion exchange);
- to praxis in the separation and identification of the mixture using chromatography analysis

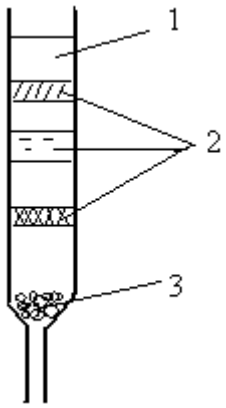
4. Literature:
4.1. Lecture materials;

Chromatographic method for the analysis

Sorption phenomenon underlying chromatographic analysis method.

Chromatography is a physical - chemical method for separating a mixture of substances, based on the different components of the mixture distribution between the mobile and stationary phases.

The method has based by the Russian scientist M.S.Tsvet in 1906, who shared chlorophyll solution into individual components by passing it through a column of adsorbent. Color got colored zones, so called chromatography method (from the Greek. Chromos - color) (Picture 16.1).



Picture 16.1 Scheme of chromatographic column

1 – adsorbent; 2 – zone of adsorbed substances; 3 – wool.

The stationary phase is basically solid. Mobile is a stream of gas or liquid.

In future, this method will be separated and unpainted solutions. Ie Chromatography is a separation method which is also used for the isolation, purification and analysis of substances.

Chromatographic analysis has its own characteristics that distinguish it from other methods of analysis:

a) Requires to analyze a small amount of a substance, sometimes hundredths ml or more molecules;

b) Can be separated substances with very similar properties such as a mixture of amino acids or sugars;

c) The high sensitivity of the method.

Classification of chromatographic methods

A. State of aggregation phases.

a) Gas chromatography, where in a mobile phase carrier gas (hydrogen, argon, etc.), which is mixed with the gas mixture under study. The stationary phase is a solid sorbent. The method applies in particular for the separation of mixtures of amino acid esters.

b) Liquid chromatography, the mobile phase is a mixture of solvents and stationary — on a carrier liquid or a solid. The method is applied for separating a mixture of proteins, nucleic acids, etc.

B. On the mechanism of separation chromatography is divided into:

a) adsorption, which is based on the ability of various substances to the adsorption;

b) distribution, based on the distribution of a mixture of substances between the stationary liquid phase and a gaseous or liquid mobile phases;

c) ion exchange, based on the ability of the assay mixture ion exchange with the adsorbent;

d) sediment, based on the different solubility of precipitation, which are formed as a result of chemical interaction with the substance of the mixture components - precipitant supported on an inert phase;

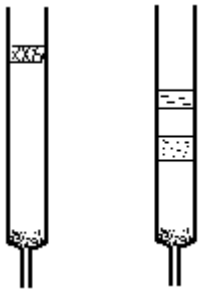
e) gel filtration method or a molecular sieve, based on the differing abilities to penetrate into the pores of the adsorbent Sephadex depending on the size of molecules (Sephadex is partially hydrolysed polysaccharide dextran). Moreover, small molecules are adsorbed and pass through the large adsorbent column;

f) an affinity based selective interaction with proteins specific substances ligands attached to the carrier Sepharose (Sepharose is partially hydrolysed polysaccharide) to which ligands are attached by enzymes, hormones, antigens, etc. In this method, a high specificity.

B. By chromatography separation technique is divided into:

a) column, the separation is conducted in a column with the adsorbent. Progress division is as follows: the prepared adsorbent column poured a small amount of a mixture of substances. Top of the column formed a mixed zone (Picture 16.2 - a). The column was then washed with solvent.

Substances start to move together with the solvent and depending on the adsorptive capacity located at different heights (Picture 16.2 - b). Substances that are weakly adsorbed, faster out of the speakers. The substances that are adsorbed more strongly by slower flow column, thus separating the mixture occurs.

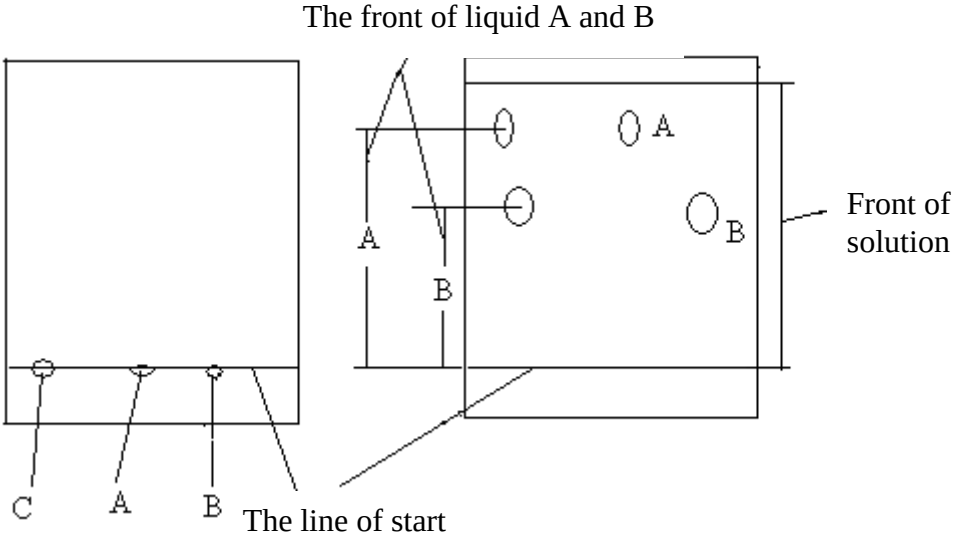


a b

Picture 16.2 Column chromatography:

a - column with a mixed area; b - column with multiple zones.

b) on paper, i.e. separation is carried out on a specially prepared paper chromatography: (Picture 16.3)



a b

Picture 16.3 Paper chromatography:

At the start line of the chromatographic strip of paper deposited a mixture of compounds C and witnesses A and B, i.e. it is a mixture of pure components (Picture 16.3 - a). Then the strip is dipped in solvent below the starting line. The solvent (mobile phase), climbing the paper captures the mixture and witnesses who rise up and depending on the adsorption capacity are located at different distances from the starting line in the form of spots (Picture 16.3 - b). When the solvent reaches the top of the strip, stop chromatography. Measure the distance from the starting line to stop solvent is solvent front. Distance from the starting line to the center of the spot of each component it is a front matter.

The ratio of substance to the front edge of the solvent is denoted R_f:

$$R_f = \frac{front \quad liquid}{front \quad solution}$$

R_f — value is characteristic of the substance, when used the same solvent and the same grade of paper. Chromatography on paper is widely used for separating mixtures of substances, especially for separating a mixture of biologically active substances - amino acids, sugars, proteins, and other bile acids, i.e. substances with very similar properties;

c) a thin layer of adsorbent, i.e. separation was performed on a thin layer of the adsorbent supported on an inert carrier, such as a glass plate. Performance technique is the same as on paper.

All types of chromatographic analysis have been recently widely used for analysis of a mixture of amino acids, proteins, monosaccharides, vitamins and other substances as well as for diagnostic purposes.

Adsorption at the solid - liquid

The solid body whose surface is adsorption, is called the adsorbent. Any solid surface exhibits adsorption properties. But it is often used as adsorbents, activated carbon, silica gel, aluminum oxide, calcium oxide, calcium carbonate, clay, starch, etc. The activated carbon adsorbent is considered universal, i.e. it absorbs the largest number of substances. It is derived from conventional or charcoal, which is heated to a high temperature without air pores, and then it was purged with carbon dioxide, to free them from various resins. The result is a very high adsorbent adsorbing surface.

A substance that is absorbed is called adsorptive.

The adsorption process is spontaneous, reversible, exothermic.

Depending on the interaction forces between the adsorbent and the adsorptive, we distinguish physical and chemical adsorption.

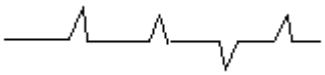
In physical adsorption forces are intermolecular attraction (or van der Waals forces) . For example, the surface of the activated carbon is physical adsorption.

In chemical adsorption (chemisorption) is a chemical interaction between the adsorbent and the adsorptive. For example, the carbon dioxide uptake of calcium oxide. Make a clear distinction between physical and chemical adsorption is not always possible, as chemical adsorption always starts with the physical .

Molecular adsorption

Adsorption of gases and dissolved substances is on the same laws. Hence we speak of adsorption from solutions, the more that these processes are most common and have a big value.

Adsorption is not the entire surface of the adsorbent and only at the active sites which are protrusions (or hollows) (Picture 16.4).



Picture 16.4 The adsorbent surface

To quantify the magnitude of adsorption using adsorption. Since the measured surface of the solid adsorbent is virtually impossible, the value is determined as the adsorption amount of the substance which is adsorbed 1 gram of adsorbent.

Factors influencing the magnitude of adsorption.

1) The nature of the adsorbent on the polar adsorbent better adsorbed polar substances. For example, silica gel absorbs polar water, alcohols and other polar substances. Ie selective adsorption process.

2) The nature of the adsorptive positively charged particles adsorb negatively charged surface of the adsorbent. For example, activated charcoal, which is positively charged, adsorb negatively charged magenta dyes and eosine. All need to be considered in the complex nature of the adsorbent and the adsorptive and the influence of the solvent. Thus, the activated carbon adsorbs better than aqueous solutions, since the water is not adsorbed charcoal adsorbs bad from an alcoholic solution, the alcohol itself as well adsorbed charcoal. For example, fuchsine is adsorbed charcoal from the aqueous solution and adsorbed from alcohol.

3) Low temperature increases adsorption of gases and substances from solutions reduced. Since the adsorption process is exothermic and the equilibrium, in accordance with Le Chatelier's principle, the equilibrium will shift toward the endothermic process, ie desorption. Thus, the adsorption process is reversible (chemical adsorption, as a rule, irreversible).

4) Concentration with increasing concentration of the adsorption is increased. Quantitatively, this dependence is expressed by the Langmuir:

$$G = G_{\infty} \frac{C}{K + C}$$

Where:

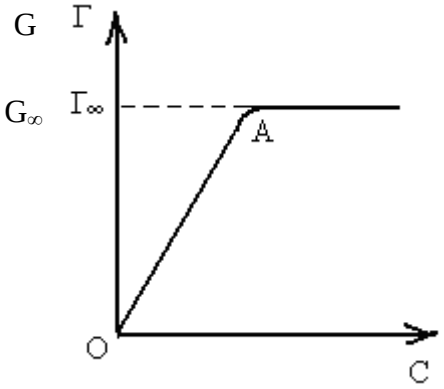
G — the adsorption;

G_∞ — maximum adsorption, when all the active sites are occupied adsorptive ;

C — equilibrium concentration of a substance that is concentration unadsorbed molecules;

K — constant of adsorption equilibrium.

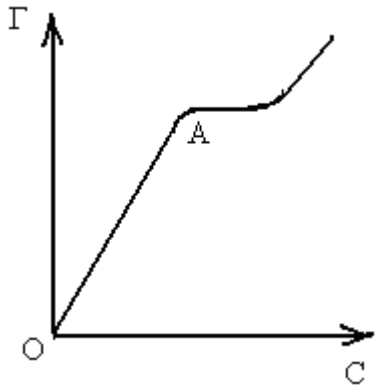
Graphically, the dependence of the adsorption isotherm shows the concentration of the Langmuir adsorption (Picture 15.10).



Picture 16.5 The adsorption isotherm

At low concentration dependence is directly proportional to (segment OA). In high concentrations, the maximum possible amount of adsorbed substance D∞. Langmuir adsorption isotherm describes sorption process in monolayer adsorptive.

For multilayer adsorption is more accurate S - shaped isotherm of Brunauer, Emmett and Teller (BET) (Picture 16.6).



Picture 16.6. S - Imaginative BET adsorption isotherm

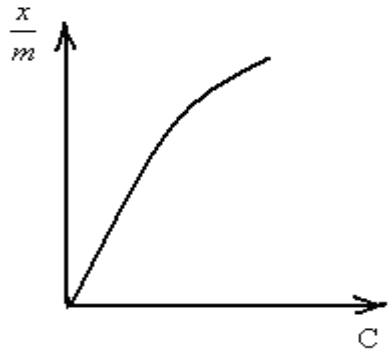
If the sorption process is the interaction between the molecules of the adsorptive on a surface of the adsorbent, it is described by the Freundlich isotherm and (Picture 16.7).

$$\frac{x}{m} = K \bullet C^{1/\pi}$$

Where: $\frac{x}{m}$ - the adsorption

C — equilibrium concentration in solution, ie, concentration unadsorbed molecules;

K and n — constants which depend on the nature of the adsorbent and the adsorptive.



Picture 16.7 Freundlich adsorption isotherm

To describe the sorption processes are more commonly used Langmuir isotherm and BET.

The biological significance of adsorption

Sorption processes are widely spread in nature, including in plants and animals. Any solid surface exhibits sorption properties. For example, plant roots absorb nutrients from the soil; photosynthesis begins with the adsorption of carbon dioxide inner side of the sheet.

Sorption processes play an important role in the human body.

Their principle is used to diagnose and treat diseases.

We give specific examples:

1) The human body sorbents are interfacial - vascular walls, intestines (surface 200 m.The surface of cells, nuclei, and vacuoles, skin enzymes)

2) Adsorption is an initial stage of absorption.

3) Antigen and antibody interact adsorption principle.

4) Substrate occurs on the surface of the enzyme at the active adsorption centers of the enzyme and desorption products of their interaction.

5) Amino acids adsorbed erythrocytes. Their total surface of 3200 m^2.

6) Adsorption therapy — the use of adsorbents for therapeutic purposes:

a) Activated carbon is used in flatulence (gas accumulation in gut);

b) Activated charcoal is used in various poisonings including radionuclides and heavy metals (enterosorption);

c) Aerosol and its derivatives polisorb, silix apply case of poisoning (their properties studied at the Department of Biological and General chemistry VNMMU Pirogov), diarrhea (enterosorption);

d) Hemosorbtion is cleaning the blood of toxic substances by passing the blood through a column with an adsorbent;

e) Lymphosorption is cleaning drainage from toxic substances, such as in violation of the kidneys;

f) Plasmasorption is cleaning plasma (separated from the pre- blood elements), by passing it through a column adsorbent;

g) The completed application therapy is applying to the wound tissues with an adsorbent which absorbs the decay products of a wound or burn area;

h) Immunoabsorbents are polymers with attached thereto biologically active substances highly specific such as enzymes, hormones, etc., are used for binding toxic substances, as well as for the diagnosis and treatment of certain diseases.

7) Face operate on the principle of adsorption. Activated coal gas masks not only adsorbs toxic gases, but is the catalyst for their expansion.

Adsorption of electrolytes

Sorption processes previously discussed concerned mainly the absorption of gas molecules or substances from the solution.

Electrolytes due to their dissociation to form adsorbed ions.

Depending on the mechanism of adsorption and ion exchange distinguish ionic adsorption.

Ion selective adsorption is (selectively by Fajans-Paneth rule): solid adsorbent adsorbs mainly those ions which exhibit affinity for the adsorbent, i.e. those that are part of it and can finish building its crystal lattice.

For example, $BaSO_4$ in the adsorbent from the solution, which contains ions of Na^+, Ca^{2+}, Cl^-, Ba^{2+}, NO_3^-, Fe^{3+}, are adsorbed ions Ba^{2+}, as they enter into the crystal lattice of the adsorbent.

Sorption of ions depends on the following factors:

1) Ion charge the higher the ion charge, the better adsorbed ion. By the ability of adsorbed ions are located in lyotropic Hofmeister series:

$$Fe^{3+} > Ca^{2+} > K^+$$

2) The degree of hydration for ions with the same charge are absorbed better than hydrated ions (larger ionic radius, the less hydrated)

$$Cs^+ > Rb^+ > K^+ > Na^+$$

3) Ion radius is the larger the radius of the ion, the stronger they are adsorbed :

$$CSN^- > I^- > Br^- > Cl^-$$

Ion adsorption is important for the structure of colloidal particles.

The ion exchange adsorption based on an exchange of ions between the adsorbent and the solution in equivalent amounts.

As the adsorbents used ion exchange resin or resins. If the exchangeable cation exchanger, it is called a cation exchanger. Conditionally it could indicate RH. Proton can go into solution , and the solution of its place is a cation which must be removed from the solution.

Scheme of the exchange is as follows:

$$RH + K^+ \rightarrow RK + H^+$$

If exchanger exchanges anions, it is called an anion exchanger. Conditionally it could indicate ROH. On the anion exchange scheme is as follows:

$$ROH + Cl^- \rightarrow RCl + OH^-$$

The biological significance of ion exchange

In humans, the ion exchange is very important. The cell membranes, nuclei and other cells in an organism involved in an ion exchange process. For exchange properties meet the carboxy (-COOH) and phosphate (PO_4^{3-}) for anion exchange groups protein amino ($-NH_2$).

Thus, when the concentration of strontium in the water and food ion exchange occurs between cations of calcium strontium on bone, this leads to bone fragility. By increasing the acidity in the mouth is calcium cation exchanged a proton tooth tissue, which leads to tooth decay.

Ion exchange is widely used in the chemical industry (separation of rare metals, the separation of rare earth metals), in pharmacy (cleaning drugs) in Biochemistry (Preparation and purification of enzymes, vitamins), and in other areas.

We give specific examples of the use of ion exchangers:

1) Demineralisation (desalting) of water-water extraction of calcium and magnesium cations, which cause water hardness.

At the core lies the demineralization reaction:

$$R^-(H^+)_2 + Ca^{2+} \rightarrow R^- Ca^{2+} + 2\,H^+$$

or $$R^-(Na^+)_2 + Mg^{2+} \rightarrow R^- Mg^{2+} + 2Na^+$$

2) Wastewater treatment is extraction of toxic substances, heavy metals, etc.;

3) Decalcification of blood is extracting calcium from the blood to prevent clotting during storage;

4) Reducing gastric acidity is Na- cation bind excess of protons in the stomach;

5) Ion-exchange milk is get removing excess calcium from cow''s milk and used as baby food.

5. The main questions of the seminar:

5.1. The adsorption of the electrolytes (selective and ion exchange).

5.2. Panet- Phayance rule.

5.3. The natural and synthetic ion-exchanger.

5.4. The role of ionic exchange in the processes of vital functions. Adsorption therapy.

6. The questions for individual learning:

6.1. Chromatography. The principles of the method.

6.2. Classification of the chromatographic analysis:

a) by the phase stage

b) by the techniques

c) by distribution mechanism.

6.3. Adsorption chromatography, ion-exchange chromatography and partition chromatography.

6.4. Application of chromatography in biology and medicine.

7. The examples of the task:

7.1.Adsorption of electrolytes.

How are the ionites called on the surface of which the exchange of cations takes place?

The answer:

Ionites are called the cationic exchanger.

7.2. Calculation of R_f of the components in the mixture.

Calculate R_f of monosaccharides if the distance moved by solvent is 21 cm, the distance moved by glucose (1) is 13 cm and the distance moved by fructose (2) is 17 cm.

The answer:

$$R_{f1} = \frac{13}{21} = 0.62$$

$$R_{f2} = \frac{17}{21} = 0.81$$

8. Homework (must be performed in the laboratory notebook):

8.1. Write the example of the adsorption phenomena in human organism.

8.2. The distance moved by solvent is 17 cm, the distance moved by amino acid is 13 cm. What is the amino acid if R_f of the following amino acids corresponds 0.84 for leucine; 0.76 for alanine; 0.91 for glycine.

***9. The control test*:**

for instance:

9.1.What is the stationary phase?

9.2. The distance moved by solvent is 43 cm, the distance moved by a substance is 28 cm. What is the carbohydrate under analysing if R_f of the following carbohydrates corresponds 0.88 for sucrose; 0.05 for fructose; 0.41 for ribose and 0.65 for glucose.

10. The algorithm of the experiments:

10.1. Paper chromatography of amino acids.

10.2. Circular paper chromatography.

11. The detailed explanation of the following experiment:

11.1.. Paper chromatography of amino acids.

Put a drop of the mixture of amino acids at the strip of the chromatographic paper about 1 cm from the base. Beside put a drop of the solution of the known amino acids at the Chromatographic paper about 1 cm from the base. The strip must be dried and dipped in the solvent (ethanol:water=7:3) and leave for 4-5 hours. Then the chromatogram is dried and revealed by and again must be dried. Calculate $R_f$of amino acids and make a conclusion.

11.2. Circular paper chromatography.

At the middle of the circular chromatographic paper drop of the mixture ($CuSO_4$, $FeCl_3$, $Co(NO_3)_2$). The cut and immerse in the water and seal the container. 10-15 min later paper draw out and filled by $K_4[Fe(CN)_6]$. Write the chemical equations. Classify the cations in the line of adsorption increasing.

12. Control test:

Sample 1.

1. What is the phenomena called adsorption and desorption?
2. Depict Langmur equation and isotherm.
3. Write the interfaces in human organism.
4. Panet-Phayance rule.
5. The distance moved by solvent is 43 cm, the distance moved by a substance is 28 cm. What is the carbohydrate under analysing if R_f of the following carbohydrates corresponds 0.88 for sucrose; 0.05 for fructose; 0.41 for ribose and 0.65 for glucose

Sample 2.

1. What is the selective adsorption?
2. Explain what is shown in the adsorption isotherm.
3. Using Al_2O_3 as the adsorbent select the cation predominantly adsorbing into the Al_2O_3 surface:
   a)Na^+
   b)Ba^{2+}
   c)Pt^{4+}
   d)Fe^{3+}
4. What is the retention time?
5. It is observed the spot with R_f =0.70. What is an analyzing alkaloid if the distance moved by solvent is 13 cm and the distances from the start line of "witnesses" are:
   a) codeine is 7.4 cm
   b)caffeine is 9.1 cm
   c) nicotine is 9.9 cm
   d) papaverine is 11.4cm

TOPIC 17: Disperse systems

***1. Actuality of the topic*:**

- the biological liquids named blood, serum, lymph present the colloidal systems where proteins, cholesterol and glycogen are in a colloid state.
- destruction of the colloid state leads to the illnesses and pathology.
- a great number of drugs are manufactured in the state of high dispersive suspension.

2. General aim: is to study the theoretical bases of coagulation and protection of colloidal systems.

3. Actual aims and abilities:

- to know the stability factors of dispersive systems;
- to know the factors influenced on stability and coagulation of dispersive systems;
- to learn the synthesis and properties of aerosols, emulsions, the low dispersive systems;
- to be capable determining of coagulation concentration.

4. Literature:

4.1. Lecture materials;

Disperse systems

The world around us are plants, animals, inanimate nature, etc. they are is dispersed systems.

Disperse systems are called systems in which one substance in the finely divided state (discontinuous phase) is distributed uniformly in another substance (dispersion medium).

Classification of disperse systems:

a) State of aggregation of the dispersed phase and the dispersion medium (Table 17.1).

System	Name	Examples
S/L	Suspensions sols	Particles in water; Sols AgCl, $Fe(OH)_3$; Blood cholesterol; Collargol, Protargolum, Almagelum
L/L	Emulsions	Benzene in water; milk, cream, butter; creams, ointments; fat droplets in the blood
G/L	Foam, Gas	Emulsion lather; oxygen foam (medical)
S/S	Solid Minerals colloidal systems	Minerals, alloys
L/S	Porous soil body	Soil, pearl, opal
G/S	Pumice solid foam	Pumice, silica gel, activated charcoal
S/G	Aerosol	Dust, smoke, smog; powders; coal, silicate, asbestos dust; tobacco smoke
L/G	Aerosols	Fog, clouds; sputtered Medicines

Table 17.1

b) Particle size (Table 17.2).

Types of disperse systems according to particle size.

Type of system	Coarsely	Colloidal	True
Particle size	$10^{-4} – 10^{-6}$ m	$10^{-7} - 10^{-9}$ m	$10^{-10} – 10^{-12}$ m
Examples	Suspensions, emulsions	Sols of metals, cholesterol	Solutions of acids, alkalis, salts

Table 17.2

a) In the interfacial interaction (see Table 17.3).

Types of disperse systems on interfacial interaction

Type of system	Hydrophilic (lipophilic)	Hydrophobic (lyophobic)
Properties	There is affinity with the solvent	There is no affinity with the solvent
	The dispersed phase is soluble	The dispersed phase is insoluble
	hydration shell	There is no hydrate shell
	It is no the surface of separation of the phases	It is the surface of separation of the phases
	Homogeneous	Heterogeneous
	Stability	Unstability
	Have charge and hydration shell	Have a charge
	Obtained by spontaneous dissolution (dispersion)	Obtained from the energy
Examples	Solution of HMC in water; rubber in benzene	Colloidal solutions, coarse system

Table 17.3

The table above shows that dispersions are very common in nature and have different properties (Table 17.4).

Comparative characterization of the properties of dispersed systems

Coarse system	Colloidal systems	True solutions
Microheterogenic	Ultramicroheterogenic	Homogenic
Opaque	Transparent	Transparent
Unstable	Relatively stable	Stable
Do not pass through the filter paper	Do not pass through the filter paper	Pass through the filter paper
Do not pass through a semipermeable membrane	Do not pass through a semipermeable membrane	Pass through a semipermeable membrane
Reflect, refract light	Scatter light (Tyndall cone yield)	Optically empty
Visible in an optical microscope	Visibility in ultramicroscope	Do not visible either in the optical & in ultramicroscopy
Grow old	Grow old	Do not grow old

Table 17.4

The human body as a heterogeneous system also applies to disperse systems. Cells, muscle and nervous tissue, biological membranes, body fluids such as blood, lymph, cerebrospinal fluid, bile - is dispersed systems. Studying the properties of dispersed systems helps to understand the processes of life, gives you the opportunity to develop models of biological membranes, nerve fibers and other biological structures.

Study of disperse systems start with colloidal systems, as they occupy an intermediate position between the coarse and true solutions. Therefore, to some extent, have the properties of both systems and, in turn, using the theory of the colloidal systems can be explained by the properties of other dispersed systems.

Colloid system

Colloidal systems (solutions) are is microheterogeneous systems with the particle size of the dispersed phase 10^{-7} - 10^{-9} m

Thermodynamically unstable colloid systems, as they have a large phase interface and, therefore, the excess surface energy. They are characterized by spontaneous processes ($\Delta G < 0$), lowering the excess energy by reducing the degree of dispersion.

Methods for the preparation of colloidal systems

Colloidal systems particle size occupy space between the coarse systems and true solutions. Therefore, they can be obtained from the coarse dispersion method systems, i.e. grinding particles, and true solutions of the condensation method, i.e. coarsening of the dispersed phase.

Dispersion methods for colloidal systems

A. Physical dispersion:

a) the use of mills of different designs for cement, flour, coffee, etc.;

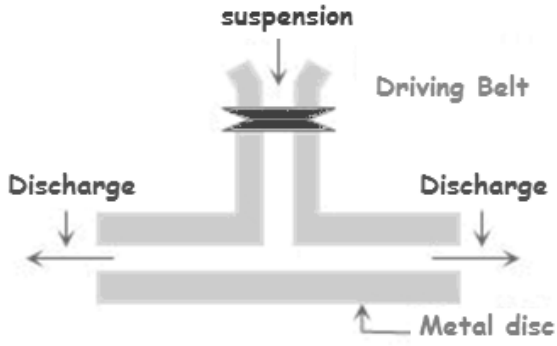
b) colloid mills for the manufacture of medicinal powders;

c) ultrasonic method is crushing due to local changes in high and low pressure. The method used to prepare the sols of metals, alloys, sulfur (for the treatment of skin diseases, as well as fine emulsions for intravenous administration);

d) electrical method by Bredige based on the formation of metal vapors by passing an electric current through the metal electrodes, which is condensed in the dispersion medium. Used to produce metal sols.

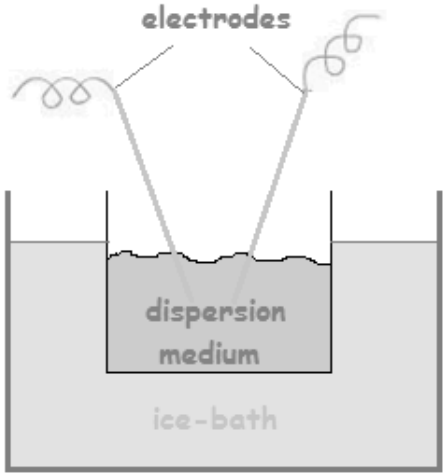
B. Physical and chemical dispersion is peptization the process of translating the freshly formed precipitate colloidal. So, if a draft freshly formed precipitate $Fe(OH)_3$ flocculent add $FeCl_3$, it turns sol ferum hydroxide $Fe(OH)_3$. This method can obtain sols $Al(OH)_3$ and $Zn(OH)_2$.

Dispersion method

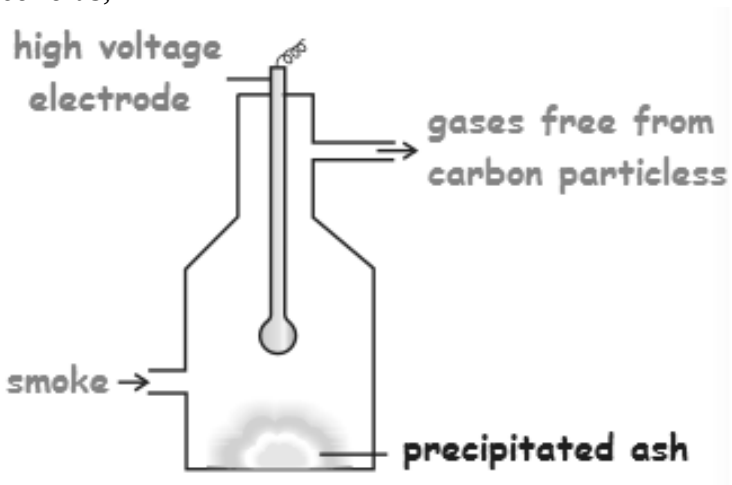


Picture 17.1: Pictorial view of colloidal mill

Peptization:



In case of lyophobic colloids;



Picture 17.2: Schematic diagram of Cottrell smoke precipitator

Condensation methods of preparation of colloidal systems

A. Physical condensation:

a) electrical method by Bredige in which a metal is vapor condensation;

b) method of solvent exchange is the replacement of the dispersion medium. For example, if sulfur alcoholic solution poured into water, then we obtain a colloidal sulfur solution in water. Used for producing sulfur sols, rosin oils.

B. Chemical condensation:

For the preparation of colloidal solutions most commonly used chemical condensation, which is used in various types of chemical reactions.

There are three conditions for obtaining sols by chemical condensation:

a) the low concentration of the starting materials;

b) the low solubility of the reaction product;

c) an excess of one of the starting materials, which acts as a stabilizer.

Examples of the preparation of sols using chemical reactions:

a) reaction of the double exchange between the salts: $BaCl_2 + Na_2SO_4 \rightarrow BaSO_4 + 2NaCl$ - got sol $BaSO_4\downarrow$;

b) the hydrolysis reaction: $FeCl_3 + H_2O \rightarrow Fe(OH)_3 + HCl$ – obtained sol $Fe(OH)_3$;

c) the reduction reaction: $Ag_2O + H_2 \rightarrow 2Ag + H_2O$ - got sol Ag;

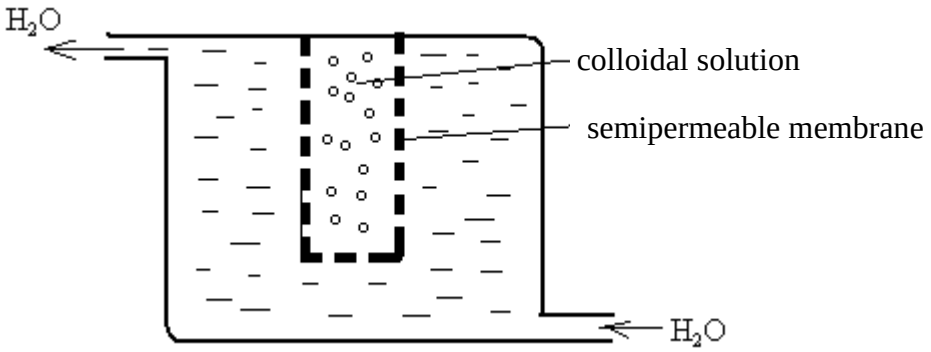
d) oxidation: $H_2S + O_2 \rightarrow S + H_2O$ - got sol S

Purification of colloidal systems

Upon receipt of the nuclei by the method of chemical condensation is taken as the excess of one of the source of electrolytes, so you need to clear them from this excess, as it can reduce the stability of sol and to cause coagulation.

There are methods of cleaning sol:

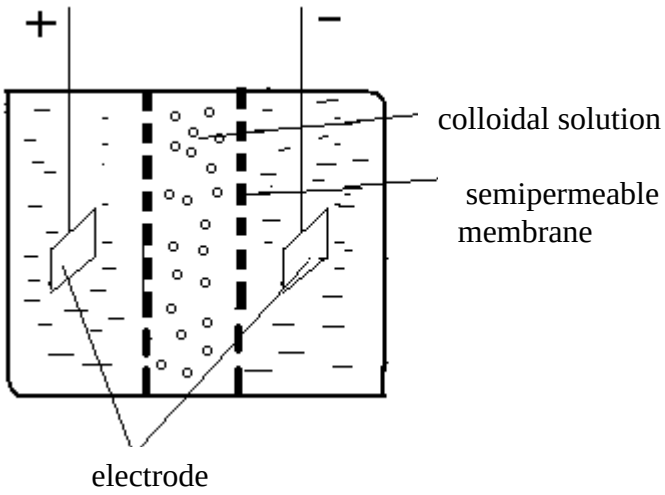
1) *Dialysis* is based on the ability of low molecular weight impurities to penetrate through a semipermeable membrane. Purification was carried out in the dialyzer (Picture 20.2)

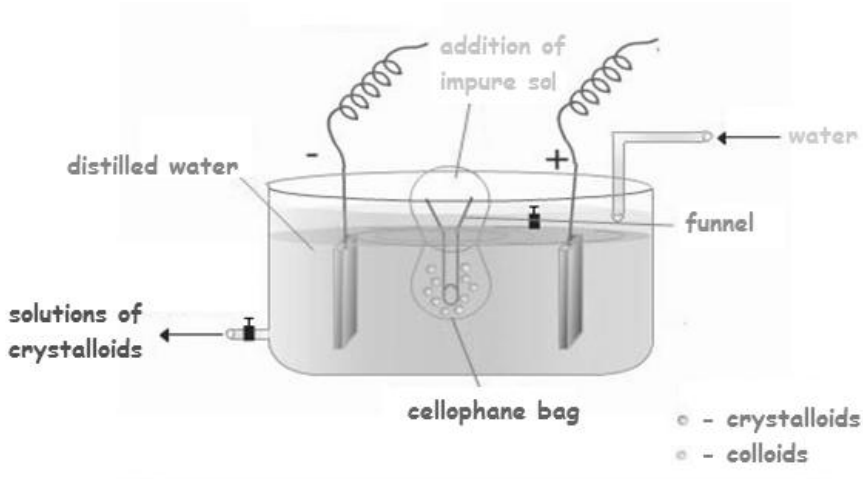


Picture 17.3 Scheme of dialyzer

Dialyser consists of two vessels. Inner receptacle whose walls are made of a semipermeable membrane is filled with a colloidal solution. In outer vessel circulates water. The low molecular weight impurities, primarily ions pass through the semipermeable membrane and the water flow removed. Dialysis takes time, but the result is a stable sol.

2) *Electrodialysis* are used to accelerate the process. Electrodialysis consists of three chambers (Picture 17.4).





Electro-dialysisused for purification of blood in case of kidney failure

Picture 17.4. Scheme of Electrodialysis

The inner chamber whose walls are made of a semipermeable membrane, filled colloid. In the chamber are placed side electrodes. When connecting voltage speed ions through the membrane increases, and dialysis is faster.

3) *Compensation dialysis* are used to determine the concentration of low molecular weight substances, particularly in biological fluids. In this case, the use of a washing liquid solutions with different concentrations of the substance to be determined. In the case when the dialysis is not, then the concentration in solution equal to the concentration of colloidal material in a washing liquid. In this way one can determine the blood sugar concentration of diabetics.

4) *Ultrafiltration* is purification of colloidal solutions by filtering them through special filters under pressure. As a result, the filter passes through the dispersion medium with impurities.

5) *Vividialysis* is cleaning the blood of toxic low molecular weight substances. Blood vessel surgically connected to the machine, which is called the "artificial kidney". Blood passes through a thin tube of semi-permeable membrane through which overlook undesirable substances to the body, and the purified blood is returned to the vessel. Thus, it is possible to purify the blood of urea, uric acid, an excess of potassium ions and other vividializa used in acute renal failure as a result of mercury poisoning drugs, sulfonamides, burns, etc.

Methods for purification of colloidal systems are widely used in pharmacy for cleaning pharmaceuticals.

STRUCTURE OF COLLOIDAL PARTICLES (MICELLES)

Colloidal solutions (or sols) - is micro heterogeneous system with particle size of 10^{-7} – 10^{-9} m.

Methods of preparation of colloidal systems:

a) variance:
- a method of colloid mill;
- ultrasonic;
- peptization.

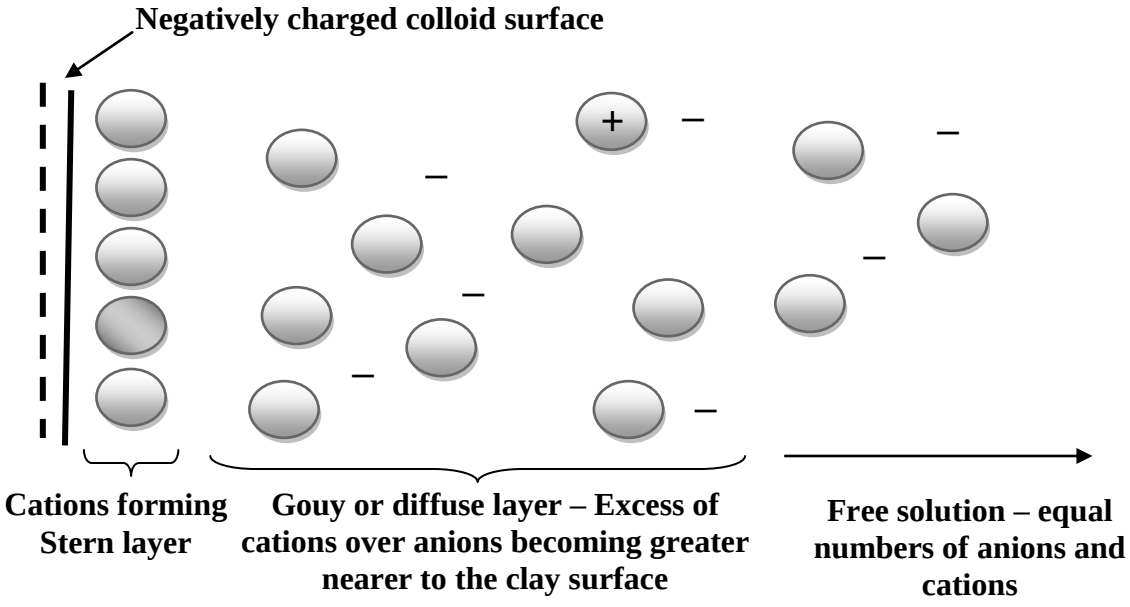
b) condensing:
- physical condensation
- method of replacing the solvent
- chemical condensation (oxidation, recovery, share, hydrolysis).

Conditions for obtaining colloidal systems by the chemical condensation:

a) low concentration of precursors;
b) the excess of one of the starting materials;
c) low solubility of one of the reaction products.

Colloidal particles are called **micelles.**

The most common method of obtaining colloidal particles is the method of chemical condensation, which uses different chemical reactions.



Picture 17.5 Electrical double layer

A) Preparation of sols of the double-exchange reaction.

a) Structure of colloidal particles, we the example of formation of micelle sol AgCl.

$$AgNO_3 + NaCl \rightarrow NaNO_3 + AgCl\downarrow$$

Components of the micelles: core, an adsorption layer, diffuse layer.

Micelle core is a collection of many water-insoluble molecules AgCl. You can write this next way as follows: m AgCl. The kernel is a solid particle. And any solid surface has adsorption properties. Kernel can adsorb ions from solution. In the formation of sol solution formed ions Na^+, NO_3^-, as well as ions Ag, which appear in the solution, if taken in excess of $AgNO_3$. Adsorption of ions is selectively according to the rule Paneth - faience. Thus, the three ions, Na^+, NO_3^-, Ag^+ selectively adsorb ions are Ag, since they show chemical affinity to the core (or part of the nucleus). Written as follows:

m AgCl n Ag^+, where n — the number of ions.

Now the particle is positively charged and attracts negatively charged ions from solution, ie, ions NO_3^- in quantity less than the ions Ag. Written as follows:

$$m\ AgCl\ n\ Ag^+\ (n - x)\ NO_3^-$$

Ag^+ ions and NO_3^- constitute an **adsorption layer**. Ions of Ag^+, which are adsorbed to the first **potential-called ions**, and the ions NO_3^- **— counterions**. Kernel, along with an adsorption layer is called **granules**. Granule has a charge, since the positively charged ions in the adsorbed layer more active:

$$[m\ AgCl\ n\ Ag^+\ (n - x)\ NO_3^-]^{X+}.$$

Granule is a particle which moves in an electric field. Micelle as a whole is electrically neutral, ie the charge of pellets is neutralized by negative ions in the amount of NO_3^- x:

$$\underbrace{[mAgCl}_{\text{core}}\ \underbrace{n\ Ag+\ (n - x)\ NO_3^-]^{X+}}_{\text{adsorption layer}}\ \underbrace{x\ NO_3^-}_{\text{diffusion layer}}$$

Thus, the micelle is formed by the stabilizing action of the ions Ag.

b) If an excess of NaCl: $AgNO_3 + NaCl \rightarrow NaNO_3 + AgCl$,

then the structure of micelles is the following:

$$\mathbf{[m\ AgCl\ n\ Cl^-\ (n - x)\ Na^+]^{x-}\ x\ Na^+}$$

Ion - the stabilizer Cl^- ions

For reactions involving multiply charged ions, it is necessary to take into account factors. For example: Ag_2SO_4 sol prepared by the reaction:

$$AgNO_3 + Na_2SO_4 \rightarrow NaNO_3 + Ag_2SO_4$$

Here are some examples of the structure of micelles :

$$\{mAg_2SO_4\ 2n\ Ag^+\ 2(n\text{-}x)NO_3^-\}^{2x-}\ 2xNO_3^-$$

AgI sol

$$AgNO_3 + KI \rightarrow NaNO_3 + AgI$$

excess

Micelle structure : $[\ m\ AgI \bullet n\ Ag^+ \bullet (n\text{-}x)\ NO_3^-\ ]^{x+} \bullet x\ NO_3^-$;

$$AgNO_3 + KI \rightarrow NaNO_3 + AgI.$$

excess

Micelle structure : $[\ m\ AgI \bullet n\ I^- \bullet (n\text{-}x)\ K^+\ ]^{x-} \bullet x\ K^+$;

c) If a solution contains multiply charged ions, it is necessary to take into account the factors:

$$Na_2SO_4 + BaCl_2 \rightarrow 2NaCl + BaSO_4\downarrow$$

$$[mBaSO_4\ nSO_4^{2-}\ 2\ (n\text{-}x)\ Na^+]^{2X+}\ 2x\ Na^+$$

A sol was prepared by an exchange reaction $BaSO_4$:

$$Na_2SO_4 + BaCl_2 \rightarrow 2NaCl + BaSO_4$$

huts

Micelle structure: $[\ m\ BaSO_4 \bullet\ n\ SO_4^{2n-} \bullet 2(n\text{-}x)\ Na^+\ ]^{2X+} \bullet\ 2x\ Na^+$.

d) Formation of sol Arsene sulphide.

$$2H_3AsO_3 + 3H_2S \rightarrow As_2S_3 + 6H_2O$$

Since hydrogen sulphide is passed through a solution of arsenic acid it is abundant and is a stabilizer: $H_2S \leftrightarrow H + HS^-$

The structure of the micelles can be written as follows:

$$\mathbf{[m\ As_2S_3\ n\ HS^-\ (n\text{-}x)\ H^+]^{x-}\ x\ H^+}$$

As_2S_3 sol

$$2Na_3AsO_3 + 3H_2S + 6HCl \rightarrow As_2S_3 + 6NaCl + 6H_2O$$

excess

Hydrogen sulphide gas was passed , i.e. it is in excess:

$$H_2S \rightarrow HS^- + H^+$$

Micelle structure: $[m\ As_2S_3 \bullet n\ HS^- \bullet (n\text{-}x)\ H^+\ ]^{x-} \bullet x\ H^+$;

B) The formation of sol hydrolysis reaction.

Hydrolysis is usually obtained from sol of metal hydroxides $Fe(OH)_3$, $Al(OH)_3$, etc. For example, the sol $Fe(OH)_3$ is prepared by adding boiling water solution $FeCl_3$:

$$FeCl_3 + H_2O \rightarrow Fe(OH)_3 + 3HCl$$

In water, salt $FeCl_3$ is hydrolyzed:

$$FeCl_3 + H_2O \rightarrow FeOCl + 2HCl$$

The resulting basic salt FeOCl dissociates:

$$FeOCl \leftrightarrow FeO^+ + Cl^-$$

Ion FeO is the stabilizer.

The structure of the micelles can be written as follows:

$$\mathbf{[m\ Fe(OH)_3\ n\ FeO\ (n\text{-}x)\ Cl^-]^{x-}\ x\ Cl^-}$$

sol of Prussian blue:

$$4\ FeCl_3 + 3K_4[Fe(CN)_6] \rightarrow \underset{\text{excess}}{} Fe_4[Fe(CN)_6]_3 + 12KCl$$

The structure of the micelles: $[\ m\ Fe_4[Fe(CN)_6]_3 \bullet n\ [Fe(CN)_6]^{4n-} \bullet (n\text{-}x)\ K^+\ ]^{4\ x\ -} \bullet 4x\ K^+$

C) The formation of sols in the dissociation of surface ionogenic groups.

For example, obtaining salt H_2SiO_3, whose molecules dissociate:

$$H_2SiO_3 \leftrightarrow H^+ + HSiO_3^-$$

The structure of the micelles can be written as follows:

$$\mathbf{[m\ H_2SiO_3\ n\ HSiO_3^-\ (n\text{-}x)\ H^+]^{x-}\ x\ H^+}$$

sol of SiO_2, on the surface of the particles of which are of H_2SiO_3 , which dissociate and allow ionic stabilizer $HSiO_3^-$:

$$H_2\ SiO_3 \rightarrow H^+ + HSiO_3^-$$

Micelle structure: $[m\ SiO_2 \bullet n\ HSiO_3^{n-} \bullet (n\text{-}x)\ H^+\ ]^{x\ -} \bullet x\ H^+$.

D) Preparation of sols by oxidation reactions.

For example, obtaining sol sulphur S.

$$H_2S + O_2 \rightarrow 2S + 2H_2O$$

Sol stabilizers are polythionic acids, which are formed during the oxidation of sulphur, for example, pentanoic acid $H_2S_5O_6$.

The structure of the micelles can be written as follows:

$$\mathbf{[mS\ n\ S_5O_6^{2-}\ 2\ (n\text{-}x)\ H^+]^{2x-}\ 2x\ H^+}$$

Sulfur sol obtained by oxidation reaction of :

$$2H_2S + O_2 \rightarrow 2S + H_2O.$$

Micelle structure: $[m\ S \bullet n\ HS^- \bullet (n\text{-}x)\ H^+\ ]^{x\ -} \bullet x\ H^+$.

E) Preparation of sols by the reduction reaction.

For example, obtaining sol sulphur.

$$KAuO_2 + 3HCHO + K_2CO_3 \rightarrow 2Au + 3HCOOK + KHCO_3 + H_2O.$$

Stabilizer is a potassium aurate $KAuO_2$.

The structure of the micelles can be written as follows:

$$\mathbf{[\ m\ Au\ \ nAuO_2^-\ \ (n\text{-}x)\ K^+\ ]^{x-}\ \ x\ K^+.}$$

As was said above — the structure of the micelles explains the theory of the electrical double layer. It occurs on the border between the granule and the diffuse layer or adsorption and diffuse layer. It is called electrokinetic or ζ-potential (Zeta-potential). ζ-potential, and simply charge granules, contributes to the mutual repulsion of the granules, which explains the stability of freshly prepared solutions of the sols. Value ζ-potential depends on the concentration of electrolytes in solution. At high electrolyte concentration of the diffuse layer decreases as a result of transition ions in the adsorption layer, and ζ-potential decreases.

Properties of colloidal systems

A. Molecular-kinetic properties of sols.

1) Brownian motion in solution sols due to thermal motion of the particles under the influence of thermal motion of the molecules of a dispersion medium. Since the size of colloidal particles is greater than the molecules and ions, the velocity of the Brownian motion in solution sols less than true solutions.

2) Diffusion in solutions sols also slowed down as a result of larger size particles.

3) The osmotic pressure due to the presence of colloidal sols and particles is calculated by Vant Hoff :

$$P_{osm.} = CRT$$

But as the concentration of solutions sols small (at high concentrations is coagulation), the value of the osmotic pressure is very low compared to the true solutions (Table 17.5)

Comparison table quantities P_{osm}. disperse systems

Solution	$P_{osm.}$
1% - solution of As_2S_3	0,0034 кPa
1% - solution of Ag	0, 045 кPa
1% - sucrose	72,5 кPa
0,9% – solution of NaCl	777,7 кPa

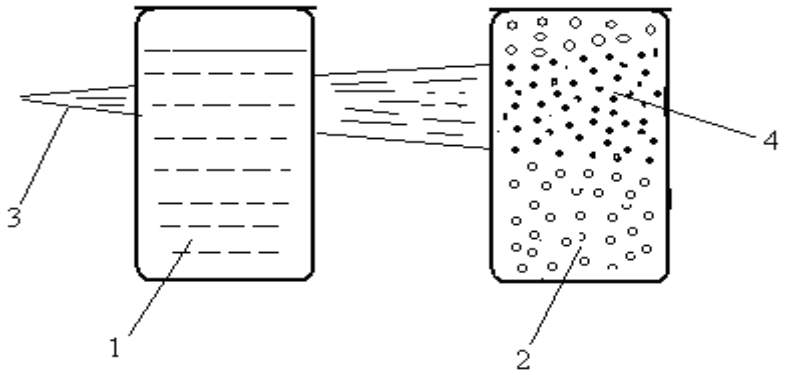
Table 17.5

B. Optical properties of sols.

1) The color of the colloidal solution is due to selective absorption of light. The colloidal solutions are painted in different colors, because the color of the colloidal solution depends on the particle size. So, As_2S_3 sol has a bright yellow color, sol Sb_2O_3 – orange, sol $Fe(OH)_3$ – red-brown. The colloidal gold solution changes its color depending on the degree of dispersion ranging from blue (larger particle) to bright red (highly dispersed sols). The color of precious stones and gems associated with their content of highly dispersed metals.

2) Opalescence is observed in the scattering of light by colloidal particles, which is manifested in the change of color. So Sol sulfur in the water shimmers of blue or yellow color.

3) The light scattering or cone Tyndall appears when the side light of a colloidal solution (Picture 17.6)

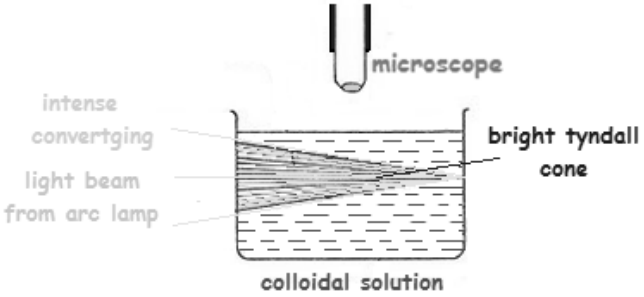


Purification of colloidal solutions:

Properties of colloids:

a) Optical properties

Size dependent change of colour in Au sol



Schematic drawing of ultra microscope

Picture 17.6. Formation of Tyndall cone

1 — solution of NaCl;
2 — a colloidal solution;
3 — light beam;
4 — Tyndall cone.

This phenomenon is explained by the fact that the particle size is less than the wavelength of the visible spectrum and thus light scattering occurs. Light beam passes through the NaCl solution without changes in a colloidal solution is dispersed (produced light path).

The blue color of the sky, sea water, tobacco smoke is also explained by light scattering due to the presence of fine impurities. Tyndall cone can be seen in the room if the light beam passes through the air, which has dust particles.

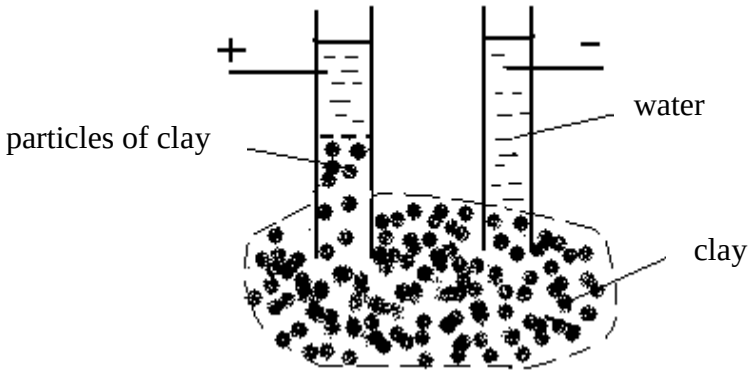
Scattering phenomenon underlies optical method: nephelometry, ultramicroscopy electron microscopy.

B. The electrokinetic phenomena.

In colloidal systems at the interface granule - diffuse layer - occurs a charge. Therefore, colloidal particles can move in an electric field. This explains the electrokinetic phenomena in sols.

1) Electrophoresis ia a directed motion of dispersed particles relative to the fixed dispersion medium in an electric field.

This phenomenon was first observed by professor at Moscow University F. Reiss. Two glass tubes filled with water, placed in a piece of wet clay. In tubes injected electrodes and electric current is passed. As a result, the clay particles are moved toward the anode (+), which was visible haze in the anode space (Picture 17.7).



Picture 17.7 Scheme of electrophoresis

Electrophoresis speed can be calculated by the Helmholtz – Smoluchowski equation

$$U = \frac{\varepsilon \bullet \xi \bullet E}{\eta}$$

Where:

U — speed electrophoresis;

ε — permittivity of the medium;

ζ — zeta potential;

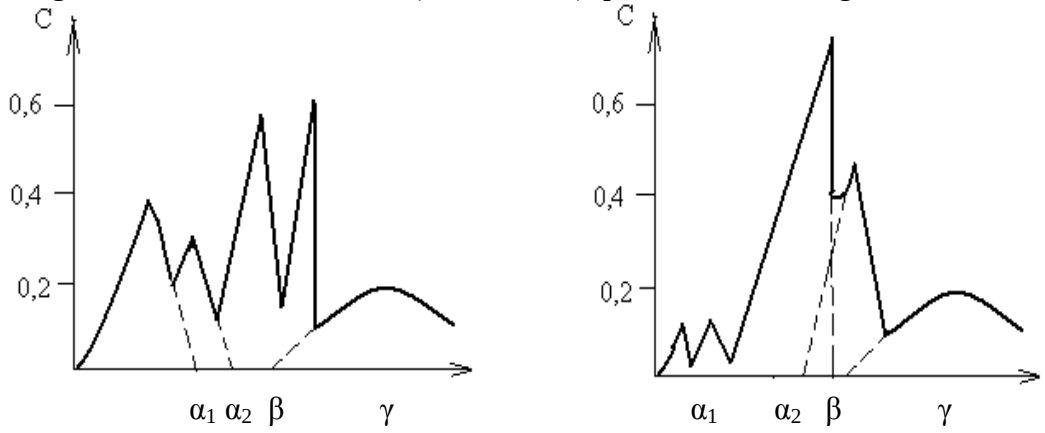
E — voltage;

η — viscosity of the medium.

Electrophoresis is widely used in various sectors of the economy: for discharge from pure kaolin clay slurry coating layer of rubber products for the capture of waste production as well as in medicine.

Electrophoresis in medicine

Electrophoresis is used in medicine for research purposes: separation of proteins, amino acids, enzymes, antibiotics, blood cell counts, bacterial cells; diagnostic purposes: compare electropherograms in health and disease (Picture 17.8), purification of drugs.



normal serum serum with lipid nephrosis

Picture 17.8. Electrophoregram serum

Electrophoresis and used for therapeutic purposes, ie administered drugs through the skin in various pathologies: rheumatism, atherosclerosis, burns and other diseases. Introduction of medicinal substances by electrophoresis has several advantages over other methods:

a) local action;

b) longer duration of action, as the drug depot is created substance;

c) a small amount of the substance used;

d) a combination of electric current and the drug.

2) Electroosmosis is moving the dispersion medium in an electric field (the water moves to the negative cathode).

Electroosmosis is used for drying the porous material, the concentration of colloidal solutions, drying of powders of drugs.

3) Occurs when the current potential within a dispersion medium of the dispersed phase relative to the fixed.

Potential flow plays a role in the process of hearing and determines the occurrence of action potentials, which are recorded on the electrocardiogram.

4) Potential sedimentation settling occurs when particles of the dispersed phase relative to the fixed dispersion medium. Potential sedimentation, settling occurs when the blood formed elements such as erythrocytes, leukocytes, platelets, which have a negative charge.

Stability and coagulation of colloidal systems

Freshly prepared colloidal solutions are relatively stable due to the same charges granules. By the charged particles are attracted dipoles of water, forming a monolayer, which does not allow particles to connect, i.e. they exhibit the disjoining pressure.

Disjoining pressure theory developed by B.V. Derjaguin

There are two types of stability of colloidal systems (N.P.Peskov) kinetic and aggregative.

Kinetic stability is the resistance deposition. Its contributes to the thermal motion of particles, i.e. diffusion and Brownian motion.

Aggregate stability is the system's ability to maintain a degree of dispersion, i.e. resistance to consolidation of the dispersed phase.

However, the action on the colloidal system to various factors, it loses its resilience, i.e. coagulation begins.

Coagulation is the coalescence of the dispersed phase.

External signs of coagulation

a) Change of color;

b) The turbidity of the solution;

c) Precipitation.

Factors causing coagulation

Coagulation occurs :

- By mechanical action;
- Changes in temperature;
- Increase in the concentration of the sol;
- The action of electrolytes.

Under the action of electrolytes causes coagulation of the coagulating ion.

Coagulating called ion which has a charge opposite to the charge of pellets.

Coagulating action depends on the charge of the coagulating ion, as a rule says Schulze- Hardy:

The higher the charge of the coagulating ions, the stronger his coagulation action and faster begins coagulation.

By the ability to coagulation action depending on the charge ions are located in lyotropic series:

$$Al^{3+} > Ca^{2+} > K^{+}$$

With the same charge coagulating ions coagulation action depends on the degree of solvation. The more solvation, the less coagulating power:

$$Rb^{+} > K^{+} > Na^{+} > Li^{+}$$

There are theories to explain the coagulation:

a) adsorption (G.Freyndlih);

b) electrostatic (compression of the diffuse layer);

c) ion exchange (Kargin);

d) physical theory (B. Derjaguin, Landau).

The mechanism of action of coagulating electrolytes following:

a) compression of the diffusion layer;

b) selective adsorption of counterions;

c) a decrease in ζ- potential;

d) reduction of the disjoining pressure;

e) an ion-exchange adsorption.

All of these factors are due to the fact that the charge reduces the ion coagulating granules and ζ-potential.

When adding a small concentration of the electrolyte coagulation may not occur. Only when a certain concentration of coagulation begins.

The lowest concentration of the electrolyte, which causes coagulation, called the threshold of coagulation.

Coagulation threshold also depends on the concentration of the sol. Determine the coagulation threshold for this sol and this electrolyte as follows: in the tubes prepared electrolyte solutions of different concentrations in each tube give a certain amount of sol and observed turbidity of the solution. The lowest concentration of electrolyte at which the coagulation, is the threshold.

Mutual coagulation

Coagulation of the sols may be observed when mixing two sols with opposite charges granules. Thus there is a mutual neutralization of granules, they lose their charge and are connected into larger aggregates that precipitate.

The mutual coagulation occurs in nature in mixing seawater and river, resulting in a sludge.

When the water treatment utilities to water add salt $AlCl_3$ and $FeCl_3$, which are formed during hydrolysis sols $Al(OH)_3$ or $Fe(OH)_3$.

They are charged positively and the particles suspended in the water are in the negative, resulting in mutual coagulation of large particles are formed, which precipitate.

The mutual coagulation may occur during mixing in the syringe two or more drug substances, which leads to the destruction of drug effect.

Coagulation in biological systems

Biological fluids such as blood, lymph, cerebrospinal fluid, etc. are dispersed systems.

1) As already mentioned erythrocytes settle out under their own gravity at a certain rate (CR).

But in the pathology in the blood appears proteins γ-globulins and others who have charge. They are adsorbed on erythrocytes, the particles become heavier and the CR increases.

2) Blood clotting is also the coagulation process.

3) An isotonic solution of NaCl isotonic solution can not be replaced, for example, $CaCl_2$, as a calcium ion and a doubly charged coagulation action is stronger.

4) Cells from malignant tumors are repelled from each other, hence, their ability to coagulate small, they are very mobile and transported to other organs to form metastases.

Colloidal protection

To stabilize the colloidal sols used protection. It consists in adding to the sol solution macromolecular compound (MMC or HMC) gelatine, polysaccharide and other gelatine molecules adsorbed on the surface of colloidal particles and thereby inform their granules sustainability factors is the charge and hydration shell.

Quantitatively, the protective effect is characterized by a protective number.

Protective mg number is the number of dry MMC, which protects the sol from 10 ml of coagulation by the action of 1 ml of a 10 % solution of NaCl.

Depending on the nature of the sol distinguish “gold”, “silver”, “ iron” protective number etc.

The biological significance of colloidal protection

Colloidal protection is important for the stabilization of dispersed systems.

1) Colloidal protection is used in the manufacture of drugs. For example, such antibacterial agents as Silver sol (Collargol – 70%) and Silver oxide (8.7% – Protargol) reserved gelatine and dextrin. Otherwise such highly concentrated sols would be unstable and precipitated.

2) The human body proteins adsorbed on cholesterol, prevent its deposition in the vessel wall.

With age, when the protective action of proteins decreases the cholesterol is deposited on the walls of blood vessels, which is one of the causes of atherosclerosis.

3) Blood carbonates and phosphates of calcium is also protected proteins and is not deposited on the walls of blood vessels, do not form stones in the kidneys. With age and a decrease in the protective effect of proteins these salts are deposited in the blood vessels (calcification) in the joints (gout).

4) Heparin increases the ζ- potential and thus prevents blood coagulation proteins.

5) Drops of blood fats and proteins are protected in a suspended state.

Coarse called heterogeneous systems with a particle size of the dispersed phase $10^{-4} – 10^{-6}$ m.

Depending on the state of aggregation of the dispersed phase and the dispersion medium are classified into types (Table 17.6).

Types of coarse systems

System	Name	Examples
S/L	Suspension	Particle of clay in water,
L/L	Emulsions	Benzene in water; milk, cream, butter; creams, ointments; drops of fat in blood
G/S	Solid foam, gas emultion	Pumice, silica gel, activated charcoal
S/G	Aerosol	Dust, smoke, smog; powders; coal, Silicate, asbestos dust; tobacco smoke
L/G	Aerosol	Fog, clouds; sputtered Medicines

Table 17.6

Consider the coarse systems that are relevant to biology in general and medicine in particular.

Aerosols

The aerosol this is a coarse system with gaseous dispersion medium and a solid or liquid dispersed phase with a particle size $10^{-4} – 10^{-6}$ m. Aerosols are prepared by spraying liquid or solid substances in the gas phase. For example, the interaction of ammonia with hydrogen chloride formed the smoke of ammonium chloride

$$NH_3 \text{ (gas)} + HCl \text{ (gas)} \rightarrow NH_4Cl \text{ (hard)}$$

Sulfuric acid “smoke” in the air in the reaction:

$$SO_3 \text{ (gas)} + H_2O \text{ (gas)} \rightarrow H_2SO_4 \text{ (liquid)}$$

The stability of the aerosol due to the presence of charge (due to ion adsorption or dissociation of ionic groups) and adsorption of the gas on the particles of the dispersed phase.

However, they are thermodynamically stable enough because of the large particle size.

In aerosol Brownian motion is faster than, for example, in colloidal solutions; they scatter and reflect light, so the fog and smoke white.

Aerosols used in the military (smoke screens); agriculture (spraying of herbicides, insecticides); technique for coating objects with paint and varnish; in household aerosols used in perfumery and deodorants etc.

The biological significance of aerosols

1) In medicine use of medicinal substance in the form of aerosols for the treatment of upper respiratory tract (inhalation). When this drug penetrates deep into tissues and high dispersion provides fast absorption.

2) Toxic effects of aerosols:

- Coal dust in mines anthracosis causes lung disease;

- Inhalation of silica dust, cement – silicosis;

- Smog is the presence of the liquid and solid phases (emissions from factory pipe) at the same time negatively affects the upper respiratory organs.

3) Pathogenic aerosols containing bacteria and viruses cause diseases such as influenza, tuberculous, meningitis, etc. Sneezing allocated 100 thousand microbes.

Powders

The powder is concentrated aerosols with the solid phase.

The powders used in agriculture as fertilizer; in industry - pulverized fuel, cement, flour.

In medicine is used powders of drugs.

Suspensions

Suspension is a type of coarse systems with dispersed solid phase and a liquid dispersion medium with a particle size $10^{-4} – 10^{-6}$ m

I.e. suspension is hydrophobic system.

Suspension get by dispersion or condensation method.

Suspensions are stabilized electrolytes, which report the charge to the particles, and the addition of the HMC, which surround the particles solvate shell.

Large particle size of the dispersed phase causes suspensions properties:

The large particle size of the dispersed phase determines the properties of the suspensions:

- weak Brownian motion;
- kinetic (sedimentation) resistance is low, after a short while the dispersed phase precipitates;
- aggregate stability is also low, because the factors of sustainability quickly destroyed;
- scatter light, so muddy.

The role of suspensions

In the industry used lime slurry, clay, dyes, varnishes. In agriculture, in the form of suspensions used insecticides and fungicides.

In medicine in the form of suspensions used streptocid (antiseptic and anti-inflammatory drug), camphor (a cardiac), menthol (irritant), sulfur (dermatology), Almagel (suspension of $Al(OH)_3$ as antacids tool), bicillin (antibiotic) and other.

Pastes

When filtering suspensions of dispersed phase concentrates on the filter and produces a highly concentrated suspension, which is called paste, and contains almost no liquid dispersion medium.

In medicine apply the paste of drugs in dermatology: zinc (drying effect), Sulsenic, Ichthyol (anti-inflammatory), and others; in hygiene - toothpaste.

Emulsions

The emulsion is coarsely dispersed systems consisting of two immiscible liquids, with a particle size of the dispersed phase 10^{-4} - 10^{-6} m.

I.e., the emulsion is a hydrophobic system. The dispersion medium is often water.

There are two types of emulsions:

b) emulsions, in which the dispersion medium is oil, and dispersed

the water phase. Indicated such a system in w / o for Example, butter.

The emulsion is produced by mixing and shaking two liquids.

From the properties of emulsions it is necessary to note the presence of the interface, the low resistance and the need for a stabilizer.

a) an emulsion in which water is the dispersion medium and dispersed phase insoluble therein a liquid which is called oil. Such a system is denoted o / w. For example, the sunflower oil in water.

b) an emulsion in which the oil is the dispersion medium and dispersed water phase. Such a system is denoted w / o, for example, butter. Emulsions prepared by mixing and shaking of the two liquids.

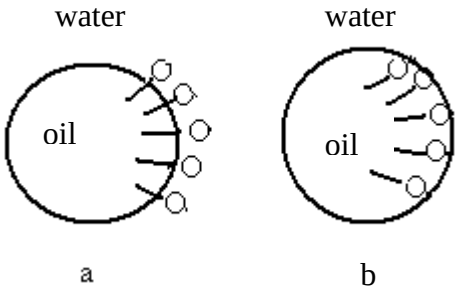
From the properties of the emulsions must note the presence of the interface, and the need for low resistance stabilizer.

Emulsion stability factor is the charge and particle size. The charge caused by adsorption or ion dissociation groups on the particle surface. The smaller the particles, the more stable emulsion. However, due to the hydrophobic nature of the system is unstable and the merging of the disperse phase particles is coalescence and then separation of the system into two layers.

To increase the stability of emulsions used emulsifiers. These surfactants (soap) or HMC (proteins) are adsorbed onto particles of the dispersed phase.

By their chemical nature emulsifiers are divided into hydrophilic and hydrophobic:

a) Hydrophilic this is are soaps, alkali, chalk, gelatine, starch. They stabilize emulsion o / w adsorbed at the interface. Emulsifier molecules are arranged so that their hydrophilic part directed to the water and hydrophobic - in oil (Picture 17.9 -a).



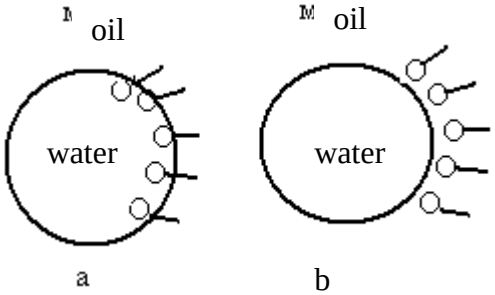
Picture 17.9 Emulsions m / v

a — hydrophilic emulsifier; b — hydrophobic emulsifier.

For example, in milk emulsifier emulsion of fat protein is casein and in latex (laticifers) is protein substances.

Hydrophobic emulsifier (Fig. 17.9 - b) does not stabilize this emulsion.

b) hydrophobic emulsifiers is carbon, sulphides and iodides of metals, rubber, cholesterol, soap polyvalent metals. They stabilize the emulsion type w / o. Hydrophobic emulsifiers are also located on the phase boundary, the hydrophilic part toward the water, and the hydrophobic - to-oil Picture 20.9 -a)



Picture 17.9. Emulsions o / w

a — hydrophobic emulsifier; b — hydrophilic emulsifier.

Thus, the mechanism of action of emulsifiers as follows:

a) adsorbed on the particles of the dispersed phase and charge ;

b) create a wrapper that prevents coalescence.

The biological significance of emulsions

Emulsions are widely used in various industries: construction, textile, chemical, food industries, etc.

The emulsions are milk, cream, mayonnaise, ice cream, latex and other.

In the human body emulsions are particles of fat in the blood, which stabilize proteins, and in the gut fat stabilized bile and fatty acids. Moreover, under the action of bile acids significantly reduced the surface tension of the droplets of fat, resulting is spontaneous fragmentation them, i.e. the process of emulsification.

Erythrocytes can also be viewed as an emulsion which is stabilized as a result of adsorption of proteins and ions.

In pharmacy apply emulsion of drugs. Moreover, the emulsion type o / w use, inside and for injection of an emulsion of oil of almonds, ground nuts, pumpkin with the addition of drugs, and type w / o — for external use: syntomycin as antibacterial action.

Semicolloids, detergents

Semicolloids call system, in which the particles of the dispersed phase can be formed of molecules and ions, as well as in the form of colloids. In such systems there is a dynamic equilibrium:

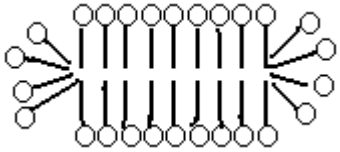
molecular solution ↔ colloidal system

In solutions of Polukarov is the process of micellization. It is that the soap solution with a concentration of 1% and above molecules form micelles, the surface of which are ionic groups, which makes the soap dissolves in the water

Semicolloids include soaps, detergents (detergents), tannins (tanning agent), dyes, alkaloids.

Semicolloids usually are amphiphilic substances, i.e. contain polar groups (carboxy, amino) and nonpolar, i.e. hydrophobic (hydrocarbyl radical).

In solutions of semicolloids going process of micellization. It consists in that the soap solution with a concentration of 1 % or more molecules combined in micelles which are arranged on the surface ionic groups, where making soap is dissolved in water (Picture 17.10).



Picture 17.10 Micelle formation in solution of soap.

Semicolloids are used as emulsifiers, stabilizers when getting vitamins, antibiotics and other biologically active substances.

5. The main questions of the seminar:

5.1. Kinetic and aggregative stability of sols, the stability factors.
5.2. Coagulation and the factors influenced on the coagulation.
5.3. Coagulation mechanism. Schulz-Hardy rule.
5.4. Coagulation ability of electrolytes. Reciprocal coagulation.
5.5. Coagulation concentration.
5.6. Colloidal stability.
5.7. Coagulation in the water purification process.

6.The questions for individual learning:

6.1. Aerosols: the preparation methods, properties, application in medicine. Poisonous action.
6.2. Suspensions: the preparation methods and properties.
6.3. Emulsion: the preparation methods and properties. Types. Emulsifying agent. Application in clinical practices. Biological role of emulsification.

7. The examples of the task:

7.1. Sol coagulation by electrolytes.

Sol can be formed after adsorbing of oxalic acid by kidneys from gastrointestinal tract

$CaCl_{2excess} + H_2C_2O_4 \rightarrow$

What is the charge of the particle?
Which kind of the following ions K^+, Mg^{2+}, NO_3^-, PO_4^{3-}, Al^{3+}exhibits the coagulation action for the particles of the given sol?
The answer:
$CaCI_{2excess} + H_2C_2O_4 \rightarrow CaC_2O_4 + 2HCI$
Sol of calcium oxalate is formed. The micelle structure is
$\{mCaC_2O_4 \cdot nCa^{2+} \cdot 2(n-x)Cl^-\}^{2X+} \cdot 2xCl^-$
When the particle has a positive charge the coagulating ions are NO_3^-, PO_4^{3-} according to Schulze-Hardy's rule.

7.2. Determination of coagulation concentration.
The coagulation concentration of $Fe(OH)_3$ sol for KI and $K_2Cr_2O_7$ electrolytes are 10.0 and 0.095 mmol/l respectively. By how many times is the coagulation ability of $K_2Cr_2O_7$ higher than KI?
The answer:
The coagulation ability of the electrolyte is the reverse value to the coagulation concentration.

$$P = \frac{1}{C}$$

$$P_{KI} = \frac{1}{10} = 0.1$$

$$P_{K_2Cr_2O_7} = \frac{1}{0.195} = 5.1$$

$$P_{KI} : P_{K_2Cr_2O_7} = 0.1 : 5.1 = 1 : 51$$

For $Fe(OH)_3$ sol the coagulation ability of $K_2Cr_2O_7$is higher in 51 times than of KI.

8 Homework (must be done performed in the laboratory notebook):
8.1. The coagulation concentrations of a sol by electrolytes are C ($NaNO_3$) = 250.0; C ($Mg(NO_3)_2$) = 20; C ($Fe(NO_3)_3$) = 0.5 (m eq/l). What are the coagulating ions? What is the charge of the sol particles?

***9. The control test*:**
for instance:
Write the structure of AgI micelle if excess KI was added to $AgNO_3$ solution.
Select the ions (Na^+, Li^+, Cl^-, SO_4^{2-}, Cr^{3+}, Pb^{2+}, CH_3COO^-, PO_4^{3-}, OH^-, Cs^+, Sr^{2+}, Br^-, Mg^{2+}) that are able to cause the coagulation of the colloid particles described in question 1.

10. The algorithm of the experiments:
10.1. Conformation of Schulze-Hardy rule.
10.2. Dependence of the coagulation concentration on the charge of coagulating ion.
10.3. Synthesis of emulsion.

11. The detailed explanation of the following experiment:
11.1. Conformation of Schulze-Hardy rule.

Three test-tubes are filled:		
1 test-tube	2 test-tube	3 test-tube
5ml $Fe(OH)_3$ sol	5ml $Fe(OH)_3$ sol	5ml $Fe(OH)_3$ sol
1 ml of KCl solution	1 ml of K_2SO_4solution	1 ml of $K_3[Fe(CN)_6]$ solution

The solution are mixed and the coagulation consecution is observed. Write the micelle structure of $Fe(OH)_3$ sol and arrange the coagulating ions in liotropic row.

11.2. Dependence of the coagulation concentration on the charge of coagulating ion.

Prepare the ammonium sulfate solutions of different concentrations:
In a first test-tube add 10 ml of ammonium sulphate (C_N=1 mol/l).
In a second test-tube add 9 ml of water and 1ml of ammonium sulphate from the first test tube.
In a third test-tube add 9 ml of water and 1ml of ammonium sulphate from the second test tube.
Analogous preparation of the forth, fifth and sixth test-tube.
Then add 2 ml of iron (III) hydroxide sol to every test-tube. Fill the table given below by marking "+" and "-".
Analogous perform the experiments with ammonium chloride. Make the conclusions.

Electrolytes	***Coagulating ion***	***Concentration of the electrolyte in the test-tube, mol/l***							***Coagulation concentration***
		1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	
$(NH_4)_2SO_4$	SO_4^{2-}								
NH_4C1	Cl^-								

11.3. Synthesis of emulsion.

The test-tube is filled by 5 ml of water and 5 drops of vegetable oil. Mix intensively. For emulsion stabilization add 5 drops of NaOH. Again shake the test-tube. Note the observation and make a conclusions.

12. Control test:

"Preparation, purification and properties of colloidal solutions"

Sample 1.

1. Write the micelle structure of the product formed after reaction of silver nitrate and calcium bromide solutions at the condition:
   a) when silver nitrate is in excess;
   b) when calcium bromide is in excess.
2. Write the classification of the dispersive systems by particle size. Write the examples.

Sample 2.

1. Write the micelle structure of the product formed after after reaction of potassium chromate and lead (II) nitrate {$Pb(NO_3)_2$}solutions at the condition:
   a) when potassium chromate is in excess;
   b) when lead (II) nitrate is in excess.
2. Write the classification of the dispersive systems by aggregative states of dispersed and dispersing phases. Write the examples.

"Coagulation of colloidal solutions. Colloidal stability."

Sample 1.

1. Write the structure of AgI micelle if the excess of KI was added to $AgNO_3$ solution.
2. Select the ions (Na^+, Li^+, Cl^-, SO_4^{2-}, Cr^{3+}, Pb^{2+}, CH_3COO^-, PO_4^{3-}, OH^-, Cs^+, Sr^{2+}, Br^-, Mg^{2+}) that are able to cause the coagulation of the colloidal particles described in question 1.
3. Write the dependence of the coagulation ability on the charge of the electrolyte cations.

4. Write the dependence of the coagulation concentration on the charge of the electrolyte anions.

Sample 2.

1. Write the structure of $BaSO_4$ micelle if the excess of $BaCl_2$ was added to Na_2SO_4 solution. Write the chemical equation.
2. Select the ions (Na^+, Li^+, Cl^-, SO_4^{2-}, Cr^{3+}, Pb^{2+}, CH_3COO^-, PO_4^{3-}, OH^-, Cs^+, Sr^{2+}, Br^-, Mg^{2+}) that are able to cause the coagulation of the colloidal particles described in question 1.
3. Write the dependence of the coagulation ability on the charge of the electrolyte anions.
4. Write the dependence of the coagulation concentration on the charge of the electrolyte anions.

TOPIC 18: Properties of biopolymers. Isoelectric point of proteins.

1. ***Actuality of the topic***: Biopolymers (proteins, polysaccharides, nucleic acids) are included in the structure of the cells performing the function of the accumulation of nutrients and energy. Nucleic acids together with proteins are the source of hereditary information, glycolproteins occasion the blood group.

2. ***General aim:*** is to estimate the polymer's property based on the chemical nature and characteristics of macromolecules.

3. Actual aims and abilities:

- to classify the polymers by type of monomers and spatial structure;
- to forecast the swelling process and the polymer's solubility on the base of thermodynamic laws.

4. Literature:

4.1. Lecture materials;

Macromolecular compounds called with a molecular weight of more than 10^4 amu

In humans, many HMC perform various biological functions:

- are catalysts of biochemical reactions - proteins;
- save up and carry genetic information - DNA;
- are reserved nutrients - glycogen;
- a protective function - antigens;
- perform structural and support functions - collagen, keratin. HMC or polymers are classified according to different criteria:

1) Origin:

a) natural are proteins, nucleic acids, polysaccharides, natural rubber;

b) artificial is collodion, cellophane, rayon, acetate silk (it cellulose derivatives);

c) synthetic is caprone, nylon, polyester, polyacrylamide. In medicine use many synthetic HMC and called biopolymers, the main requirements to which is hemocompatibility and thromboresistance;

2) In the configuration of the molecule:

a) fibrillar is muscle myosin, keratin hair, nucleic acid, cellulose;

b) globular are albumins, globulins, glycogen, starch;

3) Circuit Configuration:

a) linear is gelatin, cellulose, rubber;

b) branched is glycogen, amylopectin, natural rubber;

c) the net are proteins, phenol-formaldehyde resins;
4) Solubility in water:
a) insoluble is hair keratin;
b) soluble is albumin, globulins;
5) For medical purpose:
a) biosoluble is catgut;
b) biocompatible is blood substitute.
Disperse systems have many common properties and differences.
Table 18.1 presents comparative characteristics of some of the properties of dispersed systems.

The characteristic properties of HMC solutions, colloid and true solutions

HMC solutions	Colloidal solutions	True solutions
Get spontaneous dissolution	Obtained dispersion and condensation methods	Get spontaneous dissolution
Particle size $10^{-8} – 10^{-10}$ m	Particle size $10^{-8} – 10^{-10}$ m	Particle size less 10^{-10} m
The dispersed phase is soluble in the dispersion medium	The dispersed phase is insoluble in the dispersion medium	Molecules and ions soluble
There is a hydrated shell	There is no a hydrated shell	There is a hydrated shell
There is no surface of separation phases	The surface of separation of the phases	There is no surface of separation phases
Homogeneous	Heterogeneous	Homogeneous
Thermodynamically stable	Thermodynamically unstable	Thermodynamically stable
The resistance caused by the charge and hydrated shell	The resistance caused by the charge	Resistance due to charge intermolecular repulsion forces and hydrate shell
The concentration of the solution can be up to 15%	The concentration of the solution can be up to 1-2%	The concentration of the solution can be up to 100%
Do not pass through a semipermeable membrane	Do not pass through a semipermeable membrane	Pass through a semipermeable membrane
Brownian motion and diffusion is slow	Brownian motion and diffusion is slow	Brownian motion and diffusion is high
Osmotic pressure is higher than the colloids	The osmotic pressure is low	The osmotic pressure is high
Dry matter may swell	Dry matter does not swell	Dry matter does not swell
High viscosity	The low viscosity	Not viscous
Form jellies	Form gels	Precipitate
Give a fuzzy Tyndall cone	Give the Tyndall cone	Optically empty

Table 18.1

The solutions of HMC receive spontaneous dissolution of dry polymer in the respective solvents.
The stability of freshly prepared solutions of the HMC due to these factors:
a) the charge of the particles of the same name;
b) hydrate shell particles.
HMC for such characteristic properties: swelling of dry polymers gelation (gelation), salting, coacervation, thixotropy, syneresis.

Isoelectric state of proteins

Properties of HMC is convenient to consider the example of proteins, since they are more parametered which characterize the properties of HMC.

One of the most important properties of proteins is their isoelectric state.

In the molecule of the protein has a carboxy group - COOH, which exhibit acid properties, and the amino group $–NH_2$, which exhibits the properties of the basic amine. I.e. amphoteric protein molecule. Conditional formula of protein molecule can be written as:

$$\begin{array}{l} Pt - COOH \\ | \\ NH_2 \end{array}$$

When dissolved in water, these functional groups interact with each other and form a particle with two charges:

$$\begin{array}{l} Pt - COOH \\ | \\ NH_2 \end{array} \rightarrow \begin{array}{l} Pt - COO^- \\ | \\ {}^+NH_3 \end{array}$$

Such a particle is called amphion.

If amphion is in an acidic environment, then it is reacted anionic group:

$$\begin{array}{l} Pt - COO^- \\ | \\ {}^+NH_3 \end{array} + H^+ \rightarrow \begin{array}{l} Pt - COOH \\ | \\ {}^+NH_3 \end{array}$$

The result is a particle with a positive charge.

If amphion is in an alkaline medium, the interaction of its cationic group :

$$\begin{array}{l} Pt - COO^- \\ | \\ {}^+NH_3 \end{array} + OH^- \rightarrow \begin{array}{l} Pt - COO^- \\ | \\ NH_2 \end{array} + H_2O$$

The result is a particle with a negative charge.

If the reaction medium is gradually changing from acidic to alkaline, then at a certain pH value of the protein molecule will have an equal number of positive and negative charges and the net charge of the molecule is equal to 0.

Such a state of the protein in which it is in the form of amphion is called isoelectric state (IES).

The value of pH at which the protein is located in the isoelectric state, called the isoelectric point (IEP).

Proteins have different isoelectric point value, which depends on the ratio of functional groups (Table 18.2).

IEP OF PROTEIN

Pepsin gastric juice	2,00
Milk casein	4,60
Serum albumin	4,64
Ovalbumin	4,71
Blood globulins	4,80-6,40
Muscle myosin	5,00
Fibrinogen blood	5,40
Hemoglobin	6,60-6,87
Histone cell nuclei	8,50
Chymotrypsin	8,60
Cytochrome C	10,60

Table 18.2

Thus, the charge in the acidic environment of biopolymers it is positive, in the alkaline environment it is negative. Blood proteins most have a negative charge as blood pH of 7.36 , i.e. lies in a weakly alkaline medium.

Methods for determination of the IEP

1) Electrophoresis of protein: exploring the electrophoretic mobility of the protein in buffer solutions with different pH. In a buffer solution with a pH equal to IEP protein, the latter will not move.

2) By degree of gelation (gelling) in the tubes containing buffer solutions with different pH concentrated protein solution is poured. In vitro at pH close to the pI of the protein gelation is faster.

3) According to the degree of coagulation in test tubes with buffer solutions with different pH of the protein solution and poured alcohol as a clotting factor. In vitro at pH close to the pI of the protein faster observed turbidity.

4) The magnitude of swelling: poured into tubes and poured dry protein buffer systems with different pH. In vitro at pH close to the pI of the protein swelling is minimal.

Swelling

The Initial stage of the dissolution process is swelling of HMC.

Swelling is the increase of the volume and mass of the polymer in the result of selective absorption of low molecular weight liquid molecules HMC.

Swelling mechanism is as follows. The swelling proceeds in two stages:

a) I stage - solvation - accompanied by the absorption of a small amount of water and heat. This stage is characterized by the thermodynamical parameters: $\Delta H < 0$, $\Delta S \leq 0$, $\Delta G < 0$. Thus, when 1 g of the swollen gelatin is allocated 5.7 cal and 1 g of starch - 6.6 cal.

b) II stage - accompanied by the absorption of a large amount of water and an increase in volume of the system. This stage is characterized by thermodynamic parameters: $\Delta H = 0$, $\Delta S > 0$, $\Delta G < 0$.

Depending on the nature of the polymer and the swelling solvent can be:

a) limited when the swelling does not go into dissolution. This forms jelly. For example, gelatin in water at room temperature; seed germination.

In humans, limited swelling is observed in the formation of edema in the result of a mosquito bite or sting, as well as in inflammatory processes.

b) unlimited, when the swelling ends dissolution. In this $\Delta S > 0$, $\Delta G < 0$. For example, gelatin in hot water, the nitrocellulose in acetone, benzene rubber.

When swelling develops swelling pressure due to the increased volume. Swelling pressure is observed:

- during germination, resulting in their shell is broken;
- tree roots destroy rocks;
- swelling of legumes, grains led to the destruction of ships at ingress of water;
- ancient people for stone quarrying in the crevices of rocks killed wood wedge and watered it with water; as a result of swelling of wood developed high swelling pressure that rock burst.

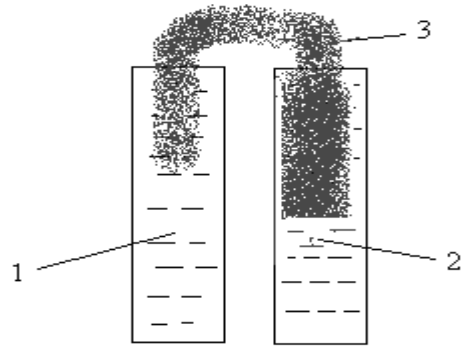
In medicine, it is used to obtain parts of the skull, filling his peas and pouring water.

Inflammations person feels pressure (bursting) in the inflammatory process, as well as mosquito bites.

Factors affecting the swelling

Swell is influenced by a number of factors.

1)Nature of HMC and the solvent. The rule of thumb: “similar dissolves at similar.” Thus, the polar molecule of gelatin (have functional groups - COOH and - NH_2) swell in polar solvent is water - but does not swell in benzene. And non-polar rubber swells in benzene, but does not swell in water (Picture 18.1).



Picture 18.1 Rubber benzene and water

1 - water ; 2 - benzene; 3 - rubber.

2) The degree of dispersion. The smaller particles of dry matter, the more it's swelling.

3) Effect of pH. In the isoelectric point of the swelling least, because the charge of the macromolecule is missing, and particles less attracted to the dipoles of water.

4) Effect of electrolytes. According to its influence electrolytes arranged in lyotropic series:

$$SCN^- > I^- > NO_3^- > Cl^- > SO_4^{2-}$$

swelling decreases →

The anion SO_4^{2-} strongly hydrated itself, so removes the hydrate shell with macromolecules, preventing swelling. Anion SCN^- not hydrated, so it contributes to swelling .

6) Temperature. As a rule, the higher the temperature, the greater the swelling. For example, gelatin and agar in hot water. But the methylcellulose is dissolved in alcohol at low temperature.

"Bound water" and its properties

In the first stage of swelling upon hydration is first formed a monolayer of water dipoles, which are attracted to the charged centers of the macromolecule. These water dipoles oriented strictly to the surface of the macromolecule and are called bound water.

Due to the orientation of the dipoles associated water has special properties

a) has an ordered structure as strictly oriented to the polar groups of the macromolecule;

b) low vapor pressure;

c) low dissolving capacity;

d) low dielectric constant - 2.2 instead of 81;

e) low pour point;

f) higher density; on the surface of the starch water density 1,28-2,45;

g) low compressibility, ie exhibits an elastic solid.

The biological significance of bound water

In living organisms, bound water determines the morphological structure of cells and tissues that support water supplies.

Amount of bound water in proteins is 0,15-0,35 g per 1 g of protein. Cardiac muscle, cerebral cortex contain 3-5% less water than blood, but has a dense consistency.

The infant up to 70% bound water, decreases with age up to 40%. Jellyfish, whose body contains only 1% of dry matter and about 99 % water, retain their shape.

Cancer cells contain 2.5 times more bound water than normal.

The biological significance of swelling

In vivo swelling is important for the digestion process, because different nutrients swell at different pH. So, in the oral cavity with a pH of 6.35 - 6,85 swell some substances, in the stomach with a pH of 0.9 to 1.5 swell other substances, in the intestine alkaline medium promotes swelling

of third substances. Thus, the change in pH promotes the swelling of various substances and digesting them.

The formation of edema, swelling of tumors is due to swelling of proteins.

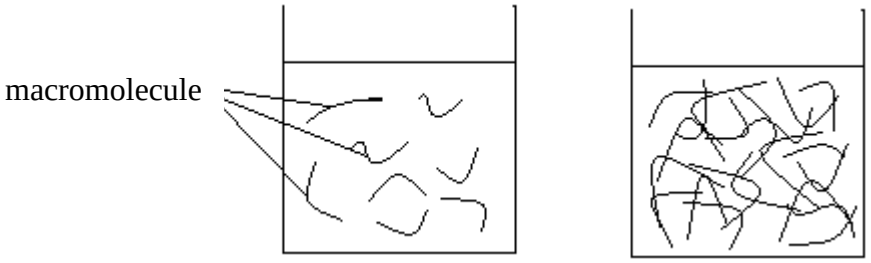
During aging the ability to swell decreases as increases the hydrophobicity of proteins, and they are not attracted to water molecules.

Gelation

As already mentioned factors sustainability solutions HMC is the charge and hydration shell. The latter being the most important factor. When standing or under the influence of various factors HMC solutions lose their stability. But it does not phase separation occurs as the coagulation, and is in the process of gelation (gelation). The product which thus formed is called a jelly.

Gelation is the process of transition of the polymer solution in a jelly with the formation of the spatial grid

The reason of gelation (gelation) in the event of ties between macromolecules, leading to the formation of the grid cells in which the solvent is. Interaction is due to hydrophobic forces (van der Waals), hydrogen bonds, ionic, covalent (Picture 18.2).



Picture 18.2. Formation a spatial grid at the gelation
a - solution of HMC; b - the spatial grid.

A number of factors contribute to gelation. Moreover, they act oppositely than when they swollen.

1) The size of the macromolecule. The larger macromolecule, is the faster connection formed between them.

2) Form of macromolecules. The longer and branched chains, are the faster gelation occurs. Albumin and globulins have a spherical shape, so they gelled after denaturation.

3) The concentration of the solution of HMC. The higher the concentration is the faster the gelatination comes, as more molecules collide with each other. But it also depends on the nature of HMC. Thus, gelatin (protein) will gelled at a concentration of 0.5%, agar-agar (polysaccharide) - 0,2%, gluten - 3-5%.

4) The pH of the solution. At the isoelectric point of gelation is faster, since the charge is zero and it macromolecule little hydrated. I.e. IEP disappears in one of the areas of sustainability

5) Temperature. The lower the temperature, the faster the gelation. But methylcellulose in water and in alcohol, nitrocellulose gelled at higher temperatures.

6) Electrolytes. Lyotropic series of electrolytes in the opposite row swelling:

$$SCN^- > I^- > NO_3^- > Cl^- > SO_4^{2-}$$

gelation increases

Sulfate anion SO_4^{2-} strongly hydrated and removes the hydrate shell as a factor of stability with macromolecules.

Time. The more time passes from the beginning of gelation, the stronger the structure formed.

The biological significance of gelation (gelation)

In humans, the process of blood clotting is gelling. At cuts when the vessel is broken under the action of enzymes produced thrombus which occludes the vessel and bleeding stops. However, if a blood clot forms in a blood vessel, it clogs it, which may lead to serious disease.

Jellies and their properties

Product gelation (gelation) is a jelly.

In humans, jellies this is: cytoplasm, leather, lens and vitreous body of the eye, horn tissue (nails, hair), ossein (protein in the bones) and others.

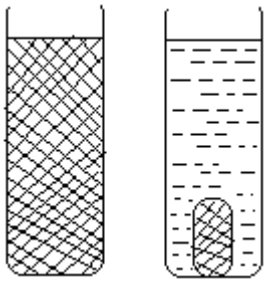
The presence of large amounts of water causes jellies following properties:

1) Thixotropy. This is the ability to liquefy and jelly go into solution of HMC and vice versa. Gelatin solution, viscose, kaolin slurry, sol $Al(OH)_3$, some of the soil under the action of external factors (shaking and stirring) can be transformed into jelly, and then pass again upon standing in solution.

In humans, thixotropic characteristic of protoplasm. Strongly expressed thixotropy for muscle protein myosin, which has a reduction in the ordered structure (resembling jelly), and for relaxation becomes more liquid.

2) Syneresis (leakage).

This phenomenon of separation of jelly into two phases, one of which has a more dense structure (dense jelly) and the liquid, which is a dilute solution of the polymer (Picture 18.3).



Picture 18.3 Syneresis phenomenon: a - solution of HMC; b - the separation of the solution into two phases.

Syneresis phenomenon is explained by strengthening of the bond between the macromolecules, contraction of mesh extrusion and fluid out of it. It's called aging gels. Syneresis explained staling of bread, liquid separation during storage confectionery (jelly).

In humans syneresis:

a) is one of the causes of aging as a result of dehydration (drying) fabric wrinkles;

b) in the process of blood coagulation protein is separated from the whey;

c) aging the cartilaginous tissues (dehydration) results in brittleness of the joints;

d) secretion glands explained syneresis.

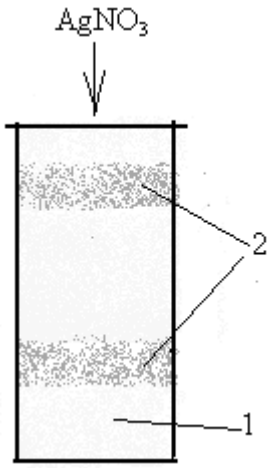
3) Diffusion in jellies. The presence of water in jellies causes chemical reactions there in. Moreover, if the thus formed insoluble materials, they are laid periodically in a ring.

For example, if a tube with a solution of agar containing potassium dichromate $K_2Cr_2O_7$, cool, then is formed coloured jelly. It poured solution Silver nitrate $AgNO_3$. Silver ions diffuse into the gelatin and potassium dichromate react with:

$$K_2Cr_2O_7 + AgNO_3 \rightarrow Ag_2Cr_2O_7\downarrow + KNO_3$$

orange

The precipitate is formed as a ring. Behind it there is a layer of agar-agar, then ring of Silver nitrate (Picture 18.4).



Picture 18.4. Periodic deposits:

1 – agar jelly with $K_2Cr_2O_7$; 2 – precipitate $Ag_2Cr_2O_7$

Such reactions are called periodic deposits. The mechanism of theim is poorly understood.

In the human body according to this principle is the formation of kidney stones (Picture 18.5)

Picture 18.5 The structure of a kidney stone

Salting

HMC solutions lose their stability during salting.

Salting is the selection in the precipitate macromolecules under the action of concentrated salts solutions.

Salting is carried out using Na_2SO_4, $(NH_4)_2SO_4$, alcohol, acetone.

Reason of salting **—** decrease of protein solubility in concentrated salt solution, resulting in removal of the hydration shell. At low concentration of large proteins are deposited. With increasing salt concentration falls proteins with lower molecular weight. Therefore, changing the salt concentration can be separated mixture of proteins.

Salting process is reversible. When water is added to the precipitated protein, it goes into the solution again.

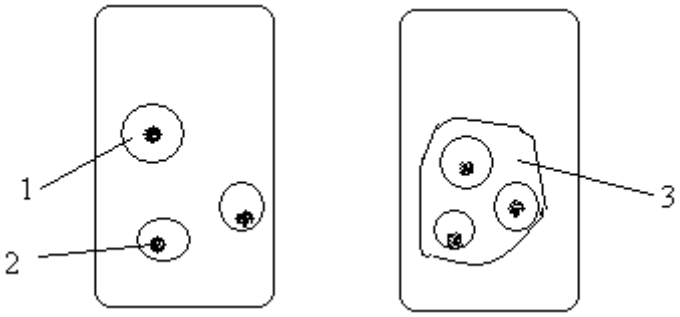
Proteins can also be precipitated using ethanol, acetone.

Salting out is used for the separation of mixtures of proteins depending on their molar mass

Coacervation

Solutions for HMC as a phenomenon characterized by coacervation (Picture 18.6).

Coacervation is a merger of hydrate shells of macromolecules with the division of the system into more and less concentrated phase



Picture 18.6 Coacervation phenomenon:

1 – hydrate shell ; 2 – molecule of HMC; 3 – coacervate with total hydration shell

More concentrated phase is called coacervate.

When coacervation occurs by mixing solutions of the protein and the polysaccharide, this is called complex coacervation.

Coacervation phenomenon underlies by A.I.Oparin theory about the origin of life on the earth.

Viscosity

Viscosity is a property of liquids and gases offer resistance when moving one portion of the liquid or gas with respect to another.

Solutions of HMC compared with colloidal and genuine solutions have high viscosity. This is due to their high hydrophilicity, i.e. macromolecules are strongly associated with the solvent.

The viscosity depends on the molecular shape. If the macromolecule is linear across the flow, it has high resistance to liquid flow. But if the particles are guided along a stream, for example, when the pressure increases, the viscosity decreases.

Uniform motion of the fluid in the tube is called laminar flow. If formed swirl, the flow becomes turbulent.

Viscosity is related to the molecular weight of dissolved polymer. Therefore, viscosity measurements are used to determine molar mass of the polymer.

H. Staudinger derived an equation which relates the specific viscosity and molar mass:

$$\eta_{\text{Sp.}} = \frac{\eta - \eta_O}{\eta_O}$$

$$\eta_{Sp.} = KCM$$

where η_{Sp} — specific viscosity

η — viscosity of the polymer solution,

η_0 — viscosity of the solvent,

C — concentration of HMC solution,

M — molar mass of HMC,

K — constant.

To determine the viscosity used devices of viscometers.

Viscosity is dependent on the solution pH. IEP viscosity near the lowest since macromolecules are rolled into a globule, which have the least resistance to flow.

The biological significance of viscosity

1) Used in medicine for viscosity measurement study its rheological properties under certain pathologies.

2) The movement of blood through the vessels is laminar, due to vascular elasticity and resilience. In case of violation of the vessel flow becomes turbulent, which contributes to the formation of a blood clot and stops bleeding.

3) Due to the disk-shaped red blood cells, they do not have a strong resistance to flow of blood through the vessels.

4) The lipid phase of membranes is considered as the liquid medium with a certain viscosity, which regulates the rate of membrane permeability, and proceeding in their enzymatic reactions

5) Hyaluronic acid (found in the joints) has a high viscosity, which prevents the penetration of pathogens into the body.

6) The viscosity of blood is 3-4 times more greater than water due to the presence of erythrocytes and various proteins. The quantity of blood viscosity of 1.2 - 2.2 poise.

Donnan membrane equilibrium

The presence of salts in the body, separate cell membrane, which leads to the redistribution of electrolytes, which obeys the equation of membrane equilibrium, Donnan.

Donnan membrane equilibrium is uneven distribution of electrolyte between the cell and the environment the presence of high-molecular compounds.

Consider the example of a redistribution of ions Na^+ and Cl^-. Pass through the membrane Na^+ and Cl^-, and protein (HMC) does not pass.

Before redistribution ion concentration is as follows:

solution (intercellular fluid) in the cell

$[Na^+]_s = [Cl^-]_s = C_s$ $[Na^+]_c = C_c$

After redistribution of some x the ions into the cell's moves :

$[Na^+]_s = [Cl^-]_s = C_{s-x;}$ $[Na^+]_c = C_c + x;$

$[Cl^-]_c = x.$

At equilibrium

$$[Na^+]_s \cdot [Cl^-]_s = [Na^+]_c \cdot [Cl^-]_c \text{ or}$$

$$(C_s - x) \cdot (C_s - x) = (C_c + x) \cdot x$$

$$x = \frac{C_s^{\,2}}{C_c - 2C_s} \qquad (1)$$

Formula 1 comes from:

1) when $[Na^+]_s >> [Na^+]_c$, C_c small quantity, then

$x = \frac{Cs^2}{2C_s} = \frac{Cs}{2}$, I.e. half of the Na^+ ions pass into the cell;

2) when $[Na^+]_s >> [Na^+]_c$, Cs means a small quantity, ie few ions will move in the cell;

3) if CP = SC, then, i.e. ions go into a third cell.

Thus, in any case, the cell enters a certain amount of ions and the osmotic pressure in to the cell is higher, there by keeping the turgor of the cell.

Donnan effect is manifested in the exchange of ions and HCO_3^- Cl^- between erythrocytes and plasma affects the extent biopotentials the absorption of drugs, etc.

Denaturation

One of the most important properties of protein denaturation is.

Denaturation is changing the nature of the protein associated with the destruction of the secondary, tertiary and quaternary structures.

or

Denaturation a partial or complete loss of biological activity associated with the destruction of secondary and tertiary and quaternary structures.

Factors that cause denaturation:

a) physical radiation, X-rays, ultraviolet rays, ultrasound, high and low temperatures (denaturation is a simple example of protein clotting when cooking eggs);

b) chemical concentrated acid and alkali salts of heavy metals.

Denaturation is accompanied by:

- increase in hydrophobicity;
- decrease in solubility;
- increase in viscosity;
- release of functional groups;
- loss of biological activity (enzyme, hormonal, immunological).

Denaturation occurs when the culinary and technological processing of materials containing proteins in the digestive process, under the action of disinfectants.

5. The main questions of the seminar:

5.1. What are the polymers?
5.2. Isoelectric state and isoelectric point of the proteins.
5.3. Protection action of proteins, protection number, biological meaning.
5.4. Swelling of polymers (the determination, mechanism, the factors). The fixed water, the properties and biological meaning.
5.5. The stability of polymers. Factors of stability.
5.6. Gelatinization of polymer solution, mechanism, factors, biological meaning.
5.7. Galantines, reaction in galantines, biological meaning.

6.The questions for individual learning:

6.1. Classification of polymers.
6.2. Salting out of the polymers, mechanism, factors, biological meaning.
6.3. Thixotropy, syneresis, coacervation, their biological meaning.

7. The examples of the task:

7.1.What is the influence of pH on gelatinization of proteins?

The answer:

The highest stage of gelatinization takes place at isoelectic point due to the neutrality of the proteins and the loss of stability is observed.

8. Homework (must be performed in the laboratory notebook):

8.1. Biological meaning of fixed water.
8.2. What are the substances extracted from blood by using salting out?

9. The algorithm of the experiments:

9.1. Determination of isoelectric point.
9.2. Determination of coagulation concentration of protected sol.
9.3. Swelling.
9.4. Influence of pH on swelling.
9.5. Influence of electrolytes on swelling.

10. The detailed explanation of the following experiment:

10.1. Determination of isoelectric point.

Concurrently 2 ml of acetate buffer with pH according to the table are added in 4 test-tubes. Then add 1 ml of 0.5% gelatine solution and mix them. Carefully add 3 ml of ethanol. Five min later, estimate the dimness of every solutions and determine the isolectric point of gelatine.

№	*pH of the system*	*0,5% gelatine solution, ml*	*Ethanol, ml*	*Dimness stage*
1	3,8	1	3	
2	4,4	1	3	
3	4,7	1	3	
4	5,1	1	3	

10.2. Determination of coagulation concentration of protected sol.

Prepare the ammonium sulfate solutions of different concentrations:		
1 test-tube	*2 test-tube*	*3 test-tube*
10 ml of ammonium (C_N=1 mol/l)	9 ml of water and 1ml of ammonium sulfate from the first test tube	9 ml of water and 1ml of ammonium sulfate from the second test tube

Analogous prepare the forth, fifth and sixth test-tube.

Then add 2 ml of iron (III) hydroxide sol. Determine the coagulation concentration. Prepare again the ammonium sulfate solutions of different concentrations and add 1 ml gelatine then 2 ml of iron (III) hydroxide sol. Determine the coagulation concentration for both cases and compare the data. Make a conclusion.

10.3. Swelling.

A piece of rubber immerse in the benzene, the second piece of rubber in water. Explain the observations.

10.4. Influence of pH on swelling.

1 test-tube	*2 test-tube*	*3 test-tube*
Dry gelatin	Dry gelatin	Dry gelatin
5 ml of HC1	5 ml of acetate buffer	5 ml ofNaOH

15 min later note the results. Make a conclusion.

10.5. Influence of electrolytes on swelling.

1 test-tube	*2 test-tube*	*3 test-tube*
Dry gelatin	Dry gelatin	Dry gelatin
5 ml of K_2SO_4	5 ml of KC1	5 ml of KSCN

15 min later note the results. Make a conclusion.

11. Control test:

Sample 1.

1. Write the determination of polymers. Examples.
2. Write the main properties of polymers that are distinguished from the properties of colloids.
3. What is configuration?

Sample 2.

1. Write the classification of polymers by nature.
2. What is limited and unlimited swelling? Swelling degree.
3. What is the phenomenon responsible for stability of polymers?

Type of reaction	Definition	Example
Reactions occurring with the change in the number of substances		
Addition	During which of the two substances form a complex.	$A + B = AB$ $2Ca + O_2 = 2CaO$ $CaO + CO_2 = CaCO_3$ $4NO_2 + O_2 + 2H_2O = 4HNO_3$ $NH_3 + H_3PO_4 = NH_4H_2PO_4$ $CH_3NH_2 + HCl = [CH_3NH_3]Cl$
Exchange	During which molecules of complex substances share their composite.	$AB + CD = AD + BC$ $Al(OH)_3 + 3HI = AlI_3 + 3H_2O$ $BaCl_2+Na_2SO_4=BaSO_4\downarrow+2NaCl$ $Na_2CO_3 + 2HNO_3 =$ $= CO_2\uparrow+ H_2O + 2NaNO_3$ $HCl + KOH = KCl + H_2O$
Substitution	While an item of simple substances replaces the element of complex substances, as a result forming a new simple and new complex substances.	$AB + C = AC + B$ $Mg + 2HCl = MgCl_2 + H_2\uparrow$ $Zn + H_2SO_{4(d)} = ZnSO_4 + H_2\uparrow$ $Fe + CuSO_4 = FeSO_4 + Cu\downarrow$
Decomposition	During which one complex substance formed by several simple or less simple substance.	$Zn(OH)_2 = ZnO + H_2O$ $CaCO_3 = CaO + CO_2\uparrow$ $2Cu(NO_3)_2=2CuO+4NO_2\uparrow+O_2\uparrow$
Reaction with heat effect		
Exothermic	Reactions run with heat release.	$4Al+3O_2=2Al_2O_3+3350,4kJ$ $N_2 + 3H_2 = 2NH_3 + 92,4kJ$
Endothermic	Reactions run with absorption of heat.	$\frac{1}{2}N_2 + \frac{1}{2}O_2 = NO - 90,25$ kJ $2C_2H_6+7O_2=4CO_2+6H_2O-2935$ kJ
Direction of the reaction		
Direct	Reactions run with the use of one of the substances.	$4Cr + 3O_2 \rightarrow 2Cr_2O_3$
Return	Reactions run under identical conditions in mutually opposite directions.	$N_2 + 3H_2 \rightleftharpoons 2NH_3$
The turnover reaction		
Reversible	Reactions that occur simultaneously forward and backward directions.	$N_2O_4 \rightleftharpoons 2NO_2$
Irreversible	Reactions in which there is only direct (formation of gas, precipitate, weak electrolyte).	$BaCl_2+H_2SO_4\rightarrow 2HCl+BaSO_4\downarrow$ $CaCO_3+2HCl\rightarrow CaCl_2+CO_2\uparrow+H_2O$
Reaction with catalyst		
Catalytic	Those who run with the participation of the catalyst.	$2SO_2 + O_2 = 2SO_3(cat\ V_2O_5)$
Non-catalytic	Those that run without the participation of the catalyst.	$2NO + O_2 = 2NO_2$
By the change in oxidation number		
With the change in the degree of oxidation (ORR)	During which atoms change oxidation states.	$Br_2 + H_2O_2 = 2HBr + O_2$ $2MnO_2 + O_2 + 4KOH \rightarrow$ $\rightarrow 2K_2MnO_4 + 2H_2O$
Without changing the oxidation state	During which the atoms do not change oxidation state.	$Na_2O + N_2O_5 = 2NaNO_3$ $KF + H_2SO_{4(c)}\rightarrow HF\uparrow+KHSO_4$

OXIDES

The main classes of inorganic compounds

As it's mentioned in the previous material all substances are divided into simple and complex, depending on their composition. Complex substances are made of atoms of different chemical elements. The composition is simple **—** the atoms of one chemical element. Simple substances are divided in turn into metals and nonmetals on the totality of the physical and chemical properties. Sharp boundary between metals and nonmetals do not exist. The substance which belongs to one group or another is a set of attributes.

<table>
<tr><td colspan="4">Substances</td></tr>
<tr><td colspan="2">Simple substances</td><td colspan="2">Complex substances</td></tr>
<tr><td>Metals</td><td>Nonmetals</td><td>Oxides</td><td>Basics</td></tr>
<tr><td rowspan="2">Nonmolecular structure.
All except mercury are solid. Have a metallic luster, mostly silver. Heat and electrically conductive.
Plastic, ductile.</td><td rowspan="2">Molecular and nonmolecular structure.
Solid, liquid and gaseous, has a matte surface, painted in different colors.
It conducts current and heat badly.</td><td>Acids</td><td>Salts</td></tr>
<tr><td colspan="2">Amphoteric hydroxides</td></tr>
<tr><td colspan="4">Oxides is a complex compound consisting of two elements, one of which is definitely the oxygen in the oxidation state -2.</td></tr>
<tr><td colspan="4">Classification of oxides</td></tr>
</table>

<table>
<tr><td colspan="3">Salifiable
— the oxides that interact with acids or bases, forming salts.</td><td>Non salifiable
CO, N_2O, NO, SiO.</td><td>Mixed</td></tr>
<tr><td>Basic — oxides, which correspond to the base.
Basic — oxides, hydrate form which is the only basis.</td><td>Amphoteric — oxides that exhibit the dual properties of the acids and bases.</td><td>Acidic — oxides, corresponding acid.
Acidic — oxides, hydrate form which is the only acid.</td><td rowspan="2">Desolator — oxides, which do not form salts (indifferent: do not interact with acids, bases, water).</td><td rowspan="2">Oxides, consisting of two or more oxides
NO_2 (N_2O_4),
ClO_2 (Cl_2O_4),
PO_2 (P_2O_4),
BrO_2 (Br_2O_4),
IO_2 (I_2O_4),
ClO_3 (Cl_2O_6),
BrO_3 (Br_2O_6),
IO_3 (I_2O_6),
Fe_3O_4 ($FeO{\cdot}Fe_2O_3$)
Mn_3O_4 ($MnO{\cdot}Mn_2O_3$),
Pb_3O_4 ($2PbO{\cdot}PbO_2$),
Pb_2O_3 ($PbO{\cdot}PbO_2$)</td></tr>
<tr><td>Li_2O, Na_2O, K_2O, Rb_2O, MgO, CaO, BaO, CrO</td><td>BeO, ZnO, Al_2O_3, Fe_2O_3, Cr_2O_3</td><td>CO_2, SO_2, SO_3, N_2O_3, N_2O_5, B_2O_3, P_2O_3,P_2O_5, As_2O_3, As_2O_5, Sb_2O_5, Mn_2O_7, MnO_3, Cl_2O, Cl_2O_3, Cl_2O_5, Cl_2O_7, Br_2O, Br_2O_3, Br_2O_5, Br_2O_7,SeO_2, SeO_3, I_2O, I_2O_3, I_2O_5, I_2O_7</td></tr>
</table>

Further examples of oxides look in the respective lectures of acids, bases, amphoteric hydroxides.		

Nomenclature **—** a system of rules, which gives an unambiguous name of the substance.

For oxides of elements of constant valence:			*For oxides of elements of constant valence:*			
The name of the item + Oxide			The name of the item + The valence + Oxide			
Li_2O	Lithium	oxide	SeO_3	Selenium	(VI)	oxide
Na_2O	Sodium	oxide	I_2O_5	Iodine	(V)	oxide
BeO	Beryllium	oxide	SO_2	Sulphur	(IV)	oxide
MgO	Magnesium	oxide	As_2O_3	Arsenic	(III)	oxide
			N_2O_3	Nitrogen	(III)	oxide

Nomenclature of mixed oxides: In this case, you specify both valence oxides.

Fe_3O_4 ($FeO \cdot Fe_2O_3$) → Iron (II, III) oxide, but RO_2: NO_2, PO_2, ClO_2, BrO_2, IO_2 – radical (IV) oxide!

Chemical properties of oxides.

I. Basic oxides — oxides of metals in low oxidation states.

Basic oxides are divided into: soluble in water (oxides of alkali and alkaline earth metals Li_2O, Na_2O, K_2O, Rb_2O, Cs_2O, Fr_2O & BeO, MgO, CaO, SrO, BaO, RaO) and **insoluble** (all others).

1. The interaction with water: (additional reaction)	$CaO + 2H_2O \rightarrow Ca(OH)_2$ $Na_2O + H_2O \rightarrow 2NaOH$

2. Interaction with acidic and amphoteric oxides to form salts: (additional reaction)

with acid	*with amphoteric*
$Na_2O + Cl_2O_3 \rightarrow 2NaClO_2$ Sodium chlorite $K_2O + SO_2 \rightarrow K_2SO_3$ Potassium sulphite $MgO + N_2O_5 \rightarrow Mg(NO_3)_2$ Magnesium nitrate	$K_2O + ZnO \rightarrow K_2ZnO_2$ Potassium zincate $MgO + Al_2O_3 \rightarrow Mg(AlO_2)_2$ Magnesium metaluminate

3. Interaction with amphoteric hydroxides to form salts and water:

$Na_2O + 2Al(OH)_3 \rightarrow 2\ NaAlO_2 + 3H_2O$ Sodium aluminate + water

$CaO + Zn(OH)_2 \rightarrow CaZnO_2 + H_2O$ Calcium zincate + water

4. Oxidative properties.

Interaction with the reducing agent with the formation of loose metal (substitution reaction) (reducing agents – H_2; C; CO and a more active metal). This reaction is used in metallurgy!

$CuO + H_2 \xrightarrow{t^0C} Cu + H_2O$

$FeO + C \xrightarrow{t^0C} Fe + CO$

$FeO + CO \xrightarrow{t^0C} Fe + CO_2$

$CuO + Zn \xrightarrow{t^0C} Cu + ZnO$

5. Reduction properties. The interaction with oxygen (additional oxidation) to form higher oxides:

$2SO_2 + O_2 \rightarrow 2SO_3$

$2NO + O_2 \rightarrow 2NO_2$

II. Acidic oxides — oxides, hydrates which are acids, so they are also called acid anhydrides. They include oxides of nonmetals and metals in higher oxidation States: CO_2, P_2O_5, CrO_3, Mn_2O_7.

Among the acidic oxides are solid

Acidic oxides — oxides, hydrates which are acids, so they are also called acid anhydrides. These include oxides of nonmetals and metals in higher oxidation states: CO_2, P_2O_5, CrO_3, Mn_2O_7.

Among the acidic oxides are solid (P_2O_5, CrO_3, Mn_2O_7); liquid (N_2O_3) and gaseous (SO_2, CO_2); they are all soluble in water except SiO_2.

1. The interaction with water to form acids: (reaction of a compound)

$SO_2 + H_2O \rightarrow H_2SO_3$ Sulphite acid

$2NO_2 + H_2O \leftrightarrow HNO_2 + HNO_3$ Nitrous & nitric acid

In the case where the anhydride several forms acids (ortho, meta):

$N_2O_3 + H_2O \rightarrow 2HNO_2$ Nitrous acid

$N_2O_5 + H_2O \rightarrow 2HNO_3$ Nitric acid

$Cl_2O + H_2O \rightarrow 2HClO$ Hypochlorous acid

$Cl_2O_3 + H_2O \rightarrow 2HClO_2$ Chlorous acid

2. Interaction with basic and amphoteric oxides (exhibit basic properties) to form a salt (addition reaction)

$Cl_2O + MgO \rightarrow Mg(ClO)_2$ Magnesium hypochlorite

$SO_3 + BaO \rightarrow BaSO_4$ Barium sulfate

$MgO + SO_2 \rightarrow MgSO_3$ Magnesium sulphite

$3Mn_2O_7 + Cr_2O_3 \rightarrow 2Cr(MnO_4)_3$ Chromium permanganate

3. The interaction of alkali with the formation of salt and water: (reaction of substitution)

$SiO_2 + 2KOH \rightarrow K_2SiO_3 + H_2O$ Potassium silicate

$Mn_2O_7 + NaOH \rightarrow NaMnO_4 + H_2O$ Sodium permanganate

$CrO_3 + Ca(OH)_2 \rightarrow CaCrO_4 + H_2O$ Calcium chromate

$SO_3 + 2NaOH \rightarrow Na_2SO_4 + H_2O$ Sodium sulfate

But!: $SO_2 + 2NaOH(conc.) = Na_2SO_3 + H_2O$

$SO_2 + NaOH(dissol.) = NaHSO_3$ Sodium bisulfite (sodium hydrogen sulfite)

4. Interaction with soda Na_2CO_3 and baking soda — $NaHCO_3$ for fusion with the formation of salt and CO_2:

$Na_2CO_3 + SO_3 \rightarrow Na_2SO_4 + CO_2\uparrow$

$6NaHCO_3 + P_2O_5 \rightarrow 2Na_3PO_4 + 6CO_2\uparrow + 3H_2O$

5. Thermal decomposition with the formation of lower oxides: (substitution reaction)

$4MnO_3 \rightarrow 2\ Mn_2O_3 + 3O_2$

6. Reduction of oxides. Interaction with the reducing agent:(addition reaction,ORR return disproportionation)

$CO_2 + C \rightarrow 2CO$ carbon (II) oxide

7. Interaction with amphoteric hydroxides with formation of salt and water:

$Br_2O_7 + Zn(OH)_2 \rightarrow Zn(BrO_4)_2 + H_2O$ perbromate zinc

$3CrO_3 + 2Al(OH)_3 \rightarrow Al_2(CrO_4)_3 + 3H_2O$ aluminum chromate

III. Amphoteric oxides — oxides exhibiting dual properties; depending on conditions demonstrate the properties of the basic and acidic oxides. They interact with acids and alkalies, insoluble in water. All amphoteric oxides solids. This include oxides of metals located in the periodic table near the diagonal (B-At), which divides the chemical elements metals and non-metals (BeO; Al_2O_3; ZnO; SnO; PbO), and oxides of metals of sub groups of the periodic system into the intermediate oxidation states (Fe_2O_3; Cr_2O_3; MnO_2).

Acidic properties:

1. Interaction with alkali during sintering with the formation of salt and water:

$BeO + 2KOH \xrightarrow{t^0C} K_2BeO_2 + H_2O$ Potassium zincate (exchange reaction)

$Fe_2O_3 + 2KOH \xrightarrow{t^0C} 2KFeO_2 + 2H_2O$ Potassium meta ferrite

in solution (formation of complex salts): (addition reaction)

$ZnO + 2KOH + HOH \xrightarrow{t^0Cp-н} K_2[Zn(OH)_4]$ Potassium **tetrahydroxo**zincate

$Al_2O_3 + 6NaOH + 3HOH \xrightarrow{t^0Cp-н} 2Na_3[Al(OH)_6]$ Sodium **hexahydroxo**aluminate or incomplete complex with a lack of alkali:

$Cr_2O_3 + 2NaOH + 3HOH \xrightarrow{t^0Cp-н} 2Na[Cr(OH)_4]$ Sodium **tetrahydroxo**crominate or till aqvacomplex:

Cr_2O_3+2NaOH +7HOH $\xrightarrow{t^0Cр-р}$ 2Na[Cr(OH)$_4$(H_2O)$_2$] sodium **diaqva**tetrahydroxocrominate

2. Interaction with basic oxides (during sintering) to form a salt and water: (addition reaction)

$ZnO + K_2O \xrightarrow{t^0C} K_2ZnO_2 + H_2O$ Potassium zincate

$Al_2O_3 + Na_2O \xrightarrow{t^0C} 2NaAlO_2 + H_2O$ Sodium metaaluminate

Basic properties:

3. Interaction with acids to form salt and water: (exchange reaction)

$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O$ Aluminium (III) sulfate

$BeO + 2HNO_3 \rightarrow Be(NO_3)_2 + H_2O$ Beryllium nitrate

4. Interaction with certain salts of alkali metals during sintering: (substitution reaction)

For example with soda

$Al_2O_3 + K_2CO_3 \xrightarrow{t^0C} 2KAlO_2 + CO_2\uparrow$ potassium metaaluminate

$ZnO + Na_2SO_3 \xrightarrow{t^0C} Na_2ZnO_2 + SO_2\uparrow$ sodium zincate

$Cr_2O_3 + 2NaHCO_3 \xrightarrow{t^0C} 2NaCrO_2 + CO_2\uparrow + H_2O$ sodium metcromate

5. Oxidation of oxides. Interaction with the reducing agent, amphoteric oxides are reduced to the free metals. (this reaction is the basis of metallurgical processes for the production of metals):

$Cr_2O_3 + 2Al \xrightarrow{t^0C} 2Cr + Al_2O_3$

$ZnO + H_2 \xrightarrow{t^0C} Zn + H_2O$

Mixed oxides.

They are conventionally divided into mixed oxides of metals and nonmetals.

I. **Mixed oxides** of non-metals **—** oxides, which correspond to two acids: NO_2 (N_2O_4); PO_2 (P_2O_4); R – Cl,Br,I: RO_2 (R_2O_4); RO_3 (R_2O_6);.

– NO_2 - nitrogen (IV) oxide (nitrogen dioxide, or "brown gas")
– PO_2 - phosphour (IV) oxide
– ClO_2 - chlorine (IV) oxide
– ClO_3 - chlorine (VI) oxide
– BrO_2 - bromine (IV) oxide
– BrO_3 - bromine (VI) oxide
– IO_2 - iodide (IV) oxide
– IO_3 - iodide (VI) oxide

1. The interaction of water with the formation of **two acids** (cold):

$2PO_2 + H_2O \rightarrow HPO_2 + HPO_3$

Phosphorous acid Phosphoric acid

$2BrO_2 + H_2O \rightarrow HBrO_2 + HBrO_3$

bromous acid bromic acid

$2IO_3 + H_2O \rightarrow HIO_3 + HIO_4$

iodic acid periodic acid

2. The interaction with the alkali with the formation of two salts of the corresponding acids (cold):

$2N_2O_4 + 2Sr(OH)_2 \rightarrow Sr(NO_2)_2 + Sr(NO_3)_2 + 2H_2O$

stroncium nitrite stroncium nitrate

$2BrO_2 + 2NaOH \rightarrow NaBrO_2 + NaBrO_3 + H_2O$

sodiumium bromite sodium bromate

$2IO_3 + 2KOH \rightarrow KIO_3 + KIO_4 + 2H_2O$

potassium iodate potassium periodate

II. **Mixed oxides of metals —** oxides, which are consisting of two or more oxides Fe_3O_4 ($FeO \cdot Fe_2O_3$), Mn_3O_4 ($MnO \cdot Mn_2O_3$), Pb_3O_4 ($2PbO \cdot PbO_2$).

Fe_3O_4 **—** magnetic iron ore (magnetite) from combustion of iron:

It's a mixture of FeO and Fe_2O_3; But mixed oxides also consider as salts formed during the interaction of basic and amphoteric oxides:

$Fe_3O_4 – Fe(FeO_2)_2$ → FeO + Fe_2O_3 → $Fe(FeO_2)$ iron (II) metaphoric

$Mn_2O_3 – Mn(MnO_3)$ → MnO + MnO_2 → $MnMnO_3$ mangan (II) metamagnet

$Mn_3O_4 – Mn_2(MnO_4)$ → 2MnO + MnO_2 → Mn_2MnO_4 mangan (II) ortomagnite

$Pb_2O_3 – Pb(PbO_3)$ → PbO + PbO_2 → $PbPbO_3$ lead (II) metaplumbate

$Pb_3O_4 – Pb_2(PbO_4)$ → 2PbO + PbO_2 → Pb_2PbO_4 lead (II) ortoplumbate

When interacting with acids are also formed two of salt:

$Fe_3O_4 + 8HBr \rightarrow FeBr_2 + 2FeBr_3 + 4H_2O$

ferum (II) bromide and ferum (III) bromide

BASES

Base is a compound, which consist of a metal atom (metal groups such as ammonium cation NH_4^+) wich is connected to one or more hydroxogroup (OH^-).

By Arrhenius: (From the point of view of electrolytic dissociation) are compounds in which aqueous solution dissociate into cations Me^{+n} and anions OH^-.

By Lewis: is a substance that provides e- pair.

By Brønsted-Lowry: (From the point of view of the proton theory): is a substance that can bind protons H^+ (a proton acceptor).

<table>
<tr><th colspan="4">Classification</th></tr>
<tr><td colspan="4">1. By acidity base — number of hydroxogroup connected with metal (or NH_4^+):
The number of hydroxide ions in the base is determined by the oxidation state of the metal.</td></tr>
<tr><td colspan="2">monoacidic:</td><td colspan="2">LiOH, KOH,NaOH, NH_4OH</td></tr>
<tr><td colspan="2">diacidic:</td><td colspan="2">$Ba(OH)_2$, $Mg(OH)_2$, $Sr(OH)_2$</td></tr>
<tr><td colspan="2">triacidic:</td><td colspan="2">$Al(OH)_3$, $Cr(OH)_3$, $Fe(OH)_3$</td></tr>
<tr><td colspan="2">tetraacid:</td><td colspan="2">$Pt(OH)_4$</td></tr>
<tr><td colspan="4">2. By dissolution in water:</td></tr>
<tr><td colspan="2">Soluble
hydroxides of alkali and alkaline-earth metals (alkali) LiOH; KOH; NaOH and ammonium hydroxide (NH_4OH)</td><td colspan="2">Insoluble
hydroxides all amphoteric metals and other metals in lower oxidation states $Mg(OH)_2$; $Al(OH)_3$; $Cr(OH)_3$; $Fe(OH)_2$; $Fe(OH)_3$; $Ni(OH)_2$; $Co(OH)_2$; $Mn(OH)_2$; $Zn(OH)_2$; $Pb(OH)_2$; $Sn(OH)_2$; $Cu(OH)_2$;</td></tr>
<tr><th colspan="4">Nomenclature</th></tr>
<tr><td colspan="4">In modern nomenclature — the name of the metal is added to the valence (if it is an element of variable valence) and the word hydroxide. This rule is used to supply the names of the bases and amphoteric hydroxides.</td></tr>
<tr><td colspan="2">Me + Hydroxide</td><td colspan="2">Me + V + Hydroxide</td></tr>
<tr><td>KOH</td><td>Potassium hydroxide</td><td>$Mn(OH)_2$</td><td>Manganese (II) hydroxide</td></tr>
<tr><td>$Mg(OH)_2$</td><td>Magnesium hydroxide</td><td>$Mn(OH)_3$</td><td>Manganese (III) hydroxide</td></tr>
<tr><td>$Cr(OH)_3$</td><td>Chromium hydroxide</td><td>$Pb(OH)_2$</td><td>Lead(II) hydroxide</td></tr>
<tr><td>$Be(OH)_2$</td><td>Berylium hydroxide</td><td>$Pb(OH)_4$</td><td>Lead(IV) hydroxide</td></tr>
<tr><td colspan="4">Physical properties of bases
All bases are solid substances. Many of them are white, although the manganese (II) hydroxide is dark brown, lead (II) hydroxide is colorless.
The physical properties of alkalis
Base — is a white crystalline substance, soluble in water; aqueous solutions of alkalis soap to the touch, caustic — corrosive to the skin, paper, fabric...
Alkali-electrolytes, which dissosiate in water to form hydroxide anions (OH^-) and cations of</td></tr>
</table>

metal (Me^{+n}), that's why their aqueous solutions are conducters of electricity — they are conductors of II type (ionic conductivity); the conduct of I type — is one of the metals (electronic conductivity).

Chemical properties of alkali

Dissociation of alkali

Strong alkali electrolytes, in aqueous solutions fully dissociate into hydroxide anions (other anions do not form!)

monoacidic dissociate at single-stage:	$NaOH \rightarrow Na^+ + OH^-$
polyacidic dissociate at few-stages:	$Ba(OH)_2 \rightarrow Ba(OH)^+ + OH^-$ $Ba(OH)^+ \rightarrow Ba(OH)^{2+} + OH^-$

The color change of the indicator

Phenolphthalein — crimson	Methyl orange — yellow	Litmus — blue

1. Interaction with acids to form salt and water (neutralization reaction)

$NaOH + HBr \rightarrow NaBr + H_2O$ (molecular equation)

$Na^+ + OH^- + H^+ + Br^- \rightarrow Na^+ + Br^- + H_2O$ (full ionic equations)

$OH^- + H^+ \rightarrow H_2O$ (short ionic equation)

$Cu(OH)_2 + H_2SO_4 = CuSO_4 + 2H_2O$ (molecular equation)

$Cu(OH)_2 + 2H^+ + SO_4^{2-} \rightarrow Cu^{2+} + SO_4^{2} + 2H_2O$ (full ionic equations)

$Cu(OH)_2 + 2H^+ = Cu^{2+} + 2H_2O$ (short ionic equation)

Depending on the quantities of substances of reaction products of diacidic base and monobasic acid can be primary or secondary salt:

I stage: $Ba(OH)_2$ unstable + $HI \rightarrow Ba(OH)I + H_2O$ barium hydroxoiodide — basic salt

II stage: $Ba(OH)_2 + 2HI \rightarrow BaI_2 + 2H_2O$ barium iodide

$Ba(OH)_2 + H_2SO_3 \rightarrow BaSO_3 + 2H_2O$ barium sulfite

or at 3 stage:

$Al(OH)_3 + 1HCl \rightarrow Al(OH)_2Cl + H_2O$

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

$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + H_2O$

2. Interaction with acidic oxides with the formation of salt and water:

$2NaOH + SiO_2 \rightarrow Na_2SiO_3 + H_2O$ sodium silicate

$Ba(OH)_2 + N_2O_5 \rightarrow Ba(NO_3)_2 + H_2O$ barium nitrate

$Cu(OH)_2 + SO_3 \rightarrow CuSO_3 + H_2O$ cuprum sulfite

$BaO + SO_3 \rightarrow BaSO_4$ barium sulfate

3. With amphoteric oxides:

a) they form a salt and water:	$2KOH + ZnO \rightarrow K_2ZnO_2 + H_2O$ (potassium zincate) $2NaOH + Al_2O_3 \rightarrow 2NaAlO_2 + H_2O$ (sodium aluminate) $Ca(OH)_2 + ZnO \rightarrow CaZnO_2 + H_2O$ (calcium zincate)
b) in solution (boiling) they form a complex salt:	$2\ KOH_{sol} + ZnO + H_2O \rightarrow K_2[Zn(OH)_4]$ potassium **tetrahydroxo**zincate $6NaOH_{sol} + Al_2O_3 + 3H_2O \rightarrow 2Na_3[Al(OH)_6]$ sodium **hexahydroxo** (III) aluminate

4. Interaction with amphoteric hydroxides with the formation of complex salts: (neutralization reaction)

$3KOH + Cr(OH)_3 \rightarrow K_3[Cr(OH)_6]$ potassium **hexahydroxo**chromate

$2NaOH + Be(OH)_2 \rightarrow Na_2[Be(OH)_4]$ sodium **tetrahydroxo**berylate

5. Interaction with dissolved salts with the formation of insoluble metal hydroxide and an alkali metal salt (method of extraction of insoluble bases):

$CuBr_2 + 2KOH \rightarrow Cu(OH)_2\downarrow + 2KBr$

or $CuBr_2 + 2KOH \rightarrow Cu(OH)Cl + 2KBr$

$Ni(NO_3)_2 + 2NaOH \rightarrow Ni(OH)_2\downarrow + 2NaNO_3$

$Fe_2(SO_4)_3 + 2NaOH \rightarrow 2Fe(OH)SO_4 + Na_2SO_4$

$Fe_2(SO_4)_3 + 4NaOH \rightarrow [Fe(OH)_2SO_4] + 2Na_2SO_4$

6. The interaction of amphoteric metals such as Zn, Be, Al)

a) is formed with the fusion of the salt of an amphoteric metal and hydrogen:	$Be + 2KOH \rightarrow K_2BeO_2 + H_2\uparrow$ potassium berylate $2Al + 2KOH + 2H_2O \rightarrow 2KAlO_2 + 3H_2\uparrow$ potassium metaluminate
b) under the action of hot dilute forms a complex salt and hydrogen	$2Al + 2KOH + 10H_2O \rightarrow 2K[Al(OH)_4(H_2O)_2] + 3H_2\uparrow$ (or $K[Al(OH)_4]$ or $K_3[Al(OH)_6]$) potassium diaquatetrahydroxoaluminate $Zn + 2NaOH + 2H_2O \rightarrow Na_2[Zn(OH)_4] + H_2\uparrow$ sodium tetrahydroxozincate

7. With some nonmetals (Cl_2; Br_2; I_2; S; Se) form two salt: (OR reaction disproportionate)

$I_2 + 2KOH \rightarrow KI + KIO + H_2O$ (on cold)

$I_2 + 2KOH \rightarrow KI + KIO_2 + H_2O$

$I_2 + 2KOH \rightarrow KI + KIO_3 + H_2O$

$I_2 + 2KOH \rightarrow KI + KIO_4 + H_2O$

$3S + 6NaOH \rightarrow 2Na_2S + Na_2SO_3 + 3H_2O$

sodium sulfide sodium sulfite

$8P + 9KOH + 3H_2O \rightarrow 5PH_3\uparrow + 3K_3PO_4$ (or acid salt KH_2PO_2)

phosphine potassium phosphate

But: $Si + 2KOH + H_2O \rightarrow K_2SiO_3 + 2H_2\uparrow$

Similarly $SiO_2 + 2KOH \rightarrow K_2SiO_3 + H_2O$

8. Interaction with acid salts with the formation of the average salt (or less acidic):

$KOH + KH_2PO_4 \rightarrow K_2HPO_4 + H_2O$

dihydrogen phosphate potassium hydrogen phosphate

$KOH + KH_2PO_4 \rightarrow K_3PO_4 + H_2O$

potassium orthophosphate

9. The decomposition of the basics. (decomposition)

When heated, the hydroxides of alkaline-earth metals and NH_4^+) are applied to:

oxide (NH_3) and water ($Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$)

$Sr(OH)_2 \rightarrow SrO + H_2O$

$NH_4OH \rightarrow NH_3 + H_2O$

Chemical properties of bases are not soluble in water.

The base that is insoluble in water is a very weak electrolyte, virtually it will not dissociate into ions in water; and change the color of indicators. It does not react with amphoteric oxides and hydroxides and salts.

1. They interact only with <u>acids</u> to form salt and water (neutralization reaction) and acidic <u>oxides:</u>

$Ca(OH)_2 + H_3PO_4 = [Ca(OH)_3^+]PO_4^{3-} + H_2O$

orthophosphate hydroxocalcium

$3Ca(OH)_2 + 2H_3PO_4 = Ca_3(PO_4)_2\downarrow + 6H_2O$

calcium ortophosphate

$Ca(OH)_2 + H_3PO_4 = CaHPO_4\downarrow + 2H_2O$

hydrophosphate sodium

$Ca(OH)_2 + 2H_3PO_4 = Ca(H_2PO_4)_2 + 2H_2O$

$Mg(OH)_2 + 2HBr \rightarrow MgBr_2 + H_2O$

$2Bi(OH)_3 + 3H_2SO_3 \rightarrow Bi_2(SO_3)_3 + 6H_2O$

$Ni(OH)_2 + SO_2 \rightarrow NiSO_3 + H_2O$

2. When heated, decompose into oxides and water:

$Co(OH)_2 \rightarrow CoO + H_2O$

$2Cr(OH)_3 \rightarrow Cr_2O_3 + 3H_2O$

But decompose at room temperature on such basis

$Hg(OH)_2 \rightarrow HgO + H_2O$

$2AgOH \rightarrow Ag_2O + H_2O$

Chemical properties of bases
Formation methods of alkali

1. The interaction of alkali and alkaline-earth metals with water:

$2K + 2H_2O \rightarrow 2KOH + H_2\uparrow$

$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2\uparrow$

2. The interaction of oxides of alkaline and alkaline-earth metals with water:

$Na_2O + H_2O \rightarrow 2NaOH$

$BaO + H_2O \rightarrow Ba(OH)_2$

3. The interaction of peroxides and hydrides of alkali and alkaline-earth metals with water:

$KH + H_2O \rightarrow KOH + H_2\uparrow$

$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2\uparrow$

4. The interaction of salts of alkaline metal with hydroxides of alkaline-earth metals – forms an alkali salt and alkaline-earth metal which is not soluble in water:

$K_2CO_3 + Ca(OH)_2 \rightarrow 2KOH + CaCO_3\downarrow$

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

5. Electrolysis of aqueous solutions of alkali metal salts:

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

6. Hydrolysis of salts formed with alkali and weak polybasic acid forms acid salt type and an alkali:

$K_2CO_3 + H_2O \leftrightarrow KHCO_3 + KOH$

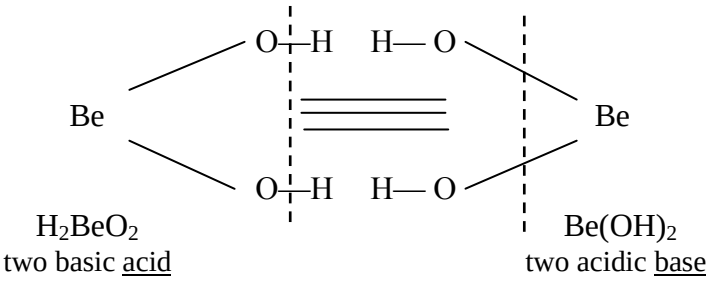
7. Production is not soluble in water — the interaction of the aqueous salt solution with an alkali:

$FeSO_4 + 2KOH \rightarrow Fe(OH)_2\downarrow + K_2SO_4$

AMPHOTERIC HYDROOXIDES

Amphoteric hydroxides (hydrated form amphoteric oxides) **—** hydroxides, which depend on conditions that show both basic and acidic properties.

The basic and acidic form of amphoteric hydroxides



BeO	H_2BeO_2	Acid properties = Basic properties
ZnO	H_2ZnO_2	
Al_2O_3	$HAlO_2$	

CuO	H_2CuO_2	Basic properties > Acid properties
PbO	H_2PbO_2	
SnO	H_2SnO_2	
Fe_2O_3	$HFeO_2$	
Cr_2O_3	$HCrO_2$	
Sb_2O_3	H_3SbO_3 $HSbO_2$	
MnO_2	H_2MnO_3	Acid properties > Basic properties
SnO_2	H_2SnO_3	
PbO_2	H_2PbO_3	

Tribasic acid amphoteric metals may exist in the form of ortho - and meta - form:

$H_3SbO_3 \longrightarrow HSbO_2 + H_2O$ ortho-antimonic acid meta-antimonious acid
$H_3CrO_3 \longrightarrow HCrO_2 + H_2O$ ortocromate metacromate

Chemical properties	
Virtually do not dissociate in water, do not change the color of indicators	
Interact: with acid oxide, base, base oxide decomposition *Do not interact:* with salts in solution, basics (weak, insoluble), amphoteric hydroxides, amphoteric oxides.	
Acidic properties	**Basic properties**
- demonstrate the properties of a weak acid. Interaction with bases (alkalis) during sintering: $Be(OH)_2 + 2NaOH \rightarrow Na_2BeO_2 + 2H_2O$ sodium beryllate $Fe(OH)_3 + NaOH \rightarrow NaFeO_2 + 2H_2O$ sodium iron oxide in solution (formation of complex salts): $3KOH + Cr(OH)_3 \rightarrow K_3[Cr(OH)_6]$ potassium **hexahydroxo**chromate $2NaOH + Zn(OH)_2 \rightarrow Na_2[Zn(OH)_4]$ sodium **tetrahydroxo**zincate	- demonstrate the properties of weak bases. Interaction with acids: $2Al(OH)_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O$ $Zn(OH)_2 + H_2SO_4 \rightarrow ZnSO_4 + 2H_2O$ acid in excess $Al(OH)_3 + 3H_2SO_4 \rightarrow Al(HSO_4)_3 + 3H_2O$ aluminium hydrogensulphate $Zn(OH)_2 + 2H_2SO_4 \rightarrow Zn(HSO_4)_2 + 2H_2O$ zinc hydrogensulphate basis in excess $2Al(OH)_3 + H_2SO_4 \rightarrow (Al(OH)_2)_2SO_4 + 2H_2O$ aluminium (III) dihydroxysulpate $Al(OH)_3 + H_2SO_4 \rightarrow Al(OH)SO_4 + 2H_2O$ aluminium (III) hydroxysulphate
Interaction with basic oxides (during sintering): $Be(OH)_2 + K_2O \rightarrow K_2BeO_2 + H_2O$ potassium beryllate $2Al(OH)_3 + Na_2O \rightarrow 2NaAlO_2 + 3H_2O$ sodium metaaluminate	Interaction with acidic oxides: $Zn(OH)_2 + ClO_3 \rightarrow ZnClO_4 + H_2O$ $2Cr(OH)_3 + 3SO_3 \rightarrow Cr_2(SO_4)_3 + 6H_2O$
Transformation of hydroxocomplex in Me $K_2[Zn(OH)_4] = 2KOH + Zn(OH)_2 = K_2ZnO_2 + 2H_2O$ $K[Al(OH)_4] = KOH + Al(OH)_3 = KAlO_2 + 2H_2O$ $Ba[Cr(OH)_4] = Ba(OH)_2 + Cr(OH)_3 = Ba(AlO_2)_2 + 2H_2O$	
Formation of hydroxocomplex from amphoteric Me $Be + Sr(OH)_2 + 2H_2O = Sr[Be(OH)_4] + H_2\uparrow$ $2Cr + Ca(OH)_2 + 6H_2O = Ca[Cr(OH)_4]_2 + H_2\uparrow$	

Formation of hydroxocomplex from amphoteric oxides & base Me $CaO + 2Al(OH)_3 + H_2O = Ca[Al(OH)_4]_2$ $ZnO + 2KOH + H_2O = K_2[Zn(OH)_4]$	
Formation	
1. The alkali salts of amphoteric metals:	
with a lack of alkali (droplets): $CrBr_3 + 3KOH \rightarrow Cr(OH)_3\downarrow + 3KBr$	**when excess alkali:** $AlI_3 + 4KOH \rightarrow KAlO_2 + 3KI + 2H_2O$
2. The action of acids on salts of amphoteric metals (Metal included in the acid residue)	
with a lack of acid: $K_2BeO_2 + 2HI \rightarrow Be(OH)_2\downarrow + 2KI$ $NaCrO_2 + HBr + H_2O \rightarrow Cr(OH)_3\downarrow + NaBr$ $2NaAlO_2 + H_2SO_4 + 2H_2O \rightarrow 2Al(OH)_3\downarrow + Na_2SO_4$	**when excess acid:** $Na_2ZnO_2 + 4HCl \rightarrow ZnCl_2 + 2NaCl + 2H_2O$ $NaCrO_2 + 4HCl \rightarrow CrCl_3 + NaCl + 2H_2O$ $2KAlO_2 + 4H_2SO_4 \rightarrow Al_2(SO_4)_3 + K_2SO_4 + 4H_2O$
3. The action of acids on complex salts of amphoteric metals:	
$K_3[Cr(OH)_6] + 3HI \rightarrow Cr(OH)_3\downarrow + 3KI + H_2O$ $Na_2[Zn(OH)_4] + H_2SO_4 \rightarrow Zn(OH)_2\downarrow + Na_2SO_4 + 2H_2O$	**when excess acid:** $Na_3[Cr(OH)_6] + 6HBr \rightarrow CrCl_3 + 3NaBr + 6H_2O$ $K_2[Cu(OH)_4] + 2H_2SO_4 \rightarrow 2CuSO_4 + 2K_2SO_4 + 4H_2O$
4. Hydrolysis of salts of amphoteric hydroxide and a weak acid: $Cr_2S_3 + 6HOH \rightarrow 2Cr(OH)_3\downarrow + 3H_2S\uparrow$ $Al_2(CO_3)_3 + 6HOH \rightarrow 2Al(OH)_3\downarrow + 2CO_2\uparrow$	

ACIDS

Acids — complex substance consisting of hydrogen atoms connected to an acidic residue.
By Arrhenius (According to the theory of electrolytic dissociation) **—** it is a compound which in aqueous solution dissociate into hydrogen cations and anions of the acid residue.
By Lewis: it is a substance that accepts e- pair
By Brønsted-Lowry (According to the proton theory) **—** it is a substance that gives the protons H^+ (proton donor);

Classification		
1. Composition:		
oxygenated:	HNO_2, H_2SO_3, H_3PO_3	
oxygen-free:	HCl, HBr, HI, H_2S	
2. By Basicity (the number of hydrogen atoms capable of substitution on metal)		
monobasic:	HCl, $HClO_2$, $HClO_3$, $HClO_4$, HNO_2,HNO_3, HPO_2, HPO_3, HBO_2	
dibasic:	H_2S, H_2SO_4, H_2CO_3, H_2SiO_3	
tribasic:	H_3PO_3, H_3AsO_3	
tetrabasic:	H_4SiO_4, $H_4P_2O_7$	
3. By Strength:		
strong:	With oxygen	Without oxygen
	$HClO_4$, HNO_3, H_2SO_4	HI, HBr, HCl ←
very strong: $\underline{EO_3}/OH/n$ $H\rightarrow O\rightarrow ClO_3$	$HClO_4$, $HMnO_4$	HCl
weak:	With oxygen EO/OH/n: $H\rightarrow OCl = O^{\delta-}$	Without oxygen ….H-F….H-F.. C≡N

	H_2CO_3, H_2SiO_3, $HClO_2$, H_2CO_3, H_2SO_3, H_3AsO_4, $HAsO_3$, H_3PO_4, HPO_3, $H_4P_2O_7$	H_2S,HF, HCN, HSCN
very weak: E/OH/n: H→O←CI	HIO, HBrO, HClO, H_3AsO_3, $HAsO_2$, H_3BO_3, HBO_2, $H_2B_4O_7$, H_2SiO_3, H_4SiO_4, H_3PO_3	
4. By concentration of the acid solutions:		
concentrated:	HNO_3 (conc.)	
dilute:	HNO_3 (dil.)	
Nomenclature		
the highest oxidation state	the average degree of oxidation	below the oxidation
- ric	- rous	-ide
Chemical properties		
The effect on the indicators:		
Phenolphthalein	Methyl orange	Litmus
colorless (color does not change)	pink	red
Dissociation of acids:		
For monobasic it takes place in one step	$HBr \rightarrow H^+ + Br^-$	
For two (or more) mainly undergo more than one step:	$H_2SO_3 \rightarrow H^+ + HSO_3^-$ $HSO_3^- \rightarrow H^+ + SO_3^{2-}$ In total: $H_2SO_3 \rightarrow 2H^+ + SO_3^{2-}$	
For three it takes place in three step	$H_3PO_4 \rightarrow H^+ + H_2PO_4^-$ $H_3PO_4 \rightarrow H^+ + HPO_4^{2-}$ $H_3PO_4 \rightarrow H^+ + PO_4^{3-}$ In total: $H_3PO_4 \rightarrow 3H^+ + PO_4^{3-}$	
For four it takes place in four step	$2H_3PO_4 \xrightarrow{t} H_4P_2O_7 + H_2O$ $H_4P_2O_7 \leftrightarrow H^+ + H_3P_2O_7^-$ $H_3P_2O_7^- \xleftrightarrow{(OH)^-} H^+ + H_2P_2O_7^{2-}$ $H_2P_2O_7^{2-} \xleftrightarrow{(OH)^-} H^+ + HP_2O_7^{3-}$ $HP_2O_7^{3-} \xleftrightarrow{(OH)^-} H^+ + P_2O_7^{4-}$	
The metals in the electrochemical series of voltages, from magnesium to the hydrogen, displace $H_2\uparrow$. Active metals, e.g. (magnesium) displace $H_2\uparrow$as with acids and water! **(dil. & conc. nitrate and conc. sulphate never displace $H_2\uparrow$):**	$Ca + 2HI \rightarrow CaI_2 + H_2\uparrow$ (the substitution reaction) $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2\uparrow$ $Zn + H_2S \rightarrow ZnS + H_2\uparrow$ $2H_2CO_3 + Mg = H_2\uparrow + Mg(HCO_3)_2$	
With some metals (mainly concentrated solutions): (redox reactions)	$3C + HNO_3 = 3CO_2\uparrow + 4NO\uparrow + 2H_2\uparrow$ $S + 6HNO_3 = H_2SO_4 + 6NO_2 + 2H_2O$	
With bases (neutralization reaction) (exchange reaction) depend on the ratio of the amounts of base and acid reaction products can be on average	$2KOH + H_2SO_4 \rightarrow K_2SO_4 + H_2O$ $3Ca(OH)_2 + 2H_3PO_4 \rightarrow Ca_3(PO_4)_2\downarrow + 6H_2O$ $Mg(OH)_2 + H_2S \rightarrow MgS\downarrow + 2H_2O$ acid in excess — sour salt	

salt.	$Mg(OH)_2 + 2H_2SO_4\ _{excess} \rightarrow Mg(HSO_4)_2 + 2H_2O$ magnesium bisulfate or magnesium hydrogen sulfate If base is in excess — main salt on $Mg(OH)_{2\ excess} + HI \rightarrow Mg(OH)I + H_2O$ only one OH group substitutes one acid residue. magnesium hydroxide $2\ Mg(OH)_{2\ excess} + H_2SO_4 \rightarrow (MgOH)_2SO_4 + 2H_2O$ magnesium hydroxo sulfate
With basic oxides: (exchange reaction)	$MgO + H_2SO_4 \rightarrow MgSO_4 + H_2O$ $Na_2O + 2HI \rightarrow 2NaI + H_2O$
With acidic oxides – displacement of one oxide with another: (exchange reaction)	$I_2O_7 + 2HPO_3 \rightarrow 2HIO_4 + P_2O_5$ $2HClO_4 + P_2O_5 \rightarrow 2HPO_3 + Cl_2O_7$ $H_2SO_4 + P_2O_5 \rightarrow 2HPO_3 + SO_3$
With amphoteric oxides: (exchange reaction)	$ZnO + 2HI \rightarrow ZnI_2 + H_2O$ $Cr_2O_3 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3H_2O$ $2H_3PO_4 + 3BaO = Ba_3(PO_4)_2 + 3H_2O$ $H_3PO_4 + BaO = BaHPO_4 + H_2O$ $2H_3PO_4 + BaO = Ba(H_2PO_4)_2 + H_2O$ $H_3PO_4 + 3BaO = (BaOH)_3PO_4$ $2HCl + ZnO = ZnCl_2 + H_2O$
Amphoteric hydroxides depend on the ratio of the amounts of base and acid reaction products which can be an average salt	$3H_2SO_4 + 2Al(OH)_3 = Al_2(SO_4)_3 + 6H_2O$ aluminium sulfate $3H_2SO_4 + Al(OH)_3 = Al(HSO_4)_3 + 3H_2O$ hydrosulfate of aluminium $H_2SO_4 + Al(OH)_3 = (Al(OH)SO_4 + 3H_2O$ hydroxosulfate of aluminium $H_2SO_4 + 2A1(OH)_3 - (Al(OH)_2)_2SO_4 + 2H_2O$ dihydroxosulfate of aluminium $2Cr(OH)_3 + 3H_2SO_3 \rightarrow Cr_2(SO_3)_3 + 6H_2O$ $Zn(OH)_2 + H_2SO_3 \rightarrow ZnSO_3 + 2H_2O$ acid in excess — sour salt $Cr(OH)_3 + 3H_2SO_3 \rightarrow Cr(HSO_3)_3 + 3H_2O$ cromium hydrogen sulfite or cromium trisulfite $Zn(OH)_2 + 2H_2SO_3 \rightarrow Zn(HSO_3)_2 + 2H_2O$ zinc bisulfite or zinc hydrogen sulfite If base is excess — main salt on $2Cr(OH)_3 + H_2SO_3 \rightarrow (Cr(OH)_2)_2SO_3 + 2H_2O$ one OH groups substitutes one acid residue chromium dihydroxosulfite $Cr(OH)_3 + H_2SO_3 \rightarrow Cr(OH)SO_3 + 2H_2O$ two OH groups substitute one acid residue chromium hydroxosulfite
Salts with weak or volatile acids (exchange reaction) only in the case where the reaction produces a weak electrolyte - insoluble salt or gas:	$H_2SO_4 + BaCl_2 \rightarrow BaSO_4\downarrow + 2HCl$ $H_2SO_4 + Na_2CO_3 = Na_2SO_4 + H_2O + CO_2\uparrow$ $HBr + AgNO_3 \rightarrow AgBr\downarrow + HNO_3$ $H_2SO_4 + K_2CO_3 \rightarrow K_2SO_4 + CO_2\uparrow + H_2O$ $2H_3PO_4 + 3K_2SiO_3 \rightarrow 2K_3PO_4 + 3\ H_2SiO_3$
Decomposition of acids (decomposition	$H_2SiO_3 \xrightarrow{t} H_2O + SiO_2$

reaction) thermal decomposition (decompose at room temperature):	$2HClO_4 \rightarrow Cl_2O_7 + H_2O$ $H_2SO_4 \rightarrow SO_3 + H_2O$ $H_2SO_3 \leftrightarrow H_2O + SO_2\uparrow$ $H_2CO_3 \rightarrow CO_2 + H_2O$ $2H_3PO_4 \overset{t}{=} 3H_2O + P_2O_5$ $2HPO_3 \rightarrow P_2O_5 + H_2O$ But: $HNO_3 \rightarrow NO_2\uparrow + O_2\uparrow + H_2O$

Interaction of oxidising acids (nitric and sulfuric) with metals:

H_2SO_4		HNO_3			
dilute	**concentrated**	**dilute**		**concentrated**	
average activity	active Me			all except Au, Pt	
from Me to H	at T with Cu, Ag, Hg	av. act.	active	av. act.	active
	Depending on the concentration				
$\mathbf{H_2}\uparrow$	$\mathbf{SO_2}$ S $H_2S\uparrow$	**NO**	NH_4NO_3	$\mathbf{NO_2}$	N_2O

Example:

$4Zn + 5H_2SO_4 (c) = 4ZnSO_4 + H_2S\uparrow + H_2O$

$3Zn + 4H_2SO_4 (c) = 3ZnSO_4 + S + 4H_2O$

$Cu + 2H_2SO_4 (c) = CuSO_4 + SO_2\uparrow + H_2O$

$8NaJ + 5H_2SO_4 (c) = 4Na_2SO_4 + H_2S\uparrow(S) + 4J_2 + 4H_2O$

$2NaBr + 2H_2SO_4 (c) = Na_2SO_4 + SO_2\uparrow + Br_2 + 2H_2O$

$2NaCl + H_2SO_4 (c) = Na_2SO_4 + 2HCl\uparrow$ (not oxidized till Cl_2)

$Mg + H_2SO_4 (d) = MgSO_4 + H_2\uparrow$

$4Ca + 10HNO_3(c) = 4Ca(NO_3)_2 + N_2O\uparrow + 5H_2O$

$Cu + 4HNO_3(c) = Cu(NO_3)_2 + 2NO_2\uparrow + 2H_2O$

$4Mg + 10HNO_3(d) = NH_4NO_3 + 4Mg(NO_3)_2 + 3H_20$

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

Formation of acids

1. Direct interaction of Me & Non metal (oxygen-free synthetic method):	$H_2 + Br_2 \rightarrow 2HBr$ $H_2 + S \rightarrow H_2S$
2. Direct interaction with water (acidic oxides):	$SO_2 + H_2O \rightarrow H_2SO_3$ $P_2O_3 + 3H_2O \rightarrow 2H_3PO_3$ $SiO_2 + H_2O \rightarrow H_2SiO_3$
3. Interaction with Non metal:	$P + HNO_2 + H_2O = H_3PO_4 + NO_2\uparrow$ $3P + 5HNO_{3(d)} + 2H_2O = 3H_3PO_4 + 5NO\uparrow$
4. The action of acids with salts, weak or volatile acids:	$H_2SO_{3conc.} + 2NaCl \rightarrow Na_2SO_3 + 2HCl\uparrow$ $2HNO_3 + FeS \rightarrow Fe(NO_3)_2 + H_2S\uparrow$ $H_2SO_{4conc.} + 2NaF \rightarrow Na_2SO_4 + 2HF\uparrow$ $H_2SO_4 + Na_2SiO_3 \rightarrow Na_2SO_4 + H_2SiO_3\downarrow$ But: **HBr and HI — not formed!!!** $2H_2S0_{4(c)} + 2NaCl \rightarrow Cl_2 + SO_2\uparrow + Na_2SO_4 + H_2O$ $5H_2SO_4 + 8NaBr \rightarrow 4Br_2 + H_2S\uparrow + 4Na_2SO_4 + 4H_2O$
5. Hydrolysis of halogen anhydride:	$PBr_5 + 4\ HOH \rightarrow 5HBr\uparrow + H_3PO_4$ phosphorus pentabromide, or anhydride of phosphoric acid $PCl_3 + 3HOH \rightarrow 3HCl\uparrow + H_3PO_3$ phosphorus trichloride phosphoric acid or chloranhydride

	SO_2Br_2+ 2HOH → 2HBr↑ + H_2SO_4 sulphur (VI) bromoxide
6. Some ORR (during heating)	$5Br_2 + I_2 + 6H_2O \rightarrow 10\ HBr + 2HIO_3$
7. The hydrolysis of the salt formed by the strong acid and weak base:	$CrCl_3 + HOH \leftrightarrow Cr(OH)Cl_2 + HCl$ (pH<7).
8. The electrolysis of an aqueous solution of salts of oxygen-containing acids:	$CuSO_4 + 2H_2O \rightarrow 2Cu + O_2\uparrow + 2H_2SO_4$

SALTS

Salts — complex compounds which are the products of complete or partial substitution of hydrogen atoms in the acid on the metal (or metal such group as NH_4^+) or hydroxogroup in the grounds on acid residue.

Classification

Salts				
Sour salt	**Average salt**	**Basic salt**	**Mixed salts**	**Double salt**
Products partial substitution of H atoms in acids at **Me**	Products complete replacement of H atoms in acids at **Me**	Products partial substitution of OH groups in the basics at **Me**	Products simultaneous substitution of OH groups in the base **of various acid residues**	Products simultaneous substitution of H atoms in acids on **various metal**
Soluble in water. Dissociate into cations Me^+ **H^+** and anions acid residue	Water-soluble salt dissociate only cations Me (NH_4^+) and anions acid residue	Dissociate into cations Me^+ anions **OH^-** and acid residues	Dissociate only cations Me^+ (NH_4^+) and anions of acid	Dissociate only on the various cations Me^+ (NH_4^+) and anions acid residue
$NaHSO_4$ $Mg(HSO_4)_2$ $Cr(HSO_4)_3$ NaH_2PO_4 Na_2HPO_4	$FeCl_2$ $Ca(NO_3)_2$ $Al_2(SO_4)_3$ Na_3PO_4 Peroxides, binary mixed oxides (Me & Non Me)	$Mg(OH)Cl$ $(MgOH)_2SO_4$ $Cr(OH)SO_4$ $(Cr(OH)_2)_2SO_4$	$MgClBr$ $Mg(OCl)_2$	$KNaSO_4$ Na_2KPO_4
Complex salts (Complex compounds)				
Average salt Nomenclature				
	Me	V	Name acid residue	Compound name
$FeBr_2$	iron	(II)	bromide	iron (III) bromide
$Ca(NO_3)_2$	calcium	(II)	nitrate	calcium nitrate
$Al_2(SO_4)_3$	aluminium	(III)	sulfate	aluminium (III) sulfate
Na_3PO_4	sodium	(I)	phosfate	sodium phosphate
NaCl	sodium	(I)	cloride	sodium cloride
KNO_3	potassium	(I)	nitrate	potassium nitrate

Sour salt					
	Me		V	Name acid residue Hydrogen	Compound name
$NaHSO_4$	potassium sodium		(I)		sodium hydrogen sulfate
$Mg(HSO_4)_2$	magnesium		(II)		magnesium hydrogen sulfate
NaH_2PO_4	potassium		(I)		potassium dihydrogen phosphate
Na_2HPO_4	potassium		(I)		potassium hydrogen phosphate
Basic salt					
	Me		V	Name base residue Hydroxo	Compound name
$Mg(OH)Cl$	magnesium		(II)		magnesium hydroxo chloride
$(MgOH)_2SO_4$	magnesium		(II)		magnesium hydroxo sulfate
$Cr(OH)SO_4$	crominum		(III)		crominum hydroxosulfate
$(Cr(OH)_2)_2SO_4$	crominum		(III)		crominum dihydroxosulfate
Mixed salt					
	Me	V	Name acid residue 1	Name acid residue 2	Compound name
CaClI	calcium	(II)	chloride	iodide	calcium chloride-iodide
$Ca(OBr)_2$	calcium	(II)	oxygen	bromide	calcium bromide-hypobromite
(CaCl(OCl)	calcium	(II)	chloride	oxygen, chloride	bleaching powder
Double salt					
	Me 1	Me 2	V	Name acid residue	Compound name
$KNaSO_4$	potassium	sodium	(II)	sulfate	potassium sodium sulphate
Na_2KPO_4	sodium	potassium	(III)	phosfate	sodium potassium phosphate
$NaFePO_4$	sodium	iron	(III)	phosfate	sodium iron (II) phosphate
Oxosalt					
	Me	V	Name acid residue 1	Name acid residue 2	Compound name
SbOCl	bismuth	(III)	oxygen	chloride	antimony (III)

					oxychloride
$ThOSO_4$	thorium	(III)	oxygen	sulphate	thorium (IV) octasulphate

Chemical properties **Sour salt**	
1) Interaction with the bases (base oxides). The neutralization reaction (to average salt): **with the same cations** → only one salt acidic salt of an alkali metal → average or less acidic salt:	$KH_2PO_4 + 2KOH \rightarrow K_3PO_4 + 2H_2O$ (the excess basis) $KH_2PO_4 + KOH \rightarrow K_2HPO_4 + 2H_2O$ (the lack of fundamentals)
acid salt of alkaline-earth metal:	$3KH_2PO_4 + 3Ca(OH)_2 \rightarrow K_3PO_4 + Ca_3(PO_4)_2 + 6H_2O$ $2KH_2PO_4 + Ca(OH)_2 \rightarrow K_2HPO_4 + CaHPO_4 + 2H_2O$ $Mg(HSO_4)_2 + 2KOH \rightarrow Mg(OH)_2\downarrow + 2KHSO_4$ or $Mg(HSO_4)_2 + 4KOH \rightarrow Mg(OH)_2\downarrow + 2K_2SO_4 + 2H_2O$ $Al(HSO_4)_3 + 3NaOH \rightarrow Al(OH)_3\downarrow + 3NaHSO_4$ or $Al(HSO_4)_3 + 6NaOH \rightarrow Al(OH)_3\downarrow + 3Na_2SO_4 + 3H_2O$
with various cations → two medium salt:	$Mg(HSO_4)_2 + Ca(OH)_2 \rightarrow MgSO_4\downarrow + CaSO_4\downarrow + H_2O$ $3KH_2PO_4 + 3Mg(OH)_2 \rightarrow K_3PO_4 + Mg_3(PO_4)_2\downarrow + 6H_2O$
with a lack of fundamentals → two acidic salt with less at. H: (only for salts tribasic acids)	$2KH_2PO_4 + Mg(OH)_2 \rightarrow K_2HPO_4 + MgHPO_4 + H_2O$ $Mn(HSO_4)_2 + 2KOH \rightarrow Mn(OH)_2\downarrow + 2KHSO_4$ $Cr(HSO_4)_3 + 3NaOH \rightarrow Cr(OH)_3\downarrow + 3NaHSO_4$
2) Interaction with acids (acidic oxides) :	$Ca(HCO_3)_2 + H_2SO_4 \rightarrow CaSO_4\downarrow + 2H_2O + 2CO_2\uparrow$ $CaHPO_4 + H_2SO_4 \rightarrow CaSO_4\downarrow + H_3PO_4$
3) Interaction with salts (exchange reaction) with average salts: (only in the case where the products are insoluble in water):	$K_2HPO_4 + SrCl_2 \rightarrow SrHPO_4\downarrow + 2KCl$ with acid salts $2KH_2PO_4 + Sr(HSO_4)_2 \rightarrow KHSO_4 + SrHPO_4\downarrow + 2H_2O$ basic salts $KHS + Cu(OH)Br \rightarrow CuS\downarrow + KBr + H_2O$ $ZnOHNO_3 + NaHS \rightarrow ZnS\downarrow + NaNO_3 + H_2O$ $2KHS + (Mg(OH))_2SO_4 \rightarrow 2MgS\downarrow + K_2SO_4 + 2H_2O$
4) Thermal decomposition:	$2KHCO_3 \rightarrow K_2CO_3 + CO_2\uparrow + H_2O$ $Mg(HCO_3)_2 \rightarrow MgCO_3\downarrow + CO_2\uparrow + H_2O$ $2K_2HPO_4 \rightarrow 2K_3PO_4 + H_3PO_4$
Basic salt	
1) Interaction with acids (acidic oxides) → (to average or less basic salt): **with the same anions (acidic residues)** → only one salt (neutralization reaction):	$Fe(OH)_2Cl + 2HCl \rightarrow FeCl_3 + 2H_2O$ (excess acid → only average salt) $Fe(OH)_2Cl + HCl \rightarrow Fe(OH)Cl_2 + 2H_2O$ (the lack of acid → only one less basic salt)
with various anions (acidic residues) → two salt (excess acid → two averrage of salt):	$3Cr(OH)_2NO_3 + 3H_2SO_4 \rightarrow Cr(NO_3)_3 + Al_2(SO_4)_3 + H_2O$ aluminum nitrate aluminum sulfate $2Cr(OH)_2NO_3 + H_2SO_4 \rightarrow CrOH(NO_3)_2 + Cr(OH)SO_4 + 2H_2O$

(the lack of acid → two less basic salt):	aluminum hydroxo nitrate aluminum hydroxo sulfate
2.) Interaction with salts: (only in the case where the products are insoluble in water): (exchange reaction) :	with acid salts $FeOHBr + NaHS \rightarrow FeS + NaBr + H_2O$ with average salts $Sn(OH)NO_3 + FeSO_4 \rightarrow SnSO_4 + Fe(OH)NO_3$
3. Thermal decomposition:	$(CuOH)_2CO_3 \rightarrow 2CuO + CO_2\uparrow + H_2O$
Average salt	
1) Interaction with acids: (exchange reaction)	$BaCl_2 + H_2SO_4 \rightarrow BaSO_4\downarrow + 2HCl$ $AgNO_3 + HBr \rightarrow AgBr\downarrow + HNO_3$ $K_2CO_3 + H_2SO_4 \rightarrow K_2SO_4 + CO_2\uparrow + H_2O$ $3K_2SiO_3 + 2H_3PO_4 \rightarrow 2K_3PO_4 + 3H_2SiO_3\downarrow$ $Mg_3N_2 + 6HBr \rightarrow 3MgBr_2 + 2NH_3\uparrow$ $Mg_3P_2 + 6HCl \rightarrow 3MgCl_2 + 2PH_3\uparrow$ $BaO_2 + HBr \rightarrow BaBr_2 + H_2O_2$ $Na_2O_2 + 2HI \rightarrow NaI + H_2O_2$
2) Acidic oxides:	$K_2SiO_3 + SO_3 \rightarrow K_2SO_4 + SiO_2\downarrow$ $MgCO_3\downarrow + CO_2 + H_2O \rightarrow Mg(HCO_3)_2$ $Al_2O_3 + Na_2CO_3 \rightarrow NaAlO_2 + CO_2\downarrow$ $K_2CrO_4 + CrO_3 \rightarrow K_2Cr_2O_7$
3)Interaction with alkalis and bases (a method of extraction of insoluble bases):	$CuSO_4 + 2KOH \rightarrow Cu(OH)_2\downarrow + 2K_2SO_4$ $NiSO_4 + 2NaOH \rightarrow Ni(OH)_2\downarrow + Na_2SO_4$ $CaBr_2 + Ca(OH)_2 \rightarrow 2Ca(OH)Br$
4) Interaction with base:	$K_2O + KPO_3 \rightarrow K_3PO_4$ $CaO + CaSiO_3 \rightarrow Ca_2SiO_4$
5) Interaction with other average salts:	$BaCl_2 + Na_2SO_4 \rightarrow BaSO_4\downarrow + 2NaCl$ $AgNO_3 + KCl \rightarrow AgCl\downarrow + KNO_3$
6) Displacement of metals from salts (more active metal in a range of activities to the left — push from salts are less active) :	$CuSO_4 + Fe \rightarrow FeSO_4 + Cu\downarrow$ $CdSO_4 + Zn \rightarrow ZnSO_4 + Cd\downarrow$
7) Reaction disproportionation (if the element acid residue is the average degree of oxidation):	$4K_2SO_3 \rightarrow K_2S + 3K_2SO_4$ $2NaBrO_2 \rightarrow NaBr + NaBrO_4$
8) Thermal decomposition of salts. The sulfate salt of without oxygen acid and alkali metal, in addition to nitrate does not decompose. In some stress of metals	nitrates to magnesium → $MeNO_2 + O_2\uparrow$ from magnesium to cuprum → $MeO + NO_2 + O_2\uparrow$ after the cuprum → $Me + NO_2 + O_2\uparrow$ ammonium salts $NH_4NO_2 \rightarrow N_2\uparrow + 2H_2O$ $NH_4NO_3 \rightarrow N_2O\uparrow + 2H_2O$ carbonates $CaCO_3 \rightarrow CaO + CO_2\uparrow$
9) Hydration salts: (formation of hydrates)	$CuSO_4 + 5H_2O \rightarrow CuSO_4 \bullet 5H_2O$ copper sulphate or cuprum (II) sulfate pentahydrate $CaCl_2 + 2H_2O \rightarrow CaCl_2 \bullet 2H_2O$ calcium chloride dehydrate

NOMENCLATURE OF INORGANIC COMPOUNDS
(CHEMICAL, TRIVIAL)

ELEMENT	ELEMENT FORMULA	CHEMICAL NAME PREFERRED IUPAC NAME	COMMON NAME
I - A group			
H	H_2O_2	Hydrogen peroxide	Dioxidane; Oxidanyl
Li	LiOH	Lithium hydroxide	Lithine
	Li_2CO_3	Lithium carbonate	Dilithium carbonate; Carbolith; Cibalith-S; Duralith; Eskalith; Lithane; Lithizine; Lithobid; Lithonate; Lithotabs Priadel; Zabuyelite
	LiCl	Lithium chloride	Lithium(1+) chloride
	Li_3N	Lithium nitride	Trilithium nitride
Na	NaOH	Sodium hydroxide	Caustic soda; Lye; Ascarite; White caustic; Sodium hydrate
	NaCl	Sodium chloride	Rock salt; Halite(mineral)
	Na_2CO_3	Sodium carbonate	Washing soda; Soda ash and Soda crystals
	$NaHCO_3$	Sodium hydrogen carbonate	Drinking soda; Baking soda; Bread soda; Cooking soda; and Bicarbonate of soda
	$NaNO_3$	Sodium nitrate	Caliche; Chile saltpeter; Nitrate of soda; Nitratine; Peru saltpeter; Soda niter; Cubic niter
	$Na_2SO_4 \cdot 10\ H_2O$	Sodium sulfate hydrated	Thenardite (mineral); Glauber's salt (decahydrate); Sal mirabilis (decahydrate); Mirabilite (decahydrate)
	$Na_2O \cdot CaO \cdot 6SiO_2$		Glass window
K	KCl	Potassium chloride	Sylvite; Muriate of potash
	$KCl \cdot NaCl$	Potassium-Sodium chloride	Silvinit
	$KCl \cdot MgSO_4 \cdot 3H_2O$	Potassium chloride and magnesium sulfate	Kainite
	KNO_3	Potassium nitrate	Saltpetre; Nitrate of potash
	KNO_3+S+C		Gunpowder black

I - B group			
Cu	Cu (92%)	Copper	Native copper
	$CuFeS_2$		Copper pyrite; Chalcopyrite (mineral)
	Cu_2S	Cuprum (I) sulfide	Cuprous sulfide; Chalcocite; Copper glance
	$CuSO_4 \cdot 5H_2O$	Cuprum sulfate hydrated	Bordeaux mixture
	Cu + Zn		Brass
	Cu + Al, Cu +Sn and other		Bronze
	$Cu(OH)_2 \cdot CuCO_3$	Copper carbonate hydroxide	Malachite
	$Cu(CH_3COO)_2 \cdot H_2O$	Cuprum acetate	Verdigris
	$Cu(CH_3COO)_2 \cdot Cu_3(AsO_3)_2$	Cuprum acetate-arsenium mixed	Paris green
II -A group			
Mg	MgO	Magnesium oxide	Magnesia; Periclase
	$3MgO \cdot 4SiO_2 \cdot H_2O$	Hydrated magnesium silicate	Talc
	$MgSO_4 \cdot 7H_2O$	Magnesium sulfate	Epsom salt (heptahydrate); English salt; Bitter salts
	$3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$		White magnesia
	CaO	Calcium oxide	Quicklime; Burnt lime; Unslaked lime; Pebble lime
Ca	$Ca(OH)_2$	Calcium hydroxide	Slaked lime; Calcium(II)hydroxide; Pickling lime; Hydrated lime; Portlandite; Calcium hydrate
	$Ca(OH)_2$	Calcium hydroxide (a saturated solution)	Quicklime water
	$Ca(OH)_2$	Calcium hydroxide (suspension)	Milk of lime
	$Ca_3(PO_4)_2$	Calcium phosphate or calcium orthophosphate	Phosphorit (mineral)
	$Ca_3(PO_4)_2 + CaF_2$ ($CaCl_2$)		Apatite (mineral)
	$CaSO_4 \cdot 2H_2O$	Calcium sulfate dihydrate	Gypsum
	$2CaSO_4 \cdot H_2O$	Dicalcium sulfate hydrate	Burnt gypsum
	$CaCO_3$	Calcium carbonate	Limestone; Calcite; Aragonite; Chalk; Marble; Pearl; Oyster
	$Ca(NO_3)_2$	Calcium nitrate	Kalksalpeter;

			Nitrocalcite; Norwegian saltpeter; Lime nitrate
Ba	$Ba(OH)_2$	Barium hydroxide	Baryta or baryta-water
II - B group			
Hg	Hg_2Cl_2	Dimercury dichloride	Mercurous chloride, Calomel
	$HgCl_2$	Mercury(II) chloride; Mercury dichloride	Mercuric chloride; Corrosive sublimate
III - A group			
B	H_3BO_3	Boric acid; Trihydrooxidoboron	Orthoboric acid; Boracic acid,; Sassolite; Optibor; Borofax; Trihydroxyborane;
Al	Al_2O_3	Aluminum oxide	Alumina; Aloxide; Aloxite or alundum
	Al_4C_3	Aluminium carbide	Aluminum carbide
	$KAl(SO_4)_2 \cdot 12H_2O$	Aluminium potassium sulfate dodecahydrate	Potassium alum; Potash alum; Alum-(K)
IV - A group			
C	C	Carbon	Coke; Diamond; Graft; Carbon; Fulleren
	CO	Carbon monoxide; Carbon(II) oxide	Carbon monooxide; Carbonous oxide; Carbonyl; Flue gas Monoxide;
	CO_2	Carbon (IV) oxide	Carbonic acid gas; Carbonic anhydride; Carbonic oxide; Carbon oxide;
	CO_2 (solid phase)	Carbon (IV) oxide	Dry ice
	H_2CO_3	Carbonic acid	Carbon dioxide solution; Dihydrogen carbonate; Acid of air; Aerial acid; Hydroxymethanoic acid
	HCN	Formonitrile (substitutive); Hydridonitridocarbon	Formic anammonide; Hydrocyanic acid; Prussic acid; Methanenitrile
	CS_2	Methanedithione	Carbon bisulfide
	CaC_2	Calcium carbide	
	$CaCO_3$	Calcium carbonate	Limestone; Calcite; Aragonite; Chalk; Marble; Pearl; Oyster
	CO -27,5%; H_2 – 9,5% CO_2 - 4% N_2 – 59%		Producer gas
Si	SiO_2	Silicon dioxide	Quartz; Silica; Silicic oxide; Silicon(IV) oxide; Crystalline silica

	SiC	Silicon carbide	Carborundum; Moissanite
V - A group			
N	NH_3	Ammonia or azane	Hydrogen nitride; Trihydrogen nitride; Nitro-Sil
	NH_4OH	Ammonium hydroxide	Ammonia solution, Ammonium hydroxide; Ammonia water; Ammonical liquor; Ammonia liquor; Aqua ammonia; Aqueous ammonia or Simply ammonia
	NH_4Cl	Ammonium chloride	Sal ammoniac; Salmiac; Nushadir salt; Sal Armagnac; Salt armoniack
	$NH_4H_2PO_4$	Ammonium dihydrogen phosphate	Monoammonium phosphate; Ammophos
	$(NH_4)_2HPO_4$	Diammonium hydrogen phosphate	Ammonium monohydrogen phosphate; Ammonium phosphate dibasic
	N_2O	Dinitrogen monoxide; nitrogen (I) oxide	Laughing gas; Sweet air; Protoxide of nitrogen; Hyponitrous oxide
	N_2O_3	Dinitrogen trioxide; nitrogen (III) oxide	Nitrous anhydride, nitrogen sesquioxide
	N_2O_5	Dinitrogen pentaoxide; nitrogen (V)oxide	Nitric anhydride; Nitronium nitrate; Nitryl nitrate; DNPO; Anhydrous nitric acid
	NO_2	Nitrogen dioxide; nitrogen (IV) oxide	Deutoxide of nitrogen
	1valueHNO_3 + 3 value HCl	Nitro-hydrochloric acid	Aqua regia
P	$Ca_5(PO_4)_3(F,Cl, OH)$		Apatite
	P_2O_3	Phosphorus(III) oxide	Phosphorus(III) oxide; Phosphorus sesquioxide; Phosphorous oxide; Phosphorous anhydride
	P_2O_5	Phosphorus pentoxide; phosphorus (V) oxide	Diphosphorus pentoxide; Phosphorus(V) oxide; Phosphoric anhydride; Tetraphosphorus decaoxide; Tetraphosphorus decoxide;
	$Ca_3(PO_4)_2$	Tricalcium	Tribasic calcium

		bis(phosphate)	phosphate
	$Ca_3(PO_4)_2 + CaF_2$ ($CaCl_2$)		Apatite (mineral)
	$Ca(H_2PO_4)_2 + CaSO_4$		Superphosphate
	$Ca(H_2PO_4)_2$	Calcium dihydrogen phosphate; Mono-calcium orthophosphate	Double superphosphate
	$CaHPO_4$	Monohydrophosphate calcium	
	$NH_4H_2PO_4$	Ammonium dihydrogen phosphate	Monoammonium phosphate; Ammophos
	$(NH_4)_2HPO_4$	Diammonium hydrogen phosphate	Ammonium monohydrogen phosphate; Ammonium phosphate dibasic
	$(NH_4)_2HPO_4 + NH_4NO_3 + KCl$	Ammonium hydrogen phosphate, Ammonium nitrate, Potassium chloride	Nitrophos
As	As_2O_3	Diarsenic trioxide;	Arsenic(III) oxide; Arsenic sesquioxide; Arseneous oxide; Arseneous anhydride; White arsenic
IV - A group			
O	O_2	Oxygen	Oxygen
	O_3	Ozone	Ozone
S	SO_2	Sulphur (IV) oxide	Sulfur dioxide
	SO_3	Sulphur (VI) oxide; Sulfur trioxide	Sulfonylideneoxidane
	FeS_2	Iron sulphide	Iron pyrite or pyrite
	ZnS	Zinc sulfide	Zincblende; Wurtzite
	PbS	Lead (II) sulfide	Plumbous sulfide; Galena; Sulphuret of lead
	Cu_2S	Copper (I) sulfide	Cuprous sulfide; Chalcocite; Copper glance
	$CaSO_4 \cdot 2H_2O$	Calcium sulfate dihydrate	Gypsum
	$Na_2SO_4 \cdot 10H_2O$	Sodium sulfate hydrated	Glauber’s salt
	$FeSO_4 \cdot 7H_2O$	Iron(II) sulfate	Ferrous sulfate; Green vitriol; Iron vitriol; Copperas; Melanterite; Szomolnokite
VI- B group			
Cr	$KCr(SO_4)_2 \cdot H_2O$	Chromium(III) potassium sulfate	Chromium alum

	$Na_2Cr_2O_7$	Sodium dichromate	Chromic acid disodium salt
	$K_2Cr_2O_7$	Potassium dichromate	Potassium bichromate; Bichromate of potash; Dipotassium Dichromate; Dichromic acid; Dipotassium salt; Chromic acid; Dipotassium salt; Lopezite;
	$PbCrO_4$	Lead(II) chromate	Yellow crowns
VII group			
F	CaF_2	Calcium fluoride	Fluorite (fluorspar) (mineral)
	Na_3AlF_6	Sodium hexafluoroaluminate	Cryolite (mineral)
	$CaF_2 \cdot Ca_3(PO_4)_2$	Calcium fluoride - calcium phosfate	Fluoapatite (mineral)
Cl	KCl	Potassium chloride	Sylvite Muriate of potash
	KCl· NaCl	Potassium-sodium chloride	Silvinit (mineral)
	$KCl \cdot MgCl_2 \cdot 6H_2O$	Potassium magnesium chloride	Carnallite (mineral)
	HCl	Hydrogen chloride	Hydrochloric acid gas; Hydrochloride
	$CaCl_2 \cdot Ca(OCl)_2$ ($CaOCl_2$)	Calcium hypochlorite	Hypochlorous acid; Calcium salt; Bleaching powder; Calcium oxychloride
	$KClO_3$	Potassium chlorate	Potassium chlorate(V); Potcrate
VII–B group			
Mn	MnO_2	Manganese(IV) oxide	Manganese dioxide; Proludic (mineral)
	$KMnO_4$	Potassium manganate(VII)	Potassium permanganate; Chameleon mineral; Condy's crystals; Permanganate of potash; Hypermangan
VIII –A group			
Fe	Fe_2O_3	Iron(III) oxide	Ferric oxide; Hematite; Ferric iron; Red iron oxide; Rouge; Maghemite; Colcothar; Iron sesquioxide; Rust; Ochre
	$2Fe_2O_3 \cdot 3H_2O$	Several hydrates of iron(III) oxide	Brown ironstone

	Fe_3O_4	Iron (II,III) oxide	Ferrous ferric oxide, Ferroso ferric oxide, Magnetite, Black iron oxide, Lodestone, rust, Iron(II) diiron(III) oxide
	FeS_2	Iron sulfide	White iron pyrite Marcasite (mineral)
	$FeCO_3$	Iron(II) carbonate	Siderite (mineral)
	$FeSO_4 \cdot 7H_2O$	Hydrous iron(II) sulfate	Iron vitriol; Melanterite (mineral)
	$(NH_4)Fe(SO_4)_2 \cdot 12H_2O$	Ammonium iron(III) sulfate	Ferric ammonium sulfate; Ferric alum
	$K_4[Fe(CN)_6] \cdot 3H_2O$	Potassium hexacyanidoferrate(II)	(Yellow) Prussiate of Potash; Potassium hexacyanoferrate (II) trihydrate; Tetrapotassium ferrocyanide trihydrate; Ferrate hexacyano tetrapotassium trihydrate
	$K_3[Fe(CN)_6] \cdot 3H_2O$	Potassium hexacyanoferrate(III)	Red prussiate of Potash; Prussian red; Potassium ferricyanide
	$Fe_4[Fe(CN)_6]_3$	Iron(III) hexacyanoferrate(II)	Berlin blue; Ferric ferrocyanide; Ferric hexacyanoferrate; Iron(III) ferrocyanide; Parisian blue
	$Fe_3[Fe(CN)_6]_2$	Iron(III) hexacyanoferrate(II)	Turnbull’s blue

THE SOLUBILITY TABLE

	OH^-	F^-	Cl^-	Br^-	I^-	S^{2-}	HS^-	SO_3^{2-}	HSO_3^-	SO_4^{2-}	HSO_4^-	NO_3^-	NO_2^-	PO_4^{3-}	CO_3^{2-}	HCO_3^-	CH_3COO^-
H^+		S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
Li^+	S	s	S	S	S	S	S	S	?	S	S	S	S	I	S	S	S
K^+	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
Na^+	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
NH_4^+	S	S	S	S	S	S	S	S	S	S	S	S	S	-	S	S	S
Ba^{2+}	S	s	S	S	S	-	S	I	S	I	?	S	S	I	I	S	S
Ca^{2+}	s	I	S	S	S	-	S	I	S	s	?	S	S	I	I	S	S
Mg^{2+}	I	I	S	S	S	-	S	s	S	S	?	S	S	S	I	S	S
Sr^{2+}	s	I	S	S	S	I	S	I	S	I	-	S	S	I	I	S	S
Al^{3+}	I	s	S	S	S	-	?	?	?	S	?	S	?	I	?	?	-
Cr^{3+}	I	I	S	S	?	-	?	-	?	S	?	S	?	I	?	?	S
Fe^{2+}	I	I	S	S	S	I	?	I	?	S	?	S	?	I	I	S	S
Fe^{3+}	I	I	S	S	?	-	?	?	?	S	?	S	?	I	?	?	-
Ni^{2+}	I	I	S	S	S	I	?	I	?	S	?	S	?	I	I	?	S
Co^{2+}	I	I	S	S	S	I	I	I	?	S	?	S	s	I	I	?	S
Mn^{2+}	I	I	S	S	S	I	?	?	?	S	?	S	?	I	I	?	S
Zn^{2+}	I	I	S	S	S	I	?	s	?	S	?	S	?	I	I	?	S
Ag^+	-	-	I	I	I	I	?	I	?	s	?	S	s	I	I	?	S
Hg^{2+}	-	-	S	s	I	I	?	I	?	-	?	S	?	I	?	?	S
Pb^{2+}	I	I	s	s	I	I	?	I	?	I	I	S	?	I	I	S	S
Sn^{2+}	I	I	S	S	s	I	?	?	?	S	?	-	?	I	?	?	-
Cu^{2+}	I	I	S	S	S	I	?	?	?	S	?	S	?	I	I	?	S

S	- soluble in water
s	- slightly soluble in water
I	- insoluble in water

THE MOLECULAR WEIGHT TABLE

	O^{2-}	OH^-	Cl^-	Br^-	I^-	NO_3^-	S^{2-}	SO_3^{2-}	SO_4^{2-}	CO_3^{2-}	SiO_3^{2-}	PO_4^{3-}
H^+		18	36,5	81	128	63	34	82	98	62	78	98
K^+	94	56	74,5	119	166	101	110	158	174	138	154	212
Na^+	62	40	58,5	103	150	85	78	126	142	106	122	164
NH_4^+		35	53,5	98	145	80	68	116	132	96	112	149
Ba^{2+}	153	171	208	297	391	261	169	217	233	197	213	601
Ca^{2+}	56	74	111	200	294	164	72	120	136	100	116	310
Mg^{2+}	40	58	95	184	278	148	56	104	120	84	100	262
Al^{3+}	102	78	133,5	267	408	213	150	294	342	234	282	112
Cr^{3+}	152	103	158,5	292	433	238	200	344	392	284	332	147
Fe^{2+}	72	90	127	216	310	180	88	136	152	116	132	358
Fe^{3+}	160	107	162,5	296	437	242	208	352	400	292	340	151
Mn^{2+}	71	89	126	215	309	179	87	135	151	115	131	355
Zn^{2+}	81	99	136	225	319	189	97	145	161	125	141	385
Ag^+	232	125	143,5	188	235	170	248	296	312	276	292	419
Pb^{2+}	223	241	278	367	461	331	239	287	303	267	283	811
Cu^{2+}	80	98	135	224	318	188	96	144	160	124	140	382

THE TABLE OF ELECTRONEGATIVITIES

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**
Rb 0,8	**Sr** 1,0	**Y** 1,3	**Zr** 1,4	**Nb** 1,6	**Mo** 1,8	**Tc**	**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**
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**
Fr 0,7	**Ra** 0,9	**Ac** 1,1															
		Ce 1,1	**Pr** 1,1	**Nd** 1,2	**Pm**	**Sm** 1,2	**Eu** 1,2	**Gd** 1,1	**Tb** 1,2	**Dy** 1,2		**Ho** 1,2	**Er** 1,2	**Tm** 1,2	**Yb** 1,1		
		Th 1,3	**Pa** 1,5	**U** 1,7													

THE PERIODIC TABLE

Hydrogen does not belongs to any definite group. It forms compounds by either donating an electron like an alkali metal or accepting an electron like a

Alkali Metals are very reactive and readily form compounds but coudn't be found free in nature. They form salts and *alkali* (acid-neutralizing) compounds such as baking soda. In pure form, they are very soft metals which catch fire contacting with water.

Alkali Earth Metals are reactive and readily form compounds but couldn't be found free in nature. Their oxides are called *alkali earth metals*. In pure form, they are soft and somewhat brittle

Transition Metals are typical metals; they are strong, shiny) and they conduct both heat and electricity.

	1	2	3	4	5	6	7	8	9
1	1 *H* 1,008 Hydrogen $1s^1$								
2	3 Li 6,941 Lithium $[He]\ 2s^1$	4 Be 9,0122 Beryllium $[He]\ 2s^2$							
3	11 Na 22,990 Sodium $[Ne]\ 3s^1$	12 Mg 24,305 Magnesium $[Ne]\ 3s^2$							
4	19 K 39,098 Potassium $[Ar]\ 4s^1$	20 Ca 40,078 Calcium $[Ar]\ 4s^2$	21 Sc 44,956 Scandium $[Ar]\ 3d^1\ 4s^2$	22 Ti 47,867 Titanium $[Ar]\ 3d^2\ 4s^2$	23 V 50,942 Vanadium $[Ar]\ 3d^3\ 4s^2$	24 Cr 51,996 Chromium $[Ar]\ 3d^5\ 4s^1$	25 Mn 54,938 Manganese $[Ar]\ 3d^5\ 4s^2$	26 Fe 55,845 Iron $[Ar]\ 3d^6\ 4s^2$	27 Co 58,933 Cobalt $[Ar]\ 3d^7\ 4s^2$
5	37 Rb 85,468 Rubidium $[Kr]\ 5s^1$	38 Sr 87,62 Strontium $[Kr]\ 5s^2$	39 Y 88,906 Yttrium $[Kr]\ 4d^1\ 5s^2$	40 Zr 91,224 Zirconium $[Kr]\ 4d^2\ 5s^2$	41 Nb 92,906 Niobium $[Kr]\ 4d^3\ 5s^2$	42 Mo 95,96 Molybdenum $[Kr]\ 4d^5\ 5s^1$	43 *Tc* [97,91] Technetium $[Kr]\ 4d^5\ 5s^2$	44 Ru 101,07 Ruthenium $[Kr]\ 4d^7\ 5s^1$	45 Rh 102,905 Rhodium $[Kr]\ 4d^8\ 5s^1$
6	55 Cs 132,91 Cesium $[Xe]\ 6s^1$	56 Ba 137,33 Barium $[Xe]\ 6s^2$	57-71 Rare Earth Metals	72 Hf 178,49 Hafnium $[Xe]\ 4f^{14}\ 5d^2\ 6s^2$	73 Ta 180,95 Tantalum $[Xe]\ 4f^{14}\ 5d^3\ 6s^2$	74 W 183,84 Tungsten $[Xe]\ 4f^{14}\ 5d^4\ 6s^2$	75 Re 186,21 Rhenium $[Xe]\ 4f^{14}\ 5d^5\ 6s^2$	76 Os 190,23 Osmium $[Xe]\ 4f^{14}\ 5d^6\ 6s^2$	77 Ir 192,22 Iridium $[Xe]\ 4f^{14}\ 5d^7\ 6s^2$
7	87 Fr [223.02] Francium $[Rn]\ 7s^1$	88 Ra [226,06] Radium $[Rn]\ 7s^2$	89-103 Actinide Metals	104 *Rf* [265,12] Ruther-fordium $[Rn]\ 5f^{14}\ 6d^2\ 7s^2$	105 *Db* [268,13] Dubnium $[Rn]\ 5f^{14}\ 6d^3\ 7s^2$	106 *Sg* [271,13] Seaborgium $[Rn]\ 5f^{14}\ 6d^4\ 7s^2$	107 *Bh* [270] Bohrium $[Rn]\ 5f^{14}\ 6d^5\ 7s^2$	108 *Hs* [277,15] Hassium $[Rn]\ 5f^{14}\ 6d^6\ 7s^2$	109 *Mt* [276,15] Meitnerium $[Rn]\ 5f^{14}\ 6d^7\ 7s^2$

Rare Earth Metals are all soft metals.

Actinide Metals are all radioactive heavy metals.

57 La 138,91 Lanthanum	58 Ce 140,12 Cerium	59 Pr 140,91 Praseodymium	60 Nd 144,24 Neodymium	61 Pm [144,91] Promethium	62 Sm 150,36 Samarium
89 Ac [227,03] Actinium	90 Th 232,04 Thorium	91 Pa 231,04 Protactinium	92 U 238,03 Uranium	93 Np [237,05] Neptunium	94 Pu [244,06] Plutonium

OF THE ELEMENTS

Nobel Gases are inactive, or inert. Each atom has exactly number of electrons which it needs to have a full outher shell, so these atoms almost never bond with other atoms. That is why these are all gases.

Halogens are reactive nonmetals and readily form compounds but couldn't be found free in nature. They combine with alkali metals to form salts (halogen means salt-former).

Nonmetals, in their solid state, are usually brittle (they break rather than bend) and they are insulators of both heat and elecricity.

10	11	12	13	14	15	16	17	18
								2 **He** 4,0026 Helium [He] 1s²
			5 **B** 10,811 Boron [He] 2s² 2p¹	6 **C** 12,011 Carbon [He] 2s² 2p²	7 **N** 14,007 Nitrogen [He] 2s² 2p³	8 **O** 15,999 Oxygen [He] 2s² 2p⁴	9 **F** 18,998 Fluorine [He] 2s² 2p⁵	10 **Ne** 20,179 Neon [He] 2s² 2p⁶
			13 **Al** 26,982 Aluminum [Ne] 3s² 3p¹	14 **Si** 28,086 Silicon [Ne] 3s² 3p²	15 **P** 30,974 Phosphorus [Ne] 3s² 3p³	16 **S** 32,066 Sulfur [Ne] 3s² 3p⁴	17 **Cl** 35,453 Chlorine [Ne] 3s² 3p⁵	18 **Ar** 39,948 Argon [Ne] 3s² 3p⁶
28 **Ni** 58,693 Nickel [Ar] 3d⁸ 4s²	29 **Cu** 63,546 Copper [Ar] 3d¹⁰ 4s¹	30 **Zn** 65,38 Zinc [Ar] 3d¹⁰ 4s²	31 ***Ga*** 69,723 Gallium [Ar] 3d¹⁰ 4s² 4p¹	32 ***Ge*** 72,63 Germanium [Ar] 3d¹⁰ 4s² 4p²	33 ***As*** 74,922 Arsenic [Ar] 3d¹⁰ 4s² 4p³	34 ***Se*** 78,96 Selenium [Ar] 3d¹⁰ 4s² 4p⁴	35 **Br** 79,904 Bromine [Ar] 3d¹⁰ 4s² 4p⁵	36 **Kr** 83,798 Krypton [Ar] 3d¹⁰ 4s² 4p⁶
46 **Pd** 106,42 Palladium [Kr] 4d¹⁰ 5s⁰	47 ***Ag*** 107,87 Silver [Kr] 4d¹⁰ 5s¹	48 ***Cd*** 112,41 Cadmium [Kr] 4d¹⁰ 5s²	49 **In** 114,82 Indium [Kr] 4d¹⁰ 5s² 5p¹	50 ***Sn*** 118,71 Tin [Kr] 4d¹⁰ 5s² 5p²	51 **Sb** 121,76 Antimony [Kr] 4d¹⁰ 5s² 5p³	52 **Te** 127,60 Tellurium [Kr] 4d¹⁰ 5s² 5p⁴	53 **I** 126,90 Iodine [Kr] 4d¹⁰ 5s² 5p⁵	54 **Xe** 131,29 Xenon [Kr] 4d¹⁰ 5s² 5p⁶
78 **Pt** 195,08 Platinum [Xe] 4f¹⁴ 5d⁹ 6s¹	79 ***Au*** 196,97 Gold [Xe] 4f¹⁴ 5d¹⁰ 6s¹	80 **Hg** 200,59 Mercury [Xe] 4f¹⁴ 5d¹⁰ 6s²	81 **Tl** 204,38 Thallium [Xe] 4f¹⁴ 5d¹⁰ 6s² 6p¹	82 **Pb** 207,2 Lead [Xe] 4f¹⁴ 5d⁵ 6s² 6p²	83 **Bi** 208,98 Bismuth [Xe] 4f¹⁴ 5d⁶ 6s² 6p³	84 **Po** [208,98] Polonium [Xe] 4f¹⁴ 5d⁷ 6s² 6p⁴	85 **At** [209,99] Astatine [Xe] 4f¹⁴ 5d⁷ 6s² 6p⁵	86 **Rn** [222,02] Radon [Xe] 4f¹⁴ 5d⁷ 6s² 6p⁶
110 ***Ds*** [287,16] Darmstadium [Rn] 5f¹⁴ 6d⁸ 7s²	111 ***Rg*** [280,16] Roentgenium [Rn] 5f¹⁴ 6d⁹ 7s²	112 ***Cn*** [285,17] Copernicium [Rn] 5f¹⁴ 6d¹⁰ 7s²	113 ***Uut*** [284,18] Ununtrium [Rn] 5f¹⁴ 6d¹⁰ 7s² 7p¹	114 ***Fl*** [289,19] Flerovium [Rn] 5f¹⁴ 6d¹⁰ 7s² 7p²	115 ***Uup*** [288,19] Unun-pentium [Rn] 5f¹⁴ 6d¹⁰ 7s² 7p³	116 ***Lv*** [293] Liver-morium [Rn] 5f¹⁴ 6d¹⁰ 7s² 7p⁴	117 ***Uus*** [294] Ununseptium [Rn] 5f¹⁴ 6d¹⁰ 7s² 7p⁵	118 ***Uuo*** [294] Ununoctium [Rn] 5f¹⁴ 6d¹⁰ 7s² 7p⁶

63 **Eu** 151,96 Europium	64 **Gd** 157,25 Gadolinium	65 **Tb** 158,93 Terbium	66 **Dy** 162,50 Dysprosium	67 **Ho** 164,93 Holmium	68 **Er** 167,26 Erbium	69 **Tm** 168,93 Thulium	70 **Yb** 173,05 Ytterbium	71 **Lu** 174,97 Lutetium
95 **Am** [243,06] Americium	96 **Cm** [247,07] Curium	97 **Bk** [247,07] Berkelium	98 **Cf** [251,08] Californium	99 **Es** [252,08] Einsteinium	100 **Fm** [257,10] Fermium	101 **Md** [258,10] Mendelevium	102 **No** [259,10] Nobelium	103 **Lr** [262,11] Lawrencium

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