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# FUNDAMENTALS OF GENERAL, INORGANIC AND BIOORGANIC CHEMISTRY

for 31.05.01 «General Medicine specialty Manual for Foreign Medical Students

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МИНИСТЕРСТВО НАУКИ И ВЫСШЕГО ОБРАЗОВАНИЯ РОССИЙСКОЙ ФЕДЕРАЦИИ

ФЕДЕРАЛЬНОЕ ГОСУДАРСТВЕННОЕ БЮДЖЕТНОЕ ОБРАЗОВАТЕЛЬНОЕ УЧРЕЖДЕНИЕ ВЫСШЕГО ОБРАЗОВАНИЯ

#### «СЕВЕРО-КАВКАЗСКАЯ ГОСУДАРСТВЕННАЯ АКАДЕМИЯ»

МЕДИЦИНСКИЙ ИНСТИТУТ

Д.Т. Джатдоева

# ОСНОВЫ ОБЩЕЙ, НЕОРГАНИЧЕСКОЙ И БИООРГАНИЧЕСКОЙ ХИМИИ

УЧЕБНОЕ ПОСОБИЕ

для обучающихся I курса по специальностям 35.05.01 «Лечебное дело».

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В учебном пособии представлены все основные и важные темы, касаемо общей и биоорганической химии для подготовки к каждому занятию курса: цель занятия, вопросы, выносимые на занятие, краткая теоретическая часть, вопросы для самоподготовки и задания для самостоятельной работы. Учебное пособие составлено в соответствии с требованиями ФГОС и предназначено для студентов первого курса специальности 31.05.01 «Лечебное дело», Медицинского института.

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#### Preface

This textbook is a theoretical material that allows you to systematize and expand knowledge on bioorganic and general chemistry. The aim is to form a systematic knowledge of the patterns of chemical behavior of the main classes of natural compounds underlying human life processes. The main objects of study are biopolymers, bioregulators and individual metabolites that play a huge role in the processes of vital activity -these are proteins, peptides, nucleic acids, polysaccharides. The textbook is compiled in accordance with the requirements of the Federal State Educational Standard and is intended for first-year students of the specialty of «General Medicine», «Pediatrics», «Dentistry» at the medical Institute.

#### Introduction

The textbook is compiled in accordance with the requirements of the Federal State Educational Standard and is intended for students of medical universities. The textbook discusses the classification and nomenclature of organic substances, as well as their properties. The manual is characterized by a concise description of some paragraphs and a complete explanation of the more complex paragraphs that cause the greatest difficulties for students and are very important in medicine, as well as related subjects, on the knowledge of which depends the understanding of subjects such as pharmacology, biochemistry, biology. This manual discusses the characteristic chemical properties of the main classes of organic compounds: alkanes, alkenes, alkynes, aromatic hydrocarbons, extreme monatomic and polyatomic alcohols, and phenols, aldehydes, ketones, unsaturated carboxylic acids and esters. Special attention is paid to biologically important substances: fats, proteins, carbohydrates and nucleic acids.

# Unit 1. Fundamentals of General and Inorganic Chemistry

# **ATOMIC MODELS**



#### **Dalton's Atomic Theory**

John Dalton, a British Chemist proposed that every matter is made up of atoms. These atoms are indivisible and indestructible i.e. they can't be broken down into smaller particles. He also suggested that all atoms of a particular matter are the same, but atoms of different elements differ in size and mass. This means atoms of each element are unique.

#### **Plum Pudding Model**

After Thomson discovered Electron he attempted to describe the structure of the atom. He postulated that an atom is a positively charged sphere in which negatively charged electrons were embedded. The popular name given to this model is the "plum pudding model" because it can be observed as a plum pudding dish where the positively charged atom signifies the pudding and the plum pieces stand for the electrons. Plum Pudding Model is also sometimes referred to as the Watermelon Model where the red edible part of a watermelon is a sphere of positive charge while the seeds of the watermelon are referred to as negatively charged electrons.

#### **Observations of Rutherford's Alpha Scattering Experiment**

The observations made by Rutherford led him to conclude that:

1. A major fraction of the  $\alpha$ -particles bombarded towards the gold sheet passed through the sheet without any deflection, and hence **most of the space in an atom is empty**.

2. Some of the  $\alpha$ -particles were deflected by the gold sheet by very small angles, and hence the **positive charge** in an atom **is not uniformly distributed**. The positive charge in an atom **is concentrated in a very small volume**.

3. Very few of the  $\alpha$ -particles were deflected back, that is only a few  $\alpha$ -particles had nearly 180° angle of deflection. So the **volume occupied by the positively charged particles in an atom is very small as compared to the total volume of an atom** 



# **Bohr's Atomic Model**

As per Bohr's model, inside an atom, there is a small nucleus that is positively charged and is surrounded by negative electrons which move around in orbits which has specific energy level. To revolve in a particular orbit, electrons must possess energy equal to the energy level of the shell. Bohr found out that the larger the distance of an electron from the nucleus, the larger its energy which means the orbits near the nucleus has smaller energy and the shell farthest from the nucleus has larger energy.



# **Bohr's Atomic Model**

#### **Schrodinger Wave Equation**

Schrodinger Wave Equation gives the equation for the total energy of the system (an atom or a molecule) whose energy doesn't change with time i.e. there is no loss or gain of energy. Mathematically, Schrodinger Wave Equation is represented as

 $H\psi = E\psi$ 

where

- H is Hamiltonian Operator in Mathematics
- *E* is the Total Energy of the System
- $\psi$  is a Wave function

#### Quantum Number

To describe the location of an electron inside an atom we need a set of 4 numbers known as Quantum Numbers. These Quantum Number helps in distinguishing different orbitals which contain electron. Orbitals that have a smaller number mean they are closer to the nucleus, have a smaller size, and have a larger probability of finding an electron. The four types of Quantum Numbers are listed below:

- Principal Quantum Number
- Azimuthal Quantum Number
- Magnetic Quantum Number
- Spin Quantum Number

Atom: The defining structure and basic units of matter of an element are called atoms. The term "atom" came from a Greek word that means indivisible because earlier atom was thought to be the smallest things in the universe that could not be divided Atomic Structure: The structure of an atom comprising a nucleus, in which the protons and neutrons are present. The negatively charged particles called electrons revolve around the center of the nucleus.

**Nucleus:** A collection of particles called protons and neutrons is called Nucleus. Protons are positively charged and neutrons, are electrically neutral. Protons and neutrons are made up of particles called quarks. The chemical element of an atom is determined by the number of protons, or the atomic number, Z, of the nucleus.

**Proton:** Positively charged particles found within atomic nuclei are given the name Proton. Rutherford discovered the proton in his famous cathode ray experiment that was conducted between 1911 and 1919. Protons are about 99.86% as massive as neutrons. The number of protons in an atom is unique for each element

**Electron:** Electrons are very tiny compared to protons and neutrons, about 1800 times smaller than either a proton or a neutron. Electrons are just 0.054% as massive as neutrons. Electrons were discovered in 1897 by Joseph John (J.J.) Thomson, a British physicist. Electrons have a negative charge and are electrically attracted to the positively charged protons

**Neutron:** Rutherford theorized the neutron's existence in 1920 and was later discovered by Chadwick in 1932. Neutrons were found during experiments where atoms were shot at a thin sheet of beryllium. Subatomic particles with no charge were released – and were named neutrons. Neutrons are uncharged particles found within all atomic nuclei

**Isotopes:** Members of the same family of an element that all have the same number of protons but different numbers of neutrons are named isotopes. The number of protons in a nucleus determines the element's atomic number on the Periodic Table. All the isotopes have unique properties, just like all family members have their own qualities.

#### *Unit* 2. Classes of inorganic chemistry

The vast majority of substances studied in the inorganic course can be considered by a simple classification depending on their composition and properties. So, hydroxides, acids, oxides and s alts are distinguished.

**Simple Oxides:** A binary compound of oxygen with another element is called an

oxide. Oxides can be classified into

a. Acidic oxides b. Basic oxides

c. Amphoteric oxides d. Neutral oxides

**a. Acidic oxides:** An oxide which dissolves in water to give an acid or reacts with a base to give a salt is called acidic oxide. For example, SO<sub>2</sub>, SO<sub>3</sub>, CO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub> etc. SO<sub>2</sub> + H<sub>2</sub>O  $\rightarrow$  H<sub>2</sub>SO<sub>3</sub>

 $SO_3 + 2NaOH \rightarrow Na_2SO_4 + H_2O$ 

Generally, oxides of nonmetals are acidic oxides.

**b. Basic oxides:** An oxide which dissolves in water to give a base or reacts with an acid to give salt is called basic oxide. For example, Na<sub>2</sub>O, CaO, BaO etc. CaO + H<sub>2</sub>O  $\rightarrow$ Ca(OH)<sub>2</sub>

 $BaO + 2HCl \rightarrow BaCl_2 + H_2O$ 

**c. Amphoteric oxides:** The oxide which reacts with a base as well as with an acid to give salt is called an amphoteric oxide. For example,  $Al_2O_3$ , ZnO, PbO, SnO, BeO.

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

**d. Neutral oxides:** The oxides which are neither acidic nor basic, are called as neutral oxides. For example, CO, NO,  $N_2O$  etc.

# Acids and Bases

Acid: a chemical compound that dissociates into a hydrogen ion and a negatively charged ion when mixed with water

Chemical that turns into H+ and something else in water

Classification of acids according to basicity					
Monobasic acids (Monoprotic) HCl, HNO <sub>3</sub>					
Dibasic acids ( Diprotic )	$H_2S, H_2SO4$				
Tribasic acids (Triprotic ) $H_3PO_4$					

# **Classification of Acids**

Depending upon the elements present, acids may be classified as follows.				
Oxyacid :	<b>Oxyacid</b> : $H_3PO_4$ , $HNO_3$			
<b>Hydracid :</b> $H_2S$ , HCl, HBr, HCN				

Brønsted–Lowry acids exhibit several key properties that distinguish them from other types of acids:

• **Proton Donors**: Brønsted–Lowry acids donate protons to other species, forming conjugate bases.

• **Arrhenius Acids**: In aqueous solutions, Brønsted–Lowry acids produce hydronium ions (H3O+).

• Acidic Solutions: Brønsted–Lowry acids form solutions with a pH less than 7, indicating their acidic nature.

The Arrhenius definition of acids and bases has the following limitations.

It defines acids and bases in terms of what happens when compounds dissolve in

water. However, similar chemistry occurs in many reactions that take place in solvents

other than water, and this definition does not work for such reactions.

It does not explain why some compounds in which hydrogen has an oxidation

number of + 1 (such as HCl) dissolve in water to give acidic solutions, whereas others (such as NH<sub>3</sub>) do so.

Only the compounds that contain the OH– ion can be classified as Arrhenius bases.

The Arrhenius definition does not explain why compounds such as  $Na_2CO_3$  have basic properties.

The electron flow shows that the species giving the electrons are the Lewis bases and the ones accepting them are the Lewis acids.

• A Lewis acid is an electron pair acceptor.

• A Lewis base is an electron pair donor.

Any base must have at least one lone pair or an electron pair in a  $\pi$  bond. That is why all bases are **Lewis bases.** Similarly, the Lewis acid must be able to accept a lone pair which is what protons do. However, the Lewis acids are not restricted to protons only

Lewis bases: OH<sup>-</sup>, NH<sub>3</sub>, CN<sup>-</sup>, H<sub>2</sub>O

Lewis acids: H<sup>+</sup>, HCl, Cu<sup>2+</sup>, CO<sub>2</sub>, SiBr<sub>4</sub>, AlF<sub>3</sub>, BF<sub>3</sub>, H<sub>2</sub>O

For examples, because Lewis acids are electron-deficient, they are also called **electrophiles**. And the Lewis bases are also called **nucleophiles** since they are electron-rich.

Classification of acids according to its strength ( degree of ionization )			
Strong acids Strong electrolytes	$H_2SO_4$ , HCl, HNO <sub>3</sub>		
Weak acids Weak electrolytes	$H_2S$ , $H_2SO_3$ , $H_2CO_3$		

**Strong electrolyte :** The electrolytes ionizing completely or almost completely are strong electrolytes. For example : strong acids, strong bases and salts.

Weak electrolyte : The electrolytes which dissociate to a smaller extent in aqueous solution are weak electrolytes. Weak acids and weak bases belong to this class

# Chemical properties of acids.

1. When a strong acid reacts with a weak acid salt, it forms a weak acid and a strong acid salt.

 $2HBr + CaCO_3 = CaBr_2 + H_2O + CO_2$ 

2. When an acid reacts with metals, it gves salt and Hydrogen gas.



3. When the acid reacts with the basic oxide, it forms salt and water .

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

4. When an acid reacts with an amphoteric oxide, it gives salt and water respectively.

 $3H_2SO_4 + Cr_2O_3 = Cr_2(SO_4)_3 + 3H_2O$ 

5. Neutralization of Acid and Base (it gives salt and water).

 $H_2SiO_3 + 2KOH = K_2SiO_3 + 2H_2O$ 

6. When an acid reacts with an amphoteric base, it gives salt and hydrogen and water

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

Base: a chemical compound that dissociates into hydroxide ion (OH-) and a positively charged ion when mixed with o water

*Chemical that turns into OH- and something else in water* Theories of Bases

• Arrhenius theory of acids – States that a base produces hydroxide ions in aqueous solutions

• Bronsted-Lowey theory – It states a base as a proton acceptor

• Lewis Theory of acids - It describes bases as electron-pair donors

#### **Types of Bases Based on Degree of Ionization**

- Strong Base
- Weak Base

• **Strong Base:** Strong Bases are those bases that dissociate completely and liberate OH- ion when dissolved in water. Some examples of Strong Bases include NaOH, KOH, etc.

• Weak Base: The bases which don't undergo complete dissociation and liberate only a fraction of OH- ion is called Weak Base. Examples of Weak bases include  $Al(OH)_3$ ,  $Cu(OH)_2$ , etc.

Chemical properties of bases:

Bases react with acids to form salt and water. This neutralization reaction can be used for the synthesis of different types of salts.

 $Cu (OH)_2 + 2HCl \rightarrow CuCl_2 + 2H_2O$ 

2. Basic oxides interact with acidic oxides

3. Basic oxides interact with solutions of various salts:

 $NiSO_4 + NaOH \rightarrow Na_2SO_4 + Ni (OH)_2 \downarrow$ 

• Reaction of Base with Metals: When alkali (base) reacts with metal, salt, and hydrogen gas is produced.

Alkali + Metal  $\rightarrow$  Salt + Hydrogen

 $2 NaOH + 2 Al + 2 H_2O \rightarrow 2 NaAlO_2 + 2 H_2$ 

• Reaction of Non-Metallic Oxides with Base: Salt and water are formed when non-metallic oxides react with a base.

Non-metallic oxide + Base  $\rightarrow$  Salt + Water

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

• Reaction of Alkalis/Base with Ammonium Salts: Ammonia is produced when alkalis react with ammonium salts.

Alkali + Ammonium salt  $\rightarrow$  Salt + Water + Ammonia

 $Ca(OH)_2 + NH_4Cl \rightarrow CaCl_2 + H_2O + NH_3$ 

pH Scale:

Denition: The pH scale measures the acidity or basicity of a solution. pH Values:

- 0 to 7: Acidic (lower values are more acidic)
- 7: Neutral
- 7 to 14: Basic or alkaline (higher values are more basic)



Salts

Definition: Salts are formed by the reaction between acids and bases. They are compounds composed of positive and negative ions.

Basic s alts are obtained if the hydroxyl groups are not completely substituted (such substances have an alkaline reaction environment) (CuOHNO<sub>3</sub>, AlOHCl<sub>2</sub>);

 $Fe(OH)_3 + HNO_3 = Fe(OH)_2NO_3 + 2H_2O;$ 

 $Fe(OH)_3 + 2HNO_3 = FeOH(NO_3)_2 + 2H_2O.$ 

Acid s alts are formed in the opposite case - with a lack of a reacting base, hydrogen partially remains in the compound  $(Ca(HCO_3)_2, Na_2HPO_4);$ 

 $KOH+H_2SO_4 = KHSO_4 + H_2O$ 

The most famous and easiest to understand are the average (or normal) samples - they are the product of complete neutralization of reagents with the formation of water and a substance with only a metal cation or its analogue and an acid residue.

 $H_2SO_4 + 2KOH = K_2SO_4 + 2H_2O;$  $Mg(OH)_2 + 2HCl = MgCl_2 + 2H_2O$ Types of salts:

Acidic salts:

Nº	Formula	Name
1.	NaHCO <sub>3</sub>	Sodium carbonate
2.	NaHSO <sub>4</sub>	Sodium bisulfate
3.	NaH <sub>2</sub> PO <sub>4</sub>	Monosodium dihydrogen orthophosphate
4.	Na <sub>2</sub> HPO <sub>4</sub>	Disodium hydrogen phosphate
5.	KHSO <sub>4</sub>	Potassium bisulfite
6.	NH <sub>4</sub> Cl	Ammonium chloride
7.	(NH4) <sub>2</sub> SO <sub>4</sub>	Ammonium sulfate

Basic Salts:

Nº	Formula	Name
	Zn(OH)Cl	Zinc chloride hydroxide
	KCN	potassium cyanide
	NaOH	sodium hydroxide
	Mg(OH)Cl	Magnesium oxychloride
	Fe(OH) <sub>2</sub> Cl	Iron(II) hydroxide
	NaOOCCH <sub>3</sub>	Sodium acetate
	Bi(OH) <sub>2</sub> Cl	bismuth oxychloride

# Neutral salts:

	Formula	Name		
Nº				
	NaCl	Sodium chloride		
	NaNO <sub>3</sub>	Sodium nitrate		
	$K_2SO_4$	Potassium sulfate		
	KCl	Potassium chloride		
	KClO <sub>3</sub>	Potassium chlorate		
	$Ca_3(PO4)_2$	Calcium phosphate		
	Na <sub>3</sub> BO <sub>3</sub>	Trisodium orthoborate		
	KClO <sub>4</sub>	Potassium Perchlorate		
	NaH <sub>2</sub> PO <sub>2</sub>	The $H_2PO_2$ - ion is derived from $H_3PO_2$		
		acid which is monobasic, hence both the		
		H atoms are not replaceable		

Double salts:

Nº	Formula	Name
	$(NH4)_2 Fe(SO_4)_2 \cdot 6H_2O$	Mohr's salt
	$K_2Cd$ (SO4) <sub>2</sub> ·6H <sub>2</sub> O	Tutton's salt
	KCeF <sub>4</sub>	Potassium cerium fluoride
	$(K_2SO_4Al_2(SO_4)_3 \cdot 24H_2O)$	Potash alum
	$K_4[YbI_6]$	Potassium Ytterbium iodide

# Mixed salts

Nº	Formula	Name
1.	Ca(ClO) <sub>2</sub>	Bleaching powder
2.	EDTA	Calcium disodium
3.	NaKSO <sub>4</sub>	Sodium potassium sulfate

Complex salts:

r		
Nº	Formula	Name
1.	$[Cu(NH_3)_4]SO_4$	Tetra amino cupric sulfate
2.	$K_4[Fe(CN)_6]$	Potassium ferrocyanide
3.	$[Cr(NH_3)_6]Cl_3]$	Hexamine chromium(III) chloride
4.	[Ni(CO) <sub>4</sub> ]	Nickel carbonyl

• Double contains a single anion in the presence of two cations. Usually such substances are obtained by merging two s alts with the same acid residue, but different metals.

• The mixed type is the opposite of the previous one: its basis is one cation with two different anions.

• Crystal hydrates - s alts, in the formula of which there is water in a crystallized state.

• Complexes are substances in which a cation, anion or both of them are presented in the form of clusters with a forming element. Such s alts can be obtained mainly from elements of subgroup B.

1. Ion exchange reaction with precipitation

 $FeCl_3 + 3KOH = 3KCl + Fe(OH)_3 \downarrow$ 

 $Na_2SO_4 + BaCl_2 = 2NaCl + BaSO_4 \downarrow$ 

 $K_2SiO_3 + 2HNO_3 = 2KNO_3 + H_2SiO_3\downarrow$ 

2. Ion exchange reaction with Evolution of a gas:  $(NH_4)_2SO_4 + 2KOH = K_2SO_4 + 2NH_3 \uparrow + 2H_2O$ 

# **3. Interaction with metals**

A more active metal is able to displace a less active metal from its salt.  $Fe + CuBr_2 = FeBr_2 + Cu$  $Mg + FeBr_2 = MgBr_2 + Fe$ 

# 4.Decomposition of mineral salts

Insoluble carbonates and lithium carbonate decompose into carbon dioxide and the corresponding metal oxide when heated:

 $Li_2CO_3 \xrightarrow{t^\circ} Li_2O + CO_2$  $MgCO_3 \xrightarrow{t^\circ} MgO + CO_2$ 

$$Fe_2(CO_3)_3 \xrightarrow{t^\circ} Fe_2O_3 + 3CO_2$$

Questions:

- 1. What are the properties of acids?
- 2. How are the basic salts formed?
- 3. What are acids, base and salt? Give an example.
- 4. What are examples of acids?
- 5. What are weak acids?

# Unit 3. Classification and nomenclature of bioorganic

# compounds

#### Nomenclature of organic compounds.

This section contains Nomenclature Rules for organic compounds, where the recommendations and requirements of the IUPAC (International Union of Pure and Applied Chemistry) are more widely and frequently applied.

In general, all three are used:

1.Trivial;

2. Rational;

3. IUPAC (International Union of Pure and Applied Chemistry) Nomenclature.

The names of compounds designated using trivial nomenclature are frequently significantly shorter and simpler than the matching IUPAC nomenclature. Organic compounds were named after the source from which they were first isolated.

For example: Urea got its name since the compound was first obtained from the urine of mammals.

Methyl alcohol was called wood spirit since it could be obtained by the destructive distillation of wood.

Acetic Acid got its name from the acetum since it is present in vinegar.

Formic acid was derived from formicus since it could be obtained by the destructive distillation of red ants.

Citric acid is named so because it is found in citrus fruits. If we consider the rational nomenclature, it was used to describe the structure of the molecule. Formic acid was first isolated from red forest ants in 1670 by the English scientist John Ray, for which it got its name.



The Chichibabina Hydrocarbon

Rational nomenclature has been used since the beginning of the 19th century. When using rational nomenclature, the names of organic compounds are based on the use of simple homologues with substituents. However, the radicals are listed in order of increasing seniority. The name ends with the name of the main organic compound.

According to rational nomenclature, alkanes, for example, are considered as derivatives of methane, alkenes, derivatives of e ethylene, and so on.



Methyl ethyl isopropyl tert-butylmethane

The IUPAC system for organic compounds remains the most rational, widespread and frequently used. The peculiarity lies in the fact that only one name is characteristic of any molecule.

$$H_2C = C - CH_3$$
  
 $CH_3$ 

Dimethylethylene

$$\underset{O}{\overset{\parallel}{\operatorname{H_3C-CH_2-CH_2-CH_2-CH_3}}}$$

Ethyl propyl ketone

# $\underset{OH}{H_3C-CH_2-CH_2-CH_2-CH_3}$

Ethyl propyl carbinol

The modern IUPAC nomenclature also has its own peculiarities, where the form of writing in English and Russian is very different, for example, in English, a number indicating the position of a multiple connection is placed before the name.

The modern IUPAC nomenclature also has its own peculiarities, where the form of writing in English and Russian is very different, for example, in English, a number indicating the position of a multiple connection is placed before the name.

The systematic nomenclature or modern nomenclature, or it is also called IUPAC, is defined by the IUPAC specifications. It begins with the name of the carbon chain (cycle), that is, from the root, with the addition of the names of the side chains, characteristic groups, suffixes, prefixes and locants to uniquely convey the structure of an organic molecule. Given the huge variety of organic compounds, which has millions of very similar molecules, sometimes strict use of systematic names can lead to difficulties. To name the molecules correctly, it is necessary to know the structure and structure, as well as the names of the initial compounds. They include heterocycles, with their monofunctional derivatives, and unsubstituted hydrocarbons.

#### **General naming principles**

I. Rules for IUPAC nomenclature of complex saturated hydrocarbons (Alkanes)

It is necessary to determine the main structure (the parent chain-the main chain or the main cyclic structure of carbon atoms).

	Name	Radical
1	isopropyl	CH-CH <sub>3</sub>
	io ob utul	
2	ISODULYI	$-CH_2-CH-CH_3$
		CH3
3	isopentyl	-CH <sub>2</sub> -CH <sub>2</sub> -CH-CH <sub>3</sub>
		$CH_3$
4	neopentyl	CH <sub>3</sub>
		$-CH_2-CH_3$
		$CH_3$
5	sec-butyl	
		CH-CH-CH
		H <sub>3</sub> C <sup>2</sup> Chi chi <sub>2</sub> chi <sub>3</sub>
6	tert-butyl	
		H <sub>3</sub> C-C-CH <sub>3</sub>
		$CH_3$

### It is necessary to get the name of some radicals

**1.** It can be represented by the longest unbranched chain of carbon atoms, regardless of how the structural formula is depicted. For example:



Hexane

Heptane

2. It is necessary to start by using a much larger number of side chains. An organic compound can have two different chains of the same length, in which case choose the one with more side chains or alkyl groups. For example,

$$\begin{array}{c} H_{3}C-CH-CH-CH_{2}-CH_{2}-CH_{3}\\ CH_{3} CH_{2}\\ CH_{3} \end{array} \qquad \qquad CH_{3}-CH + CH_{2}-CH_{2}-CH_{2}-CH_{3}\\ CH_{3} CH_{2} CH_{3} CH_{2} CH_{3} CH_{3} CH_{2}-CH_{3} \end{array}$$

In this case, it should be named as hexane with two alkyl substituents (correct). If you call it hexane with one alkyl substituent, it will be wrong.

**3**. The main carbon structure is numbered: from the end of the carbon chain to which the carbon atom carrying the substituent is closer, if there are several substituents, from the end where there are more of them

# $\begin{array}{c} H_3C-CH_2-CH_2-CH_2-CH_2-CH_3\\ \overset{|}{C}H_3\end{array}$

correct

5. It contains the main characteristic group, if there are several of them, then the main goal of which is the most senior characteristic group.

	Name	Suffix	Alkanes	Suffix	Alkenes	Suffix	Alkynes
Number	of the						
of C	root						
atoms			C-C		C=C		C≡C
in a		-an(e)	$sp^3$	_en(e)	$sp^2$	_vn(e)	sp
chain		-an(c)	1	-011(0)	1	-yn(c)	I
1	meth	-ane	Methane				
2	Eth	-ane	Ethane	-ene	Ethene	-yne	Ethyne
3	Prop	-ane	Propane	-ene	Propene	-yne	Propyne
4	But	-ane	Butane	-ene	Butene	-yne	Butyne
5	Pent	-ane	Pentane	-ene	Pentene	-yne	Pentyne
6	Hex	-ane	Hexane	-ene	Hexene	-yne	Hexyne
7	Hept	-ane	Heptane	-ene	Heptene	-yne	Heptyne
8	Oct	-ane	Octane	-ene	Octene	-yne	Octyne
9	Non	-ane	Nonane	-ene	Nonene	-yne	Nonyne
10	Dec	-ane	Decane	-ene	Decene	-yne	Decyne

The names of characteristic groups (functional groups), if they are minor, are also indicated in prefixes.

IUPAC name	Word	Primary	Secondary	Organic
	root	suffix	suffix	compound

Ethanol	Eth	2 C	ane	ol	CH <sub>3</sub> -CH <sub>2</sub> -OH
Propanamine	Prop	3 C	ane	amine	CH <sub>3</sub> -CH <sub>2</sub> - CH <sub>2</sub> -NH <sub>2</sub>
Butanoic acid	But	4 C	ane	oic acid	CH <sub>3</sub> -CH <sub>2</sub> - CH <sub>2</sub> -COOH

For example,

$$H_3C-CH-CH-CH_3$$
  
Br Cl

2-Bromo-3-chlorobutane

$$\begin{array}{c} H_3C-CH_2-CH-CH-(CH_2)_4-CH-CH_3\\ CH_2 \ CH_3 \end{array} \\ \begin{array}{c} H_1\\ Br\\ CH_3\end{array}$$

2 - Bromo - 8 - ethyl - 7 - methyldecane

#### 4. Name of the complex alkane.

The prefixes indicate the number of identical structural elements in the formula. For example: "di"-two, "three" -three, "tetra"-four, the names of the others coincide with the numerals of the Greek language "penta"- 5, "hexa"- 6 so on

2,3-dimethylpentane

#### 5. Alphabetical order of the simple substituents.

When two or more simple substituents are present in an organic compound, it is necessary to arrange the prefixes in alphabetical order and remember that their names must be written before the name of the parent alkane.

#### 6. Numbering of the different substituents in equivalent positions.

It should be borne in mind that if there are two different substituents in equivalent positions, the numbering of this chain should begin in such a way that the first substituent in alphabetical order will be indicated by a smaller number.

#### **II. Rules for IUPAC nomenclature for Alkenes and Alkynes.**

The IUPAC nomenclature for unsaturated hydrocarbons differs slightly, and in the presence of double and triple bonds, the following rules must be observed:

1. Regardless of the location, the chemical compound must have a multiple bond.

2. If double and triple connections are present at the same time, numbering should begin with the connection that comes first.

3. If you have to choose between double and triple bonds, it is preferable to start with a double bond.

#### III. There are IUPAC nomenclature rules for organic compounds with one functional group but with multiple bonds and substituents.

There are special rules for naming compounds containing double and triple bonds i.e. multiple bonds as well as containing substituents

1. As a parent chain, it is always necessary to choose the longest chain that will contain a functional group as well as the maximum number of multiple chemical bonds.



In this case, there are four atoms in the parent chain that are isolated, not five

2. The parent chain must be numbered in such a way that the smallest possible number indicates the functional group, only after that it is necessary to indicate double and triple links, despite the fact that this violates the smallest rule of summation.

$$H_3C-CH_2-C-CH_2-CH-CH_3$$
  
O CH<sub>3</sub> > C=O group gets lowest number 3

3. Numbering always starts with a functional group, whatever the functional group is, it is assigned the number 1.

- COOH, 
$$-$$
 CHO,  $-$ CN  $-$  COOR,  $-$  CONH<sub>2</sub>,  $-$  COCl, etc

**1.** In an organic compound, if there is only one functional group, then its location can be omitted if there is no ambiguity, but in this case, this numericallocant is always included when another numerical locant appears in the same name. For example,



$$\begin{array}{c} CH_2 - OH \\ CH - OH \\ H_2 - OH \\ CH_2 - OH \end{array} Propane-1, 2, 3-triol$$

An organic compound may have more than one similar complex substituent in which case all prefixes such as d 3 tetra and so on are replaced etc. are replaced by bis, tris, tetrakis, etc. For example,



2,2-Bis (2-hydroxyethoxy)ethanoic acid

#### V. Rules for IUPAC Nomenclature of Polyfunctional Compounds.

There are separate rules for organic compounds that have several functional groups, such compounds are called fully functional compounds. The names of the functional groups are given below

**1. Principal functional group.** An organic compound may contain several functional groups. In this case, priority rules or senior rules are used, all except the main functional group are considered substituents.. The choice of the principal functional group is made on the basis of the following order of preference.

1.Sulphonic acid

- 2. Carboxylic acid
- 3.Anhydrides
- 4. Esters
- 5. Acid chlorides
- 6. Acid amides
- 7. Nitriles
- 8. Aldehydes
- 9. Ketones
- 10. Alcohols
- 11.Amines
- 12.Ethers

13.Alkenes 14.Alkynes.

Functional groups containing halogens (fluoro, chloro, bromo, iodo), nitro (–  $NO_2$ ), nitroso (– NO), and alkoxy (– OR) are always treated as substituent groups.

In such cases, the main functional group is indicated by adding a secondary suffix to the root of the word, and all secondary ones are indicated by using prefixes to the root of the word.

Table of priority						
Structure	Class	Functional group	Suffix			
CH <sub>3</sub> -COOH	Carboxylic acid	-COOH	-oic acid			
CH <sub>3</sub> - CN	Nitrile	-CN	-nitrile			
HC <sup>#O</sup> H	Aldehyde	-С-Н	-al			
$H_3C-C-CH_3$	Ketone	-C-	-one			
O		0				
CH <sub>3</sub> -OH	Alcohol	-OH	-ol			

Let's summarize schematically how to name organic compounds correctly.

prefixes + root + suffixes

stru		ructure name		unsaturatin	group
substituents	+	parent +		saturation /	+ main

**Problems.** 

$$H_3C-CH_2-CH-CH-C \sim O$$
  
 $CH_3 NH_2 OH$ 

Name the organic compound according to IUPAC

Answer. 2- amino-3-methylpentanoic acid

Name the following organic compounds by the substitutive nomenclature



2.

3.

$$H_3C-C-CH_3$$

Saturated hydrocarbons

# Unit 4.Alkanes.

Alkanes are saturated hydrocarbons, and all the free valence carbon atoms are occupied by hydrogen atoms. The General formula of Alkanes CnH2n+2

In alkanes, the carbon atom is in a state of sp<sup>3</sup> hybridization and forms 4 sigma bonds.

Number of Carbons	Name	Formula	Structure
1	Methane	CH <sub>4</sub>	CH <sub>4</sub>
2	Ethan	$C_2H_6$	CH <sub>3</sub> -CH <sub>3</sub>
3	Propane	C <sub>3</sub> H <sub>8</sub>	CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>3</sub>
4	Butane	$C_4 H_{10}$	CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>
5	Pentane	C <sub>5</sub> H <sub>12</sub>	CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>
6	Hexane	C <sub>6</sub> H <sub>14</sub>	CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>
7	Heptane	C <sub>7</sub> H <sub>16</sub>	CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>
8	Octane	C <sub>8</sub> H <sub>18</sub>	CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>
9	Nonane	CH <sub>4</sub>	CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>3</sub>
10	Decane	C <sub>2</sub> H <sub>6</sub>	CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>3</sub>

The name of the radicals is formed from the name of the corresponding alkane, if you reduce the number of hydrogen atoms by one atom.

Na	me	Structure	Name	Radical
1	Methane	CH <sub>4</sub>	methyl	-CH <sub>3</sub>
2	Ethane	C <sub>2</sub> H <sub>6</sub>	ethyl	-CH <sub>2</sub> -CH <sub>3</sub>
3	Propane	C <sub>3</sub> H <sub>8</sub>	propyl	-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>
4	Butane	C <sub>4</sub> H <sub>10</sub>	butyl	$-CH_2-(CH_2)_2-CH_3$
5	Pentane	C <sub>5</sub> H <sub>12</sub>	pentyl	$-CH_2-(CH_2)_3-CH_3$
6	Hexane	C <sub>6</sub> H <sub>14</sub>	hexyl	-CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>4</sub> -CH <sub>3</sub>
7	Heptane	C <sub>7</sub> H <sub>16</sub>	heptyl	-CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>5</sub> -CH <sub>3</sub>
8	Octane	C <sub>8</sub> H <sub>18</sub>	octyl	-CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>6</sub> -CH <sub>3</sub>
9	Nonan	$C_9H_{20}$	nonyl	-CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>7</sub> -CH <sub>3</sub>
10	Decane	$C_{10}H_{22}$	decyl	$-CH_2-(CH_2)_8-CH_3$

#### Isomerism and nomenclature.

Alkanes are characterized only by structural isomerism and isomerism of the carbon skeleton or chain isomerism.

Isomers are substances with the same qualitative and quantitative composition of molecules, but different structures, and therefore different properties.

# Isomers

**1.** Butane -  $C_4H_{10}$ 

H<sub>3</sub>C-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub> Butane

H<sub>3</sub>C-CH-CH<sub>3</sub> CH<sub>3</sub> Methylpropane or Isobutane

**2.** Pentane  $-C_5H_{12}$ 

```
H_3C - CH_2 - CH_2 - CH_2 - CH_3
```

Methylbutane

Pentane or isopentane



$$CH_3$$
  
 $H_3C-C-CH_2-CH_3$   
 $CH_3$   
2,2- dimethylbutane

**Dhysical properties of Allyanes**. The first four

**Physical properties of Alkanes**. The first four hydrocarbons  $CH_4$ -  $C_4H_{10}$  - are gases, the next ten are liquids  $C_{15}H_{10}$ -  $C_{15}H_{32}$ , higher homologs are solids.

# Chemical properties.

Alkanes are characterized by substitution, cleavage, oxidation, and other reactions.

**1.** Halogenation of alkanes

 $Cl_2 \rightarrow Cl_{\bullet} + Cl_{\bullet}$  -This is called the **initiation step**   $Cl_{\bullet} + CH_3_{\bullet} \rightarrow CH_3Cl$  chain -propagating **steps**   $CH_3_{\bullet} + CH_3_{\bullet} \rightarrow C_2H_6$ **Free radical substitution** 

$$CH_4 \xrightarrow{hv} Cl - CH_3 \xrightarrow{hv} Cl - CH_2 - Cl \xrightarrow{hv} Cl_2 CH - Cl \xrightarrow{hv} Cl_2 CH - Cl \xrightarrow{hv} Cl_2 CH - Cl \xrightarrow{hv} Cl_2 Cl - Cl_2 Cl \xrightarrow{hv} Cl_2 CH - Cl_2 Cl_2 Cl \xrightarrow{hv} Cl_2 Cl \xrightarrow{hv} Cl_2 Cl \xrightarrow{hv} Cl_2 Cl \xrightarrow{hv} Cl_2 CH - Cl_2 Cl_2 Cl \xrightarrow{hv} Cl_2 Cl \xrightarrow{hv} Cl_2 Cl \xrightarrow{hv} Cl_2 CH - Cl_2 Cl_2 Cl \xrightarrow{hv} Cl_2 Cl \xrightarrow{hv} Cl_2 CH - Cl_2 Cl_2 Cl \xrightarrow{hv} Cl_2 CH - Cl_2 Cl_2 Cl \xrightarrow{hv} Cl_2 CH - Cl_2 Cl_2 Cl \xrightarrow{hv} Cl_2 Cl \xrightarrow{hv} Cl_2 CH - Cl_2 Cl \xrightarrow{hv} Cl_2 Cl \xrightarrow{hv} Cl_2 CH - Cl_2 Cl \xrightarrow{hv} Cl_2 Cl \xrightarrow{hv} Cl_2 CH - Cl_2 Cl \xrightarrow{hv} Cl_2 CL - Cl_2 Cl \xrightarrow{hv} Cl_2 CH - Cl_2 Cl \xrightarrow{hv} Cl_2 Cl \xrightarrow{hv} Cl_2 CH - Cl_2 Cl \xrightarrow{hv} Cl_2 Cl \xrightarrow{hv} Cl_2 CH - Cl_2 Cl \xrightarrow{hv} Cl_2 Cl \xrightarrow{hv} Cl_2 Cl \xrightarrow{hv} Cl_2 CH - Cl_2 Cl_2 Cl \xrightarrow{hv} Cl \xrightarrow{hv} Cl_2 Cl \xrightarrow{hv} Cl$$

Chloromethane dichloromethane

.

chloroform carbon tetrachloride

H<sub>3</sub>C-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH  
H<sub>3</sub>C-CH<sub>2</sub>-CH<sub>2</sub>-CH  
$$\stackrel{\frown}{-HCl}$$
  
H<sub>3</sub>C-CH-CH<sub>3</sub>  
 $\stackrel{\downarrow}{Cl}$ 

Propane  $\rightarrow$  1-chloropropane + 2-chloropropane 2. Nitration. Konovalov's reaction OTT

$$\begin{array}{c} H_{3}C-CH-CH_{2}-CH_{3}+HNO_{3} \xrightarrow{t^{\circ}} H_{3}C-CH_{2}-CH_{2}-CH_{3}+H_{2}O\\ CH_{3} & NO_{2} \end{array}$$

Isopentane + nitric acid  $\rightarrow$  2-methyl-2-nitrobutane + water

# **2.** Sulfonation reaction

$$CH_3-CH_3+H_2SO_4 \rightarrow CH_3-CH_3-SO_3 H$$

# **3.** Oxidation reaction

$$CH_4 + 2O_2 \xrightarrow{t^\circ} CO_2 + 2H_2O$$

# 4. Catalytic oxidation by atmospheric oxygen

$$2CH_4 + O_2 \xrightarrow{t^\circ, p, \kappa a_T} 2H_3C - OH$$

methanol

$$CH_4 + O_2 \xrightarrow{t^\circ, p, \text{ KAT}} HC \xrightarrow{H} HC H_2O$$

formaldehyde

$$2CH_4 + 3O_2 \xrightarrow{t^\circ, p, \text{ Kar}} 2HC \bigvee_{OH} OH + 2H_2O$$

5. Reactions of dehydrogenation and dehydrocyclization  $CH_4 \xrightarrow{t} C+2H_2$ 

$$2 \text{CH}_4 \xrightarrow{1500^{\circ}\text{C}} \text{HC} = \text{CH} + 3 \text{H}_2$$
  
Acetylene

 $CH_3-CH_2-CH_2-CH_3 \xrightarrow{t} CH_3-CH=CH-CH_3+H_2$ Butene

$$H_3C - (CH_2)_4 - CH_3 \xrightarrow{t^\circ, Pt} \checkmark + 4H_2$$

benzene

# 6. Cracking reactions $H_3C-CH_2-CH_2-CH_2-CH_3 \xrightarrow{450-550^\circ C} H_3C-CH_3 + H_2C=CH-CH_3$

Saturated hydrocarbon

unsaturated hydrocarbon

#### **Problems**

**1.** Write the formulas of alkane isomers  $C_8H_{18}$ . Name them.

2. Describe the physical properties of Alkanes.

3. What chemical reactions are characteristic of Alkanes?

**4.** What is the difference between the name of a radical and the name of an alkane?

5. What is the feature of the substitution reaction in Alkanes?

# **Unit 5. The Alkenes**

Alkenes are hydrocarbons that contain one double bond. They have the general formula: CnH2n

Alkenes are hydrocarbons of a non-cyclic structure in which two carbon atoms are in the state of sp2 hybridization and are connected to each other with a double bond.

Isomers of alkenes (E-Z Isomerism)

The bond angles are at about  $120^{\circ}$ , and rotation about the C=C axis is restricted, since twisting through  $90^{\circ}$  would mean the p-orbitals would no longer

overlap and the  $\pi$ -bond would be broken. The restriction of rotation produces isomers called E-Z isomers (geometric isomers or cis-trans isomers) For E-Z isomerism (cis-trans isomerism) to occur there must be a double bond and two different groups on each of the double bonded carbon atoms The E-Z (cis / trans) isomers will be chemically very similar, though not quite identical, and will have slightly different melting and boiling points. [Note that a third isomer, 2methylpropene, which has two methyl groups attached to the same carbon atom, is a structural isomer of these, as is but-1-ene] E- and Z- vs cis-trans nomenclature The cis trans system breaks down with examples like; The E-Z naming system is more useful than the cis-trans system. The naming of the isomer is determined by priorities. Each atom on the double bond is given a priority determined by its atomic number. The smaller the atomic number the lower the priority – hydrogen in the example above. If atoms with the lowest priority are on the same side on each end of the C=C the isomer is called the Z-isomer. (Z=Zusammen (together)). If atoms with the lowest priority are on the same side on each end of the C=C the isomer is called the E-isomer. (E=Entgegen (opposite)

This is called the pi,  $\pi$ , bond. The electron clouds in ethene can be represented as shown below.



#### Physical properties of Alkenes.

The first four  $(C_2H_4-C_4H_8)$  representatives are gases, the next ten are liquids  $(C_5H_{10}-C_{16}H_{32})$ , followed by solids.

#### Chemical properties.

If we compare alkenes and alkanes, alkenes are more reactive due to the presence of the C=C double bond. It is possible for the double bond to break, allowing each carbon to form a new bond, which is often energetically favourable. Halogens, hydrogen halides, hydrogen and potassium manganate (VII) will produce addition reactions with alkenes. Addition of hydrogen (hydrogenation) Alkenes react with hydrogen in the presence of a nickel catalyst at t=  $150^{\circ}$ C

Hydrogenation (reduction) of an alkene



1. Hydrogenation

$$H_2C = CH - CH_3 + H_2 \xrightarrow{N_1} H_3C - CH_2 - CH_3$$

Propane

# 4. Halogenation

$$\begin{array}{c} H_2C = CH_2 + Cl_2 \rightarrow Cl - CH_2 - Cl_2 - Cl \\ 1,2 \text{-dichloroethane} \\ H_3C - CH = CH - CH_3 + Br_2 \rightarrow H_3C - CH - CH - CH_3 \\ & Br & Br \\ \end{array}$$

2,3-dibromobutane

# 5. Hydrohalogenation

$$\begin{array}{c} H_2C = CH_2 + HCl \rightarrow H_3C - CH_2 - Cl \\ Chloroethane \\ H_2C = CH - CH_3 + HBr \rightarrow H_3C - CH - CH_3 \\ Br \end{array}$$

2-bromopropane

When addition of a hydrogen halide takes place, if the alkene is not symmetrical, the hydrogen adds to the carbon that already has the most hydrogen. This is called Markovnikoff's rule

$$H_{2}C = CH_{2} + H_{2}O \xrightarrow{H_{2}SO_{4}} H_{3}C - CH_{2} - OH$$
  
ethanol  
$$H_{2}C = CH - CH_{2} - CH_{3} + H_{2}O \xrightarrow{H_{2}SO_{4}} H_{3}C - CH - CH_{2} - CH_{3}$$

butanol-2

# **6.** Oxidation reaction

$$H_2C = CH_2 + 3O_2 \xrightarrow{t^\circ} 2CO_2 + 2H_2O$$
  
Carbon dioxide

$$2H_2C = CH_2 + O_2 \xrightarrow{Ag} 2O \left( \begin{array}{c} CH_2 \\ CH_2 \end{array} \right)$$

ethylene oxide

$$2H_2C = CH_2 + O_2 \xrightarrow{PdCl_2, CuCl_2} 2H_3C - C \xrightarrow{PdCl_2, CuCl_2} H_3C - C \xrightarrow{PdCl_2} H_3C - C \xrightarrow{PdCl_$$

acetaldehyde

polyatomic alcohol

The discoloration of the potassium permanganate solution is a qualitative reaction to a double bond

$$3 \text{CH}_2 = \text{CH} - \checkmark + 2 \text{KMnO}_4 + 4 \text{H}_2\text{O} \xrightarrow{0^{\circ}\text{C}} \rightarrow 3 \checkmark - \text{CH} - \text{CH}_2 + 2 \text{MnO}_2 + 2 \text{KOH}$$

Alkenes with terminal double bonds are characterized by the following reactions

$$H_{2}C \neq CH-CH_{3} + 2KMnO_{4} + 3H_{2}SO_{4} \xrightarrow{t^{o}}$$
$$\rightarrow H_{3}C-C \bigvee_{OH}^{0} + CO_{2} + K_{2}SO_{4} + 2MnSO_{4} + 4H_{2}O_{4}$$
acetic acid

Double bond at tertiary carbon, R'R=. The unit is oxidized to the ketone R'-CO-R:

$$5H_{3}C-C=CH-CH_{3}+6KMnO_{4}+9H_{2}SO_{4} \xrightarrow{t^{\circ}}$$

$$CH_{3} \rightarrow 5H_{3}C-C-CH_{3}+5 \xrightarrow{O}_{HO}C-CH_{3}+3K_{2}SO_{4}+6MnSO_{4}+9H_{2}O$$

$$5H_{2}C = C - CH_{3} + 8KMnO_{4} + 12H_{2}SO_{4} \xrightarrow{t^{\circ}}$$
  

$$CH_{3}$$
  

$$\rightarrow 5H_{3}C - C - CH_{3} + 5CO_{2} + 4K_{2}SO_{4} + 8MnSO_{4} + 17H_{2}O$$

**1.Double bond at secondary carbon**, R–CH =. The link is oxidized to the R–JUICE group, and a carboxylic acid salt is formed:

$$3H_3C-CH \neq CH-CH_2-CH_3 + 8KMnO_4 \xrightarrow{t^{\circ}}$$
  
 $\rightarrow 3H_3C-C \bigvee_{OK}^{\circ} + 3 \bigvee_{KO}^{\circ} C-CH_2-CH_3 + 8MnO_2 + 2KOH + 2$ 

2. Double bond at the H<sub>2</sub>C= It is oxidized to potassium carbonate:  $3H_2C=CH-CH_3+10KMnO_4 \xrightarrow{t^o}$ 

$$\rightarrow 3 H_3 C - C \bigvee_{OK}^{\#O} + 3 K_2 CO_3 + 10 MnO_2 + KOH + 4 H_2 O$$

**+**0

$$H_{3}C-C=CH-CH_{3}+2KMnO_{4} \xrightarrow{\mathsf{L}} CH_{3}$$
$$\rightarrow H_{3}C-C-CH_{3}+\mathcal{O}_{KO}C-CH_{3}+2MnO_{2}+KOH$$

4. Polymerization of ethylene

$$nH_2C = CH_2 \xrightarrow{\text{Kat}} (-CH_2 - CH_2 - )_n$$
polyethylene

#### **Problems.**

**1.** Write the formulas of alkane isomers  $C_5H_{10}$ . Name them.

2. Compare the reactivity of Alkanes and Alkenes.

**3.** What type of hybridization is typical for alkenes?

**4.** Is the addition reaction or substitution reaction most characteristic of Alkanes?
**5.** What is the name of the oxidation reaction of alkenes with potassium permanganate (with alkali)?

# Unit 6. Alkadienes

Alkadienes or Dienes hydrocarbons (alkadienes)-these are hydrocarbons, in the molecules of which there are two double bonds between carbon atoms. They have the general formula :  $C_nH_{2n-2}$ .(n $\geq$ 3)

Depending on the relative position of the double bonds in the molecules, alkadienes are divided into two types:

**1.Cumulated dienes** 

2. Conjugated dienes

3. Unconjugated dienes

# **Chemical properties.**

Alkadienes with conjugated bonds differ in chemical properties of alkenes as it differs from other types of alkadienes. The chemical behavior of these compounds is explained by the coupling effect. This term refers to the formation of a single electron cloud as a result of the mutual overlap of four non-hybridized pclouds.

## Addition reactions.

## **Hydrogenation**

 $H_2C = CH - CH = CH - CH_3 + H_2 \xrightarrow{N_1} H_3C - CH = CH - CH_2 - CH_3$ 

Halogenation  $H_2C=CH-CH=CH_2+Cl_2 \rightarrow Cl-CH_2-CH=CH-CH_2-Cl$ 

Hydrohalogenation  $H_2C=CH-CH=CH_2 + HCl \rightarrow Cl-CH_2-CH=CH-CH_3$ 

Polymerization

$$\begin{array}{c} H_2C = C - CH = CH_2 \xrightarrow{\text{Kar}} (-CH_2 - C = CH - CH_2 -)_n \\ CH_3 & CH_3 \end{array}$$

Oxidation reaction



n-isoprene

isoprene rubber

When polymerization of compounds with conjugated bonds is dominated by 1,4-addition, which results in a regular unsaturated polymer.

## Problems.

- **1.** What is the peculiarity of alkadienes?
- 2. What explains the polymerization reaction of alkadienes?
- 3. What groups are alkadienes divided into?
- 4. What factors determine the chemical properties of alkadienes?
- **5.** Specify the differences in the chemical properties of alkenes alkadienes

# Unit 7. Alkynes.

Alkynes are non-cyclic hydrocarbons in whose molecules carbon atoms are in a state of sp hybridization and are connected to each other with a triple bond.

They have the general formula :  $C_nH_{2n-2}$ . (n $\geq 2$ )

Alkynes are characterized by: chain isomerism, triple bond position isomerism, interclass isomerism between alkynes and alkadienes.

sine representatives of this group.				
Name	Structure	Formula		
acetylene (ethine)	HC≡CH	$C_2H_2$		
propin	$HC \equiv C - CH_3$	$C_3H_4$		
butin-1	$HC \equiv C - CH_2 - CH_3$	$C_4H_6$		

Some representatives of this group:

Trivial names It is useful to know the historically established traditional (trivial) names of the following substances:

# $H_2C = CH - C \equiv CH$ vinyl acetylene

The numbering is carried out from the end to which the triple bond is closest, regardless of the positions of the substituents. For example:



2,5-dimethyl-5-ethyloctin-3

# **Chemical properties.**

1. Hydrogenation reaction  

$$HC \equiv CH + 2H_2 \xrightarrow{Ni} H_3C - CH_3$$
  
Ethan

## 2. Halogenation



## 3. Hydrohalogenation reaction

$$HC = CH + 2HCl \rightarrow \underbrace{Cl}_{Cl}CH - CH_{3}$$
1,1-dichloroethane

The reaction proceeds according to Markovnikov's Rule, geminal dihaloalkanes are formed:

$$HC \equiv C - CH_3 \xrightarrow{HC1} H_2C = C - CH_3 \xrightarrow{HC1} H_3C - C - CH_3$$

#### **4.** Kucherov reaction (hydration)

The reaction is carried out in an acidic environment in the presence of mercury salts. A special case: acetylene, acetylene hydration gives an aldehyde (ethanal), the remaining alkynes, according to Markovnikov's Rule, give ketones:

$$HC \equiv CH + H_2O \xrightarrow{H^*, Hg^{2^*}} H_3C - C \xrightarrow{H} H_3C + H_2O \xrightarrow{H^*, Hg^{2^*}} H_3C - C \xrightarrow{H} H_3C - C - CH_3$$

**5.** Trimerization Acetylene and its homologues form arenas when heated with a catalyst. In this case, acetylene gives benzene and its homologues form substituted arenes.:



benzene



trimethylbenzene

Dimerization of acetylene Acetylene dimerization is carried out in the presence of an aqueous ammonia solution CuCl, the dimer vinyl acetylene is formed:

$$2HC \equiv CH \xrightarrow{CuCl, NH_4Cl} H_2C = CH - C \equiv CH$$

#### **1.Oxidation reactions**

Like alkanes, alkynes burn in air, and are completely oxidized to carbon dioxide and water.

$$2\text{HC} \equiv \text{CH} + 5\text{O}_2 \stackrel{\text{t}^\circ}{\longrightarrow} 4\text{CO}_2 + 2\text{H}_2\text{O}$$

1. Triple bond at secondary carbon, R-C=. The unit is oxidized to the carboxyl group R-COOH, and a carboxylic acid is formed.:

$$5H_{3}C-C \neq C-CH_{3} + 6KMnO_{4} + 9H_{2}SO_{4} \xrightarrow{t^{\circ}}$$
$$\rightarrow 10H_{3}C-C \swarrow OH + 3K_{2}SO_{4} + 6MnSO_{4} + 4H_{2}O$$

2. Triple bond at primary carbon,  $HC\equiv$ . The link is oxidized to oxidized to carbon dioxide and water:

$$5HC \equiv C - CH_2 - CH_3 + 8KMnO_4 + 12H_2SO_4 \xrightarrow{t^o} 5H_3C - CH_2 - C \swarrow O_{OH} + 5CO_2 + 4K_2SO_4 + 8MnSO_4 + 12H_2O$$

3. Special case: acetylene oxidation. In the first stage, acetylene is oxidized to oxalic acid without breaking the chain. But oxalic acid, in turn, is oxidized by permanganate to carbon dioxide, so it is better to carry out oxidation in a neutral environment (see below):

In a neutral environment The harsh oxidation of alkenes without the addition of acid is similar. The only difference is that the potassium hydroxide formed during the decomposition of permanganate neutralizes the oxidation products. Instead of carboxylic acids, their salts are formed:  $H_3C-C \equiv C-CH_2-CH_3 + 2KMnO_4 \xrightarrow{t^\circ}$ 

$$\rightarrow H_3C - C O + O C - CH_2 - CH_3 + 2MnO_2$$

Carbonates are formed instead of carbon dioxide. If the potassium ions from the decomposition of permanganate are not enough to form an average carbonate, bicarbonate is formed.:

$$3 \text{HC} = \text{C} - \text{CH}_3 + 8 \text{KMnO}_4 \xrightarrow{\text{t}^\circ} \\ \rightarrow 3 \text{H}_3 \text{C} - \text{C} \bigvee_{OK}^{\not O} + 2 \text{K}_2 \text{CO}_3 + \text{KHCO}_3 + 8 \text{MnO}_2 + \text{H}_2 \text{O}$$

Acetylene in a neutral medium gives potassium oxalate:

$$3 \text{HC} = \text{CH} + 8 \text{KMnO}_4 \xrightarrow{\text{t}^\circ} 3 \frac{\text{O}}{\text{KO}} \text{C} - \text{C} \frac{\text{O}}{\text{OK}} + 2 \text{KOH} + 8 \text{MnO}_2 + 2 \text{H}_2\text{O}$$

6.Substitution reaction

# $HC \equiv CH + 2CuCl = Cu - C \equiv C - Cu + 2HCl$

copper acetylenide

## Problems.

1. What are the chemical properties of alkyne?

2. What are the properties that alkynes share?

**3.** What is the difference between alkene and alkyne?

4. What are some examples of alkane, alkene, and alkyne?

5. Is CIS-TRANS isomerism possible for alkynes?

6. Suggest ways to obtain acetylene from inorganic substances. Write the equations of the corresponding reactions.

7. With the help of some reagents and under what conditions it is possible to obtain butyn-2 from butene-2? Write down the reaction equations.

8. Why in all the works connected with the acetylene is strongly prohibited to use copper or its alloys in reactors, tools, communications, etc.?

# Unit 8. Aromatic hydrocarbons

Aromatic hydrocarbons, also called arenes, are substances whose molecules contain one or more benzene rings, cyclic structures with a special natural bond between carbon atoms. The molecular formula of benzene is  $C_6H_6$ . In 1865, the first structural formula of benzene was proposed by the German scientist A. Kekule



All carbon atoms in benzene are in the sp3 hybridization state.

A benzene ring containing a closed system of conjugated double bonds has a planar structure and specific properties, which is why hydrocarbons containing such a ring are classified into a separate class of aromatic hydrocarbons (arenes).

Since the double bonds in the ring are delocalized, they are often referred to as a ring in a hexagon .A large number of organic molecules (including important biological compounds) contain a benzene ring. Benzene is the simplest representative of arenes.

The simplest multinucleated aromatic hydrocarbons are

Chemical properties. Addition reactions 1. Halogenation of arenes in the light



```
Hexachlorane
```

## 2. Hydrogenation reaction



Cyclohexane

A special case, different from reactions with homologues

## Substitution reactions

3. Nitration of Arenes



Nitrobenzene

4. Sulfonation

$$+ H_2 SO_{4 \text{ Kohu}} \rightarrow - SO_3 H + H_2 O$$

Benzenesulfonic Acid

5. Halogenation (catalytic)



Chlorobenzene

6. Alkylation is the substitution of hydrogen atoms in a benzene molecule by a strong radical to form benzene homologues. Alkyl halides are most often alkylating reagents. This method of alkylation of aromatic hydrocarbons was developed jointly by Sh.Friedel and D. Crafts in 1877.

**Friedel-Crafts reaction.** 



7. Alkylation of benzene by alkenes



8.Oxidation reaction



## **Problems.**

*1.* What determines the chemical properties of aromatic hydrocarbons?

2. What is the peculiarity of Friedel Kravets' reaction?

**3.** Explain why addition reactions are more typical for aromatic hydrocarbons than for unsaturated hydrocarbons?

4. Describe the physical properties of aromatic hydrocarbons.

**5.** What type of hybridization is typical for carbon atoms in a benzene molecule?

# Unit 9. Alcohols and Phenols.

Alcohols are derivatives of hydrocarbons in which one or more hydrogen atoms are replaced by the hydroxyl group -OH. General formula saturated monatomic alcohols: :  $C_nH_{2n+1}OH$  or  $C_nH_{2n+2}O$ 

Alcohols are stable, in the molecules of which the OH group is bound to sp3 by hybridized carbon atoms, with no more than one OH group associated with each carbon atom.

The systematic name of the simplest alcohol is based on: – the root, which indicates the length of the chain (memo: list of roots), – a suffix indicating the presence/absence of multiple connections, – the second suffix is "ol", this suffix indicates a hydroxyl group and, accordingly, belonging to the class of alcohols.

 $CH_3OH$ methanol $CH_3CH_2OH$ ethanol $CH_3(CH_2)_2OH$ propanol $CH_3(CH_2)_3OH$ butanol $CH_3(CH_2)_4OH$ pentanol $CH_3(CH_2)_5OH$ hexanol $CH_3(CH_2)_6OH$ heptanol $CH_3(CH_2)_7OH$ octanol $CH_3(CH_2)_9OH$ decanol

If the alcohol is unsaturated, a locant is added to the first suffix (if necessary), indicating the position of the multiple bond.:

H<sub>3</sub>C-CH-CH=CH-CH<sub>3</sub> OH

penten-3-ol-2

By the way, the hydroxyl group is a functional group, it takes precedence over multiple bonds or non-functional substituents when choosing numbering, so in the example above, the numbering was conducted not from the end to which the double bond is closer, but from the one to which the –OH group is closer. Also, the hydroxyl group has priority when choosing the parent chain (it should be in it), for example:



5-methyl-2-propylhexanol-1

However, if the molecule contains a higher-priority functional group, it becomes the senior one, and the hydroxyl group is indicated as a "hydroxy" (sometimes simply "oxy") substituent before the root along with the rest of the substituents.:



2-hydroxy-4-methylhexanoic acid

In this example, the carboxyl group takes precedence over the hydroxyl group, the substance should be classified as carboxylic acids, numbering goes from right to left.

Radical functional nomenclature Within the framework of this nomenclature, the hydrocarbon part of the molecule is considered as a radical with a hydroxyl group and is indicated before the alcohol construction:

 $HO-CH_2-CH_3$   $H_3C-CH_2-CH_2-OH$ 

ethyl alcohol

propyl alcohol

H<sub>3</sub>C-CH-CH<sub>2</sub>-CH<sub>3</sub> OH OH sec-butyl alcohol

isopropyl alcohol



Classification According to the degree of carbon substitution at which the hydroxyl group is located, alcohols are divided into primary, secondary, and tertiary:



According to the number of hydroxyl groups, alcohols are divided into monatomic and polyatomic. Polyatomic, in turn, is sometimes subdivided into diatomic, triatomic, and so on. For more information about polyatomic alcohols, see the corresponding paragraph below.



Aromatic, alicyclic and aliphatic alcohols are also distinguished by the structure of the chain.:



By the presence of multiple bonds: marginal and unsaturated alcohols. Among unsaturated alcohols, enols are particularly distinguished – alcohols, the hydroxyl group of which is located directly at the double bond: –CH=CH–OH. The corresponding paragraph below is devoted to their special properties.

The interclass isomers of such alcohols are esters. For example, both of these substances meet the gross formula  $C_3H_8O$ :

H<sub>3</sub>C-CH-CH<sub>3</sub> OH  $H_3C - CH_2 - O - CH_3$ methyl ethyl ether propanol-2

Alcohols are also characterized by structural isomerism: the isomerism of the carbon skeleton and the isomerism of the functional group position.



The general formula of unsaturated alcohols with one multiple bond:  $C_nH_{2n}O$ . Their interclass isomers are aldehydes, ketones, and cyclic alcohols:



The interclass isomers of aromatic alcohols are phenols:





The alcohol molecule, unlike the hydrocarbon molecules, is polar. Oxygen is a very strong nonmetal with a high electronegativity of 3.5, it attracts a common electron pair from carbon and especially from hydrogen. Due to the proximity of common electron pairs, the oxygen atom acquires some excess negative charge (it is designated  $\delta$ -, such as "a little minus"), and carbon and hydrogen deprived of electrons acquire some positive charge ( $\delta$ +).



This difference between the poles of a molecule (the negative and positive regions of the molecule) is called polarity. On the contrary, for example, alkanes consist only of elements whose electronegativity is close to 2.4 & 2.1, all bonds between these atoms are weakly polar, this is not enough for the molecule to have pronounced poles, such molecules are called nonpolar. The polarity of alcohol molecules determines two important features in their physical properties: Hydrogen bonds (dotted line) 1. Alcohols, as polar substances, are well soluble in polar solvents, for example, ethanol is well soluble in water. Conversely, alcohols themselves are often used as good polar solvents. 2. Alcohols have a relatively high boiling point (significantly higher than that of hydrocarbons with the same molecular weight). This is due to the presence of hydrogen bonds between alcohol molecules (green dotted line in Fig.). The positively charged hydrogen of the hydroxy group is electrostatically attracted to the negatively charged oxygen of the neighboring molecule. These hydrogen bonds prevent the substance from evaporating. Lower monatomic alcohols are colorless bitter liquids with a pungent unpleasant odor. They are poisonous or harmful to health. Polyhydric alcohols have no unpleasant odor and even taste sweet.

Chemical properties Acidic and basic properties.

**1.**Alcoholss are Bronsted OH –acids and O-H chemical bond is cleaved under the impact of active metals or their hydrides with formation of salts

 $2H_3C-CH_2-OH+2Na \rightarrow 2H_3C-CH_2-ONa+H_2$ 

2. Reactions with electrophilic site participation

All reaction conditions depend on the alcohol structure and the hydrogen halide nature. HI > HBr > HCl The reaction takes place in a highly acidic environment (as a rule, concentrated  $H_2SO_4$  is used, or an excess of hydrogen halide itself). The alcohol group is replaced by a halogen, and haloalkanes are formed.:

$$\begin{array}{l} H_{3}C-CH_{2}-OH+HCl \xrightarrow{H_{2}SO_{4 \text{ конц}}} H_{3}C-CH_{2}-Cl+H_{2}O\\ H_{3}C-CH_{2}-OH+HBr_{\mu_{3}6} \rightarrow H_{3}C-CH_{2}-Br+H_{2}O \end{array}$$

# 7. Reaction with CH-acidic site participation (elimination). Zaitsev's rule.

$$\begin{array}{c} H_{3}C-CH-CH-CH_{2}-CH_{3} \xrightarrow{180^{\circ}C, H_{2}SO_{4 \times OH4}} H_{3}C-CH=C-CH_{2}-CH_{3}+H_{2}O \\ OH CH_{3} & CH_{3} \\ & 3-methylpentene-2 \end{array}$$

## 4. Intermolecular dehydration

$$\begin{array}{l} H_{3}C-CH_{2}-\overrightarrow{OH+H}O-CH_{2}-CH_{3} \xrightarrow{140^{\circ}C, H_{2}SO_{4 \text{ KOHU}}} \\ \rightarrow H_{3}C-CH_{2}-O-CH_{2}-CH_{3}+H_{2}O \end{array}$$

diethyl ether

# 5. Esterification

$$H_{3}C-C \bigvee_{OH}^{\mu O} + HO-CH_{2}-CH_{3} \xrightarrow{H_{2}SO_{4}} H_{3}C-C \bigvee_{O-CH_{2}-CH_{3}}^{\mu O} + H_{2}O$$

ethyl acetate

#### 6. The Catalytic Amination of Alcohols

$$H_3C - CH_2 - OH + NH_3 \xrightarrow{t^\circ, kat} H_3C - CH_2 - NH_2 + H_2O$$

Amination of alcohols with ammonia

**7. Dehydrogenation** (when alcohol vapors are passed over the catalyst at temperature  $300-400^{\circ}$ C)

Primary alcohols converted to aldehydes, secondary alcohols converted to ketones:

$$H_3C - OH \xrightarrow{t^{\circ}, Cu} HC H^{\circ} + H_2$$

Dehydrogenation (oxidation) of an alcohol  $H_{3}C-CH-CH_{3} \xrightarrow{t^{e}, Cu}_{OH} H_{3}C-C-C-CH_{3} + H_{2}$ 

## 8. Oxidation with copper(II) oxide

It forms an aldehyde or ketone (if the alcohol was secondary)

$$H_3C-CH_2-OH+CuO \xrightarrow{t^{e}} H_3C-C \xrightarrow{\not O} H+Cu+H_2O$$

#### 9. Catalytic oxidation by oxygen

This is another way to produce an aldehyde or ketone.:  

$$2H_3C-CH-CH_2-CH_3+O_2 \xrightarrow{t^\circ, Cu} 2H_3C-C-CH_2-CH_3+2H_2O$$
  
OH

**10. Oxidation** with permanganate or bichromate Oxidation with strong laboratory oxidizing agents always proceeds to the end (to the non-oxidizable product). If it is a primary alcohol (except methanol), the oxidation continues to carboxylic acid.:

$$5H_{3}C-CH_{2}-OH+4KMnO_{4}+6H_{2}SO_{4} \rightarrow$$
  
$$\rightarrow 5H_{3}C-C \bigvee_{OH}^{\not O}+2K_{2}SO_{4}+4MnSO_{4}+11H_{2}O$$

11. Oxidation H<sub>3</sub>C-CH<sub>2</sub>-OH +  $3O_2 \xrightarrow{t^\circ} 2CO_2 + 3H_2O$ 

Nomenclature.

For the nomenclature of alcohols in general, see the corresponding paragraph above. The number of hydroxyl groups is indicated by multiple prefixes "di", "three", "tetra", and so on before the suffix "ol", then the locants are listed.:



The most important polyatomic alcohols have trivial names:



C

Sorbitol

Lower polyatomic alcohols are colorless, odorless, and sweet-tasting liquids.

Chemical properties Polyatomic alcohols have all the properties of monatomic alcohols, for more information see the corresponding paragraph above, here we will focus on the features of polyatomic alcohols.

1.Reaction with Alkalis.

Alcoholates are formed

$$\begin{array}{ccc} CH_2 - OH \\ \downarrow \\ CH_2 - OH \end{array} \xrightarrow[]{} \begin{array}{c} NaOH \\ \longleftarrow \end{array} \xrightarrow[]{} \begin{array}{c} CH_2 - ONa \\ CH_2 - OH \end{array}$$

# 2. Qualitative reaction with copper(II) hydroxide



# 3. Production of nitroglycerin

$$\begin{array}{c} \mathrm{CH}_2-\mathrm{OH}+3\,\mathrm{HNO}_{3\,\mathrm{conc}} \rightarrow \mathrm{CH}_2-\mathrm{O}-\mathrm{NO}_2+3\,\mathrm{H}_2\mathrm{O}\\ \mathrm{CH}-\mathrm{OH} & \mathrm{CH}-\mathrm{O}-\mathrm{NO}_2\\ \mathrm{CH}_2-\mathrm{OH} & \mathrm{CH}_2-\mathrm{O}-\mathrm{NO}_2 \end{array}$$

4.Formation of Lipids conc

$$\begin{array}{c} CH_2 - OH + 3 \\ CH - OH \\ CH_2 - OH \\ H_3C - (CH_2)_{14} - CH_3 \rightarrow \\ H_3C - (CH_2)_{14} - C - O - CH_2 \\ H_3C - (CH_2)_{14} - C - O$$

tripalmitoylglycerin

5. Oxidation

# $5CH_2-OH + 10 KMnO_4 + 15 H_2SO_4 \rightarrow$ $CH_2-OH \rightarrow 10 CO_2 + 5K_2SO_4 + 10 MnSO_4 + 30 H_2O$

## Problems.

- 1. How does alcohol act as an acid?
- 2. Is alcohol acidic or basic?
- 3. How do you show that alcohol can act as an acid and a base?
- 4. Is alcohol acid or base?
- 5. Why is water more acidic than alcohol?

# Unit 9. Phenols.

Phenols are derivatives of aromatic hydrocarbons in which one or more hydroxyl groups are directly bound to the benzene core, that is, OH at the benzene core (phenols should not be confused with aromatic alcohols).

The simplest representative of the class is called that.:



The systematic names of other phenols are constructed by listing the radicals before the word "phenol" with an indication of their locants. If there is only one substitute, ortho-, meta-, and para locants characteristic of arenas are more often used.:



meta-ethylphenol paraphenylphenol

If there are several substitutes, digital locations are used. The numbering is based on the hydroxyl group, the numbering direction is chosen so that the first lockout is the smallest.:



Polyatomic phenols In the systematic nomenclature of polyatomic phenols, benzene is used as the basis for the name, and hydroxy groups with their positions are indicated as "hydroxy" substituents:



The simplest diatomic phenols have trivial names:



# **Chemical properties.**

Phenols are very insidious compounds. They are often confused with alcohols, but their properties are very different from those of alcohols. These differences are listed below.



Reactions with alkalis and active metals The acidic properties of phenols are stronger than alcohols, phenols react not only with metals, but also with alkalis, and phenolates are formed.:



sodium phenolate

Polyatomic phenols react reversibly with alkalis, monosubstituted phenolates predominate without a strong excess of alkali (by analogy with acid salts of weak acids):



Phenols do not enter into dehydration and esterification reactions. To obtain phenol esters and esters, alternative methods of dehydration and esterification are used: first, phenol is converted to phenolate, and the phenolates are further alkylated or acylated:

## Williamson's reaction .

Phenolates derived from phenols are alkylated with haloalkanes, which is a method of producing phenolic esters.:



Acylation with halides

For this reaction, it is also necessary to first obtain phenolate, then it is acylated with halide anhydride, so that phenolic esters can be obtained.

$$\begin{array}{|c|} & & & \\$$

Substitution reactions in the nucleus As aromatic compounds, phenols enter into substitution reactions, with the hydroxyl group facilitating substitution in ortho and para positions, for example, halogenation:



## Problems.

- 1. What are the chemical properties of Phenols?
- 2. What are some examples of chemical properties?
- 3. Do phenols exhibit acidic or basic properties to a greater extent?
- 4. What is the difference between phenols and alcohols?
- 5. What is a trivial name for hydroxybenzene?

# Unit 10. Aldehydes and Ketones

Carbonyl compounds are a common name for organic substances with a carbonyl group (C=O) in a molecule. Since the chemical properties of carbonyl compounds strongly depend on the location of the carbonyl group in the chain, this group of compounds is considered as two separate classes: aldehydes and ketones. In aldehydes, the carbonyl group is located at the end of the chain, while in ketones it is not at the end.

Aldehydes are organic compounds whose molecules contain an aldehyde group associated with a hydrocarbon radical



The general formula of aldehydes and ketones:  $C_nH_{2n}O$ 

Aldehydes

Ketones



Thus, aldehydes and ketones are interclass isomers to each other, and unsaturated alcohols and cyclic alcohols are also their interclass isomers.

We start counting carbon atoms from a functional group.

Nomenclature.

The systematic name of the aldehyde is based on: – the root, which indicates the length of the chain (memo: list of roots), – a suffix indicating the presence/absence of multiple connections, – the ending is "al", this indicates the terminal carbonyl group and, accordingly, belonging to the class of aldehydes. For example, see the analysis of the name "butanal" on the right.

$$H_{3}C - CH_{2} - C$$

If the molecule contains substituents, they are listed before the root indicating the locants, numbering is based on the aldehyde group.:



4,5-dimethylhexanal

If the carbonyl group is not the oldest in the molecule, it is referred to before the name as an oxo substituent (an alternative version of keto).:



3-oxopropanoic acid

The same should be done if both an aldehyde and a keto group are present in the molecule at the same time. The aldehyde group is older, so the compound is considered an aldehyde, and the keto group is referred to as a substituent.

4-oxohexanal

If the carbonyl group is a radical, it is called a formyl:



3-Formyl glutaric acid

Trivial names of aldehydes are the same root as the trivial names of the corresponding acids, only "fatty acid" is replaced by "aldehyde". Another way is to use the roots of carboxylic acid anions ("acetate", "butyrate"...), replacing the suffix "at" with "aldehyde":

Formula	Name
CH <sub>2</sub> O	methanal
$C_2H_4O$	ethanal
C <sub>3</sub> H <sub>6</sub> O	propanal
$C_4H_8O$	butanal
$C_5H_{10}O$	pentanal

Aldehydes can be classified by the presence/absence of multiple bonds (marginal/unsaturated), cycles (aliphatic/alicyclic), aromatic structures, by the number of aldehyde groups (monoaldehydes/dialdehydes/polyatomic aldehydes), by the presence of non-aged functional groups. Here we will limit ourselves to mentioning the most important groups of aldehydes.: Unsaturated aldehydes have multiple bonds in the molecule, they combine the properties of aldehydes and alkenes/alkynes.:



#### acrolein (propenal)

Aromatic aldehydes have a benzene core in the molecule, the simplest aromatic aldehyde.:



Dialdehydes have two aldehyde groups in the chain, ending in "dial":



Aldose monosaccharides (carbohydrates) are a special type of aldehydes with hydroxyl groups for all carbons except carbonyl group carbon:



The interclass isomers of such aldehydes are ketones, unsaturated alcohols, unsaturated esters, and cyclic alcohols. For example, these three substances correspond to the gross formula  $C_3H_6O$ :



Of the two types of structural isomerism, aldehydes are characterized by carbon skeleton isomerism.:





**Chemical Properties.** 

Oxygen of the carbonyl group is bound to carbon by a  $\sigma$ -bond and a  $\pi$ -bond. The  $\pi$  bond is less strong, it breaks easily, due to which carbonyl compounds (both aldehydes and ketones) are prone to addition reactions.Let's start with them.: 1. Hydrogenation The reaction takes place in the presence of a catalyst:

$$H_3C - C \xrightarrow{\mu O}_H + H_2 \xrightarrow{Ni}_H H_3C - CH_2 - OH$$

#### Addition of alcohols.

The reaction proceeds with primary alcohols in an acidic environment, semi-acetals are formed.

$$H_{3}C-CH_{2}-OH + \bigcup_{H}^{O}C-CH_{3} \xrightarrow{H^{+}}$$

$$HO = HO = H_{3}C-CH_{2}-O$$

$$H_{3}C-CH_{2}-O = O$$

The reaction can continue to produce acetals:

HO  
H<sub>3</sub>C-CH<sub>2</sub>-O  
CH-CH<sub>3</sub> + HO-CH<sub>2</sub>-CH<sub>3</sub> 
$$\xrightarrow{H^+}$$
  
 $\xrightarrow{H_3C-CH_2-O}$   
H<sub>3</sub>C-CH<sub>2</sub>-O  
CH-CH<sub>3</sub> + H<sub>2</sub>O

#### **Oxidation.**

This is how aldehydes differ from ketones. Ketones are very resistant to oxidation, but aldehydes are oxidized even by weak oxidizing agents. The general principles of aldehyde oxidation are here. 3. The reaction of the "silver mirror" This is a qualitative reaction to aldehydes, using Tollens reagent (an ammonia solution of silver oxide). Since ammonia is present in the solution, the oxidation does not proceed to the carboxylic acid, but to its salt.:

$$H_{3}C - C \bigvee_{H}^{\not O} + 2 \left[ Ag(NH_{3})_{2} \right] OH \rightarrow H_{3}C - C \bigvee_{ONH_{4}}^{\not O} + 2Ag \downarrow + 3NH_{3} + H_{2}O$$

A sign of the reaction is the loss of silver plaque on the glass of the test tube. The exception is methanal, which is oxidized to ammonium carbonate. 4. Oxidation with copper(II) hydroxide Another qualitative reaction:

$$H_{3}C-CH_{2}-C \swarrow O H_{2} \rightarrow H_{3}C-CH_{2}-C \swarrow O H_{2} \rightarrow H_{2}C + Cu_{2}O \downarrow + 2H_{2}O \downarrow +$$

A sign of the reaction is the precipitation of a red–brown precipitate of copper  $\mbox{oxide}(I)$ 

Oxidation with permanganate or bichromate In an acidic environment:

$$5H_{3}C-C \bigvee_{H}^{0} + 2KMnO_{4} + 3H_{2}SO_{4} \rightarrow$$
$$\rightarrow 5H_{3}C-C \bigvee_{OH}^{0} + K_{2}SO_{4} + 2MnSO_{4} + 3H_{2}O$$

In the neutral :

$$3H_3C - C \bigvee_H^{O} + 2KMnO_4 \rightarrow 2H_3C - C \bigvee_{OK}^{O} + O G C - CH_3 + 2MnO_2 + H_2O$$

# Hydrogen addition reaction

$$H_3C - C \searrow^{0} H + 2H^0 \rightarrow H_3C - CH_2 - OH$$

Production of phenol-formaldehyde resins



Ketones are carbonyl compounds in which the carbonyl group (C=O) is associated with two hydrocarbon radicals.

$$R_1 - C - R_2$$
  
O

Ketones should not be confused with another class of carbonyl compounds: aldehydes. In aldehydes, the carbonyl group is located at the end of the hydrocarbon chain. The properties of the compound strongly depend on the location of the carbonyl group, therefore aldehydes and ketones are considered as two separate classes.

Formula	Name	Structure
C <sub>3</sub> H <sub>6</sub> O	acetone (propanone)	$H_3C-C-CH_3$
C <sub>4</sub> H <sub>8</sub> O	butanone (methyl ethyl ketone)	$H_3C - C - CH_2 - CH_3$
C <sub>5</sub> H <sub>10</sub> O	Pentanone-2 (propylmethyl ketone)	$H_3C - C - CH_2 - CH_2 - CH_3$
C <sub>6</sub> H <sub>12</sub> O	hexanon-2 (butylmethyl ketone)	$H_3C - C - (CH_2)_3 - CH_3$

The systematic name of ketone is based on: – the root, which indicates the length of the chain (memo: list of roots), – a suffix indicating the presence/absence of multiple connections, – ending with "oh", this indicates the presence of a non-terminal carbonyl group (keto group), – the location of the keto group (if necessary). For example, see the analysis of the name "pentanon-2" on the right.

$$H_{3}C - C - CH_{2} - CH_{2} - CH_{3}$$

Pentanon-2

If the molecule contains substituents, they are listed before the root indicating the locants, numbering is conducted from the end to which the keto group is closer.:

$$\begin{array}{c} H_3C-CH_2-C-CH-CH-CH_3\\ O & CH_3 & CH_3\\ \end{array}$$

4,5-dimethylhexanone-3

The same should be done if both an aldehyde and a ketones group are present in the molecule at the same time. The aldehyde group is older, so the compound is considered an aldehyde, and the keto group is referred to as a substituent.:



If the ketone is polyatomic, multiple prefixes are added.:



butadion



Radical functional nomenclature The carbonyl group is taken as the basis of the molecule, and the word ketone is used as the basis of the name, the remaining parts of the molecule are considered as radicals and are listed at the beginning of the name.:



Classification, isomerism, general formula Ketones can be classified by the presence/absence bonds of multiple (marginal/unsaturated), cycles (aliphatic/alicyclic), aromatic structures, by the number of carbonyl groups (monoketones/diketones/polyatomic ketones), by the presence of non-aged functional groups. Here we will limit ourselves to mentioning the most important groups of ketones .:

Unsaturated ketones have multiple bonds in the molecule:



Aromatic ketones have a benzene core in the molecule:



Butyrophenone

Diketones have two carbonyl groups in the chain:



pentanedione-2,4

Ketose monosaccharides (carbohydrates) are a special type of ketones with hydroxyl groups at all carbons except carbonyl group carbon:



The interclass isomers of such ketones are aldehydes, unsaturated alcohols, unsaturated esters, and cyclic alcohols. For example, these three substances correspond to the gross formula : C<sub>3</sub>H<sub>6</sub>O



Unlike aldehydes, ketones have both types of structural isomerism.:





Pentanon-2



H<sub>3</sub>C-C-CH-CH<sub>3</sub> O CH<sub>3</sub>

Methylbutanone

## **Chemical Properties.**

Oxygen of the carbonyl group is bound to carbon by a  $\sigma$ -bond and a  $\pi$ -bond. The  $\pi$  bond is less strong, it breaks easily, due to which carbonyl compounds (both aldehydes and ketones) are prone to addition reactions. Let's start with them:

#### 1. Hydrogenation



## 3. Addition of alcohols.

The reaction with primary alcohols **in the presence of an acid**, semiacetals are formed:

$$\begin{array}{c} \text{OH} \\ \text{H}_{3}\text{C}-\text{C}-\text{CH}_{3} + \text{CH}_{3} - \text{OH} \xrightarrow{\text{H}^{+}} \text{H}_{3}\text{C} \xrightarrow{\text{O}} - \text{CH}_{3} \\ \text{O} \\ \text{O} \\ \text{CH}_{3} \end{array}$$

## **3. Oxidation.**

Ketones, unlike aldehydes, are very resistant to oxidation, possible only in severe oxidation, and then it goes slowly. During oxidation in an acidic environment, one of the  $\sigma$ -bonds in the carbonyl group breaks, and the fragments are oxidized to carboxylic acids or carbon dioxide. Moreover, since there are two  $\sigma$ -bonds in the carbonyl group, the rupture is random, and a mixture of products is formed.:

$$H_{3}C \stackrel{?}{\leftarrow} CH_{2}-CH_{3} \stackrel{[O], t^{\circ}}{\longrightarrow} H_{3}C-CH_{2}-C \stackrel{\#O}{\searrow} H_{2}C-CH_{2}-C \stackrel{\#O}{\searrow} H_{2}C$$

Similarly, severe oxidation occurs in a neutral environment, but instead of acids, their salts are formed, for example:

$$3H_{3}C-C-CH_{3}+8KMnO_{4} \xrightarrow{t^{\circ}}$$

$$\longrightarrow 3H_{3}C-C \bigvee_{OK}^{\not O} + 2K_{2}CO_{3} + KHCO_{3} + 8MnO_{2} + 4H_{2}O$$

## 4. Addition

When ketones are reduced, secondary alcohols are formed.

$$\begin{array}{c} H_{3}C-C-CH_{3}+2H^{0} \rightarrow H_{3}C-CH-CH_{3} \\ O \\ OH \end{array}$$

## **Questions:**

- What is the difference between an aldehyde and a ketone?
- How can you prepare an aldehyde from a ketone?

• How do you distinguish between aldehyde and ketone?

•What is the difference between carbonyl compounds, aldehydes, and ketones?

• What is the difference between aldehyde and acetone?

• What can aldehyde and ketone be distinguished by?

# Unit 11. Carboxylic acid.

Carboxylic acids are organic substances containing a carboxyl group – COOH (structural image on the right).

−C<sup>∦O</sup> OH

Carboxylic acid molecules are polar due to the presence of two electronegative oxygen atoms



- They also participate in hydrogen bonding due to the presence of the carbonyl group (C=O) and the hydroxyl group.
- When placed in nonpolar solvents, these compounds form *dimers via hydrogen bonding* between the hydroxyl group of one carboxylic acid and the carbonyl group of the other.

General formula of marginal monobasic carboxylic acids: CnH2nO2

0	2
Carboxylic Acid	Common Name
НСООН	Formic acid
CH <sub>3</sub> COOH	Acetic acid
CH <sub>3</sub> –CH <sub>2</sub> –COOH	Propionic acid
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COOH	Butyric acid
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> COOH	Valeric acid
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOH	Palmitic acid
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> COOH	Stearic acid

## Nomenclature

The systematic name of carboxylic acid is based on: – the root, which indicates the length of the chain (memo: list of roots), – a suffix indicating the presence/absence of multiple connections, – the "heavy acid" construction, this indicates a carboxyl group and, accordingly, belonging to the class of carboxylic acids.

$$H_3C - CH_2 -$$

butanoic acid

However, it so happens that acids are most often referred to by trivial names.

We can see carboxylic acids are in natural sources.

- Formic acid (HCOOH) contains in the ant venom.
- Acetic acid (CH<sub>3</sub>COOH) contains in the vinegar.

For example, it is rare that you hear the systematic "ethanoic acid" instead of the traditional "acetic acid". Therefore, I recommend learning the trivial names of the first six homologues from this list, and the important fatty acids palmitic acid (C16) and stearic acid (C18). If there are substituents in the molecule, they are listed before the name of the parent chain, indicating their locations (if necessary). The numbering in the chain begins with the carboxyl group:

$$\begin{array}{cccc} H_{3}C-CH_{2}$$

Carboxylic acids often use an alternative numbering in Greek letters. Moreover, the numbering is offset: the second atom of the chain receives the first letter "alpha"



 $\alpha$ -chlorvaleric acid (or 2-chloropentanoic acid)

If the carboxyl group is outside the parent chain, then it is referred to in the name as a "carboxy" substituent. This happens, for example, if there are three carboxyl groups in an acid at once.:



3-hydroxy-3-carboxypentanedioic acid (citric acid)

The interclass isomers of such acids are, for example, esters, unsaturated or cyclic diols, aldehydes with a hydroxy group. For example, these three substances correspond to the gross formula  $C_2H_4O_2$ :



Carboxylic acids are also characterized by structural isomerism (carbon skeleton isomerism):



butyric acid

Isobutyric acid

Unsaturated carboxylic acids are characterized by cis-trans isomerism.

In the figure, you can compare the structure of the functional group of alcohols and carboxylic acids. Alcohol has only a hydroxyl group, in which the strong nonmetal oxygen "pulls off" common electron pairs ( $C \rightarrow O \leftarrow H$ ).



The carboxyl group consists of two functional groups, a carbonyl group and a hydroxyl group. The common electron pairs of the C=O carbonyl group double bond are shifted to more electronegative oxygen. This makes the carbon of the carboxyl group electron-deficient, and it is less willing to give up an electron pair to the oxygen of the hydroxyl group. (In the figures, the red arrows indicate the direction of the actual displacement of the common electron pairs, and the green arrow shows the relative displacement of the electron pair (explanation here). Let me remind you that the acidic properties of the molecule depend on the degree of polarity of the O  $\leftarrow$  H bond. If the bond is sufficiently polar, the substance tends to dissociate along this bond, for example, alcohol dissociation.: R-OH  $\rightleftharpoons$  R-O- + H+ But in alcohol, oxygen receives electrons from both carbon and hydrogen, which makes both bonds (C  $\rightarrow$  O  $\leftarrow$  H) comparatively not very polar. Therefore, the acidic properties of alcohols are so weak that they form alcoholates only with active metals and do not even react with alkalis. In acid, oxygen of the OH group does not receive an electron pair from carbon, so what should it do? Logically: to pull electrons away from hydrogen even more strongly. In the carboxyl group, the O  $\leftarrow$  H bond is more polar than in alcohol, so the acids dissociate better.: R-COOH  $\rightleftharpoons$  R-COO- + H+ Carboxylic acids react with both active metals, basic oxides, and alkalis. Although it should be noted that carboxylic acids are still classified as weak, their dissociation is not complete.

## **Physical properties**

Another consequence of the structure of the carboxyl group is that carboxylic acid molecules tend to form hydrogen bonds, and hydrogen bonds prevent the substance from evaporating, which means that carboxylic acids have a relatively high boiling point. The simplest acids are colorless liquids with a pungent odor. Due to the presence of polar bonds, lower carboxylic acids are well soluble in polar solvents. for example, in water. However, the longer the hydrocarbon chain, the worse the solubility. Higher fatty acids (stearic acid, oleic acid, etc.) have a very large nonpolar hydrocarbon "tail", due to its hydrophobicity higher fatty acids are insoluble: in water they form micelles w – microscopic droplets.

## Chemical properties.

#### Acidic properties.

Carboxylic acids are considered weak, they do not dissociate completely:



## 1. Reactions with Metals.

Metals to the left of hydrogen in the Range of metal activity replace hydrogen in carboxylic acid:  $2H_3C-C \bigvee_{OH}^{\checkmark O} + 2K \rightarrow 2H_3C-C \bigvee_{OK}^{\checkmark O} + H_2 \uparrow$ 

## 2. Reactions with basic oxides

$$2H_{3}C-CH_{2}-C\swarrow O + BaO \rightarrow \left[H_{3}C-CH_{2}-C\swarrow O \right]_{2}Ba^{2+} + H_{2}O$$

3. Reactions with Alkali

$$\begin{array}{c} H_{3}C-CH-C \swarrow O \\ H_{3}C-CH-C \swarrow O \\ CH_{3} \end{array} + NaOH \rightarrow H_{3}C-CH-C \swarrow O \\ CH_{3} \end{array} + H_{2}O$$

The reaction also occurs with ammonia, ammonium salts are formed.:

$$H_{3}C-(CH_{2})_{3}-C_{OH}^{\#O}+NH_{3}\rightarrow H_{3}C-(CH_{2})_{3}-C_{OH}^{\#O}$$

### **4.**Reactions with salts of volatile or unstable acids.

Carboxylic acids displace carbonic acid from carbonates, because carbonic acid is unstable, the reaction continues with the release of carbon dioxide:

$$HC_{OH}^{\#O} + NaHCO_3 \rightarrow HC_{ONa}^{\#O} + CO_2\uparrow + H_2O$$

5. Esterification The reaction takes place with alcohols in an acidic environment (usually sulfuric acid is added), esters are formed.

$$H_{3}C-C \bigvee_{OH}^{\not O} + HO-CH_{2}-CH_{3} \xrightarrow{H_{2}SO_{4}} H_{3}C-C \bigvee_{O-CH_{2}-CH_{3}}^{\not O} + H_{2}O$$

## 6. Production of amides.

The reaction occurs with ammonia when heated. The amino group replaces the hydroxyl group, and amides are formed. Attention: without heating, it will not be replaced, but neutralized, and an ammonium salt will be obtained.

$$H_{3}C-CH-C \bigvee_{OH}^{\#O} + NH_{3} \xrightarrow{t^{\circ}} H_{3}C-CH-C \bigvee_{OH}^{\#O} + H_{2}O$$

$$\downarrow_{CH_{3}}^{H} OH \xrightarrow{I} H_{3}C-CH-C \bigvee_{OH}^{\#O} + H_{2}O$$
Isobutyramide

# 7. Acid halide formation
$$H_{3}C - C_{OH}^{\#O} + PCl_{5} \rightarrow H_{3}C - C_{Cl}^{\#O} + HCl + POCl_{3}$$

As a result of the reaction acid halides are formed.

#### 8. Dehydration, production of symmetrical anhydrides



acetic anhydride

#### 9. Acid anhydride formation (Alpha halogenation).

In the presence of a red phosphorus catalyst, the halogenation of carboxylic acids is selective, substitution occurs at the  $\alpha$ -position:

$$H_{3}C-CH_{2}-CH_{2}-C\overset{\#O}{\searrow} + Cl_{2} \xrightarrow{P_{\text{KPBCHEW}}} H_{3}C-CH_{2}-\overset{O}{CH} - C\overset{\#O}{\searrow} + HCl_{1}$$

#### 10. Decomposition of certain acids.

Most carboxylic acids are thermally stable, the most important exceptions are:







с<sup>"О</sup> t°  $+ CO_2$ 

Benzoic acid

#### 11. Oxidation.

Formic acid and strong oxidizing agents

Most carboxylic acids are resistant to oxidation, the most important exceptions are: Formic acid

$$5\text{HC}_{OH}^{\#O} + 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow 5\text{CO}_2 + 2\text{MnSO}_4 + \text{K}_2\text{SO}_4 + 8\text{H}_2\text{O}_4$$

Formic acid has a CHO group and exhibits aldehyde properties.

Oxalic acid  

$$5 \xrightarrow{O} C - C \xrightarrow{O} OH + 2KMnO_4 + 3H_2SO_4 \rightarrow$$
  
 $\rightarrow 10 CO_2 + 2MnSO_4 + K_2SO_4 + 8H_2O$ 

None of other carboxylic acids are oxidized and give  $CO_2$  and  $H_2O$  like HCHO acid.

## Unsaturated carboxylic acids.

For unsaturated carboxylic acids, instead of the suffix "an", the suffixes "en" or "in" are used, indicating the locus of the multiple bond (if necessary):



$$CH_2 = CH - CH - CH_2 - C$$
  
 $CH_3 OH$ 

3-methylpentene-4-acid

The following unsaturated fatty acids are important

$$O_{HO} = C - (CH_2)_6 - CH_2 + C = C + CH_2 - (CH_2)_4 - CH_3$$
palmitoleic acid (hexadecene-9-acid, 16 carbons)
$$O_{HO} = C - (CH_2)_6 - CH_2 + C = C + CH_2 - (CH_2)_6 - CH_3$$
noleic acid (octadecene-9-acid, 18 carbons)
$$O_{HO} = C + CH_2 + C = C + CH_2 + C = C + CH_2 - (CH_2)_3 - CH_3$$
noleic acid (octadecadiene-9, 12 - acid, 18 carbons)
$$O_{N} = C + CH_2 + C + CH_2 + C + CH_2 + C + CH_2 + CH_2$$



linolenic acid (octadecatriene-9,12,15-acid, 18 carbons)



arachidonic acid (eicosatetraene-5,8,11,14-acid, 20 carbons)

These are natural unsaturated fatty acids. All of them are cis isomers. Fatty acids form esters with glycerol – fats. There are marginal and unsaturated fatty

acids. Vegetable fats contain more unsaturated fatty acids than animal fats (olive oil contains 80% oleic acid, linseed oil: 60% linoleic acid). Please note: all double bonds in natural unsaturated fatty acids are isolated.

#### Chemical properties.

Unsaturated carboxylic acids combine both the properties of carboxylic acids (neutralization with bases, esterification, formation of amides, anhydrides, etc.) and the properties of unsaturated compounds (halogenation, hydrogenation, oxidation, etc.). \* A special property of carboxylic acids with a double bond in the  $\alpha$ , $\beta$  position is that their asymmetric addition reactions go against the Markovnikov



Hydrohalogenation is against Markovnikov's rule: the halogen goes to the βposition.

Dibasic and polybasic carboxylic acids.

Polybasic carboxylic acids (polycarboxylic acids) contain two or more carboxyl groups. Polybasic acids are dibasic (dicarboxylic), tribasic (tricarboxylic), etc. The name of dibasic acids is based on the root corresponding to the length of the chain, and additionally "dionic acid". I recommend remembering the trivial names of the first five dibasic acids (well, at least oxalic acid should definitely be remembered):

$C_2H_2O_4$	oxalic acid (ethanedioic acid)	O HO C - C OH
$C_3H_4O_4$	malonic acid (propanoic acid)	$HO C - CH_2 - C O OH$
$C_4H_6O_4$	succinic acid (butanedioic acid)	$O$ $C - CH_2 - CH_2 - C$ $O$ $OH$
$C_5H_8O_4$	glutaric acid (pentanedioic acid)	$O_{HO} C - (CH_2)_3 - C_{OH} O$

$$C_6H_{10}O_4$$
 adipic acid  
(hexanedioic acid)  $O_6C - (CH_2)_4 - C_0O_0H_0$ 

Important unsaturated carboxylic acids (these are cis- and trans-isomers of butenedioic acid):



The most important tribasic acid is citric acid, which plays a central role in the energy metabolism of living organisms.:



The systematic name of citric acid is formed as follows: we select the main chain with two carboxyl groups at the ends, the root "pentanedioic acid" is obtained, and the third carboxyl group is referred to as the "carboxy" substituent, it turns out "3-hydroxy-3-carboxypentanedioic acid".

#### Chemical properties of polybasic acids

Polybasic carboxylic acids are slightly stronger than monobasic acids. However, even polybasic acids are considered weak: they dissociate stepwise, and the degree of dissociation decreases sharply with each step. Without an excess of alkali, acidic salts predominate:



Esterification of polybasic acids can give esters of both one and several carboxyl groups, for example:

$$\begin{array}{c} O \\ HO \end{array} C - C \\ OH \end{array} + 2HO - CH_2 - CH_3 \xrightarrow{H_2SO_4} \\ \longrightarrow \\ H_3C - CH_2 - O \\ O \\ O - CH_2 - CH_3 \end{array} + 2H_2O$$

oxalic acid diethyl ether

# Aromatic carboxylic acids.

The most important monobasic aromatic acids:



The three isomers of the dibasic aromatic carboxylic acid have their own trivial names:



Phthalic acid





Terephthalic acid

The systematic name of monobasic carboxylic acids can be constructed as follows: we choose the carboxyl group as the main chain, and we mention the benzene ring as a substitute for "phenyl", for example, the systematic name of benzoic acid: "phenyl muric acid" (although no one calls it that). This will not work with dibasic acids, so there is an alternative way: use the endings "carboxylic acid", for example, isophthalic acid (Fig. above) is called "benzenedicarboxylic-1,3 acid". Even carboxylic acids with a bunch of carboxyl groups can be called this way.:



benzene hexacarboxylic acid (mellitic acid)

#### **Chemical properties.**

Aromatic carboxylic acids have all the properties of aliphatic acids, here we will limit ourselves to describing specific properties. Catalytic halogenation As an aromatic compound, benzoic acid is capable of substitution reactions into the core. However, the carboxyl group of benzoic acid is a deactivating meta-agent. That is, firstly, the reaction is difficult (worse than with activating orientants), and secondly, the halogen is predominantly in the meta-position.:



Thermal decomposition The carboxyl group in the benzene core is thermally unstable, decarboxylation occurs when heated.:

$$\left\langle \right\rangle - C \left\langle O \right\rangle + CO_2 + CO_2$$

## **Questions:**

- What happens when a carboxylic acid is heated?
- How does carboxylic acid react with HI?
- Why are carboxylic acids more acidic than phenol?
- Are carboxylic acids saturated organic compounds?
- What is the mechanism of reduction of carboxylic acid?
- What are some industrial uses for carboxylic acids?
- What carboxylic acid has the lowest pH?
- What are the uses of carboxylic acids?

# Unit 12. Ethers

Esters are derivatives of acids in which the hydrogen of the hydroxyl group is replaced by a hydrocarbon radical. Esters can also be considered as condensation products of carboxylic acid and alcohol

$$R_1 - C_0^{\#O}$$

$C_4H_8O_2$	propyl ether of formic acid (propylformate)	H C-O-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>
$C_4H_8O_2$	ethyl ether of acetic acid (ethyl acetate)	$H_3C - C \sim O - CH_2 - CH_3$
$C_4H_8O_2$	methyl ester of propionic acid (methylpropionate)	$H_3C-CH_2-C_0^{\mu O}O-CH_3$

 $\sim$ 



The systematic name of the ester consists of: – the name of the hydrocarbon radical that replaces hydrogen in the initial acid, – the construction "ether", – the name of the carboxylic acid in the genitive case. The trivial names of esters are constructed from the trivial names of the corresponding acids. For example, "ethyl ether of ethanoic acid"  $\rightarrow$  "ethyl ether of acetic acid". An alternative way to name esters also begins with the name of the radical, but instead of the name of the acid, the name of its anion is used (the list of acid anions is here), for example:



Isopropyl acetate

C″ `0-CI -CH<sub>3</sub>

methyl benzoate

# Esters of dicarboxylic acids.

Dicarboxylic (dibasic) acids can form esters with one or two alcohol molecules. For example, two variants of oxalic acid ester:





Dimethyloxalate

#### **Polyatomic alcohol esters**

Polyatomic alcohols are also capable of forming esters with acids. The most important representatives of this group are glycerol esters. Glycerin is able to form esters with one acid molecule, as well as with two or three:



Syllabic esters of glycerol and three fatty acids are called fats (triglyceride):



General formula of saturated aliphatic esters:  $C_nH_{2n}O_2$ 

Esters are the interclass isomers of carboxylic acids:





**Chemical properties** 

#### **1.Acid hydrolysis**.

In an acidic environment, esters are hydrolyzed to the initial alcohol and carboxylic acid.:

$$H_{3}C-C \bigvee_{O-CH_{2}-CH_{3}}^{\mu O} + H_{2}O \xrightarrow{H_{2}SO_{4}} H_{3}C-C \bigvee_{OH}^{\mu O} + HO-CH_{2}-CH_{3}$$

This reaction is reversible, the reverse reaction is esterification.

#### 2. Saponification.

Unlike acid hydrolysis, saponification (alkaline hydrolysis) is an irreversible reaction, since it is not the acid itself that is formed, but its salt.:

$$H_{3}C-C^{\#O}_{O-CH_{3}} + KOH \rightarrow H_{3}C-C^{\#O}_{OK} + CH_{3}-OH$$

methyl acetate methanol

Saponification of fats is of particular importance, it is a method of producing soap and glycerin.:

$$\begin{array}{ccc} H_{3}C-(CH_{2})_{16}-C-O-CH_{2} \\ & O \\ & CH-O-C-(CH_{2})_{16}-CH_{3} + 3NaOH \rightarrow \\ H_{3}C-(CH_{2})_{16}-C-O-CH_{2} \\ & O \\ &$$

1,2,3-O-tripalmitoylglycerin Glycerin

sodium palmitate

#### 3. Ammonolysis.

Ammonolysis is similar to hydrolysis (all these reactions are varieties of solvylizaw), only instead of the hydroxyl group of water, an amino group is added to the acidic residue of the ether, and an amide is formed:



propanol

#### **4.Reduction.**

Strong reducing agents are used. The acid residue is reduced to alcohol, resulting in two alcohols. In a simplified way, the reaction can be written as follows:

$$\begin{array}{ccc} H_{3}C-C & & +4H^{0} \rightarrow \\ O-CH_{2}-CH_{2}-CH_{3} & & \\ & \rightarrow H_{3}C-CH_{2}-OH+HO-CH_{2}-CH_{2}-CH_{3} \\ & & \text{propyl acetate} & \text{ethanol} & & \text{propanol} \end{array}$$

#### **Problems.**

**1.** Define and write the esterification reaction

**2.** What explains the fact that acid and alkaline hydrolysis reactions are more typical for Esters?

**3.** What chemical reactions are most characteristic of Esters?

4. Write the reaction that produces propionic acid and methyl alcohol

## Unit 13. Lipids

Lipids are an extensive group of natural organic compounds that are insoluble in water but highly soluble in natural solvents such as acetone, ether, benzene, and chloroform. More than 40 different classes of lipids are known, but we will consider the most important of them based on the properties that determine the functions in living organisms. Bioorganic chemistry is a science that studies the relationship between the structure of organic substances and their biological functions. The biological functions of lipids are diverse. Structural or plastic -lipids are part of the structural components of the cell and largely determine their properties. They are also not only structural components of the central nervous system, but also the most important participants in functional activity. Phospholipids, glycolipids and cholesterol, due to their amphiphilicity of molecules, are involved in the formation of cell membranes -performing a plastic function, determining their permeability to ions of nonelectrolyte and water.

The brain is characterized by a high lipid content. Brain cells are 60% fat. The brain contains unique membrane structures, myelin sheaths, which have the highest lipid content compared to other tissues or subcellular structures.1,500 different lipids have been found in myelin from the structures of the human central nervous system, 30 of which are present in significant amounts. The composition of myelin lipids includes: 43% phospholipids, 29% galactolipids, 28% cholesterol. The study of the general patterns of membrane composition is greatly hampered by the fact that membranes of different origins vary greatly in their content of lipids of different types. However Phospholipids are present in almost all membranes, regardless of their origin, and their content ranges from 40 to 90% of the total amount of lipids in the membrane. Another very important property is the oxidative cleavage of triacylglycerols, which provides the human and animal

bodies with the energy necessary for other vital processes. In addition, fat accumulations play an important protective role: they protect organs and tissues from mechanical damage, serve as a heat-saving and electrical insulating material. Cerebrosides and gangliosides are involved in the processes of recognizing chemical signals and bringing them to intracellular effects., that is, they perform a receptor-mediating role. Lipids also have a regulatory signaling function performed by (steroids). Derivatives of polyunsaturated fatty acids: prostaglandins, thromboxanes and leukotrienes are tissue hormones, Cholesterol is not only a structural component of membranes, but also a precursor of steroid hormones, bile acids and vitamin D3. Acyl exchange reactions are also directly related to many processes, affecting the activity of a number of enzymes, prostaglandin synthesis, and photoreceptor sensitivity. There is also a risk of depression, allergies, osteoarthritis, osteoporosis, and decreased immunity due to impaired lipid metabolism. If you look at the statistics of recent years, mortality from cardiovascular diseases is in the first place, which is associated with the development of atherosclerosis as a result of increased lipids in the blood, It has been proven that hypertension, atherosclerosis and their consequences (stroke, heart attack), inflammatory joint diseases and many other serious diseases develop due to disorders in the body prostaglandin balance. Fats have long been used for the preparation of medicinal and cosmetic products, although today the study of individual classes continues. The first elemental analysis of fats was performed by A. Lavoisier, who showed that fats and oils consist mainly of carbon and hydrogen

According to their ability to hydrolyze, lipids are divided into saponifieble (hydrolyzed) and unsaponifiable (non-hydrolyzed - steroids, terpenes). Depending on the component composition, saponifieble lipids on: simple and complex. Simple lipids are hydrolyzed to form 2 components of higher fatty acids and alcohols, and complex lipids are hydrolyzed to form three or more components of higher fatty acids, alcohols, and other substances such as carbohydrates, nitrogenous substances, and phosphoric acid. Saponified lipids are divided into simple and complex, as mentioned above, the simple ones include: waxes, fats (oils) ceramides. Complex lipids include phospholipids, sphingolipids, and glycolipids.

**Lipid Examples:** One of the most necessary and well-known lipids is cholesterol, paraffin, cortisol, estrogen, phospholipids, from which the cell membrane is built, are especially important. The figure shows the structural formula, on the right are the molecular models of the two fatty acids stearic acid and oleic acid.



An essential structural component, i.e., the basic unit that makes up most lipids, are fatty acids. Biologically important lipids include numerous carboxylic acids of the marginal and unsaturated series, which differ from each other in the degree and nature of the branching of the carbon chain, the number and position of double bonds, the nature and number of other functional groups, and the length of the carbon chain. The composition and structure of fatty acids have a great influence on their properties: molecular weight, neutralization number, solidification and melting point, oxidation ability, iodine number, solubility in water, density and other properties

## FATTY ACIDS

Saturated

Formula	Common Name
---------	-------------

 $CH_3(CH_2)_{10}CO_2H$  lauric acid

CH<sub>3</sub>(CH<sub>2</sub>)<sub>12</sub>CO<sub>2</sub>H myristic acid

CH<sub>3</sub>(CH<sub>2</sub>)<sub>14</sub>CO<sub>2</sub>H palmitic acid

 $CH_3(CH_2)_{16}CO_2H$  stearic acid

CH<sub>3</sub>(CH<sub>2</sub>)<sub>18</sub>CO<sub>2</sub>H arachidic acid

Unsaturated<br/>FormulaCommon NameCH\_3(CH\_2)\_5CH=CH(CH\_2)\_7CO\_2Hpalmitoleic acidCH\_3(CH\_2)\_7CH=CH(CH\_2)\_7CO\_2Holeic acidCH\_3(CH\_2)\_4CH=CHCH\_2CH=CH(CH\_2)\_7CO\_2Hlinoleic acidCH\_3CH\_2CH=CHCH\_2CH=CHCH\_2CH=CH(CH\_2)\_7CO\_2Hlinoleic acid

 $CH_3(CH_2)_4(CH=CHCH_2)_4(CH_2)_2CO_2H$ 

arachidonic acid

Lipids also include amino alcohols and monoatomic, diatomic, and polyatomic alcohols:

Serin

HO-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub> Ethanolamine

$$\begin{array}{c} CH_3\\ H_3C - \overset{|}{N^+} - CH_2 - CH_2 - OH\\ CH_3\end{array}$$

choline

# $CH_2-CH-CH-CH=CH-(CH_2)_{12}-CH_3$ OH NH<sub>2</sub> OH Sphingosine

CH<sub>2</sub>-OH CH-OH CH<sub>2</sub>-OH Glycerin

$$\begin{array}{c} CH_2-OH+3 & O \\ CH-OH & HO \\ CH-OH \\ CH_2-OH \end{array} \xrightarrow{H_2SO_4} H_3C-C-O-CH_2 & +3H_2O \\ H_3C-C-O-CH_2 & O \\ H_3C-C-O-CH_2 &$$

A lipid molecule or triglycerides is formed by a glycerol molecule and three molecules of higher fatty acids

#### **Fats and Oils**

#### **Triacylglycerols** (Triglycerides)

When all three hydroxyl groups of glycerol are esterified with fatty acids, the structure is called a triacylglycerol:



The difference between fat and oil is that fat contains saturated fatty acids while oil contains saturated fatty acids.

#### Plasmalogens.

There are two types of essential phospholipids: plasmanyl and plasmenyl phospholipids. Plasmanyl phospholipids have an ester bond at the sn-1 position with an associated group. Plasmenylphospholipids have an ester bond at the sn-1 position with an alkenyl group. The latter are called plasmalogens and they They are found in many human tissues, as mentioned above, especially in the nervous, immune and cardiovascular systems. In human cardiac tissue, about 30-40% of choline glycerophospholipids are plasmalogens. However, it must be remembered that 32% of glycerophospholipids in the adult heart, 20% in the brain, and up to 70% of ethanolamine-glycerophospholipids in the myelin sheath are plasmalogens.



Phospholipid molecules form a two-layered membrane structure that separates the inside of the cell from surrounding fluids. It most often consists of phospholipids, but it contains many other components, such as cholesterol, which contribute to its structural integrity. Sphingomyelins are also membrane lipids. They are the main component of the myelin sheath surrounding nerve fibers.





#### **Chemical properties**



## Acid hydrolysis of esters

$$\begin{array}{ccc} H_{3}C-(CH_{2})_{16}-C-O-CH_{2} & & \\ O & CH-O-C-(CH_{2})_{16}-CH_{3}+3\,H_{2}O \xrightarrow{t^{\circ},\ H^{*}} \\ H_{3}C-(CH_{2})_{16}-C-O-CH_{2} & & \\ O & & \\ H_{3}C-(CH_{2})_{16}-C-O-CH_{2} & & \\ O & & \\ O & & \\ O & & \\ CH_{2}-OH & +3 & \\ CH_{2}-OH & +3 & \\ HO & C-(CH_{2})_{16}-CH_{3} \\ HO & & \\ CH_{2}-OH & \\ CH_{2}-OH & & \\ CH_{2}-$$

#### **Questions:**

- 1. What are compound lipids?
- 2. What is the difference between lipids and derived lipids?
- 3. What is the difference between simple lipids and compound lipids?
- 4. What are the functions of compound lipids?

## Unit 13. Carbohydrates.

Carbohydrates are natural organic compounds that are divided into three monosaccharides, large groups: oligosaccharides, and polysaccharides. Carbohydrates are oxygen-containing organic substances that contain carbonyl and hydroxyl groups in their composition. Carbohydrates are a wide class of organic compounds, one of the most important classes of organics for all living beings on Earth. The simplest carbohydrates, monosaccharides, contain a carbonyl group in the molecule (they come with both an aldehyde group and a keto group), as well as several hydroxyl groups. Thus, monosaccharides combine the properties of both carbonyl compounds and polyatomic alcohols. More complex carbohydrates are built from several (oligosaccharides, a special case is disaccharides) or many (polysaccharides) monosaccharides (more precisely, their residues), more details about this in the relevant paragraphs below. Carbohydrates are an important source of energy for living beings, they make up a large part of the biomass of organisms, especially plants. Glucose is a product of plant photosynthesis, so carbohydrates are a key link in the transfer of carbon from inanimate nature to biomass. Monosaccharides (monoses) are the simplest carbohydrates. The monosaccharide molecule contains a carbonyl group and several hydroxyl groups. Aldoses and ketoses. There are two main types of monosaccharides: aldoses are carbohydrates with an aldehyde group, and ketoses are carbohydrates with a keto group.



Classification by chain length Another classification of carbohydrates, monosaccharides— is based on the length of the carbon skeleton. Glucose and fructose are hexatomic carbohydrates, hexoses ("hexa" – six). The simplest carbohydrates are dioses and trioses:



Glycolaldehyde is the only diose and the only monosaccharide that is not a polyatomic alcohol.

#### The enantiomers.

The second type of stereoisomers are optical isomers, or enantiomers. Enantiomers are mirror images of each other, which cannot be "superimposed" on each other.

Each monosaccharide has enantiomers, conventionally designated by the symbols B and D. All natural monosaccharides are D-enantiomers, for example, natural glucose is exactly D-glucose. If L-glucose enters the body, enzymes will not be able to use it in biological processes. A trivial example: your left and right hands are very similar, almost a copy, but still they are not the same, they will not match when superimposed. Thus, your right and left hands are "enantiomers" to each other.

Фруктоза



Most important pentose is ribose, and its derivative, deoxyribose, is also of great importance. These substances are involved in the formation of RNA and DNA, respectively.:



#### Deoxyribose

Semi-acetal (cyclic) shapes, Heurs projection Let me remind you that alcohols can react with carbonyl compounds to form semi-acetals. Carbohydrates contain both a carbonyl group and an alcohol group, so they can form cyclic semi-acetals.:



Formation of an internal (cyclic) hemiacetal in glucose.

This is a reversible reaction, but the equilibrium is shifted to the right. For example, glucose in solution is 99% in cyclic form. The cyclic form of a carbohydrate is a heterocyclic compound with oxygen as a heteroatom. Various natural monosaccharides form, as a rule, six-membered and five-membered heterocycles. Formally, these cycles can be considered as derivatives of piran and furan heterocycles, hence the name of the cycle forms. The carbohydrate that formed the six-membered cycle is pyranose (pyranose form), the five-membered is furanose (furanose form):



Among biologically important furanoses, in addition to fructose, we will single out ribose and its derivative, deoxyribose, these are the structural units RNK and DNK, respectively.:



#### Chemical properties of monosaccharides.

Since monosaccharides contain both a carbonyl group and several alcohol groups, they combine the chemical properties of aldehydes/ketones and polyatomic alcohols. Here are the most important reactions. 1. The formation of cyclic semi–acetals is a reaction involving both a carbonyl group and one of the alcohol groups of a monosaccharide. Due to this reaction, cyclic forms of monosaccharides are formed.:



2. All aldoses, like aldehydes, are easily oxidized to acids. The product of glucose oxidation is gluconic acid. For example, oxidation by copper(II) hydroxide during heating

$$\begin{array}{cccc} H & O & OH \\ H - C & H + 2Cu(OH)_2 \xrightarrow{t^e} & O & OH \\ H - C - OH & H - C - OH \\ HO - C - H & HO - C - H \\ H - C - OH & H - C - OH \\ H - C - OH & H - C - OH \\ H - C - OH & H - C - OH \\ H - C - OH & H - C - OH \\ H - C - OH & H - C - OH \\ C H_2 OH & C H_2 OH \end{array}$$

The reaction of the "silver mirror" with glucose is also possible.



3. When interacting with copper(II) hydroxide without heating, glucose behaves like polyatomic alcohols. A complex compound is formed with a characteristic bright color, in the case of glucose – blue. 4. Polyatomic alcohols are formed during hydrogenation or reduction of monosaccharides.:



5. There are several types of fermentation of carbohydrates, in particular glucose. Alcoholic fermentation is most widely used:



Lactic acid fermentation is also important. :



Glucose

lactic acid

6. Strong water-removing agents, such as concentrated sulfuric acid, charring monosaccharides:



7. Severe oxidation of monosaccharides goes down to carbon dioxide:

$$\begin{array}{c} CH_2OH\\ C=O\\ 5HO-C-H + 24 \text{ KMnO}_4 + 36 \text{ H}_2\text{SO}_4 \rightarrow\\ H-C-OH\\ H-C-OH\\ CH_2OH\\ \rightarrow 30 \text{ CO}_2 + 24 \text{ MnSO}_4 + 12 \text{ K}_2\text{SO}_4 + 66 \text{ H}_2O\end{array}$$

8. In plant and animal organisms, monosaccharides condense into oligosaccharides or polysaccharides. These are complex biochemical processes involving enzymes. For more information about the products of such syntheses, see the relevant articles below.

#### Disaccharides, oligosaccharides.

Disaccharides (dioses) are a special case of oligosaccharides, the molecules of which consist of two monosaccharide residues. The general formula of disaccharides:  $C_n(H_2O)_{n-1}$ 

The most famous disaccharide is sucrose, the substance that makes up dietary sugar. Sugar beet and sugar cane are the most sucrose–rich. These two plants are the main sources of sucrose in the food industry. In addition, sucrose is found in many fruits and berries. Sucrose is formed by residues of D-glucose and D-fructose:



From the point of view of organic chemistry, the formation of a disaccharide is the production of a simple ether. The two hydroxyl groups form a simple ether bond with the loss of water:



 $\alpha$ -D-glucopyranose  $\beta$ -D-fructofuranose sucrose. A very simplified equation.

This bond has a special feature: at least one of the hydroxyl groups involved in condensation (and both in sucrose) is semi-acetal. The semi-acetal hydroxyl was formed during the formation of the cycle of each monomer, in more detail here. From the point of view of organics, condensation of a semi-acetal with alcohol is acetalization, so disaccharides can be considered acetals.



 $\beta$ -lactose or  $\beta$ -D-galactopyranosyl-(1,4)- $\beta$ -D-glucopyranose

Maltose consists of two glucose residues connected through the first and fourth atoms, it is a  $(1\rightarrow 4)$ -glycoside bond:



 $\alpha$ -maltose or  $\alpha$ -D-glucopyranosyl-(1,4)- $\alpha$ -D-glucopyranose

Cellobiose is very similar to maltose, it is also two glucoses connected by a  $(1\rightarrow 4)$ -glycosidic bond. But the glycoside bond of maltose is formed by the semiacetal hydroxyl of  $\alpha$ -D-glucopyranose, this bond is also called the  $\alpha$ -glycoside bond.In cellobiose,  $\beta$ -D-glucopyranose is involved in this connection, respectively, there is a  $\beta$ -glycoside bond.:



 $\beta$ -cellobiose or  $\beta$ -D-glucopyranosyl-(1,4)- $\beta$ -D-glucopyranose

#### **Chemical properties of disaccharides**

Hydrolysis of disaccharides is possible without enzymes; in an acidic environment, disaccharides break down into their constituent monomers.:



Sucrose hydrolysis underlies the production of artificial honey. Honey consists mainly of glucose and fructose. Disaccharides are divided into reducing and non-reducing ones. Reducing disaccharides are those containing a free aldehyde group in the molecule. Aldehydes, unlike ketones, have reducing properties, therefore reducing disaccharides give a positive test for qualitative reactions with oxidizing agents, for example, "silver mirror". Of the non–reducing disaccharides listed above, these are sucrose and trehalose. This is logical: sucrose consists of fructose, which does not have an aldehyde group at all, and glucose, whose aldehyde group is "linked" by a glycosidic bond with fructose. Lactose, maltose, and cellobiose have at least one unrelated aldehyde group (clarification). Another characteristic property of carbohydrates is complete dehydration by strong water–removing agents. The general formula of carbohydrates is Cn(H2O)m, so after dehydration, only carbon remains. See, for example, a video of sugar charring with sulfuric acid.



Oligosaccharides Disaccharides (bioses) are a special case of oligosaccharides. Carbohydrates consisting of 2-10 monosaccharide residues are considered oligosaccharides. In addition to disaccharides, trisaccharides, tetrasaccharides, etc. are distinguished.

### **Polysaccharides**

Polysaccharides are carbohydrates formed by a large number of monomeric units. The polysaccharide units are monosaccharide residues. The general formula of polysaccharides:  $C_n(H_2O)_{n-m+1}$ ,

where m is the number of monosaccharide residues. Most often, natural polysaccharides are built from glucose residues. In this case, the general formula of polysaccharides is simplified:  $(C_6H_{10}O_5)_n$ .

Starch Starch is a mixture of two polysaccharides: amylose and amylopectin



Starch

Qualitative reaction to starch: a sample with iodine gives a blue color

#### Amylase

The simplest component of starch is amylose. The connection between glucose residues is the same as that of maltose: an  $\alpha$ -glycoside bond at positions 1 $\rightarrow$ 4. Amylose forms long, unbranched chains of hundreds of monomers.



Glycogen Glycogen is a storage polysaccharide. Glycogen is sometimes called "animal starch": starch accumulates in plants, and glycogen is deposited in the cytoplasm of animal and fungal cells. Glycogen mainly accumulates in liver and muscle cells. The structure of glycogen is very similar to the branched component of starch, amylopectin. As for the latter, glycogen is characterized by branchings formed by  $1\rightarrow 6$ -bonds. But glycogen is more branched than starch amylopectin.



Cellulose Cellulose (fiber) consists of residues of the  $\beta$ -anomer of glucose –  $\beta$ -D-glucopyranose, 1 $\rightarrow$ 4 the bond between such chain links is called  $\beta$ -glycoside. In this way, cellulose differs from starch and glycogen, in which the units are connected by an  $\alpha$ -glycosidic bond.



Cellulose

#### **Problems.**

1. What groups are carbohydrates divided into?

2. How cyclic forms are formed, give an example?

3. What is the name of a qualitative reaction for Carbohydrates?

4. Write the disaccharide formulas and name them

5. What is the feature of the structure of polysaccharides, write down the formulas of polysaccharides and name them

# Unit 14. Amino acids and Proteins

Amino acids are carboxylic acids with the amino group NH2, or amino groups. The simplest amino acid is aminoethanoic acid (glycine).:



According to the position of the amino group in the chain,  $\alpha$ -amino acids,  $\beta$ -amino acids,  $\gamma$ -amino acids, and so on are distinguished.:



#### γ-aminobutyric acid

#### Proteinogenic amino acids.

Of all the amino acids, the most important are the 20 amino acids used in the genetic code of living beings. Of these 20 proteinogenic  $\alpha$ -amino acids, proteins are constructed for all organisms on Earth. Let's list the most important of these amino acids:

	$NH_2$ – $CH$ – $COOH$
NH <sub>2</sub> -CH <sub>2</sub> -COOH	CH <sub>3</sub>

Glycine

 $\begin{array}{c} {\rm H_2N-CH-COOH}\\ |\\ {\rm CH_2-SH} \end{array}$ 

 $\begin{array}{c} \mathsf{H_2N} - \mathsf{CH} - \mathsf{COOH} \\ | \\ \mathsf{CH} - \mathsf{CH}_3 \\ | \\ \mathsf{CH}_3 \end{array}$ 

Alanine

Cysteine Cys

Valine Val

 $\begin{array}{c} {\sf H}_2{\sf N} \,-\, {\sf CH} \,-\, {\sf COOH} \\ & | \\ {\sf CH}_2 \\ & | \\ {\sf CH} \,-\, {\sf CH}_3 \\ & {\sf CH}_2 \\ {\sf CH}_3 \\ \\ {\sf CH}_3 \\ \end{array} \qquad \begin{array}{c} {\sf NH}_2 \,-\, {\sf CH} \!-\, {\sf COOH} \\ & | \\ {\sf CH} \,-\, {\sf CH}_3 \\ & {\sf CH}_2 \\ & | \\ {\sf CH}_3 \\ \end{array}$ 



Isoeucine





**Methionine Met** 





Serine

## Phenylalanine



Arginine Arg

Lysine Lys





**Tryptophan Trp** 



Condensation of amino acids, production of peptides.

glycine

The condensation reaction of amino acids with the formation of peptides is of great biological importance. The carboxyl group of one amino acid forms an amide bond with the amino group of another amino acid, forming a dipeptide consisting of two amino acid units. Such a special case of an amide bond is called a peptide bond.:

$$\begin{array}{c} H_{2}N-CH-C \xrightarrow{\#O} + H \\ OH + H \\ CH_{3} \end{array} N-CH_{2}-C \xrightarrow{\#O} OH \xrightarrow{\text{аппарат}} \\ OH \xrightarrow{\text{клетки}} \\ \rightarrow H_{2}N-CH-C - NH-CH_{2}-C \xrightarrow{\#O} H \\ CH_{3} \end{array} H_{2}O + H_{2}O \\ \end{array}$$

Alanine glycine alanylne

The dipeptide can condense with a third amino acid to form a tripeptide.:



Synthesis can continue until the formation of protein w, a polypeptide consisting of dozens of amino acids. In the body, protein biosynthesis from amino acids takes place on ribosomes with the participation of a complex enzyme apparatus. Proteins are the structural basis of organisms of living beings.

If we consider proteins, proteins consist of peptides, peptides in turn consist of amino acids, proteins of various forms may have different structures and have a more complex structure that will consist of several units connected into a single whole. Proteins perform a huge number of functions in the cell. No biochemical reaction is possible without proteins.

Proteins or proteins are high-molecular nitrogen-containing biopolymers constructed from alpha amino acid residues, which are associated with all the main manifestations of life. Proteins consist of a peptide, and peptides are built from alpha amino acids connected by a peptide or amide bond. They are formed either as a result of protein hydrolysis or the polycondensation reaction of alpha amino acids to form amide bonds.

The primary structure of a protein is a sequence of amino acid residues of a polypeptide chain. Relatively conventionally, proteins are considered to include polypeptides containing polypeptide chains of more than 50 amino acid residues with a molecular weight of 5,000 to several million. Compounds with fewer amino acid residues are called peptides.



The secondary structure of the protein arises as a result of the formation of intramolecular hydrogen bonds between the hydrogen atoms of the amino group and the oxygen atoms of the carbonyl groups, the polypeptide chains of many injections twist into a spiral, 3.6 amino acid residues account for one turn of the spiral. During the formation of a spiral, the radicals of amino acid residues are located outside, which makes it possible to form a tertiary protein structure.



B. Secondary structure

The tertiary structure of the protein determines the configuration of the protein macromolecules and represents the spatial packaging of the helix, a globule that is stabilized by bonds of various types between individual sections of the polypeptide chains. It is the tertiary structure that largely determines certain biological functions of the protein.



Some proteins are characterized by the formation of associates of several polypeptide chains, each of which has a specific primary, secondary, and tertiary structure. The polypeptide chains of the subunit in the quaternary structure are not

covalently bound. There are hydrogen, ionic, hydrophobic and other bonds between them. For example, blood protein hemoglobin is a complex protein whose macromolecule consists of four polypeptide chains connected to four non-protein formations -heme. Each gem contains one iron atom that can attach one oxygen molecule.

**Protein Examples:** Hemoglobin, Collagen, Enzymes, Keratin, Albumin, Myoglobin, Fibrin

#### Problems.

**1.** What function do proteins perform in the body?

**2.** What is the difference between the primary structure and the secondary structure of proteins?

**3.** What compounds are formed as a result of protein hydrolysis?

**4.** What is the name of the chemical bond that binds amino acids and peptide chains together?

5. Which amino acids differ in structure from other amino acids?

# Unit 15.Nucleic Acids.

Nucleic acids are natural biopolymers and nucleotides. They play a huge role in the storage and transmission of genetic information in living organisms. Nucleic acids are high molecular weight organic compounds.

Nucleic acids consist of nucleotides whose molecules are constructed from phosphoric acid residues, a monosaccharide (ribose or deoxyribose) and a nitrogenous base (purine or pyrimidine).

Nitrogenous bases are divided into 2 groups purine and pyrimidine. Purine rings with two rings – Adenine and Guanine, and pyrimidine rings with one ring-Cytosine, Thymine, Uracil.



There are two types of nucleic acids: deoxyribonucleic acid and ribonucleic acid. They differ from each other both in molecular weight, as well as in the composition of nitrogenous bases, sugars, stability, and functions.

If we compare DNA and RNA monomers, then DNA contains the nitrogenous base Thymine, and RNA contains Uracil, if we compare carbohydrates, then DNA contains deoxyribonucleic acid, and RNA contains ribonucleic acid. The RNA chain is single, the DNA chain is double



Nucleotides are phosphorylated nucleosides, which are divided into ribonucleotides and deoxyribonucleotides.



Upon hydrolysis of the nucleotide, a nucleoside is obtained


The DNA molecule carries hereditary information, and the RNA molecules transmit the received information, as well as participate in the management of the synthesis of various proteins. Nucleic acids are high molecular weight compounds that consist of mononucleotides. The nucleotide, in turn, consists of a carbohydrate, a nitrogenous base, and a phosphoric acid residue.

The nitrogenous bases of the 2 polynucleotide dna chains are interconnected in pairs using hydrogen bonds strictly according to the principle of complementarity. Thymine combines with Adenine, Cytosine combines with Guanine. The principle of complementarity is the principle of spatial correspondence to each other. In 1927, the principle of complementarity was proposed by Niels Bohr. It is also necessary to remember Chargaff's Rules - these are patterns in the analysis of the content of nitrogenous bases in DNA from various organisms- the sum of purine nucleotides is equal to the sum of pyrimidine nucleotides



3'

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## **Problems.**

- 1. What is the difference between DNA and RNA?
- 2. What functions does DNA perform in the body?
- 3. What nitrogenous bases are included in DNA?
- 4. What nitrogenous bases are included in RNA?
- 5. What groups are nitrogenous bases divided into?

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## ОСНОВЫ ОБЩЕЙ, НЕОРГАНИЧЕСКОЙ И БИООРГАНИЧЕСКОЙ ХИМИИ

УЧЕБНОЕ ПОСОБИЕ

для обучающихся I курса по специальностям 35.05.01 «Лечебное дело».

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