MASARYK UNIVERSITY

Faculty of Medicine

OVERVIEW
OF CHEMISTRY

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CONTENTS

This textbook has been created for the foreign students who intend to study general medicine or dentistry at Medical Faculty of Masaryk University. It is a brief review of the required knowledge of chemistry to guide students in the preparation to the entrance tests. We know that chemistry is not easy for students, and moreover, high school chemistry has different concepts in different countries all over the world. The last chapter shows typical questions of entrance test, together with correct answers. The authors hope that *Overview of Chemistry* will be useful for all applicants who are ready to go to Brno.

1 BASIC CHEMICAL TERMS

Elementary Particles of Matter, Substances, Elements, Compounds

Substance is a specific kind of matter, which exhibits stable physical characteristics at definite conditions. All substances are built up by atoms.

Atom is the smallest electrically neutral particle, which still keeps the chemical characteristics (quality) of the corresponding element. It consists from a positively charged nucleus and negatively charged electron shell. The arrangement of electrons in the shell influences the chemical characteristics of an atom.

Molecule is the smallest part of a pure substance, which still keeps the chemical characteristics of this substance. It is electroneutral, characterized by a specific composition (nature and number of the present atoms) and structure (their mutual arrangement in space, kind of bonds). Di- or polyatomic molecules of one type of chemical element have homoatomic composition (they contain one kind of atoms e.g. H_2, O_2, N_2, Cl_2). Molecules of compounds have heteroatomic composition, e.g. HCl, H_2O etc. In some substances (e.g. solid substances with crystal structure), the individual molecules are not identifiable. In this case, we formally appoint the smallest part of the substance (the smallest numerical ratio of atoms), the composition of which still describes the composition of the whole substance, and we call it **formula unit** (e.g. a pair of ions Na^+ and F^- in sodium fluoride, carbon atom in diamond, Si atom and two O atoms in silicon dioxide etc.). From this formula unit (the repeating part) the name of the substance is derived.

According to the composition are distinguished chemically pure substances and mixtures (homogeneous, colloid, and heterogeneous). In the nature, substances occur usually in the form of mixtures.

A chemically pure substance (chemical individual) consists of identical particles with stable characteristic properties (boiling point and melting point, density, refractive index, specific rotation etc.). We distinguish two groups of chemically pure substances – elements and compounds.

An element is a chemically pure substance consisting of atoms with the same proton/atomic number. If the element is formed by atoms with the same mass number, it is called **nuclide**. Atoms of the given element can be non-combined (noble gases), form molecules (gaseous oxygen O_2), or they are combined altogether to form more complex structures (covalent bonds – diamond, metal bonds – metals, covalent bonds and van der Waals forces – graphite).

A compound is a chemically pure substance consisting of two or more different atoms. The atoms can be arranged in isolated molecules (gaseous carbon dioxide) or they can form more complex structures (crystalline structures – sodium chloride).

A mixture (dispersion system) consists of several different, chemically pure substances. The mixture can be homogeneous (formed by only one phase – air, solutions), colloid (e.g. egg white in water) or heterogeneous (more phases physically separated from each other – water with sand).

Expressing the Amount of Substance and Their Structural Elements

The amount of any substance (chemical element, compound, mixture) can be expressed in several ways: mass (m), volume (V) or the number of basic structural particles (atoms, ions, molecules).

Atomic and Molar Mass

Mass (m) is an additive quantity, which does not depend on the temperature and pressure. The mass of the structural particles can be expressed in common mass units (kg, g). The **absolute mass of an atom** (the value of its resting mass) is very small, about 10^{-27}–10^{-25} kg. Thus, the absolute quantities are impractical for everyday use. Mass can be more conveniently expressed by comparing to standard (object with a mass similar to the mass of these particles). This standard was stated during the last correction in 1961 to be the atom of a carbon nuclide ^{12}C. Exactly 1/12 of the mass of this atom $m(^{12}C)$ was determined as an accessory unit. It is the **atomic mass unit** (symbol **u**). The value of its mass is called the **atomic mass constant** (symbol m_u).

$$m_u = 1/12 \, m(^{12}C) = 1/12 \cdot 1.99 \cdot 10^{-26} \, kg = 1.660\,56 \cdot 10^{-27} kg = 1 \, u$$

The absolute atomic masses are not as important from the chemical point of view as the ratio (the relative amount), under which the atoms react with each other. Therefore, we most frequently use the relative (proportional) expression of mass (related to the 1/12 of the mass of the carbon nuclide ^{12}C).

The relative atomic mass (A_r) is a dimensionless number representing how many times the mass of a given atom (X) is higher than the atomic mass constant m_u. It is given by the ratio between the (absolute) mass of one atom $m(X)$ in kg to the atomic mass constant m_u in kg.

For the given element X it is accepted that:

$$A_r(X) = \frac{m(X)}{m_u}$$

Example: Calculate the relative mass of the hydrogen, carbon and silver atoms, if you know their mass: $m(H) = 1.67 \cdot 10^{-27}$ kg, $m(C) = 1.99 \cdot 10^{-26}$ kg, $m(Ag) = 1.77 \cdot 10^{-25}$ kg.
$A_r(H) = 1.67 \cdot 10^{-27}$ kg $/ 1.66 \cdot 10^{-27}$ kg $= 1.007$
$A_r(C) = 1.99 \cdot 10^{-26}$ kg $/ 1.66 \cdot 10^{-27}$ kg $= 12.01$
$A_r(Ag) = 1.79 \cdot 10^{-25}$ kg $/ 1.66 \cdot 10^{-27}$ kg $= 107.8$

The relative molecular mass (M_r) is sum of the relative atomic masses of all atoms present in the molecule. It is equal to the ratio of the molecular mass $m(XY)$ in kg to the atomic mass constant m_u in kg.

Volume

Volume, as the expression of the amount of substances, is most frequently used in case of liquids or gases. It is additive quantity only in case of ideal systems in gaseous state, where the individual particles do not affect each other. The effect of temperature and pressure on the volume is very significant.

Avogadro's law is of great importance for calculations of ideal gas volume: at the same pressure and temperature, equal volumes of different gases contain the same number of particles. In simplified calculations, the gaseous substances will be assumed to be ideal.

Substance Amount

The substance amount (n) is the quantity related to the number of particles (N). If we used one molecule (ion, atom) in calculations as the unit for quantity of a substance, we would deal with very large numbers. Therefore in chemistry is used one **mole** as the basic unit of the substance amount. It contains exactly the same number of elementary entities (molecules, atoms, ions, electrons) as there are atoms in exactly 12 g of the carbon nuclide ^{12}C. This number is expressed by the **Avogadro's constant** $N_A = 6.022 \cdot 10^{23}$ mol^{-1}. The substance amount (n) is then calculated as $n = N / N_A$. The mole is one of the seven SI base units. When the mol is used, the kind of elementary entities must be always specified.

Example: a) Calculate the substance amount, which is represented by $3.0115 \cdot 10^{23}$ carbon atoms.
$n = N / N_A = 3.0115 \cdot 10^{23} / 6.022 \cdot 10^{23} = 0.5$ mol $\Rightarrow 3.0115 \cdot 10^{23}$ carbon atoms is 0.5 mol.
b) Calculate what number of molecules is contained in 10 moles of CO_2.
$N = n \cdot N_A = 10 \cdot 6.022 \cdot 10^{23} = 6.022 \cdot 10^{24}$ molecules $\Rightarrow$ 10 mol of CO_2 contain $6.022 \cdot 10^{24}$ molecules.

Molar Quantities

Quantities related to the mole are called **molar** (mass, volume, charge).

The molar mass (M) is the (absolute) mass of $6.022 \cdot 10^{23}$ particles, e.g. 1 mole of a given substance expressed in **g mol^{-1}**. It can be calculated by multiplying the absolute mass of an atom or molecule by the Avogadro's constant: $M = m_x N_A$ where m_x is a mass of one atom or molecule.

Because the atomic mass can be expressed as the product of the relative atomic mass and atomic mass unit, it follows that $M = A_r \cdot u \cdot N_A$, which after substitution gives:

$$M = A_r \cdot 1.66 \cdot 10^{-27} \cdot 6.022 \cdot 10^{23}\, \text{kg mol}^{-1} = A_r \cdot 1.66 \cdot 10^{-24} \cdot 6.022 \cdot 10^{23}\, \text{g mol}^{-1}$$

Because the product $1.66 \cdot 10^{-24} \cdot 6.022 \cdot 10^{23}$ is approximately equal to one, it implies that the mass of one mole of substance M **is numerically equal to the relative atomic or molecular mass, but it is expressed in grams.** If we know the mass of a substance containing a certain number of moles of this substance, the molar mass is expressed by the equation:

$$M = \frac{m}{n}$$

The molar volume of a gas (V_M) is the volume of one mole of an ideal gas under standard conditions (0 °C, 101.3 kPa). It is equal to **22.41 mol^{-1}**. It is calculated by dividing the volume of a gas (V) by the quantity of a substance (n):

$$V_M = \frac{V}{n}$$

The molar charge is the electric charge of one mole of charged particles with one elementary charge and it is the product of the elementary charge and the Avogadro's constant N_A. **The elementary charge** is the smallest possible charge of a particle (the absolute quantity of the charge of an electron or proton) and it is equal to **1.602 · 10^{-19} C** (coulombs). Then the charge of one mole of particles with one elementary charge is **Faraday's constant** $F = 1.602 \cdot 10^{-19}\, \text{C} \cdot 6.022 \cdot 10^{23} = $ **96 485 C mol^{-1}**.

2   STOICHIOMETRIC CALCULATIONS

Calculations based on chemical formula
Chemical formula informs about composition of given substance. The relative molecular mass, the molar mass and the mass fraction (or %) of element can be derived from chemical formula.

Example 1: What information can be derived from chemical formula of ethanol C_2H_5OH?

1 molecule of C_2H_5OH is composed of: 2 carbon atoms, 6 hydrogen atoms, 1 oxygen atom.
relative atomic masses of the elements: H 1.01, C 12.01, O 16.00
The relative molecular mass of one molecule: $(2 \times 12.01) + (6 \times 1.01) + (1 \times 16) = 46,08$
$M_r (C_2H_5OH) = 46.08$.
The molar mass of ethanol: $M (C_2H_5OH) = 46.08\, \text{g /mol}$
molar mass M (in grams per mole) is numerically equal to the molecular (see Chapter 1).

The composition of ethanol:
In 46,08 g of C_2H_5OH (1 mol) 24.02 g of C, 6.06 g of H, 16.00 g of O are contained.
The mass fraction of elements in C_2H_5OH: 24.02/46.08 of C; 6.06/46.08 of H; 16.00/46.08 of O,
that is: 0.5213 of C; 0.1315 of H; and 0.3472 of O.

The percentage composition of ethanol: 52.13 % of C, 13.15 % of H, and 34.72 % of O.

Example 2: What is the mass fraction of water in sodium sulfite heptahydrate?

Formula of the crystalline salt: $Na_2SO_3 \cdot 7 H_2O$
The relative molecular mass: $M_r = 252.2$
The molar mass: $M = 252.2$ g/mol
There are seven molecules of water per one formula unit, $M_r(H_2O) = 18$
One mol of the compound contains: $18 \times 6 = 126$ g of H_2O
Mass fraction of water: $126/252.2 = 0.4996$
Water incorporated in a crystal lattice of the salt represents 50.0 % (rounded to three digits) of its mass.

Example 3: What is the mass of 1,5 mol of sodium?

Relative atomic mass: $Ar (Na) = 23$, molar mass: $M (Na) = 23$ g/mol.
The relationship between the mass of a pure substance (m) and number of moles (n) is described by the relation $m = n \times M$
The mass of Na: $1.5 \times 23 = 34.5$ g. The mass of 1.5 mol of sodium is 34.5 g.

Example 4: Which of the following is equivalent to the greater number of moles: 1 kg of hydrogen peroxide, or 1 kg of water?

$Mr (H2O2) = 34.0$, $Mr (H2O) = 18.0$.
Molar mass of hydrogen peroxide $M (H_2O_2) = 34$ g/mol
Molar mass of water $M (H_2O) = 18$ g/mol
The numbers of moles of the substance is calculated as $n = m/M$
Number of moles of water $n (H2O) = 55.6$ mol
Number of moles of peroxide $n (H2O2) = 29.4$ mol
Substance amount of water is larger then that of hydrogen peroxide.

Example 5: Calculate the volume of 1 kg of carbon dioxide (at standard conditions).

$Mr (CO2) = 44$ $M (CO2) = 44$ g/mol
Number of moles CO_2 $n = m/M$ $n = 1000$ (g) $/ 44$ (g/mol) $= 22.73$ mol
The molar volume of gas (V_M) $= 22.41$ mol^{-1} at standard conditions (see Chapter 1)
The molar volume of CO_2 $V = V_M \times n = 22.41 \times 22.73 = 509.37$ l
One kg of CO_2 has the volume 509.37 litres.

Calculations based on Chemical Equations

The chemical equations provide information about the proportions between the reacting substances. All stoichiometric calculations are based on the balanced equation for the reaction.

Example 1: What information can be derived from the following chemical equation?
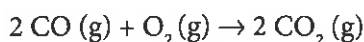
$2\,CO\,(g) + O_2\,(g) \rightarrow 2\,CO_2\,(g)$
2 molecules of CO react with 1 molecule of O_2 to yield 2 molecules of CO_2
2 moles of CO react with 1 mol of O_2 to yield 2 moles of CO_2
56.02 g of CO react with 32 g of O_2 to yield 88.02 g of CO_2
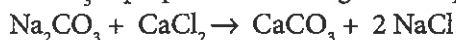44.8 l of CO react with 22.4 l of O_2 to yield 44.8 l of CO_2
The mol ratio for reactants $n(CO)/n(O_2)$ is always 2/1
The mass ratio for reactants $m(CO)/m(O_2)$ is always 56.02/32= 1.75

Example 2: How many grams of sodium carbonate and calcium chloride are needed to produce 200 g of calcium carbonate?

$M_r\,(Na_2CO_3) = 106.0;\ M_r(CaCl_2) = 111.0;\ M_r\,(CaCO_3) = 100.1$
$CaCO_3$ is prepared according to the equation (precipitation reaction):
$Na_2CO_3 + CaCl_2 \rightarrow CaCO_3 + 2\,NaCl$
1 mol of Na_2CO_3 react with 1 mol of $CaCl_2$ to yield 1 mol of $CaCO_3$
The amount of $CaCO_3$ needed $m/M = 200/100.1 = 1.998$ mol
The same amount of reactants must be used:
$m(Na2CO3) =$ 1.998 mol $\times$ 106.0 g mol-1 = 211.8 g
$m(CaCl2) = 1.998$ mol $\times$ 111.0 g mol-1 = 221.8 g
We need 211.8 g of Na_2CO_3 and 221.8 g of $CaCl_2$ to prepare 200 g of calcium carbonate.

Example 3: Calculate the volume of hydrogen (at standard temperature and pressure) which is produced in a reaction of 10.0 g of metallic zinc with an excessive amount of hydrochloric acid. $Ar(Zn) = 65.4$

The balanced equation is: $Zn + 2\,HCl \rightarrow ZnCl_2 + H_2$
1 mol of Zn yields 1 mol = 22.4 l of H_2
The amount of Zn $n = m/M = 10/65.4 = 0.153$
The volume of hydrogen produced will be $V(H_2) = 0.153$ mol $\times$ 22.4 l mol-1 = 3.427 litres.

Example 4: How many grams of silver chloride can be formed when solutions containing 50 g of $CaCl_2$ and 100 g of $AgNO_3$ are mixed? Which of the reactants is in excess and how many grams of this reactant remain unreacted?

$Mr(AgNO_3) = 169.9$, $Mr(CaCl_2) = 111.0$, $Mr(AgCl) = 143.3$.
The balanced equation is (precipitation reaction):

$CaCl_2$ + 2 $AgNO_3$ → 2 AgCl + $Ca(NO_3)_2$
1 mol 2 moles 2 moles 1 mol

50 g $CaCl_2$ represents $n(CaCl_2) = m/M = 50/111 = 0.450$ mol.
As $CaCl_2$ and $AgNO_3$ react in molar ratio 1:2, we would need 0.9 mol of $AgNO_3$
but 100 g $AgNO_3$ represents only $n(AgNO_3) = m/M = 100/169.9 = 0.589$ mol, so $AgNO_3$ is the limiting reactant.
The yield of AgCl cannot be higher than 0.589 mol, which is 0.589 (g) × 143.3 (g/mol) = 84.404 g.
$CaCl_2$ is in excess, only 0.589/2 mol will react, which is 0.294 × 111.0 = 32.634 g
the unreacted amount of it equals 50 − 32.634 = 17.366 g.
The yield of AgCl will be 84.404 g. Calcium chloride is in an excess and 17.366 g will remain unreacted.

Example 5: Calculate the volume of 0.05 M sulfuric acid needed to neutralize 500 ml of 0.4 M sodium hydroxide.

The balanced equation of neutralization is:

H2SO4 + 2 NaOH → Na2SO4 + 2 H2O
1 mol 2 mol
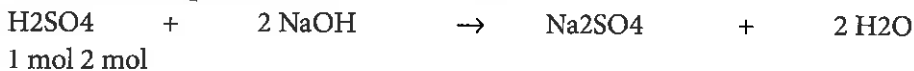
500 ml of NaOH with $c = 0.4$ mol/l represents $n = c \times V = 0.4 \times 0.5 = 0.2$ mol
As the mol ratio for reactants $n(H_2SO_4) / n(NaOH) = 1:2$, it can be derived that we need 0.1 mol of H_2SO_4.
The volume of sulfuric acid solution needed would be $V = n/c = 0.1/0.05 = 2$ litres.
The volume of sulfuric acid will be two litres.

3 ATOMIC STRUCTURE

An atom is the smallest representative particle of an element. Each element has a unique kind of atoms that differs from the atoms of all other elements. The chemical behavior of an atom is directly related to its atomic structure. Atoms are composed of three major kinds of **subatomic particles:**

Characteristics of the basic particles of an atom

Particle	Symbol	Absolute mass (kg)	Relative mass	Charge (C)
Electron	e	$9.109 \cdot 10^{-31}$	$5.486 \cdot 10^{-4}$	$-1.602 \cdot 10^{-19}$
Proton	p	$1.673 \cdot 10^{-27}$	1.007	$+1.602 \cdot 10^{-19}$
Neutron	n	$1.675 \cdot 10^{-27}$	1.009	0.000

An atom consists of a very small, extremely dense, and positively charged **nucleus** around which negatively charged **electrons** of relatively very low masses are moving (Rutherford 1911). Nuclei are clusters of protons and neutrons. For a neutral atom, the number of protons always equals the number of electrons.

Atomic Nucleus

The number of protons in the nucleus is represented by the proton (atomic) number Z. This number defines the position of an element in the periodic table. The number of all nucleons is given by the nucleon (mass) number A. According to the convention, each nuclide can be characterized by the expression $_Z^A X$. Atoms with the same atomic and different nucleonic number are called isotopes. The majority of natural elements exist as a mixture of several isotopes, one usually predominating over the others. For example hydrogen is in the form of three isotopes $_1^1 H$ (protium), $_1^2 H$ (D, deuterium), $_1^3 H$ (T, tritium), and the participation of the isotope $_1^1 H$ is 99.985 %. Tabulated relative atomic masses are stated as the mean values of the given mixture of isotopes. Isotopes do not differ in the number of valence electrons; therefore, they do not differ in their chemical properties. However, their physical properties can be different.

The existence of isotopes is reflected in the average mass of an atom of an element: The relative atomic masses (weights) listed in tables are the **average relative masses** of an atom of elements determined by considering the contribution of each natural isotope.

Most naturally occurring nuclides are stable and retain their structure indefinitely.

However, some nuclides spontaneously decay over time – they are radioactive. **Radioactivity** depends on the instability of nuclei which decay by giving off nuclear particles (alpha or beta accompanied, in some cases by gamma radiation) and forming new nuclei with different atomic numbers.

for example: $_1^3 H \rightarrow _2^3 He + \beta^-$

(β^- particle is a high-speed electron emitted from the original nucleus when a neutron decays to form a proton)

The nuclear sciences deal with the structure and behavior of atomic nuclei. On the contrary, chemistry deals with the structure and behavior of atoms and molecules, with the chemical reactions of elements and compounds supposing atomic nuclei to be mostly indefinitely stable.

Electronic Configuration of Atoms

In neutral atoms, the number of electrons surrounding the nuclei and forming their electron "covering" or "casing" equals the number of protons in atomic nuclei. The most stable arrangement of the electrons in the atom (i.e. the one having the lowest energy) is called the **electron configuration**. Each element has a unique electronic configuration; the differences in it give different elements different chemical and physical characteristics.

Electronic Structure

Several models have been created to describe the composition of the electron shell, trying to explain the physical and chemical properties of the elements satisfactorily. Recently, the quantum-mechanical model (wave mechanical) model of the atom is accepted.

According to this theory, the electron moving in three-dimensional space surrounding the nucleus has the properties of a mass particle and a wave at the same time and its movement is characterized by the wave function Ψ (psi). The energy of electrons is quantized, which means, that electrons appear to be only in certain energetic states. Their way of movement is not exactly defined, but they are found in some areas of the atom with a certain degree of probability. The border area, which encloses the place with the highest probability of the presence of an electron with a certain energetic content, is called orbital and it is defined as the square of the wave function. In order to fully define the electron in a certain orbital, we use four quantum numbers (see Table).

Quantum numbers and types of orbital

Quantum number			Subshell quantum number l	
Name	Symbol		Value	Orbital type
Principal	n		0	s
Subshell	l		1	p
Magnetic	m		2	d
Spin	s		3	f

The principal quantum number n describes the main energy level, in which the electron is present in its ground state. Values of n range from 1 to 7 in the unexcited states of the known elements. As n increases, electrons are generally farther from the nucleus and have higher potential energy. The electrons with the same principal quantum number are contained in the same electron layer (sphere, shell).

The subshell quantum number l designates the different energy subshells within the main level. It also indicates the general shape of orbitals and its size in connection with the main quantum number. Only certain values of l are allowed. These depend on n: $l = 0, 1, 2, ..., (n - 1)$ for the given n. The size of orbital of the same type increases with the increasing value of the main quantum number. Instead of subshell quantum numbers we use letters to describe the type of orbital (see Table 2.3). The spatial shapes of orbitals s, p and d are represented on Fig.
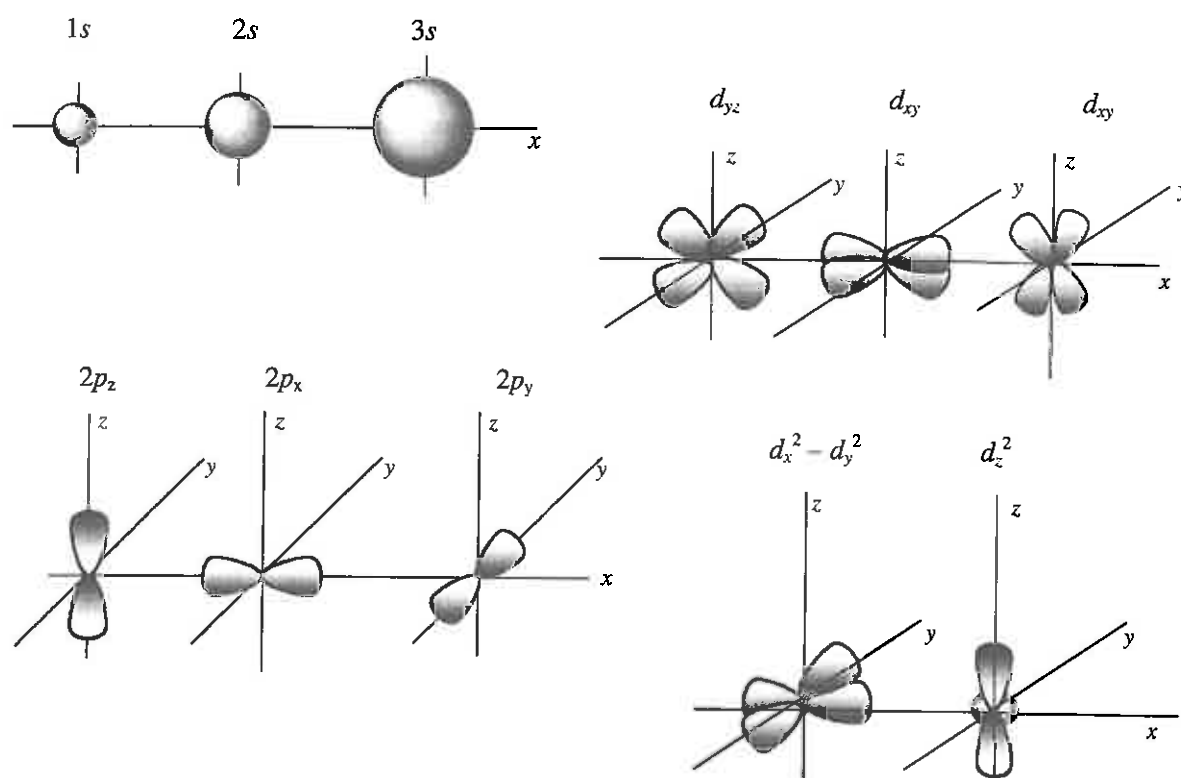

Fig.: Spatial shapes of orbitals s, p and d

The number of orbitals present in a certain electron shell is given by the main quantum number n. Thus in the electron shell with $n = 1$ are found just orbitals of type s, in the shell $n = 2$ orbitals s and p, in the next layer with

$n = 3$ orbitals s, p and d, etc. We usually place the main quantum number in front of the letter characterizing the given orbital, e.g. $1s$, $2s$, $2p$, etc.

The magnetic quantum number m determines the energy shift of an atomic orbital due to an external magnetic or electric field (it denotes the energy levels available within a subshell). The number of allowed values of m is limited and depends upon l. The orbital with the subshell quantum number l has magnetic quantum numbers with values from $-l$ to $+l$ including zero. The number of orbitals in each subshell equals the number m. For the given l, it is thus $(2l + 1)$ values in total. For example, for the p-orbital ($l = 1$) m reaches values -1, 0 and 1. It means that we have three p orbitals in total, which differ in the value of their magnetic quantum number (see Fig.). The probability of the occurrence of electrons is symmetrically distributed along the x-, or y- or z-axes of set of coordinates, and therefore, these orbitals are called p_x, p_y and p_z. Orbitals with the same main and subshell quantum numbers differ only in m, i.e. orbitals of the same type lying in the same electron subshell, do not differ in energy, and are called degenerate.

Quantum numbers and their mutual relationships

Quantum number			Type of orbital	Maximal number of electrons
Main	Subshell	Magnetic		
1	0	0	$1s$	2
2	0	0	$2s$	2
	1	$-1, 0, +1$	$2p$	6
3	0	0	$3s$	2
	1	$-1, 0, +1$	$3p$	6
	2	$-2, -1, 0, +1, +2$	$3d$	10
4	0	0	$4s$	2
	1	$-1, 0, +1$	$4p$	6
	2	$-2, -1, 0, +1, +2$	$4d$	10
	3	$-3, -2, -1, 0, +1, +2, +3$	$4f$	14

The spin quantum number characterizes the spin momentum of an electron in the given orbital. It has only two possible values $+1/2$ and $-1/2$.

Rules for Assigning Electrons to Atomic Orbitals
There are three rules according to which can be with few exceptions determined the electron configuration of an element.

The first rule is called **the building up principle (aufbau principle)**. Electrons are added to orbitals in the order of increasing energy.

Following this principle, the orbitals are filled in this sequence: $1s$, $2s$, $2p$, $3s$, $3p$, $4s$, $3d$, $4p$, $5s$, $4d$, $5p$, $6s$, $5d$, $4f$, $6p$, ...

The second rule, which specifies the building up of the electron shell, is **the Pauli exclusion principle**. No two electrons can have the same four quantum numbers. One orbital can contain two electrons with the opposite spin maximally and they create an electron pair. According to this rule, the smallest repulsive forces are between two electrons in one orbital only if they have the opposite spin.

The third rule of filling up of the orbitals is called **the Hund's rule**. Orbitals of equal energy (degenerate orbitals) are each occupied by a single electron before a second electron, which will have the opposite spin quantum number, enters any of them. Unpaired electrons in degenerate orbitals have the same spin.

The Electron Configuration of Elements

Following the above-mentioned rules we can predict the electron distribution of any element and demonstrate the relationship between the configuration of the electron shell of an element and its position in the periodic table.

The electron building up of the first 18 elements of the periodic table

	1s	2s	2p	3s	3p	3d	4s	4p
H	↑							
He	↑↓							
Li	↑↓	↑						
Be	↑↓	↑↓						
B	↑↓	↑↓	↑					
C	↑↓	↑↓	↑ ↑					
N	↑↓	↑↓	↑ ↑ ↑					
O	↑↓	↑↓	↑↓ ↑ ↑					
F	↑↓	↑↓	↑↓ ↑↓ ↑					
Ne	↑↓	↑↓	↑↓ ↑↓ ↑↓					
Na	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑				
Mg	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓				
Al	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑			
Si	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑ ↑			
P	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑ ↑ ↑			
S	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑ ↑			
Cl	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑			
Ar	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓			
K	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓		↑	
Ca	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓		↑↓	
Sc	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑	↑↓	
Ti	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑ ↑	↑↓	
V	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑ ↑ ↑	↑↓	
Cr	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑ ↑ ↑ ↑	↑↓	
Mn	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑ ↑ ↑ ↑ ↑	↑↓	
Fe	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑ ↑ ↑ ↑	↑↓	
Co	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑ ↑ ↑	↑↓	
Ni	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓ ↑ ↑	↑↓	
Cu	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑	↑↓	
Zn	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	
Ga	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑
Ge	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑ ↑
As	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑ ↑ ↑
Sc	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑ ↑
Br	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑
Kr	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓

The electron sphere with the main quantum number $n = 1$ can be filled by two electrons at most, into the orbital 1s. Elements with the corresponding configuration, i.e. hydrogen and helium, lie in the first period. The electron shell with the main quantum number equal to 2 contains s and p orbitals. The p orbitals are according to the Hund's principle filled up with one electron first. Elements with the gradually filling 2s and 2p orbitals lie in

the second period, the last element is neon with a fully filled $n = 2$ electron shell. Similarly, in the third electron layer the $3s$ and $3p$ orbitals are being filled in first, the corresponding elements lie in the third period.

Following the building up principle, when the orbitals $3s$ and $3p$ are fully filled in, the other electrons enter firstly into the $4s$ orbitals and after they are full, the layer $3d$ begins to fill in. Therefore, in the fourth period we have ten elements with the gradually filling $3d$ orbitals, i.e. the first line of the transition elements ($_{21}$Sc–$_{30}$Zn). Thus in the fourth period we have 18 elements in total. Similarly, the fifth period contains elements with the filling $4d$ orbitals and the sixth period elements with the gradually filling $5d$ and $4f$ level.

Valence Electrons and Chemical Properties of Elements

The chemical behaviour of atoms is largely due to interactions between electrons. Electrons, which have the greatest influence on chemical properties of elements, are found in the outermost filled electron shell and are called the valence electrons. (In the case of the transition metals the valence electrons are also those in the $(n - 1)$, respectively $(n - 2)$ sphere). Their number and space arrangement decide about the formation of chemical bonds between atoms. The number of electrons in an atom's outermost valence shell governs its bonding behaviour. Therefore, elements with the same number of valence electrons are grouped together in the periodic table of the elements. According to the type of outermost filled orbital the elements are usually divided into s-elements (there are only ns orbitals in the valence shell), p-elements (valence electrons are in the orbitals ns and np) and d-elements (valence electrons are in orbitals ns and $(n - 1)d$).

Generally, the fewer electrons in an atom's valence shell, the more reactive it is. Group 1 metals are therefore very reactive, with cesium, rubidium, and francium being the most reactive of all metals. Every atom is much more stable, or less reactive, with a full valence shell. This can be achieved one of two ways: either an atom can share electrons with neighbouring atoms, a covalent bond, or it can remove electrons from other atoms, an ionic bond.

Elements, whose valence shell is entirely filled with electrons, are always found at the end of the period and they have the highest chemical stability (resistance to the chemical changes). They are called noble (inert) gases. Except helium with the configuration $1s^2$, all noble gases have configuration $ns^2\,np^6$.

The Periodic Table of the Elements

By arranging the elements according to the value of their proton number, we get the natural row of elements. Elements with the similar properties occur in regular intervals – periods. Explanation of the structure of atoms and the electron configuration of elements showed, that the periodic table corresponds with the periodicity of the building up of the electron shell of atoms.

Similar properties of the elements result from the similar arrangement of electrons in the outer electron layer of an atom (the valence electrons). The elements in the periodic table are arranged into seven horizontal rows – called **periods** – and eighteen vertical columns – **groups**.

The number of a period is equal to the main quantum number n of the last electron shell.

The **first period** contains just two elements, electrons occupy the $1s$ orbital.

The second up to the sixth period always begins with the element with one valence electron (an alkali metal) and ends with the element with completely filled ns and np orbitals (a noble gas).

The **second and third** period each contains eight elements, only ns and np orbitals with the main quantum numbers 2 and 3 are being filled.

The **fourth and fifth** period each contains eighteen elements; ns, np, and besides that also $(n - 1)d$ orbitals are being filled.
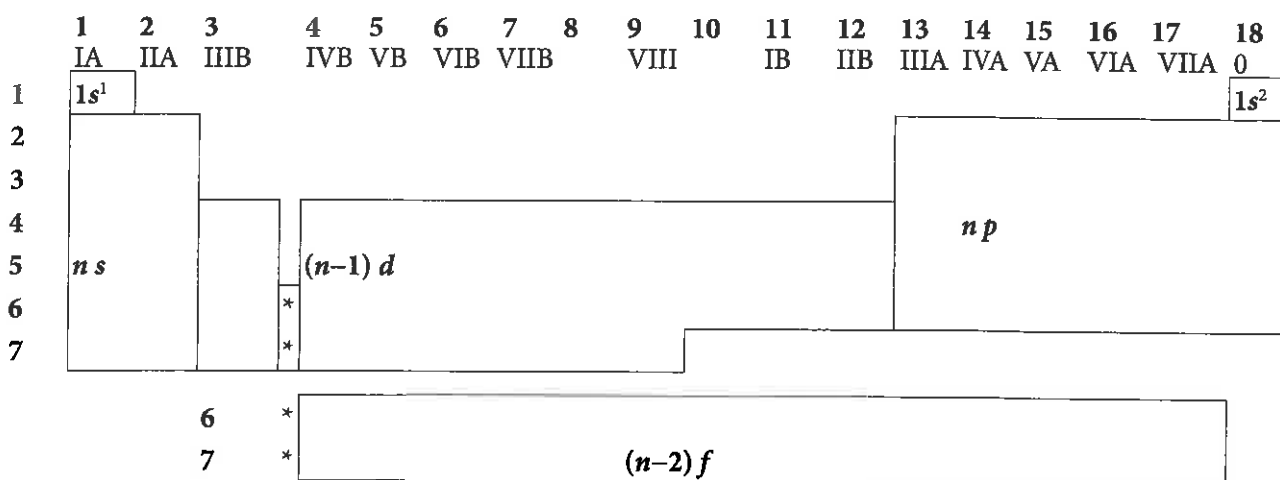
The **sixth** (and probably also the **seventh**, still incomplete) period includes 32 elements, because also $(n - 2)f$ orbitals are being occupied.

	1	2	3		4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA	IIA	IIIB		IVB	VB	VIB	VIIB		VIII		IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc		22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y		40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	*	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt									

		58	59	60	61	62	63	64	65	66	67	68	69	70	71
6	*	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
7	*	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

The table can be divided into several blocks. The elements of the s-block and p-block in which all inner orbitals fully are occupied and the ns and np orbitals are filling are called **representative elements** (also **main group elements**). The elements in which electrons enter $(n - 1)d$ or $(n - 2)f$ orbitals as proton numbers increase are referred to as **transition elements**. They form the d block (the d-transition elements) and the f block (the f-transition elements, inner transition elements).

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA	IIA	IIIB	IVB	VB	VIB	VIIB		VIII		IB	IIB	IIIA	IVA	VA	VIA	VIIA	0

Groups of elements (vertical columns) have their numbers. According to the IUPAC rules, the group numbers from 1 to 18 are used. Two rows of the inner transition $(n–2)f$ elements (lanthanides and actinides) are taken as a part of the group 3.

The older way that is sometimes still in use signs the groups with the Roman numerals I–VIII and these groups are distinguished by letters as A groups (groups of representative elements, representative or main groups) and the groups of transition elements (B groups). The group of the noble **gases** VIIIA is usually referred to as the zero group.

The elements comprising each group have equal numbers of the valence electrons localized mostly in the same types of orbitals (but of the different main quantum number n).

Representative elements are elements of the groups 1 and 2 (s-elements) and 13 to 18 (p-elements). According to the old marking system the elements of the main groups IA to VIIIA (0); in this marking system, the number of valence electrons equals to the number of the group; the only exception is helium with two valence electrons.

d-**Transition elements** comprise three ten-member series in the fourth to the sixth period, the groups 3 to 12 (the groups IIIB to VIIIB, IB and IIB). Either the atoms of those elements do not have the d orbitals completely occupied, or they can form ions with incomplete d orbitals. All the transition elements are metals characterised by the variable oxidation numbers, high variety of colours of their compounds and easy formation of coordination compounds.

f-**Transition elements** (inner transition elements) comprise two fourteen-member series lines in the sixth and seventh period, they are inserted between the groups 3 and 4 (IIIB and IVB). *Lanthanides* (rare earth elements) are the inner transition elements of the sixth period (with proton numbers 58 to 71); *actinides* are the inner transition elements of the seventh period (proton numbers 90 to 103). The only reason why f-block of elements is drawn separately from the other blocks is the easy graphic arrangement.

In representative elements of the same *period*, there are increasing numbers of valence electrons in the same valence shell with the increase in proton numbers. The atomic radii decrease (and ionization energies increase) because of the increase in the electrostatic attraction of valence electrons by the positively charged nuclei.

Elements of the same *group* have usually an equal configuration of the valence electrons so that they have many similarities in properties. However, some of their properties differ due to the increasing atomic radii and the decrease in ionization energy.

Table Distinctive names of some groups of representative elements

Alkali metals	Li, Na, K, Rb, Cs, Fr
Alkaline earth metals	Ca, Sr, Ba, Ra
Chalcogens	O, S, Se, Te, Po
Halogens	F, Cl, Br, I, At
Noble gases	He, Ne, Ar, Kr, Xe, Rn

Which Properties Can Be Derived from the Location of Elements in the Periodic Table?

Orbital radius of atoms, important for thinking about the spatial arrangement of molecules, varies periodically with the increasing proton number. Electrostatic attractive forces between the positive charge of the nucleus and the negative charge of electrons in its shell decisively influence the orbital atomic radius. In periods, the atomic radius **decreases** with the growing proton number (from left to right); and it **increases** with the increasing proton number in groups (from top to bottom).

Reactivity of elements (the ability to participate in the chemical reactions with other elements)

Very stable, energetically convenient configuration is $1s^2$ in helium as well as the octet ns^2p^6 in atoms of other noble gases; therefore, they have so low reactivity. The other elements reach more stable configuration of electrons in the chemical reactions. One of the possibilities includes sharing of the valence electrons between two atoms (formation of the covalent or coordination bond, Chapter 3), another involves accepting new electrons or their removal (creating of ions, see ionic bond, Chapter 3).
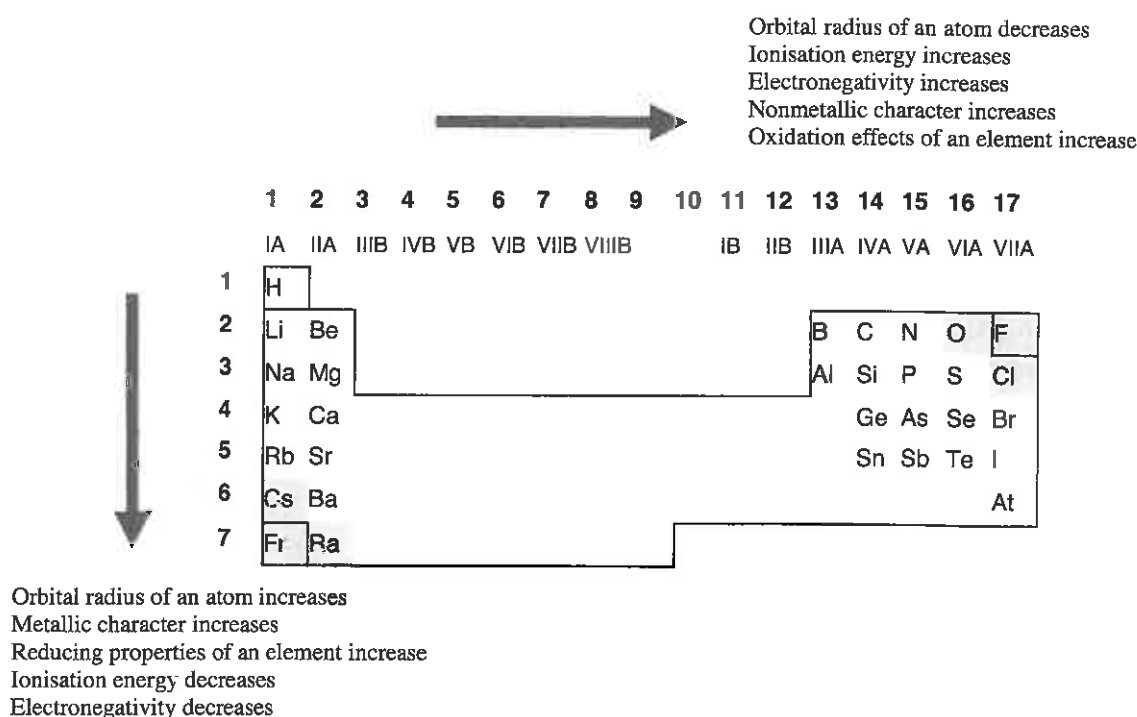
The measure of tendency of an atom to lose one (or more) valence electron and thus form a cation is the value of **ionisation energy**, the measure of tendency to accept electrons into the valence shell and thus create a stable anion is the **electron affinity**. From these quantities, the values of **electronegativity** can be obtained. Electronegativity of an element is the ability of an atom in a covalent bond to attract the bonding electron pair to itself.

All three above-mentioned characteristics are periodical properties of the elements, because they depend on the electron configuration of an atom. The value of electronegativity **increases** in periods together with the

increasing proton number, whereas it **decreases** in groups with the growing atomic radius (see the diagram on the next page).

The type of bond (polarity of the bond) in the compound depends on the difference of electronegativities of the participating elements as well as their reactivities. A strong polar ionic bond originates most easily between large atoms of elements exhibiting very low electronegativity (electropositive elements) and small atoms of elements with high electronegativity.

Reactivity of the electropositive elements is the greater, the smaller is the difference between their electron configuration and that of the previous noble gas, and the bigger is their atomic radius. Thus, the most electropositive elements are the alkali metals (group 1) with high proton numbers, cesium, and francium, found in the left bottom part of the periodic table.

Orbital radius of an atom decreases
Ionisation energy increases
Electronegativity increases
Nonmetallic character increases
Oxidation effects of an element increase

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA
1	H																
2	Li	Be											B	C	N	O	F
3	Na	Mg											Al	Si	P	S	Cl
4	K	Ca												Ge	As	Se	Br
5	Rb	Sr												Sn	Sb	Te	I
6	Cs	Ba															At
7	Fr	Ra															

Orbital radius of an atom increases
Metallic character increases
Reducing properties of an element increase
Ionisation energy decreases
Electronegativity decreases

The value of electronegativity of elements of the same period increases with the growing proton number. The most reactive highly electronegative elements are fluorine, chlorine and oxygen in the group 16 and 17 (group VIA and VIIA). These elements most easily form anions with the electron configuration of the following noble gas by accepting electrons. Elements in the middle of the table have medium values of electronegativity; their ability to form covalent bonds with other elements is generally low and the bonds have low polarity.

Metals and non-metals. Elements with low electronegativity and a small number of valence electrons in the ns or np orbitals are metals. Metallic bonding in an elemental metal is the attraction between positive metal ions and surrounding, freely mobile valence electrons (Chapter 3). All the s-block elements, all the transition elements, and some of the p-block elements are metals. The border between metals and non-metals in the periodic table is not sharp, approximately represented by the **diagonal from boron to astatine**. Non-metals are only to the right of the diagonal and above, to the left and below are metals. Elements lying on the diagonal and some in the close neighbourhood (germanium, selenium, and antimony) are semiconducting elements. These semi-metals resemble metals in appearance; in chemical behaviour they are more like the non-metals.

Oxidizing or reducing properties of elements depend on the ability to release or accept valence electrons. The most electropositive elements (alkali metals and alkaline earth metals) are strong reducing agents in their elementary state – they easily give their valence electrons to other substances and reduce them. Elements with high electronegativity (F, O, Cl) are strong oxidation agents.

Oxidation Numbers of Elements in Compounds

- Hydrogen has oxidation number I in all its compounds except the ionic hydrides (compounds with the most electropositive metals, in which hydrogen reaches oxidation number –I).
- Oxygen has oxidation number –II in most compounds, but in peroxides –I, and in superoxides –½.
- In p-elements (groups 13 to 17, i.e. IIIA–VIIA), the highest possible positive value of the oxidation number is equal to the number of the valence electrons (i.e. 3 to 7); exceptions are oxygen, as mentioned above, and fluorine (it exhibits very high electronegativity, so that it does not reach the positive oxidation number at all).
- Only non-metals achieve negative oxidation numbers in their compounds. Boron reaches –III, the other elements in groups 14 to 17 have oxidation numbers equal to the number of electrons missing to reach the octet $ns^2\,np^6$.
- Metals have only positive oxidation numbers in their compounds. The alkali metals have always I, the alkaline earth metals always II.

4 CHEMICAL BONDS

Compounds are composed of atoms, which are held by chemical bonds forming the molecules or crystalline structures. When a chemical bond is formed, the electrons are redistributed to form a new, energetically more convenient arrangement. The strength of the chemical bond is measured by the energy needed to its cleavage, which is equal to the energy released when this bond is formed. It is called bond energy and is given in kJ mol⁻¹. The basic types of chemical bond are **covalent** and **ionic**.

Covalent Bond

The covalent bond is characteristic for **non-metal** elements. The bond energy of the covalent bonds is usually in the range of 200–1000 kJ mol⁻¹. The lengths of covalent bonds are (in most organic compounds) between 0.07–0.12 nm.
The principle of the covalent bond is the sharing of one or more electron pairs between two atoms. When these atoms approach so close, that two of their orbitals, each containing one electron, are overlapped, the bond is

created (an exception is the donor-acceptor bond, see later). Effective overlapping (and the formation of a bond) occurs, when the sharing of atoms creates a stable and energetically more favourable electron configuration, usually corresponding with the electron configuration of the nearest noble gas. The sharing of one electron pair between two atoms creates a **single** bond. Overlapping occurs on the join line of the nuclei of the reacting atoms where the highest electron density is also located. This bond is called σ **bond**. The overlapping is most frequent between *s*, *p*, and *d* orbitals mutually or between *s*, *p*, *d* and hybridized orbitals (see later).

Formation of single covalent bond in the molecule of hydrogen and bromine (unpaired electron is signed with a dot).

H· + H· → H—H
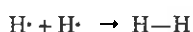
s-s overlapping on the join line of the nuclei

|B̅r̅· + ·B̅r̅| → |B̅r̅—B̅r̅|
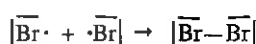
p-p overlapping on the join line of the nuclei

A higher number of shared electron pairs between the two atoms implicate the formation of a **multiple** covalent bond. The multiple covalent bonds consist of one σ (sigma) bond and one or two π (pi) bonds. A π bond is created by overlapping of the valence orbitals (*p* or *d*) elsewhere than on the join line between the two nuclei. In the case of these bonds, the highest electron density is above and under the symmetry plane of the orbitals, which lies on the join line of the nuclei (Fig.).
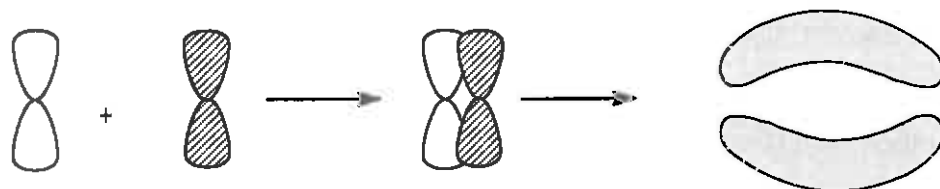
Fig. Formation of a π bond by a *p-p* overlapping outside the nuclear join line

Multiple bonds are typical for carbon in organic compounds. However, they are also found in a number of inorganic compounds, especially those with nitrogen, oxygen, sulfur. Multiple covalent bonds are stronger than single bonds, but the bond energy of a double bond is not equal to the doubled energy of the single bond, etc. The bond energy of the C—C bond in ethane is e.g. 347 kJ mol^{-1}, the C=C bond in ethene 598 kJ mol^{-1} and bond in ethyne equals to 820 kJ mol^{-1}.

Hybridization of Orbitals

The spatial arrangement of some polyatomic molecules cannot be explained only based on interaction and overlapping of orbitals containing unpaired electrons.

For example, carbon with the configuration of the valence electrons being $2s^2 2p^2$ should theoretically create the compound CH$_2$ with hydrogen, which would be formed by overlapping of unpaired electrons in *p* orbitals of the carbon atom with 1*s* electrons of hydrogen. The valence angle between the two bonds would be 90° (it would correspond with the angle between the two *p* orbitals of carbon). However, it is known that carbon forms in majority of its compounds four equivalent bonds and the bond angles are approximately 109°.

To explain the differences between the observed and expected shapes of molecules and bond angles **the hybridization theory** was created. Hybridization is the mixing of the atomic orbitals on a single atom to give a new set

of orbitals, called hybrid orbitals, on the atom. In terms of the quantum theory, this represents the combination of mathematical functions that describe the atomic orbitals involved in bonding. The result is a new description of the probable electron density about the atom. In terms of energy, hybridization represents the mixing of higher energy and lower energy orbitals to form orbitals of intermediate energy.

The example is the formation of two hybrid orbitals sp by combining atomic orbitals s and p.
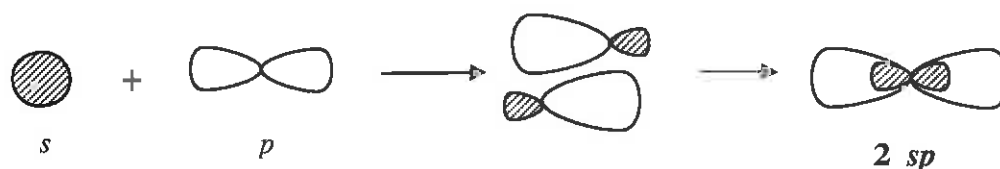
Fig. The formation of two hybrid orbitals sp

It is obvious, that hybridization of a certain number of the regular atomic orbitals creates the same number of hybrid orbitals. However, all valence orbitals of an atom need not be hybridized, some orbitals, even when they are filled with electrons, may remain unhybridized. This is valid especially in the case of atoms, which create multiple bonds: **Orbitals, whose overlapping creates π bonds, do not participate in the hybridization.** Because each type of hybridization results in the characteristic space arrangement of the hybrid orbitals, the molecular geometry can be predicted using this theory.

Basic Types of Hybrid Orbitals

Hybrid orbitals sp are formed from one s orbital and one p orbital, as was mentioned above. The angle between the axes of these orbitals is 180°, all molecules are of the AB_2 type, in which the orbitals of the central atom are in the sp hybrid state and have linear shape. The example is $BeCl_2$. Hybridization sp occurs also in carbon atoms, which form a triple bond (e.g. ethyne $CH{\equiv}CH$).

Hybrid orbitals sp^2 consist of one s orbital and two p orbitals. The geometric arrangement of these three sp^2 hybrid orbitals is in a flat plane with 120° angles between them.
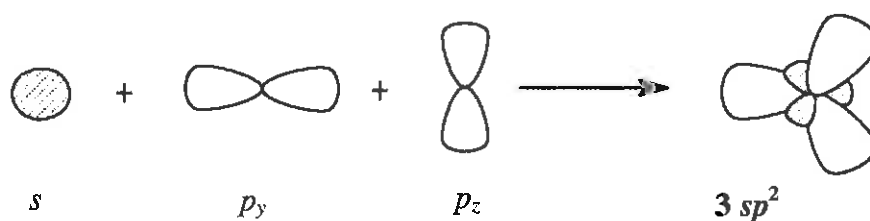
Fig. The formation of three hybrid orbitals sp^2

Molecules, in which the central atom with the sp^2 hybridization covalently binds three other atoms, are planar. The example is BF_3. The hybridization of sp^2 type helps to explain the bond angles and spatial arrangement of carbon compounds with a double bond (e.g. ethene $CH_2{=}CH_2$).

Hybrid orbitals sp^3 are formed by the energetic unification of one s orbital and three p orbitals. The geometric arrangement of four hybrid orbitals is called tetrahedral. There is a 109.5° angle between all orbitals.
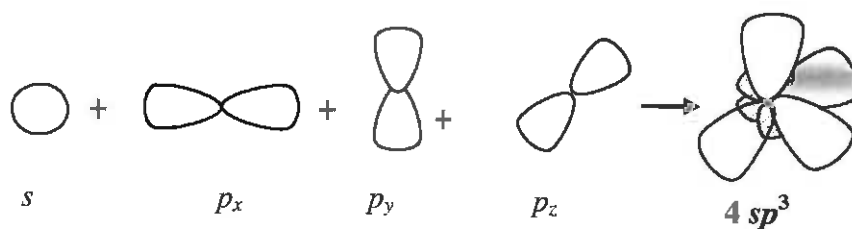
Fig. The formation of four hybrid orbitals sp^3

A typical example is the hybridization of carbon in all organic compounds where a carbon atom is bonded to four other atoms.
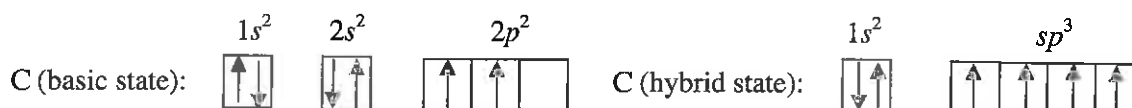
The hybridization of this type helps to explain the shape of molecules such as H_2O and NH_3. In these molecules, the central atoms (O, N) are in sp^3 hybridization. However, some of the hybrid orbitals are filled with a pair of electrons, which does not take part in any bonding (free electron pair). This causes the change of bond angles in the molecule.

In the molecule of NH_3, one of the four hybrid sp^3 orbitals of nitrogen is filled with a free electron pair, which tends to take more space than the hybrid orbital. This leads to the compression of the tetrahedral shape of the rest of the molecule – the measured angles between N–H bonds are 107.3°. Similarly, in the molecule of water with two free electron pairs on oxygen the bond angles are 104.5°. This phenomenon is sometimes called the umbrella effect.

One hybrid orbital sp^3 filled with a free electron pair
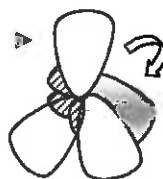
Molecular Orbitals Theory

Another theoretical method, which explains the properties molecules of elements and compounds, is the theory of molecular orbitals. It is based on the presumption that during the bonding of atoms the interaction between the atomic orbitals leads to the formation of **molecular orbitals (MO)**. These new orbitals play a similar role in molecules as the atomic orbitals in atoms – they are the permitted areas, in which the electron is allowed to move in the vicinity of several atomic nuclei. The filling of the molecular orbitals follows the same rules as the filling of the atomic orbitals (the building up principle, the Hund's principle, and the Pauli exclusion principle). A combination of a certain number of atomic orbitals forms the same number of molecular orbitals. Orbitals formed from the atomic s orbitals or p orbitals, in which most of electron density is located between the nuclei are called σ, orbitals formed by a combination of the remaining atomic p-orbitals are called π. The molecular orbitals with lower energy than the original atomic ones are called **bonding**. Orbitals with higher energy than in the case of atomic orbitals are called **antibonding** and are symbolized by asterisk *. Orbitals with the energy nearly equal to the energy of the original atomic orbitals are called **nonbonding**. Electrons found in the bonding orbitals contribute to the stability of the bond, whereas the antibonding orbitals act against it. The scale of stability is the **bond order**, which is according to the MO theory calculated by the expression:

Bond order = 1/2 (number of bonding electrons – number of antibonding electrons)

In the molecule of hydrogen H_2 two atomic $1s$ orbitals combine to form the bonding σ_{1s} and the antibonding σ_{1s}^* orbitals:

Molecular orbitals

Atomic orbital

Atomic orbital

σ_{1s}^*

$1s$

$1s$

$\uparrow\downarrow$

σ_{1s}
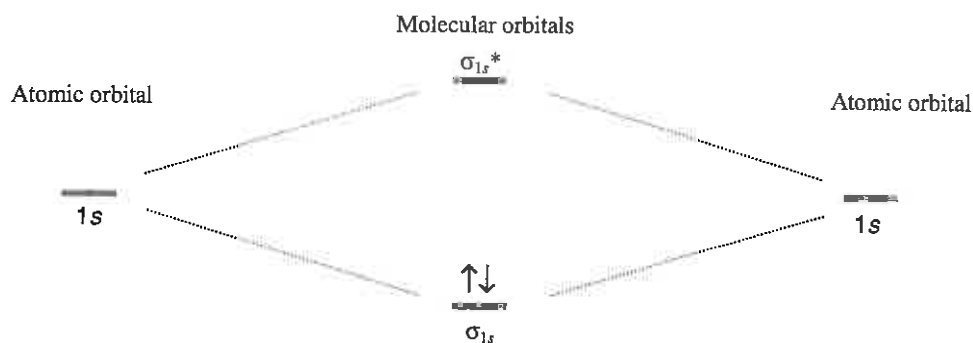
Electrons fill only the bonding orbitals; therefore, the molecule of H_2 is stable.
With the help of the MO theory, we can explain the paramagnetic properties of the dioxygen molecule and the difference in the electron building of the triplet and singlet oxygen.

Atomic orbitals   Molecular orbitals   Atomic orbitals

$\sigma_{2p_z}^*$

$\uparrow$ $\uparrow$

$\pi_{2p_x}^*$ $\pi_{2p_y}^*$

$2p_x$ $2p_y$ $2p_z$

$\uparrow\downarrow$ $\uparrow\downarrow$

π_{2p_x} π_{2p_y}

$2p_x$ $2p_y$ $2p_z$

$\uparrow\downarrow$

σ_{2p_z}

$\uparrow\downarrow$

σ_{2s}^*

$2s$

$2s$

$\uparrow\downarrow$

σ_{2s}

$\uparrow\downarrow$

σ_{1s}^*

$1s$

$1s$

$\uparrow\downarrow$

σ_{1s}
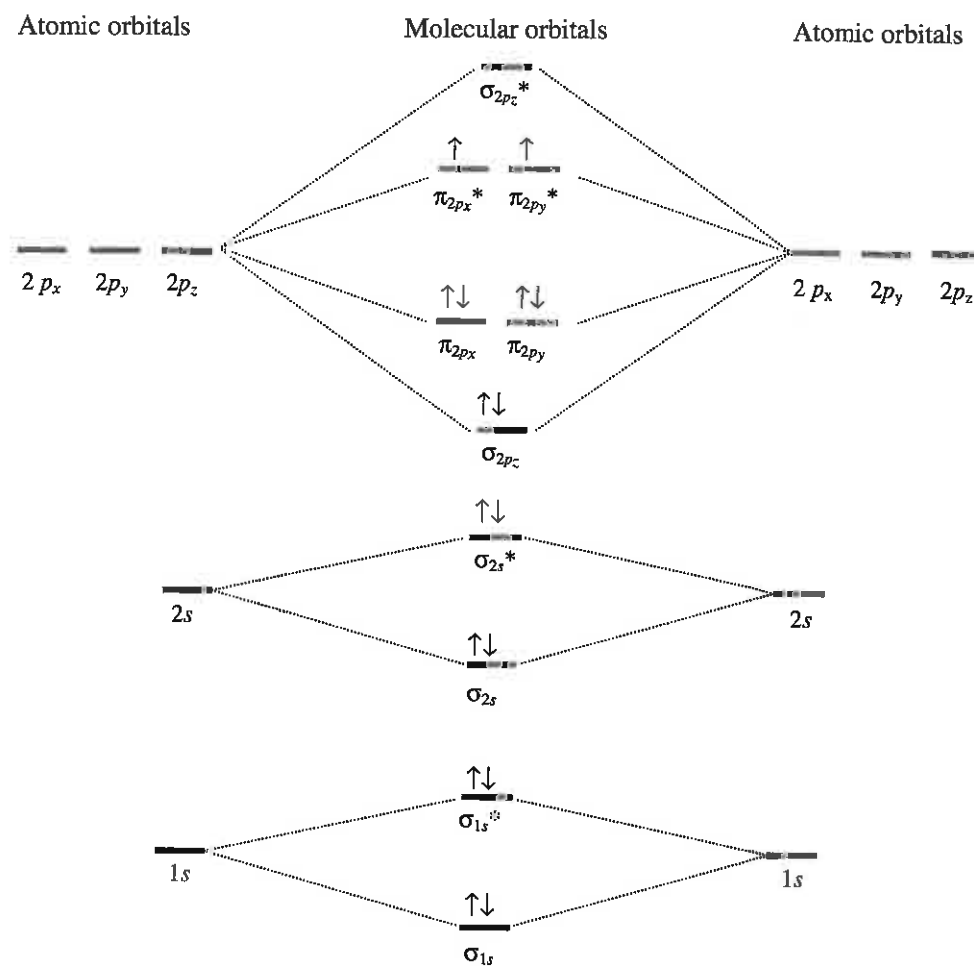
Fig. Electron arrangement of the oxygen molecules according to the MO theory

The arrangement of electrons in the dioxygen molecule predicted by the MO theory explains a number of its properties. The oxygen molecule in its ground state is a biradical – it contains two unpaired electrons with the same spin. The spin multiplicity calculated by the expression $nS + 1$ (where S is the total spin and n the number of unpaired electrons) equals to three, therefore oxygen in its ground molecular state is identified as triplet ($^3O_2$). Common diatomic oxygen has a relatively low reactivity in comparison with the other "radicals"– this is explained by the fact, that both unpaired electrons have the same spin. When energy is added, oxygen can be changed to the singlet form $^1O_2$, which is much more reactive.

The distribution of electrons in the antibonding π_{2p}^* orbitals in the different forms of oxygen

Triplet dioxygen $^3O_2$		Singlet dioxygen $^1O_2$		Superoxide $\cdot O_2^-$	
↑	↑	↑↓	–	↓↑	↑
π_{2px}^*	π_{2py}^*	π_{2px}^*	π_{2py}^*	π_{2px}^*	π_{2py}^*

Polarity of Bonds and Molecules

If the covalent bond binds two equal atoms, e.g. in the diatomic molecules of gases (N_2, O_2, F_2), the shared electrons are distributed uniformly between both atoms; such a bond is called **nonpolar**.

A polar bond is formed when two different atoms are bonded and the shared electron pair is distributed unequally between them. How unequally the electrons are shared depends on the relative abilities of the two different atoms to attract electrons. Then one atom acquires a partial negative charge ($-\delta$) and the other partial positive charge ($+\delta$). The degree of this attraction is given by the **electronegativity** of the atom. The electronegativities of elements vary in the range from 0.7 (Cs) to 4.1 (F). The electronegativities of the most important non-transition elements are presented in the Table below.

Table Electronegativities of elements

		H 2.2				
Li 1.0		C 2.5	N 3.1	O 3.5	F	4.1
Na 0.9	Mg 1.2	Si 1.8	P 2.1	S 2.4	Cl	3.0
K 0.8	Ca 1.0				Br	2.8
					I	2.5

The polarity of bond can be derived from the difference of electronegativities of both elements. The generally used rule says that if this difference is lower than 0.4 the bond is assigned as **non-polar** (less than 5 % of the ionic character). If the difference is 0.4–1.7 (less then 50 % of ionic character), the bond is classified as **polar**. The polarity of the individual bonds influences the total polarity of the molecule, i.e. the distribution of the positive and negative charge in the whole molecule. The measure of polarity is the dipole moment. In diatomic compounds, the dipole moment of the bond is equal to the dipole moment of the molecule (N_2, HI). The polarity of polyatomic molecules depends on their molecular geometry; the dipole moment is given by the vector sum of dipole moments of the individual bonds. It means that a molecule can be **non-polar**, even when if it contains **polar** covalent bonds (e.g. molecules of CO_2, CCl_4).

Besides substances with a permanent dipole moment, there exist easily polarizable substances. By the action of an electric field (neighbourhood of the ion or permanent dipole) can be affected the distribution of electrons in the molecules. Thus, induced dipoles are formed, the dipole moment of which depends on the intensity of

the electric field E and on the character of the substance $\mu_i = \varepsilon\, E$. The constant ε is called polarizability. It is a quantity characteristic for each substance. Easily polarized molecules include organic compounds with multiple bonds (polarization of the π binding electrons), mainly with conjugated systems of multiple bonds and/or the nonbinding electron pairs.

Valence of Elements

Each element has a characteristic valence that determines the number of covalent bonds it can form. Atoms of hydrogen, which contain only 1 electron, can form only one covalent bond. To derive the bonding capacity of the other **non-metals** in compounds with more electropositive elements we can use a simple rule. The typical valence is equal to the **negative oxidation number** of the appropriate non-metal: four for carbon and silicon (group IV A), three for nitrogen and phosphorus (group V A), two for oxygen and sulfur (group VI A) and one for halogens.
In compounds consisting of a non-metal with **more electronegative** elements cannot be used this rule, because the valence of the given non-metal can be higher or lower. Thus e.g. in NO nitrogen is bivalent, in PCl_5 phosphorus pentavalent (10 shared electrons), etc.

Coordinate Covalent Bond

Except the typical covalent bond there can exist a special type – **coordinate covalent bond.** In this type of covalent bond, both electrons are provided to a bond by the same atom. The **donor atom** has a **free electron pair**, i.e. a pair of electrons still not involved in any bond, and the **acceptor atom** has a **free valence orbital** and accepts an electron pair for to be shared in the bond. Therefore, this bond is also named as the donor-acceptor or dative bond.
For example, a hydrogen ion unites with an ammonia molecule by coordinate covalent bond to form ammonium ion NH_4^+:
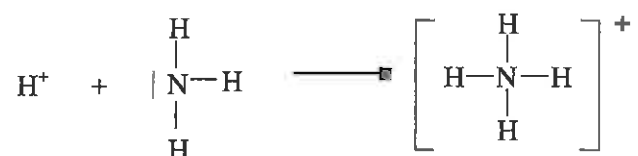
All N–H bonds in the ammonium cation are equivalent, it is impossible to distinguish among the electrons once the bond has formed. Note that in the ammonium cation nitrogen is fourvalent.
The coordinate covalent bond is mostly found in the complex compounds. The acceptor of the electron pair is usually a cation or atom of a transition metal; it is referred to as the **central atom**. Donors of the electron pairs (molecules, anions) are called **ligands**. The number of ligands bonded to the central atom gives the **coordination number**. It varies from 2 to 8. The most frequently occurring compounds have coordination numbers 6 or 4. For example, iron ion has most often the coordination number 6.

Ionic Bond

The ionic bond is the extreme form of the polar covalent bond. The shared electrons are pulled into the vicinity of the more electronegative atom, so that 2 ions are created. The cation and anion with opposite charges are attracted by electrostatic forces.
An approximate definition states that the ionic bond exists between atoms with the difference of electronegativities greater than 1.7. This value corresponds with more than 50 % of the ionic character of the bond. The ionic character never reaches 100 %.
Besides the typical binary salts (NaCl, KF) the ionic bond occurs in other salts of inorganic and organic acids, which are formed by cations and anions such as NH_4^+, NO_3^-, SO_4^{2-}. In these particles, e.g. $NH_4^+NO_3^-$, the character of the bond is ionic.

Ionic and Covalent Compounds

According to the type of chemical bond, we divide compounds into **ionic** and **covalent**.

Ionic compounds are crystalline substances in solid state. The ions are bound by strong electrostatic forces in the crystals; therefore, they have high melting and boiling points. Most salts are well soluble in water and their solutions and melts conduct electric current (electrolytes). In the solid state there are no free molecules, they form ion lattices. The chemical formula of the ionic compound, e.g. NaCl, is only the simplest record of the stoichiometric ratio of ions in the crystal.

Covalent compounds are much less polar than the ionic compounds. They include mainly molecular substances, where the chemical formula really expresses the smallest particle of the compound (CO_2, CH_3OH). They occur as gases, liquids, and solids with relatively low melting and boiling temperature. The typical covalent compounds are e.g. all carbohydrates. In solid state, they form molecular lattices.

Certain substances such as diamond (crystalline carbon), carborundum (SiC) and quartz (SiO_2) resemble molecular compounds, except that they are very hard and have very high melting points. In these materials, no discrete molecules are present but individual elements are interconnected by strong covalent bonds. They form network covalent substances, sometimes called **covalent crystals**

Metallic Bond

The metallic bond exists between metal atoms in solid state. The model of the metallic bond supposes that the metal crystal consists of the cations distributed in the space lattice. Positively charged metal ions are held in their position by the charge of easily mobile valence electrons (electron "sea"). This explains the very good electric and thermal conductivity of metals, malleability, and ductility.

Intermolecular Forces

By these interactions we understand the attractive forces **between molecules** (or between the parts of a macromolecule), which influence the consistence of substances. The energy of these interactions is much lower than the energy of the covalent bonds and the ionic interactions in the crystal lattices – therefore they are defined as the **weak** non-bonding interactions or **non-covalent bonds.** The strength of the intermolecular forces determines the physical state of substance and affects its solubility. Their biological importance lies in maintaining the secondary, tertiary or quaternary structure of biopolymers, stability of the supramolecular structures such as biomembranes, in the specific biological interactions (the binding of a substrate to an enzyme, an antibody to antigen, a hormone to protein receptor) etc.

Hydrogen Bonds

Hydrogen bonds (hydrogen bridges) are the strongest intermolecular forces. They are found in substances, in which the hydrogen atom is bonded to a strongly electronegative atom – nitrogen, oxygen, or fluorine. The electronegative atom strongly attracts the shared electron pair; the small hydrogen atom has little electron density around it. Under these circumstances, the hydrogen atom carries a partial positive charge and is able to form a weak bond with a free electron pair of the electronegative atom of the other molecule. In formulas, it is marked by punctuation: XH...Y. The bond energy is greater than in the case of other non-covalent interactions, it reaches up to several tens of kJ mol^{-1}. The presence of the hydrogen bonds in a certain system leads to the increase of intermolecular attractive forces.

The hydrogen bonds can be **intermolecular** and **intramolecular.** Large numbers of hydrogen bonds are formed between C=O and –NH groups of peptide chains. They play important role in the formation of the secondary structures (α–helix, β–structure).

Intramolecular bridges in 2-nitrophenole
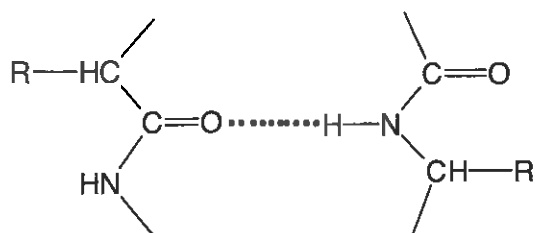
Intramolecular bridges between peptide chains

Hydrogen bonds have special importance for the properties of water. Because oxygen in H_2O has two lone pairs of electrons and two covalently bonded hydrogen atoms, each water molecule is able to form hydrogen bonds with up to four other molecules at the same time. Thus aggregates (clusters) with a different number of molecules and with circular or spatial arrangement are formed. They have tetrahedral arrangement in ice – each molecule binds four others and six-membered rings are formed. The crystal lattice is relatively loose (lower density of ice, increase of volume).
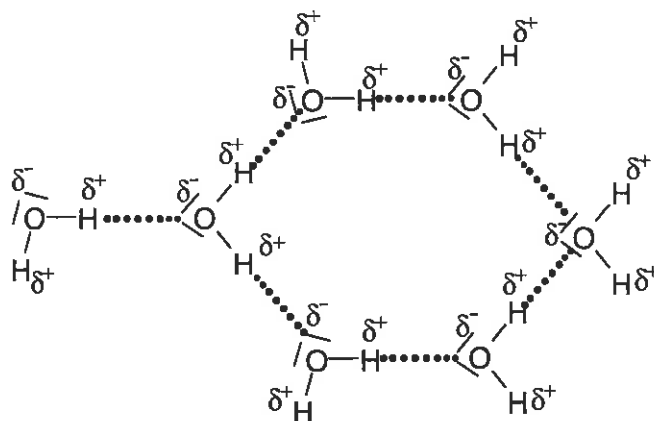
The formation of hydrogen bonds between the purine and pyrimidine bases is important in the replication of DNA.

Van der Waals Forces
The term van der Waals forces are used for weak intermolecular interactions including **electrostatic and dispersion** interactions.
Electrostatic interactions are based on attractive coulombic forces between positive and negative electrical charges. The charge can be either total, in ions, or partial, in dipoles.
Ion-ion interactions. (They cannot be confused with ionic bonds in the crystal lattice of ionic compounds). These interactions include the formation of ion pairs (**salt bridges**) in solutions. Ion pairs are formed e.g. during interaction of side amino acid chains in proteins, of the $-COO^-...^+NH_3$ type. This interaction is important mainly for the association of subunits participating in the quaternary structure of proteins.
Ion-dipole or dipole-dipole interactions. They are weaker than the previous interactions. In polar substances, they are responsible for their lower volatility in comparison with the analogical non-polar compounds. They cause the solvation of ions in polar solvents. They participate in the stabilization of the tertiary structure of proteins. They contribute to the solubility of polar substances in polar solvents.

Dipole-induced dipole interaction. In non-polar molecules, especially if they contain easily polarizable structures, a weak dipole moment is induced in the electric field of ions or in the close vicinity of the permanent dipoles. Formation of this dipole moment results in corresponding electrostatic attractive forces.

Dispersion forces (London forces) occur in non-polar substances (carbohydrates, gaseous elements including noble gases). Dispersion forces are the result of momentary changes (distortions) in the symmetry of electron cloud in the molecule. In a large collection of molecules, at any given moment collisions occur, with resulting polarization of the molecules. As soon as a slight positive charge is produced at one end of the molecule, it induces a slight negative charge in one end of the molecule next to it – induced dipole. Dispersion forces are attraction between fluctuating dipoles in atoms and molecules that are very close together. The probability of attraction is greater for long molecules than for spherical ones. In nonpolar substances (hydrocarbons, O_2, N_2, H_2, inert gases), the dispersion forces are the only intermolecular interactions. They are responsible for the condensation of gases at low temperature. The bond energy induced by the van der Waals forces is 2 or 3 orders lower than the energy of the covalent or ion bonds.

Hydrophobic interactions are the bonds formed between the hydrophobic (non-polar) molecules of substances in an aqueous environment. When you add some drops of oil to water, the drops combine to form a larger drop. Water molecules are attracted to each other and are cohesive because they are polar molecules. Oil molecules are non-polar and thus have no charged regions on them. This means that they are neither repelled nor attracted to each other. The attractiveness of the water molecules for each other then has the effect of squeezing the oil drops together to form a larger drop. This results in the increase of their order and the decrease of entropy of the system. The bond energy of the individual interactions is imperceptible, but if they occur in large quantities, they reach considerable strength. This type of interactions is important in the structure of biomolecules, e.g. in the stabilization of biological membranes and the tertiary structure of proteins.

5   NOMENCLATURE OF INORGANIC COMPOUNDS

The International Union of Pure and Applied Chemistry (IUPAC) designated the official system of inorganic nomenclature. In this system, most of the compounds are considered to be composed of two parts, one positive, and the other negative. The positive part is named and written first; the **negative** part, generally non-metallic, follows.

The Names of Cations

Monoatomic cations originate by the removal of one or more electrons from an atom. The name of a cation consists of the name of the element and the word *ion* (or cation).

Na^+	sodium ion	Ca^{2+}	calcium ion
K^+	potassium ion	Al^{3+}	aluminium ion

If more than one type of cation exists, a Roman numeral inside parenthesis denotes the oxidation number (the charge on the ion). There is an older rule still used, by which the names of elements are transformed into adjectives by combining the Latin stem of element's name with the suffixes *-ous* for the lesser charge and *-ic* for the greater charge.

Fe^{2+}	iron(II) ion ferrous ion	Cu^+	copper(I) ion cuprous ion
Fe^{3+}	iron(III) ion ferric ion	Cu^{2+}	copper(II) ion cupric ion

The names of **polyatomic cations** are expressed by one noun with the suffix _-onium_. NH_4^+ cation is called ammonium. The name ammonium ion is more frequently used for alkylated ammonium ions in organic chemistry.

NH_4^+	ammonium	$CH_3NH_3^+$	methylammonium ion
PH_4^+	phosphonium	$(CH_3)_2NH_2^+$	dimethylammonium ion
H_3O^+	hydrated proton (or oxonium)	$(CH_3)_3NH^+$	trimethylammonium ion
H_3S^+	sulfonium	$(CH_3)_4N^+$	tetramethylammonium ion

The Names of Anions

The name of a monatomic anion consists of adjective formed from the stem of the name of the element modified with the suffix _-ide_ and the noun _ion_ (or anion).

Cl^-	chloride ion	O^{2-}	oxide ion
F^-	fluoride ion	S^{2-}	sulfide ion
I^-	iodide ion	N^{3-}	nitride ion
H^-	hydride ion	C^{4-}	carbide ion

Exceptions that use the –ide ending are, e.g. hydroxide anion OH^-, cyanide ion CN^-, peroxide anion O_2^{2-}, and superoxide anion-radical $\cdot O_2^-$. These anions take the ending –ide, even though they are not monoatomic.

The name of an oxoanion consists of the stem of the element other than oxygen to which the suffix _-ite_ or _-ate_ is added followed with the noun _ion_ (or anion). The –ite ending represents the lower and the –ate the higher oxidation state. When an element has only one oxidation number, such as C in carbonate, the –ate suffix is used. In cases where there are more than two oxoanions of particular element, the names are further modified with the prefixes _hypo-_ and _per-_. Hypo– is placed before the stem when the element has a lower oxidation number than in the –ite anion; per– is used as a prefix before the stem when the element has a higher oxidation number than in the –ate anion.

CO_3^{2-}	carbonate ion	SO_3^{2-}	sulfite ion
SiO_4^{4-}	silicate ion	SO_4^{2-}	sulfate ion
PO_4^{3-}	phosphate ion		
CrO_4^{2-}	chromate ion	ClO^-	hypochlorite ion
		ClO_2^-	chlorite ion
NO_2^-	nitrite ion	ClO_3^-	chlorate ion
NO_3^-	nitrate ion	ClO_4^-	perchlorate ion

The names of anions that contain hydrogen. Such anions are formed by the diprotic and polyprotic acids (acids that contain more than one hydrogen atom). They are named by using the word _hydrogen_ with the multiplying prefix, when needed.

HS^-	hydrogen sulfide ion	HCO_3^-	hydrogen carbonate ion (formerly bicarbona-
HSO_3^-	hydrogen sulfite ion	HPO_4^{2-}	te)
HSO_4^-	hydrogen sulfate ion	$H_2PO_4^-$	hydrogen phosphate ion
			dihydrogen phosphate ion

The Names of Compounds
Ionic compounds

The majority of these compounds contain a cation of a metallic element (or ammonium) and an anion which is either monoatomic or an oxoanion. Their names consist of two parts: the first is the name of the cation followed by the anion name; the words "ion" are omitted. This type of naming is used, above all, for ionic oxides, ionic hydrides, hydroxides, and salts.

Na_2O	sodium oxide		FeS	iron(II) sulfide
ZnO	zinc oxide		As_2S_3	arsenic(III) sulfide
			KCN	potassium cyanide
CaH_2	calcium hydride			
			$NaNO_2$	sodium nitrite
KOH	potassium hydroxide		KNO_3	potassium nitrate
$Mg(OH)_2$	magnesium hydroxide		$CaCO_3$	calcium carbonate
$Cu(OH)_2$	copper(II) hydroxide		$Al_2(SO_4)_3$	aluminium sulfate
$Al(OH)_3$	aluminium hydroxide		$NaHCO_3$	sodium hydrogen carbonate
			$K_2Cr_2O_7$	potassium dichromate
NaF	sodium fluoride		$AlPO_4$	aluminium phosphate
$CaCl_2$	calcium chloride		Mg_2SiO_4	magnesium silicate
NH_4Br	ammonium bromide		$KMnO_4$	potassium permanganate
KI	potassium iodide		Na_2HPO_4	(di)sodium hydrogen phosphate
			$Ca(H_2PO_4)_2$	calcium dihydrogen phosphate

Salts with more than one positive or negative ion:

$CaMg(CO_3)_2$	calcium magnesium carbonate	MgCl(OH)	magnesium chloride-hydroxide
NH_4MgPO_4	ammonium magnesium phosphate	$BiNO_3(O)$	bismuth(III) nitrate-oxide
$KAl(SO_4)_2$	aluminium potassium sulfate		

Acids

Acids are hydrogen-containing covalent compounds that liberate hydronium (hydrated ions H^+) when dissolved in water.

Acids derived from binary hydrogen compounds. The chemical bond that exists between two nonmetals is predominantly covalent. Binary compounds of hydrogen and certain nometals (group 16 and 17, sulfur and halogens) are volatile, mostly gases (called hydrogen sulfide, hydrogen chloride, etc.). However, when dissolved in water these compounds have acid properties. Then they are given acid name composed of the stem of the nonmetal with the prefix _hydro-_, the suffix _-ic_, and the noun _acid_.

H_2S (_g_) hydrogen sulfide (sulfane) $\longrightarrow$ H_2S (_aq_) hydrosulfuric acid
HF (_l_) hydrogen fluoride $\longrightarrow$ HF (_aq_) hydrofluoric acid
HCl (_g_) hydrogen chloride $\longrightarrow$ HCl (_aq_) hydrochloric acid
HI (_g_) hydrogen iodide $\longrightarrow$ HI (_aq_) hydroiodic acid

Oxoacids. The name of an oxoacid consists of the stem of the element other than oxygen to which the suffix _-ous_ or _-ic_ is added followed with the noun _acid_. The –ous ending represents the lower and the –ate the higher oxidation state. When an element has only one oxidation number, such as boron, the –ic suffix is used. In cases where there are more than two oxidation states of particular element, the names are further modified with the prefixes _hypo-_ and _per-_. Hypo– is placed before the stem when the element has a lower oxidation number than in the –ous acid; per– is used as a prefix before the stem when the element has a higher oxidation number than in the –ic acid.

H_3BO_3	boric acid		H_2SO_3	sulfurous acid
H_2CO_3	carbonic acid		H_2SO_4	sulfuric acid
H_4SiO_4	silicic acid			
$H_2Cr_2O_7$	dichromic acid		HClO	hypochlorous acid
			H_3PO_3	phosphorous acid
HNO_2	nitrous acid		H_3PO_4	phosphoric acid
HNO_3	nitric acid		$H_4P_2O_7$	diphosphoric acid

Binary covalent compounds containing two nonmetals

Unless the compound is a covalent hydride that has its specific name (e.g. BH_3 borane, CH_4 methane, NH_3 ammonia, PH_3 phosphane), the least electronegative element is named first, followed by the stem of a more electronegative element with the ending _–ide_. When there is a need to distinguish between two or more compounds of the particular couple of elements, common multiplying prefixes are used.

H_2S (g)	hydrogen sulfide		N_2O	dinitrogen monoxide
CO	carbon monoxide		NO	nitrogen monoxide
CO_2	carbon dioxide		NO_2	nitrogen dioxide
ICl_3	iodine trichloride		N_2O_5	dinitrogen pentoxide

Table Simplified outline of some suffixes (and prefixes) in the names of inorganic salts and acids

Oxidation number of the element other than oxygen in the anion	The second noun in a name of a compound	Name of the corresponding acid
Negative value (binary compounds)	–ide	hydro– –ic acid
Positive value (oxoanions, oxoacids) – only one oxidation state possible	–ate	–ic acid
Positive value (oxoanions, oxoacids) – two or more oxidation states:		
the least value	hypo– –ite	hypo– –ous acid
the lower oxidation number	–ite	–ous acid
the higher (typical) oxidation number	–ate	–ic acid
the highest value	per– –ate	per– –ic acid

6   CHEMICAL REACTIONS

A chemical reaction is a process that leads to the transformation of one set of chemical substances to another.

Reaction types

According to the number of substances that take part in chemical reactions, there are four simple types of chemical reactions:

1. Simple **combination reactions (synthesis)**, in which two (or more) reactants combine to form one product, $A + B \rightarrow C$.

Example: reaction of carbon with oxygen during coal burning

$C + O_2 \rightarrow CO_2$
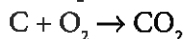
2. **Decomposition reactions**, opposites to the previous type. A compound is decomposed into smaller compouns or elements, $C \rightarrow A + B$,
Example: thermal decompositions of some inorganic compounds
$CaCO_3 \rightarrow CaO + CO_2$
3. **Displacement reactions** occur when an element is displaced out of a compound by a more reactive element,
$A + BC \rightarrow AC + B$.
Example: displacements of hydrogen from water by sodium
$2 Na + 2 H_2O \rightarrow 2 NaOH + H_2\uparrow$
4. **Partner-exchange reactions** (rearrangement reactions, conversions) are very common: molecules of two reactants exchange some atoms or groups of atoms so as to give two new compounds,
$AC + BD \rightarrow AD + BC$.
Example: formation of an insoluble salt
$BaCl_2 + H_2SO_4 \rightarrow 2 HCl + BaSO_4\downarrow$,
If a small molecule (esp. water) is one of the products in a reaction between two organic compounds, the reaction is usually referred to as **condensation**. The opposite – a cleavage of certain organic compounds in the reaction with water is called **hydrolysis** of that compound,
CH3CO–O–CH3 + H2O $\rightarrow$ CH3COOH + CH3OH (hydrolysis of an ester).
Reactions in which the exchange of H^+ ions between the reactants occurs are **acid-base reactions**.
Oxidation-reduction reactions (redox reactions) are the reactions in which some atoms of the reactants change their oxidation numbers because of the exchange of electrons.
Chemical reactions differ very much in their speed as well as in energy changes accompanying the reactions as a consequence of bond cleavage and formation.
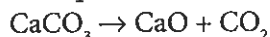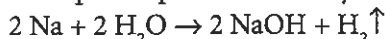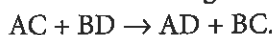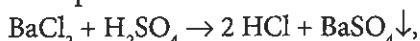
Chemical kinetics

The speed, with which the reactants are transformed to products during chemical reaction, is called the rate of a chemical reaction. The rate of a chemical reaction could be defined according to the decrease of the concentration reactants or the increase of the concentration of products per unit time. Since the reactants are disappearing as the products are appearing, the rate of loss of a reactant is, by convention, designated as being negative whilst the rate of appearance of a product, positive:
In the common equation $aA + bB \leftrightarrows cC + dD$
the rate is expressed by the relation:

$$v = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

E.g. for reaction $H_2O_2(l) \rightarrow H_2O(l) + \frac{1}{2}O_2(g)$ the reaction rate may be measured in terms of either the concentration-of-peroxide decrease or the volume-of-oxygen increase per second.
The dependence of the reaction rate on the concentration of reactants determined from the experimental data is expressed in **the kinetic equation**. The common formulation of the kinetic equation is

$$v = k [A]^\alpha [B]^\beta$$

Values α and β are so called partial reaction orders, in general they are not identical to coefficients a and b in the stoichiometric equation of the reaction and they are obtained only from the experimental measurements. The sum of stoichiometric coefficients $\alpha + \beta$ is defined as **the reaction order**.
Reaction, whose kinetic equation is $v = k [A]$, is the reaction of **the 1st order**, reaction described by kinetic equation $v = k [A] [B]$, is the reaction of **the 2nd order** etc. The reaction order need not be expressed as entire value, e.g. for the reaction with kinetic equation expressed as $v = k [A]^{0.5} [B]$, the reaction order will be 1.5.
As follows from the kinetic equation the rate of any reaction does not remain constant. Because of the decreasing

concentration of a reactant (or reactants), the velocity of reactions gradually decreases and the reactions go to completion unless they are reversible.

The rate of a chemical reaction increases
- with increasing temperature,
- with an increase in the concentration of reactants,
- when a catalyst is used,
- with the decreasing concentrations of reaction products which are continuously removed (in reversible reactions).

Many reactions are reversible and do not go to completion at which all reactants disappear. So after some of the products are created, the reverse reaction starts at which products begin to react to form the reactants. At the beginning of the reaction, the rate of reactants changing into products is higher than the rate of products changing into reactants. Therefore, the net change is a higher number of products. After some time, the opposing reactions will have equal reaction rates and the ratio between reactants and products will appear fixed. This is called chemical equilibrium. Even though the reactants are constantly forming products and vice-versa the amount of reactants and products does become steady.

Equilibrium might be reached at a point where the number of reactant molecules remaining is much larger than the number of product molecules – such reaction is described as "not going very far toward completion". On the other hand, the reaction might come to equilibrium at a point where only few reactant molecules remain and the system contains mainly products – such reaction is described as "favorable in the forward direction" (going to the right).

The equilibrium state of a closed system is after the completion of the chemical reaction quantitatively described by the equilibrium constant K. The value of this constant is always the same for the given reaction and temperature (and in case of systems composed of gaseous components the given pressure).

For the general reaction: $aA + bB \leftrightarrows cC + dD$
the numerical value of the equilibrium constant is expressed as

$$K_c = \frac{k_1}{k_2} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where the brackets denote the concentrations of the substances at equilibrium (in moles per litre, if they are solutes in the solution). The presented equation is called the law of chemical equilibrium or the Guldberg-Waage equation. Its verbal formulation is: The product of the concentrations of reaction products exponentiated by its stoichiometric coefficients divided by the product of the concentration of reactants exponentiated by stoichiometric coefficients is in the equilibrium state a constant quantity.

The value of the equilibrium constant implies the state of the reaction system in the equilibrium:
- If $K > 1$, products prevail in the equilibrium reaction mixture.
- If $K < 1$, reactants prevail at equilibrium.
- Reactions with values of K near 1, are called typically reversible reactions.
- If the value of K is extremely high, it means that practically all reactants are changed to products at equilibrium – these reactions are sometimes regarded as irreversible.
- On the other hand, if K is very low, reaction almost does not proceed in the given direction. Thus the reaction going on in the opposite direction is then preferred.

Catalysts are substances which, in relatively small amounts, can accelerate chemical reactions without being changed themselves. They act by diminishing the energy of activation needed for a particular reaction. Catalysts cause a system to reach an equilibrium more quickly, but they do not change the value of the equilibrium constant.

Reaction energy

As a consequence of both bonds cleavage and formation, chemical reactions are accompanied by energy changes.

To characterize processes taking place at constant pressure we use a state quantity **enthalpy H**, which expresses the heat content of the system. The change of enthalpy ΔH equals to heat accepted or released during the reaction proceeding at the constant pressure:

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

According to the quantity of the heat of reaction we distinguish **exothermic** reactions, when the heat is released ($\Delta H < 0$) and **endothermic** reactions ($\Delta H > 0$), when the heat is consumed.

The enthalpy H is a state value; its change is given only by the difference between the enthalpy of a system in the initial and the final state. Therefore, ΔH does not depend on the path taken between the two states. This principle is included in two thermo-chemical laws (Lavoisier-Laplace's and Hess's)

The application of these laws enables us to calculate the heat of any reaction with the using tabulated values.

Example: Calculate the reaction heat of the oxidation of ethanol to acetaldehyde. The heat of combustion of ethanol is $-1\ 371$ kJ mol^{-1}. The heat of combustion of acetaldehyde is -116 kJ mol^{-1}.

Solution: Equations of the oxidation processes:
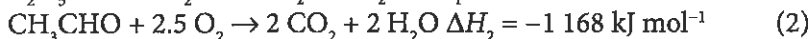
$C_2H_5OH + 3\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O\ \Delta H_1 = -1\ 371$ kJ mol^{-1} (1)
$CH_3CHO + 2.5\ O_2 \rightarrow 2\ CO_2 + 2\ H_2O\ \Delta H_2 = -1\ 168$ kJ mol^{-1} (2)
Subtraction of the second equation (2) from the first equation (1) gives:
$C_2H_5OH - CH_3CHO + 1/2\ O_2 \rightarrow H_2O\ \Delta H = \Delta H_1 - \Delta H_2 = -1\ 371 - (-1\ 168)$ kJ mol^{-1}
And after the correction:
$C_2H_5OH + 1/2\ O_2 \rightarrow H_2O + CH_3CHO \quad \Delta H = -203$ kJ mol^{-1}
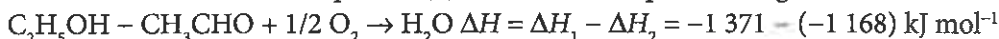
The reaction heat, when ethanol is oxidized to acetaldehyde, is -203 kJ mol^{-1}.

Do not confuse enthalpy change (heat absorbed or evolved) with free enthalpy (Gibbs energy) change ΔG. The latter expresses energy capable to do some useful work, the real driving force of chemical reactions and will not be mentioned in this overview.

Remember well that there is no relationship between the velocity of chemical reactions and the energy changes accompanying them. Some highly exothermic reactions may proceed very slowly and vice versa.

7   SOLUTIONS. ELECTROLYTES. ACIDS AND BASES

Solutions are homogenous mixtures consisting of two or more components. In liquid solutions, the liquid substance in which the components are dispersed is called the solvent. Biochemistry deals mainly with *aqueous* solutions, others are named non-aqueous. The dissolved substances are called **solutes**. If particles of solute are ions or small molecules, the solutions are classified as **analytical solutions** (sometimes as "true" solutions). If particles of solute are greater in size (about 1-500 nm, e.g. macromolecules of proteins, polysaccharides, associates of molecules of detergents etc.), solutions are assigned as **colloid solutions**.

The quantitative composition of a solution may be expressed in several ways. The most often are:

Quantity	Symbol	Definition[a]	Units
Molarity	c_B	n_B/V	$mol\ l^{-1}$, $mmol\ l^{-1}$
Mass concentration	ρ_B	m_B/V	$g\ l^{-1}$, $mg\ l^{-1}$
Mass fraction	w_B	m_B/m	$kg\ kg^{-1}$, $g\ g^{-1}$

[a] V volume of the solution, m mass of the solution, m_r mass of the solvent

Molarity (molar concentration, substance concentration) defines the substance amounts n_B (number of moles) of the solute B in the given volume of the solution (V). The molar concentration of substance B is specified by the symbol c_B, $c(B)$ and or $[B]$.

$$c_B = \frac{n_B}{V}$$

In practice, we usually express the molar concentration in $mol\ l^{-1}$ or their fractions ($mmol\ l^{-1}$, $\mu mol\ l^{-1}$). In the British texts the unit $mol\ l^{-1}$ is specified by the symbol M, thus e.g. the solution NaOH with concentration 0.5 $mol\ l^{-1}$ can be expressed as 0.5 M NaOH.

The composition of solutions expressed by the molar concentration is dependent on the temperature (in the equation used for calculation is the volume of a solution which changes with temperature). The molar concentration of aqueous solutions decreases with the increasing temperature. Solutions of equal molar concentration contain in the same volume the same number of molecules and ions of the dissolved substance.

The mass concentration (ρ_B) defines the mass of the solute B (m_B) in the given volume of the solution (V). The mass concentration is mostly used in case when M_r is unknown, e.g. to express the total concentration of proteins in blood serum. The mass concentration in solutions is usually related to 1 liter, e.g. the amount of ions in mineral waters is given in $mg\ l^{-1}$, the highest acceptable concentration of toxic substances in the wastewaters in $\mu g\ l^{-1}$.

$$\rho_B = \frac{m_B}{V}$$

Density (symbol ρ without index) defines the mass of a substance (e.g. solution) divided by its volume:

$$\rho = m/V.$$

The mass fraction (w_B) is defined as the ratio of the mass of the solute B (m_B) to the total mass of the solution (m). The mass of solute and solution is substituted in the same units. The composition of solutions expressed by the mass fraction is not dependent on temperature.

$$w_B = \frac{m_B}{m}$$

The mass fraction is usually expressed in **mass percents**. It is the mass of a substance in grams, which are dissolved in 100 g of the solution (mass %, % w/w).

$$w_B = 100\frac{m_B}{m}\ \%$$

35

Example 1: 200 ml of a sodium hydroxide solution contains 20 g NaOH.
Calculate the molar concentration of NaOH. $Mr(NaOH) = 40$.

molar concentration is calculated as $c_B = \dfrac{n_B}{V}$

number of moles can be calculated as $n_B = \dfrac{m_B}{M}$

n (NaOH) = 20 (g)/40 (g/mol) = 0.5 mol c (NaOH) = 0.5 (mol) /0.2 (l) = 2.5 mol/l
Molar concentration of NaOH is 2.5 mol/l.

Example 2: How many grams of sodium chloride and water are required to prepare 500 g of 0.5% NaCl solution?

Mass fraction w is calculated as $w_{NaCl} = \dfrac{m_{NaCl}}{m}$

w_{NaCl} is the mass fraction of NaCl: 0.5 % = 0.005
m is the total mass of the solution: 500 g
m_{NaCl} is calculated: $m_{NaCl} = w_{NaCl} \times m = 0.005 \times 500 =$ **2.5 g NaCl**
The mass of water makes the difference between the mass of NaCl and the required mass of solution:
500 g – 2.5 g = **497.5 g H_2O**
The solution is prepared by dissolving of 2.5 g of NaCl in 497.5 of water.

Example 3: What is the molar concentration of a 50% NaOH solution (which has the density 1.525 g/ml)?
$M(NaOH)$ = 40 g/mol.
The density of a solution is calculated as m/V, where m is the mass of the solution and V is the volume of the solution. The density 1.525 g/ml means that the mass of each litre of the solution equals 1525 g.

From relation $w_{NaOH} = \dfrac{m_{NaOH}}{m}$ follows that $m(NaOH) = 0.5 \times 1525 = 762.5$ g

One litre of the solution contains 762.5 g of NaOH.
Number of moles n (NaOH) = m/M = 762.5/40 = 19.06 mol
The molar concentration $c = n/V$ = 19.06/1 = 19.06 mol/l.

Example 4: What is the mass percent of a component B in a solution that has been prepared by mixing 100 g of a 10% solution with 200 g of a 20% solution of the same compound B?
The first solution has mass m_1, the mass fraction of compound B is w_1. The mass of compound B is $m_{B1} = m_1 w_1$
The second solution has mass m_2, the mass fraction of compound B is w_2. The mass of compound B is $m_{B2} = m_2 w_2$
The final solution has total mass $m = m_1 + m_2$, the mass fraction of B is w_3.
The mass of compound B in final solution must be a sum of masses added by both solutions $m_B = m_{B1} + m_B$
and at the same time is valid $m_B = m w_3$
From it follows: $m1 w1 + m2 w2 = (m1+m2) w3$
For the given solution: 100 g × 0.1 + 200 g × 0.2 = (100 g + 200 g) $w3$ and $w3$ = 0.1666 = 16.7 %
The concentration of the new solution is 16.7 %.

> **Example 5:** What volume of a NaOH solution (c = 0.5 mol/l) should be used to prepare, by dilution, 2 litres of a NaOH solution with a concentration of 0.2 mol/l?
>
> When the volume of a solution is increased by adding water, the concentration of the solution decreases with the increasing volume of the solution, since the amount of solutes in the solution does not change. The idea is that the volumes may change but the number of moles does not. This means that the original number of moles and the final number of moles are the same.
>
> The following expression can be used: $n = c_1 V_1 = c_2 V_2$ where subscript 1 refers to the original solution and subscript 2 to the final solution.
>
> The volume of NaOH solution is $V_1 = c_2 V_2 / c_1 = 0.8 l$. The result shows that 800 ml of the original NaOH solution should be diluted by adding water to make up the final volume of 2 litres.

Substances in Aqueous Solutions, Electrolytes

Pure water is not a good conductor of electricity, but the presence of compounds (called electrolytes) that release ions when dissolved is the cause of an increase in electrical conductance of water. Substances can be classified as follows:

non-electrolytes, molecular compounds which do not form any ions in solutions (e.g. glucose, saccharose, ethanol).

electrolytes, which form ions when they dissolve. However, electrolytes differ in the extent to which they form ions:

Weak electrolytes are molecular compounds that ionize in solutions only to a slight extent and concentrations of ions are low when compared with concentrations of unionized molecules. The formation of ions is a reversible chemical reaction involving a chemical **equilibrium**, the position of which can be expressed through the ionization constants K.

All weak acids and weak bases (as acetic acid, ammonia, water) are weak electrolytes.

Strong electrolytes are compounds (mostly ionic, only some are molecular) that dissolve in water and completely ionize. In their solutions, there are hydrated cations and anions and no undissociated molecules or formula units besides molecules of water.

Remember that most of the soluble salts, common soluble hydroxides (sometimes called strong bases) and all the strong acids are strong electrolytes. The former two groups are ionic, the latter consists of molecular compounds (e.g. HCl, HNO3, H2SO4, HClO4).

The most common strong acids:

HCl, HBr, HI, H_2SO_4, HNO_3, $HClO_3$, $HClO_4$, CF_3COOH, CCl_3COOH, $R-SO_3H$, $R-O-SO_3H$

Nearly all of the nonlisted inorganic acids and all carboxylic acids may be regarded as weak acids.
The most common strong hydroxides:

NaOH, KOH, $Mg(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$, $(NR_4)^+OH^-$

Soluble hydroxides of other metals and other soluble bases, namely ammonia, all types of amines and other nitrogenous bases should be considered weak bases.

Classification of compounds into three groups:

Compound type	Dissociation	Particles in solution	Examples
Strong electrolyte	full	only ions	Strong acids, strong hydroxides, most of soluble salts
Weak electrolyte	partial	ions and molecules	Weak acids, weak soluble hydroxides, weak nitrogen bases
Non-electrolyte	none	only molecules	Polar, mostly organic molecules

Ions in solutions of electrolytes can react with each other. When we mix solutions of two or more electrolytes, the interactions between ions can result in new equilibrium. There may be formed non-dissociated or insoluble compounds or ions which may exchange their electrons in redox reactions. Such reactions can be expressed by ionic equations. According to the character, we can distinguish acid-base, precipitation, complex-forming, and redox ionic reactions.

Acids and Bases

Acid-base reactions occur between acids and bases and include the transfer of proton (H^+) from an acid to a base.

According to the Brønsted and Lowry's theory, an acid is a proton donor, a base is a proton acceptor. When H^+ is released from the acid, its conjugate base is formed. Acid and its conjugate base form a **conjugate pair**:

$$HA \rightarrow H^+ + A^-$$
acid   conjug. base

conjugate pair

Example: $HNO_3 \rightarrow H^+ + NO_3^-$
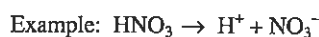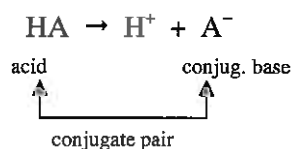
Nitrate anion is the conjugate base of nitric acid.

When a base accepts proton it is transformed into the conjugate acid.

$$B + H^+ \rightarrow BH^+$$
base   conjug. acid

conjugate pair

Example: $NH_3 + H^+ \rightarrow NH_4^+$
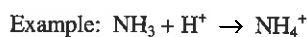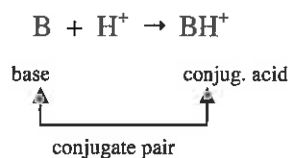
Ammonium cation is the conjugate acid of ammonia.

Protons H^+ are not able to exist independently, therefore they are not free in the solution, but only in the hydrated form as H_3O^+ or $H(H_2O)_n^+$. However, to simplify equations and calculations, these ions are often described as hydrogen ions by the symbol H^+.

The ability of an acid to release H^+ is exhibited only in the presence of a base, which is able to accept this proton. On the other hand, the properties of a base are displayed only in acidic environment. The conjugate pair cannot exist separately, but always in the combination with another conjugate pair. Generally, each acid-base reaction can be described as the combination of two separate reactions:

$$1^{st}\text{ conjugate pair}$$

$$\text{HA} \quad + \quad \text{B} \quad \rightarrow \quad \text{A}^- \quad + \quad \text{BH}$$

acid base conjug. base conjug. acid
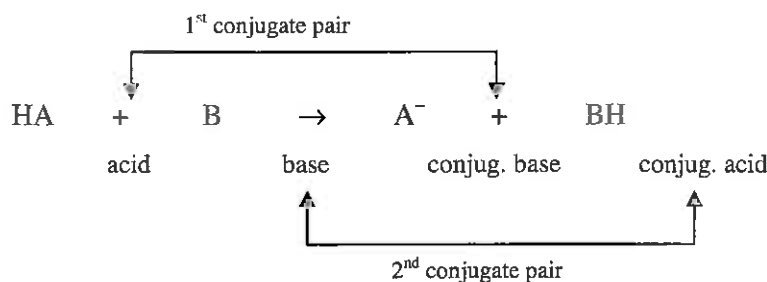
$$2^{nd}\text{ conjugate pair}$$

In aqueous solutions, the second conjugate pair is derived from water that behaves as an amphiprotic solvent. **Amphiprotic** substances have the properties of both acids and bases.
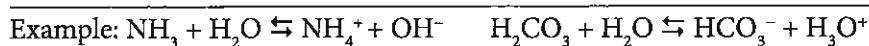
Example: $NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$ $H_2CO_3 + H_2O \leftrightarrows HCO_3^- + H_3O^+$
The ammonium cation is the conjugate acid to NH_3 Water behaves as a base (oxonium cation
and H_2O is an acid (its conjugate base is OH^-).   is its conjugate acid)

The Ionization of Water

Water (chemically pure) belongs to very weak electrolytes (very small electric conductivity indicates weak dissociation of water molecules into ions). Water molecules have amphiprotic character, they can release or bind protons. The transfer of protons can proceed also between two molecules of water. This process is called **self-ionization (autoprotolysis)**:

$$2\,H_2O \leftrightarrows H_3O^+ + OH^-$$
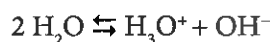
and is characterized by the equilibrium constant K_c:

$$K_c = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

The equilibrium of the reaction lies well to the left side ($K_c = 10^{-16}$). The concentration of non-dissociated water molecules can be considered as constant and practically equal to the total concentration of water (55.5 mol l^{-1}). We can include the concentration of water into K_c and we get a new constant called **the ion product of water** K_w:

$$K_w = K_c[H_2O]^2 = [H_3O^+][OH^-]$$

In the temperature range 20–25 °C, $K_w = 10^{-14}$ mol^2 l^{-2}.

Acidity of Solutions, pH Calculations

In pure water, concentrations of H^+ ions and OH^- ions are equal, $[H+] = [OH-] = 1.0 \times 10^{-7}$ mol/L. All aqueous solutions that have equal concentrations of H+ and OH- are said to be **neutral**.
Acidic solutions are those with hydronium concentrations greater than 1×10^{-7} mol/L and [OH-] less than 10^{-7} mol/L, **alkaline** (or **basic**) solutions are characterized by [H+] less than 10^{-7} mol/L .
Since possible concentrations cover a wide range, the **pH scale** has been introduced for hydronium concentrations:
pH is defined as the negative decimal logarithm of the hydronium ion concentration,

$$\text{pH} = -\log[H+]$$

For any found value of pH, the corresponding [H+] equals 10-pH.
Similarly can be defined the pOH quantity for hydroxide ions, i.e. pOH = −log [OH⁻]. The pH and pOH quantities are in relation given by the ion product of water in the logarithmic form:

$$\log 10^{-14} = \log [H^+] + \log [OH^-]$$

and after conversion:

$$14 = pH + pOH$$

In neutral solutions, when [H⁺] = [OH⁻], pH = 7. Acidic solutions have pH < 7 (with the increasing acidity the pH decreases) and in basic solutions pH > 7 (with the increasing basicity of the solutions, [H⁺] decreases and the pH increases). From the known concentration of the hydrogen (or hydroxide) ions, we can calculate pH. On the other hand, from the given pH we can calculate the concentration of H⁺ using the relation: $[H^+] = 10^{-pH}$.

Calculations of pH

In all calculations, we have to distinguish between strong and weak acid (base).
Strong acids: As strong acids are fully ionized in aqueous solutions, the concentration of H+ equals the concentration of an acid if it is monoprotic.
Then $\qquad$ **pH = -log $c$acid** (for $c$acid > 10-6 mol/L)
Strong hydroxides (soluble ionic hydroxides) also fully dissociate when dissolved. In their solutions, the concentration of OH- ions equals the concentration of a compound, [OH-] = $c$base.
pOH = -log c_{base}
From the ionic product of water, [H+] = 10-14/[OH-],
then $\qquad$ **pH = 14 + log $c$base** (for cB >10-6 mol/L).

Note that there is an exponential relationship between the concentration c of a strong acid or base and the corresponding pH value; then any n-fold change in the c value will cause the ±log n increment to the pH value. Calculations of pH values of weak acid and weak base solutions must consider the particular values of the dissociation constants K. For example, the pH value of a weak acid solution can be found using the expression pH = ½ pKa - ½ log $c$acid.

Example 1: Calculate the pH of a solution at which the concentration of H⁺ ions is 0,003 mol/l.
From the definition $\qquad$ pH = -log[H⁺]
$\qquad\qquad\qquad\qquad$ pH = -log 0.003 = **2.52**
pH of the solution is 2.52.

Example 2: Calculate the concentration of hydrogen ions in a solution if pH = 4.3.
From the definition [H+] = 10-pH
On a calculator display, input -4.3 and select the function 10^x
you will get [H+] = 5.0 × 10-5 mol/l
The concentration of H⁺ in the solution is 5 × 10⁻⁵ mol/l.

Example 3: A solution of nitric acid has concentration c = 0.02 mol/l. Calculate the pH.
From the definition $\qquad\qquad\qquad$ pH = − log [H⁺] = − log c_{acid}
$\qquad\qquad\qquad\qquad\qquad\qquad$ pH = − log 0.02 = 1.7

Example 4: A solution of sulfuric acid has concentration $c = 0.02$ mol/l. Calculate the pH.

From the definition $\qquad$ **pH** $= - \log [H^+]$

However, sulfuric acid is strong **diprotic** acid, the concentration of H^+ in its solution is $2 \times c_{acid}$

Then $\qquad$ pH $= - \log [H^+] = -\log 2\, c_{acid}$

$\qquad\qquad\qquad$ pH $= - \log (2 \times 0.02) = 1.4$

pH of the solution is 1.4 (the pH of a solution of strong diprotic sulfuric acid is lower than the pH of strong monoprotic nitric acid with the same concentration. The difference in pH is $- \log 2 = 0.3$).

Example 5: A solution of sodium hydroxide has concentration $c = 0.02$ mol/l. Calculate the pH.

NaOH is a strong hydroxide, we will firstly calculate pOH

From the definition $\qquad$ pOH $= - \log [OH^-] = - \log c_{base}$

$\qquad\qquad\qquad$ pOH $= - \log 0.02 = 1.7$

$\qquad\qquad\qquad$ pH $= 14 - pOH = 14 - 1.7 = 12.3$.

pH of the solution is 12.3. (Remember: pH of the base cannot be acidic!)

Example 6: A solution of calcium hydroxide has concentration $c = 0.02$ mol/l. Calculate the pH.

$Ca(OH)_2$ is a base, we will firstly calculate pOH.

From the definition: pOH $= - \log [OH^-]$

However, $Ca(OH)_2$ is strong **dibasic** hydroxide, the concentration of OH^- in its solution is $2\, c_{base}$

Then $\qquad\qquad\qquad$ pOH $= - \log [OH^-] = - \log 2\, c_{base}$

$\qquad\qquad\qquad$ pOH $= - \log (2 \times 0.02) = 1.4$

$\qquad\qquad\qquad$ pH $= 14 - pOH = 14 - 1.4 = 12.6$

pH of the solution is 12.6.

Example 7: What is the pH of a HCl solution with a mass concentration of 0.75 g/l ?

Firstly, it is necessary to calculate the molar concentration, $Mr(HCl) = 36.5$;

$c = n/V \; n = m/M \; n = 0.75/36.5 = 0.02$ then $c = 0.02/1 = 0.02$ mol/l

pH $= - \log c_{acid} = - \log 0.02 =$ **1.7**

The pH of the solution is 1.7.

Hydrolysis of Ions

Solutions of salts usually behave as strong electrolytes, during dissolution in water they completely dissociate to ions. Resulting ions may react with water and the pH of a solution changes. Whether such reaction occurs depends on salt origin. Anions of strong acids and cations of strong hydroxides do not react with water; dissociated ions ("strong ions") will be only hydrated.

Anions of weak acids and cations of weak bases react with water to form corresponding weak acids and bases, respectively, until the equilibrium given by K_A and K_B, respectively, is established. This reaction is defined as the **hydrolysis of salts.**

Both events mentioned above (dissociation of salts and hydrolysis of ions) must be distinguished from each other. At first salt dissociates when dissolved in water and after that dissociated ions can be hydrolyzed. Salts are products of the neutralization reaction between an acid and a base. They can be divided into four types:

A. Salts of weak acids and strong hydroxides

e.g. CH_3COONa, KCN, Na_2CO_3, $NaHCO_3$, KNO_2

Salt dissociates to cation and anion in an aqueous solution, e.g. $CH_3COONa \rightarrow Na^+ + CH_3COO^-$. The cation of this salt (Na^+) comes from the strong hydroxide, does not react with water, it is found in a hydrated form in the solution. The anion of this salt (CH_3COO^-) originates from the weak acid, and therefore it is the subject of hydrolysis, reacts with water to form acetic acid until the equilibrium is established:

$$CH_3COO^- + H_2O \leftrightarrows CH_3COOH + OH^-$$
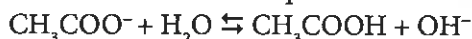
The solution of this salt has **slightly alkaline reaction** due to some excess of OH^- ions by hydrolysis of the anion of the weak acid.

B. Salts of weak bases and strong acids

e.g. NH_4Cl, $(NH_4)_2SO_4$, NH_4NO_3, $(CH_3)_3NHCl$, C_5H_5NHCl (pyridinium chloride), $CuSO_4$, $FeCl_3$

There are two groups of salts in this category. One group possesses ammonium cation or other protonized nitrogenous base, the second group are salts derived from weak hydroxides. The first event is dissociation. In the first group e.g. $NH_4Cl \rightarrow NH_4^+ + Cl^-$. Anion of this salt ($Cl^-$) originates from the strong acid, it does not react with water, and it is found in the hydrated form in the solution. Cation of this salt is the subject of hydrolysis: $NH_4^+ + H_2O \leftrightarrows NH_3 + H_3O^+$.

The solution of this salt has **slightly acidic reaction** in water, created by the surplus of the H_3O^+ ions, which resulted from the hydrolysis of ammonium cation.

Salts of the second type contain cation derived from weak hydroxides, e.g.: $FeCl_3 \leftrightarrows Fe^{3+} + 3\ Cl^-$. Anion ($Cl^-$) comes from the weak acid, it does not react with water, it is found in the hydrated form in the solution. Iron cation makes a complex hexaaqua ion: $Fe^{3+} + 6\ H_2O \leftrightarrows [Fe(H_2O)_6]^{3+}$. Hydrated cations can act as Brønsted acids by loss of H^+ from coordinated water molecule:

$[Fe(H_2O)_6]^{3+} + H_2O \leftrightarrows [Fe(H_2O)_5OH]^{2+} + H_3O^+$
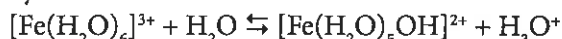
The solution of this salt has **slightly acidic reaction**. Excess of H_3O^+ ions comes from the hydrolysis of complex aqua-cation.

C. Salts of weak acids and weak bases

e.g. CH_3COONH_4, NH_4NO_2, $CuNO_2$, aluminium lactate

After the salt is dissociated in water to ions, they are both independently the subject of hydrolysis, both hydroxide and oxonium ions arise. The value of pH of this salt solution depends on that component which is relatively stronger.

D. Salts of strong acids and strong hydroxides

e.g. NaCl, Na_2SO_4, $Ca(NO_3)_2$, KI

The salts of strong acids and strong hydroxides are completely dissociated in aqueous solutions. Cations and anions **do not hydrolyze**, they are found in hydrated forms in solutions. The value of pH of these solutions remains **neutral**.

Hydrolysis of salts – summarization:

Type of the salt (salt was formed from:)		pH of a salt in aqueous solution
Acid	Hydroxide	
strong	weak	acidic
weak	strong	alkaline
weak	weak	approx. neutral
strong	strong	neutral

Example: Select the salt whose aqueous solution will have alkaline pH:
$NaNO_3$, KBr, NH_4Cl, Na_2CO_3, Na_2SO_4, $FeCl_3$, $CaCl_2$.
Among the salts, only Na_2CO_3 is the salt of strong base (NaOH) and weak acid (H_2CO_3).

8 OXIDATION AND REDUCTION

Oxidation Number

The oxidation number (also oxidation state) acquired by a particular element in its compounds serves as a useful characteristic in chemistry. Elements in their natural state, uncombined with other elements, have their oxidation numbers equal to zero (0). This also holds for diatomic elements. The oxidation number of an element in a simple ion (in ionic compounds) expresses the number of electrons lost by an atom to produce a cation or the number of electrons gained to produce a simple anion and, therefore, it is determined by the charge of the ion. For example, in the ferric ion (in FeCl3), iron has the oxidation number +III (or +3). The oxidation number of an element in a molecular compound or of a polyatomic ion is the hypothetical charge the atom will have if shared electrons in covalent bonds are assigned to a more electronegative element. The algebraic sum of the oxidation numbers of elements in a molecular compound equals zero and, in a polyatomic ion, it equals the charge of the ion.

Oxidation-Reduction Reactions

Oxidation-reduction reactions (often shortly referred to as redox reactions) are reactions in which **transfer of electrons** from one reactant to another takes place.
Oxidation is the loss of electrons by a species or a substance in a reaction, resulting in an increase in the oxidation number of the element.
Reduction is the gain of electrons by a species or a substance in a reaction, resulting in a decrease in the oxidation number of an the element.
The reactant that causes another reactant to be oxidized is called an **oxidant** (oxidizing agent). It should be noted that an oxidant is reduced in the reaction because it accepts electrons lost by an oxidized species. The reactant that causes another reactant to be reduced is a **reductant** or reducing agent. Analogically, a reductant is oxidized because it donates electrons to an acceptor that is thus reduced.
The reduction of any reactant does not occur without another reactant being oxidized at the same time; similarly, the number of electrons spent for the reduction must be the same as that of electrons released by the reductant. For example, the reaction of copper with silver ions (silver nitrate solution):

$$-2\,e$$
$$Cu + 2\,Ag^+ \rightarrow Cu^{2+} + 2\,Ag$$
$$+2e$$
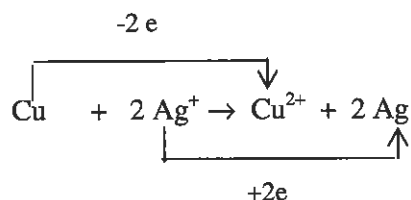
Oxidation numbers of copper   0 - reduced form   II – oxidized form
of silver I - oxidized form   0 - reduced form

The redox reaction can be formally separated into two **half-reactions** (half-equations) that are analogous to conjugate pairs in acid-base reactions. It is useful to deduce both half-reactions before writing the balanced equation of any redox reaction:

and (taken twice)

$$Cu \rightarrow Cu^{2+} + 2\,e^-$$
$$Ag^+ + e^- \rightarrow Ag$$

In each of the half-reactions, there is a pair of species consisting of the oxidized and the reduced form (e.g. Cu^{2+}/ Cu and Ag^+/Ag) called a **redox pair** or a **half-cell**.

All oxidation and reduction processes are potentially reversible. An oxidized form of the pair can act as a potential oxidant and its reduced form can act as a potential reducing agent. Those abilities will be realized if a redox pair meets (i.e. is mixed with) another redox pair of which either the oxidized form has a greater affinity to electrons than the reduced form of the former pair, or the reduced form has a less affinity to electrons than the oxidized form of the former one.

Oxidizing and reducing agents vary in their ability to react with other agents very much. Their tendency to gain or lose electrons (the strength of oxidizing and reducing agents) is expressed by **standard electrode potentials** of the particular redox pairs. The potentials can be measured by comparing them, in a galvanic cell, with the standard H^+/H half-cell the potential of which equals zero by convention.

The negative cell voltages indicate that the reduced form in a measured half-cell is a stronger reducing agent than hydrogen is. The most negative electrode potentials have redox pairs of the elements placed in the lower left-hand corner of the Periodic Table (alkali metals, alkaline earth metals – the electropositive elements) and *vice versa*, fluorine, chlorine, and oxygen as the most electronegative elements have the most positive standard electrode potentials and, therefore, they are the strongest oxidation agent of all elements.

Metallic elements are usually arranged in an electromotive series according to the values of their standard electrode potential: Na, Mg, Al, Zn, Fe, Pb, **H**, Cu, Hg, Ag, Au, Pt.

In the elemental state, metals placed on the left are reducing agents, they can release their valence electrons and produce cations more easily than metals on the right (the former can displace the latter from their compounds).

Redox pair	$E°$ (V)
$K^+ + e^- \rightarrow K$	−2.92
$Ca^{2+} + 2\,e^- \rightarrow Ca$	−2.87
$Na^+ + e^- \rightarrow Na$	−2.71
$Mg^{2+} + 2\,e^- \rightarrow Mg$	−2.37
$Al^{3+} + 3\,e^- \rightarrow Al$	−1.66
$Zn^{2+} + 2\,e^- \rightarrow Zn$	−0.76
$Fe^{2+} + 2\,e^- \rightarrow Fe$	−0.44
$\mathbf{2\,H^+ + 2\,e^- \rightarrow H_2}$	**0.00**
$Cu^{2+} + 2\,e^- \rightarrow Cu$	0.34
$I_2 + 2\,e^- \rightarrow 2\,I^-$	0.54
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.76
$NO_3^- + 3\,H^+ + 2\,e^- \rightarrow HNO_2 + H_2O$	0.94
$Br_2 + 2\,e^- \rightarrow 2\,Br^-$	1.07
$ClO_4^- + 2\,H^+ + 2\,e^- \rightarrow ClO_3^- + H_2O$	1.19
$O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O$	1.23
$Cr_2O_7^- + 14\,H^+ + 6\,e^- \rightarrow 2\,Cr^{3+} + 7\,H_2O$	1.33
$Cl_2 + 2\,e^- \rightarrow 2\,Cl^-$	1.36
$MnO_4^- + 8\,H^+ + 5\,e^- \rightarrow Mn^{2+} + 4\,H_2O$	1.51
$H_2O_2 + 2\,H^+ + 2\,e^- \rightarrow 2\,H_2O$	1.77
$F_2 + 2\,e^- \rightarrow 2\,F^-$	2.56

9 BRIEF SYNOPSIS OF INORGANIC CHEMISTRY

Group I.A Elements

Group IA consists of hydrogen and the alkali metals. However, hydrogen, because of its unique properties, is usually classified separately from this group.

Hydrogen

Hydrogen is diatomic and is the lightest element. It is believed to be the most abundant element in the universe. In the Earth's crust, hydrogen ranks one third among all the elements (after oxygen and silicon) in atomic percent, and ninth in percent by mass. On Earth, virtually all hydrogen is bound in molecules (esp. in water and organic compounds) and traces of gaseous hydrogen are occasionally found in the lower atmosphere. Hydrogen occurs naturally as a mixture of three isotopes – protium ^1H, deuterium ^2H (< 0.02 %), and radioactive tritium ^3H (10^{-15} %, β-emitter).

Hydrides are simple binary compounds of hydrogen. They are formed with both metals and nonmetals. Solid ionic hydrides are formed with the highly electropositive elements such as the alkali and alkaline-earth metals; they contain the hydride ion H^- (oxidation number -I, e.g. sodium hydride, Na^+H^-). The hydrides formed by nonmetals are volatile covalent hydrides. They include familiar compounds such as polar hydrogen halides (HX), **water** (H_2O), sulfane (H_2S), **ammonia** (NH_3), methane (CH_4), and other **hydrocarbons**.

Hydrogen ion H^+ (hydronium, proton)

has a unique role in relation to acidity in aqueous solutions. Only compounds that release hydrogen cation in a solution are acidic. Protons are ionizable from any species in which they are bonded to the highly electronegative elements (halogens, oxygen, sulfur) through a polar covalent bond.

Gaseous elemental hydrogen can be prepared from acids or from water in reactions with metals posessing a negative electrode potential, for example

$$Zn + HCl \rightarrow ZnCl_2 + H_2$$
$$Na + H_2O \rightarrow NaOH + H_2$$
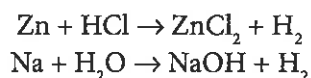
Alkali metals

The electron configuration of lithium, sodium, potassium, rubidium, cesium, and francium is ns^1 (s^1 elements). These elements show only one oxidation number, I, in their compounds. They all have marked metallic properties.

Alkali metals in their elemental state are strong reducing agents. Because of their great reactivity, the alkali metals **sodium** and **potassium** exist in nature only as Na^+ and K^+ ions in compounds or dissolved in seawater and brine wells.

The other alkali metals are rare. In animals, the sodium ion is the principal extracellular cation whose major role is to maintain osmotic pressure and regulate water balance, whereas potassium is the principal intracellular cation.

Sodium and potassium compounds are ionic, most of them dissolve in water readily. They produce characteristic coloring of the flame: sodium compounds yellow, potassium a pale violet one.

The most common compounds are sodium chloride, NaCl (table salt), hydroxides NaOH and KOH (strong soluble hydroxides, common lyes), sodium carbonate, Na2CO3 (soda) and potassium carbonate, K2CO3 (potash, both caustic substances), sodium hydrogen carbonate, NaHCO3 (baking soda).

Group II.A Elements

The alkaline-earth metals Be, Mg, Ca, Sr, Ba and radioactive Ra have the electron configuration ns^2 and show only one oxidation number, II. They closely resemble the alkaline metals in that they are too reactive to remain in the elemental state.

Insoluble **calcium** and **magnesium** minerals are very common in nature, esp. calcite, $CaCO_3$ (found as limestone, marble, chalk), dolomite ($MgCO_3 \cdot CaCO_3$), various silicates and phosphates. Soluble Ca and Mg compounds are responsible for the so-called hardness of water.

In human body approximately 1 kg of calcium is bound as hydroxoapatite $Ca_5(PO_4)_3OH$ in the bones and teeth. Free Ca^{2+} as well as Mg^{2+} ions in the body fluids play an important role in muscle contraction, blood clotting, etc. Magnesium is a constituent of the leaf pigment chlorophyll in green plants.

Calcium and magnesium compounds

Calcium oxide, CaO (lime) is prepared from limestone by calcining at 1000 °C :
$$CaCO_3 \rightarrow CaO + CO_2$$
Lime is mixed with other oxides to give cement or it reacts with water to give a strong calcium hydroxide, $Ca(OH)_2$ (slaked lime) which is only sparingly soluble (lime water). Wet calcium hydroxide reacts with CO_2, forming solid calcium carbonate:
$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$
Calcium phosphate $Ca_3(PO_4)_2$ is a major constituent of apatites in the bones.
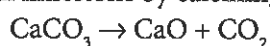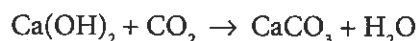
Calcium sulfate dihydrate, $CaSO_4 \cdot 2H_2O$ (gypsum) is only slightly soluble in water but it transforms into hemihydrate, $CaSO_4 \cdot \frac{1}{2}H_2O$, by heating. The latter pulverized and mixed with water is used as plaster ("of Paris") which turns into a solid dihydrate form again.

The other alkaline-earth metals compounds are toxic (except for insoluble $BaSO_4$ used as a contrast substance for X-ray examination of the digestive tract).

The isotope Sr-90 is present in nuclear fallout, it can be absorbed by the human body and concentrates in the bones creating a radiation hazard.

Transition Elements (Group III.B – II.B)

The transition elements (or the d-block elements) are those which build their (n-1)d orbitals. In the d-block, there are three series of ten transition elements in the 4th, 5th, and 6th period and one incomplete series in the 7th period. The configuration of their valence electrons can be described generally as ns2 (n-1)d1-10.

Common properties of transition elements

All the d-elements are metals; because of the higher number of valence electrons, these metals are denser and also have higher melting temperatures than the metals of Groups IA and IIA.

Many of the d-elements exhibit the multiplicity of their oxidation numbers; in the higher oxidation states, some of the d-element oxides are acidic and can form stable polyatomic oxyanions if hydrated.

Typical feature is an existence of many colored cations, and oxoanions, respectively.

They have a tendency to combine covalently with anions, and even with some neutral compounds, to form complex species by coordination.

Metal ion complexes (coordination complexes) include the central ion of a transition metal to which a certain number of negatively charged or neutral ligands (unshared electron pair donors) are covalently attached like, for example, the hexacyanoferrate(II) ion (ferrocyanide ion):
$$Fe^{2+} + 6\ CN- \rightarrow [Fe(CN)_6]^{4-}$$
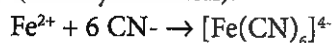
Group VIB elements – chromium (Cr), molybdenum (Mo) and tungsten (W)
are metals of great hardness which exhibit great resistance to corrosion and possess six valence electrons in the subshells ns and (n-1)d.

Chromium forms compounds in which positive oxidation numbers, from II to VI, can be acquired. The III and VI states are most common and stable.

Chromium(III) oxide, Cr_2O_3, and hydroxide, $Cr(OH)_3$, are amphoteric the Cr^{3+} and $[Cr(OH)_4]-$ ions exist only in acidic and strongly alkaline solutions, respectively. Chromium(VI) oxide, CrO_3, is a chromic acid anhydride and a strong oxidant, as the are chromates and dichromates (CrO_4^{2-} and $Cr_2O_7^{2-}$ ions). All chromium compounds are colored, itch the skin and are toxic. Nevertheless, chromium, as well as molybdenum, are essential trace elements for mammals.

Molybdenum and tungsten tend to form compounds with the highest oxidation number VI, molybdates and tungstates (e.g. $(NH_2)_2MoO_4$ and Na_2WO_4), used as oxidants in laboratories.

Group VIIB elements – manganese (Mn), technetium (Tc) (and rhenium).

In this family, **manganese** is the element of major importance and versatility. It exists in five oxidation states, from II to VII, differing in colours of aqueous ions.

Manganese(II) salts (Mn^{2+} ion) are pale pink, insoluble manganese(IV) oxide, MnO_2, is dark brown to black, manganates(VI) are green and permanganate(VII) ions, MnO_4^-, are deep purple. Potassium permanganate, $KMnO_4$, is a familiar and strong oxidizing agent widely used in organic chemistry and in treatment of water polluted by oxidizable impurities.

Group VIIIB elements, groups 8-10, the three triades:

the iron family:	iron, Fe, cobalt, Co, nickel, Ni (in the 3d series),
the platinum group elements:	ruthenium, rhodium, palladium (in the 4d series),
	osmium, iridium, platinum (in the 5d series).

Elements of the iron family

are more similar to each other in chemical properties and less similar to the elements of the platinum group (below them in the periodic table).

Iron, next to aluminium is the most abundant metal in the Earth's crust; it occurs mainly in the form of oxides. Iron shows oxidation numbers II or III in its compounds; the latter state is more stable. In the presence of oxygen, Fe^{2+} ions in solutions are readily oxidized to Fe^{3+} (ferric) ions and their color turns to reddish brown. Both ferrous and ferric ions react with water (see hydrolysis of salts) and their solutions are slightly acidic. Iron rusts when exposed to oxygen and moisture. Rust is primarily a hydrous ferric oxide, $Fe_2O_3 \cdot xH_2O$.

Fe, as well as Co and Ni form a variety of complex species of which the most common are anionic, such as stable hexacyanoferrate(II) (ferrocyanide) and hexacyanoferrate(III) ions.

Iron ions are essential for humans (synthesis of hemoglobin, myoglobin, and cytochromes). Sources of iron in the diet include liver, lean meat, whole-grain cereals and legumes.

Cobalt is an essential trace element, mainly as a constituent of vitamin B_{12} (cyanocobalamin).

Nickel is used as a catalyst in hydrogenation reactions (see hardening of plant oils). In their compounds, cobalt and nickel show oxidation number II.

Platinum-group

These elements are very noble, heavy, complex forming, and so non-reactive that they are found free in nature. They are used in special laboratory equipment because of their resistance to acids and aqueous bases. Most of them will dissolve only in *aqua regia* (a solution of concentrated hydrochloric acid and concentrated nitric acid) to form chlorocomplexes such as $[PtCl_6]^{2-}$.

Some platinum metals are useful as catalysts for various organic reactions such as hydrogenation. Platinum is used in catalytic convertors of engine exhaust.

Group I B elements – copper (Cu), silver (Ag), and gold (Au)
have the electron configuration ns1(n-1)d10. The oxidation state I exists for each of the elements but, contrary to all expectations, it is common only to silver: oxidation number II is more common in copper compounds and oxidation number III in gold compounds. The group IB elements are resistant to oxidation; they do not dissolve in non-oxidizing acids such as hydrochloric acid. Conversely, their cations are readily reduced acting as oxidants (those metals are to the right /below/ of the hydrogen in the electromotive series).

Copper is an essential trace element for both animals and plants. Larger doses of copper compounds are toxic, as are those of other trace elements.

Copper(II) salts are mostly blue because of formation of the hydrated ion $[Cu(H_2O)_4]^{2+}$.

Silver – only silver(I) nitrate dissolves in water, other Ag(I) compounds are of very low solubility, e.g., silver halides (AgCl, AgBr, AgI). Precipitation of white AgCl is a sensitive test for the presence of either Ag+ or Cl- in solutions.

Group IIB elements – zinc (Zn), cadmium (Cd), and mercury (Hg)
have the electron configuration ns2(n-1)d10, i.e., there is a stable configuration of 18 electrons in their (n-1) energy level. The oxidation number of these elements is II and mercury also exhibits an unstable diatomic cation Hg22+ with the oxidation number I.

Mercury is the only metal that is liquid at room temperature. Elemental mercury and all soluble compounds of Hg and Cd are extremely toxic. Mercury forms alloys, called amalgams, with most of the metals. Amalgam alloys with silver are used in dentistry. Mercury(I) chloride, Hg_2Cl_2, known as calomel, has been used in medicine for a long time.

Zinc is a component of many alloys, such as of yellow brass (Cu+Zn). Zinc oxide, ZnO (used in dermatology and in dental zinc-oxide cements), as well as hydroxide, $Zn(OH)_2$, are amphoteric. Upon addition of excess OH-, zinc hydroxide re-dissolves to form zincate solutions:

$Zn(OH)_2 + OH- \rightarrow [Zn(OH)_3]-$
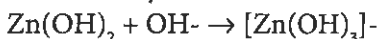
Zinc is an essential trace element for animals; it is a constituent of numerous enzymes.

Group III.A Elements

Boron, aluminium, gallium, indium and thallium are representative of p-block elements. Their valence electron configuration is ns2np1 (simply p1 elements) and in their compounds they acquire mostly the oxidation number III (thallium I).

Boron is the only nonmetallic element in the group and its oxide is acidic; the other elements exhibit metallic properties. Boric acid, H_3BO_3, is a white solid, poorly soluble in water and of very weak acidity (its solution is used as eyewash). The salts, borates, e.g. sodium tetraborate, $Na_2B_4O_7 \cdot 10H_2O$ (borax), contain polyborate anions. Boron carbide, B_4C (carbon tetraboride), is an extremely hard material.

Aluminium is the third most abundant element in the Earth's crust, the other Group IIIA elements are rare. It is an extremely important material in modern technology. Although it has a low redox potential, this metal does not corrode due to the formation of a thin, transparent oxide film on its surface. Aluminium oxide, Al_2O_3 (alumina), is used as an adsorbent in laboratories and, similarly to hydroxide, $Al(OH)_3$, exhibits amphotheric properties:

$Al(OH)_3 + 3 H^+ \rightarrow Al^{3+} + 3 H_2O$ aluminium cation (as usual for metals)

$Al(OH)_3 + OH- \rightarrow [Al(OH)_4]-$ tetrahydroxoaluminate anion.
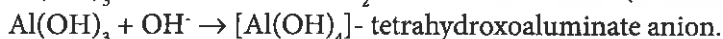
Aluminium hydroxide is used as a constituent of some common antacid medications. It is also present in complex salts containing mono- and trivalent ions known as alums, such as $KAl(SO_4)_2 \cdot 12H_2O$ (give the IUPAC name of this compound).

Thallium and its compounds are highly toxic.

Group IV. A Elements

Carbon, silicon, germanium, tin, and lead are characterized by the half-filled valence shell (configuration ns2 np2). Carbon has nonmetallic properties, Si and Ge are semiconducting metalloids, and Sn and Pb are typical metals.

Carbon

Carbon is the 15th most abundant elements in the Earth's crust, and the fourth most abundant element in the universe by mass after hydrogen, helium, and oxygen. It is present in all known forms of life, and in the human body carbon is the second most abundant element by mass (about 18.5%) after oxygen. In the elemental form, carbon occasionally occurs as diamond but more commonly as graphite or in non crystalline forms such as coke, charcoal, carbon black and lampblack. In this chapter, only some simple carbon compounds are considered. Most of the carbon compounds will be described in the next chapters dealing with organic chemistry.
Carbon is not a very reactive element; it exhibits the oxidation number -IV and IV in most of its simple compounds. Carbides are binary compounds of carbon and metals or metalloids, e.g., calcium carbide, CaC_2, is an ionic compounds reacting with water to release acetylene, C_2H_2.
Hydrogen cyanide, HCN, is an extremely toxic and volatile liquid. It is a very weak acid and its salts are cyanides. Hydrides of carbon are **hydrocarbons**.

Oxides of carbon

Carbon monoxide CO, is released by an incomplete combustion of carboniferous substances, for instance, in automobile exhausts. It reacts with hemoglobin in the blood to form carbonylhemoglobin which interfere with the transport mechanism for oxygen. It possesses reducing properties and reacts with transition metals to give covalent metal carbonyls and with chlorine forming carbonyl chloride, $COCl_2$ (phosgene), a highly toxic, suffocating gas.
Carbon dioxide, CO_2, is a dense, colourless gas released to the atmosphere by combustion of organic materials (either by biochemical reactions in living organisms or by burning or decay). Its content in the air is about 0.03% by volume. CO_2 dissolves in water to form a weak acid solution (e.g. carbonated beverages) known as carbonic acid but most of CO_2 exists in solution as hydrated CO_2 molecules and only few of them react with water to form H_2CO_3. Solidified CO_2 is used as dry ice which sublimes at -78 °C. Carbon dioxide should not be viewed as a toxic compound but if there are more than 10% CO_2 in the inhaled air, respiration is depressed or stopped even if a sufficient amount of oxygen is present.

Carbonates

CO_2 reacts with hydroxides and **basic** oxides to give carbonates. The reaction is used for setting mixtures of gases free of CO_2, e.g. in various respirators with an closed circuit:

$$2\,NaOH + CO_2 \;\rightarrow\; Na_2CO_3 + H_2O$$
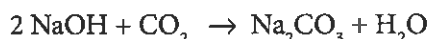
Two series of salts are derived from the diprotic carbonic acid. Hydrogen carbonates (HCO_3^- ion, incorrectly also bicarbonates) are mostly soluble. The solutions are slightly alkaline due to hydrolysis of the anion. Hydrogen carbonates exist only in slightly acidic to slightly alkaline solutions because of being amphoteric; they evolve CO2 by adding an acid (the displacement of the weak and unstable carbonic acid by a stronger acid) and lose hydronium in strongly alkaline solutions:

$$CO_2 + H_2O \;\underset{H^+}{\overset{OH^-}{\rightleftharpoons}}\; HCO_3^- \;\underset{H^+}{\overset{OH^-}{\rightleftharpoons}}\; CO_3^{2-}$$
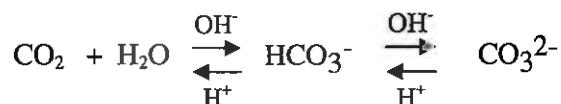
Hydrogen carbonate ions play a very important role as constituents of the buffer system in the blood.

Carbonates of alkali metals dissolve in water forming strongly alkaline solutions (hydrolysis of CO_3^{2-} ion), the others are mostly insoluble. Calcium carbonate, $CaCO_3$ (limestone), is converted to soluble $Ca(HCO_3)_2$ by the slow action of the ground water containing CO_2 (creating limestone caverns):

$$CaCO_3 + H_2O + CO_2 \leftrightarrows Ca(HCO_3)_2$$
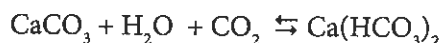
The resulting $Ca(HCO_3)_2$ solution may be reconverted to $CaCO_3$ (forming stalactites and stalagmites of limestone caves).

Other familiar carbonates are: sodium carbonate Na_2CO_3 (soda), potassium carbonate, K_2CO_3 (potash), ammonium carbonate, $(NH_4)_2CO_3$, and sodium hydrogen carbonate, $NaHCO_3$ (baking soda).

Silicon is the second most abundant element in the Earth's crust. Stable covalent Si–O bonds in a variety of silicon compounds are said to form the framework for the mineral world. The oxidation number IV is typical for silicon compounds. Hydrides called silanes (e.g. SiH_4, Si_2H_6) are analogous to simple alkanes but they are much more reactive than those hydrocarbons.

Silicon dioxide, SiO_2 (silica, or its pure crystalline form quartz), is a slightly acid oxide with a network structure of which the basic structural unit is a tetrahedral SiO_4. Glasses are made by a reaction of silica with basic and other oxides. Strong hydroxides etch silica to form soluble sodium (or potassium) silicate, Na_2SiO_3, from which a very weak silicic acid, H_4SiO_4 (orthosilicic acid), can be displaced by acidification. By polymerization, this forms a hydrated gel, known as silica gel when dried, which is widely used as an adsorbent, desiccative agent, or dehumidifier.

The bulk of rocks of the Earth's crust consist of silicate minerals of very complex structures, mostly aluminosilicates (e.g. feldspar minerals, micas, asbestos). By the action of water and CO2, these minerals gradually decay to form various clays (e.g. kaolin) and earths mixed with silica particles.

A valuable group of silicon compounds are the polymeric silicones, alkylated polysiloxanes, which may be quite non-polar solids, rubbers, greases or oils.

Tin and **lead** exhibit the oxidation numbers II and IV in their compounds. The hydroxides of both metals, Sn(OH)2, Sn(OH)4, and Pb(OH)2 are amphoteric. Lead itself and all its compounds are toxic. Recent concern over the effects of lead pollution has resulted in gradual removal of lead compounds from paints and gasoline (tetraethyllead has been widely used as an antiknock additive).

Group V.A Elements

Nitrogen, phosphorus, arsenic, antimony, and bismuth possess the valence electron configuration ns^2np^3 (p^3 elements), i.e., they all have five outer-shell electrons. There is an increase in metallic character going down the group: nitrogen is a gaseous diatomic element with a high electronegativity value, phosphorus is a non-metal, As and Sb are metalloids and Bi is distinctly metallic in character.

Nitrogen

Nitrogen is a diatomic element which occurs in the elemental state as a major constituent of the atmosphere (78% by volume). Many nitrogenous compounds are essential constituents of the living cells: amino acids and proteins, nucleic acids, biogenic amines, etc.

Nitrogen is a colorless, odorless, nontoxic gas. In its molecule, N_2, the atoms are joined by a very strong triple bond,. Therefore, molecular nitrogen is of low reactivity at ordinary temperatures. The most common oxidation states of nitrogen are -III, III, and V, but all the oxidation numbers from -III to V can be present in nitrogen compounds. Binary nitrogen compounds have ionic, metallic or, most frequently, covalent characters.

Ionic nitrides are formed by the very electropositive metals; these nitrides contain the N^{3-} anion and hydrolyze to form ammonia.

Ammonia

is the most important binary compound, NH_3, which is a covalent nitride as well as a hydride. It is an irritant and toxic gas, well soluble in water where it forms a monohydrate, $NH_3 \cdot H_2O$, by joining a molecule of water through a hydrogen bond. Since the nitrogen atom of ammonia has one unshared electron pair, it is able to bind the hydronium ion by coordination and exhibits the properties of a weak base, the forming ammonium ion:

$$NH_3 + H_2O \leftrightarrows NH_4^+ + OH-$$

ammonia (weak base)　　　　　　ammonium (conjugate acid of ammonia)

Almost all ammonium salts are soluble in water and, except for their volatility and hydrolysis of ammonium ion, they resemble alkali-metal salts. Similarly to the other weak or volatile bases which can be displaced from their salts, ammonia is evolved from ammonium salts by adding a strong hydroxide, for example:

$$(NH_4)_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2\,H_2O + 2\,NH_3$$
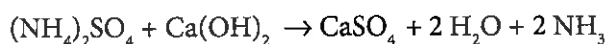
Transition-metal ions readily bind ammonia as ligands and form complex amminemetal ions, e.g. diammine-silver (I) ion, $[Ag(NH_3)_2]+$ or tetraamminecopper(II) ion, $[Cu(NH_3)_2]^{2+}$.

Oxides of nitrogen

Five nitrogen oxides are known in which nitrogen exhibits positive oxidation numbers from I to V. Three of them are more important. Dinitrogen oxide, N_2O (nitrous oxide, "laughing gas"), is used as an anesthetic for minor surgery or in aerosol dispensers. Nitrogen monoxide, NO (nitric oxide), is readily oxidized in the air to the brown gas NO_2, nitrogen dioxide. By cooling, this gives a colourless solid dimer, N_2O_4. Both these oxides are air pollutants generated as by-products in most manufacturing processes and as exhaust gases, when nitrogen and oxygen combine at high temperatures of fossil fuel combustion.

Oxoacids of nitrogen

Having the oxidation number III and V, these oxidizing agents take part in numerous redox reactions.
Nitrous acid, $HNO2$, is a weak and unstable acid. When its solution is heated, it decays into the nitric acid (V) and nitric oxide (II) by disproportionation. Nitrites are toxic and heat resistant.
Nitric acid, HNO_3, is a strong acid and a powerful oxidizing agent, especially when concentrated. It is produced in the reaction of nitric oxide with water by disproportionation:

$$3\,N^{IV}O_2 + H_2O \rightarrow 2\,HN^VO_3 + N^{II}O$$
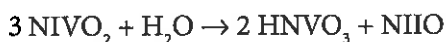
Nitric acid dissolves almost all metals (except for gold and platinum), for example:

$$3\,Cu + 8HNO_3 \rightarrow 3\,Cu(NO_3)_2 +\ 2NO +\ 4H_2O$$
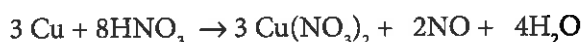
Nitrates are the salts of nitric acid and nearly all are readily dissolved in water. However, they are not toxic even though high doses of nitrates (water pollution by fertilizers) may be harmful to humans because of their reducibility to toxic nitrites.
Animals as well as higher plants are unable to utilize elemental nitrogen for syntheses of their body constituents. Higher plants require nitrates taken up from the soil, animals must obtain amino acids or proteins (synthesized by the plants) as the source of nitrogen for the proteosynthesis. After they stop living, proteins of their tissues are decomposed by bacterial putrification to simple inorganic compounds of nitrogen. One part of the compounds is retained in soil or water, the other part is reduced to the elemental nitrogen and released to the atmosphere. This complex of events is known as the nitrogen cycle. It is quite obvious that for the amount of

nitrogen compounds obtainable for the higher forms of life, the supplementation of the nitrogen cycle by oxidation of new doses of the elemental nitrogen is critical. This is provided by the so-called nitrogen fixation, i.e., by the action of certain species of soil bacteria capable to convert N2 into nitrates. Further, certain amounts of nitric oxide are formed in the atmosphere during electrical storms and, finally, agricultural technologies supply nitrogen compounds to soil in the form of manufactured nitrogen fertilizers (like ammonia, ammonium nitrate, and urea).

Phosphorus

Phosphorus is a widely spread element occurring mainly in the form of phosphates in rocks and soil. It is the only group V.A element not found free in nature. In its compounds, phosphorus exhibits the oxidation numbers -III, I, III and, most commonly, V.

Elemental phosphorus can be prepared in two principal allotropic forms: white phosphorus is tetra-atomic (P4), highly reactive, flammable and soluble in non-polar solvents; red phosphorus is polymeric, rather non-reactive and insoluble. The former is toxic and the latter is nontoxic.

Binary compounds

Although these compounds are numerous, they are usually too reactive to be found in nature. They occur as phosphorus tri- and pentahalides, ionic phosphides (P^{3-} ion), phosphine, PH_3 (hydrogen phosphide), a toxic gas resembling ammonia in its basicity, etc. Phosphorus forms two solid acidic oxides, phosphorus(III) oxide, P_4O_6 ("trioxide") and phosphorus(V) oxide, P_4O_{10} ("pentoxide").

Oxoacids

There are three oxoacids of phosphorus: monoprotic hypophosphorous acid, H_3PO_2, diprotic phosphorous acid, H_3PO_3, and the most common phosphoric acid, H_3PO_4 (orthophosphoric or trihydrogenphosphoric acid). The latter is weak and triprotic, very stable and nonvolatile. By heating, it gradually loses water to form multinuclear acids, e.g., diphosphoric acid, $H_4P_2O_7$ (formerly pyrophosphoric) or metaphosphoric acids $(HPO_3)x$ which have a cyclic structure.

Phosphates

This name is used for the salts of trihydrogenphosphoric acid which are of three series. Dihydrogen phosphates with H2PO4- ions form acidic aqueous solutions. Hydrogen phosphates which contain HPO42- ions and (normal) phosphates with PO_4^{3-} ions form, if they dissolve, alkaline solutions due to the hydrolysis of anions. All kinds of dihydrogen phosphates dissolve in water. From hydrogen phosphates and phosphates, only those of alkali metals are soluble (see Appendix to this Chapter). The kind of phosphate ions in a particular solution depends on the value of pH; phosphate ions bind or release hydronium ions by adding an acid or a base to the solution. Hydrogen and dihydrogen phosphate ions comprise an efficient buffer system within the cell. Calcium phosphate, $Ca_3(PO_4)_2$ (phosphorite as a mineral), is a substantial constituent of the bones and teeth of animals, where it mostly occurs in the form of hydroxyapatite, $Ca_5(PO_4)_3OH$.

Phosphorus is an essential element for living organisms. Phosphates also play an important role as constituents of nucleic acids and nucleotides (e.g. ATP, adenosine triphosphate), phospholipids of biologic membranes and phosphorylated metabolic intermediates (e.g. phosphorylated monosaccharides). Phosphates are involved in energy transfer as well as in control of enzyme activity. A sufficient intake of phosphate is provided by a diet which includes meat, dairy products and legumes.

Arsenic, antimony, bismuth and their compounds are mostly toxic and have no biological importance. Examples of their compounds: Arsine, AsH_3, is an unstable gas. Arsenic(III) oxide, As_4O_6, is poorly soluble, very slightly acidic and amphoteric, forming arsenite anions in alkaline solutions and arsenic(III) cations in strongly acidic solutions. Bismuth(III) salts readily undergo hydrolysis and give insoluble "basic" salts of the type of bismuth nitrate oxide, $BiNO_3(O)$ (also oxynitrate or subnitrate occasionally used in medicine).

Group VIA Elements

The atoms of oxygen, sulfur, selenium, tellurium and radioactive polonium have six valence electrons in the configuration $ns^2\, np^4$ (p^4 elements). They acquire the oxidation number -II when combined with hydrogen or metals and (except for oxygen) the oxidation number IV and VI in compounds with nonmetals. Oxygen and sulfur are typical nonmetals, Se and Te are considered to be metalloids, polonium exhibits typical properties of metals.

Oxygen

is the most abundant element in the Earth's crust, either as a constituent of silicate or other rocks, water and organic compounds or as the diatomic elemental oxygen (O_2, dioxygen) in the atmosphere (21% by volume). Oxygen plays a central role in the chemistry of living matter. It is an essential oxidant for heterotrophs which utilize organic compounds rich in hydrogen as the only source of energy by combining them with oxygen to produce water and CO_2. The depletion of oxygen in the atmosphere is constantly replenished by photosynthesis provided by green plants.

Oxides

Oxygen combines directly with nearly all elements to generate oxides. The properties of an oxide depend on the difference between the high electronegativity of oxygen and that of another element.

Ionic oxides are, above all, the oxides of alkali and alkaline-earth metals. They are solid, nonvolatile and basic substances. The oxide anion (O^{2-}) readily reacts with water to form the strong base OH-.

Covalent oxides are the oxides of transition metals, metalloids and nonmetals. Many of them form vast covalent networks (they are rather hard, nonvolatile solids) and few of them are typical molecular compounds (possessing high volatility; some are gaseous or liquid).

Oxides may also be classified, according to the product of oxide hydration, into the distinct groups of basic, acid-forming, amphoteric and non-hydratable oxides:

Basic oxides are only oxides of metals, including all the ionic oxides and covalent oxides of metals in which they exhibit the lower oxidation numbers; they form hydroxides when hydrated. For example,

$$MgO + H_2O \rightarrow Mg(OH)_2$$
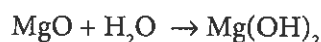
Amphoteric oxides are covalent oxides of some metals and metalloids, exhibiting a low oxidation number (e.g. ZnO, Al_2O_3, SnO, PbO, As_2O_3). They form salts with both acids and strong hydroxides.

Acid oxides are only covalent oxides; they react with water to give oxoacids, oxides of nonmetals and some oxides of metals with the higher oxidation numbers (e.g. CrO_3, MoO_3, Mn_2O_7) belong to this group. For example,

$$SO_2 + H_2O \rightarrow H_2SO_3$$
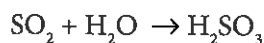
Exceptionally, there are few molecular covalent oxides (e.g. CO, N_2O) that neither react with water nor form salts with hydroxides.

Water is the most common compound of oxygen, essential for terrestrial life. Molecules of water in liquid and solid states associate forming hydrogen bonds. Water is a very weak electrolyte (an ampholyte, see Autoprotolysis of water and Hydrolysis of ions, (p. 46-49). It is bound to various transition-metal ions by coordination to form stable aquacomplexes (e.g. $[Cu(H_2O)_4]^{2+}$).

Peroxides are not very stable compounds in which two oxygen atoms bond together showing an unusual oxidation number -I. Hydrogen peroxide, H_2O_2, takes part in various redox reactions (a familiar oxidant). It decays by disproportionation, particularly in the presence of metallic catalysts:

$$2\,H_2O_2 \rightarrow 2\,H_2O + O_2$$
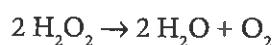
Some alkali and alkaline earth metals form ionic peroxides which contain the peroxide anion O_2^{2-}.

Ozone, O_3 (trioxygen), is an unstable allotropic form of oxygen created when an electric discharge passes through oxygen gas. It is an air pollutant in the lower atmosphere, but in the stratosphere it serves as an efficient ultraviolet light filter for the Earth.

Sulfur

Sulfur is found naturally in the elemental state (S_8, several allotropic forms) and in many compounds in which it mostly exhibits oxidation numbers -II, IV, and VI.

Binary compounds, sulfides

Sulfur combines directly with hydrogen and metals and is reduced to the oxidation state -II. Hydrogen sulfide, H_2S (sulfane) is a foul-smelling (odour of rotten eggs) and extremely poisonous gas. Dissolved in water, it is a weak diprotic acid acting as a reducing agent. Its salts are sulfides (S^{2-} ion) or hydrogen sulfides (HS^- ion). Not speaking of Group IA and IIA elements, the metallic sulfides are insoluble and occur widely in nature as important ores (PbS, ZnS, HgS, FeS_2, etc.). H_2S can be prepared from any sulfide by acidification:

$$S^{2-} + 2\,H^+ \rightarrow H_2S$$

The oxides and oxy acids of sulfur

Sulfur dioxide, SO_2 is a gas irritant to the eyes and respiratory tract. It is formed when sulfur-containing substances (esp. fossil fuels, solid waste) are burnt, and it acts as a primary air pollutant. A part of it produces SO_3 and the two oxides, dissolved in water, result in an acid rain which is extremely harmful to forests and lake water. SO_2 dissolves in water and partly reacts with it forming the unstable and weak sulfurous acid:

$$SO_2 + H_2O \rightarrow H_2SO_3$$
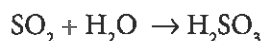
Its salts are sulfites used as reductants.

Sulfur trioxide is an anhydride of sulfuric acid:

$$SO_3 + H_2O \rightarrow H_2SO_4$$
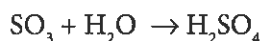
Sulfuric acid is a strong, diprotic and nonvolatile acid. A dilute sulfuric acid solution reacts with metals as any other non-oxidizing strong acid, e.g., its hydronium is reduced (molecular H_2 is evolved) by metals situated above hydrogen in the electromotive series. Hot concentrated sulfuric acid is a strong oxidant, although not as strong as nitric acid; in reaction with less reducing metals, sulfur is usually reduced from the oxidation state VI to IV, for example:

$$Cu + 2\,H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2\,H_2O$$

Concentrated H_2SO_4 is also a powerful dehydrating agent able to remove water even from carbohydrates and some organic compounds that contain hydrogen and oxygen.

Sulfuric acid forms two series of salts – sulfates, SO_4^{2-}, and hydrogen sulfates, HSO_4^-. Sulfates are mostly soluble (exception for the Ca subfamily and Pb).

Thiosulfates, e.g., $Na_2S_2O_3$, are salts of diprotic thiosulfuric acid (the thio- prefix indicates the S-for-O substitution). As reducing agents, they are used for fixing baths (as hypo) in photography or for rendering harmless elemental halogens by reduction.

Group VII.A Elements

Fluorine, chlorine, bromine, iodine and radioactive astatine have the electron configuration $ns^2 np^5$ (seven valence electrons), which is the cause of their high electronegativity values.

All halogens are diatomic nonmetals not found in nature in the elemental state (F_2 and Cl_2 are gases, Br_2 is a liquid, I_2 is a solid) because they tend to react readily as strong oxidants generating halide anions, X^-. Halogens with lower atomic weights can displace halogens with higher atomic weights in their halides by oxidation. Elemental fluorine is the strongest oxidizing agent at all, so that it cannot be prepared from fluorides by chemical oxidation.

Elemental Cl_2 or many compounds that are able to release it are used as common antiseptics (water treatment plants, swimming pools, etc.).

Iodine is insoluble in water but it dissolves easily in organic solvents; its alcohol solution, known as tincture of iodine, or compounds able to release gradually elemental I_2 are widely used as antiseptics or disinfectants.

Hydrogen halides and metal halides

As polar covalent hydrides, they are highly volatile. HF is a liquid (it boils at 19 °C) because of forming hydrogen bonds, the others are irritating gases. When introduced into water, hydrogen halides dissociate and give solutions of strong hydrochloric, hydrobromic and hydroiodic acids, respectively (except for HF which is only weakly acidic in solutions).

Hydrofluoric acid is unique in its ability to react with SiO_2 to give soluble H_2SiF_6 and thus to etch glass. The most of their salts with metals, ionic halides, dissolve in water; there are only few exceptions (e.g. silver halides, Hg_2Cl_2, CaF_2). Sodium chloride is an important component of our food, the chloride ion is a major anion in the extracellular fluid of mammals. The intake of a small amount of fluorides in food is necessary for the development of sound teeth in children, iodide intake is needed for sufficient biosynthesis of the thyroid hormone.

Halogen oxo acids and their salts

Halogen oxides are very unstable and of no special importance. Halogens, with the exception of fluorine, form oxoacids in which they usually exhibit oxidation numbers I, V and VII.

Elemental chlorine, bromine and iodine disproportionate in cold aqueous solutions to give a mixture of hydrohalic (HX^{-I}) and hypohalous acid, HX^IO, for example,

$$Cl_2 + H_2O \rightarrow HCl + HClO \quad \text{(hypochlorous acid)}$$

All oxo acids of halogens are strong oxidizing agents, as well as their salts. Calcium hypochlorite, $Ca(ClO)_2$, prepared by introducing chlorine into a slaked lime is used as disinfectant.

Chloric acid, $HClO_3$, and perchloric acid, $HClO_4$, are strong acids. Potassium chlorate, $KClO_3$, is explosive in the solid state when rubbed with organic compounds.

Noble Gases

(He, Ne, Ar, Kr, Xe, Rn)

These elements are characterized by a very stable configuration in their outermost electron shells (helium duplet $1s^2$, octets ns^2np^6). Their chemical activity is so low that they were called "inert gases" till, in the sixtieth, several compounds of krypton and xenon were synthesized.

All noble gases are colourless, odourless, and exist as monoatomic species. Noble gases constitute a component of air (total fraction about 1 % by volume, mostly argon).

Radon, a product of the radioactive decay of radium, is an intense alpha emitter.

Appendix: Solubility of the Common Salts

The solubility of ionic compounds – a simplified survey

Anion	Cation	
	Soluble salt	Insoluble salt
Nitrate (NO_3^-)	all cations	–
Hydrogen carbonate (HCO_3^-)	all cations	–
Dihydrogen phosphate ($H_2PO_4^-$)	all cations	–
Carbonate (CO_3^{2-})	Na^+, K^+, NH_4^+	other cations
Hydrogen phosphate (HPO_4^{2-})	Na^+, K^+, NH_4^+	other cations
Phosphate (PO_4^{3-})	Na^+, K^+, NH_4^+	other cations
Sulfide (S^{2-})	Na^+, K^+, NH_4^+	other cations
Hydroxide (OH^-)	Na^+, K^+	other cations
Chloride (Cl^-)	other cations	Ag^+, Hg_2^{2+}, Pb^{2+}
Sulfate (SO_4^{2-})	other cations	Ca^{2+}, Ba^{2+}, Sr^{2+}, Pb^{2+}
Oxalate $(COO)_2^{2-}$	Na^+, K^+, NH_4^+	Ca^{2+}
Hydrogen urate	–	Na^+, NH_4^+

10 INTRODUCTION TO ORGANIC CHEMISTRY

Organic chemistry comprises the chemistry of carbon compounds. Carbon atoms exhibit a unique property called catenation, which means that they can form covalent bonds with other carbon atoms. There exist a variety of carbon chains of different lengths (simple, branched, cyclic), to which hydrogen atoms are nearly always bonded (hydrocarbons); besides carbon and hydrogen, the compounds in human body include atoms of oxygen, nitrogen, sulfur, phosphorus, and a few others. Carbon compounds can be classified according to the carbon skeleton or the groups attached. According to the carbon skeleton, there are three main classes:

Acyclic compounds: aliphatic, open chain structures either unbranched or branched, both saturated and unsaturated (i.e. having double or triple bonds), e.g. ethane, ethanol, butyric acid.
Carbocyclic compounds: closed rings of carbon atoms that may have branches attached to them and may contain multiple bonds, they are divided into two subgroups – alicyclic, and aromatic compounds (i.e., those with a ring stabilized by the fully conjugated system of double bonds) e.g. cyclohexane, naphthalene.
Heterocyclic compounds: at least one atom in the ring is a heteroatom, an atom that is not carbon, e.g. pyridine, pyrrole.

Classification according to the functional groups: hydrocarbons, halogen derivatives, compounds with oxygen group (alcohols, phenols, aldehydes, ketones, carboxylic acid), sulfur (thiols, sulfides), nitrogen (e.g. amines, amides, nitrocompounds), and various combinations.

Common properties of organic compounds

Most of the bonds in organic compounds are covalent. Consequently, organic compounds are mostly typical covalent compounds exhibiting various degrees of polarity; only some of them are ionic (salts of organic acids and bases). The **polarity of a covalent bond** depends on the difference in electronegativities of the two bonded atoms. Typical non-polar bonds are C–C and C–H, hydrocarbons do not exhibit any substantial dipole moment. With the increasing difference in electronegativities of bonded atoms, the polarity of a bond increases and the atoms acquire partial electric charges ($\delta+$, $\delta-$). For example, the molecule of ethanol CH_3-CH_2-OH is polar because the C–O bond is quite polar and the O–H bond is even more polar than the C–H bonds.

Note that a polar bond is a prerequisite for the **polarity of a molecule**, but not all molecules with polar bonds must necessarily be polar. Dipole moments of individual bonds are vectors. When more polar bonds are present in a molecule, the resulting dipole moment of the molecule depends on the spatial arrangement of polar bonds. In some symmetrical molecules, internal cancelling of partial dipoles results in an overall absence of polarity. For example, tetrachloromethane CCl_4 is non-polar because of the symmetrical tetrahedral geometry of four polar C–Cl bonds.

Reactivity of organic compounds depends on bond energy as well as on bond polarity and other given conditions. Covalent bonds can be split in a symmetrical **homolytic cleavage**; the result is a free radical, which has a single (unpaired) electron to offer for bonding: X-Y $\rightarrow$ ·X + ·Y.
Another type of bond splitting is an asymmetrical **heterolytic cleavage**; one of the products is the nucleophile having an unshared electron pair to offer for bonding, the second is the electrophile able to form a new bond by accepting a pair of electrons: X-Y $\rightarrow$ $|$X⁻ + Y⁺.

Reactions in organic chemistry are commonly divided according to the reaction mechanism and the resulting change of the substance (condensation, hydrolysis etc.). According to mechanism we recognise four basic types of reactions: addition, elimination, substitution, and rearrangement.
During **addition** the multiple bonds are removed, the hybrid state of C is changed ($sp^2 \rightarrow sp^3$). E.g. CH_2=CH_2 + Cl_2 $\rightarrow$ CH_2Cl-CH_2Cl (chloration of ethane to 1,2-dichloroethane).
In **elimination** the multiple bond is formed and hybrid state of carbon is changed ($sp^3 \rightarrow sp^2$), e.g. elimination of water from ethanol gives ethene: $CH_3CH_2OH \rightarrow CH_2$=$CH_2$ + H_2O.
In **substitution** the hybridization state is not changed. The H atom in the molecule is substituted by another atom (group), e.g. chloration of methane gives chloromethane: CH_4 + Cl_2 $\rightarrow$ CH_3Cl + HCl.
In **molecular rearrangement** atoms and groups migrate within one molecule; carbon chain is altered, the number of atoms is the same (e.g. glucose $\rightarrow$ fructose).

Condensation is the linkage of two molecules with elimination of a small molecule. E.g. the reaction of carboxylic acid with alcohol produces ester and water: R-COOH + R'-OH $\rightarrow$ R-COOR' + H_2O.
Hydrolysis is the reaction of a substrate with water. Two smaller product molecules are formed from one molecule of substrate. The subjects of hydrolysis are esters, amides, proteins, lipids, polysaccharides, polynucleotides etc. Hydrolysis usually needs the catalytic amount of acid, base or enzyme. E.g. hydrolysis of an ester gives acid and alcohol: R-COOR' + H_2O $\rightarrow$ R-COOH + R'-OH.
Redox reactions in organic chemistry are connected with the change of oxidation number of carbon, which gets in organic compounds values from –IV to III. Redox transformations of a substrate can principally occur in six ways (see the table):

Oxidation	Reduction
Loss of electron(s)	Gain of electron(s)
Loss of 2 H atoms (dehydrogenation)	Accepting 2 H atoms (hydrogenation)
Gain of oxygen (oxygenation)	Loss of oxygen (deoxygenation)

Very often, in biochemical processes, oxidations proceed by **dehydrogenation**. Two H atoms are eliminated from a substrate to form a double bond product.

Isomerism of organic compounds

The qualitative and quantitative composition of a compound is given by its empirical formula (the simplest stoichiometric ratio of elements comprising the molecule) or, more exactly, by its molecular formula (the number of different atoms comprising the molecule). However, there is a vast number of organic compounds with identical molecular formulas but different physical and chemical properties related to different arrangements of their atoms (structure). The structure of a particular compound can be understood as:

- **constitution** is the sequence of atoms and bonds within the molecule, described by its structural (constitutional) formula and which does not consider a spatial arrangement of atoms
- **configuration** takes into account the spatial arrangement of the atoms attached to double bonds (*cis/trans*), cyclic systems (*cis/trans*), or stereogenic centres (D/L);
- **conformation** considers all the spatial arrangements of a particular compound (conformers) that can exist due to rotation about single bonds.

Isomerism means the existence of two or more compounds (isomers) with identical molecular formulas but different structures.

Structural (constitutional) isomers

Constitutional isomers are compounds which have the same molecular but different structural formula. They may differ from each other in the arrangement of their chains (straight unbranched or branched), in the position of double bonds, in the presence of a cycle instead of one double bond etc.

Tautomerism is a special type of isomerism in which a rapid rearrangement of hydrogen and a bonding electron pair takes place (see keto and enol forms of aldehydes).

Example: the C_2H_6O formula can be ethanol (CH_3-CH_2-OH) or dimethyl ether (CH_3-O-CH_3).

Stereoisomers

Stereoisomers have the same order of attachment of atoms but different arrangements of atoms in space. Isomers can be interconverted only by breaking and remaking of covalent bonds. There are two kinds of stereoisomerism: geometrical and optical. Geometrical isomerism occurs, if each carbon of the double bond has two different atoms or groups attached. Two different forms (*cis*, *trans*) exist because rotation at double bonds is restricted:

oleic acid   elaidic acid
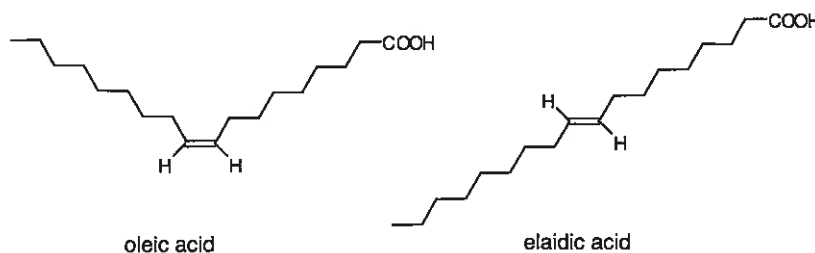
Two H atoms are either on the same side of the double bond (*cis*-isomer, oleic acid) or on the opposite sides (*trans*-isomer, elaidic acid).

Optical isomerism, chirality

Any carbon atom with four different groups (or atoms) attached to it is called the **stereogenic** carbon atom (chiral centre). These dissimilar substituents can be arranged in two different ways to provide two distinct configurations which are non-superimposable on mirror images of each other. Such isomers are called **enantiomers** or optical antipodes. In most properties they behave identically, both exhibit optical activity (one of them is levorotatory, the other dextrorotatory). The example given is L- and D-amino acid.

Conformers (rotamers) are the different arrangements (conformations) of a particular compound which result from free rotation about the carbon-carbon single bonds without breaking any bond. The energy barrier to rotation is, however, mostly small enough to allow free rotation in saturated compounds. Although different conformers cannot be isolated, the rotational arrangement of groups has an influence on chemical reactivity. Conformations in which large groups are as far apart as possible are generally the most stable ones.

Nomenclature of Organic Compounds

There are many **common** names of organic compounds which do not contain any structural information. These names were usually based on source material (citric acid, formic acid, lactate, caffeine, urea). **Semisystematic** names express certain chemical features, e.g. acet_one_ is a ketone, cholester_ol_ is a steroid alcohol. The complete structural information is contained in **systematic names**, which are based on the principles of IUPAC (International Union of Pure and Applied Chemistry).

A part of the structure in molecule is taken as the **basic structure**, whereas the other parts are substituents, which replace some of hydrogen atoms of basic structure. The basic structure can be acyclic, cyclic or heterocyclic; only H atoms are bound to the atoms of the chain. **Substituents** are atoms or groups (e.g. -OH, -NH$_2$, -COOH, methyl). Unsaturation of structure is expressed by the suffix _-ene_ for a double bond, and _-yne_ for a triple bond instead of _-ane_ (for saturated skeleton). The presence of substituents in the basic structure is expressed by one suffix, one or more prefixes and locants. **Suffix** is a part of name, which expresses the present substituent with the highest priority, which determines the character of the compound. The hierarchy of the types of compounds for the application of the suffix is shown in the table below:

1.	Onium cations	8.	Aldehydes
2.	Carboxylic acids, sulfonic acids	9.	Ketones
3.	Acid anhydrides	10.	Alkohols, phenols, thiols
4.	Esters	11.	Hydroperoxides
5.	Acid halogenides	12.	Amines
6.	Amides	13.	Ethers, sulfides
7.	Nitriles	14.	Peroxides, disulfides

The other substituents (with lower priorities) are denoted by **prefixes**. The presence of a higher number of the same substituents in the basic structure is expressed by multiple prefixes _di-, tri-, tetra-_ etc.

Locant is the number (1, 2, 3 …) or the symbol of an element (e.g. _N-_, _O-_), which describes the position of the substituent(s) in the basic structure. Locants are placed just in front of the part of the name, to which they are directly related, for example: 1,2-dichloroethane, propane-2-ol, but-2-ene, cyclohex-2-ene-1-ol, _N_-methylbenzamide. To determine the name of an organic compound from the structural formula we follow several general steps:

1. Find basic structure, the main chain has the highest number of characteristic groups and multiple bonds.
2. Determine, which of the characteristic groups will be expressed by the suffix as the main one.
3. Name the basic structure.
4. Name the main group by the suffix.
5. Determine other substituents and to name them by prefixes.
6. Determine locants, so that the main group has the lowest locant.
7. Set individual parts, prefixes are arranged in the alphabetical order.

Prefixes and suffixes for some characteristic groups are presented in the following table.

Type of compound	Group	Prefix	Suffix
Onium cation	- [a]	-	-onium
Carboxylic acids	-COOH	carboxy-	-oic / -carboxylic acid
Sulfonic acids	$-SO_3H$	sulfo-	-sulfonic acid
Salts of carboxylic acids	$-COO^-$	-	-(o)ate, -carboxylate
Esters	-COOR	R-oxycarbonyl-	R-(o)ate, R-carboxylate
Amides	$-CONH_2$	carbamoyl-	-(carbox)amide
Nitriles	$-C\equiv N$	cyano-	-(carbo)nitrile
Aldehydes	-CH=O	formyl-	-al, -carbaldehyde
Ketones	>C=O	oxo-	-one
Alcoholes, phenoles	-OH	hydroxy-	-ol
Thiols	-SH	sulfanyl-	-thiol
Amines	$-NH_2$	amino-	-amine
Ethers	-OR	R-oxy-	-ether
Sulfides[b]	-SR	R-sulfanyl-	-
Halogenderivates[b]	-F, -Cl, -Br, -I	fluoro-, chloro-, bromo-, iodo-	-
Nitroderivates[b]	$-NO_2$	nitro-	-

[a] E.g. RNH_3^+ alkylammonium, ROH_2^+ alkyloxonium, R_3S^+ trialkylsulfonium. [b] Exclusively as prefixes.

Example:
basic structure: *hexane*
suffix group: -COOH (*-oic acid*)
prefix groups: $-NH_2$ (*amino*), multiple prefix: *di*
locants: 2,6
complete set = systematic name: 2,6-diaminohexanoic acid (lysine)
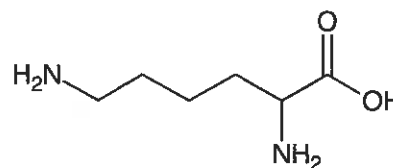
Hydrocarbons
Compounds which contain only carbon and hydrogen atoms are called hydrocarbons. Saturated hydrocarbons involve only single bonds, unsaturated hydrocarbons contain carbon-carbon double and/or triple bonds. Aromatic hydrocarbons are a special class of cyclic and unsaturated hydrocarbons.

Saturated hydrocarbons (alkanes and cycloalkanes)

Alkanes are represented by the general formula C_nH_{2n+2}, where n corresponds to the number of carbon atoms. Alkanes make a homologous series in which each member differs from the preceding one by a methylene group $-CH_2-$. Example of homologous series of unbranched alkanes is given in the table:

C	Alkane	Alkyl(s)
1	Methane CH_4	methyl CH_3-, methylene $-CH_2-$
2	Ethane CH_3-CH_3	ethyl CH_3-CH_2-, ethylene $-CH_2-CH_2-$
3	Propane $CH_3-CH_2-CH_3$	propyl $CH_3-CH_2-CH_2-$, isopropyl (propane-2-yl) $(CH_3)_2CH-$
4	Butane $CH_3-CH_2-CH_2-CH_3$	butyl, butane-2-yl
5	Pentane $CH_3-CH_2-CH_2-CH_2-CH_3$	pentyl, pentane-2-yl, pentane-3-yl

In branched alkanes, the systematic name is derived from the longest continuous chain of carbon atoms (basic structure) which is numbered from the end of the sequence closest to the branches; side branches are named as alkyl substituents to the parent alkane (basic structure).

E.g.: 3-methylhexane
(neither 2-ethylpentane nor 4-methylhexane)
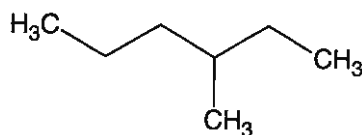
There is a usage rule in organic chemistry used to distinguish among carbon atoms according to their position in the carbon chain. A carbon atom joined directly to another carbon atom (the terminal carbon atom) is called a primary carbon (1°) atom. A carbon attached directly to two other carbons is called a secondary carbon (2°), and any carbon that is joined directly to three other carbons is a tertiary carbon (3°, representing the branch point of a chain).

Properties of alkanes. Because C–H and C–C bonds of all types are almost entirely non-polar, all hydrocarbons are very non-polar compounds, insoluble in water, less dense than water. They are separated from natural gas or petroleum (oil).

Reactions of alkanes. Alkanes are relatively inert, they do not react with acids, bases, oxidants, and reductants. They react with oxygen and halogens only at higher temperatures:

1. **Oxidation and combustion.** Alkanes, as well as other hydrocarbons, burn with excess oxygen to form carbon dioxide and water. The reaction evolves considerable heat (is very exothermic), alkanes are efficient fuels. E.g. $CH_4 + 2 O_2 \rightarrow CO_2 + 2 H_2O +$ energy ($\Delta H = - 883$ kJ/mol).
If not enough oxygen is available, incomplete combustion occurs forming soot (elemental carbon), toxic CO and other compounds.

2. **Halogenation** is example of substitution. Halogens heated with alkanes can give many different halogen derivatives (an example of chlorination was given earlier).

3. **Elimination** (dehydrogenation) yields alkenes during the thermal or catalytic cleavage of petroleum, e.g.: $CH_3-CH_3 \rightarrow H_2 + CH_2=CH_2$.

Cycloalkanes have monocyclic or polycyclic structures. The five- and six-membered rings are common because of little or no strain due to deformations of bond angles. **Cyclopentane** has a nearly planar ring of five carbon atoms. **Cyclohexane** forms two most stable **chair** conformations which are interconvertible by rotation of the carbon-carbon bonds through a less stable **boat** conformation.
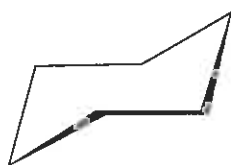
chair conformation
(simplified formulas without H atoms)
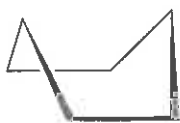
boat conformation

real structure of cyclohexane

Unsaturated hydrocarbons

Alkenes and cycloalkenes contain one carbon-carbon double bond, two double bonds are present in alkadienes and there are also alkatrienes, tetraenes and even polyenes. When two or more double bonds are present in a molecule, properties depend on their relative positions.

Isolated double bonds are separated by two or more single bonds; they do not influence each other. Very important compounds are those with **conjugated** bonds which alternate with single bonds (double bonds are separated by a single bond). The most common is **isoprene** (2-methylbuta-1,3-diene), a building unit of many naturally occurring compounds (isoprenoids, terpenes).
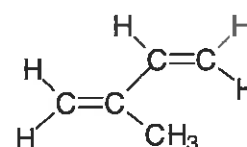
isopren

Nomenclature. The simplest alkene of the homologous series is ethene, $CH_2=CH_2$ (trivial name ethylene is quite common), followed by propene (commonly propylene), four isomeric butenes: but-1-ene, *cis*-but-2-ene, *trans*-but-2-ene (geometric isomers), 2-methylpropene. The chain is numbered from the end nearest to the multiple bond and its position is indicated by a lower-numbered carbon of that bond. In branched unsaturated hydrocarbons, the parent structure is the longest chain that includes most of the multiple bonds and the position of the multiple bond is designated by a number which takes preference (lower number) over that for alkyl substituents,

E.g. 2-ethyl-3-methylbut-1-ene, notice that the main chain has four carbons, not five:

2-ethyl-3-methylbut-1-ene
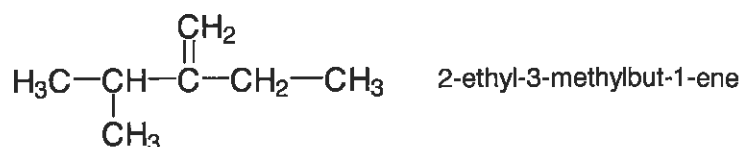
Monovalent groups are generally *alkenyls*. For instance, *vinyl* from ethene $H_2C=CH-$ (ethenyl, as it would be logical, is not allowed), 1-propenyl (prop-1-en-1-yl) $CH_3-CH=CH-$, and 2-propenyl (prop-2-en-1-yl) $CH_2=CH-CH_2-$ (*allyl*) from propene. Notice that the lower number is ascribed to the carbon with the free valence.

The reactions of alkenes are typical for any compound that includes an isolated double bond.

1. **Addition reactions** are the most common reactions with unsaturated compounds. The π-bond of the multiple bond is broken, the reactant attached and the saturated product results, examples are given in the table:

Reaction	Reagent	Product
Hydrogenation	H_2	alkane
Chloration	Cl_2	dichloroalkane
Hydration	H_2O	alkohol

$$H_3C-CH_2-OH \xleftarrow{\;H_2O\;} \underset{\underset{\text{ethene}}{}}{\overset{\overset{H}{}}{\underset{H}{}}C=C\overset{H}{\underset{H}{}}} \xrightarrow{\;H_2\;} H_3C-CH_3$$

ethanol   ethene   ethane
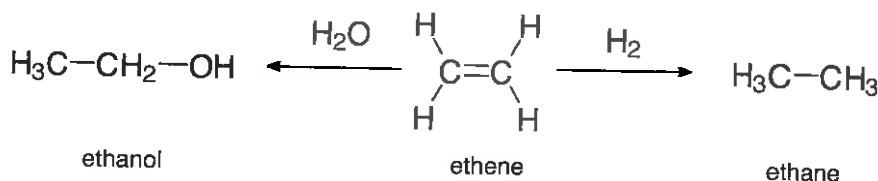
If an asymmetrical reagent (HBr, H_2O) is added to an asymmetrical alkene, the hydrogen in the reagent goes to the carbon atom with a greater number of hydrogen atoms (Markovnikov's rule).

Alkenes can undergo addition polymerization. Low-molecular unsaturated monomers join each other to produce high-molecular polymers as natural or synthetic rubber, neoprene, polyethylene, teflon, polystyrene, polyvinyl chloride (PVC), polymethacrylate, etc. However, not all polymers are adducts, another class of polymers is produced by condensation reactions as polyamides, polyesters, polyethers, not speaking of natural biopolymers (polysaccharides, proteins, and nucleic acids).

2. **Oxidation** of alkenes may convert them to dihydroxycompounds, called glycols (alkanediols), or may lead to breaking the double bond and forming two carbonyl compounds.

Alkynes possess one or more triple bonds. Their reactivity is similar but somewhat lower than that of alkenes. The simplest compound is gaseous **ethyne**, H-C≡C-H, common name **acetylene**. It can be prepared from calcium carbide CaC_2 and water and exhibits a slightly acidic character. It might be assumed that vinylalcohol, $H_2C=CH-OH$, is the product of ethyne hydration. However, acetaldehyde is the product because of a rearrangement of unstable enol to its more stable carbonyl form, keto-enol tautomerism ($H_2C=CH-OH \leftrightarrows CH_3-CH=O$).

Aromatic hydrocarbons (arenes)

form a distinct group of hydrocarbons which comprise one or more benzene rings. In benzene, C_6H_6, all six carbons of the cycle as well as six hydrogen atoms lie in the same plane and all bond angels are 120° (hybridization sp²). Six π-electrons of the unhybridized carbon p-orbitals are delocalized within the molecular orbital spread over the ring which makes the ring very stable. In spite of the occasional use of Kekule's formula of benzene (with three double bonds), all the six carbon-carbon bonds of the ring are equivalent; benzene is a resonance hybrid.
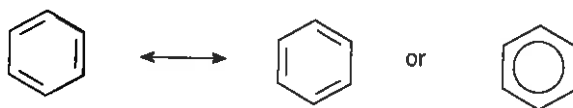
Nomenclature. The names of arenes are frequently common: benzene, toluene (methylbenzene), xylene (dimethylbenzene), styrene (vinylbenzene). The position in disubstituted benzenes can be described by locants or prefixes: 1,2- (*ortho-, o-*), 1,3- (*meta-, m-*) or 1,4- (*para-, p-*). The general name of univalent aromatic residue is *aryl* (Ar-), derived from benzene *phenyl*, toluene *o-, m-* or *p-tolyl*, naphthalene *1-naphthyl* or *2-naphthyl*. Bivalent residues from benzene are *o-, m-* or *p-phenylenes*. If the valence in the aliphatic remnant of the side chain is free, it is *phenylalkyl*, in case of toluene it is *benzyl* (NOTE benzoyl is acyl of benzoic acid).
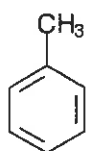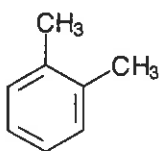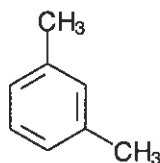
toluene   *o* xylene   *m* xylene   styrene
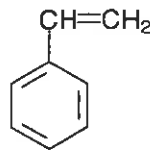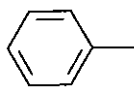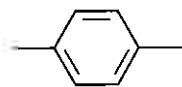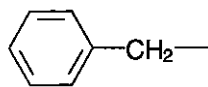
phenyl   *p* phenylene   benzyl   *p* tolyl
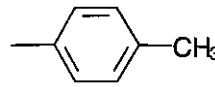
Reactions of arenes. Reactions of the side-chains attached to benzene rings are similar to the reactions of other hydrocarbons. Benzene-ring reactions are different, arenes do not behave as other unsaturated hydrocarbons due to the molecular π-orbital.

1. Addition reactions do not occur readily.

2. **Substitutions** are the major type of reaction of the aromatic ring, hydrogen atom(s) can be replaced with a halogen atom (halogenation), with a nitro group $-NO_2$ (nitration), or an acidic $-SO_3H$ group (sulfonation). Any substituent attached to the ring polarizes the ring directing so other substituents which may react to certain positions on the ring.

3. The benzene ring resists to oxidation. Oxidation of side chains, if present, takes place as well as oxidation of some of the fused rings in polynuclear arenes.

Polycyclic aromatic hydrocarbons (PAH) have more fused benzene rings. The most common of them are naphtalene (two rings), anthracene (three rings condensed linearly), and its isomer phenanthrene (three rings condensed forming an angle).
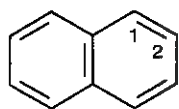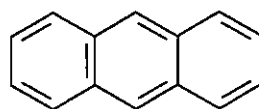
naphthalene   anthracene   phenanthrene
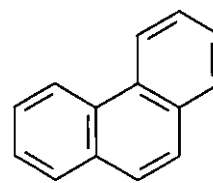
Some of them are carcinogenic. They are found in coal tar, soot or tobacco smoke but also can be formed by overheating unsaturated fatty acids in fats during barbecuing and frying.

11   ORGANIC COMPOUNDS WITH FUNCTIONAL GROUPS

Organic Halogen Compounds

Organic halogen compounds are found only exceptionally as constituents of the living matter. They are synthesized, as industrial chemicals, from hydrocarbons by substitution or addition reactions. Many bromoalkanes and iodoalkanes are common alkylating agents, which react with nucleophiles. Chlorinated and fluorinated hydrocarbons are much less reactive. Many of them are effective non-polar solvents for hydrophobic compounds.

Chloroform $CHCl_3$ (trichloromethane), **trichloroethene** $Cl_2C=CHCl$, **tetrachloromethane** CCl_4 are excellent solvents for degreasing or in dry cleaning. The former two act as anaesthetics but, because of their toxicity, they have been replaced by more safe compounds; CCl_4 is very toxic (damaging the liver tissue).

Chlorofluorocarbons (CFCs, formerly known as Freons), e.g. CCl_2F_2 (dichlorodifluoromethane), were used as refrigerants in air conditioners, refrigerators and freezers or as propellants in aerosol dispensers. Unfortunately, chlorine atoms released from CFCs in the stratosphere by the action of UV radiation damage the ozone layer and, therefore, the use of them must be restricted.

Vinyl chloride $H_2C=CHCl$ (chloroethene), and **tetrafluoroethylene** $F_2C=CF_2$ represent the raw material for synthetic polymers PVC and Teflon, respectively.

Many halogen compounds are potent antiseptics (e.g. chlorhexidine), insecticides (the best known is DDT, dichlorodiphenyltrichloroethane) and herbicides (wheed killers, e.g. 2,4-dichlorophenoxyacetic acid). Their excessive use may result in accumulation in the environment.

Alcohols

are hydroxy derivatives of hydrocarbons, one or more H atoms (attached to different carbon atoms) are replaced by hydroxyl group -OH. The three types of alcohols are distinguished:
primary alcohol $R-CH_2-OH$, secondary alcohol R^1R^2CH-OH, and tertiary alcohol $R^1R^2R^3C-OH$.

Primary alcohols always contain $-CH_2OH$ group, **secondary alcohols** have the CH-OH group and **tertiary alcohols** have a hydroxyl attached to the carbon at a branching point.

According to the number of hydroxyl groups, there are monohydric, dihydric, and polyhydric alcohols. Alcohols with two adjacent OH groups are **glycols** (e.g. ethylene glycol, $HO-CH_2-CH_2-OH$). The simplest trihydric alcohol is **glycerol**. Polyhydric alcohols are mostly formed by reduction of monosaccharides and are called **alditols** (e.g. glucitol).

An unstable class of compounds are **enols,** in which hydroxyl group is attached to a carbon-carbon double bond, for instance, as in "vinyl alcohol" $CH_2=CH-OH$. In fact, these compounds are tautomers of more stable carbonyl compounds.

Nomenclature of alcohols. In the IUPAC system, the name of a hydrocarbon is completed with the ending *-ol* (*-diol*, *-triol*) and with the proper locant(s): CH_3CH_2OH is ethanol,
$(CH_3)_2CHCH_2OH$ is 2-methylpropane-1-ol, $HO-CH_2-CH_2-OH$ is ethane-1,2-diol (ethylene glycol).

Properties of alcohols. Lowest alcohols are very polar and miscible with water, the hydrophilic character diminishes with the increasing number of carbon atoms and increases with the number of hydroxyl groups. Water-soluble alcohols form clusters due to hydrogen bonds.

1. Alcohols behave like **neutral compounds** in water (**non-electrolytes**). However, in the absence of water, they react with alkali metals to give unstable alkoxides, e.g.:
$CH_3OH + Na \rightarrow ½ H_2 + CH_3O^- Na^+$ (sodium methoxide).
Alkoxides are readily hydrolyzed to alcohols and alkali hydroxide when traces of water are present.
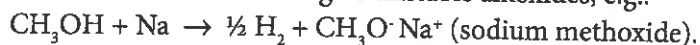
2. Dehydration of alcohols (elimination of water) gives, depending on temperature, ethers or alkenes:
dehydration of two molecules yields an ether: $2\ CH_3OH \rightarrow CH_3\text{-O-}CH_3 + H_2O$,
intramolecular elimination of water yields an alkene: $CH_3CH(OH)CH_3 \rightarrow CH_3CH=CH_2 + H_2O$.
3. In reaction with acids, alcohols yield esters and water. Methanol, for example, reacts with acetic acid: $CH_3OH + CH_3COOH \rightarrow H_2O + CH_3CO\text{-}OCH_3$.
Esters are named as "alkyl salts" of the acid. In the reaction shown above, the ester is methyl acetate. See also carboxylic acids.
Inorganic acid esters are analogous compounds; for example, primary alcohol and sulfuric acid give alkyl sulfate and water: $R\text{-}CH_2OH + HO\text{-}SO_3H \rightarrow R\text{-}CH_2\text{-O-}SO_3H + H_2O$.
Phosphate esters of monosaccharides (e.g. glucose 6-phosphate) are intermediary metabolites of glucose, pentose phosphates are constituents of nucleotides (purine or pyrimidine base is attached to ribose 5-phosphate) and also phospholipids are phosphate esters. In the cells, there exist different esters of diphosphoric and triphosphoric acids (nucleoside di- and triphosphates, ADP and ATP, high-energy phosphates) which are important as carriers of energy. Esters of phosphoric and sulfuric acids occur in the living system largely as anions, unless all ionizable groups of those polyprotic acids are completely esterified. A well known inorganic ester is glycerol trinitrate (so-called nitroglycerine) used as an explosive or a vasodilating drug.
4. In reactions with carbonyl compounds (aldehydes or ketones), alcohols give hemiacetals.
5. Oxidation of alcohols (dehydrogenation, two H atoms are eliminated) produces corresponding carbonyl compounds. Primary alcohols form aldehydes which are easily oxidized to carboxylic acids:
Secondary alcohols form ketones:
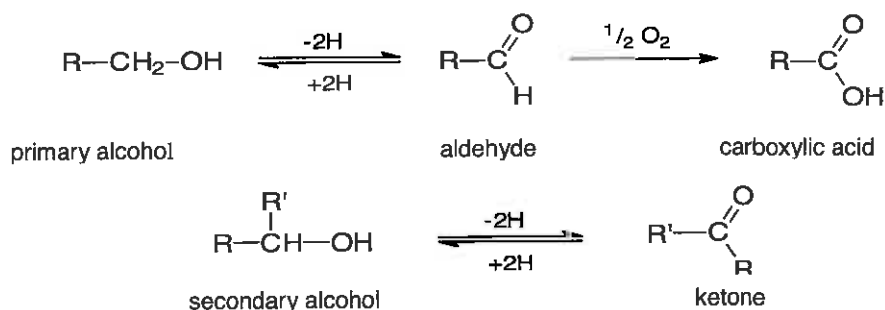
Ketones cannot be further oxidized by dehydrogenation. Tertiary alcohols also cannot be oxidized by dehydrogenation. Under vigorous oxidating conditions, their molecule is split into two products.

Phenols

have the hydroxyl group attached directly to an aromatic ring, Ar-OH. Properties are similar to alcohols: they give ethers when alkylated and they form esters and hemiacetals in reactions with acids and carbonyl compounds, respectively. Phenols behave as weak acids in aqueous solutions and form phenoxides (phenolates) in reactions with sodium hydroxide. In contrast to alcohols, monohydric phenols cannot be simply oxidized into corresponding carbonyl compounds. On the other hand, oxidation of polyhydric phenols to quinones is very easy, if they contain two hydroxyl groups in *ortho-* or *para*-positions.
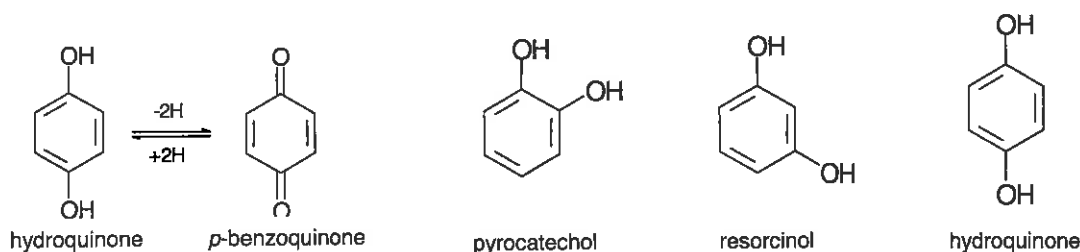
Many naturally occurring compounds are phenols, for example, the amino acid tyrosine, hormones adrenaline (epinephrine), thyroxine, and estrogens as well as tocopherol (vitamin E). Phylloquinone (vitamin K) which plays a role in the blood-clotting, is a derivative of 1,4-naphthoquinone.

Ethers

The general formula of ethers is R-O-R, two alkyls are bonded to an oxygen atom. Ethers are not very reactive and may be regarded as products of alcohol dehydration (see above).

CH_3-O-CH_3 dimethyl ether (methoxymethane)

CH_3-O-CH_2CH_3 ethyl methyl ether (methoxyethane)

CH_3CH_2-O-CH_2CH_3 diethyl ether (ethoxyethane, commonly ethyl ether or just ether)

CH_3-O-C_6H_5 methyl phenyl ether (methoxybenzene, anisole)

Cyclic ethers are named as heterocyclic compounds (tetrahydrofuran, tetrahydropyran, Chapter 12).

Thiols and Alkyl Sulfides

These compounds are sulfur analogues of alcohols, phenols, and ethers.

Nomenclature. Thiols are sulfur analogues of alcohols; they contain monovalent group -SH. The names of thiols are formed similarly to alcohols: the suffix –*thiol* is added to the name of the hydrocarbon (ethanethiol CH_3CH_2-SH, butanethiol $CH_3CH_2CH_2CH_2$-SH). If -SH is not the main group, the prefix *sulfanyl-* is used, e.g. 2-amino-3-sulfanylpropanoic acid (cysteine).

Properties of thiols are similar to those of alcohols: they give alkyl sulfides when alkylated, they form thioesters and hemithioacetals in reactions with acids and carbonyl compounds, respectively. However, thiols differ from alcohols that they are:

- less polar (no hydrogen bonds with water) and weakly acidic in aqueous solutions, thus can make salts (capture of toxic mercury and arsenic ions),
- are easily oxidized (dehydrogenated) that two molecules form an alkyl disulfide R-S-S-R, with an intermolecular disulfide bridge (also interchain disulfide cross-links in proteins), e.g.

$2 R-SH + \frac{1}{2} O_2 \rightarrow R-S-S-R + H_2O$

$2 R-SH + H_2O_2 \rightarrow R-S-S-R + 2 H_2O$
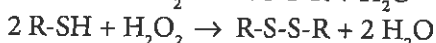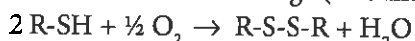
The reverse reaction is also easily accomplished by reducing agents. By using strong oxidants, the sulfur atom of thiols acquires the highest oxidation number VI and sulfonic acids $R-SO_3H$ are formed. These acids contain the sulfo group $-SO_3H$ bonded to alkyl or aryl and, in contrast to carboxylic acids, they are strong acids. Do not confuse sulfonic acids in which the sulfur atom is attached directly to carbon atom, e.g., CH_3-SO_3H (methanesulfonic acid), with alkyl sulfates that are esters of sulfuric acid and an alcohol, e.g., CH_3-O-SO_3H (methyl sulfate). SH-compounds are biologically important because of their roles in redox reactions and formation of disulfide cross-links. The most common compounds are **cysteine** (amino acid) and **glutathione** (tripeptide). Many of the organic sulfur compounds have very intensive odours: the scent of the pole-cat (or skunk) is mainly due to butanethiol, the pungent flavours of onion and garlic are due to alkyl sulfides and disulfides.

Aldehydes and Ketones

The term **carbonyl group** means a carbon-oxygen double bond C=O. Carbonyl groups are found not only in aldehydes and ketones but also in carboxylic acids and their derivatives. Aldehydes always contain the monovalent group -CH=O, ketones always contain the carbonyl group combined with two alkyl (aryl) groups.
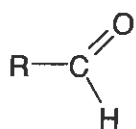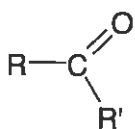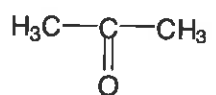
aldehyde   ketone   keto form of acetone   enol form of acetone
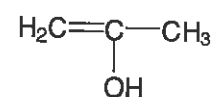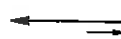
Tautomerism occurs in both aldehydes and ketones, one H atom and the double bond migrate reversibly. The carbonyl form is more stable and the enol form cannot be isolated.

Nomenclature. The systematic names of aldehydes are formed by adding the suffix -al to the name of hydrocarbon (butanal, propandial etc.). In cyclic aldehydes, the suffix -carbaldehyde is added to the name of the cyclic system (cyclohexanecarbaldehyde, naphthalenecarbaldehyde). Common names are used for some aldehydes (formaldehyde, acetaldehyde, benzaldehyde, glyceraldehyde, malondialdehyde). The names of ketones are formed by adding the suffix -one to the name of hydrocarbon (propanone, cyclohexanone, pentane-2,4-dione). For quinoid compounds we use the suffix -quinone (p-benzoquinone). Some ketones have common names, e.g. acetone CH_3-CO-CH_3.

Reactivity of carbonyl compounds

The carbonyl group of aldehydes and ketones is polar, both aldehydes and ketones undergo the following addition reactions:

1. Addition of hydrogen (using metal hydrides) is the reduction of carbonyl compounds to primary and secondary alcohols.

2. Addition of an alcohol results in formation of an unstable **hemiacetal** or hemiketal:
R-CH=O + HO-R' → R-CH(OH)-OR'
Notice that monosaccharides form intramolecular hemiacetals (cyclic forms) in the same way.
A hemiacetal may further react with another molecule of alcohol (this second step is not an addition because it involves elimination of water) to produce more stable **acetals** (or ketals):
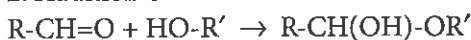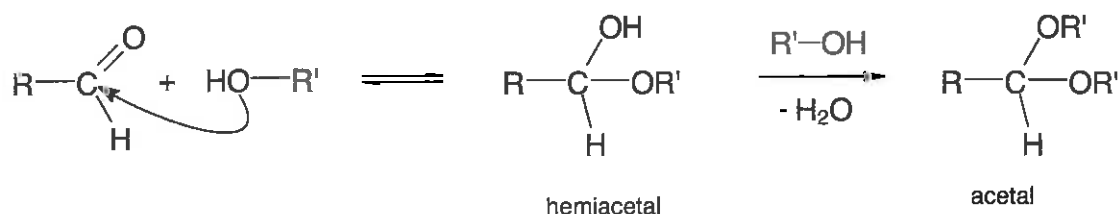
The acetals of saccharides are called glycosides, i.e., the reaction above may also be applied to formation of glycosidic bonds.

3. Reaction with ammonia or amines produces **imines** and water:
R-CH=O + NH_3 → R-CH=NH + H_2O
R-CH=O + R^1-NH_2 → R-CH=N-R^1 + H_2O
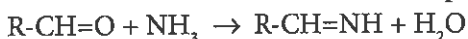
4. Oxidation: Aldehydes (unlike ketones) exhibit marked reducing properties because they are very easily oxidized to the corresponding carboxylic acids. On the contrary, ketones strongly resist oxidation (they cannot be oxidized without breaking the carbon skeleton).

Carboxylic Acids

The functional group of carboxylic acids is the monovalent carboxyl group -COOH. It is formally made by combining carbonyl and hydroxyl groups. However, this combination acquires new quality that differ from alcohols and carbonyl compounds. Carboxylic acids are classified according to:
- the carbon skeleton: acyclic, aromatic acids, alicyclic and heterocyclic acids;
- the number of carboxyl groups: monocarboxylic, di-, tri-, polycarboxylic acids;
- the presence of other functional groups, substituted acids as hydroxy, oxo, and amino acids.

Nomenclature. To obtain the systematic name of a carboxylic acid, the final –*e* in the name of the corresponding hydrocarbon is replaced with the suffix –*oic* (or –*dioic*) *acid*. For cyclic acids, the suffix –*carboxylic acid* is used, e.g. benzenecarboxylic acid (benzoic acid). The names of tri- and polycarboxylic acids are formed in the similar way (propane-1,2,3-tricarboxylic acid). Many carboxylic acids have common names, namely those of biochemical importance.

The names of anions and salts of acids are derived from the systematic or common names by replacing the final –*ic* in the name of acid with the suffix –*ate*, e.g., acetate, butanoate (butyrate), hexanoate, butandioate (succinate), stearate. The names of salts consist of the name of a cation and an anion: sodium benzoate, calcium oxalate, magnesium stearate.

The group that is left after removal of hydroxyl from R-COOH, is called an **acyl** R-CO-. To derive the name of an acyl, the final –*ic* in the name of acid is replaced with the suffix -*oyl* (-*yl*): hexanoic acid – hexanoyl, formic acid – formyl, acetic acid – acetyl, succinic – succinyl, palmitoic acid – palmitoyl, oleic acid – oleoyl.

The systematic IUPAC and common names of some acids, the names of their anions, and acyls are presented in the tables below.

Some saturated monocarboxylic acids

C	Formula	Acid	Anion	Acyl
1	$HCOOH$	formic	formate	formyl
2	CH_3COOH	acetic	acetate	acetyl
3	CH_3CH_2COOH	propanoic (propionoic)	propionate	propionyl
4	$CH_3CH_2CH_2COOH$	butanoic (butyric)	butyrate	butyryl
5	$CH_3(CH_2)_3COOH$	pentanoic (valeric)	pentanoate	pentanoyl
6	$CH_3(CH_2)_4COOH$	hexanoic (caproic)	hexanoate	hexanoyl
12	$CH_3(CH_2)_{10}COOH$	dodecanoic (lauric)	dodecanoate	dodecanoyl
14	$CH_3(CH_2)_{12}COOH$	tetradecanoic (myristic)	tetradecanoate	tetradecanoyl
16	$CH_3(CH_2)_{14}COOH$	Hexadecanoic (palmitic)	palmitate	palmitoyl
18	$CH_3(CH_2)_{16}COOH$	octadecanoic (stearic)	stearate	stearoyl
20	$CH_3(CH_2)_{18}COOH$	eicosanoic (arachidonic)	eicosanoate	eicosanoyl

Some dicarboxylic acids

C	Formula	Acid	Anion	Acyl
2	$HOOC-COOH$	ethandioic (oxalic)	oxalate	oxalyl
3	$HOOC-CH_2-COOH$	propandioic (malonic)	malonate	malonyl
4	$HOOC-(CH_2)_2-COOH$	butandioic (succinic)	succinate	succinyl
5	$HOOC-(CH_2)_3-COOH$	pentandioic (glutaric)	glutarate	glutaryl
6	$HOOC-(CH_2)_4-COOH$	hexandioic (adipic)	adipate	adipoyl
4	$HOOC-CH=CH-COOH$	*trans*-butendioic (fumaric)	fumarate	fumaroyl
4	$HOOC-CH=CH-COOH$	*cis*-butendioic (maleinic)	maleinate	maleinyl

There are two types of aromatic carboxylic acids: arenecarboxylic acids, e.g. benzoic (benzenecarboxylic), phthalic (benzene-1,2-dicarboxylic), 1-naphthoic (naphthalene-1-carboxylic), and arylalkanoic acids, e.g. phenylacetic, cinnamic (*trans*-3-phenylpropenoic).

| benzoic acid | phthalic acid | 1-naphthoic acid | phenylacetic acid | cinnamic acid |
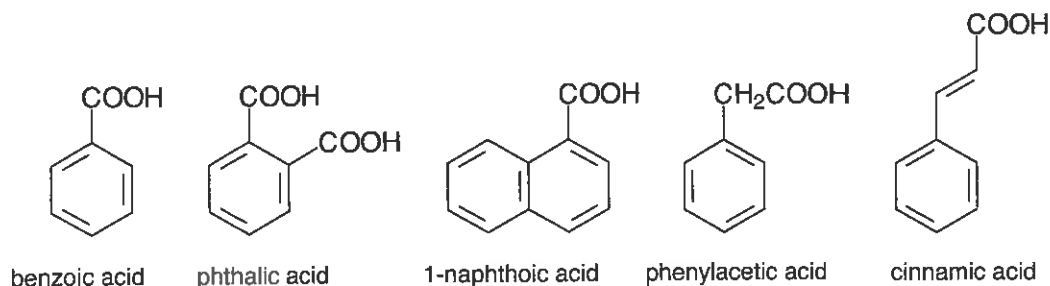
Properties and reactivity of carboxylic acids

The carboxyl group is very polar, it can both donate and accept H atom in hydrogen bonds. The short-chain aliphatic monocarboxylic acids dissolve readily in water, higher homologues (C>6) are water-insoluble. The aliphatic monocarboxylic acids with long chains are called fatty acids because of their appearance.

1. **Acidity.** In aqueous solutions, the carboxyl group partly dissociates:

$$R\text{-}COOH + H_2O \leftrightarrows R\text{-}COO^- + H_3O^+$$
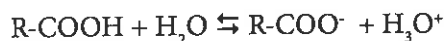
This equilibrium is shifted to the left. Nearly all carboxylic acids are weak acids. If they neutralize bases, the carboxyl groups will become carboxylate ions. Some acids are water-insoluble but they will dissolve in sodium hydroxide solutions since all the alkali salts of carboxylic acids dissolve in water. The alkali soaps of fatty acids are soaps.

2. Strong reductants are capable of reducing carboxylic acids to primary alcohols.

3. Carboxylic acid are involved in many different reactions in which the hydroxyl in a carboxyl group is replaced by another functional group. In such reactions, carboxyl loses its acidity. The products are called acid derivatives: acyl halides, acid anhydrides, esters, amides, and nitriles. All of them can be converted to the corresponding carboxylic acids through hydrolysis.

Carboxylic Acid Derivatives

| acyl halide | acid anhydride | ester | thioester | amide | *N*-alkylamide |
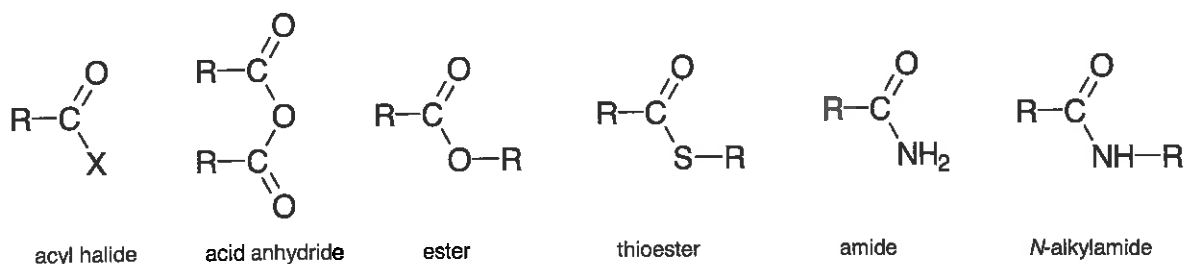
Acyl halides are produced by replacement of the hydroxyl in a carboxyl group by a halogen atom. Acyl halides are too reactive to take part in biological processes. They are used as acylating agents.

Acid anhydrides are produced by removing water from two carboxyl groups which may originate from either one monocarboxylic acid or two different acids. Some dicarboxylic acids easily form cyclic anhydrides when heated. All anhydrides exhibit high reactivity and are potent acylating agents.

E.g. acetic anhydride: $2\ CH_3COOH \rightarrow CH_3CO\text{-}O\text{-}COCH_3 + H_2O$

Esters are derived from an alcohol and carboxylic acid with elimination of water. The hydroxyl of the carboxyl is replaced by the alkoxy (-OR) or aryloxy (-OAr) group, general formula R-CO-O-R'.

An example of esterification: $CH_3COOH + HO\text{-}CH_2CH_3 \rightarrow CH_3CO\text{-}O\text{-}CH_2CH_3 + H_2O$

Esters of carboxylic acid are named as alkyl (aryl) carboxylates, so the example is ethyl acetate.

Esters are mostly non-polar compounds, insoluble in water. Hydrolysis of esters gives parent acid and alcohol. Esters are widely distributed in nature. Many simple esters are responsible for the pleasant odour of a lot of fruits and flowers. A very important group of esters involves fats and vegetable oils, the esters of long-chain fatty acids and glycerol.

Amides can be prepared by the acylation of ammonia or amines. The general formula of amide from ammonia is $R\text{-}CO\text{-}NH_2$; those derived from amines are R-CO-NHR or $R\text{-}CO\text{-}NR_2$.

N-alkylamide
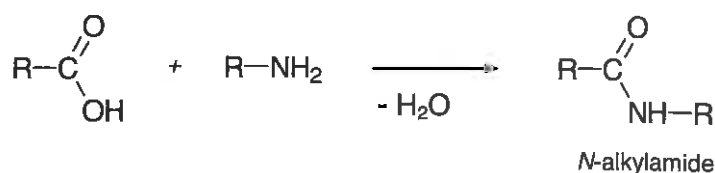
Simple amide can be prepared by heating ammonium salts of acids:

$R\text{-}COO^- NH_4^+ \rightarrow R\text{-}CO\text{-}NH_2 + H_2O$.

Names of amides are based upon the names of related acids. The suffix –(o)ic acid is replaced by the suffix -amide. If the nitrogen atom bears substituents, these are located by a capital N before the name of the substituent. For example, $CH_3CO\text{-}NHCH_3$ is N-methylacetamide.

Intramolecular cyclic amides of 4- and 5-amino acids are called **lactams**.

4-aminobutanoic acid   butano-4-lactam
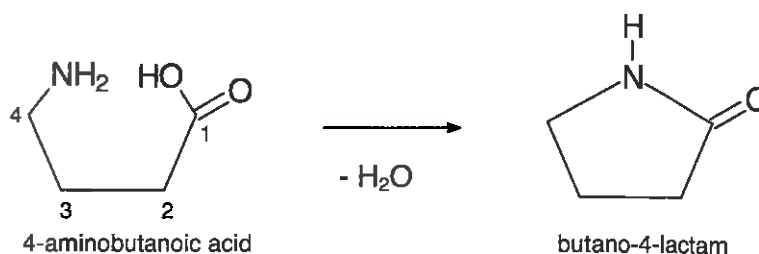
Properties of amides are influenced by the presence of a very polar group causing that nearly all unsubstituted amides are solids. In contrast to amines, amides are not basic and not very reactive. Hydrolysis of amide bonds gives carboxylic acid and amine or ammonia. Dehydration of unsubstituted amides produces nitriles ($R\text{-}CONH_2 \rightarrow R\text{-}C{\equiv}N + H_2O$). Amides occur widely in nature, mainly as proteins and peptides. The peptide bond in proteins is a specific type of the amide bond formed in the reaction of the α-amino group of an amino acid with the α-carboxyl of another amino acid.

Glutamine and asparagine are the monoamides of glutamic and aspartic acids, respectively. They are both standard (coded) amino acids.

Paracetamol CH_3CO-NH-C_6H_4-OH (acetaminophen), is the most common analgesic and antipyretic.

Urea NH_2CONH_2 is the diamide of carbonic acid. In mammals, it is excreted into urine as an end product of amino acid catabolism. Nearly all α-amino nitrogens of metabolized proteins are eliminated from the body in this way. Gentle heating of urea produces biuret:

$2\ H_2N$-CO-$NH_2 \rightarrow H_2N$-CO-NH-CO-$NH_2 + NH_3$.
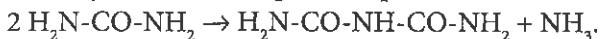
Guanidine, $(NH_2)_2C$=NH (iminourea), is a relatively strong base, present in the side chain of the basic amino acid arginine.

Nitriles contain a cyano group, -C≡N, and may be regarded as alkyl and aryl derivatives of hydrogen cyanide (HCN). The general formula is R-C≡N. These organic cyanides are real acid derivatives, because they can be formed by dehydration of amides and can again reconvert to amides, if subjected to hydrolysis. Nitriles are only rarely found in natural products. Despite their structural relationship to HC≡N, nitriles are only moderately toxic. **Acetonitrile**, CH_3-C≡N, is a common solvent.

Substituted Carboxylic Acids

In addition to carboxyl, substituted acids have another functional group such as halogen, hydroxyl, oxo or amino group. The presence of two different groups in molecules is often the cause of chirality, hence numerous naturally occurring substituted acids exhibit optical activity.

Halogen acids are mostly prepared as raw materials for organic syntheses. Halogen atoms in the aliphatic chain of carboxylic acids increase the strength of acid. E.g. trichloroacetic acid, CCl_3COOH, is a strong acid (used occasionally as a reagent for deproteinization).

Hydroxy acids

When 4- and 5-hydroxy acids are heated, stable five- and six-membered rings, respectively, are produced through formation of intramolecular esters called **lactones**. For example, 5-hydroxypentanoic acid forms a six-membered lactone:

5-hydroxypentanoic acid   pentano-5-lactone
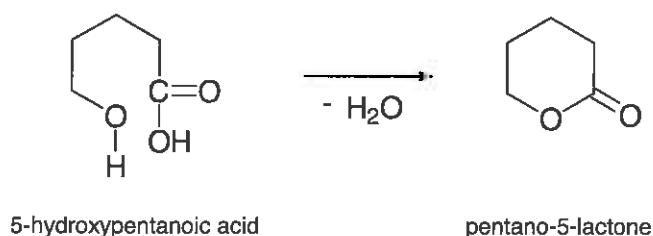
Lactic acid CH_3-$CH(OH)$-$COOH$ (2-hydroxypropanoic acid, *acidum lacticum*, anion lactate) is a syrupy liquid. Lactate is the end product of glycolysis under anaerobic conditions, e.g. in the muscle that is working with high intensity. Lactate is the product of lactic fermentation of sugars (kefir milk, yoghurt, sauerkraut). Dehydrogenation of lactate gives pyruvate; the reaction is reversible, it needs the cofactor NAD^+ and enzyme lactate dehydrogenase.

lactate   pyruvate
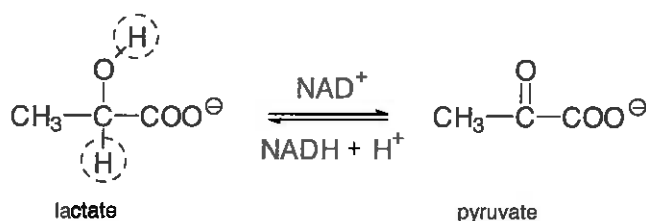
Tartaric acid, HOOC-CH(OH)-CH(OH)-COOH (2,3-dihydroxybutanedioic acid), contains two chiral centers but both of them are equivalent. Tartaric acid occurs in grapes, wine, and fruit juices.

Malic acid HOOC-CH$_2$-CH(OH)-COOH (hydroxybutandioic acid, *acidum malicum*, salts malates) was primarily isolated from apples (Lat. *malum*). It is the intermediate of the citric acid cycle, in which it is produced by the hydratation of fumarate. Dehydrogenation of malate with NAD$^+$ cofactor gives oxaloacetate:

malate   oxaloacetate
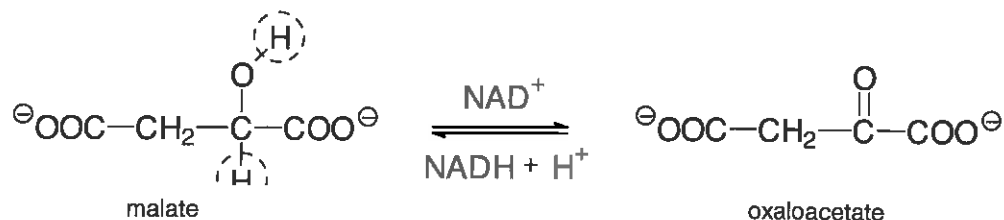
Citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid, *acidum citricum*, salts citrates) is a triprotic hydroxy acid. It is abundant in fruits and vegetables. In the mitochondria, it is formed by the condensation of acetyl-coenzyme A with oxaloacetate in the first reaction of the citric acid cycle. The next step is the isomeration to isocitric acid. Citric acid is produced by industrial biotechnology in huge quantities required for food industry; citric acid is an acidulant in numerous soft drinks. The solution of trisodium citrate (natrii citras) serves as an anticoagulant, because citrate binds Ca^{2+} ions and so prevents blood clotting.

citric acid   isocitric acid
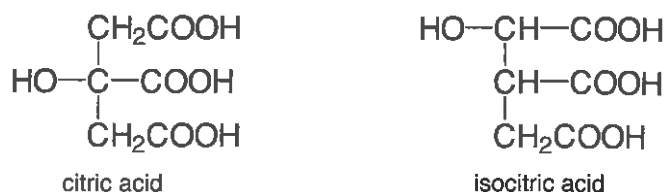
Salicylic acid (2-hydroxybenzoic acid, *acidum salicylicum*) was first isolated from the willow tree (Lat. *salix*). It is a colourless crystalline substance, almost insoluble in water. It has antiseptic, antipruritic, and anti-inflammatory effects. It is used mainly in dermatology.
Acetylsalicylic acid (2-acetoxybenzoic acid) is an important and famous derivative of salicylic acid. In doses about 0.5 – 3.0 g/day it is a commonly used analgesic-antipyretic (e.g. Aspirin). In doses about 50 mg/day it prevents the aggregation of blood platelets.

salicylic acid   acetylsalicylic acid
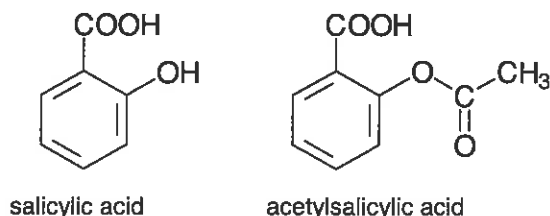
Oxo acids

contain at least one oxo group (carbonyl group) in their carbon chains, designated by the prefix *oxo-* in systematic names. They react as both ketones and enols (keto-enol tautomerism).
Pyruvic acid is the simplest oxo-carboxylic acid, CH$_3$-CO-COOH (2-oxopropanoic acid). It is the key intermediate in the glucose metabolism, yielding lactic acid by hydrogenation.
Oxaloacetic acid, HOOC-CO-CH$_2$-COOH (2-oxobutanedioic acid), and its homologue **2-oxoglutaric acid**, HOOC-CO-CH$_2$-CH$_2$-COOH (2-oxopentanedioic acid), are both intermediates of the citric acid cycle and amino acid metabolism.

Acetoacetic acid, CH_3-CO-CH_2-COOH (3-oxobutanoic acid), is an important intermediate in the metabolism of fatty acids. It is easily decarboxylated to acetone.

Amino acids

have both acidic carboxyl groups and the basic amino groups. Therefore they are amphoteric and exist as dipolar ions (amphions) in neutral solutions. 4-Amino and 5-amino acids are able to form intramolecular cyclic amides called **lactams** (see above). Amino acids in proteins (twenty coded amino acids) are L-α-amino acids, R-CH(NH_2)-COOH, and have common names. E.g. 2-aminopropanoic acid is **alanine**. Details about their structures and names will be given in Chapter 15.

Amines

can be derived by replacing one or more H atoms in the molecule of ammonia by the alkyl groups or aryl groups. Amines are divided into primary R-NH_2, secondary R^1-NH-R^2, and tertiary $R^1R^2R^3N$. Some secondary or tertiary amines may have nitrogen enclosed in a cycle.

Nomenclature. The names of primary amines consist of the names of alkyl or alkanes and the suffix *-amine* or *-diamine*, e.g.: CH_3-CH_2-NH_2 ethylamine (ethanamine),
NH_2-$CH_2CH_2CH_2CH_2$-NH_2 tetramethylendiamine (butane-1,4-diamine).
The names of secondary (tertiary) amines are formed according to scheme *di(tri)alkylamine, alkyl¹alkyl²amine, alkyl¹alkyl²alkyl³amine* or *N*-substituted primary amines:
CH_3-NH-CH_3 dimethylamine,
$(CH_3)_2$N-$CH_2CH_2CH_3$ dimethylpropylamine (*N,N*-dimethylpropanamine).
Some aromatic amines have trivial names, e.g. aniline, benzidine.
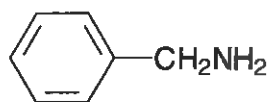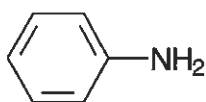
benzylamine   aniline   benzidine
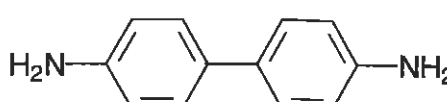
Basicity of amines. The lone electron pair of nitrogen gives a weakly basic character and nucleophilic properties to amines. In the aqueous solutions, amines behave as bases and their solutions are alkaline (R-NH_2 + H_2O ⇆ R-NH_3^+ + OH^-). Aliphatic amines are stronger bases compared to ammonia. On the other hand, aromatic amines, with regard to the conjugation of the unshared electron pair of nitrogen in the aromatic cycle, are weaker bases compared to ammonia. In the series of aliphatic amines we can observe the steric effect of alkyls influencing the basicity of trialkylamines. Thus, the basicity of amines decreases in the following order:
dialkylamines > alkylamines > trialkylamines > NH_3 > arylamines.

The reaction of amines with acids gives alkylammonium salts: R-NH_2 + HCl → R-NH_3^+ Cl^-.
A base liberates a free amine from the salt: R-NH_3^+ Cl^- + NaOH → R-NH_2 + H_2O + NaCl.
Alkylammonium salts hydrolyze to acidic reaction: R-NH_3^+ + H_2O ⇆ R-NH_2 + H_3O^+.

Alkylation of amines. Alkylation of primary amines produces secondary dialkylamines, then tertiary trialkylamines. Further alkylation gives **quaternary ammonium salts** R_4N^+ X^-. The tetravalent nitrogen atom does not have the lone electron pair, therefore it is not basic. The solutions of tetraalkylammonium salts are neutral. On the contrary, tetraalkylamonium hydroxides R_4N^+ OH^- are strong hydroxides, like NaOH.
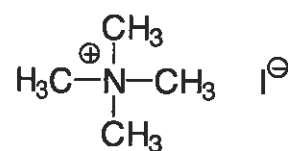
tetramethylamonium iodide

Reaction with aldehydes and ketones. The reaction of primary amines with carbonyl compounds gives unstable alkylamino compounds, which are stabilized by the removal of water to form N-substituted imino compounds called Shiff´s bases R-CH=N-R¹. Amines react with the anomeric (hemiacetal) hydroxyl of saccharides to give N-glycosides.

Oxidation. Some amines are sensitive to oxidation agents. They can produce various compounds. Oxidative deamination of primary amines, catalyzed by monoamine oxidases, is the way of inactivation of some biogenic amines.

Reaction with nitrous acid. Primary aromatic amines give diazonium salts with nitrous acid (in the presence of a strong acid). This reaction is called diazotation. Arenediazonium salts react with aromatic amines or phenols to **azo compounds** (Ar-N=N-Ar). Secondary amines give **nitrosamines** $R^1R^2 N-N=O$, compounds having a nitroso group -N=O bound to nitrogen. Nitrosoamines are considered as cancerogenic agents, their formation in the body is partially caused by nitrites consumed in meat products (smoked food, pates, etc.).

$$R-\underset{\underset{R'}{|}}{N}H \;+\; HO-N{=}O \;\xrightarrow[-H_2O]{H^+}\; R-\underset{\underset{R'}{|}}{N}-N{=}O$$

secondary amine   nitrosamine
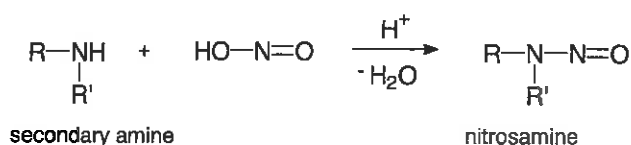
Some Important Amines

Ethylenediamine $H_2N-CH_2-CH_2-NH_2$ is used for the production of **ethylenediaminetetraacetic acid** (EDTA), an important chelating agent, which forms chelates with polyvalent cations of metals. It is used as an additive to washing powders (it softens water, because it binds Ca^{2+} ions) and reagent in analytical chemistry.
Aniline $C_6H_5-NH_2$ (phenylamine) is an oily liquid, which is important as raw material in the chemical industry.

$$\begin{array}{ccc} HOOC-CH_2 & & CH_2-COOH \\ \diagdown & & \diagup \\ & N-CH_2-CH_2-N & \\ \diagup & & \diagdown \\ HOOC-CH_2 & & CH_2-COOH \end{array}$$

EDTA
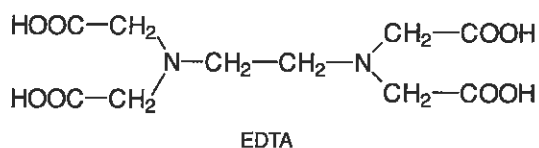
Aniline is a relatively toxic compound. It causes oxidation of hemoglobin to methemoglobin and the subsequent hemolysis, the premature destruction of erythrocytes.

Biogenic Amines

are formed by decarboxylation of coded amino acids. This reaction needs an enzyme (decarboxylase) and a cofactor (pyridoxal phosphate). Biogenic amines usually exhibit various physiological effects.

$$R-\underset{\underset{NH_2}{|}}{C}H-COOH \;\xrightarrow[-CO_2]{}\; R-CH_2-NH_2$$
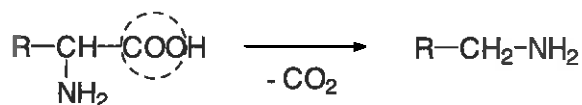
Ethanolamine $H_2N-CH_2CH_2-OH$ (2-aminoethanol) is produced by the decarboxylation of serine, it belongs to the building components of some phospholipids (phosphatidylethanolamine). Its methylation produces choline. **Histamine**, 2-(imidazole-4-yl)ethylamine, is the decarboxylation product of histidine. It plays an important role in inflammatory and allergic reactions and acts as a neurotransmitter in the CNS. **Tyramine** and

tryptamine are formed by the decarboxylation of tyrosine and tryptophane, they are important for the formation of hormones and a range of alkaloids in plants.
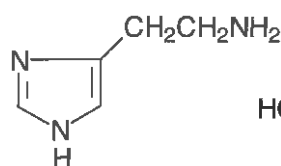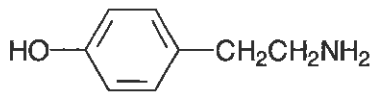
histamine   tyramine   tryptamine
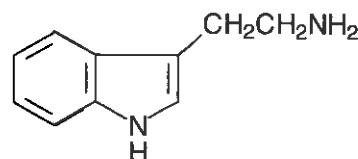
Catecholamines

The decarboxylation of 3,4-dihydroxyphenylalanine (DOPA) gives **dopamine** (3-hydroxytyramine). Further transformations give hormones of the adrenal cortex **noradrenaline** and **adrenaline**. Moreover, noradrenaline is the neuromediator on the adrenergic synapses. The above mentioned three substances with important physiological and pharmacological effects are called **catecholamines** (they have the structure of o-diphenols similar to pyrocatechol, benzene-1,2-diol).
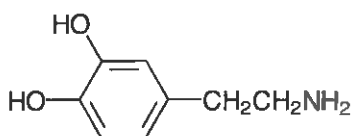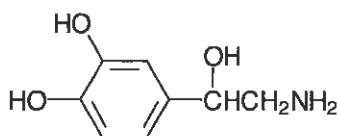
dopamine   noradrenaline   adrenaline
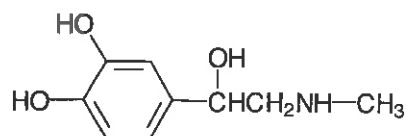
Phenethylamines are natural or synthetic derivatives of phenethylamine (2-phenylethylamine), which is produced by decarboxylation of phenylalanine. Their common feature is the substantial central stimulative effect (ephedrine, amphetamine, metamphetamine, ecstasy etc.)

Quaternary Ammonium Salts

Choline (2-hydroxyethyl)trimethylammonium, is the component of phosphatidylcholines and sphingomyelins. The positive charge on the nitrogen atom is compensated by any physiological anion, most often by a chloride. **Acetylcholine** (ester of choline and acetic acid) belongs among important neurotransmitters; it is the transmitter substance on cholinergic synapses.
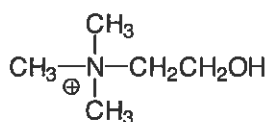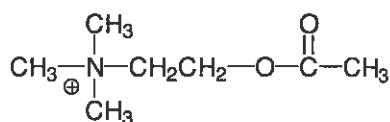
choline   acetylcholine

Nitro compounds

Nitro compounds contain a nitro group $-NO_2$ bound to the carbon atom of an alkyl ($R-NO_2$, nitroalkanes) or aryl ($Ar-NO_2$, nitroarenes). The presence of the nitro group is expressed by the prefix *nitro-*, e.g. nitromethane CH_3-NO_2, nitrobenzene $C_6H_5-NO_2$.

It is important to note the structural similarity with the esters of nitric acid (alkyl nitrates) $R-O-NO_2$ and nitrous acid (alkyl nitrites) $R-O-N=O$. Nitro compounds are usually toxic substances with a yellow colour and nearly all of synthetic origin. Aromatic nitro compounds are usually prepared by the reaction of a hydrocarbon with the mixed acid (HNO_3 and H_2SO_4). The reduction of aromatic amino acids gives aromatic amines.

Nitrobenzene $C_6H_5-NO_2$ is a yellow liquid of a bitter almond odour, insoluble in water. It is poisonous, dangerous to inhale and easily absorbed by the skin. It transforms hemoglobine to methemoglobine (oxidizes Fe^{2+} to Fe^{3+}).

Trinitrotoluene (2,4,6-trinitrotoluene, TNT) is one of the most important explosives. In other polynitro compounds we can also observe their strong oxidation properties. The typical examples are **hexogen** (1,3,5-trinitro-1,3,5-triazacyclohexane) and its homologue **octogen**.

Picric acid (2,4,6-trinitrophenol) is a crystalline substance of a rich yellow colour, poorly soluble in water. Its salts picrates are explosive, especially picrates of heavy metals. Because of the negative mesomeric effect of three nitro groups, picric acid is a relatively strong acid.

TNT   hexogen   octogen   picric acid
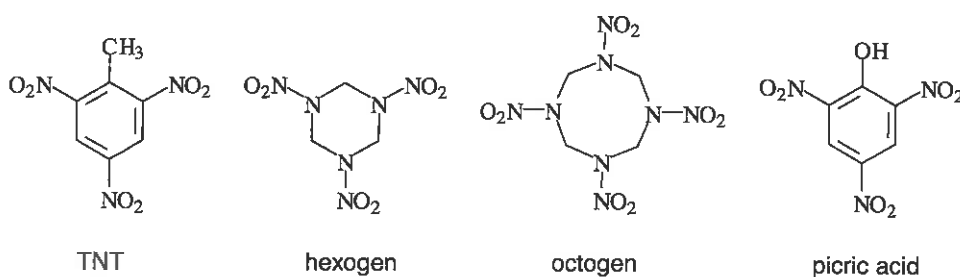
12 HETEROCYCLIC COMPOUNDS

Heterocyclic compounds have in addition to C atoms in the cycle also one or more atoms of other elements (heteroatoms), most often nitrogen, oxygen and sulfur. Derivatives of heterocycles are widespread in the nature. The five- and six-membered heterocycles are the most stable. The bonding angles in these heterocycles are close to those corresponding with sp^3 and sp^2 hybridization. Saturated heterocycles have often properties similar to that of the aliphatic compounds (cyclic ethers, cyclic secondary amines). Maximally unsaturated heterocycles are substantially more stable. If they possess the π-molecular orbital with a sextet of delocalized electrons, the cycle is in its stability similar to benzene and the compound has aromatic character. A range of heterocyclic compounds have trivial names, which are commonly used instead of the systematic names. Numbering the heterocycles starts from the heteroatom, the order of preference being O > S > N. Below we present the main heterocycles and their common names.
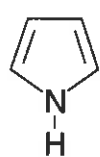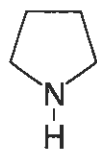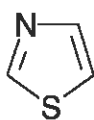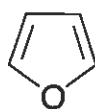
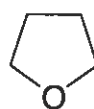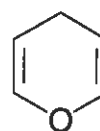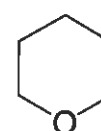pyrrole   pyrrolidine   imidazole   pyridine   pyrimidine   pyrazine
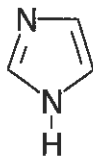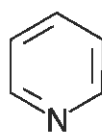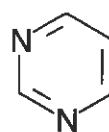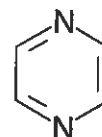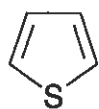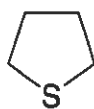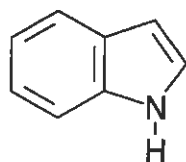
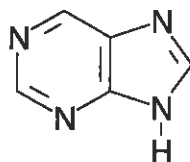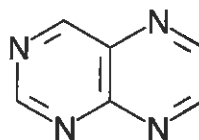thiophene   thiolane   thiazole   furan   tetrahydrofuran   pyran   tetrahydropyran
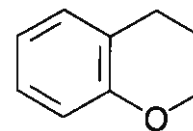
indole   purine   pteridine   chroman

Pyrrole is a five-membered heterocycle with one nitrogen atom. The free electron pair of nitrogen participates in conjugation with two double bonds. The consequence is planarity and aromatic character of the ring and the fact, that basicity of nitrogen is practically diminished. The biochemically important pyrrole derivatives are **cyclic tetrapyrroles** (red heme, green chlorophyll, pink cyanocobalamine). Degradation of heme results in the formation of **linear tetrapyrroles** (green biliverdin, orange bilirubin, urobilinoids).

The basic structure of heme is cyclic tetrapyrrole **porphin**, four pyrrole rings are joined by four methine bridges =CH– in the positions 2 and 5 (positions α). The derivatives of porphin with various substituents are called **porhyrins**. Porphin and porphyrins are planar, completely conjugated systems of double bonds and therefore intensively coloured.
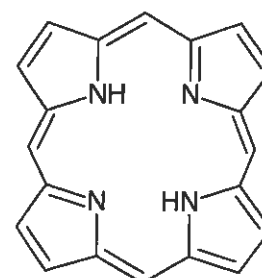
Pyrrolidine is formed by the complete hydrogenation of pyrrole, it has properties of the secondary amines. It is markedly basic, protonization produces pyrrolidinium cation. Its derivatives include amino acids **proline** (pyrrolidin-2-carboxylic acid) and its derivative **4-hydroxyproline**, both are contained in the protein collagen.

pyrrolidine   pyrrolidinium   proline   4-hydroxyproline
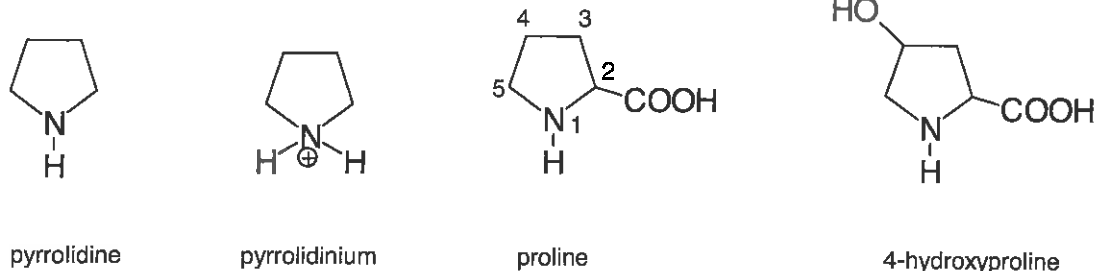
Indole is benzopyrrole. Similarly to pyrrole, it is not basic. The essential amino acid **tryptophan** is 2-amino-3-(3-indolyl)propanoic acid. Its derivative is the biogenic amine **tryptamine** and **serotonin** (5-hydroxytryptamine), the mediator of the nervous excitement in the brain.

indole   tryptophane   tryptamine (R = H), serotonin (R = OH)
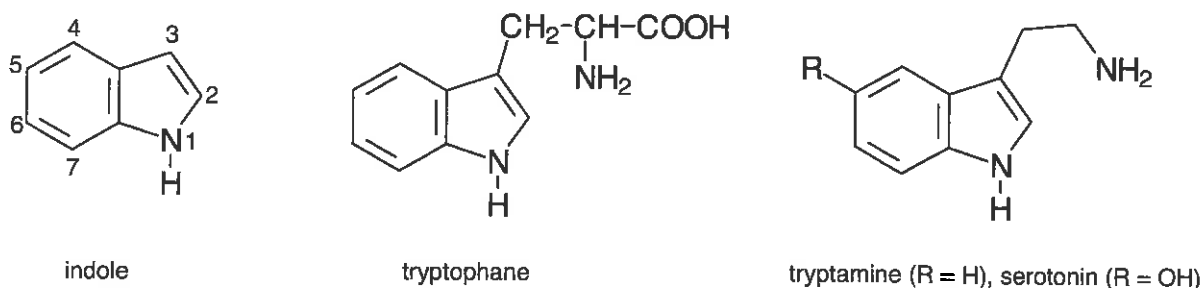
Imidazole is weakly basic. The nitrogen atom N3 can bind proton to form imidazolium cation. The N1 nitrogen atom is not basic, because its electron pair participates in conjugation with the double bonds. The imidazole derivative is the essential amino acid **histidine**, 2-amino-3-(4-imidazolyl)propanoic acid. The protonized imidazole is imidazolium and its acid-base transformations are the principle of buffer functions of proteins. The decarboxylation of histidine provides **histamine**, one of the mediators of inflammatory and allergic reactions.

imidazole   imidazolium   histidine   histamine
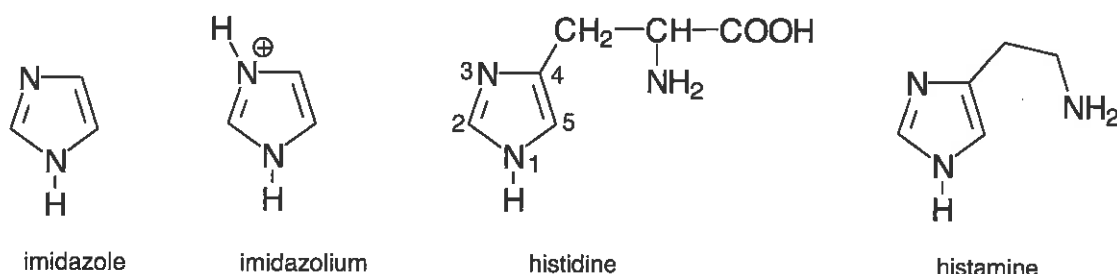
Pyridine itself has no biochemical importance. **Nicotinic acid** (pyridine-3-carboxylic) and its amide, **nicotinamide**, are included in the group of B vitamins. Sometimes they are given a common name niacine. Nicotinamide is the component of NAD^+ (nicotinamide adenine dinucleotide) that is coenzyme of many dehydrogenases. NAD^+ contains pyridinium ring bound to C1 of ribose, the nitrogen atom is tetravalent with a positive charge (oxidized form of coenzyme). In the dehydrogenation reactions two hydrogen atoms are removed from the

substrate. One is bound to position 4 of the pyridinium ring as hydride anion H⁻ to produce electroneutral reduced form NADH. The second hydrogen is released to surroundings as a proton H⁺.

| nicotinic acid | nicotinamide | part of NAD⁺ (oxidized form) | part of NADH (reduced form) |
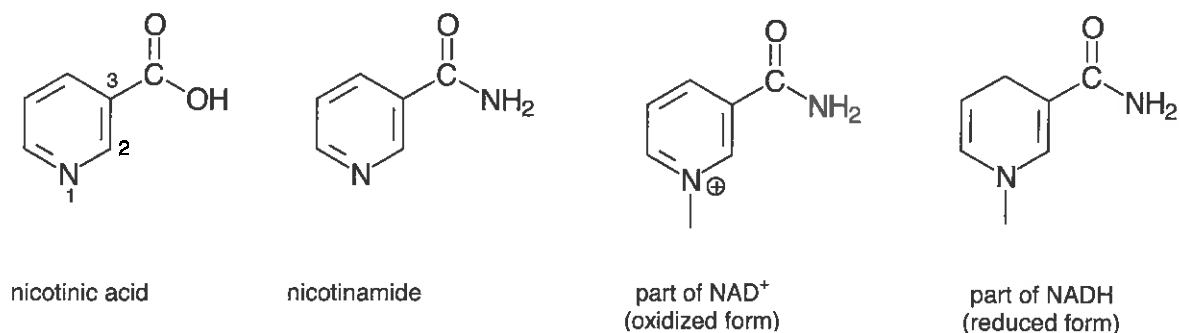
Vitamin B₆ is the name given to three related derivatives of 3-hydroxy-5-hydroxymethyl-2-methylpyridine. All of them have primary alcohol group and phenolic hydroxyl and the same biological activity but differ in the group bound at C4. **Pyridoxine** has a primary alcohol group, **pyridoxal** an aldehyde group, and **pyridoxamine** an aminomethyl group. Pyridoxal-5-phosphate is the coenzyme of aminotransferases and decarboxylases in the transformation of amino acids.


| pyridoxine | pyridoxal | pyridoxamine |
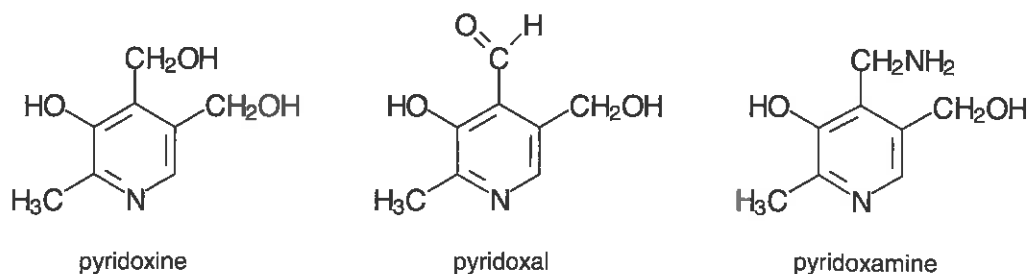
Three pyrimidine derivatives **cytosine** (2-hydroxy-4-aminopyrimidine), **uracil** (2,4-dihydroxy pyrimi dine), and **thymine** (2,4-dihydroxy-5-methylpyrimidine) are components of nucleic acids and some important nucleosides and nucleotides. These compounds exist in two tautomeric forms. The lactam form is the more stable and prevailing to the lactim form with the enolic hydroxyl.

| cytosine | thymine | uracil (lactim) | uracil (lactam) |
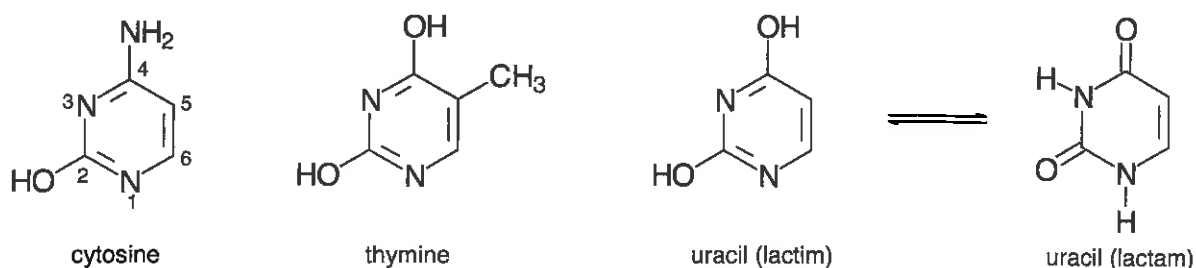
Purine is the condensed system of pyrimidine and imidazole. It has special numbering. Its derivatives are **adenine** (6-aminopurine) and **guanine** (2-amino-6-hydroxypurine), most widespread purine bases in the nucleic acids and nucleosides. Both bases are linked by *N*-glycosidic bond through nitrogen N9 to pentose.


purine   adenine   guanine
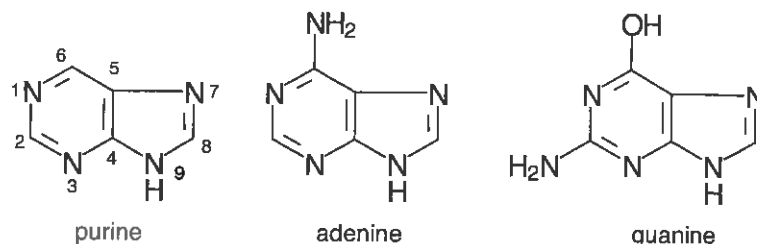
Hydroxyderivatives of purine are formed from the purine bases during the catabolism of nucleotides in cells, adenine gives **hypoxanthine** (6-hydroxypurine) and guanine **xanthine** (2,6-dihydroxypurine). Both these substances are hydroxylated by xanthine oxidase to uric acid.

hypoxanthine   xanthine   uric acid   ammonium hydrogen urate
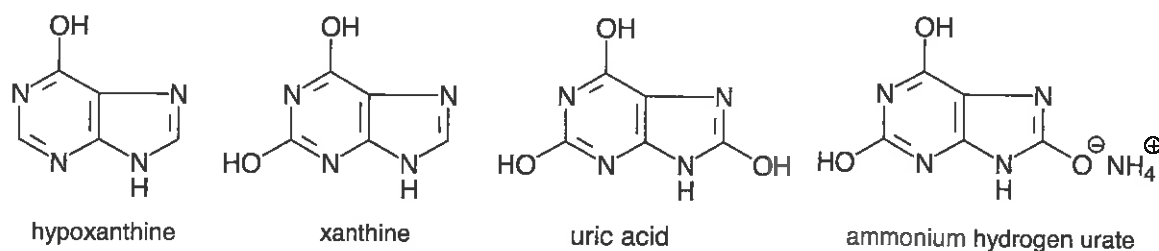
Uric acid (2,6,8-trihydroxypurine, *acidum uricum*, salts urates) is a very weak diprotic acid with substantial reducing properties. It belongs to the natural antioxidants, which reduce reactive oxygen species in the body. It is only slightly soluble in water, mainly at pH < 5.5. The solubility of uric acid rapidly increases with alkalization, when its salts hydrogen urates are formed, in the strongly alkaline environment also urates. Uric acid and hydrogen urates can precipitate in the efferent urinary tract and form renal stones (urate urolithiasis). Adult man excretes up to 1 g of uric acid or urates daily. Under pathological conditions it is deposited into the joints and tissues (gout).

N-Methylderivatives of xanthine are well-known alkaloids **caffeine, theobromine**, and **theophylline**. They are called methylxanthines.

Pteridine is the condensed system of pyrimidine and pyrazine. The pteridine derivatives include co-factors of many enzymes: pterin cofactors, folate and flavine coenzymes. **Folic acid** (pteroylglutamic, *acidum folicum*, folate) contains trisubstituted pteridine, *p*-aminobenzoic acid, which is via the amide bond linked to glutamic acid. Animals are not able to synthesize this acid, it is an important **essential** factor (vitamin). Its lack in food causes anaemia.

folic acid
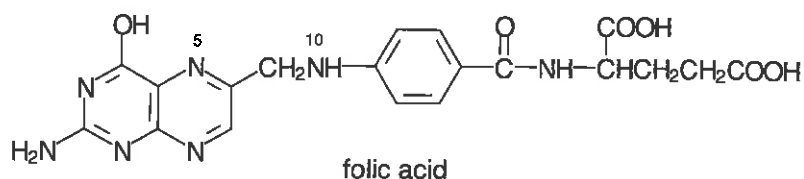
Benzopteridine has one more benzene ring attached. Its 2,4-dioxoderivative is **isoalloxazine**, the part of **ribo-flavin** (6,7-dimethyl-9-ribitylisoalloxazine, vitamin B_2).

benzo[*g*]pteridin   isoalloxazin   riboflavin
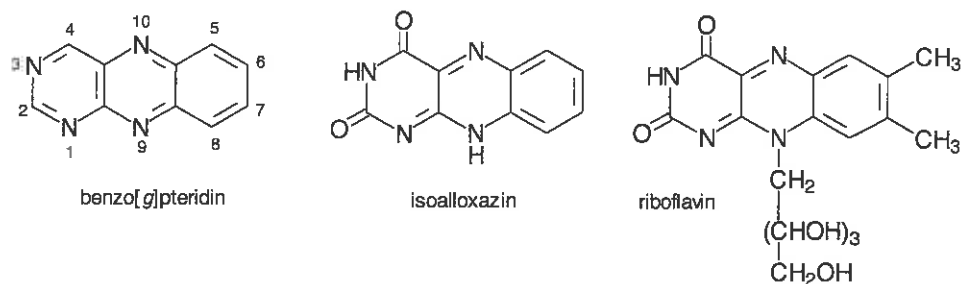
Riboflavin is a yellow vitamin (from the Latin *flavus*), which is the component of cofactors FAD (flavin adenine dinucleotide) and FMN (flavin mononucleotide) of some dehydrogenases. Their function is to remove two hydrogen atoms from the -CH_2-CH_2- fragment in the molecule of substrate and to bind them to the nitrogen atoms of a cofactor. The example is the dehydrogenation of succinate to fumarate.

Oxygen containing heterocycles

The five-membered **furan** has no biochemical importance. The hydrogenated furan is **tetrahydrofuran** and is used as a solvent. The tetrahydrofuran ring is the base of cyclic forms of monosaccharides called **furanoses** e.g. ribose is D-ribofuranose. The six-membered **pyran** has no biochemical importance. The pyran ring occurs in many plant substances, mainly condensed with the benzene ring. The saturated cycle is **tetrahydropyran** and is present in the cyclic forms of monosaccharides called **pyranoses. Tocopherol** (vitamin E) is the mixture of several substances derived from **chroman** (the saturated pyran condensed to the benzene ring).

Sulfur containing heterocycles

Thiophene itself has no biochemical importance. **Thiolane** (tetrahydrothiophene) is the component of biotin. Biotin is important for the carboxylation reactions, e.g. the carboxylation of pyruvate gives oxalacetate (substrate of the citrate cycle). The carboxyl group of carboxybiotin is bound to nitrogen.

1,2-Dithiolane is the five-membered saturated heterocycle with two sulfur atoms. Its derivative is the **lipoic acid** (1,2-dithiolane-3-pentanoic), which is the cofactor for the oxidative decarboxylation of pyruvate and other 2-oxoacids. In the reduced form (dihydrolipoic) it has two -SH groups.

Thiazole is the five-membered heterocycle with the N and S atoms in positions 1,3. **Thiamine** (vitamin B_1) contains substituted pyrimidine connected by the methylene group to nitrogen of the substituted thiazole. Because nitrogen in thiamine is tetravalent, it has positive charge. Thiamine diphosphate is the cofactor during the oxidative decarboxylation of pyruvate and other 2-oxoacids.
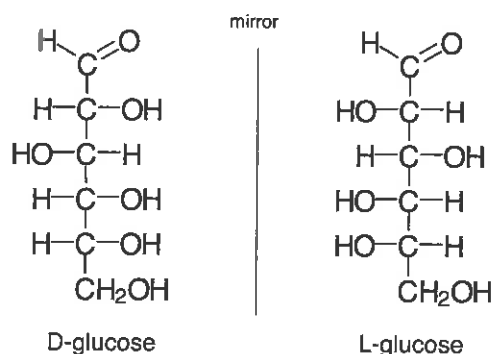
13 SACCHARIDES

Saccharides are polyhydroxyaldehydes and polyhydroxyketones. **Monosaccharides** (simple sugars) cannot be hydrolyzed to smaller carbohydrate units. **Disaccharides** contain two monosaccharide units joined by O-glycosidic bond. **Polysaccharides** contain thousands of monosaccharide units.

Monosaccharides are classified according to the nature of carbonyl group and number of atoms. If the group is an aldehyde, the sugar is an aldose. If it has oxo group, the sugar is a ketose. The general names are formed from the Greek numeral referring to the number of C atoms. Aldoses have the ending -*ose* (triose, tetrose, pentose, hexose), ketoses have ending -*ulose* (tetrulose, pentulose). The simplest monosaccharides are **glyceraldehyde** and **dihydroxyacetone**. Glyceraldehyde has one chiral carbon (C2), therefore makes two enantiomers, which are mirror images. These are called D and L.
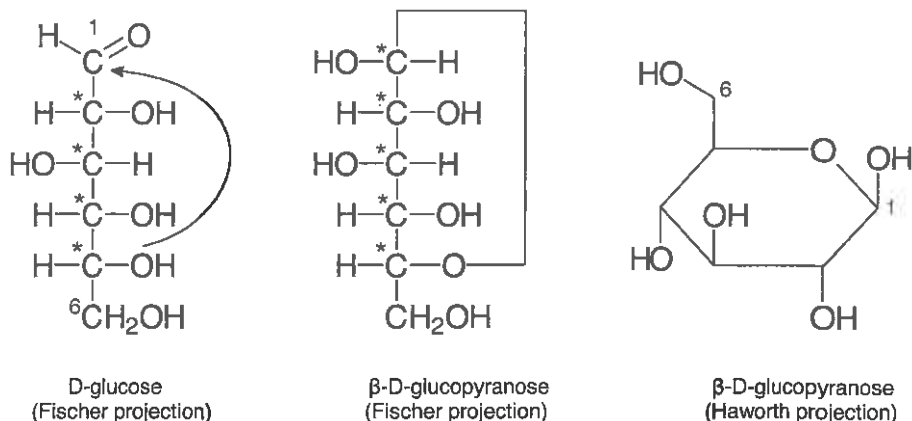
D-glyceraldehyde

dihydroxyacetone
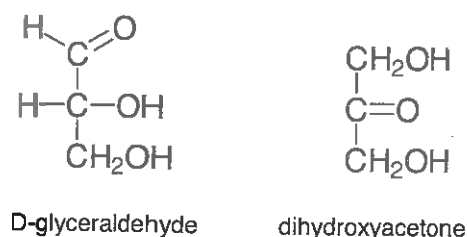
Configuration of Monosaccharides

The monosaccharides with the higher number of carbon atoms have more chiral center in the molecule and the number of their possible stereoisomers is also higher. Fischer projections are used to identify the configuration at the chiral centers of a sugar. The sugar is oriented so that the carbon skeleton is vertically aligned with the aldehyde or keto group at the top and the alcohol at the bottom, so that vertical substituents are shown below the plane of the page, while horizontal substituents are shown above. The projections of the vertical and horizontal substituents are shown as plain vertical and horizontal lines, giving the Fischer projection of the chiral center. Monosaccharide is assigned to the D or the L series according to the configuration at the highest-numbered centre of chirality. This asymmetrically substituted carbon atom is called the configurational carbon. E.g., in pentoses it is carbon number 4, in hexoses number 5. Thus if the hydroxy group projects to the right in the Fischer projection (on the same side as in D-glyceraldehyde), the sugar belongs to the D series. If the OH group on the configurational carbon is to the left in the Fischer projection, then the compound is L-sugar. **Enantiomers** are pairs of stereoisomers, which differ in configuration at all chiral centres. They rotate the plane of polarized light by the same value, but in opposite direction. As seen from the formulas bellow, D- and L-glucose differ in configuration at all four chiral carbon atoms. **Racemate** is the optically inactive mixture of two enantiomers in ratio 1:1.

mirror

D-glucose

L-glucose

Cyclic forms of monosaccharides

Molecules of monosaccharides spontaneously form cyclic forms in solutions. The intramolecular addition of the hydroxyl group to carbonyl occurs and **cyclic hemiacetals** are produced. In case of aldohexoses it is usually hydroxyl group at C5, in aldopentoses at C4. The resulting oxygen heterocycle is the derivative of hydrogenated pyran or furan and is generally called **pyranose** (six-membered) or **furanose** (five-membered), respectively. Cyclic forms are preferred in solutions.

D-glucose
(Fischer projection)

β-D-glucopyranose
(Fischer projection)

β-D-glucopyranose
(Haworth projection)

After monosaccharide cyclizes, the carbonyl carbon becomes a new chiral center with two possible configurations. The two newly formed stereoisomers are designed as α and β. The carbon atom is known as the anomeric carbon and the α and β forms are called **anomers**. The configuration of cyclic forms can be expressed by Fischer projection (α-anomer has the same configuration on C1 and the last chiral C, β-anomer reverse configuration), but Haworth projections are used more often.

Rules for drawing Haworth projections
The atoms of a heterocycle lie in one plane, perpendicular to the plane of the paper, with the bottom margin closer to the observer. Bonds directed upwards from the atom are above the plane of the cycle, bonds directed downwards are below the plane. Anomeric carbon is on the right-hand end, oxygen heteroatom is behind. The atoms are numbered clockwise around the ring. Groups that appear to the right of the modified Fischer projection appear below the plane of the ring; those on the left appear above. In the Haworth projections, α-anomer of D-monosaccharides has -OH group below the plane of the cycle, β-anomer above the plane. The -CH$_2$OH group is directed upwards in D-sugars. The hydrogen atoms are often not displayed.

Properties of monosaccharides
All monosaccharides are highly polar, well soluble in water. They do not dissociate in the aqueous solutions, they are typical **non-electrolytes**. They are mostly sweet.

D-Ribose and **2-deoxy-D-ribose** are structural components of nucleotides and nucleic acids. Both monosaccharides occur in furanose forms.
**Deoxyribose** lacks the hydroxyl group in position 2.
D-Glucose is the most important and in the form of polymers the most abundant sugar in the nature. Free glucose can be found in sweet fruits (about 1-5 %) and honey (~ 30 %). Humans have free glucose in blood (3.3-5.5 mmol/l).
D-Mannose is 2-epimer of D-glucose, i.e. these sugars differ only in the configuration of C-2. Mannose is present in some plants, e.g. in polysaccharides of carob. In human body, it is a component of glycoproteins.
D-Galactose differs from D-glucose in configuration at C-4, thus it is the 4-epimer of glucose. It occurs in lactose (milk sugar), glycolipids, and glycoproteins. In plants it is found in gums (fibre).
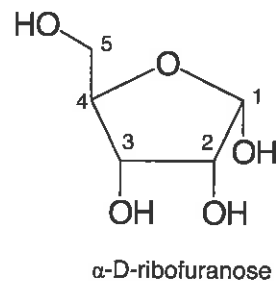

α-D-ribofuranose
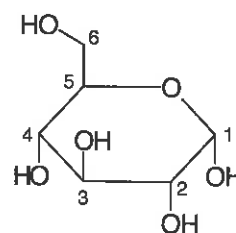
α-D-glucopyranose

D-Fructose is the most widespread ketohexose. Configuration at C3-C5 is identical with D-glucose. It is found mainly in fruits (3-6%) and honey (~ 40%). Free fructose exists mostly in the pyranose form; fructofuranose occurs only in sucrose, polysaccharides (inulin), and phosphoric esters.

β-D-mannopyranose   β-D-galactopyranose   D-fructose   β-D-fructofuranose
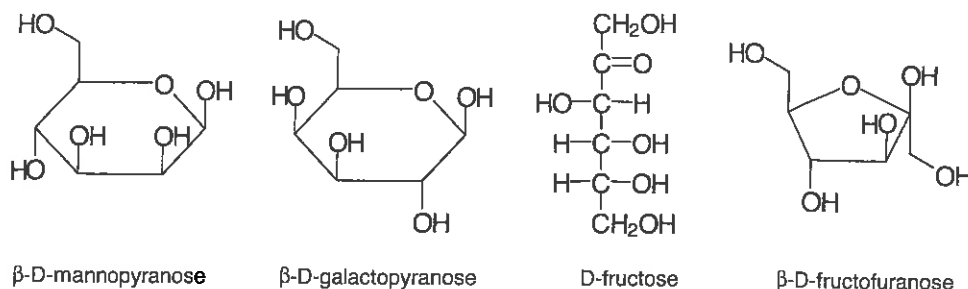
Reactions of monosaccharides

Esterification. Alcohol groups can be esterified by various acids. In biochemistry, **esters of phosphoric acid** are of special importance. In the metabolic pathways, monosaccharides occur primarily in phosphorylated forms, e.g. glucose 6-phosphate, fructose 1,6-bisphosphate, ribose 5-phosphate.

Oxidation. All monosaccharides are relatively easily oxidized, mainly in the alkaline environment, therefore they have substantial reducing properties. The most easily oxidized group is the aldehyde group of aldoses, so the polyhydroxy **aldonic acids** are formed.

Under stronger oxidation, both the aldehyde and primary alcohol groups are oxidized and dicarboxylic **aldaric acids** are obtained (they have no biochemical importance).

If the aldehyde group is protected against oxidation, only the primary alcohol group is oxidized to produce **uronic acids** (see scheme).
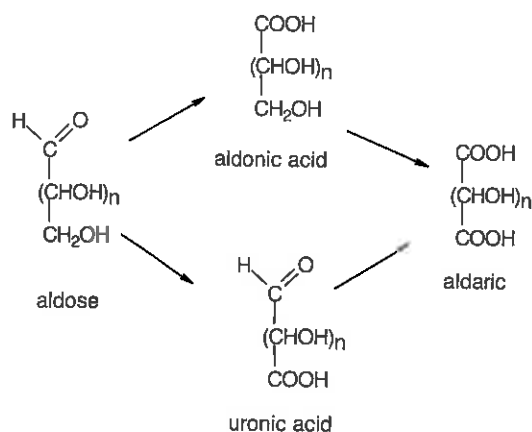
Glucuronic acid is the component of proteoglycans in connective tissues. Glucuronic acid also forms glycosides with a number of substances increasing their solubility and their excretion to urine or bile (conjugation reactions). **Galacturonic acid** is present in plants and fruits as a component of pectins (dietary fibre).


D-glucuronic acid   D-galacturonic acid
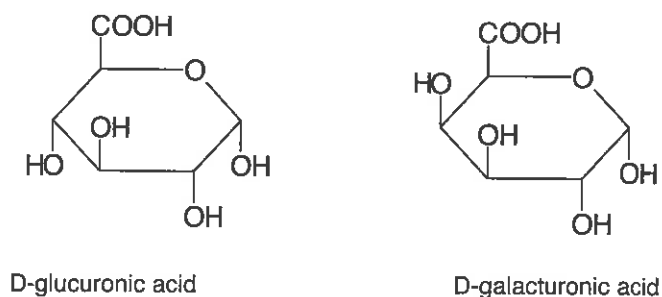
Reduction. Reduction, i.e. hydrogenation of the carbonyl group of aldoses and ketoses produces **sugar alcohols (alditols).** Although they are formed from sugars and have sweet taste, they are not real sugars; they have no reducing properties and do not provide any other reactions conditioned by the presence of carbonyl or anomeric hydroxyl. Aldoses give only one sugar alcohol by reduction, e.g. **glucitol** is formed from glucose. Fructose gives a mixture of glucitol and mannitol, which differ in configuration at C-2.
Ribitol, part of riboflavin, vitamin B_2, is made from ribose.

Formation of glycosides. Glycosides are derivatives of the cyclic forms of monosaccharides, which are formed by reaction of anomeric hydroxyl with oxygen or nitrogen containing compound with the simultaneous release of water. Glycosides formed by reaction of anomeric hydroxyl with alcohol are **O-glycosides**, the bond is O-glycosidic. If the glycosidic bond is formed between monosaccharides, it gives oligo/polysaccharides. The simplest O-glycoside is methyl-β-D-glucoside. Glycosides formed by reaction of anomeric hydroxyl with nitrogen of amines are **N-glycosides.** The residue formed from cyclic forms of monosaccharides after the removal of anomeric hydroxyl is generally called *glycosyl* (e.g glucopyranosyl). The names of glycosides are formed in various ways, if the non-sugar component (aglycon) is simple, the name is *alkyl-glycoside* or *glycosylamine*.


methyl-β-D-glukosid   α-D-glukosylamin
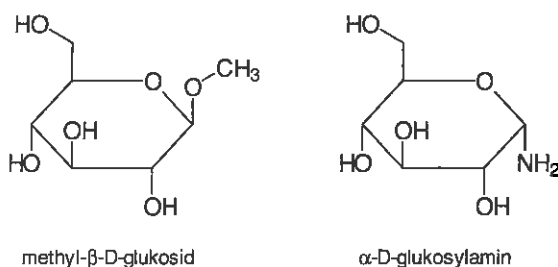
Disaccharides

are formed from two identical or different monosaccharides joined by O-glycosidic bond. Anomeric hydroxyl of one molecule can join to some alcoholic hydroxyl or anomeric hydroxyl of the second molecule. In the first case, the result is **reducing disaccharide**, which exists in two anomeric forms and is able to form glycosides with other compounds. If the glycosidic bond is formed between two anomeric hydroxyls of both molecules, it results in **non-reducing** sugars.
Sucrose (β-D-fructofuranosyl-α-D-glucopyranoside, beet/cane sugar) is a non-reducing disaccharide, the only nutrient we take in pure form.
Maltose, 4-O-(α-D-glucopyranosyl)-D-glucopyranose, is formed during digestion of starch and is present in malt.

sucrose

maltose
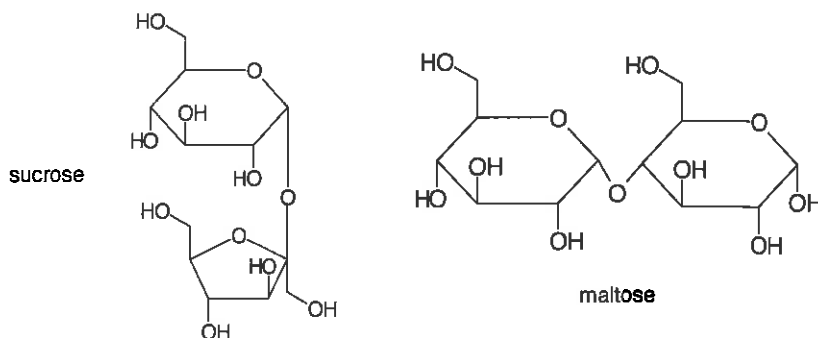
Cellobiose, 4-O-(β-D-glucopyranosyl)-D-glucopyranose, has its glucosyl residue also bound in position 1→4, but it is the β bond. It is produced during partial hydrolysis of cellulose.
Lactose (milk sugar) is 4-O-(β-D-galactopyranosyl)-D-glucopyranose. It is the most important sugar contained in milk of all mammals; in cow milk 4-6 %, in human milk 6 %.

Polysaccharides

consist of several hundreds or thousands of monosaccharide units. The molecules of monosaccharides are linked by α- or β-glycosidic bonds, most often 1→4 or 1→6.

Starch is the storage substance of plants contained mainly in cereals, potatoes, rice. Starch dissolves in hot water to make a colloidal solution. Starch is the mixture of amylose and amylopectin. **Amylose** consists of glucose units joined by α-1,4-glycosidic bonds. **Amylopectin** is the main component of starch (70-80 %). It also consists of glucose units linked by α-glycosidic bond. However, the molecule of amylopectin is branched, side chains bind by α-1,6 bond to the main 1→4 chain.

Glycogen, also called „animal starch", is the storage substance contained in the liver (5-10 %) and in the muscles (1 %) of animals. It is formed by synthesis from sugars taken in food. It is the ready source of glucose, whose breakdown provides the organism with energy.

Cellulose is formed from unbranched chains, the molecules of glucose are joined by β-1,4-glycosidic bond. The basic unit is cellobiose. It is not digestible for humans and most animals, because they do not have enzymes, which cleave β-glycosidic bonds. Cellulose is passed through the digestive tract as fibre. Enzymes, which cleave cellulose, are contained only in microorganisms. If some animals use cellulose as a nutrient, its cleavage is almost always done by the microflora; e.g. in the paunch of ruminants. The pure cellulose is used in medicine as dressing cotton-wool.

14 LIPIDS AND STEROIDS

Lipids are derivatives of fatty acids. They have lipophilic (hydrophobic) character, are insoluble in water and soluble in non-polar organic solvents (for example, trichloroethene $Cl_2C=CHCl$, chloroform $CHCl_3$, tetrachloromethane CCl_4). Lipids can be classified as **simple lipids** (triacylglycerols, waxes) and **complex lipids** (glycerophospholipids, sphingophospholipids, glycosphingolipids).

Fatty acids

Fatty acids (FA) are aliphatic monocarboxylic acids. Almost all fatty acids have an unbranched chain with even number of carbons, because they are synthesized from two-carbon units (acetyl-coenzyme A). According to the length of carbon chain, fatty acids are classified as short chain fatty acids with up to 6 carbon atoms, medium chain FA (8-10 C), and long chain fatty acids with more than 12 C atoms. According to the number of double bonds, they are distinguished as **saturated fatty acids** (SAFA), **monounsaturated fatty acids** (MUFA), and **polyunsaturated fatty acids** (PUFA). Double bonds are isolated, separated by a single methylene group. Configuration on the double bonds is *cis*. Chemical formulas of fatty acids are commonly presented in a simplified way. The abbreviated designation includes the number of carbon atoms, number of double bonds, and locations of the double bonds in parenthesis. For example, α-linolenic acids, is recorded as 18:3(9,12,15). Other way is 18:3 (*n*-3), where *n*-3 marks the location of the last double bond, relative to the end methyl group (see scheme).
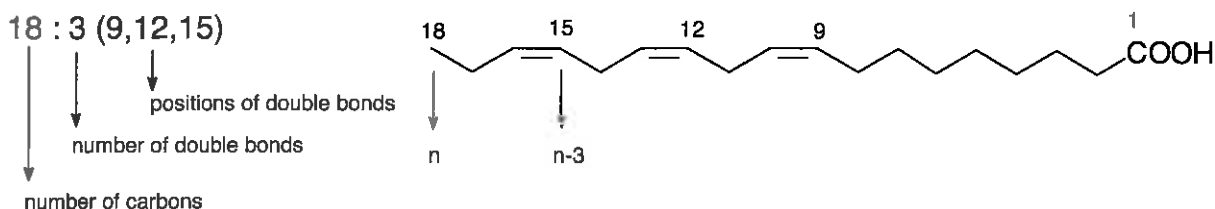
The following tables show the most important fatty acids.

Selected saturated fatty acids (SAFA)

Abbreviated record	Common name	Systematic name	Occurrence
4:0	butyric	butanoic	milk fat
6:0	capronic	hexanoic	milk fat
12:0	lauric	dodecanoic	coconut fat
14:0	myristic	tetradecanoic	coconut fat
16:0	palmitic	hexadecanoic	nearly all fats
18:0	stearic	octadecanoic	nearly all fats
20:0	arachidic	eicosanoic	nearly all fats
24:0	lignoceric	tetracosanoic	sphingolipids

Selected unsaturated fatty acids (MUFA, PUFA)

Abbrev. record	Series	Common name	Systematic name	Occurrence
16:1(9)	n-7	palmitoleic	*cis*-9-hexadecenoic	vegetable oils
18:1(9)	n-9	oleic	*cis*-9-octadecenoic	vegetable oils
18:2(9,12)	n-6	linoleic	*all-cis*-9,12-octadecadienoic	vegetable oils
18:3(9,12,15)	n-3	α-linolenic	*all-cis*-9,12,15-octadecatrienoic	fish oil
20:4(5,8,11,14)	n-6	arachidonic	*all-cis*-5,8,11,14-eicosatetraenoic	phospholipids
20:5(5,8,11,14,17)	n-3	EPA	*all-cis*-5,8,11,14,17-eicosapentaenoic	fish oil
24:1(15)	n-9	nervonic	*cis*-15-tetracosaenoic	sphingolipids

Unsaturated fatty acids are important for chemical and physical properties of lipids. It is well known that the more double bonds (*cis*-configuration) in a lipid, the more liquid character the lipid has: the melting point of triacylglycerols becomes lower.

Essential polyunsaturated fatty acids. Unsaturated fatty acids, MUFA and PUFA are formed from saturated fatty acids by **desaturation,** in humans only in positions between C-9 and C-1. Essential fatty acids are **linoleic** and α-**linolenic acid**. Linoleic acid (n-6) is converted by a series of elongation and desaturation reactions to arachidonic acid and, similarly, α-linolenic acid (*n*-3) into eicosapentaenoic acid. The main source of essential fatty acids are plant oils, in our diet mainly soya, sun-flower, and rape seed. The content of essential fatty acids in olive oil is significantly lower. It is advisable to say that oils with high content of polyunsaturated fatty acids should not be used for frying or fritting because of little resistance against autooxidation. Other important sources of *n*-3 polyunsaturated fatty acids, especially α-linolenic acid, are fish oils.

Simple lipids

are composed only of fatty acids and alcohol. **Triacylglycerols** are esters of glycerol and fatty acids, they are the main components of naturally occurring fats and oils. They exist always as a mixture of various molecular types of triacylglycerols. The acyl residues in the molecule of triacylglycerols are typically not identical, usually

there are two or three different residues in one molecule that vary by chain length and degree of saturation. Their positions are not random, unsaturated fatty acid are primarily bonded to the C-2. They are considered as *O*-acylderivates of glycerol.

1,3-distearoyl-2-oleoyl-*sn*-glycerol
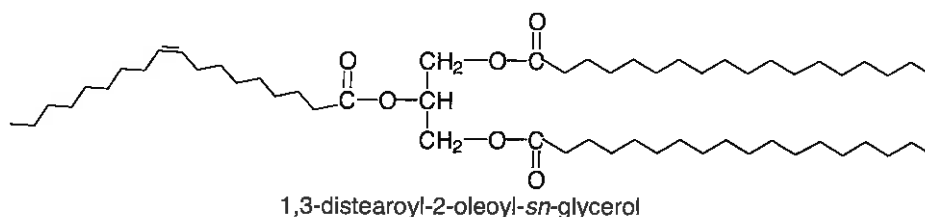
Properties of triacylglycerols. Triacylglycerols are markedly **non-polar** compounds, insoluble in water. By shaking liquid fat (oil) with water the emulsions are formed. Milk is an example of a stable natural emulsion; milk fat is dispersed in small droplets stabilized by proteins and phospholipids.

Hydrolysis of ester bond of triacylglycerols leads to release of their components. It is performed by heating with a mineral acids; glycerol and mixture of fatty acids are the products. Another way is hydrolysis of triacylglycerols by boiling with alkaline hydroxides which is called saponification. As a result glycerol and soaps (a mixture of salts of fatty acids) are obtained. The hydrolysis of lipids in organism is catalyzed by enzymes lipases.
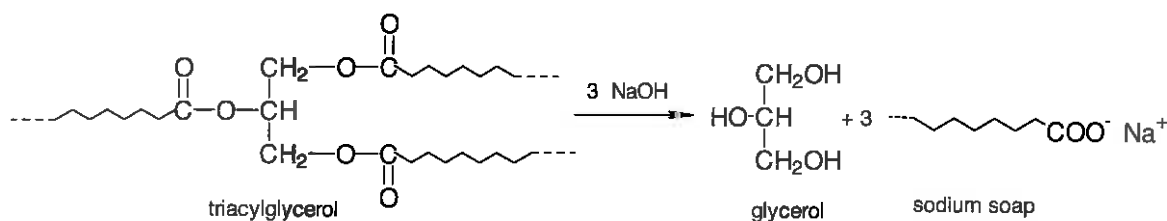

Waxes are natural mixtures of esters of long chain saturated fatty acids and long chain fatty alcohols. Often the number of carbons in alcohol is the same as in the acid. Waxes are much more hydrophobic than triacylglycerols and they are solid at a room temperature.
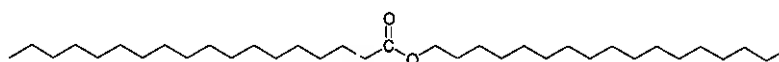

Complex lipids

Their molecules contain a **non-polar part** formed from fatty acid chains and a **polar part**. All complex lipids therefore belong to **natural tensides**. Their overall polarity has a wide range, from neutral glyco- lipids to ionized phospholipids. They have various functions in living organisms. The most significant role is the formation of **phospholipid bilayer** of all membranes.
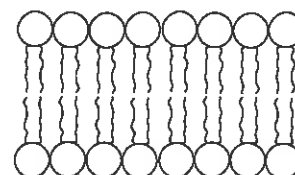

Phospholipids contain phosphoric acid that forms two ester bonds; one with alcohol group of substituted glycerol or sphingosine, the second binds another component, most commonly choline. Phosphate group has a negative charge at a physiologic pH. If the other component is a nitrogen base, phospholipid is **dipolar (amphoteric)** – it has a positive charge on nitrogen. Polar/non-polar character of phospholipids is important for stabilization of phase interface and properties of membranes. At a phase interface, membranes are oriented with a hydrophilic end into water phase and with hydrophobic end to non-polar phase (air, lipids or other non-polar molecules.).

Glycerophospholipids are distinguished from each other by their polar component, which is bonded to phosphate by its hydroxyl. According to this compound, glycerophospholipids are classified as phosphatidylcholines (lecithins), phosphatidylethanolamines, phosphatidylserines, phosphatidylinositols, and phosphatidylglycerols.

phosphatidylcholine
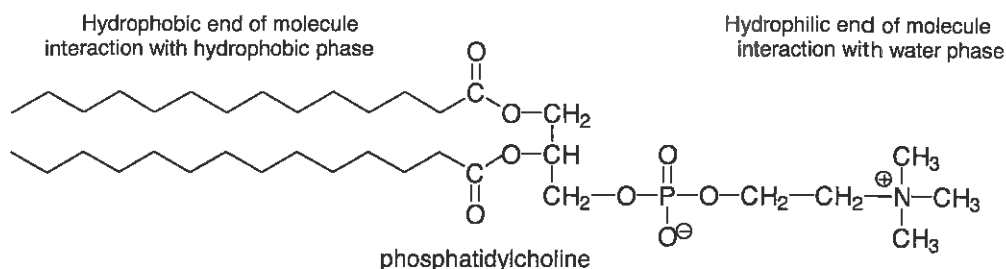
Phosphatidylcholines and **phosphatidylethanolamines** are dipolar phospholipids. They are the main component of plasmatic membranes and membranes of cellular organels. **Phosphatidylserines** are acidic phospholipids, they have two negative and one positive charge. **Phosphatidylinositols** contain *myo*-inositol, a cyclic alcohol with six hydroxyl groups.

Sphingophospholipids are derivatives of **sphingosine**, 18C-aminoalcohol. The simplest derivative is **ceramide**, *N*-acylsphingosine. Long chain fatty acids is attached by amide bond to sphingosine. In **sphingomyelin**, phosphate is attached to primary alcohol group of sphingosine, choline is bound as an ester to phosphate.


sfingosine

ceramide
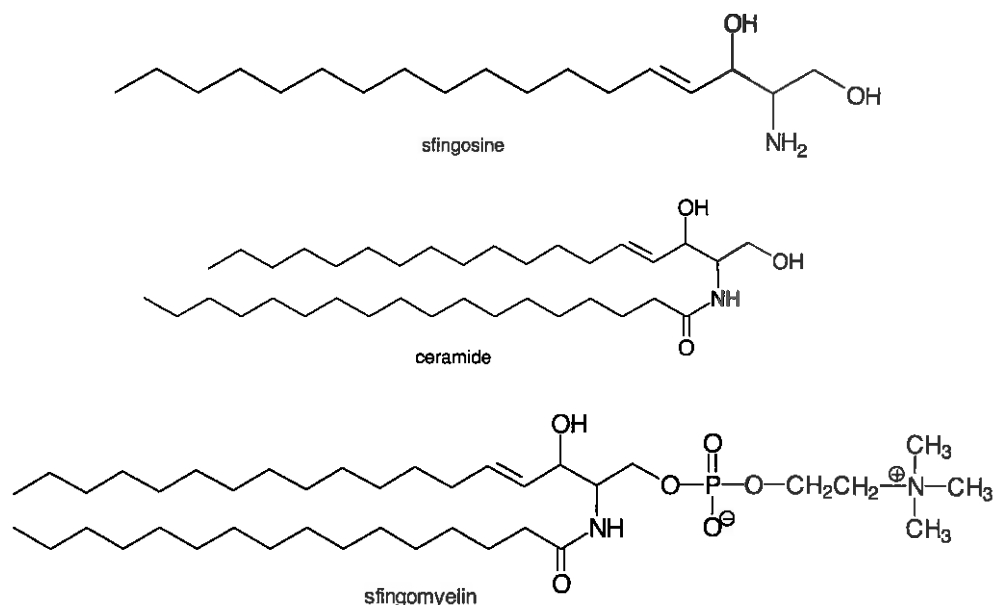
sfingomyelin

Sphingomyelins belong to amphotheric phospholipids. Sphingomyelins are the main type of phospholipids in myelin sheet of axons of neural cells, which gave them their group name. They are a permanent component of plasmatic membranes of almost all cell types. **Glycosphingolipids** are complex lipids. Saccharide component, monosaccharide or oligosaccharide (polar part of the molecule) is glycosidically linked to a lipid component.

Steroids

are a group of biologically important compounds, widely spread in all eukaryotic cells. Steroids are mostly very hydrophobic, similar to lipids. The 17C skeleton is made from condensated alicyclic rings, perhydrocyclopenta[*a*]

phenanthrene, called **sterane**. Rings of steroid skeleton are indicated with letters A to D, their carbons are numbered in a specific manner.
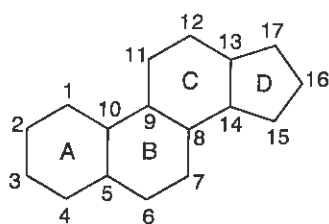
sterane
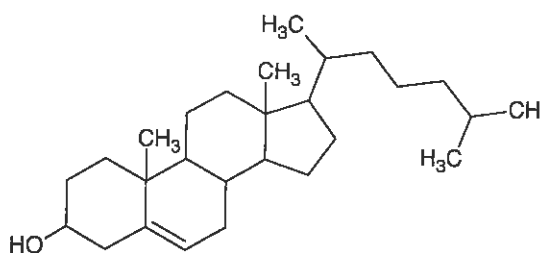
cholesterol

Cholesterol has 27 carbons, in position 17 it has eight-carbon branched alkyl. In adult human body, there are about 250 g of cholesterol, a considerable part is in the brain, and also in the cell membranes. Even though it has one hydroxyl group, it is rather hydrophobic, in water insoluble. In blood plasma, it is transported together with other lipids as a part of lipoproteins. From the total concentration of cholesterol (about 5 mmol/l) only a part of it is free cholesterol, as most of it make hydrophobic esters with unsaturated fatty acids. Cholesterol is the substrate for calciol, bile acids, and steroid hormones.

Calciol is vitamin D, in which the ring B (C9-C10 bond) is broken by the effect of UV radiation. In human liver, a small amount of cholesterol transforms into 7-dehydrocholesterol and from that, in dermal capillary exposed to sun radiation, **calciol** is formed. Calciol is precursor of **calcitriol**, nowadays ranked among steroid hormones. In cells of intestinal mucosa, calcitriol induces the synthesis of protein for the resorption of Ca^{2+} from food. A rich source of calciol is cod liver oil, fish oil, butter, egg yolks, milk, and liver. In case of vitamin D deficit, growing and remodelling bones are insufficiently mineralized (rachitis in children, osteomalacy in adults).

Bile acids originate from cholesterol in the liver. Bile acids differ in the number and the position of hydroxyl groups, which are almost always in positions 3, 7, and 12. Main bile acids are **cholic** and **chenodeoxycholic** acid. They are discharged into bile as **conjugated** bile acids, amides made by binding carboxyl to -NH_2 group of glycine or taurine. Cholate is thus converted into more polar and better soluble glycocholate or taurocholate. Bile acids are effective tensides, thus emulsify fat into small micelles.

Steroid hormones are classified as hormones of adrenal cortex, **corticoids**, and **sex hormones**, male androgens and female estrogens and gestagens.

Glucocorticoids are hormones, which play crucial role in adaptation of the organism to the state evoked by stress. They increase glucose concentration in blood by stimulating liver gluconeogenesis, synthesis of glucose from some amino acids (provide thus the most easily exploitable nutrient for tissues, therefore the name glucocorticoids). They also make amino acids more easily available by suppressing proteosynthesis and supporting breakdown of proteins, e.g. in muscles, bones and cells of lymforeticular system. They have catabolic effect on protein metabolism. The main hormone is **cortisol**.

Mineralocorticoids play an important role in managing Na^+ and K^+ ions and therefore in osmolality and the volume of extracellular fluid regulation. In kidney tubules, reverse resorption of ions Na^+, thus their retention in body and increased discharge of K^+ ions is supported. The most effective hormone of this group is **aldosterone**.

Sex hormones influence reproduction and development of secondary sex features. Most of these hormones are produced by gonads.

Androgens are male sex hormones, In males, they are produced mainly by Leydig testicular cells. The typical representative is **testosterone**. Androgens influence development of external male genitals and development of secondary sex characteristics. Their metabolic effect is **generally anabolic**. They support growth, especially by stimulation of proteosynthesis – the growth of muscle mass.

Estrogens are female sex hormones originated in ovaries. The most active is **estradiol**, initiates proliferation of uterine mucosa in the first half of the menstrual cycle, development of female secondary sex characteristics. During menopause their function decreases radically.

Gestagens are synthesized in corpus luteum and placenta. The most important one of them is **progesterone**. It prepares the uterine epithelium for nidation of fertilized egg in the second half of the menstrual cycle and prevents further ovulation. During pregnancy the production of progesterone is many times increased. It also supports and evokes structural changes in mammary gland.

15 AMINO ACIDS AND PROTEINS

All coded (standard) amino acids are carboxylic acids with amino group bound to α-carbon, i.e. carbon C2 neighbouring with carboxyl. An exception is proline, which has secondary amino group -NH- as a part of pyrrolidine ring. Except glycine, the α-carbon of standard amino acids is **chiral**, isoleucine and threonine have also the second chirality centre; amino acids are therefore optically active. In proteosynthesis, only amino acids that have on α-carbon configuration L are built into polypeptide chains.
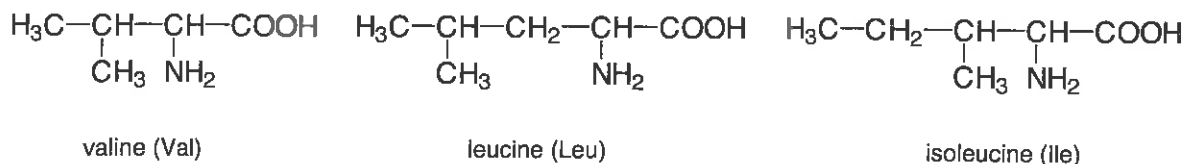

α-amino acid   L-amino acid   D-amino acid
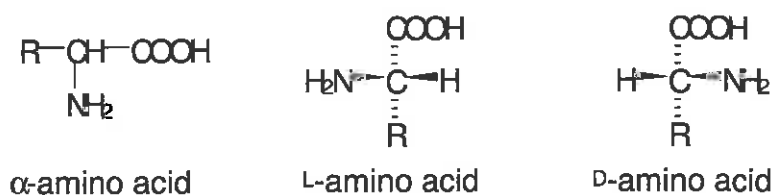
Standard amino acids differ from each other just by the substituent R on the α-carbon, called a **side chain**. Side chains of amino acids determine secondary and tertiary structure of proteins. According to the polarity of side chain and its behaviour under physiological pH ($\sim$ 7.4) amino acids are divided into following four groups: **non-polar, polar, basic,** and **acidic** amino acids. In proteins, non-polar side chains are mutually bound by hydrophobic interactions, polar groups create hydrogen bonds, acidic and basic groups stabilize tertiary or quaternary structure of proteins by electrostatic interactions.

Amino acids with non-polar side chains (Gly, Ala, Val, Leu, Ile, Phe, Pro, Trp, Met)

Glycine (aminoacetic acid) is the simplest amino acid and the only one that is not chiral. Glycine is especially abundant in collagen. **Alanine** (2-aminopropanoic acid) has a close relation to pyruvate by transamination.


glycine (Gly)   alanine (Ala)
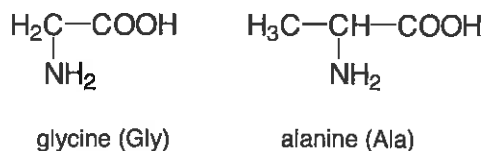
Valine (2-amino-3-methylbutanoic acid), **leucine** (2-amino-4-methylpentanoic acid), and **isoleucine** (2-amino-3-methylpentanoic acid) have quite similar characteristics, especially isomers leucine and isoleucine. They are essential for animals, because they cannot synthesize their branched carbon chain.

$$H_3C-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{NH_2}{|}}{CH}-COOH \qquad H_3C-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\underset{NH_2}{|}}{CH}-COOH \qquad H_3C-CH_2-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{NH_2}{|}}{CH}-COOH$$

| valine (Val) | leucine (Leu) | isoleucine (Ile) |

Phenylalanine (2-amino-3-phenylpropanoic acid) has in the side chain a very non-polar aromatic residue phenyl. It is essential acid, animal cells cannot synthesize aromatic skeleton *de novo*.

Proline (pyrrolidine-2-carboxylic acid) is α-amino acid very unusual, it does not have a primary amino group -NH_2, but secondary amino group -NH- as a part of pyrrolidine ring. Carbon chain that closes the five-membered heterocycle is non-polar. A major amount of proline is in collagen.

Tryptophan, 2-amino-3-(3-indolyl)propanoic acid, contains a condensed aromatic system of indol (benzopyrrol), heteroatom of nitrogen is not basic like in pyrrole.
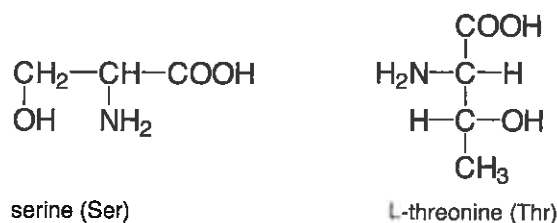

| phenylalanine (Phe) | proline (Pro) | tryptophan (Trp) |
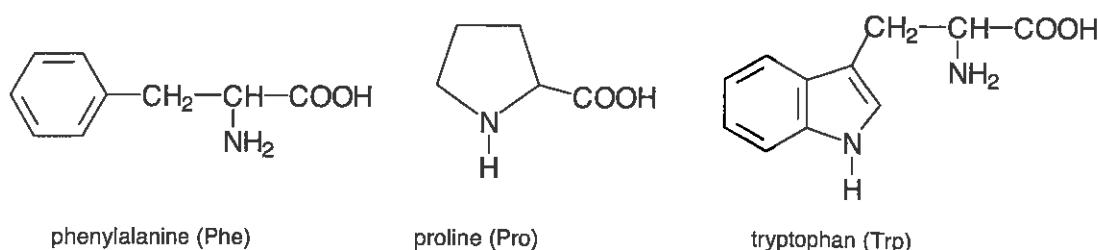
Methionine (2-amino-4-methylsulfanylbutanoic acid) has in its side chain a -S-CH_3 group (belongs among dialkylsulfides). It is very valuable, essential amino acid. The methyl group bound to S atom is used for methylations. During methylation reactions, **homocysteine** (the cysteine homolog) is a by-product, from which methionine can be regenerated again.


| methionine (Met) | homocysteine |
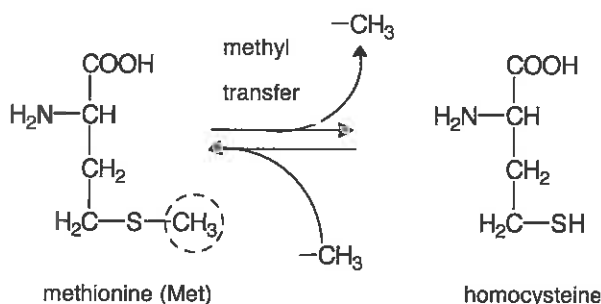
## Amino acids with a polar side chain (Ser, Thr, Asn, Gln, Tyr, Cys)

Serine (2-amino-3-hydroxypropanoic acid) and serine homolog, four-carbon **threonine** (2-amino-3-hydroxybutanoic acid) can esterically bind phosphoric acid by their hydroxyl, which is important in the regulation of protein function. Essential threonine has two chiral centres.

$$\underset{\underset{OH}{|}}{CH_2}-\underset{\underset{NH_2}{|}}{CH}-COOH \qquad \qquad \underset{\underset{CH_3}{|}}{\overset{\overset{COOH}{|}}{H_2N-\underset{|}{C}-H}}\underset{}{}$$

| serine (Ser) | L-threonine (Thr) |

Asparagine (4-amide of aspartic acid) and **glutamine** (5-amide of glutamic acid) are neutral amino acids, amide group -CO-NH$_2$ is neither basic nor acidic (amides are non-electrolytes). Amide bond is easily hydrolyzed, releases ammonia and aspartic (glutamic) acid.
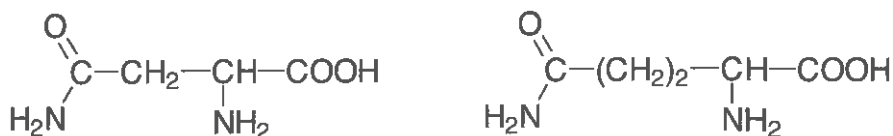
Tyrosine is 2-amino-3-(4-hydroxyphenyl)propanoic acid. Unlike phenylalanine it is not essential amino acid, it is formed by hydroxylation of phenylalanine. Tyrosine is the precursor of e.g. melanine pigments, hormones adrenaline, and iodinated thyronines.


tyrosin (Tyr)
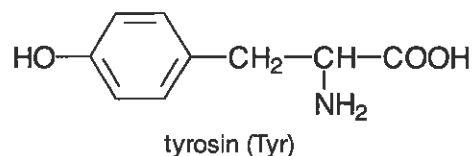
Cysteine (2-amino-3-sulfanylpropanoic acid) has a –SH group, whose very weak acidity is not used in the range of physiological values pH. On the contrary, -SH group easily undergoes to dehydrogeneration. Two cysteine molecules are oxidized to a disulfide **cystine**. Reaction is reversible and important for all compounds that contain cysteine residues. In proteins, **disulfide bridges** are made this way. A tripeptide glutathione (GSH) contains cysteine and its reduced form works in cells as important antioxidant.


cysteine (Cys)   cysteine (Cys)   cystine
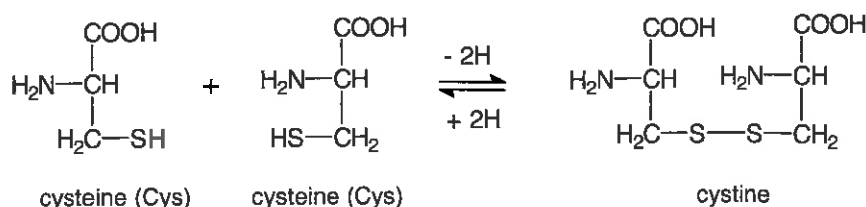
Basic amino acids (Lys, Arg, His)

Lysine (2,6-diaminohexanoic acid), essential amino acid, has the second amino group in its side chain. Side chains of lysine are vitally important for making covalent inter-chain bonds in collagen (cross bridges) and elastin (desmosine). **Arginine** (2-amino-5-guanidinepentanoic acid) contains a guanidine (iminourea) group, which contains three nitrogen atoms. Nitrogen bound by double bond (imino nitrogen) is quite basic. In the liver, arginine is an intermediate of ureosynthesis.


lysine (Lys)   arginine (Arg)
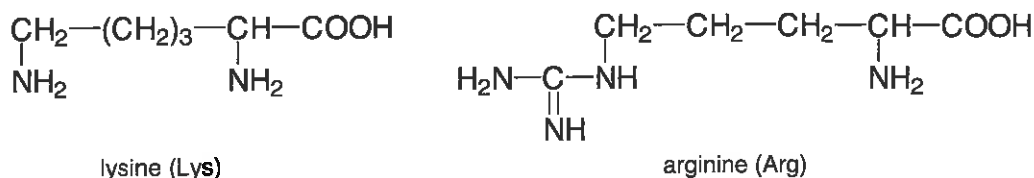
Histidine (2-amino-3-(4-imidazolyl)propanoic acid) contains imidazole in the side chain. Heterocyclic nitrogen N3 causes that imidazole ring is a weak base. Side chains of histidine in proteins are the only ones that act as donors or acceptors of protons (**protein buffers**) under physiological pH. Apart from this, in haemoglobin, side chain of histidine provides bond of heme iron to globin. Free histidine provides histamine by decarboxylation. Side groups of basic amino acids give positive charges to proteins under physiological pH values.
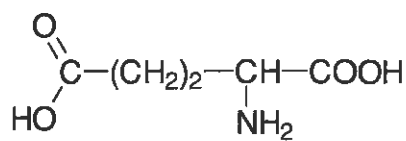

histidin (His)
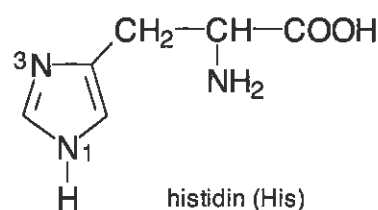
Acidic amino acids (Asp, Glu)

Aspartic acid (2-aminobutanoic acid, aspartate) and **glutamic acid** (2-aminopentanoic acid, glutamate) carry the second acidic (carboxyl) group in their side chain. Under physiological pH values, ionized carboxyl groups provide proteins with negative charges.
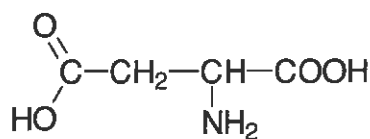

aspartic acid (Asp)   glutamic acid (Glu)

Peptides

Amino acids have ability to link together in peptides and proteins. The **peptide bond** –CO-NH– is the special type of an amide bond between the α-carboxyl group of one amino acid and the α-amino group of another amino acid; water is excluded in the reaction. A peptide bond can undergo hydrolysis and the initial reactants are released.
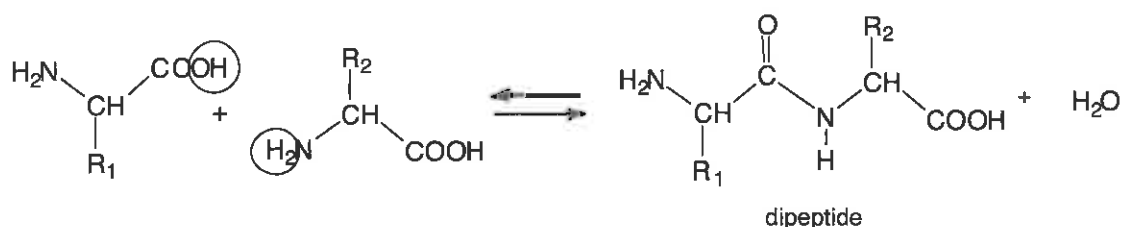
dipeptide

Peptide bond has its specific features caused by the delocalization of π-electrons of carbonyl and the unshared electron pair of nitrogen atom. The peptide bond –CO-NH– has partly the character of a double bond: it is slightly stronger than a single bond and slightly weaker than a double bond; the rotation about the bond C–N is restricted. The atoms of the group –NH-CO– have a planar geometry. By linking amino acids through peptide bonds, a **linear peptide chain** originates. There is a free α-amino group at one of the ends (N-terminus) and a free α-carboxyl group at the opposite end (C-terminus). The **main chain** of peptides consists of the regularly alternating sequences -NH-C$^{\alpha}$H-CO-. **Side chains** R of individual amino acid residues attached to C$^{\alpha}$-atoms are branching off from the main chain.
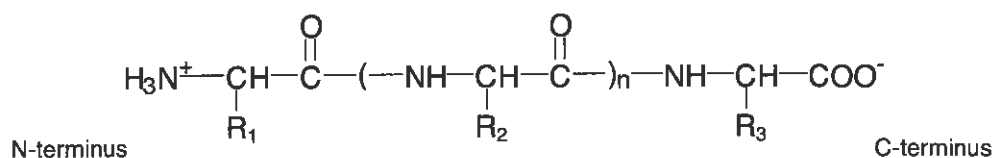
Proteins

From the quantitative point of view, proteins are polypeptides consisting of more than about one hundred amino acids. Proteins exhibit a qualitatively higher order of organization. A specific protein has its unique conformation. This conformation corresponds with the specific biologic function of the protein, retains certain stability and still is flexible due to interactions with molecules in its surroundings. The largest protein chains may comprise a few thousands of amino acids, some proteins consist of more than one polypeptide chain.

Protein Structure

Primary structure is the sequence of amino acid residues in the polypeptide chains.

Secondary structure is the spatial arrangement of atoms of the main chain without any regard to its side chains and to the interactions of the segment with other remote parts. Right-handed α-**helix** is an important structure in most globular proteins. There are 3.6 amino acid residues per turn. Intra-chain hydrogen bonds stabilize the helix. They bind oxygen atoms of CO groups and nitrogens of peptide bonds so that the C=O group of the amino acid residue i forms a hydrogen bond with the NH group of the amino acid residue $i + 4$, i.e. of the fourth that succeeds. The amino acids side chains are on the outside of the helix.

Another important secondary structure is the β-**strand** (β-structure). The main chains are considerably stretched. The peptide bond planes of the chain incline regularly up and down as if the chain ran on the surface of a folded sheet of paper. The side chains point alternately up and down. The stabilization of β-strands is usually provided by linking two or more β-strands by hydrogen bonds between the adjacent strands. These relatively flat structures, combined from two or more chains, are called **pleated sheets** (or β-**sheets**). Most of them adopt a somewhat twisted shape.

Supersecondary structures occur in proteins frequently; they consist of various combinations of segments with regular secondary structure of α-helix or β-strand, which are quite stable. Segments of β-strands and α-helices form units e.g. βαβ and βαβαβ.

Tertiary structure of a protein molecule is the spatial arrangement of all protein atoms, the complete description of its unique native conformation and external shape. Tertiary structure is a result of stabilizing interactions between side chains R of segments with various secondary structures. Polar groups occur on the molecular surface, exposed to water; that is why globular proteins are mostly soluble. Most hydrophobic groups are hidden within the compact inner of molecules. In molecules of globular proteins with long polypeptide chains, relatively independent compact globular parts occur, called **domains**. They have specific and independent biological function, e.g. for catalytic or regulatory domains of enzymes, the binding domain for NAD^+ in all dehydrogenases etc.

Molecules of some proteins have also **quaternary structure**, i.e. they comprise several independent globular subunits. These subunits are bound only by non-covalent interactions. Quaternary structure is then understood as the number and spatial arrangement of subunits in the oligomeric molecule (assembly of contacts and interactions between subunits). Subunits can be identical or different; their number is various, usually even. An example of a hetero-tetrameric protein is **hemoglobin A**; the molecule consists of four subunits, which are very similar but not identical, of type α and β ($α_2β_2$), each of the subunits binds one heme.

Protein classification

Globular proteins are members of a numerous family of proteins with various biological functions. They are usually soluble in water (unlike fibrous proteins); in solutions, they exist as individual, on others independent molecules. Protein molecules have oval or even spherical shape. Main polypeptide chain and most non-polar side chains are in the compact inner of molecules, most polar side chains are exposed on the surface of molecules, in contact with water.

Fibrous proteins create microscopic fibrils. Many fibrous proteins do not dissolve in water, a few of them are extraordinary resistant to chemicals. They function as internal scaffolding within cells (cytoskeleton), they give strength to connective tissues, resistance to the skin. Muscle proteins **actin** and **myosin** are components of contractile system which realizes muscle work. **Keratin** is a representative of α-helical fibrous proteins. In mammals, it is main component of horny outer layer of the skin as well as of skin adnexa (hair and hairiness, fingernails, even horns and hooves). **Collagen** is the major fibrous protein in extracellular ground substance in all types of connective tissue (tenuous connective tissue, tendons, cartilages, and bones) and the most abundant protein in the body. It has very great tensile strength. Boiling in water transforms insoluble collagen, by partial

hydrolysis, into soluble **gelatin**; it gives gel (aspic) by cooling. **Elastin** is the fibrous protein, which prevails over collagen in certain types of connective tissue (e.g., elastic layer of large arteries, lungs, and skin). **Fibroin** is the stringy, insoluble protein of silk (produced by silkworms) and spider webs.

Membrane proteins differ in their association with the membrane structure. **Integral proteins** are embedded more or less in hydrophobic inner of the phospholipid bilayer and may even extend completely through the membrane (penetrating, transmembrane proteins). **Peripheral** membrane proteins are loosely attached to the membrane surface by electrostatic attractions to hydrophilic electrically charged polar heads of the bilayer lipids or to the groups on surfaces of integral proteins.

Denaturation is the loss of specific biological functions. The cause of it can be even a gentle change in its native conformation, disruption of some non-covalent interactions, which stabilize the tertiary and secondary structure, without any change in the primary structure. Denaturation can be evoked by many influences. **Physical** factors are heating (hard-boiled eggs), mechanical effects (whipped egg whites), high pressure, UV radiation, ultrasound. Examples of **chemical** influences are acids, bases, cations of heavy metals, tensides, and certain organic acids. Denaturation of proteins usually decreases their solubility considerably.

16 ENZYMES

Enzymes are proteins that function as biological **catalysts**. As all other catalysts, enzymes, in very small amounts, accelerate chemical reactions by decreasing the activation energy needed for the reaction. Enzymes do not change the equilibrium constant, they only cause that the system reaches the equilibrium more quickly.
In enzymatic reactions, the reactants are called **substrates**. Enzymes (E) then bind proper substrates (S) transiently to a restricted region of enzyme molecule called **active site**. The interactions are non-covalent (H-bonds, electrostatic, hydrophobic) and even covalent bonds. In the enzyme-substrate (E-S) complex, the reactant proximity and local concentration is enhanced, which can result in an increase of local reaction rate. After the reaction is completed, the product (P) is released from the active site.

$$E + S \leftrightarrows E\text{-}S \rightarrow E + P.$$

Enzymes are the most effective catalysts known. Nevertheless, their catalytic activity is lost on denaturation of protein. Some enzymes have a tightly bound non-protein component called **prosthetic group** or need a loosely linked **coenzyme** to be fully active. Many prosthetic groups and coenzymes are derived from vitamins. Unlike other catalysts, enzymes are highly specific in the reaction type. They act on either one substrate or more structurally related compounds. The catalytic activity of enzymes can be regulated.

Factors affecting the rate of enzymatic reactions
In every chemical reaction, the rate increases with increasing temperature and concentration of reactants. However, there are some differences in enzyme-catalyzed reactions.

Temperature. The rate usually becomes approximately double for each 10 °C rise in temperature. At higher temperatures, the rate increase is stopped by the effect of enzyme denaturation. So many enzymes become inactive at temperatures higher than 60 °C.

pH. The pH values affect the ionization of either enzymes or ionizable substrates. There is an optimal pH at which each enzyme exhibits its highest activity. Most intracellular enzymes have very often pH optima close to neutral value. Exceptions are with digestion enzymes, e.g. pepsin in the stomach works at pH about 1.5, a rather acidic environment.

Concentration. The reaction rate is directly proportional to **enzyme concentration** as well as to the **substrate concentration.** Although, at very high substrate concentrations, the reaction rate is independent of it, the enzyme is saturated with substrate. The reaction then proceeds at a constant rate.

Some enzymes require **activators,** substances other than substrates, to exhibit higher activity. On the other hand, **inhibitors** specifically reduce the catalytic activity of enzymes. Inhibitors can be reversible or irreversible. Many important drugs and toxins (e.g. Aspirin, cyanides, CO, H_2S, heavy metal cations) belong to enzyme inhibitors.

Enzyme nomenclature and classification

Some enzymes catalyzing the hydrolysis of proteins still retain their historical names, e.g. pepsin, trypsin, chymotrypsin, thrombin, rennin. The other enzymes have common names formed by adding the suffix –*ase* to the substrate name (urease, amylase, peroxidase).

The IUPAC-IUB Enzyme Commision has developed the systematic nomenclature of enzymes that is rather complicated to be discussed here. However, a simplified set of trivial names is recommended as an alternative convenient for common use. Those names consist of the name of substrate and the type of reaction catalyzed + the suffix –*ase*. For example, lactate dehydrogenase is the enzyme catalyzing the dehydrogenation of lactate to pyruvate as well as the opposite reaction.

Enzyme classification is based on the six major classes of enzymes:

1. **Oxidoreductases** catalyze redox reactions: dehydrogenases, dioxygenases, hydroxylating monooxygenases, various oxidases, reductases, and peroxidases. According to substrate specifity, there are subclasses acting on alcohols, amines, aldehydes, etc.
2. **Transferases** catalyze the transfer of groups from one substrate to another, e.g. amino group (aminotransferases), alkyl/aryl groups, acyltransferases, and phospho-, glycosyl-, nucleotidyltransferases.
3. **Hydrolases** are able to perform the hydrolysis of esters, glycosides, amides, acid anhydrides, etc. exhibiting more or less substrate specifity. Many of them are important digestive enzymes. Hydrolases acting on esters bonds are called esterases (e.g. lipases, phosphatases, ribonucleases). Those acting on glycosidic bonds are glycosidases (e.g. amylases). Hydrolases splitting peptide bonds are peptidases and proteinases (pepsin, trypsin).
4. **Lyases** catalyze the non-hydrolytic removal of small groups from the substrate without presence of any other reactant or the addition of a small molecule to a double bond. These reactions are accompanied by scission (or formation) of carbon-carbon bond (e.g. carboxy-lyases called decarboxylases), carbon-oxygen bond (dehydration of H_2CO_3 or hydration of CO_2 by carbonate dehydratase) or carbon-nitrogen bond (e.g. ammonia-lyases).
5. **Isomerases** catalyze intramolecular bond changes in substrates (isomerisation). For instance, racemases and epimerases, *cis-trans* isomerases, intramolecular oxidorecuctases, and transferases.
6. **Ligases (synthetases)** catalyze a linkage of two substrates (formation of new bonds) simultaneously with the hydrolysis of ATP that supplies the energy for the reaction. For example, peptide synthetases or kinases (forming phosphate ester bonds).

17 VITAMINS

Humans obtain nutrients from food (saccharides, proteins, lipids). Besides those, food has to contain other components, which are essential because they cannot be synthesized in the body: essential amino acids, minerals, and vitamins. Vitamins can be classified by their water/fat solubility. This classification can help us to guess in what type of food vitamin can be found. Balanced diet of fresh foods usually contains essential amounts of vitamins. Low intake of vitamins can lead to **hypovitaminoses** with unspecific symptoms or more serious disorders with characteristic symptoms (avitaminosis). Vitamin **deficit** can happen also due to malabsorption in GIT. Excess of hydrophilic vitamins from food is usually excreted from the body by urine. On the other hand, vitamins soluble in fats can be deposit for longer time, vitamin A and D in liver, partly vitamin K and tocopherols in fat tissue. Repeated high doses of retinol or calciol can be toxic (hypervitaminoses).

Fat soluble vitamins

They have non-polar (hydrophobic) character because they are either hydrocarbons (isoprenoids) (A and D) or they contain isoprenoid chain in their molecule (E and K). In plant and animal food they are dissolved in fats. They are absorbed from the intestine together with dietary fats. During prolonged maldigestion, the absorption of vitamins is reduced; it results in hypovitaminosis, even though vitamin intake is sufficient. Lipophilic vitamins come into circulation as parts of chylomicrons.

Retinol (vitamin A) is formed by degradation of provitamin β-carotene, found in vegetables and fruits. There is some reserve of retinol (in ester form) in the liver. Aldehyde **retinal** is a component of rhodopsin of rod cells in the retina. **Retinoic acid** takes part in cell regulation of gene expression. One of the first symptons of retinol deficit is worse night sight (night-blindness).

Calciol (vitamin D) is formed in skin under UV light from 7-dehydrocholesterol and converted to hormone **calcitrol**. This hormone has a central function in Ca^{2+} and phosphate regulation. Calciol deficiency results in insufficient mineralization of bones. Serious deficiency in children causes rachitis (rickets), in adults osteomalacia. The best source of calciol is sea fish oil.

Tocopherol (vitamin E) is antioxidant, inhibits peroxidation of unsaturated fatty acids of membrane lipids and lipoproteins.

Phylloquinone (vitamin K) is essential for the biosynthesis of prothrombin, blood coagulation factors, and proteins necessary for bone mineralization. Vitamin K is therefore used for prevention or treatment of increased bleeding. It is produced y colon microflora.

Water soluble vitamins

are not stored in the body (with and exception of B_{12}), their excess is excreted by urine and therefore they have to be continuously supplemented with food. They are parts of **enzyme cofactors.**

L-Ascorbic acid (vitamin C) is an important reducing agent (antioxidant). It is easily oxidized (dehydrogenated) into biologically inactive L-dehydroascorbic acid. Vitamin C takes part in hydroxylation reactions in the synthesis of collagen, bile acids, and adrenaline by keeping metal ions of metaloenzymes in reduced form. It increases iron resorption in GIT. People with low intake of vitamin C get easily tired, they are more susceptible to small infections, swelling and bleeding of gums. Extreme avitaminosis is scurvy.

Thiamine (vitamin B_1) is is essential for degradation of all nutrients, mainly saccharides. Extreme avitaminosis is rare, but in Southeast Asia it is well know as beri-beri disease.

Riboflavin (vitamin B_2) is a component of flavin adenine dinucleotide (FAD), cofactors of flavin dehydrogenases.

Pyridoxin is a part of a prostetic group of enzymes which take part in amino acid transformation (aminotrans-ferases, decarboxylases).

Niacin is a name for two derivates of pyridine: **nicotinic acid** (pyridine-3-carboxylic acid) and its amide **nicotinamide**. Nicotinamide is a part of pyridine nucleotides, NAD^+, coenzyme transferring hydrogen in reactions catalyzed by many dehydrogenases.

Cobalamin (vitamin B_{12}) has a very complex structure with tetrapyrrole corrin system and a central cobalt ion. It is produced only by bacteria, it is found in animal products not in plant food. It is necessary for degradation of some amino acids and for methylation reactions.

Folic acid (folate) is a converted to tetrahydrofolate, cofactor transferring one-carbon residues in various oxidation states. Deficiency of folates is usually caused by insufficient resorption and results in abnormal blood count (megaloblastic anemia, thrombocytopenia).

Pantothenic acid contains β-alanine. It is very common in nature, therefore abundant in all foods. It is found as a part of **coenzyme A** and multienzyme complex synthesizing fatty acids.

Biotin (vitamin H) serves as a cofactor of carboxylation reactions. Biotin is found in common foods, main part of needed amount is synthesized by colon microflora.

Overview of vitamins is presented in the following table.

Common name	Letter	Deficit symptoms	Main food sources
Retinol	A	night blindness	liver, butter, egg yolk, coloured vegetable and fruits
Calciol	D	rickets	butter, fish oil, eggs (**partly formed in skin**)
Tocopherol	E	-	plant oils, nuts, seeds, germ oil
Phylloquinone	K_1	bleeding	vegetable, liver (**partly formed by intestinal bacteria**)
L-Ascorbic acid	C	scurvy	fresh fruits and vegetables, potatoes
Thiamine	B_1	neurological disorders	meat, eggs, wholemeal cereals, yeast
Riboflavin	B_2	angular stomatitis	eggs, milk, liver, yeast, cereals
Pyridoxin	B_6	-	meat, liver, cereal germs, yeast
Niacin	B_3	pellagra	meat, liver (**partly formed in cells from tryptophan**)
Cobalamin	B_{12}	anemia	only animal products
Folic acid	B_{11}	anemia	leafy vegetables, liver
Pantothenic acid	B_5	-	liver, milk, eggs
Biotin	H	-	egg yolk, liver (**partly formed by intestinal bacteria**)

18 NUCLEOTIDES AND NUCLEIC ACIDS

Nucleosides
are compounds, in which heterocyclic nitrogen base and pentose are linked by *N*-glycosidic bond, with the removal of water. The sugar component is **ribose** or **deoxyribose**, nitrogen bases include purine bases **adenine** and **guanine** (and hypoxanthine) or pyrimidine bases **uracil, cytosine**, and **thymine**. These bases exhibit tautomerism, but in cells with pH approximately 7, the hydroxyl group exists mainly in its lactam (i.e. oxo) form, amino groups of guanine and cytosine remain in the lactim form.
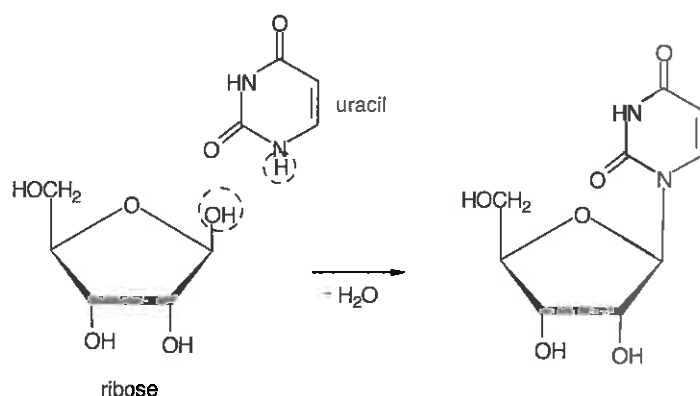
Nucleosides have trivial names, which are derived from names of bases (see the table). The names of purine nucleosides end by *-osine* (adenine → adenosine), the pyrimidine nucleosides end by *-idine* (uracil → uridine). Carbon atoms of pentose are numbered 1'- 5', so that they differ from the numbering of the base. Purine bases are usually glycosylated on the nitrogen N9, pyrimidine base on N1. The *N*-glycosidic bond has β configuration, the glycosyl is thus β-D-ribofuranosyl. The table shows the names of nucleosides/nucleotides with ribose, in the case of thymine with deoxyribose.

Base	Nucleoside	Nucleotide
Adenine	adenosine (A)	adenosine 5'-monophosphate (AMP)[a]
Guanine	guanosine (G)	guanosine 5'-monophosphate (GMP)
Hypoxanthine	inosine (I)	inosine 5'-monophosphate (IMP)
Cytosine	cytidine (C)	cytidine 5'-monophosphate (CMP)
Uracil	uridine (U)	uridine 5'-monophosphate (UMP)
Thymine	deoxythymidine (dT)	deoxythymidine 5'-monophosphate (dTMP)

[a]AMP is sometimes called adenylic acid (adenylate).

Nucleosides are highly polar compounds, soluble in water. Their *N*-glycosidic bond can be, like in other glycosides, hydrolyzed by diluted acids, it is stable in alkaline environment.


adenosine (A) guanosine (G) inosine (I)
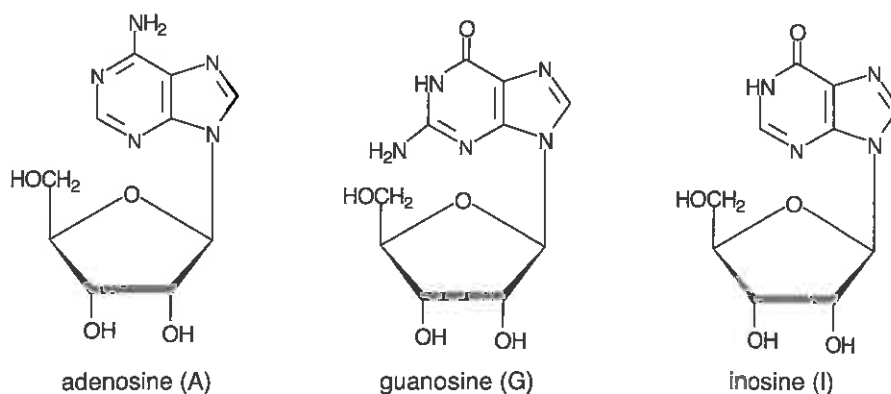
Nucleotides

are derivatives of nucleosides, phosphoric acid is bound to ribose by ester bond, most often in the positions 5' or 3'. General name of a nucleotide is nucleoside phosphate. In solutions with pH 7.0 we find **nucleoside monophosphates** as anions with two negative charges. **Nucleoside diphosphates** and **nucleoside triphosphates** have phosphate groups linked by **anhydride bonds.**

Energy accumulated by the formation of two anhydride bonds makes nucleoside triphosphates to be **high-energy** compounds, the most universal is **adenosine-5'-triphosphate (ATP)**. The hydrolysis of ATP to ADP and phosphate is a very exergonic reaction: $ATP + H_2O \rightarrow ADP + P_i + energy$.

The Gibb's energy released in this reaction is used to drive many biochemical processes, enzymatically catalyzed endergonic reactions, to create concentration gradients on membranes, for muscle contraction, etc. Thus ATP in cells presents a prompt source of chemical energy.
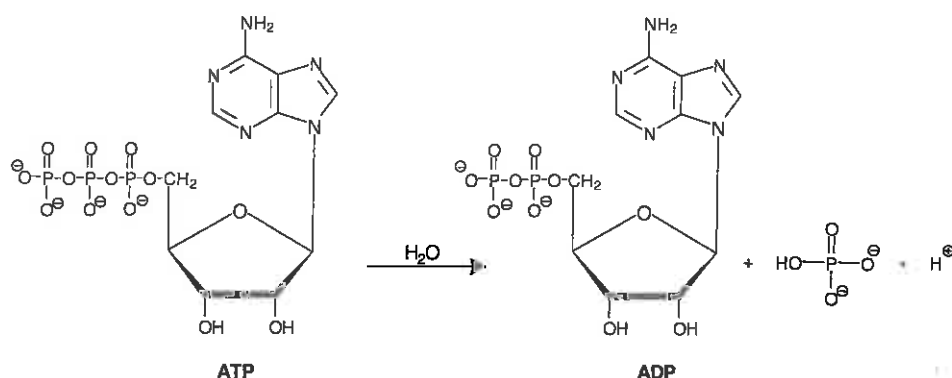
Nucleotide coenzymes

Nucleotides structurally include also coenzymes of redox reactions NAD⁺ and FAD. As **pyridine nucleotide** we take the coenzyme **NAD⁺** (nicotinamide adenine dinucleotide). Most flavoproteins contain flavin adenine dinucleotide, **FAD**. Another important compound, which contains adenine nucleotide is **coenzyme A** (CoA-SH). It is the cofactor for the transfer of acyl groups.

Nucleic acids

are polynucleotides made of tens up to millions of nucleotides inked by the **3',5'-phosphodiester bonds**. A 5'-phosphate group is attached to a 3'-OH group of the following nucleotide. Chains of all nucleic acids are made of regularly sequenced phosphate-pentose groups with purine or pyrimidine bases attached to their anomeric carbons (C1') by *N*-β-glycosidic bonds. Polynucleotide chains have polarity (direction). Each chain has its 5'end and 3'end; there is a free phosphate group at C5 of the 5'end, on the other side of the chain there is a free hydroxyl group at C3 of pentose.
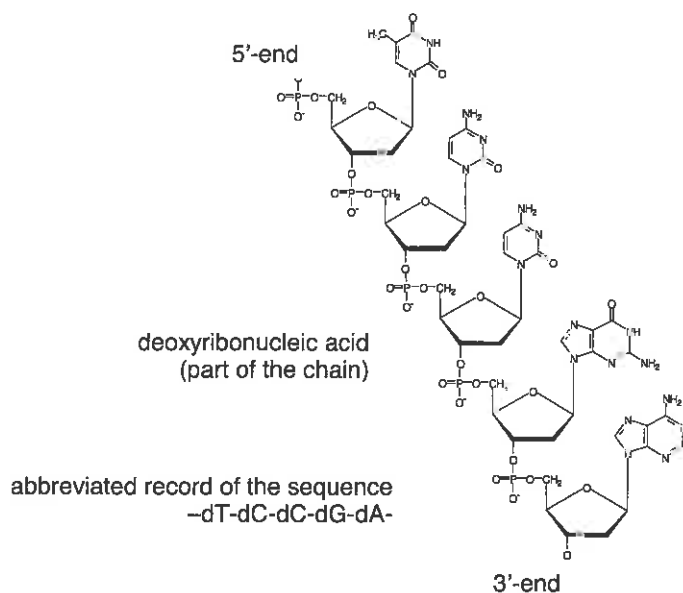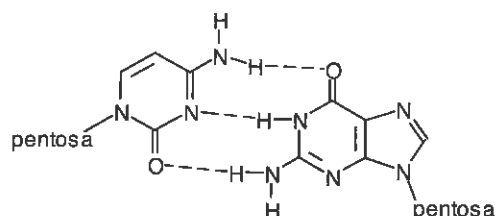
Deoxyribonucleic acids (DNA)

DNA molecules are carriers of genetic information. DNA molecules are extremely long polynucleotides which, besides deoxyribose and phosphoric acids, are made of purine bases adenine and guanine and pyrimidine bases, cytosine and thymine. Thymine is typical for deoxyribonucleic acids while ribonucleic acids contain uracil on its place. DNA molecules are double-stranded, strands are antiparallel, which means that the direction of bonds is 5'→3' in one strand and 3'→5' in the other strand. Both polynucleotide strands are **complementary** to each other; opposite nucleotides are held by hydrogen bonds between bases. Hydrogen bonds are formed between adenine – thymine and guanine – cytosine pairs.
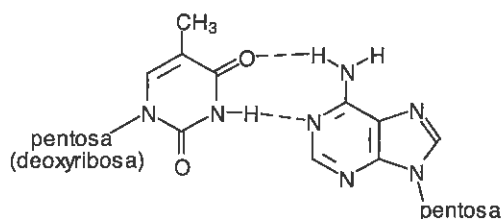
thymine-adenine (two H bonds)   cytosine-guanine (three H bonds)

The two polynucleotide chains are twisted around longitudinal axis and form a **double-helix**. The skeleton of DNA molecule is formed by **phosphodiester bonds** between deoxyribose and phosphate. Phosphate groups with negative charges protrude from the surface into the space. Purine and pyrimidine bases are oriented inside the double helix.

Ribonucleic acids (RNA)

RNA chain is similar to DNA; 3',5'-phosphodiester bonds connect ribonucleotides. There is uracil instead of thymine and in some RNAs we can find other modified bases. RNA molecules are shorter compared to DNA and they are, in animal cells, only single stranded. However, there are some parts which are double stranded – arms (this occurs when there are complementary sequences). According to their function, there are three types of RNA: messenger RNA (mRNA), ribosomal RNA (rRNA), and transfer RNA (tRNA). They differ by molecular size and the structures of bases. They all have specific functions in protein synthesis.

Messenger RNAs (mRNA) take only few percent of the total cellular RNA, but they present a very diverse group. The mRNA carries the transcribed genetic information from structural genes. It serves as a template for protein synthesis on ribosomes. Each protein synthesized in the cell has its specific mRNA, which represents a transcript of one gene. The primary structure of polypeptide chain is defined by nucleotide sequence of the gene made up by triplets of bases. Each of the 20 coded amino acids is represented in the mRNA by a triplet of bases called **codon**.

Ribosomal RNAs (rRNA) are the most abundant in cells, they form up to 80 % of all cellular RNA. They are found in different types which can be distinguished by size, base composition, and specific sedimentation constant (S). rRNAs are structural compounds of ribosome subunits on which translation takes place. There are four different types of rRNA in eukaryotic organisms; the small subunit contains one molecule 18S-RNA, large subunit contains one of each 5S-, 5,8S- and 28S-rRNA. Molecular mass of mRNA corresponds to about 100-5000 nucleotides and there are many arms and loops made. The biological half time of rRNA is very long compared to mRNA.

Transfer RNAs (tRNA) are the smallest type of RNA. The function of tRNA is to bond a specific amino acid and transfer it to ribosome in the correct order of polypeptide chain. There are at least 20 different tRNA in each cell,

that means there is at least one tRNA for each of the 20 standard amino acids. In all tRNA there is a significant amount of unusual or **minor bases**. Those are chemically modified bases, for example methylated guanosine or hydrogenated uridine. Minor bases are necessary for formation of secondary and tertiary structures of tRNA. If we draw the secondary structure of tRNA in two dimensions it resembles a cloverleaf. The 3'-end with a CCA sequence forms an ester bond with acyl of amino acid by its 3'-hydroxyl of adenosine. During protein synthesis, **translation**, tRNA carrying a corresponding amino acid binds by its **anticodon** to the complementary codon of mRNA. Hydrogen bonds are formed between chains of opposite polarity.

19 ENERGY AND METABOLISM

Living organisms require a continuous influx of energy to carry out their various multiple functions. The processes of gaining and utilizing energy are called metabolism. Metabolism involves two kinds of chemical reactions:

Exergonic reactions (releasing free energy) are mostly the conversions (oxidations) of hydrogen-rich nutrients to energy-poor CO_2 and H_2O. Since more complex compounds are degraded to simple products, the reactions are called **catabolic**.

Endergonic processes (biosynthesis of complex molecules – **anabolic** reactions, performance of mechanical or osmotic work etc.) can occur only when they are coupled to exergonic reactions. Only plants are able to acquire energy from the Sun to perform the endergonic synthesis of saccharides from carbon dioxide and water through photosynthesis.

Photosynthesis in plants converts light energy into chemical energy. Energy-poor compounds CO_2 and H_2O are converted to glucose while releasing oxygen. The complex process of photosynthesis catalyzed by chlorophyll can be expressed by overall reaction: $6\ CO_2 + 6\ H_2O \rightarrow C_6H_{12}O_6 + 6\ O_2$. Saccharides then serve as an energy source for the organisms that have produced them as well as for chemotrophs. These consume plants and oxidize hydrogen-rich saccharides to water and CO_2.

Free energy released during exergonic oxidations is conserved by the synthesis of energy-rich phosphates. Adenosine triphosphate (ATP) synthesized from adenosine diphosphate (ADP) and inorganic phosphate, is the most universal carrier of free energy. The breakdown of ATP to ADP and inorganic phosphate (P_i) is highly exergonic: **$ATP + H_2O \rightarrow ADP + P_i + energy$**.

This reaction powers the work done by living systems (mechanical work, synthesis of large biomolecules etc.). Animals are chemotrophs which obtain their free energy by oxidation of hydrogen-rich nutrients (saccharides, lipids, proteins). Dioxygen, a common oxidant, is consumed for the oxidation of hydrogen of the nutrients to produce water ($4\ H + O_2 \rightarrow 2\ H_2O$). Carbon dioxide is produced by decarboxylations of some acids. Most of the free energy released during the catabolism of nutrients is conserved through the synthesis of ATP, the remaining part is released as heat.
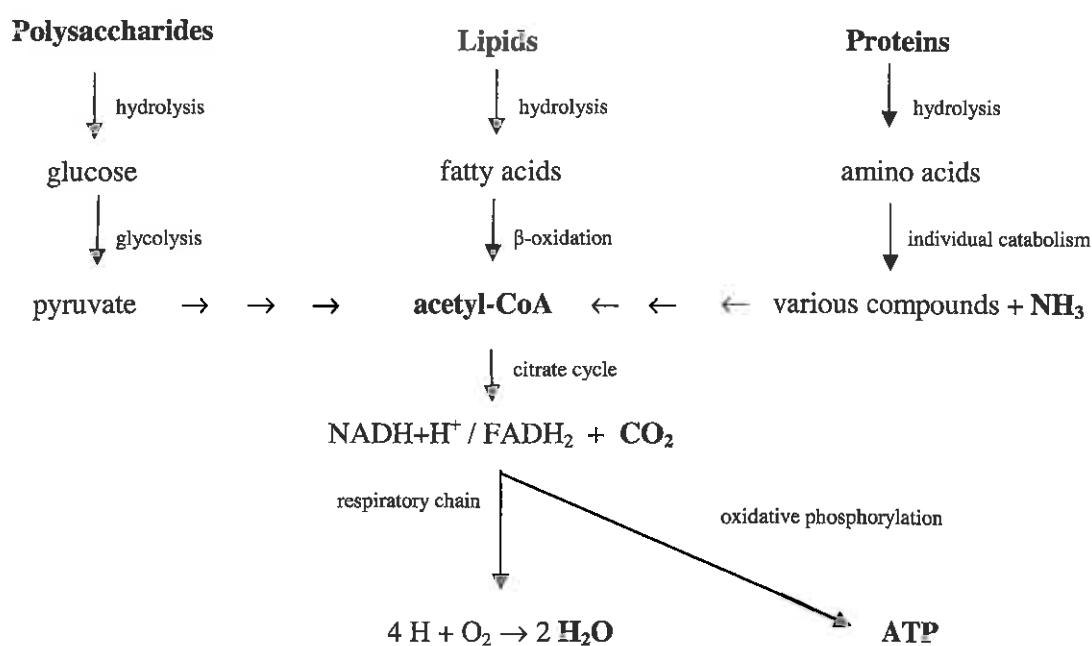
The catabolism of glucose can be simply described as $C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O$. In animal cells, this reaction is carried out in a complex series of nearly twenty consecutive reactions that are carefully controlled. However, it is interesting that diverse nutrients (saccharides, lipids, proteins) are converted to only a few common intermediates that are further catabolized in the common way to CO_2 and H_2O. The three stages can be distinguished in the generation of energy from the oxidative degradation of complex nutrients.

1. Hydrolysis of complex nutrients into smaller units. It does not supply any useful free energy in the form of ATP. Polysaccharides (starch) give glucose, triacylglycerols are hydrolyzed to glycerol and fatty acids, proteins to amino acids.
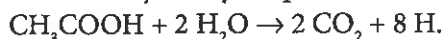
2. In specific multistep pathways, molecules of simple nutrients undergo partial oxidation (dehydrogenations) and are converted into acetyl coenzyme A (acetyl-CoA) and a few other amphibolic intermediates. The term amphibolic means that the compounds may still serve as a starting material for some anabolic pathways, for example, the synthesis of fatty acids or steroids. In the second stage, a small amount of ATP is formed only in the catabolism of glucose (glycolysis).

3. The last stage is the irreversible oxidation of acetyl-CoA to CO_2 in the citric acid cycle. ATP is generated as a consequence of reoxidation of NADH and $FADH_2$ by O_2 in the mitochondrial respiratory chain (oxidative phosphorylation).

Polysaccharides   **Lipids**   **Proteins**

$\downarrow$ hydrolysis $\downarrow$ hydrolysis $\downarrow$ hydrolysis

glucose   fatty acids   amino acids

$\downarrow$ glycolysis $\downarrow$ β-oxidation $\downarrow$ individual catabolism

pyruvate $\rightarrow$ $\rightarrow$ $\rightarrow$ **acetyl-CoA** $\leftarrow$ $\leftarrow$ $\leftarrow$ various compounds + **NH₃**

$\downarrow$ citrate cycle

$NADH + H^+ / FADH_2 + CO_2$

respiratory chain   oxidative phosphorylation

$4 H + O_2 \rightarrow 2 H_2O$ **ATP**
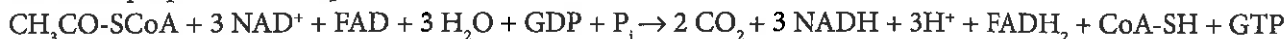
Citric Acid Cycle

occurrs in the matrix of mitochondria and oxidizes the acetyl group of acetyl coenzyme A to two molecules of CO_2. Hydrogen atoms concomitantly generated in the form of reduced coenzymes $NADH + H^+$ and $FADH_2$ are then transferred into the respiratory chain and are oxidized to water. The result of the citric acid cycle can be described by a very simplified reaction:

$CH_3COOH + 2 H_2O \rightarrow 2 CO_2 + 8 H.$

The more proper balance equation is:

$CH_3CO\text{-}SCoA + 3 NAD^+ + FAD + 3 H_2O + GDP + P_i \rightarrow 2 CO_2 + 3 NADH + 3H^+ + FADH_2 + CoA\text{-}SH + GTP$

It is a complex series of sequential reactions. First, acetyl (C_2 unit) from acetyl-CoA is condensed with oxaloacetate (C_4 dicarboxylic acid) to give citrate (C_6 tricarboxylic acid). Citric acid is then isomerized, dehydrogenated, and decarboxylated to give 2-oxoglutarate (C_5) that converts, being further oxidized and decarboxylated to succinyl-CoA. Other intermediates are succinate, fumarate, malate. The cyclic process is closed by oxaloacetate which can be condensed again with another acetyl group.
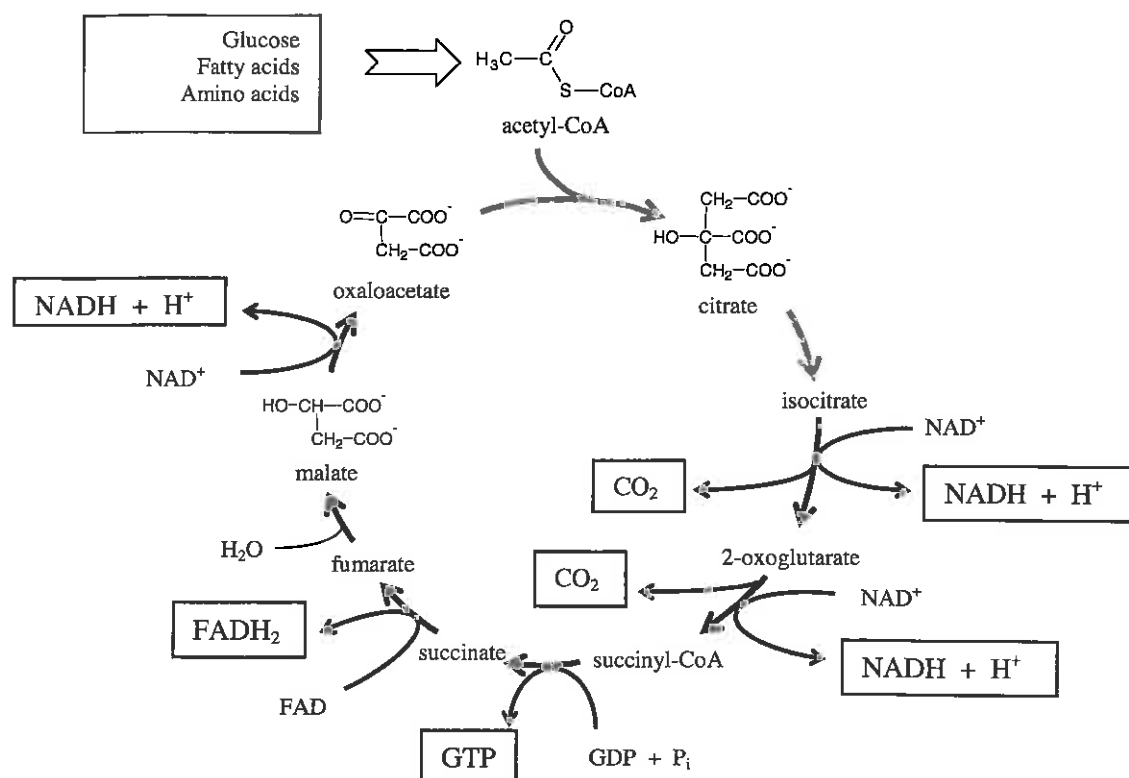
Each acetyl group entering the cycle is thus completely oxidized to two CO_2 molecules. The resulting eight atoms of hydrogen, 8 H = 3 (NADH+H$^+$) + FADH$_2$, are the substrates for the respiratory chain.

Respiratory Chain and Oxidative Phosphorylation

The respiratory chain is the final phase of oxidative degradation of nutrients. Atoms of hydrogen removed from amphibolic metabolites through dehydrogenations in the form of reduced coenzymes NADH+H$^+$ and/or FADH$_2$ pass into the mitochondrial respiratory chain. The reduced coenzymes are reoxidized and **electrons** from these hydrogen atoms participate in the consecutive reduction of several oxidoreductases (complexes) in the inner mitochondrial membrane, before they **reduce dioxygen** to water (4 e$^-$ + 4 H$^+$ + O$_2$ → 2 H$_2$O). The last step is catalyzed by cytochrome oxidase.

In this electron transport, H$^+$ ions are expelled from the mitochondrion through the inner mitochondrial membrane. An electrochemical proton gradient across the membrane is generated and represents a special form of free energy. This energy drives phosphorylation, the synthesis of ATP from ADP and inorganic phosphate: **ADP + P$_i$ + energy of H$^+$-gradient → ATP + H$_2$O.**

Since the phosphorylation is tightly coupled to the terminal oxidation of reduced coenzymes by oxygen, it is called **oxidative phosphorylation.** Oxidation of each NADH+H$^+$ yields 3 molecules ATP, oxidation of FADH$_2$ only 2 ATP molecules. Although some ATP is generated also in other processes (e.g. anaerobic glycolysis), oxidative phosphorylation is the major source of ATP. The total free-energy yield of one acetyl group oxidation to CO_2 and H$_2$O is utilized for generation of 12 ATP.

Metabolism of Saccharides

Saccharides are the main nutrients for humans, with starch prevailing in the human diet. Digestion of starch begins in the mouth and is completed in the small intestine. Both saliva and pancreatic juice contain α-amylase

that acts as a catalyst of the hydrolytic splitting of $\alpha(1\rightarrow4)$ glycosidic bonds. Due to amylase and other glycosidases, starch, dextrines, and maltose are decomposed to glucose that is readily absorbed and enters the blood circulation.

Glycolysis is the major pathway for utilization of glucose in the cytosol of all cell types. It can occur in the presence or absence of oxygen. After phosphorylation to glucose 6-phosphate, glucose is converted, in several steps, into pyruvate. Under **anaerobic** conditions, pyruvate is reduced to lactate in order to reoxidize 2 molecules of NADH formed in the previous reactions. The net energy yield of anaerobic glycolysis is not large and it may be expressed as follows:

$C_6H_{12}O_6 \rightarrow 2\ CH_3\text{-}CH(OH)\text{-}COOH + 2\ ATP$.
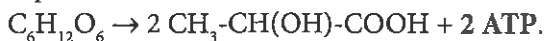
Under **aerobic** conditions, pyruvate is oxidatively decarboxylated to acetyl coenzyme A. Further oxidation to CO_2 in the citric acid cycle generates reduced coenzymes that yield water and ATP as a consequence of oxidative phosphorylation. The complete aerobic degradation of glucose to CO_2 and water generates a great amount of free energy captured as ATP while the remaining energy is lost as heat:

$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O + \textbf{38 ATP}$.

If cells are sufficiently supplied with glucose, the amount of glucose not immediately oxidized can be either stored in the form of glycogen (liver, muscles) or used for the synthesis of fat reserves.

Scheme of glucose metabolism
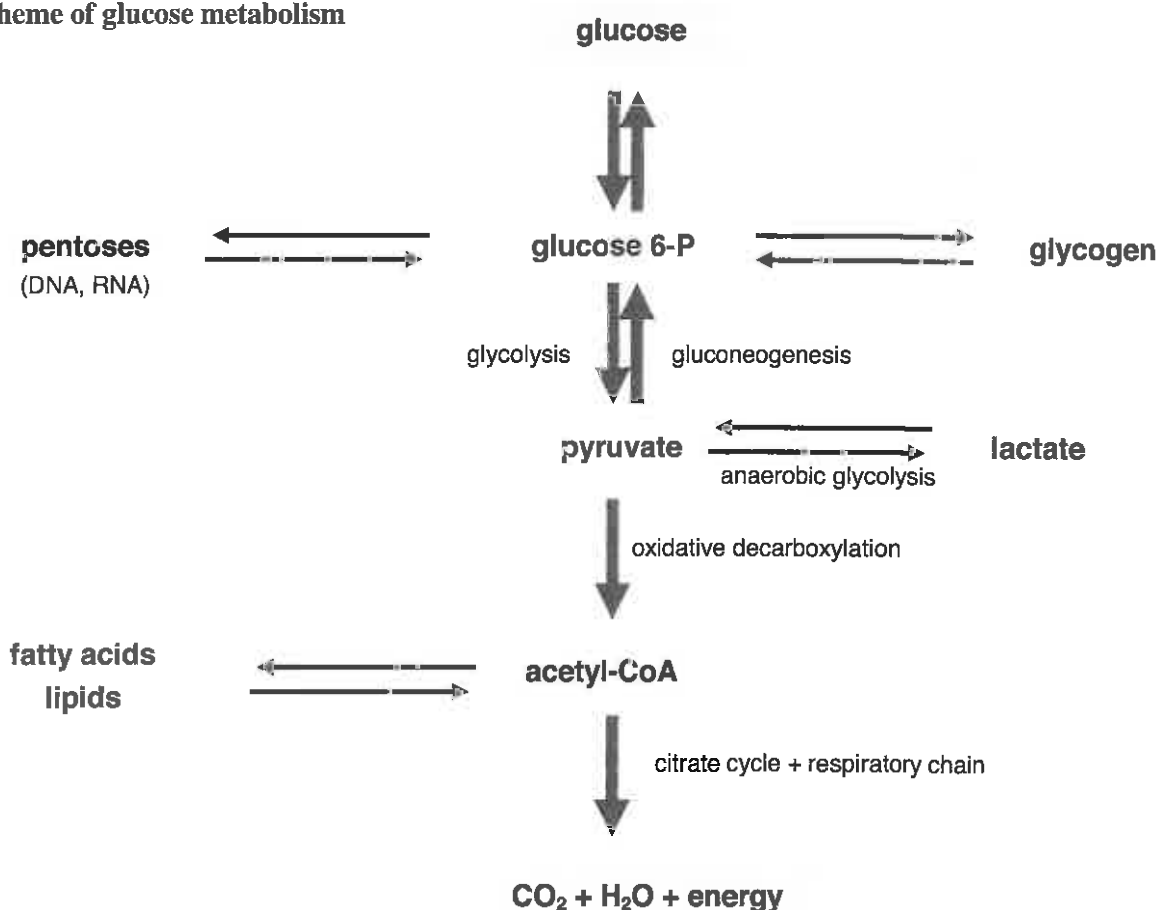

Metabolism of Lipids

Fat (triacylglycerols) is a normal constituent of the diet and is also the chief form of storage of energy-providing compounds in many animal species. Triacylglycerols have a high energy content (38 kJ/g). Glucose or starch can yield only about 16 kJ/g.

Digestion of dietary fat. In the small intestine, fat is emulsified due to the presence of bile acids and hydrolyzed to free fatty acids and monoacylglycerols by the action of pancreatic lipase.
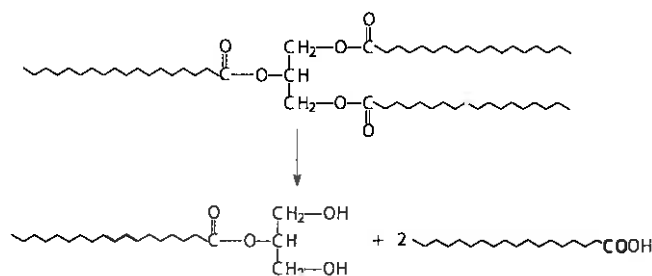
After absorption, triacylglycerols are resynthesized within the mucosal cells and enter the bloodstream as complex micelles called lipoproteins (**chylomicrons**). Most of the fat undergoes again the hydrolysis of ester bonds catalyzed by lipoprotein lipase and the resulting components enter the cell. Within cells, glycerol may be oxidized and then metabolized through the glycolytic pathway. Fatty acids are broken down oxidatively to acetyl groups (acetyl-CoA) that enter the citric acid cycle.

β-Oxidation. The oxidative degradation of fatty acids takes place within mitochondria. It is a repeating series of reactions simply named β-oxidation. Firstly, a fatty acid has to be activated through joining to coenzyme A (the required energy is obtained from hydrolysis of one ATP):

R-COOH + HS-CoA + ATP + H_2O → R-CO-S-CoA + AMP + 2 P_i.
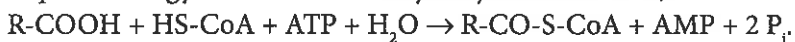
Acyl-CoA (R-CO-S-CoA) then undergoes four successive reactions:
(1) dehydrogenation ($FADH_2$ is produced) to α,β-unsaturated acyl-CoA,
(2) addition of water resulting in β-hydroxyacyl-CoA,
(3) dehydrogenation (producing NADH) to β-oxoacyl-CoA,
(4) cleavage of the bond between α- and β-carbon by the action of free coenzyme A.
Since the initial acyl-CoA has been shortened by two carbons, these can now be further oxidized in the same four steps. The second product is **acetyl-CoA**, which can be completely oxidized in the citric acid cycle. The cycle repeats till the long-chain fatty acyl-CoA is degraded to molecules of acetyl-CoA. The cycle produces $FADH_2$ and NADH+H⁺ which are reoxidized in the respiratory chain producing ATP. Each turn also sends one acetyl group into the citric acid cycle which, via the respiratory chain, yields more ATP molecules by complete oxidation than are produced by β-oxidation. For example, the complete oxidation of palmitic acid to CO_2 and H_2O yields 129 ATP, from which only 35 ATP represent the yield of β-oxidation.

If there is a high production of acetyl-CoA derived from glucose, and a low demand for energy, the synthesis of fat is initiated. Fatty acids are synthesized from acetyl-CoA due to the pathway that has some similarity to a reversal of the β-oxidation pathway.

Scheme of β-oxidation
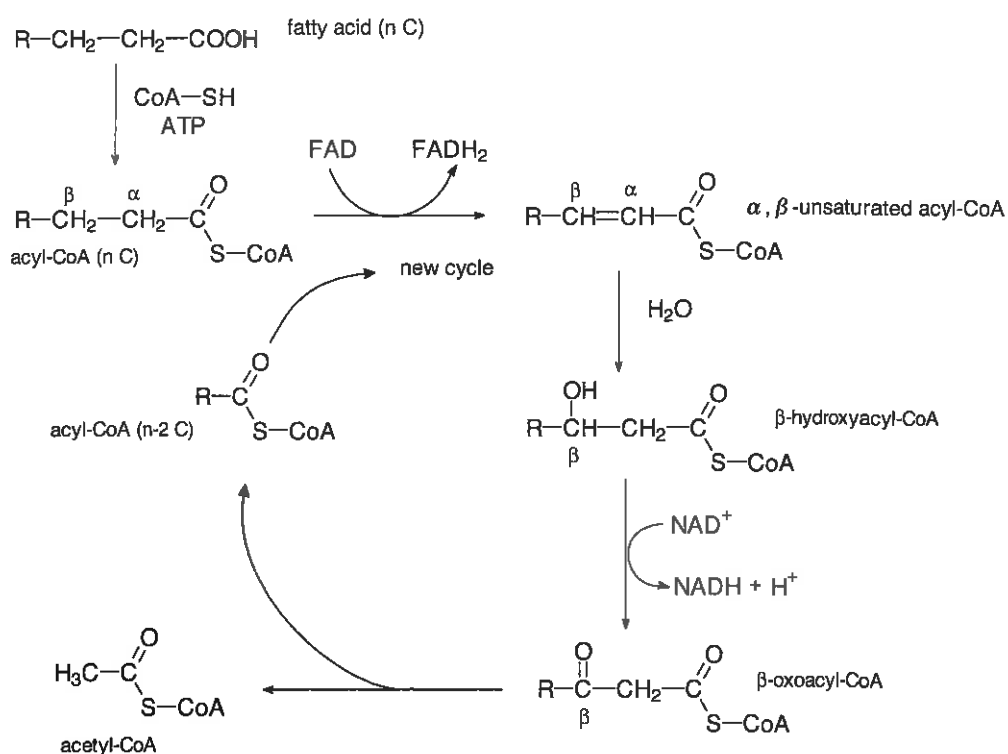
Metabolism of Proteins and Amino Acids

Humans, like other animals, require a certain minimum intake of proteins or amino acids in order to grow and prosper. Some of the twenty coded amino acids cannot be synthesized in animal cells at all. These essential amino acids must be supplied by the diet. Other amino acids may be manufactured from the amphibolic intermediates.

Digestion. Protein digestion is initiated in the stomach and continues in the small intestine. Proteins are subjected to the action of proteolytic enzymes which catalyze the hydrolysis of peptide bonds. **Proteinases** (formerly endopeptidases) hydrolyze peptide bonds within the main structure of proteins or large peptides thus producing peptides of various length, e.g. pepsin in the acid content of stomach, trypsin and chymotrypsin, constituents of the pancreatic secretion, in the alkaline chymus in the small intestine. **Peptidases** (formerly exopeptidases) then degrade peptides to free amino acids: **carboxypeptidases** cleave peptide bonds next to C-terminal amino acids, **aminopeptidases** attack the amino-terminal peptide bonds. All proteolytic enzymes are secreted as inactive proenzymes (zymogens, e.g. pepsinogen,) that are activated after being secreted into the lumen of the digestive tract. Free amino acids, the end products of protein digestion, are readily absorbed and enter the blood. They are supposed to form the general **amino acid pool** which can be used by the cell by the three ways:

(1) to synthesize proteins (for cell division, growth, renewing or reparation of tissues),
(2) to synthesize important non-protein low-molecular nitrogen compounds, like purines, pyrimidines, heme, biologically active amines, hormones etc.
(3) to provide free energy supply when other resources are exhausted.

Catabolism of amino acids

begins with removal of the α-amino nitrogen by transamination or deamination. The resulting carbon skeleton is then oxidatively degraded to amphibolic intermediates that can enter the citric acid cycle for complete oxidation to water and CO_2. The α-amino nitrogen, in fact highly toxic **ammonia**, is converted to **urea**. Urea is excreted as non-toxic end product.

The synthesis of proteins

from amino acids takes place on the surface of ribosomes. The process is called **translation** because the information from the nucleotide sequence of mRNA is translated accurately into the sequence of amino acids of the corresponding specific protein. Free amino acids must be first activated by the formation of aminoacyl esters with the specific type of tRNA which has the corresponding anticodon:

amino acid + tRNA + ATP $\rightarrow$ aminoacyl-tRNA + AMP + 2 P_i.
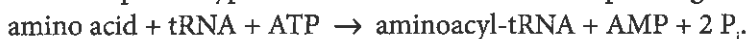
Theoretically, there should exist at least twenty specific tRNAs, one for each of the twenty amino acids, but they are, in fact, about sixty since there are 64 coding triplets. The synthesis is initiated after binding mRNA and the first aminoacyl-tRNA (methionyl-tRNA), attached to the starting codon of mRNA, upon the surface of a ribosome. Then the next aminoacyl-tRNA binds, by its anticodon, to the second codon of mRNA. The peptide bond is formed by transfer of the first aminoacyl (or peptidyl, in further steps) to the free amino group of the next aminoacyl-tRNA. During this stage, termed elongation, the ribosome moves along the mRNA. In the last stage, termination, the complete polypeptied chain is released from the last tRNA after the termination codon in the mRNA sequence has been reached. In eukaryotic cells, syntheses of different proteins occur either on free ribosomes or on ribosomes attached to the membranes of endoplasmic reticulum.

Hormones

are substances that, released from certain types of cells, possess regulatory functions and affect the metabolism even of very remote cells (target tissues). The name endocrine tissue (or gland) was given to the tissues which are specialized in the secretion of hormones into the blood.

However, it appeared that there are many other cell types that produce and release substances (local hormones, cytokines, growth factors, etc.) into the blood or interstitial fluid acting in the same way as classic hormones. Neurotransmitters similarly provide intercellular communication between neurons and other cells. In spite of a wide diversity in the specific responses of target cells, all those signaling molecules have only a limited number of different mechanisms of action on the cell.

According to structure and solubility, hormones can be classified as:

(1) Proteins, peptides, and simple derivatives of amino acids. They are polar, hydrophilic, and therefore, they do not enter the target cells. After binding a hormone to specific protein receptor on the outer surface of the cell membrane, intracellular events follow that can be a consequence formation of another signaling molecule (a second messenger).

(2) Steroid and thyroid hormones are simple but hydrophobic compounds. They can diffuse into cells and their action is mediated by interactions with specific intracellular protein receptors. They are translocated into nucleus where they interact with DNA.

Examples of Hydrophilic Hormones

The anterior pituitary secretes several hormones that regulate the growth and function of other endocrine glands: **Growth hormon** (somatotropin) is essential for postnatal growth, because it stimulates protein synthesis. Two **gonadotropins** (follicle-stimulating and luteinizing hormone) regulate synthesis and secretion of

steroid sex hormones in the gonades they are a.polypeptide adrenocorticotropic hormone (**ACTH**) and thyroid-stimulating hormone (TSH) stimulating the adrenals and the thyroid, respectively. The anterior pituitary itself is under control of hypothalamic hormones (called releasing and release-inhibiting factors).

The posterior pituitary releases **oxytocin** (a nonapeptide) that causes contraction of some smooth muscles and **vasopressin** (antidiuretic hormone) that inhibits excretion of water by the kidney.
Parathyroid hormone (PTH) is formed in the parathyroid glands. It regulates the level of calcium and phosphate ions in the blood.

The pancreatic hormones **insulin** and **glucagon** formed in the endocrine portion of the pancreas (the islets of Langerhans) are both polypeptides chiefly involved in regulating the saccharide metabolism. Insulin decreases the blood glucose level and diabetes mellitus is due to insufficient action of insulin. Glucagon opposes the actions of insulin.

Adrenaline (epinephrine), a derivative of tyrosine, the major product of the adrenal medulla, is released in response to severe stress and regulates many functions of cardiopulmonary system.

Examples of Hydrophobic Hormones
Thyroxine and triiodothyronine, derivatives of tyrosine, are produced in the thyroid gland. They enhance general protein synthesis and in this way mostly increase the rate of metabolic processes.

Steroid hormones are chiefly produced from cholesterol in the adrenal cortex and in the gonades, i.e. in the testes and ovaries. The adrenal cortex secretes glucocorticoids, such as cortisol, mineralocorticoids, such as aldosterone, and some androgens. **Cortisol** is the essential component of adaptation to severe stress since it increases the rate of metabolism to ensure necessary nutrients. **Aldosteron** regulates the electrolyte balance and osmolality of the internal environment. The gonadal sex hormones are of three types. The male hormones, androgens, principally **testosterone**, are anabolic hormones increasing the synthesis of proteins besides their crucial function in reproduction. The female hormones, estrogens, such as **estradiol** and progestins, such as **progesterone**, determine the frequency of ovulation and the menstrual cycle, support pregnancy and the development of the mammary gland.

20 MODEL TEST QUESTIONS

Select just one statement from the five possible answers (a – e).
The statement „e) no answer is correct" is not given to save the space.

Inorganic formulas, chemical calculations based on formulas and equations, substance amount

1. Select the formula of copper(I) nitrite:
a) $Cu(NO_2)_2$ b) Cu_2NO_2 c) $CuNO_2$ d) $CuNO_3$

2. Select the formula of calcium hypochlorite:
a) $CaClO_2$ b) $CaCl_2$ c) $CaHClO$ d) $Ca(ClO)_2$

3. Select the formula of barium manganate:
a) $BaMnO_4$ b) Ba_3Mn_2 c) $BaMnO_3$ d) $Ba(MnO_4)_2$

4. Select the formula of magnesium hydrogen sulfite:
a) $Mg(HS)_2$ b) $Mg(HSO_4)_2$ c) $MgHSO_4$ d) $MgHSO_3$

5. Select the formula of iron(II) phosphate:
a) Fe_3PO_4 b) $Fe_3(PO_4)_2$ c) $Fe_2(PO_4)_3$ d) $FePO_4$

6. Select the formula of chromium(III) hydrogen sulfate:
a) $Cr_2(HSO_4)_3$ b) $Cr(HSO_4)_2$ c) $Cr_3(HSO_4)_2$ d) $Cr(HSO_4)_3$

7. Select the formula of magnesium diphosphate:
a) $Mg_3(PO_4)_2$ b) $Mg_2P_2O_7$ c) $Mg_3P_2O_4$ d) MgP_2O_8

8. Select the formula of barium sulfite:
a) BaS_2 b) $Ba(HSO_3)_2$ c) $Ba_2(SO_3)_3$ d) $BaSO_3$

9. Select the formula of calcium hydrogen phosphate:
a) $Ca_3(HPO_4)_2$ b) $CaHPO_4$ c) $Ca(HPO_4)_2$ d) $Ca(H_2PO_4)_2$

10. Calculate the mass fraction of oxygen, $w(O)$, in hydrogen peroxide:
a) 0,94   b) 0,89   c) 0,50   d) 0,21

11. Calculate the mass fraction of oxygen, $w(O)$, in glucose ($M_r = 180$):
a) 0,53   b) 0,58   c) 0,70   d) 0,36

12. Calculate the mass fraction of nitrogen, $w(N)$, in ammonium nitrate ($A_r(N) = 14,0$):
a) 43,8 %   b) 35,0 %   c) 21,9 %   d) 17,5 %

13. Calculate the mass of potassium in 87 g of anhydrous potassium sulfate ($A_r(K) = 39,1$; $A_r(S) = 32,1$):
a) 39,0 g   b) 19,5 g   c) 22,4 g   d) 6,17 g

14. Calculate the mass of silver in 3,50 g of silver nitrate ($A_r(Ag) = 108$; $A_r(N) = 14,0$):
a) 1,63 g   b) 3,10 g   c) 0,55 g   d) 2,22 g

15. Calculate the mass of calcium sulfate containing 10 g of calcium ($A_r(Ca) = 40,1$; $A_r(S) = 32,1$):
a) 67,9 g   b) 34,0 g   c) 44,0 g   d) 18,0 g

16. The Avogadro's constant expresses:
a) the mass of atomic mass unit   b) the volume of one mole of gas
c) the number of particles in one mole of substance   d) the number of molecules in one litre of gas

17. Calculate the substance amount in 1 g of tetrachloromethane ($A_r(Cl) = 35,5$)
a) 145 mmol   b) 6,49 mmol   c) 21,0 mmol   d) $3,91.10^{24}$ mmol

18. Calculate the substance amount in 1 kg of water:
a) 55,5 mol   b) 1 mol   c) 18,0 mol   d) $44,6.10^{-3}$ mol

19. Calculate the number of oxygen atoms in 0,4 mol of KNO_3:
a) $1,45.10^{24}$ b) $1,45.10^{23}$ c) $7,23.10^{24}$ d) $7,23.10^{22}$

20. Calculate the number of hydrogen atoms in 1 g of water:
a) $3,34.10^{22}$ b) $5,37.10^{22}$ c) $6,69.10^{22}$ d) $1,32.10^{25}$

21. Calculate the mass of 6,72 m^3 of nitrogen ($t = 0$ °C, $p = 101,3$ kPa) ($A_r(N) = 14,0$)
a) 4,20 kg   b) 8,40 kg   c) 4,20 g   d) 22,4 g

22. Calculate the mass of 3,36 m^3 of helium ($t = 0$ °C, $p = 101,3$ kPa)
a) 1,2 kg   b) 300 g   c) 480 g   d) 600 g

23. Calculate the mass of CO_2 produced by the complete combustion of 20 g of ethyne (acetylene):
a) 33,8 g   b) 44,8 g   c) 67,7 g   d) 89,6 g

24. Calculate the mass of CO_2 produced by the complete combustion of 1 g of glucose ($M_r = 180$):
a) 1,66 g   b) 1,20 g   c) 0,60 g   d) 0,50 g

25. Calculate the volume of hydrogen ($t = 0$ °C, $p = 101,3$ kPa) released from 16,35 g of zinc in excess of hydrochloric acid ($A_r(Zn) = 65,4$):
a) 11,2 dm^3 b) 5,60 dm^3 c) 2,24 dm^3 d) 0,50 dm^3

26. Calculate the volume of CO_2 produced by the complete combustion of 9 g of ethyne (acetylene) ($t = 0$ °C, $p = 101,3$ kPa):
a) 7,75 dm^3 b) 5,22 dm^3 c) 10,4 dm^3 d) 15,5 dm^3

The structure of atom, the configuration of electrons, the types of bonds, polarity of molecules

1. Determine the number of neutrons in $^{35}_{17}Cl$ nuclide:
a) 35   b) 17   c) 52   d) 18

2. Determine the values of the subshell quantum number l, if $n = 3$:
a) -1, 0, +1   b) 0, 1, 2, 3   c) +1/2, -1/2   d) -2, -1, 0, +1, +2

3. Select the electron configuration of aluminium:
a) [He] $2s^2 2p^1$ b) [Ne] $2s^2 2p^2$ c) [He] $2s^2 2p^3$ d) [Ne] $3s^2 3p^1$

4. Select the electron configuration of calcium:
a) [Ar] $4s^2$ b) [Ne] $3s^2$ c) [Ne] $4s^2$ d) [Ar] $3s^2$

5. Which element has the electron configuration [Ne] $3s^2 3p^1$?
a) phosphorus   b) sodium   c) aluminium   d) boron

6. Which element has the electron configuration [Ne] $3s^2 3p^2$?
a) Mg   b) P   c) Ti   d) Si

7. How many electrons are there in the valence sphere of sulfur atom?
a) 2   b) 16   c) 14   d) 6

8. How many valence electrons are there in the element with proton number of 17 ?
a) 17   b) 7   c) 1   d) 3

9. How many valence electrons are there in the element with proton number of 15 ?
a) 3   b) 5   c) 7   d) 15

10. How many valence electrons are there in the element with proton number of 19 ?
a) 19   b) 7   c) 4   d) 3

11. Which element belongs to the p^2 elements?
a) Sn   b) Se   c) Sb   d) Sr

12. Which element belongs to the p^3 elements?
a) B   b) Cr   c) Au   d) Sb

13. Which element belongs to the p^4 elements?
a) Si   b) Ti   c) Se   d) Br

14. Locate the least electronegative elements in the periodic table:
a) right bottom part of the table   b) left bottom part of the table
c) the region of transition elements   d) left top part, near hydrogen

15. Select the compound with covalent bonds:
a) Na_2O b) $CaCl_2$ c) K_2S d) SiO_2

16. What is the shape of molecule with sp-hybridized central atom?
a) linear   b) planar   c) tetrahedral   d) bipyramidal

17. What is the shape of molecule with sp^3-hybridized central atom?
a) linear   b) planar   c) tetrahedral   d) octahedral

18. Select the complex compound:
a) $Mn(NO_3)_2$ b) Na_3FeF_6 c) $KAl(SO_4)_2$ d) AuBr

19. Select the substance with intermolecular hydrogen bonds:
a) CH_4 b) H_2 c) H_2S d) H_2O

20. Select the substance with intermolecular hydrogen bonds:
a) H_2O b) NH_3 c) CH_4 d) H_2

21. Select the ionic compound:
a) CO_2 b) P_2O_5 c) N_2O_3 d) MgO

22. Select the ionic compound:
a) KBr   b) SiC   c) HF   d) H_2

23. Select the ionic compound:
a) HF   b) SiO_2 c) CO_2 d) CaO

Solutions – concentrations, electrolytes, acids, bases, pH

1. Calculate the mass of glucose in 240 g of 0,80% solution:
a) 2,50 g   b) 3,33 g   c) 3,00 g   d) 2,00 g

2. Calculate the mass % of the solution prepared from 3 kg of substance and 12 kg of water:
a) 20 %   b) 25 %   c) 40 %   d) 36 %

3. Calculate the mass % of the solution prepared from 600 g of NaOH and 2,4 kg of water:
a) 40 %   b) 20 %   c) 16 %   d) 25 %

4. Calculate the mass of water needed to make 10% solution from 2 kg of 40% solution:
a) 2 kg   b) 4 kg   c) 8 kg   d) 10 kg

5. Calculate the mass of water needed to make 20% solution from 50 g of glucose.
a) 125 g   b) 250 g   c) 150 g   d) 320 g

6. Calculate the mass of NaCl needed to make 40% solution from 3 kg of water:
a) 1 200 g   b) 1 333 g   c) 2 000 g   d) 750 g

7. Calculate the mass of sucrose needed to make 25% solution from 3 kg of water:
a) 1286 g   b) 100 g   c) 833 g   d) 750 g

8. 200 cm³ of solution contains 10 g of alanine ($M_r = 89,0$). The molarity of alanine is:
a) 0,56 mol.dm⁻³   b) 1,78 mol.dm⁻³   c) 0,11 mol.dm⁻³   d) 2,2 mol.dm⁻³

9. What volume of 2 M H_2SO_4 contains 40 mmol H_2SO_4?
a) 50 cm³   b) 20 cm³   c) 80 cm³   d) 40 cm³

10. Calculate the mass of NaCl after evaporating 250 cm³ of 0,5 M solution ($M_r = 58,5$):
a) 29,2 g   b) 73,1 g   c) 7,31 g   d) 14,6 g

11. Calculate the mass of iron(II) chloride in 300 cm³ of 0,1 M solution (A_r(Fe) = 55,8; A_r(Cl) = 35,5):
a) 7,61 g   b) 4,87 g   c) 5,48 g   d) 3,80 g

12. Calculate the mass of NaOH in 400 cm³ of 0,25 M solution (A_r(Na) = 23,0):
a) 4 g   b) 16 g   c) 23 g   d) 40 g

13. Calculate the mass of HCl ($M_r = 36,5$) in 120 g of 4,1 M solution (solution density 1068 g.dm⁻³):
a) 18,0 g   b) 19,2 g   c) 30,8 g   d) 18,6 g

14. To neutralize 16 cm³ of 0,5 M HCl you need:
a) 60 cm³ of 0,20 M NaOH   c) 20 cm³ of 0,40 M NaOH
b) 40 cm³ of 0,25 M NaOH   d) 16 cm³ of 0,25 M NaOH

15. To neutralize 100 cm³ of 0,2 M sulfuric acid you need:
a) 200 cm³ of 0,20 M $Ba(OH)_2$
b) 100 cm³ of 0,10 M $Ba(OH)_2$
c) 80 cm³ of 0,25 M $Ba(OH)_2$
d) 80 cm³ of 0,50 M $Ba(OH)_2$

16. To neutralize 250 cm³ of 0,20 M KOH you need:
a) 250 cm³ of 0,40 M sulfuric acid
b) 200 cm³ of 0,25 M sulfuric acid
c) 400 cm³ of 0,25 M sulfuric acid
d) 250 cm³ of 0,10 M sulfuric acid

17. To neutralize 80 cm³ of 10 mM calcium hydroxide you need:
a) 1 cm³ of 80 mM HCl
b) 8 cm³ of 100 mM HCl
c) 16 cm³ of 150 mM HCl
d) 4 cm³ of 400 mM HCl

18. Calculate the volume of 0,2 M HCl needed to neutralize 0,404 g of KOH ($M_r = 56,1$):
a) 11,3 cm³   b) 18,0 cm³   c) 36,0 cm³   d) 72,0 cm³

19. Electrolytic dissociation is:
a) decomposition of electrolyte by electric current
b) decomposition of substance to positive and negative ions
c) the movement of ions to inversely charged electrodes
d) redox reaction on electrodes

20. Select the strong electrolyte:
a) NH_4Cl b) NH_3 c) CH_3COOH d) H_2CO_3

21. Select the weak electrolyte:
a) NH_4Cl b) $KMnO_4$ c) NH_3 d) HNO_3

22. What is the molarity of NaCl, if the concentration of sodium ions is 150 mmol.dm⁻³ ?
a) 225 mmol.dm⁻³   b) 75 mmol.dm⁻³   c) 150 mmol.dm⁻³   d) 300 mmol.dm⁻³

23. NaOH solution has pH = 12,0. Calculate the molarity of sodium ions:
a) 10 mmol.dm⁻³   b) 5 mmol.dm⁻³   c) 0,1 mmol.dm⁻³   d) 1 mmol.dm⁻³

24. Calculate the concentration of chloride ions in 15 mM barium chloride:
a) 7,5 mmol.dm⁻³   b) 5,0 mmol.dm⁻³   c) 30 mmol.dm⁻³   d) 15 mmol.dm⁻³

25. What is the molarity of sodium sulfate solution, if sodium ion concentration in this solution is 18 mmol.dm⁻³ ?
a) 27 mmol.dm⁻³   b) 18 mmol.dm⁻³   c) 12 mmol.dm⁻³   d) 9 mmol.dm⁻³

26. The molarity of potassium sulfate solution is 0,04 mol.dm^{-3}. What volume of this solution contains 1 mmol of potassium ions?
a) 6,25 cm^3 b) 12,5 cm^3 c) 25 cm^3 d) 50 cm^3

27. The value of the ionic product of water K_w is:
a) 55,4.10^{14} b) 1,0.10^{-14} c) 14,0   d) 2,0.10^{-7}

28. Select the species which can be a Brønsted acid in aqueous solution:
a) SO_4^{2-} b) NH_3 c) OH^- d) HPO_4^{2-}

29. Consider dissolving ammonia in water. Which species makes the conjugate pair with ammonia?
a) OH^- b) H_2O c) H_3O^+ d) NH_4^+

30. Consider dissociation of acetic acid in water. Which species makes the conjugate pair with CH_3COO^- ion?
a) H_2O b) H_3O^+ c) OH^- d) H^+

31. Which species makes the conjugate pair with CH_3-NH_2 in aqueous solution?
a) H_2O b) H_3O^+ c) HCl d) OH^-

32. Select the conjugate pair:
a) $HCOOH; HCOO^-$ b) $HCOOH; OH^-$ c) $HCOOH; H_2O$ d) $HCOOH; H_3O^+$

33. Select the conjugate pair:
a) $NH_4^+; OH^-$ b) $NH_3; H_2O$ c) $H_2O; H_3O^+$ d) $H_2O; NH_3$

34. Select the weak acid:
a) HBr b) H_2SO_4 c) HNO_3 d) H_3BO_3

35. Which acid is <u>not</u> the weak one?
a) H_3BO_3 b) H_3PO_4 c) HBr d) $HClO$

36. Is there a strong acid among the following compounds?
a) H_2S b) $HCOOH$ c) HF d) C_6H_5OH

37. Calculate the concentration of OH^- ions, if pH = 9,0.
a) 1.10^{-9} mol.dm^{-3} b) 1.10^{-5} mol.dm^{-3} c) 5.10^{-5} mol.dm^{-3} d) 9.10^{-5} mol.dm^{-3}

38. What is the pH of calcium hydroxide solution, if c = 2 mmol.dm^{-3} ?
a) 12,70   b) 11,30   c) 9,00   d) 10,70

39. NaOH solution has pH = 11,0. Calculate the pH, if the solution is diluted by adding 9 volume portions of water.
a) 10,0   b) 10,9   c) 11,1   d) 12,0

40. Hydrochloric acid, pH = 2,60, was diluted 4x, that is by adding threefold volume of water. Calculate the concentration of H^+ ions in diluted solution.
a) 1,0.10^{-2} mol.dm^{-3} b) 2,51.10^{-3} mol.dm^{-3} c) 0,63.10^{-3} mol.dm^{-3} d) 0,40.10^{-3} mol.dm^{-3}

41. Hydrochloric acid, $c = 0.01$ mol.dm⁻³, was diluted by adding the same volume of water. What is the pH of diluted acid?

a) 1,70   b) 2,50   c) 2,30   d) 4,00

42. Select the salt which undergoes hydrolysis in aqueous solution:

a) KBr   b) $Fe(NO_3)_3$ c) K_2SO_4 d) $CaCl_2$

43. Which substance provides alkaline aqueous solution?

a) CH_3COONa b) H_2S c) CH_3OH d) C_6H_5OH

44. Which substance provides alkaline aqueous solution?

a) $(NH_4)_2SO_4$ b) CH_3OH c) Na_2SO_4 d) $NaHCO_3$

45. Which substance provides alkaline aqueous solution?

a) NH_4Cl b) NaBr   c) Na_2SO_4 d) CH_3OH

46. Which aqueous solution (concentration of each 0,1 mol.dm⁻³) can react with the same volume of HCl (0,1 mol.dm⁻³) to give solution with pH = 7,0 ?

a) CH_3OH b) NH_3 c) CH_3COOH d) C_6H_5OH

Periodic system, properties of elements, redox reactions

1. Determine the configuration of calcium electrons:

a) $[Ar]\ 3s^2$ b) $[Ne]\ 3s^2$ c) $[Ne]\ 4s^2$ d) $[Ar]\ 4s^2$

2. How many valence electrons are there in phosphorus?

a) 13   b) 5   c) 3   d) 15

3. Select non-transition element:

a) Cd   b) Mn   c) Ti   d) U

4. Select the element from the group IV (14) of periodic system:

a) tin   b) chromium   c) selenium   d) antimony

5. Select the element from the group VI (16) of periodic system:

a) molybdenum   b) bismuth   c) uranium   d) chromium

6. Select the transient element (*d*-element):

a) As   b) Bi   c) Al   d) Pb

7. Select the transient element (*d*-element):

a) Mn   b) Ra   c) Pb   d) As

8. Select the acidic (acid-forming) oxide:

a) Ag_2O b) CO   c) Mn_2O_7 d) N_2O

9. Select the acidic (acid-forming) oxide:
a) CrO_3 b) MgO c) Bi_2O_3 d) CO

10. Select the amphoteric oxide:
a) BaO b) Ag_2O c) Al_2O_3 d) SiO_2

11. The volume fraction of CO_2 in air is:
a) 0,5 %   b) 3 %   c) 0,03 %   d) 1 %

12. What is the product of the reaction between hydrochloric acid and sodium sulfide?
a) sulfur   b) sulfane   c) sulfur dioxide   d) chlorine

13. Select the formula of gypsum (plaster):
a) $Ca(OH)_2$ b) $CaCO_3$ c) $CaSO_4.2H_2O$ d) $CaSO_4.0,5H_2O$

14. Determine the concentration of $CaSO_4$ in its satutared aqueous solution, if you know the solubility product $K_s(CaSO_4) = 3,0.10^{-5}\ mol^2.dm^{-6}$.
a) $5,5.10^{-3}\ mol.dm^{-3}$ b) $3,0.10^{-5}\ mol.dm^{-3}$ c) $7,5.10^{-6}\ mol.dm^{-3}$ d) $6,0.10^{-10}\ mol.dm^{-3}$

15. The solubility of lead sulfate is given by the solubility product $K_s(PbSO_4) = 2,0.10^{-8}\ mol^2.dm^{-6}$. Calculate the substance amount of $PbSO_4$ needed to make 1 dm^3 of saturated solution in water.
a) $4,0.10^{-16}\ mol$ b) $1,4.10^{-4}\ mol$ c) $2,0.10^{-8}\ mol$ d) $1,0.10^{-8}\ mol$

16. Select the redox reaction:
a) $KCl + AgNO_3 \rightarrow AgCl + KNO_3$ b) $CaCl_2 \rightarrow Ca^{2+} + 2 Cl^-$
c) $Ba + Cl_2 \rightarrow BaCl_2$ d) $NaOH + HNO_3 \rightarrow H_2O + NaNO_3$

17. Complete the equation $2\ Cu^{2+} + ...\ I^- \rightarrow ...\ CuI + ...\ I_2$ with the lowest stoichiometric coefficients and express the coefficient of I^-:
a) 3   b) 4   c) 2   d) 5

18. Complete the equation $...\ SO_2\ (g) + ...\ O_2\ (g) \rightarrow$ ..... and determine how many mols of SO_2 are oxidized by one mol of dioxygen:
a) 0,5 mol   b) 1 mol   c) 2 mol   d) 4 mol

19. Complete the stoichiometric coefficients a, b, c in equation $a\ NH_3 + b\ Cl_2 \rightarrow c\ NH_4Cl + N_2$:
a) 4; 2; 4   b) 8; 3; 6   c) 2; 1; 1   d) 6; 3; 6

Organic chemistry – nomenclature, isomerism, structure and properties of compounds

1. Determine the correct name of hydrocarbon:
a) 1,1,1,3-tetramethylbutane
b) 2,2-dimethyl-1-isopropylpropane
c) 2,2,4-trimethylpentane
d) isooctane

2. Determine the correct name of hydrocarbon:
a) 2-propylbut-1-ene   b) 3-methylidenhexane   c) 3-propylbut-3-ene   d) 2-ethylpent-1-ene

3. Determine the correct name of hydrocarbon:
a) 3-methyl-4-vinylheptane
b) 3-(2-butyl)hex-1-ene
c) 4-ethyl-3-propylpent-1-ene
d) 4-methyl-3-propylhex-1-ene

4. Determine the correct name of hydrocarbon:
a) phenyltoluene
b) biphenyl
c) diphenylmethane
d) benzylbenzene

5. Determine the correct name of the residue -CH$_2$-CH$_2$- :
a) ethenyl   b) diethyl   c) ethylene   d) dimethylene

6. Vinyl is:
a) divalent residue of ethane
b) monovalent residue of ethene
c) acyl of vinilic acid
d) type of plastic (polymeric material)

7. Determine the name of CH$_3$-CO-O-CH$_2$CH$_2$CH$_2$CH$_3$:
a) butyl methyl ketone   b) methyl butyrate   c) acetyl butyl ether   **d) butyl acetate**

8. Determine the name of the given compound:
a) 1-bromo-2-chloroisobutane   b) 3-bromo-4-chloro-4,4-dimethylbutane
c) 2-bromo-1-chloro-l,l-dimethylbutane   d) 3-bromo-2-chloro-2-methylpentane

9. Determine the number of isomers of tetrachlorobenzene:
a) 2   b) 4   c) 6   d) 8

10. Determine the number of isomeric dihydroxybenzoic acids:
a) 6   b) 3   c) 4   d) 8

11. Select the isomer of xylene:
a) ethylbenzene   b) styrene   c) octatriene   d) methylheptadiene

12. Find the isomer of methyl acetate:
a) propionic acid
b) ethylester of carbonic acid
c) dihydroxyacetone
d) propenal (acrylaldehyde)

13. Find the isomer of cyclohexene:
a) hexa-2,4-diene
b) 1,3-dimethylcyclobutane
c) 2-methylpent-1-ene
d) methylcyclopentane

14. Diethyl ether and butan-2-ol are:
a) tautomers
b) *cis-trans* isomers
c) configurational isomers
d) constitutional isomers

15. Find the tautomer of vinylalcohol:
a) propionaldehyde   b) acetic acid   c) acetaldehyde   d) acetone

16. Find *cis-trans* isomers:
a) hexene + cyclohexane
b) vinylalcohol + acetaldehyde
c) fumaric acid + maleinic acid
d) phthalic acid + terephthalic acid

17. Two enantiomers differ in:
a) melting point and boling point
b) molecular mass
c) direction of optical rotation
d) constitution

18. Rotation along C-C bond in a part of molecule affords:
a) constitutional isomers   b) optical isomers   c) various conformations   d) tautomers

19. Select the principal feature of electrophilic reagent – an electrophil has:
a) negative charge
b) free valence electrons
c) nonbonding electron pair
d) unoccupied valence orbital

20. Nucleophilic reagent is characterized by:
a) nonbonding electron pair
b) positive charge
c) one electron in valence orbital
d) unoccupied valence orbital

21. Alkenes typically exhibit addition reactions. Select the reagent which does not react with alkenes:
a) H_2 b) H_2O c) Cl_2 d) HBr   e) no answer is correct, all reagents can add to alkenes

22. Determine the name of hydrocarbon:
a) phenylethylene   b) styrene   c) benzylethane   d) vinylbenzene

23. Select the molecular formula of styrene:
a) C_8H_8 b) C_8H_{10} c) C_8H_{12} d) C_8H_{14}

24. Select the molecular formula of 1,3-cyclohexadiene:
a) C_6H_{10} b) C_6H_8 c) C_6H_{14} d) C_6H_{12}

25. Which compound is produced by the oxidation of toluene?
a) cresol   b) phthalic acid   c) cyclohexanone   d) benzoic acid

26. Select the least polar compound:
a) benzoquinone   b) benzaldehyde   c) cyclohexadiene   d) aniline

27. Select the molecular formula of phenanthrene:
a) $C_{10}H_8$ b) $C_{14}H_{12}$ c) $C_{18}H_{14}$ d) $C_{14}H_{10}$

28. Select the molecular formula of naphalene:
a) $C_{14}H_{10}$ b) $C_{10}H_{10}$ c) $C_{14}H_{12}$ d) $C_{10}H_{18}$

29. Select the molecular formula of anthracene:
a) $C_{18}H_{14}$ b) $C_{10}H_8$ c) $C_{14}H_{12}$ d) $C_{14}H_{10}$

30. Select the product of reaction: but-1-ene + HCl:
a) 1,2-dichlorobutane b) 1-chlorobutane c) 2-chlorobutane d) isobutylchloride

31. Select the product of addition of water to cyclohexene:
a) benzenediol b) phenol c) cyclohexanediol d) benzylalcohol

32. Select the systematic name of chloroform:
a) monochloroethane b) formylchloride c) tetrachloromethane d) trichloroethene

33. How many hydrogen atoms are there in the structure depicted?
a) 3 b) 6 c) 7 d) 8

34. The compound HO-CH$_2$-CH$_2$-CH$_2$-OH belongs to:
a) alkoxides b) primary alcohols c) secondary alcohols d) sugar alcohols (alditols)

35. Find the secondary alcohol:
a) ethyleneglycol b) pentane-3-ol c) ethanol d) 2-methyl-propane-2-ol

36. Determine the number of carbon atoms in benzylalcohol:
a) 7 b) 6 c) 8 d) 9

37. Isopropylalcohol can be made by the reduction of:
a) acetaldehyde b) ethyl methyl ketone c) acetone d) propionaldehyde

38. Find the product of glycerol oxidation:
a) 3-hydroxypropanoic acid b) 2,3-dihydroxypropanal c) acetone d) lactic acid

39. Find the product of benzene-1,4-diol dehydrogenation:
a) hydroquinone b) 1,4-benzenedicarboxylic acid
c) 1,4-xylene d) 1,4-benzoquinone

40. Find the product of glyceraldehyde reduction:
a) dihydroxyacetone b) glyceric acid
c) propionaldehyde d) propane-1,2,3-triol

41. Find the product of benzaldehyde reduction:
a) cyclohexanol b) toluene c) benzene d) phenol

42. Which compound is easily oxidized under mild conditions:
a) CH$_3$CH$_2$CH$_2$-CH=O b) (CH$_3$)$_2$C(OCH$_3$)$_2$ c) CH$_3$CH$_2$-O-CH$_2$CH$_3$ d) CH$_3$CH$_2$-CO-CH$_2$CH$_3$

43. Find the product of cyclohexanone reduction:
a) phenol b) benzoic acid c) benzylalcohol d) cyclohexanol

44. Acetal is formed by:
a) hydration of aldehyde b) aldol condensation
c) reaction of alcohol and aldehyde d) dehydration of acetic acid

45. The compound H$_2$N-CH$_2$-CH$_2$-NH$_2$ belongs to:
a) primary amines   b) secondary amines   c) tertiary amines   d) dimethylamines

46. Dimethylamine belongs to:
a) primary amines   b) diamines   c) secondary amines   d) amides

47. Determine the name of (CH$_3$)$_3$N:
a) trimethylnitride   b) trimethylamine   c) trimethylnitrile   d) trimethylazide

48. Find the formula of nitro compound:
a) C$_6$H$_5$-NO$_2$ b) C$_6$H$_5$-O-NO$_2$ c) C$_6$H$_5$-O-N=O   d) C$_6$H$_5$-N=O

49. Find the product of nitrobenzene reduction:
a) benzylamine   b) phenol   c) aniline   d) benzyl nitrite

50. Find the correct description of diazotization:
a) diazonium salts are decomposed to phenol and nitrogen
b) aromatic amines and phenols make azodyes
c) aldehydes react with aromatic hydrazines
d) aromatic amines and nitrous acid give reactive salts

51. Find the group typical for azo-compounds:
a) -N$^+$≡N   b) -N=O   c) -N=N-   d) -NH-NH$_2$

52. Select the carboxylic acid from the following acids:
a) phthalic acid b) uric acid c) ascorbic acid d) picric acid

53. Find the unsaturated (alkenoic) acid:
a) pyruvic   b) phthalic   c) citric   d) acetoacetic

54. The simplest dicarboxylic acid is:
a) malic   b) lactic   c) citric   d) oxalic

55. Which acid is not dicarboxylic?
a) tartaric   b) aspartic   c) succinic   d) fumaric   e) no answer is correct, all acids are dicarboxylic

56. Find the tricarboxylic acid:
a) phthalic   b) tartaric   c) oxaloacetic   d) picric

57. The compound CH$_3$-CO-CH$_2$-CO-O-CH$_2$-CH$_3$ belongs to:
a) acid anhydrides   b) esters   c) ethers   d) acetals

58. Determine the correct name of the structure depicted:
a) phenyl acetyl ether   b) phenyl acetate   c) methyl benzoate d) phenyl methyl ketone

59. Select the hydroxy carboxylic acid:
a) fumaric acid   b) oleic acid   c) phthalic acid   d) acrylic acid

60. What is produced by the dehydrogenation of lactic acid?
a) maleinic acid   b) malonic acid   c) acetone   d) pyruvic acid

61. Select the true statement: Esters can be made from hydroxy carboxylic acids ...
a) only exceptionally   b) with acids and alcohols
c) only with alcohols   d) only with acids

62. Determine the product of oxidation of lactic acid:
a) 2-hydroxypropanal   b) 2-hydroxypropanoic acid
c) 3-oxopropanoic acid   d) acetoacetic acid

63. What is the common name of CH_3-CO-CH_2-COOH ?
a) malic acid   b) pyruvic acid
c) oxaloacetic acid   d) acetoacetic acid

64. Urea is derived from:
a) oxalic acid   b) formic acid
c) uric acid   d) H_2CO_3

65. Which compound is chiral and exhibits optical rotation?
a) citric acid   b) salicylic acid
c) malic acid   d) pyruvic acid

66. Find the common name for HOOC-CH_2-CH(OH)-COOH
a) lactic acid   b) oxaloacetic acid
c) acetoacetic acid   d) tartaric acid

67. Which heterocycle does <u>not</u> contain heteroatom of oxygen?
a) pyran   b) furan   c) pyrazole   d) dioxan
e) no answer is correct, all compounds have oxygen heteroatom

68. Select the name of the heterocycle depicted:
a) imidazole   b) pyrrole   c) pyridine   d) indole

69. Select the name of the heterocycle depicted:
a) thiazole   b) pyrazole   c) pyrimidine   d) pyrrolidine

70. Which of the compounds is five-membered heterocycle with two N atoms?
a) pyran b) pyrazole   c) pyridine   d) pyrimidine

71. How many nitrogen heteroatoms are there in pyrimidine?
a) 4   b) 3   c) 2   d) 1

72. Select the name of the heterocycle depicted:
a) pyrimidine   b) pyridine   c) purine d) imidazole

73. Select the name of the heterocycle depicted:
a) benzofuran   b) indole   c) quinoline   d) purine

74. Select the name of the heterocycle depicted:
a) purine   b) pyrimidine   c) indole   d) quinoline

75. Find the molecular formula of indole:
a) $C_3H_4N_2$ b) $C_5H_4N_4$ c) $C_7H_6N_2$ d) C_8H_7N

76. Find the molecular formula of imidazole:
a) $C_3H_4N_2$ b) C_4H_4N c) $C_5H_{11}N$ d) $C_4H_{10}N_2$

77. How many nitrogen heteroatoms are there in purine?
a) 1   b) 2   c) 3   d) 4

78. Which heterocycle contains two different heteroatoms?
a) imidazole   b) indole   c) pyrazole   d) thiazole

79. Select the five-membered heterocycle with two N atoms:
a) pyran   b) pyridin   c) pyrazole   d) pyrimidine

80. Select the name of the heterocycle depicted:
a) pyridine   b) pyran   c) pyrrolidine   d) furan

81. Select the name of the heterocycle depicted:
a) thiamin   b) thiophene   c) imidazole   d) thiopental

82. Select the name of the heterocycle depicted:
a) quinoline   b) indole   c) purine   d) benzoquinone

Saccharides, lipids, amino acids, proteins, nucleic acid, enzymes, metabolism

1. How many chiral atoms are there in acyclic (Fisher) structure of D-ribose?
a) 2   b) 3   c) 4   d) 5

2. How many chiral atoms are there in acyclic (Fisher) structure of D-galactose?
a) 5   b) 4   c) 3   d) 6

3. Select the name of monosaccharide:
a) β-D-glucopyranose
b) β-D-ribofuranose
c) β-D-glucofuranose
d) β-D-fructofuranose

4. Select the type of bond in polysaccharides:
a) peptide   b) ether   c) ester   d) glycosidic

5. Hydrolytic cleavage of lactose provides:
a) galactose + maltose   b) maltose + fructose   c) glucose   d) glucose + galactose

6. Hydrolytic cleavage of sucrose provides:
a) fructose + maltose   b) galactose + glucose   c) glucose   d) glucose + fructose

7. Select the non-reducing saccharide:
a) lactose   b) ribose   c) maltose   d) fructose

8. Select the reducing disaccharide:
a) maltose   b) galactose   c) fructose   d) amylose

9. Select the pair of reducing sugars:
a) fructose + maltose b) lactose + sucrose c) sucrose + glucose d) maltose + amylose

10. Which polysaccharide is not D-glucan?
a) cellulose   b) glycogen   c) maltodextrin   d) amylose
e) no answer is correct, all are D-glucans

11. Which compound is not polysaccharide?
a) starch   b) amylose   c) amylopectin   d) cellulose
e) no answer is correct, all are polysaccharides

12. Systematic name of palmitic acid is:
a) hexadecanoic acid   b) eicosanoic acid
c) octadecanoic acid   d) hexadecenoic acid

13. The hydrogenation of oleic acid gives:
a) palmitic acid   b) linolenic acid   c) stearic acid   d) linoleic acid

14. Select the common name of *cis,cis*-9,12-octadecadienoic acid:
a) linolenic acid   b) oleic acid
c) palmitic acid   d) stearic acid

15. Select the common name of *cis*-9-octadecenoic acid:
a) linolic acid   b) butyric acid   c) oleic acid   d) stearic acid

16. Soaps are:
a) esters of fatty acids and glycerol
b) mixtures of fatty acids and glycerol
c) the salts of higher fatty acids
d) salts of alkanesulfonic acids

17. Soaps are made by:
a) the esterification of glycerol with carboxylic acids
b) hydrogenation of plant oils
c) alkaline hydrolysis of fatty acids
d) saponification of glycerol

18. Which natural substances often contain choline?
a) phospholipids   b) bile acids   c) esters of cholesterol   d) waxes

19. Select the purine base:
a) guanine   b) uracil   c) thymine   d) cytosine

20. Which heterocycle makes the skeleton of cytosine?
a) purine   b) pyridine   c) imidazole   d) pyrimidine

21. What are the components of nucleosides?
a) nitrogen base and phosphate   b) nitrogen base and pentose
c) nitrogen base, pentose, and phosphate   d) pentose and phosphate

22. Which compound is <u>not</u> nucleoside:
a) guanosine   b) uridine   c) cytosine   d) adenosine
e) no answer is correct, all compounds are nucleosides

23. What type of bond is between base and other parts of nucleotide?
a) glycosidic   b) macroergic   c) ester   d) hydrogen

24. What type of bond is between nucleotides in nucleic acids?
a) glycosidic   b) hydrogen   c) ester   d) amide

25. Transcription is the transfer of information from the nucleotide sequence ...
a) of mRNA into primary structure of proteins
b) of RNA into DNA sequence
c) of mRNA into tRNA anticodone
d) of DNA into primary structure of proteins

26. Translation is the transfer of information from the nucleotide sequence ...
a) of DNA into daughter molecule of DNA before cell division
b) of mRNA into primary protein structure on ribosome
c) of mRNA into DNA sequence during cell division
d) of DNA into mRNA sequence

27. Select the common name of amino acid depicted:
a) valine   b) leucine   c) lysine   d) isoleucine

28. Select the common name of amino acid depicted:
a) threonine b) proline   c) serine d) cysteine

29. Select the common name of amino acid depicted:
a) glutamic acid   b) glutamine   c) proline   d) aspartic acid

30. Select the name of compound depicted:
a) pyrrol-2-carboxylic acid   b) pyrrolidin-2-one   c) proline   d) butano-2-lactam

31. Determine the common name for 2,6-diaminohexanoic acid:
a) lysine   b) aspartic acid   c) arginine   d) glutamine

32. Select the common name of amino acid depicted:
a) lysine   b) leucine   c) arginine   d) isoleucine

33. Select the common name of amino acid depicted:
a) tyrosine   b) tryptophan   c) histidine   d) phenylalanine

34. Select the common name of amino acid depicted:
a) tryptophan   b) histidine   c) phenylalanine   d) tyrosine

35. Determine the number of chiral C atoms in serine:
a) 3   b) 2   c) 1   d) none

36. Select the correct name of dipeptide shown:
a) threonyl-leucine   b) lysyl-serine
c) leucyl-valine   d) valyl-isoleucine

37. Select the correct name of dipeptide shown:
a) lysyl-serine   b) seryl-valine
c) leucyl-threonine   d) alanyl-arginine

38. What type of bond is typical for proteins?
a) ester   b) peptide   c) disulfide   d) glycosidic

39. Which interaction stabilizes the secondary structure of proteins?
a) hydrogen bonds   b) peptide bonds   c) disulfide bridges   d) ionic interactions

40. Which interaction is <u>not</u> involved in the stabilization of tertiary protein structure?
a) disulfide bridges   b) hydrogen bonds
c) peptide bonds   d) hydrophobic (van der Waals) forces
e) no answer is correct, all interactions are involved

41. Enzymes catalyzing the cleavage of peptide bonds in proteins belongs to:
a) oxidoreductases   b) lyases   c) hydrolases   d) ligases

42. Trypsin is enzyme which catalyzes:
a) hydrolytic cleavage of ester bonds   b) oxidative cleavage of unsaturated bonds
c) hydrolytic cleavage of polysaccharides   d) decarboxylation of amino acids

43. Amylase, catalyzing the cleavage of glycosidic bonds in starch, belongs to:
a) hydrolases   b) lyases   c) ligases   d) transferases

CHEMISTRY – correct answers (answer „e" means "no aswer is correct")

Inorganic formulas, chemical calculations based on formulas and equations, substance amount

1c, 2d, 3a, 4e, 5b, 6d, 7b, 8d, 9b, 10a, 11a, 12b, 13a, 14d, 15b, 16c, 17b, 18a, 19e, 20c, 21b, 22d, 23c, 24c, 25b, 26d

The structure of atom, the configuration of electrons, the types of bonds, polarity of molecules

1d, 2e, 3d, 4a, 5c, 6d, 7d, 8b, 9b, 10e, 11a, 12d, 13c, 14b, 15d, 16a, 17c, 18b, 19d, 20a, 21d, 22a, 23d

Solutions – concentrations, electrolytes, acids, bases, pH

1e, 2a, 3b, 4e, 5e, 6c, 7e, 8a, 9b, 10c, 11d, 12a, 13e, 14c, 15c, 16d, 17d, 18c, 19b, 20a, 21c, 22c, 23a, 24c, 25d, 26b, 27b, 28d, 29d, 30e, 31e, 32a, 33c, 34d, 35c, 36e, 37b, 38b, 39a, 40c, 41c, 42b, 43a, 44d, 45e, 46e

Periodic system, properties of elements, redox reactions

1d, 2b, 3e, 4a, 5e, 6e, 7a, 8c, 9a, 10c, 11c, 12b, 13d, 14a, 15b, 16c, 17b, 18c, 19b

Organic chemistry – nomenclature, isomerism, structure and properties of compounds

1c, 2d, 3d, 4c, 5c, 6b, 7d, 8d, 9e, 10a, 11a, 12a, 13a, 14d, 15c, 16c, 17c, 18c, 19d, 20a, 21e, 22e, 23a, 24b, 25d, 26c, 27d, 28e, 29d, 30c, 31e, 32e, 33e, 34b, 35b, 36a, 37c, 38b, 39d, 40d, 41e, 42a, 43d, 44c, 45a, 46c, 47b, 48a, 49c, 50d, 51c, 52a, 53e, 54d, 55e, 56e, 57b, 58b, 59e, 60d, 61b, 62e, 63d, 64d, 65c, 66e, 67c, 68e, 69e, 70b, 71c, 72a, 73b, 74a, 75d, 76a, 77d, 78d, 79c, 80b, 81e, 82e

Saccharides, lipids, amino acids, proteins, nucleic acid, enzymes, metabolism

1b, 2b, 3b, 4d, 5d, 6d, 7e, 8a, 9a, 10e, 11e, 12a, 13c, 14e, 15c, 16c, 17e, 18a, 19a, 20d, 21b, 22c, 23a, 24c, 25e, 26b, 27b, 28c, 29d, 30c, 31a, 32a, 33b, 34d, 35c, 36c, 37a, 38b, 39a, 40c, 41c, 42e, 43a

OVERVIEW OF CHEMISTRY

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