КИЇВСЬКИЙ НАЦІОНАЛЬНИЙ УНІВЕРСИТЕТ ІМЕНІ ТАРАСА ШЕВЧЕНКА

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НАВЧАЛЬНИЙ ПОСІБНИК З АНГЛІЙСЬКОЇ МОВИ ДЛЯ СТУДЕНТІВ-ХІМІКІВ

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Навчальний посібник з англійської мови призначено для студентів хімічних спеціальностей вищих закладів освіти. Тематика матеріалу охоплює низку теоретичних і практичних питань сучасної органічної, фізичної та високомолекулярної хімії. Укладений на основі комунікативних принципів, посібник включає завдання для читання й обговорення, підстановчі, тренувальні і творчі вправи на засвоєння лексики, у тому числі спеціальної термінології, фонетичні і граматичні вправи, завдання на письмо і переклад. а також проблемні питання для дискусій. Посібник може бути використаний як під час аудиторних занять, так і для самостійної роботи студентів.

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CONTENTS

Preface	4
1. Heterogeneity of Astroglia	5
2. Biosensors	19
3. Electrophilic Aromatic Substitution	29
4. Lipids	40
5. Asymmetric Synthesis	53
6. Nanopores	65
7. Molecular Imprinting Technology	78
8. Dye-Sensitized Solar Cells	90
9. Catalysis	103
10. Amino Acids	114
11. The Mass Spectrum	124
12. X-Ray Crystallography	134
13. The Nature of Physical Chemistry	145
14. Activated Carbon	157
15. Biodegradable Drug Delivery Systems	168
16. Plastic Recycling	179
17. Aldehydes and Ketones	189
18. Fullerenes	200
19. Bibliography	212

PREFACE

The present-time labour market requires highly qualified and competitive chemists whose foreign language competence and communication skills are part and parcel of their professional activity. The era of growing international communication and imminent global integration creates an urgent need for specialists possessing profound English-language knowledge as a comparative advantage to meet the demands of today's competitive work-related environment.

This manual is intended for university chemistry students to facilitate their mastering of English for specific purposes, to ensure their foreign language competence and communication skills, as well as to enhance the learners' confidence, accuracy and fluency in using the English language in their future professional discourse.

The book consists of eighteen units, each including the following sections: pre-reading, while-reading and post-reading activities to develop learners' reading comprehension and speaking skills, activities focusing on grammar and lexis, and final tasks, which contain certain points for discussions, debates etc., as well as roleplays to ensure developing the students' speaking and communication skills. Each unit comprises a number of tasks aimed at enriching the topical vocabulary, including scientific terms, as well as pronunciation drills, open-end questions to the texts, critical thinking and discussion tasks, writing and translation tasks etc.

The study material is based on authentic printed publications covering a set of fundamental and up-to-date issues related to organic, physical and polymer chemistry to facilitate expanding the learners' professional scope in their majoring field.

Unit 1

HETEROGENEITY OF ASTROGLIA

I. Pre-reading activities

Task 1. Discuss the following questions:

- 1) Have you ever heard about astroglia?
- 2) What do you know about star-like cells in the human body?
- 3) What is a neuron?
- 4) What do you know about nerve cells?
- 5) What is the soma?
- 6) What is the difference between nerve cells and somatic cells?

Task 2. Pronounce the following international words and guess what they mean:

astrocyte ['astrə(U)sait] (n)	astroglia /ə'str ¤glı ə/ (n)
archetypal [a:kI'taıp(ə)l] (adj.)	bipolar [baı'pəʊlə(r)] (adj.)
membrane ['mεmbreIn] (n)	profile ['prəʊfaıl] (n)
protein /'prəʊti:n/ (n)	neuroglial [njʊə'rɒglɪəl] (adj.)
neuron ['njʊərɒn] (n)	heterogeneous [hɛtərə(ʊ)'dʒinɪəs] (adj.)
morphology [mɔː'fɒlədʒi] (n)	physiological [fIziə'lbd3Ik(ə)l] (adj.)
protoplasmic [prəʊtəʊ'plazmɪk] (adj.)	fibrous ['faıbrəs] (adj.)
radial ['reIdIəl] (adj.)	process ['prəUsəs] (n)
dendrite ['dɛndrait] (n)	capillary [kə'p 1 ləri] (n)
glial ['glaıəl], ['glıəl] (adj.)	oligodendrocyte [\mathcal{D} IIG \Rightarrow (\mathcal{U})'d ϵ ndr \Rightarrow sait] (n)
somatic [səʊ'mætık] (adj.)	homogeneous [hɒmə(ʊ)'dʒinɪəs ,-'dʒɛn-] (adj.)
fibrous ['fa 1 brəs] (adj.)	variety [və'raIətI] (n)
vertebrate ['v3:tIbrət] (n)	variable ['vɛərɪəbl] (adj.)
retina ['rɛtɪnə] (n)	ordinary [' ว1 d(ə)n(ə)r 1] (adj.)

Task 3. Match the synonyms:

1. soma	a) variety
2. fibrous	b) unusual; striking
3. filament	c) detailed and complicated
4. unequivocal	d) star-like
5. elaborate [I'læb(ə)rət]	e) thread
6. remarkable	f) unambiguous; definite
7. heterogeneity	g) stringy ['striŋi]
8. cortex	h) body
9. ovoid	i) egg-shaped
10. stellate ['stɛleIt, -lət]	j) bark

Task 4. Match the opposites:

1. mature	a) ordinary
2. specific	b) simple
3. acquire	c) common
4. complicated	d) lose
5. remarkable	e) young

Task 5. Guess from the context what the underlined words mean:

- 1. It works well in cultured astrocytes, but <u>in situ</u> the levels of GFAP expression vary quite considerably.
- 2. Fibrous astrocyte processes also send numerous <u>extensions</u> ('perinodal' processes) that contact axons at nodes of Ranvier.
- 3. <u>Protoplasmic astrocyte</u> density in the cortex varies between $10\ 000\ \text{and}\ 30\ 000\ \text{per}\ \text{mm}^3$.
- 4. Thus astrocytes display a remarkable <u>heterogeneity</u> in their morphology and function.
- 5. An archetypal <u>morphological feature</u> of astrocytes is their expression of intermediate filaments, which form the cytoskeleton.
- 6. Other regions of the CNS contain many different populations of <u>astroglial cells</u>.
- 7. The majority of Müller glial cells have a characteristic <u>morphology</u>, extending longitudinal processes along the line of rods and cones.

Task 6. Match the English words and phrases on the left with their Ukrainian equivalents on the right:

r
а) біла речовина
b) зіркоподібні клітини
с) рецептори сітківки ока
d) сіра речовина
е) шлункова стінка
f) нюхова цибулина
g) мікрогліальні клітини
h) сітківка
і) мозочок
j) нижчі хребетні тварини
k) поверхня м'якої мозкової оболонки
l) синаптичні нервові закінчення
m) кровоносні судини
n) віментин (білок)

II. While-reading activities

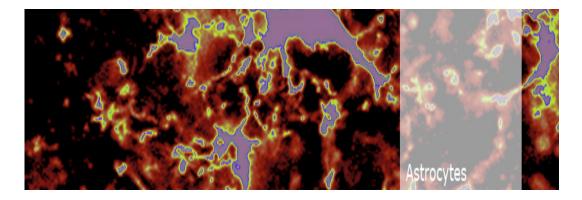
Task 7. Read the text and answer the questions:

- 1. What can you say about astrocytes?
- 2. What do the acronyms GFAP and CNS mean?
- 3. What kinds of astrocytes are known today?

Heterogeneity of Astroglia

Astrocytes (literally 'star-like cells') are the most numerous and diverse neuroglial cells in the CNS. While most neuroscientists think they know what an astrocyte is, there is no uniform and unequivocal definition of an astrocyte. Not all astrocytes are star-like cells, not all of them express the specific marker: glial fibrillary acidic protein (GFAP), not all contact brain capillaries. Astrocytes are actually the cell population in the brain which are left over after one would remove neurons, oligodendrocytes and microglial cells. Thus, astrocytes display a remarkable heterogeneity in their morphology and function. Conceptually astroglial cells are as heterogeneous as neurons, and astrocytes in different brain regions may have very different physiological properties.

Morphology of astrocytes is highly heterogeneous. Some astrocytes do have a star-like appearance, with several primary (also called stem) processes originating from the soma, although many more morphological profiles exist (see the picture below).



An archetypal morphological feature of astrocytes is their expression of intermediate filaments, which form the cytoskeleton. The main types of astroglial intermediate filament proteins are glial fibrillary acidic protein (GFAP) and vimentin; expression of GFAP is commonly used as a specific marker for the identification of astrocytes. It works well in cultured astrocytes, but *in situ* the levels of GFAP expression vary quite considerably: for example, GFAP is expressed by virtually every Bergmann glial cell in the cerebellum whereas only about 15–20 percent of astrocytes in the cortex of mature animals express GFAP.

Protoplasmic astrocytes are present in gray matter. They have many fine processes (approx ~50 μ m long), which are extremely elaborate and complex. The processes of protoplasmic astrocytes contact blood vessels, forming so-called 'perivascular' endfeet, and form multiple contacts with neurons. Some protoplasmic astrocytes also send processes to the pial surface, where they form 'subpial' endfeet. Protoplasmic astrocyte density in the cortex varies between 10 000 and 30 000 per mm³; the surface area of their processes (in rodents) may reach up to 60 000--80 000 μ m², and cover most of neuronal membranes within their reach.

Fibrous astrocytes are present in white matter. Their processes are long (up to $300 \ \mu$ m), though much less elaborate as compared to protoplasmic astroglia. The processes of fibrous astrocytes establish several perivascular or subpial endfeet. Fibrous astrocyte processes

also send numerous extensions ('perinodal' processes) that contact axons at nodes of Ranvier. The density of fibrous astrocytes is $\sim 200\ 000\ cell\ per\ mm^3$.

The second big group of astroglial cells is the radial glia, which are bipolar cells, each with an ovoid cell body and elongated processes. Radial glia usually have two main processes, one of them forming endfeet at the ventricular wall and the other at the pial surface. Radial glia are a common feature of the developing brain, as they are the first cells to develop from neural progenitors. From very early embryonic stages radial glia also form a scaffold, which assists in neuronal migration. After maturation, radial glia disappear from many brain regions and transform into stellate astrocytes, although radial glial cells remain in the retina (*Müller glia*) and in lower vertebrates such as turtles.

The retina contains specialized radial glia called Müller cells, which make extensive contacts with retinal neurones. The majority of Müller glial cells have a characteristic morphology, extending longitudinal processes along the line of rods and cones. In humans, Müller glial cells occupy up to 20 percent of the overall volume of the retina, and the density of these cells approaches 25 000 per mm² of retinal surface area. Each Müller cell forms contacts with a clearly defined group of neurons organized in a columnar fashion; a single Müller cell supports ~16 neurones in human retina, and up to 30 in rodents.

The cerebellum contains specialized semi-radial glia called Bergmann glia. They have relatively small cell bodies (~15 μ m in diameter) and 3-6 processes that extend from the Purkinje cell layer to the pial surface. Early in development these cells have contacts to the ventricular surface and are true radial glial cells, but with the development of the granular layer, they acquire the classical morphology of Bergmann glial cells. Usually several (~8 in rodents) Bergmann glial cells surround a single Purkinje neuron and their processes form an ensheathment of the Purkinje cell dendrites. The processes of Bergmann glial cells are extremely elaborate, and they form close contacts with synapses formed by parallel fibres on Purkinje neuron dendrites. Each Bergmann glial cell provides coverage for up to 8000 of such synapses.

Other regions of the CNS contain many different populations of astroglial cells. Velate astrocytes are found in the cerebellum, where

they form a sheath surrounding granule neurones; each velate astrocyte enwraps a single granule neurone. A similar type of astrocyte is also present in the olfactory bulb. Interlaminar astrocytes are specific to the cerebral cortex of higher primates. Their characteristic peculiarity is a very long single process (up to 1 mm) that extends from the soma located within the supragranular layer to cortical layer IV. Tanycytes are specialized astrocytes found in the periventricular organs, the hypophysis and the raphe part of the spinal cord. Astroglial cells in the neuro-hypophysis are known as pituicytes; the processes of these cells surround neuro-secretory axons and axonal endings under resting conditions. Perivascular and marginal astrocytes are localized very close to the pial matter, where they form numerous endfeet with blood vessels; they form the pial and perivascular glia limitans barrier, which assists in isolating the brain parenchyma from the vascular and subarachnoid compartments. Ependymocytes, choroid plexus cells and retinal pigment epithelial cells line the ventricles or the subretinal space.

(From: http://www.networkglia.eu/en/astrocytes (adapted from: Kettenmann H.; Verkhratsky A. (2011) Neuroglia - Living Nerve Glue, Fortschritte der Neurologie und Psychiatrie 79: 588-597).

III. Post-reading activities

Task 8. Complete the following sentences using the text:

- 1) ______ and _____ are localized very close to the piamater.
- 2) ______ are specific to the cerebral cortex of higher primates.
- 3) ______ are found in the cerebellum, where they form a sheath surrounding granule neurones; each velate astrocyte enwraps a single granule neurone.
- 4) The cerebellum contains specialized semi-radial glia called _____.
- 5) The retina contains specialized radial glia called _____.
- 6) Conceptually ______ are as heterogeneous as neurons and astrocytes in different brain regions may have very different physiological properties.
- 7) ______ are specialized astrocytes found in the periventricular organs, the hypophysis and the raphe part of the spinal cord.
- 8) Velate astrocytes are found in the _____.

Task 9. Find and analyze all the definitions given in the text.

Task 10. Answer the questions about the text:

- 1) What is the morphology of astrocytes?
- 2) What astrocytes are present in gray matter?
- 3) What is the name of specialized radial glia in the retina?
- 4) What astrocytes are specific to the cerebral cortex of higher primates?
- 5) What is Bergmann glia?
- 6) Are all astrocytes star-like cells?
- 7) What astrocytes are present in white matter?

Task 11. Are the following statements about the text true or false? *Explain why:*

- 1) Fibrous astrocytes are present in gray matter.
- 2) The cerebellum contains specialized semi-radial glia called Bergmann glia.
- 3) Astrocytes do not display any heterogeneity in their morphology and function.
- 4) An archetypal morphological feature of astrocytes is their expression of intermediate filaments, which form the cytoskeleton.
- 5) Interlaminar astrocytes are localized very close to the pial matter, where they form numerous endfeet with blood vessels.
- 6) Astrocytes form the pial and perivascular glia limitans barrier, which assists in isolating the brain parenchyma from the vascular and subarachnoid compartments.
- 7) Müller glial cells occupy about 30 percent of the overall volume of the retina.
- 8) The density of Müller glial cells approaches 25 000 per mm² of retinal surface area.

IV. Focus on grammar and lexis

Task 12. Here are the answers to some questions about the text. Write the questions:

- 1) Yes, the morphology of astrocytes is highly heterogeneous.
- 2) They have relatively small cell bodies (\sim 15 µm in diameter) and 3 to 6 processes that extend from the Purkinje cell layer to the pial surface.

- 3) They form close contacts with synapses formed by parallel fibres on Purkinje neuron dendrites.
- 4) It is up to 1 mm.
- 5) Glial fibrillary acidic protein.
- 6) Up to 30 percent of the overall volume of the retina.

Task 13. Put the words in the right order to make sentences:

- 1) of astrocytes proportion in the is well defined the brain not.
- 2) within astrocytes have the field of made such discoveries area of research neuroscience an important.
- 3) glial are they known as cells also astrocytic.
- 4) playing a role radial glia present during development in neuron migration are mostly.
- 5) the brain regulate they the of electrical impulses transmission within.

Task 14. Correct the mistakes. There is one mistake in each of the following sentences. Find it and write the corrected sentences:

- 1) The majority of Müller glial cells has a characteristic morphology, extending longitudinal processes along the line of rods and cones.
- 2) Early in development this cells have contacts to the ventricular surface and are true radial glial cells.
- 3) With the development of the granular layer they acquiring the classical morphology of Bergmann glial cells.
- 4) Thus astrocytes displays a remarkable heterogeneity in their morphology and function.
- 5) Most neuroscientists think they know what astrocyte is.
- 6) There is any uniform and unequivocal definition of an astrocyte.
- 7) Each Müller cell form contacts with a clearly defined group of neurons organized in a columnar fashion.
- 8) A single Müller cells supports ~16 neurones in human retina, and up to 30 in rodents.

Task 15. Fill in the gaps with the suitable preposition:

- 1) Other regions _____ the CNS contain many different populations _____ astroglial cells.
- 2) A similar type of astrocyte is also present ____ the olfactory bulb.
- 3) .After maturation, radial glia disappear ____ many brain regions and transform ____ stellate astrocytes, although radial glial cells remain ____ the retina (*Müller glia*) and ____lower vertebrates such as turtles.
- 4) Astrocytes display a remarkable heterogeneity _____ their morphology and function.
- 6) The second big group _____ astroglial cells are the radial glia, which are bipolar cells each _____ an ovoid cell body and elongated processes.

Task 16. Translate from Ukrainian into English:

- 1) Астроцити це підтип гліальних клітин у центральній нервовій системі.
- 2) Деякі форми астроцитів існують у центральній нервовій системі, у тому числі: волокниста (у білій речовині), протоплазмова (у сірій речовині) і радіальна.
- 3) Радіальні глії розташовані у зонах, що є перпендикулярними до вісі шлуночків.
- 4) Астроцити виробляють калієві канали з високою щільністю.
- 5) Добре відомо, що неправильне накопичення позаклітинного калію спричиняє епілептичну активність нейронів.
- 6) Астроцити забезпечують нейрони поживними речовинами, такими як лактат.

Α	В
1) protoplasm	a) the outer layer of the cerebrum (the cerebral cortex), composed of folded grey matter and playing an important role in consciousness
2) dendrite	b) a small fluid-filled bladder or vacuole within the body
3) oligodendrocyte	c) relating to the sense of smell

Task 17. Match the terms in A with their definitions in B:

4) cortex	d) a groove, ridge, or seam in an organ or tissue, typically marking the line between two halves
5) axon	e) the colourless material comprising the living part of a cell, including the cytoplasm, nucleus, and other organelles
6) olfactory	f) (Lat. "tender mother") the delicate innermost
[v l'fækt(ə)ri]	layer of the membranes surrounding the brain and spinal cord
7) cerebellum	g) a long, slender projection of a nerve cell that typically conducts electrical impulses away from the neuron's cell body
8) raphe ['re 1 fi]	h) a membrane or membranous structure,
(pl. raphae ['reIfi])	typically covering another structure or partly obscuring an opening
9) Pia mater (the pia)	i) a glial cell similar to an astrocyte but with
[paɪə meɪtər], [piə mɑtər]	fewer protuberances, producing myelin in the central nervous system
10) velum ['viləm] (pl. vela [-lə])	j) (Latin for "little brain") a major feature of the hindbrain of all vertebrates
11) vesicle	k) (Lat.) in the original place:
['vɛsɪk(ə)l, 'vi-]	in the appropriate position
12) in situ [In 'sItju]	1) a short branched extension of a nerve cell, along which impulses received from other cells at synapses are transmitted to the cell body.

V. Final tasks

Task 18. Discuss the following ideas with your group-mates:

- 1. How much is the brain's response to injury different than that of other organs?
- 2. Under what circumstances might you see a reactive astrocyte?
- 3. What is gliosis?
- 4. What are the functions of astrocytes?
- 5. What do gliosis and astrocytes represent on an MRI of the brain?
- 6. What defines astrocytes?
- 7. What are the causes and effects of encephalomalacia?

Task 19. Use the key phrases given below to talk about astroglia:

Star-like cells, neuroglial cells, CNS, glial fibrillary acidic heterogeneity, remarkable astroglial GFAP. protein. cells. physiological properties, protoplasmic astrocytes, fibrous astrocytes, radial glia, Müller cells, Bergmann glia, velate astrocytes, interlaminar perivascular tanycytes, marginal and astrocytes. astrocytes. Ependymocytes, choroid plexus cells, retinal pigment, epithelial cells, gliosis, MRI of the brain.

VI. Individual reading: supplementary text

Task 20: Read the text and answer the following questions:

- 1. What mechanisms are implicated in the release of gliotransmitters?
- 2. What do astrocytes express?
- 3. How can glutamate released from astroglia affect neuronal excitability?

The Concept of Gliotransmission

Astrocytes and other glial cells can release a variety of transmitters into the extracellular space. These transmitters are currently classified as gliotransmitters although in fact they are the same molecules utilized by neurons such as glutamate, ATP, GABA and D-serine. Only taurine and possibly kinurenicacis may represent substances uniquely released by glia being thus true gliotransmitters. Several different mechanisms have been implicated in the release of a gliotransmitter. These mechanisms include: (i) diffusion through high-permeability channels (e.g. volume-activated Cl-channels, unpaired connexin (a transmembrane protein) "hemichannels" or P2X₇ poreforming purinoceptors; (ii) through transporters, e.g. by reversal of excitatory amino acid transporters or exchange via the cystine-glutamate antiporter or organic anion transporters; and (iii) through Ca^{2+} -dependent exocytosis.

The first documented description of secretion from astrocytes was made by a French neuroanatomist Jean Nageotte who in 1910 proposed that astroglial cells may release substances into the blood, acting like an endocrine gland. Recently, exocytotic release from astroglial cells was confirmed in numerous experiments. It appeared that astrocytes express proteins important for exocytosis such as synaptobrevin 2, syntaxin 1, synaptosome-associated protein of 23 kDa. astrocytes express transporters In addition. required for neurotransmitter accumulation in the secretory vesicles. These include the vacuolar type of proton ATPase (V-ATPase), which drives protons into the vesicular lumen creating the proton concentration gradient necessary for glutamate / ATP transport into vesicles, and the three known isoforms of vesicular glutamate transporters (VGLUTs) -1, 2 and 3, and vesicular nucleotide transporters (VNUT). Immunoelectron microscopy studies demonstrated that VGLUTs 1 or 2 in astrocytes in situ associate with small clear vesicles with a mean diameter of ~30 nm. Astrocytes also have large dense core granules with diameters of ~115 nm, containing the secretory peptide secretogranin II and ATP. Functionally, exocytotic release of transmitters for astrocytes was deduced from several types of experiments in vitro and in situ. In particular, Ca²⁺-dependent exocytotic glutamate release from astrocytes can trigger several neuronal responses including an elevation of neuronal $[Ca^{2+}]_i$ and generation of a slow neuronal inward current mediated by NMDA receptors. In addition, glutamate released from astroglia can affect neuronal excitability, possibly modulate synaptic transmission and synchronise synaptic events. It should be stated, however, that the role and relevance of gliotransmission for information processing in the brain remains controversial. (From: http://www.networkglia.eu/en/astrocytes)

(FIOIII. http://www.networkgila.eu/en/astrocyte

Task 21: Write a summary of the text.

VII. Additional texts

Did you know that glutamate is synthesized within astrocytes as a by-product of the tricarboxylic acid (TCA) cycle?

Task 22: Read the text and make up 2-3 key questions based on it:

Amino Acids as Astrocytic Transmitters

Gliotransmitters are chemicals released from glial cells fulfilling the following set of criteria: 1) they are synthesized by and / or stored in glia; 2) their regulated release is triggered by physiological and / or pathological stimuli; 3) they activate rapid (milliseconds to seconds) responses in neighboring cells; and 4) they play a role in (patho)physiological processes. The criteria for a chemical released from neurons to be classified as a neurotransmitter have been frequently modified. Since transmitter release from glia was demonstrated at a much latter time than that from neurons, only recently has the above-mentioned set of criteria been put forth to establish what compounds qualify as gliotransmitters.

As mentioned before, astrocytes can release a variety of gliotransmitters into the extracellular space using several different mechanisms, e.g. exocytotic mechanism(s) underlying the release of three classes of gliotransmitters: (i) amino acids, such as, glutamate and D-serine; (ii) nucleotides, like adenosine 5'-triphosphate; and (iii) peptides, such as, atrial natriuretic peptide and brain-derived neurotrophic factor. It is clear that astrocytes are endowed with elements that qualify them as cells communicating with neurons and other cells within the CNS by employing regulated exocytosis.

Glutamate is synthesized within astrocytes as a by-product of the tricarboxylic acid (TCA) cycle. Since astrocytes possess the enzyme pyruvate carboxylase, they can synthesize glutamate *de novo*. Glutamate is converted from the TCA cycle intermediate, α -ketoglutarate, usually via transamination of another amino acid, such as, aspartate. D-serine is converted from L-serine by the action of serine racemase, an enzyme found predominately in astrocytes.

Glutamate packaged in vesicles is released from the astrocyte when the vesicle fuses with the plasma membrane. This fusion process is mediated by synaptotagmin 4 and SNARE proteins, such as syntaxin 1 and synaptobrevin.

Evidence for Ca^{2+} -dependent glutamate release from astrocytes was first shown using high performance liquid chromatography to monitor the release of this transmitter from cultured astrocytes. Astrocytes were equilibrated for prolonged periods of time (40–60 minutes) either in a solution containing normal external free Ca^{2+} (2.4 mM), or in a solution depleted of external free Ca^{2+} (24 nM); the latter solution caused a depletion of internal Ca^{2+} stores and prevented Ca^{2+} entry from the extracellular space. Addition of the Ca^{2+} ionophore, ionomycin, in the presence of normal external Ca^{2+} , caused an increase in the release of glutamate from astrocytes. Stimulation of astrocytes, bathed in a solution depleted of free Ca^{2+} , failed to cause an increase in glutamate release. These data indicate that elevated intracellular Ca^{2+} concentration ($[Ca^{2+}]_i$) is sufficient and necessary to stimulate glutamate release. Consistent with the former finding, other stimuli that directly increased astrocytic $[Ca^{2+}]_i$, including mechanical stimulation, photostimulation, and photolysis of Ca^{2+} cages, all caused release of glutamate.

The majority of intracellular Ca²⁺ necessary for glutamate release originates from endoplasmic reticulum (ER) internal stores, since Ca²⁺-dependent glutamate release from astrocytes is most prominently reduced in the presence of thapsigargin. Diphenylboric acid 2-aminoethyl ester (2-APB) solution, a cell-permeant inositol 1,4,5-trisphosphate (IP₃) receptor antagonist, greatly reduce exocytotic glutamate release from astrocytes, implicating the role of IP₃sensitive internal stores in mediating Ca²⁺-dependent glutamate release from astrocytes. Similarly, ryanodine/caffeine-sensitive ER stores play a role, as well, since the treatment of astrocytes with ryanodine, at concentrations that block the release of Ca²⁺ from the ryanodine/caffeine- sensitive stores, also attenuates mechanicallyinduced glutamate release. Furthermore, the sustained presence of caffeine, which depletes ryanodine/caffeine stores, also reduces mechanically-induced glutamate release. Thus, Ca²⁺-dependent glutamate release from astrocytes requires co-activation of IP_3 - and ryanodine/caffeine-sensitive internal Ca^{2+} stores, which operate jointly.

(From: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC2862866/)

Task 23. Analyze the text for the key phrases to be used in the following-up discussion. Write down the phrases in your exercise-book.

Task 24. Read the text again for more details and put 5-7 questions (wh-questions / open-end questions).

Task 25. Pair-work. Ask your partner the questions you have made up. Check if the answers are correct.

Task 26. Team-work. Divide into two teams and discuss the text during 5-7 minutes. Choose a presenter in each team to present the main ideas of the text in front of the class. Which of the teams presents best?

Unit 2

BIOSENSORS

I. Pre-reading activities

Task 1. Discuss the following questions.

- 1) What do you know about biosensors?
- 2) Do you have any relatives or friends who are suffering from diabetes? What do they use to check blood glucose?
- 3) What examples of using living organisms for the detection of hazardous chemicals do you know?

Task 2. Pronounce the following international words after your teacher and guess their meaning:

biosensor	canary [kə'nɛərɪ]
sensitive element	fluorometer [flʊə'rɒmɪtə, flɔː-]
transducer [trænz'dju:sə(r)]	receptor [rI'septə(r)]
reader device	xenobiotic [zenə(ʊ)baı'btik]
detector	biomimetic [,baıəʊmı'mɛtık]
electronic nose	glucose ['glukəus]

Task 3. Match the synonyms:

- sensitive (adv)
 detection (n)
 response (n)
 toxic (adv)
 biological (adv)
 bind (v) *Task 4. Match the* opposites:

 specific (adv)
 - 2)impossible (v)

- a) reply (n)
- b) living (adv)
- c) poisonous (adv) ['p**JI**z(ə)nəs]
- d) susceptible (adv)
- e) associate (v)
- f) finding (n)

a) biochemicals (n)

b) reductase [re'dAkteIz] (n)

3) xenobiotics (n)	c) general (adv)
4) user-friendly (adv)	d) conceal (v)
5) display (v)	e) unclear (adv)
6) oxidase (n) ['oxIdeIz]	f) likely (v)

Task 5. Guess from the context what the underlined words mean:

- 1) Other <u>evanescent</u> wave biosensors have been commercialised using waveguides where the <u>propagation</u> constant through the waveguide is changed by the absorption of molecules to the waveguide surface.
- 2) An immunosensor utilizes the very specific binding <u>affinity</u> of antibodies for a specific compound or antigen.
- 3) The recognition process is based on the principle of <u>complementary</u> base pairing, adenine:thymine and cytosine:guanine in DNA.
- 4) An important part in a biosensor is to attach the biological elements to the surface of the sensor. The simplest way is to functionalize the surface <u>in order to coat</u> it with the biological elements.

Task 6. Match the English phrases on the left with their Ukrainian equivalents on the right:

1) biosensor reader device	а) клітинна відповідь на ліганд
2) the analyte under study	b) застосовуваний для
	розпізнавання
3) to break blood glucose down	с) аналіт, що вивчається
4) used to fingerprint	d) бере участь у клітинній
	передачі
5) involved in cellular signaling	е) зчитувальний біосенсорний
	пристрій
6) cellular response to ligand	f) розкладання глюкози у крові

II. While-reading activities

Task 7. Read the text and answer the questions:

- 1) What are the main parts of a biosensor?
- 2) How do commercial electronic noses use biological elements?
- 3) What are the advantages of a live-cell biosensor for CAMP?

The Biosensor



A biosensor is an analytical device used for the detection of an analyte that combines a biological component with a physicochemical detector. It consists of:

• the sensitive biological element (e.g. tissue, microorganisms, organelles, cell receptors, enzymes, antibodies, nucleic acids, etc.), a biologically derived material or biomimetic component that interacts (binds or recognizes) the analyte under study. The biologically sensitive elements can also be created by biological engineering;

• the transducer or the detector element (which works in a physicochemical way; optical, piezoelectric, electrochemical, etc.) that transforms the signal resulting from the interaction of the analyte with the biological element into another signal (i.e., transduceing) that can be more easily measured and quantified;

• the biosensor reader device with the associated electronics or signal processors that are primarily responsible for the display of the results in a user-friendly way. This sometimes accounts for the most expensive part of the sensor device, however it is possible to generate a user friendly display that includes transducer and sensitive element (ex. holographic sensor). The readers are usually custom-designed and manufactured to suit the different working principles of biosensors.

A common example of a commercial biosensor is the blood glucose biosensor, which uses the enzyme glucose oxidase to break blood glucose down. In doing so it first oxidizes glucose and uses two electrons to reduce the FAD (a component of the enzyme) to FADH2. This in turn is oxidized by the electrode in a number of steps. The resulting current is a measure of the concentration of glucose. In this case, the electrode is the transducer and the enzyme is the biologically active component.

Recently, arrays of many different detector molecules have been applied in so-called electronic nose devices, where the pattern of response from the detectors is used to fingerprint a substance. In the Wasp Hound odor-detector, the mechanical element is a video camera, and the biological element is five parasitic wasps that have been conditioned to swarm in response to the presence of a specific chemical. Current commercial electronic noses, however, do not use biological elements.

A canary in a cage, as used by miners to warn of gas, could be considered a biosensor. Many of today's biosensor applications are similar in that they use organisms which respond to toxic substances at much lower concentrations than humans can detect to warn of their presence. Such devices can be used in environmental monitoring, trace gas detection and in water treatment facilities.

Biological biosensors often incorporate a genetically modified form of a native protein or enzyme. The protein is configured to detect a specific analyte and the ensuing signal is read by a detection instrument, such as a fluorometer or luminometer. An example of a recently developed biosensor is one for detecting cytosolic concentration of the analyte CAMP (cyclic adenosine monophosphate), a second messenger involved in cellular signaling triggered by ligands interacting with receptors on the cell membrane. Similar systems have been created to study cellular responses to native ligands or xenobiotics (toxins or small molecule inhibitors). Such "assays" are commonly drug discovery development by pharmaceutical and used in biotechnology companies. Most CAMP assays in current use require lysis of the cells prior to measurement of CAMP. A live-cell biosensor for CAMP can be used in non-lysed cells with the additional advantage of multiple reads to study the kinetics of receptor response. (From: https://en.wikipedia.org/wiki/Biosensor).

III. Post-reading activities

Task 8. Complete the following sentences using the text:

- 1) The readers are usually ______ and _____ to suit the different working principles of biosensors.
- 2) A common example of a commercial _____ is the blood glucose _____, which uses the enzyme glucose oxidase to break _____ down.

- 3) Many of today's biosensor applications ______, in that they use organisms which respond to ______ at much lower concentrations than humans can detect to ______ their presence.
- 4) An example of a recently developed biosensor is one for detecting ______ of the analytecAMP (cyclic adenosine monophosphate), a ______ involved in cellular signaling triggered by ligands interacting with receptors on the cell membrane.

Task 9. Read and analyze the definitions given in the text.

Task 10. Are the following statements true or false? Explain why:

- 1) A common example of a commercial biosensor is a canary in a cage.
- 2) Current commercial electronic noses use a large amount of biological elements.
- 3) The protein is configured to detect a specific analyte and the ensuing signal is read by a detection instrument, such as a fluorometer or luminometer.

IV. Focus on grammar and lexis

Task 11. Here are the answers to some questions about the text. Write the questions:

- 1) The mechanical element is a video camera, and the biological element is five parasitic wasps.
- 2) They incorporate a genetically modified form of a native protein or enzyme.
- 3) A second messenger involved in cellular signaling.
- 4) To study cellular responses to native ligands or toxins, or small molecule inhibitors.

Task 12. Put the words in the right order to make correct sentences:

- 1) The be created engineering by elements also sensitive biologically biological can.
- 2) The usually readers principles and manufactured are the different to suit working custom-designed biosensors of.
- 3) Been cellular study to Similar have to responses or systems ligands xenobiotics native created.

Task 13. Correct the mistakes. There is one mistake in each sentence:

- 1) The sensitive biological element, a biologically derived material or biomimetic component that interact the analyte under study.
- 2) Recently, arrays of many different detector molecules have been applied in so called electronic nose devices, where the pattern with response from the detectors is used to fingerprint a substance.
- 3) More CAMP assays in current use require lysis of the cells prior to measurement of CAMP.

Task 14. Fill in the gaps with a suitable preposition:

- 1) The transducer or the detector element that transforms the signal resulting _____ the interaction ___ the analyte with the biological element _____ another signal that can be more easily measured and quantified.
- 2) This is oxidized _____ the electrode ____ a number of steps.
- 3) A live-cell biosensor __ CAMP can be used __ non-lysed cells with an advantage of multiple reads to study the kinetics __ receptor response.
- 4) The pattern _____ response _____ the detectors is used to fingerprint a substance.

Task 15. Translate into English:

- 1) Чутливий біологічний елемент, отриманий біологічно матеріал або біоміметичний компонент взаємодіють з досліджуваним аналітом (зв'язуються або розпізнають його).
- 2) Для цього він спочатку окиснює глюкозу і використовує два електрони, щоб відновити ФАД (компонент ферменту) у ФАД-Н2.
- 3) У детекторі запахів «Оси-гончаки», механічним елементом є відеокамера, а біологічним елементом – п'ять паразитних ос, які збиваються у рій у відповідь на присутність певної хімічної речовини.
- Такі пристрої можуть бути використані в моніторингу навколишнього середовища, виявленні слідів газів і у водоочисних спорудах.
- 5) Такі аналізи зазвичай використовуються в розробці нових ліків у фармацевтичних і біотехнологічних компаніях.

V. Final tasks

Task 16. Discuss the following ideas with your group-mates:

- 1) What are the advantages of using living cells or their fragments in constructing of chemical sensors?
- 2) What do you think about the rate of research works in the direction of development of multipurpose electronic nose (you can see one of such devices in the film "*Richie Rich*")?
- 3) What do you think about the use of plants and animals (especially mammals) in such biosensor studies?

Task 17. Use the phrases below and retell the text in your own words:

sensitive biological element; detector element; biosensor reader device; blood glucose biosensor; a canary in a cage; biosensor enzymes; cyclic AMP; living cells.

VI. Individual reading: supplementary text

Task 18: Read the article and answer the following questions:

- 1. What are the work lines of the research group from Alicante?
- 2. How can measuring some biological parameters far from the lab improve the living standards? Make your own assumptions.
- 3. What, in your opinion, are the difficulties of introducing such biosensor devices to the public?

Monitoring glucose levels in the field



The need for low-cost portable devices to measure substances of medical or biological interest (blood sugar levels, for instance) is growing, primarily within the health sector and such areas as food quality and environmental monitoring. Sending samples off to a clinical chemistry laboratory for analysis is expensive, and it takes a long time for the results to reach the patient. Devices for use in the field, at point-of-care or in non-hospital settings would constitute an efficient alternative were they able to give accurate readings under non-laboratory conditions.

This is the challenge addressed by the Electrocatalysis and Polymer Electrochemistry research group at the University of Alicante, Spain. As reported in 2015, they develop biosensors designed to detect neurotransmitters, like dopamine, adrenaline, norepinephrine, and metabolites, such as glucose, vitamin C and uric acid. Specifically, they are working on electrochemical biosensors that can be used directly on physiological fluids (blood, urine, saliva, etc.) and afford the same precision and reliability as lab testing.

Often, the perfectly normal presence of other chemical substances in these fluids can interfere with the detection process and lead to false positives, which is the main reason samples are sent off to specialist laboratories. To avoid these false positives, the university researchers are developing materials that have a high affinity with the molecule whose concentrations are being measured. Two main lines of work are being pursued.

The first is the development of "third-generation" biosensors that can be used to control glucose levels in diabetics: "We have immobilized a model protein with silica layers using the sol-gel method. Silica, or silicon oxide, is very common and very cheap – it is the main component of sand. By modulating the composition of these silica layers, we have been able to induce a direct electrochemical reaction between the protein and the sensor electrode. This innovative approach means we will be able to target other proteins, including glucose oxidase, and develop new substance-control devices," explains one of the group's researchers, Francisco Montilla.

The second comprises work on biomimetic sensors. These work like biosensors, but do not contain the biomolecules, such as proteins, that are a necessary part of typical electrochemical biosensors. "Despite the fact that biosensors offer some very interesting properties, they also have efficiency issues: they remain relatively expensive and, more importantly, no protein has been found in nature which can target their metabolic activity to a specific molecule," Montilla tells us. The reserchers are modifying sensor electrodes with silica layers that act like selective filters and can be manufactured bespoke for a given molecule.

(From: <u>https://phys.org/news/2015-11-efficient-biosensors-glucose-field.html</u>)

VII. Additional texts

Did you know that biosensors can be used for military purposes at times of biological attacks, with the main motive being to sensitively and selectively identify organisms posing threat in virtually real time called biowarfare agents (BWAs), namely: bacteria (vegetative and spores), toxins and viruses?

Task 19: Read the text and put your questions to cover its content:

Types of Biosensors

Biosensors started in the 1960s by the pioneers Clark and Lyons. Various types of biosensors being used are enzyme-based, tissuebased, immunosensors, DNA biosensors, and thermal and piezoelectric biosensors.

The first enzyme-based sensor was reported by Updike and Hicks in 1967. Enzyme biosensors have been devised on immobilization methods, i.e. adsorption of enzymes by van der Waals forces, ionic bonding or covalent bonding. The commonly used enzymes for this purpose are oxidoreductases, polyphenol oxidases, peroxidases, and aminooxidases.

The first microbe-based or cell-based sensor was actualized by Diviès. The tissues for tissue-based sensors arise from plant and animal sources. The analyte of interest can be an inhibitor or a substrate of these processes. Organelle-based sensors were made using membranes, chloroplasts, mitochondria, and microsomes.

Immunosensors were established on the fact that antibodies have high affinity towards their respective antigens, i.e. the antibodies specifically bind to pathogens or toxins, or interact with components of the host's immune system.

The DNA biosensors were devised on the property that singlestrand nucleic acid molecule is able to recognize and bind to its complementary strand in a sample. The interaction is due to the formation of stable hydrogen bonds between the two nucleic acid strands.

Magnetic biosensors include miniaturized biosensors detecting magnetic micro- and nanoparticles in microfluidic channels using the magnetoresistance effect. They have great potential in terms of sensitivity and size. Thermal biosensors or calorimetric biosensors are developed by assimilating biosensor materials into a physical transducer.

Piezoelectric biosensors are of two types: the quartz crystal microbalance and the surface acoustic wave device. They are based on the measurement of changes in resonance frequency of a piezoelectric crystal due to mass changes on the crystal structure.

Optical biosensors consist of a light source, as well as numerous optical components to generate a light beam with specific characteristics and to beeline this light to a modulating agent, a modified sensing head along with a photodetector.

Genetically-encoded biosensors, using green fluorescent protein and the subsequent autofluorescent protein (AFP) variants, are userfriendly, easy to engineer, manipulate and transfer into cells. Singlechain FRET (Förster resonance energy transfer) biosensor is another example. They consist of a pair of AFPs, which are able to transfer fluorescence resonance energy between them when brought close together. Different methods may be used to regulate changes in FRET signals based on intensity, ratio or lifetime of AFPs. Peptide and are easily manufactured through synthetic protein biosensors enzymatic followed by labelling chemistry with synthetic fluorophores. Due to their independence of genetically-encoded AFPs, they are readily utilized to control target activity and constitute attractive alternatives and have an added advantage of being able to enhance signal-to-noise ratio and sensitivity of response through introduction of chemical quenchers and photoactivatable groups. (From: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC4862100)

Task 20. Analyze the text for the key phrases to be used in the following-up discussion. Write down the phrases in your exercise-book.

Task 21. Read the text again for more details and put 5-7 questions (wh-questions / open-end questions).

Task 22. Pair-work. Ask your partner the questions you have made up. Check if the answers are correct.

Task 23. Team-work. Divide into two teams and discuss the text during 5-7 minutes. Choose a presenter in each team to present the main ideas of the text in front of the class. Which of the teams presents best?

Unit 3

ELECTROPHILIC AROMATIC SUBSTITUTION

I. Pre-reading activities

Task 1. Discuss the following questions:

- 1) What do you know about electrophilic aromatic substitution?
- 2) What reagents are needed?
- 3) What types of such substitution exist?
- 4) What are the reaction mechanisms in such substitution?

Task 2. Pronounce the following international words after your teacher and guess their meaning:

electrophilic [i'lektrə'filik] (adj.)	kinetics [kən'etiks] (n)
acylation [æsi'le 1 ∫n] (n)	electron [i'lektrə:n] (n)
carbocation [karbo'ke $I \int n$] (n)	benzaldehyde [ben'zaldəhaid] (n)
stoichiometric [stɔɪ'kiəu'metrɪk] (adj)	steric ['sterik; 'sti(ə)r-] (adj.)
regioselectivity ['rid3ioselek'tiviti] (n)	aromatic [arə'matik] (adj.)
concentrated[kansən'treItId] (adj)	conjugation [kɒndʒʊ'geɪ∫(ə)n] (n)
resonance $['rez(ə)nən(t)s](n)$	cyanate ['saIəneit] (adj.)
ipso- ['IpsəU] (prefix)	ortho- ['ɔ:(r)θə] (prefix)
nitroamide ['naitro'(ə)maid] (n)	functional ['fʌŋk∫ənl] (adj.)

Task 3. Match the synonyms:

1) amount	a) model
2) conduct	b) substance
3) key	c) speed
4) predict	d) carry out
5) route	e) quantity
6) compound	f) foresee
7) pattern	g) important
8) rate	h) course

Task4. Match the opposites:

1) addition	a) nucleophilic
2) acid	b) base
3) ipso-	c) elimination
4) electrophilic	d) deactivated
5) activated	e) diluted
6) concentrated	f) ortho -

Task 5. Guess from the context what the underlined words mean:

- 1. Factors specific to organic reactions are those that determine the stability of reactants and products such as <u>conjugation</u>, <u>hyperconjugation</u> and <u>aromaticity</u> and the presence and stability of <u>reactive intermediates</u> such as <u>free radicals</u>, <u>carbocations</u> and <u>carbanions</u>.
- 2. The Wohler synthesis is the <u>conversion</u> of <u>ammonium cyanate</u> into <u>urea</u>.
- 3. Electron donating groups are generally <u>ortho/para directors</u> for <u>electrophilic aromatic substitutions</u>, while electron <u>withdrawing</u> groups are generally meta directors with the exception of the <u>halogens</u> which are also ortho/para directors as they have <u>lone</u> <u>pairs</u> of electrons that are shared with the aromatic ring.
- 4. Unlike the other halogens, iodine does not serve as a <u>base</u> since it is positive.
- 5. Heating the reaction mixture is sufficient to <u>hydrolyze</u> the nitroamide back to the nitroamine.

Task 6. Match the English phrases on the left with their Ukrainian equivalents on the right:

1) aromatic ring	а) ключовий напівпродукт
2) electron density	b) ароматичне кільце
3) key intermediate	с) дезактивуючий замісник
4) nitronium ion	d) ароматичне сульфонування
5) patterns of regioselectivity	е) електронна густина
6) aromatic sulfonation	f) підвищена реактивність
7) deactivating substituent	g) модель регіоселективності
8) increased reactivity	h) йон нітронію

II. While-reading activities

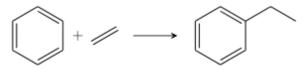
Task 7. Read the text and answer the questions:

- 1. What is electrophilic substitution?
- 2. How many types of substituents exist in an aromatic ring?
- 3. What is resonance structure?

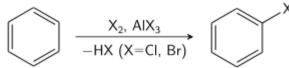
Electrophilic aromatic substitution

Electrophilic aromatic substitution (S_EAr) is an organic reaction in which an atom that is attached to an aromatic system (usually hydrogen) is replaced by an electrophile. Some of the most important electrophilic aromatic substitutions are aromatic nitration, aromatic halogenation, aromatic sulfonation, and acylation and alkylating Friedel–Crafts reactions.

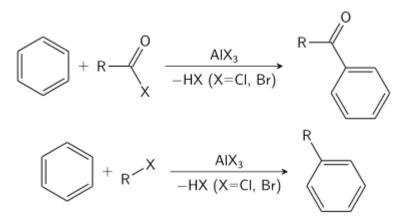
The most widely practiced example of this reaction is the ethylation of benzene:



Approximately 24,700,000 tons were produced in 1999. (After dehydrogenation and polymerization, the commodity plastic polystyrene is produced.) In this process, solid acids are used as catalyst to generate the incipient carbocation. Many other electrophilic reactions of benzene are conducted, although on much smaller scale, they are valuable routes to key intermediates. The nitration of benzene is achieved via the action of the nitronium ion as the electrophile. The sulfonation with fuming sulfuric acid gives benzenesulfonic acid. Aromatic halogenation with bromine, chlorine, or iodine gives the corresponding aryl halogen compounds catalyzed bv the corresponding iron or aluminum trihalide.



The Friedel–Crafts reaction can be performed either as an acylation or as an alkylation. Often, aluminium trichloride is used, but almost any strong Lewis acid can be applied. For the acylation reaction a stoichiometric amount of aluminum trichloride is required.



Both the regioselectivity and the speed of an electrophilic aromatic substitution are affected by the substituents already attached to the benzene ring. In terms of regioselectivity, some groups promote substitution at the ortho or para positions, while other groups increase substitution at the meta position. These groups are called either ortho– para directing or meta directing. In addition, some groups will increase the rate of reaction (activating) while others will decrease the rate (deactivating). While the patterns of regioselectivity can be explained with resonance structures, the influence on kinetics can be explained by both resonance structures and the inductive effect.

Substituents can generally be divided into two classes regarding electrophilic substitution: activating and deactivating towards the aromatic ring. Activating substituents or activating groups stabilize the cationic intermediate formed during the substitution by donating electrons into the ring system, by either inductive effect or resonance effects. Examples of activated aromatic rings are toluene, aniline and phenol.

The extra electron density delivered into the ring by the substituent is not equally divided over the entire ring, but is concentrated on atoms 2, 4 and 6 (the ortho and para positions). These positions are thus the most reactive towards an electron-poor electrophile. The highest electron density is located on both ortho and para positions, though this increased reactivity might be offset by steric hindrance between substituent and electrophile. The final result of the electrophilic aromatic substitution might thus be hard to predict, and it is usually only established by doing the reaction and determining the ratio of ortho versus para substitution.

On the other hand, deactivating substituents destabilize the intermediate cation and thus decrease the reaction rate. They do so by withdrawing electron density from the aromatic ring, though the

positions most affected are again the ortho and para ones. This means that the most reactive positions (or, least unreactive) are the meta ones (atoms 3 and 5). Examples of deactivated aromatic rings are nitrobenzene, benzaldehyde and trifluoromethylbenzene. The deactivation of the aromatic system also means that generally harsher conditions are required to drive the reaction to completion. An example of this is the nitration of toluene during the production of trinitrotoluene (TNT). While the first nitration, on the activated toluene ring, can be done at room temperature and with dilute acid, the second one, on the deactivated nitrotoluene ring, already needs prolonged heating and more concentrated acid, and the third one, on very strongly deactivated dinitrotoluene, has to be done in boiling concentrated sulfuric acid.

Functional groups thus usually tend to favor one or two of these positions above the others; that is, they direct the electrophile to specific positions. A functional group that tends to direct attacking electrophiles to the meta position, for example, is said to be metadirecting.

(From: https://en.wikipedia.org/wiki/Electrophilic aromatic substitution)

<u>III. Post-reading activities</u>

Task 8. Complete the following sentences using the text:

- 1) In this process, solid acids are used as ______ to generate the incipient carbocation.
- 2) The nitration of benzene is achieved via the action of the nitronium ion as the _____.
- 3) Often, aluminium trichloride is used, but almost any strong _____acid can be applied.
- 4) The extra electron density delivered into the ring by the substituent is not equally divided over the entire ring, but is concentrated on atoms 2, 4 and 6 (the ortho and _____ positions).
- 5) They do so by withdrawing _____ density from the aromatic ring, though the positions most affected are the ortho and para ones.

Task 9. Read and analyze the definitions given in the text.

Task 10. Answer the questions about the text:

- 1) What are the most important aromatic electrophilic substitutions?
- 2) What is the key intermediate of aromatic substitution reactions?

- 3) How many positions of subsituents in aromatic ring are?
- 4) How many classes of substituents in aromatic ring are?
- 5) What is the effect of meta-substients?
- 6) What examples of deactivated aromatic rings do you know?
- 7) Why is dilute acid needed for the nitration of trinitrotoluene?

Task 11. Are the following statements true or false? Say why:

- 1) Acylation and alkylation reactions of benzene ring are called Friedel-Crafts reactions.
- 2) Nitrobenze is easier nitrated then benzene.
- 3) Carbanion is the key intermediate in electrophilic aromatic substitution.
- 4) Meta-orientants have electron withdrawing effect.
- 5) Resonance effect is enough for explaining kinetics of aromatic electrophilic substitution.
- 6) Trinitrotoluene is prepared by sulfonation of benzene.
- 7) The extra electron density delivered into the ring by the substituent is equally divided over the entire ring.

Task 12. Make a list of all the chemicals, chemistry terms, procedures, experiments, equipment (glassware) you can find in the text. Check all the examples in your class.

IV. Focus on grammar and lexis

Task 13. Here are the answers to some questions about the text. Write the questions:

- 1) In this process, solid acids are used as catalyst to generate the incipient carbocation.
- 2) Both the regioselectivity and the speed of an electrophilic aromatic substitution are affected by the substituents already attached to the benzene ring.
- 3) The final result of the electrophilic aromatic substitution might be hard to predict.
- 4) Examples of deactivated aromatic rings are nitrobenzene, benzaldehyde and trifluoromethylbenzene.
- 5) A functional group that tends to direct attacking electrophiles to the meta position, for example, is said to be meta-directing.

Task 14. Put the words in the right order:

- 1) reactive these are positions electrophile thus towards the most an electron-poor.
- 2) ring substituents can aromatic classes divided into two regarding electrophilic be substitution: and activating deactivating activating towards the generally.
- 3) on the deactivating cation hand, substituents intermediate destabilize the and thus decrease other rate reaction.

Task 15. Correct the mistakes There is one mistake in each of the following sentences. Find it and write the corrected sentences:

- 1) These groups is called either ortho-para directing or meta directing.
- 2) These positions are thus the more reactive towards an electronpoor electrophile.
- 3) On the other hand, deactivating substituents have destabilize the intermediate cation and thus decrease the reaction rate.
- 4) The deactivation of the aromatic system also means can that generally harsher conditions are required to drive the reaction to completion.
- 5) The first nitration, on the activated toluene ring, can be have done at room temperature and with dilute acid.
- 6) The second nitration, on the deactivated nitrotoluene ring, need prolonged heating and more concentrated acid.
- 7) The third nitration, on very strongly deactivated dinitrotoluene, have to be done in boiling concentrated sulfuric acid.

Task 16. Complete these sentences with the correct preposition forming phrasal verbs:

- 1) You must not to give _____ if your first experiment isn't successful.
- 2) Before work is started fume cupboard must be turned ____.
- 3) Don't hesitate to ask your mentor about anything you look _____.
- 4) If a problem with reaction arises try to work it ____.
- 5) Sometimes it feels like there is no exit it's a point when you are about to come up _____ solution.

V. Final tasks

Task 17. Discuss the following ideas with your group-mates:

- 1) Do you agree that aromatic electrophilic substitution plays an important role in organic synthesis? Explain your point of view.
- 2) How do you understand the statement "organic chemistry is the science of living organisms"? Work in pairs and share your points of view.
- 3) What is the main purpose of investigating kinetics of organic reactions? Provide some evidence to support your opinion.

Task 18. Use the phrases below to retell the text in your own words:

Aromatic ring, electron density donating and withdrawing groups, Friedel-Crafts reaction, carbocation, key intermediate, nitration, metaand ortho- directing groups, activating and deactivating effects, trinitrotoluene, dilute or concentrated acid.

VI. Individual reading: supplementary text

Task 19: Read the text and answer the following questions:

- 1. Where are organic reactions used?
- 2. What are the factors governing organic reactions?
- 3. How is the selectivity of organic reactions reached?

Organic reactions are chemical reactions involving organic compounds. The basic organic chemistry reaction types are addition reactions, elimination reactions, substitution reactions, pericyclic reactions, rearrangement reactions, photochemical reactions and redox reactions. In organic synthesis, organic reactions are used in the construction of new organic molecules. The production of many manmade chemicals such as drugs, plastics, food additives, fabrics depend on organic reactions.

The oldest organic reactions are combustion of organic fuels and saponification of fats to make soap. Modern organic chemistry starts with the Wöhler synthesis in 1828. In the history of the Nobel Prize in Chemistry awards have been given for the invention of specific organic reactions such as the Grignard reaction in 1912, the Diels-Alder reaction in 1950, the Wittig reaction in 1979 and olefin metathesis in 2005. Organic chemistry has a strong tradition of naming a specific reaction to its inventor or inventors and a long <u>list</u> of so-called named reactions exists, conservatively estimated at 1000. A very old named reaction is the Claisen rearrangement (1912) and a recent named reaction is the Bingel reaction (1993). When the named reaction is difficult to pronounce or very long as in the Corey-House-Posner-Whitesides reaction it helps to use the abbreviation as in the CBS reduction. The number of reactions hinting at the actual process taking place is much smaller, for example the ene reaction or aldol reaction.

Another approach to organic reactions is by type of organic reagent, many of them inorganic, required in a specific transformation. The major types are oxidizing agents such as osmium tetroxide, reducing agents such as Lithium aluminium hydride, bases such as lithium diisopropylamide and acids such as sulfuric acid.

Factors governing organic reactions are essentially the same as that of any chemical reaction. Factors specific to organic reactions are those that determine the stability of reactants and products such as conjugation, hyperconjugation and aromaticity and the presence and stability of reactive intermediates such as free radicals, carbocations and carbanions.

An organic compound may consist of many isomers. Selectivity in terms of regioselectivity, diastereoselectivity and enantioselectivity is therefore an important criterion for many organic reactions. The stereochemistry of pericyclic reactions is governed by the Woodward– Hoffmann rules and that of many elimination reactions by the Zaitsev's rule.

Organic reactions are important in the production of pharmaceuticals. In a 2006 review it was estimated that 20% of chemical conversions involved alkylations on nitrogen and oxygen atoms, another 20% involved placement and removal of protective groups, 11% involved formation of new carbon-carbon bond and 10% involved functional group interconversions.

(From: <u>https://en.wikipedia.org/wiki/Organic_reaction</u>)

VII. Additional texts

Did you know that despite possessing multiple double bonds, aromatic compounds do not undergo addition reactions due to the great stability of the ring systems that result from complete π electron delocalization (resonance)?

Task 20: Read the text and put your questions to cover its content:

Aromatic compounds react by electrophilic aromatic substitution reactions, in which the aromaticity of the ring system is preserved. For example, benzene reacts with bromine to form bromobenzene.

All electrophilic aromatic substitution reactions share a common mechanism. This mechanism consists of a series of steps:

1. An electrophile — an electron seeking reagent — is generated. For the bromination of benzene reaction, the electrophile is the Br+ ion generated by the reaction of the bromine molecule with ferric bromide, a Lewis acid.

2. The electrophile attacks the π electron system of the benzene ring to form a non-aromatic carbocation.

3. The positive charge on the carbocation that is formed is delocalized throughout the molecule.

4. The aromaticity is restored by the loss of a proton from the atom to which the bromine atom (the electrophile) has bonded.

5. Finally, the proton reacts with the FeBr $_4$ ⁻ to regenerate the FeBr $_3$ catalyst and form the product HBr.

Although the delocalized pi electrons in aromatic rings are much less reactive than those in isolated or conjugated alkenes, they can undergo electrophilic reactions given a powerful enough electrophile. Electrophilic addition to aromatic double bonds, however, is not generally observed – this would be energetically unfavorable because it would result in a loss of aromaticity in the product.

Rather, aromatic double bonds undergo electrophilic substitution reactions, (abbreviated S_EAr), which are mechanistically very similar to the substitutive addition-elimination reactions of alkenes. The product of an S_EAr reaction, like the starting compound, is aromatic.

Because the starting point in an S_EAr reaction is inherently low in energy (due to aromaticity), the activation energy for the first electrophilic step – in which aromaticity is temporarily lost in the carbocation intermediate – is correspondingly high. This is why aromatic pi bonds are significantly less reactive in electrophilic steps compared to the π bonds of nonaromatic alkenes.

As a consequence, S_EAr reactions tend to share two basic characteristics. First, the electrophilic partner needs to be highly reactive – this serves to increase the energy of the starting point and

decrease the activation energy. The electrophile in an enzymatic S_EAr reaction is usually a carbocation.

A second common characteristic that we can see in many S_EAr reactions is that the aromatic substrate is often activated by the presence of one or more electron-donating heteroatom-containing substituents.

The heteroatom – generally a nitrogen or an oxygen – stabilizes the positive charge on the intermediate, which by Hammond's postulate also lowers the energy of the transition state and therefore the activation energy.

An example of an S_EAr reaction can be found in the biosynthetic pathway for a kind of compound found in fungi called 'ergot alkaloids' (the term 'alkaloid' refers to a diverse family of amine-containing biomolecules, and 'ergot' is a type of fungus). These alkaloid compounds in fungi often have potent hallucinogenic effects when ingested by humans. In an interesting historical note, it has been speculated that the bizarre behavior of some of the young women accused in the Salem witchcraft trials may have been caused by their accidental consumption of fungus-tainted grain.

A key step in fungal alkaloid biosynthesis is a condensation between the aromatic side chain of the amino acid tryptophan and dimethylallyl diphosphate, an isoprenoid building block molecule.

(From: <u>https://www.cliffsnotes.com/study-guides/chemistry/organic-chemistry-</u> <u>ii/reactions-of-aromatic-compounds/electrophilic-aromatic-substitution-</u> <u>reactions</u> and https://chem.libretexts.org > ... > 15: Electrophilic reactions)

Task 21. Analyze the text for the key phrases to be used in the following-up discussion. Write down the phrases in your exercise-book.

Task 22. Read the text again for more details and put 5-7 questions (wh-questions / open-end questions).

Task 23. Pair-work. Ask your partner the questions you have made up. Check if the answers are correct.

Task 24. Team-work. Divide into two teams and discuss the text during 5-7 minutes. Choose a presenter in each team to present the main ideas of the text in front of the class. Which of the teams presents best?

Unit 4

LIPIDS

I. Pre-reading activities

Task 1. Discuss the following questions:

- 1) What do you know about lipids and fats?
- 3) What can you say about prokaryotes and eukaryotes?
- 4) Have you heard about glycosylation reactions? What are they?
- 5) What is a liposome?
- 6) What is the difference between hydrophilic and hydrophobic substances?

Task 2. Pronounce the following international words after your teacher and guess what they mean:

nanotechnology [nænətek'nɔlədʒɪ] (n)	hydrophobic [haIdrə'fəubIk] (adj.)
liposome ['lɪpəsəum; 'lī-] (n)	isoprene [aIsəpr i:n] (n)
protein ['prəuti:n] (n)	steroid ['ster JI d] (n)
iso- [aIsə] (prefix)	reductive [rI'd^ktIv] (adj.)
organelle [ɔ:gə'nel] (n)	condensation [k⊃nden'seI∫(ə)n]
eukaryotic [ju:kær ɪ' ɔtɪk] (adj.)	oxidative ['DksIdətIv; 'deI-] (adj.)
prokaryotic [prəukær I' >t I k] (adj.)	vesicle ['vɛsık(ə)l, 'vi-] (n)
polypropylene [pɔlɪ'prəupɪli:n] (n)	micelle [mI'sel] (n)

Task 3. Match the synonyms:

- 1. fats
- 2. application
- 3. obtained
- 4. core
- 5. formation
- 6. behavior
- 7. term

- a) construction
- b) action
- c) lipids
- d) name
- e)center
- f) use
- g) gotten (got)

Task 4. Match the opposites:

1. hydrophobic	a) tail
2. small	b) combined
3. eukaryotic	c) reductive
4. head	d) hydrophilic
5. oxidative	e) large
6. distinct	f) prokaryotic

Task 5. Guess from the content what the underlined words mean:

- 1. Although the term lipid is sometimes used as a synonym for fats, fats are a <u>subgroup</u> of lipids called triglycerides.
- 2. The glycerophospholipids are the main structural component of biological membranes, such as the <u>cellular plasma membrane</u> and the intracellular membranes of organelles.
- 3. In an aqueous system, the polar heads of lipids align towards the polar, aqueous environment, while the hydrophobic tails minimize their contact with water and tend to cluster together, forming a vesicle; depending on the concentration of the lipid, this biophysical interaction may result in the formation of <u>micelles</u>, <u>liposomes</u>, or <u>lipid bilayers</u>.
- 4. Micelles and bilayers form in the polar medium by a process known as the <u>hydrophobic effect</u>.
- 5. Lipids also form the basis of steroid hormones.
- 6. Polyprenols and their phosphorylated derivatives play important transport roles, in this case the transport of oligosaccharides <u>across</u> membranes.

Task 6. Match the English phrases on the left with their Ukrainian equivalents on the right:

Α	В
1. broadly defined	а) мати тенденцію групуватись
2. using an approach	b) ліпідний бішар
3. intracellular membranes	с) використовуючи підхід
4. ester linkage	d) реакції глікозилювання
5. glycosylation reactions	е) у широкому сенсі
6. to tend to cluster	f) естерний зв'язок
7. lipid bilayer	g) внутрішньоклітинні мембрани

<u>II. While-reading activities</u>

Task 7. Read the text and answer the questions:

- 1. What are the main biological functions of lipids?
- 2. How many building blocks do lipids consist of?
- 3. What do you know about "fat-soluble" vitamins?

Lipids

Lipids are a group of naturally occurring molecules that include fats, waxes, sterols, fat-soluble vitamins (such as vitamins A, D, E, and K), monoglycerides, diglycerides, triglycerides, phospholipids, and others. The main biological functions of lipids include storing energy, signaling, and acting as structural components of cell membranes. Lipids have applications in the cosmetic and food industries as well as in nanotechnology.

Lipids may be broadly defined as hydrophobic or amphiphilic small molecules; the amphiphilic nature of some lipids allows them to vesicles, multilamellar / unilamellar form structures such as liposomes, or membranes in an aqueous environment. Biological lipids originate entirely or in part from two distinct types of biochemical subunits or "building blocks": ketoacyl and isoprene groups. Using this approach, lipids may be divided into eight glycerolipids, categories: fatty acids, glycerophospholipids, saccharolipids, and polyketides (derived sphingolipids. from condensation of ketoacyl subunits); and sterol lipids and prenol lipids (derived from condensation of isoprene subunits).

Although the term "lipid" is sometimes used as a synonym for fats, fats are a subgroup of lipids called triglycerides. Although humans and other mammals use various biosynthetic pathways to both break down and synthesize lipids, some essential lipids cannot be made this way and must be obtained from the diet.

Eukaryotic cells are compartmentalized into membrane-bound organelles that carry out different biological functions. The glycerophospholipids are the main structural component of biological membranes, such as the cellular plasma membrane and the intracellular membranes of organelles. The glycerophospholipids are amphiphilic molecules (containing both hydrophobic and hydrophilic regions) that contain a glycerol core linked to two fatty acid derived "tails" by ester linkages and to one "head" group by a phosphate ester linkage. While glycerophospholipids are the major component of biological membranes, other non-glyceride lipid components such as sphingomyelin and sterols are also found in biological membranes.

A biological membrane is a form of lamellar phase lipid bilayer. The formation of lipid bilayers is an energetically preferred process when the glycerophospholipids described above are in an aqueous environment. This is known as the hydrophobic effect. In an aqueous system, the polar heads of lipids align towards the polar, aqueous environment, while the hydrophobic tails minimize their contact with water and tend to cluster together, forming a vesicle; depending on the concentration of the lipid, this biophysical interaction may result in the formation of micelles, liposomes, or lipid bilayers. Phase behavior is an area of study within biophysics and is the subject of current academic research. Micelles and bilayers form in the polar medium by a process known as the hydrophobic effect. When dissolving a lipophilic or amphiphilic substance in a polar environment, the polar molecules become more ordered around the dissolved lipophilic substance, since the polar molecules cannot form hydrogen bonds to the lipophilic areas of the amphiphile.

Triglycerides, stored in a dipose tissue, are a major form of energy storage both in animals and plants The complete oxidation of fatty acids provides high caloric content, about 9 kcal/g, compared with 4 kcal/g for the breakdown of carbohydrates and proteins. Migratory birds that must fly long distances without eating use stored energy of triglycerides to fuel their flights.

The "fat-soluble" vitamins (A, D, E and K) – which are isoprenebased lipids – are essential nutrients stored in the liver and fatty tissues, with a diverse range of functions. Polyprenols and their phosphorylated derivatives play important transport roles, in this case the transport of oligosaccharides across membranes. Polyprenol phosphate sugars and polyprenol diphosphate sugars function in extracytoplasmic glycosylation reactions, in extracellular polysaccharide biosynthesis and in eukaryotic protein N-glycosylation. Cardiolipids are a subclass of glycerophospholipids containing four acyl chains and three glycerol groups that are particularly abundant in the inner mitochondrial membrane. They are believed to activate enzymes involved with oxidative phosphorylation. Lipids also form the basis of steroid hormones.

(From: <u>https://www.coursehero.com/file/17951522/Lipids/</u>)

III. Post-reading activities

Task 8. Complete the following sentences using the text:

- 1) The main biological functions of lipids ______ storing energy, signaling, and acting as structural components of _____.
- 2) Lipids may be broadly defined as _____ or amphiphilic small molecules.
- 4) Although the term lipid is sometimes used as a ______ for fats, fats are a ______ of lipids called triglycerides.
- 5) The glycerophospholipids are the main structural component of ______, such as the cellular plasma membrane and the intracellular membranes _____.
- 6) Micelles and bilayers form in the _____ by a process known as the _____.
- 7) Triglycerides, stored in a_____, are a major form of energy storage both in _____ and plants.
- 8) Polyprenols and their _____ play important transport roles, in this case the transport of oligosaccharides _____ membranes.

Task 9. Read and analyze the definitions given in the text.

Task 10. Answer the questions about the text:

- 1) How many subtypes of lipids exist?
- 2) What examples of lipid application do you know?
- 3) Why is aggregation of lipids possible?
- 4) Can sphingomyelin be a source of energy?
- 5) What is the difference between hydrophobic and hydrophilic parts of a lipid molecule?
- 6) Where are triglycerides stored?
- 7) What is the role of cardiolipids?

Task 11. Are the following statements true or false? Say why:

- 1) Fats are a group of naturally occurring molecules that include lipids, waxes, sterols, fat-soluble vitamins, monoglycerides, diglycerides, triglycerides, phospholipids, and others.
- 2) A biological organelle is a form of lamellar phase lipid bilayer.

- 3) The term "lipid" is sometimes used as a synonym for fats.
- 4) Polyprenols and their phosphorylated derivatives play important transport roles, e.g. the transport of oligosaccharides across membranes.
- 5) The glycerophospholipids are amphiphilic molecules that contain a glycerol core linked to two fatty acid derived "head" by ester linkages and to one "tails" group by a phosphate ester linkage.
- 6) The formation of lipid bilayers is an energetically preferred process when the glycerophospholipids are in an aqueous environment.
- 7) Lipids have applications in the cosmetic and food industries as well as in nanotechnology.
- 8) Cardiolipids are a subclass of glycerophospholipids containing four acyl chains and three glycerol groups that are particularly abundant in the inner mitochondrial membrane.

Task 12. Make a list of all the chemistry terms, procedures, methods, and nomenclature you can find in the text. Check all the examples in your class.

IV. Focus on grammar and lexis

Task 13. Here are the answers to some questions about the text. Write the questions:

- 1) Lipids have applications in the cosmetic and food industries as well as in nanotechnology.
- 2) They are glycerophospholipids.
- 3) The major form of energy storage both in animals and plants are triglycerides.
- 4) They are believed to activate enzymes involved with oxidative phosphorylation.
- 5) They may be divided into eight categories: fatty acids, glycerolipids, glycerophospholipids, sphingolipids, saccharolipids, and polyketides; sterol lipids and prenol lipids.

Task 14. Put the words in the right order to make correct sentences:

- 1) of phase of study within biophysics and is the subject current is an area academic research behavior.
- 2) steroid also form the lipids of hormones basis.

- 3) provides high the caloric complete content, about 9 kcal/g oxidation of fatty acids.
- 4) membranes of organelles the are the main structural component cellular plasma of biological membranes, such as the membrane and the glycerophospholipids intracellular.
- 5) cell membranes the main biological functions, and acting as structural components of lipids include of storing energy, signaling.

Task 15. Correct the mistakes. There is one mistake in each of the following sentences. Find it and write the corrected sentences:

- 1) A biological organelles is a form of a lamellar phase lipid bilayer.
- 2) When dissolving a lipophilic or amphiphilic substance in a polar environment, the polar molecules becoming more ordered around the dissolve lipophilic substance,
- 3) Although the term lipids is sometimes use as a synonym for fats, fats are a subgroup of lipids called triglycerides.
- 4) Eukaryotic cells compartmentalized into membrane-bound organelle that carry out different biological functions.
- 5) The formation of lipid bilayer are an energetically preferred process when the glycerophospholipids are in an aqueous environment.

Task 16. Fill in the gaps with the suitable preposition:

- 1) Lipids are a group _____ naturally occurring molecules that include fats, waxes, sterols, fat-soluble vitamins (A, D, E, and K), monoglycerides, diglycerides, triglycerides, phospholipids, etc.
- 2) Phase behavior is an area _____ study _____ biophysics and it is the subject ____ current academic research.
- 3) Triglycerides, stored _____ a dipose tissue, are a major form _____ energy storage both _____ animals and plants.
- 4) Using this approach, lipids may be divided _____ eight categories.
- 5) Micelles and bilayers form a polar medium ____ a process known _____ the hydrophobic effect.

Task 17. Translate from Ukrainian into English:

 Ліпі́ди — це група органічних речовин, що входять до складу живих організмів і характеризуються нерозчинністю у воді та розчинністю в неполярних розчинниках.

- 2) Люди та тварини мають спеціальні біохімічні шляхи для біосинтезу та розщеплення ліпідів, проте деякі з цих речовин є незамінними і мусять надходити в організм із їжею.
- Сучасна номенклатура і класифікація ліпідів, що використовується в дослідженнях у галузі ліпідоміки, ґрунтується на поділі їх на вісім основних груп.
- 4) Ацилгліцериди це естери трьохатомного спирту гліцеролу та жирних кислот.
- 5) Основною групою структурних ліпідів є фосфоліпіди, які залежно від спирту, що входить до їх складу, поділяються на гліцерофосфоліпіди та сфінгофосфоліпіди.

Task 18. Match the words in A with their definitions in B:

Α	В
1) lamellar	a) an organic compound made by replacing the
[lə'melə] (adj.)	hydrogen of an acid by an alkyl or other organic group
2) isoprene	b) any of a number of organized or specialized
['aɪsə(ʊ)pri:n]	structures within a living cell
3) organelle	c) having a thin layer, membrane, or plate of tissue,
	especially in bone
4) spermaceti	d) a volatile liquid hydrocarbon obtained from
[spərmə'set 1] (n)	petroleum, whose molecule forms the basic structural
	unit of natural and synthetic rubbers, chem. formula:
	CH2=C(CH3)CH=CH2
5) malleable	e) of or relating to the immediate surroundings of
[ˈmælɪəbl]	something
6) solubilize	f) able to be hammered or pressed permanently out of
['sɒljʊbɪlaɪz]	shape without breaking or cracking (of metal etc.)
7) homologous	g) make (a substance) soluble or more soluble
[həˈmɔləgəs]	
8) immiscible	h) having the same functional group but differing in
[I'mIsIb(ə)l]	composition by a fixed group of atoms
9) ambient	i) a white waxy substance produced by the sperm
['æmb 1 ənt]	whale, formerly used in candles and ointments.
10) ester ['ɛstə]	j) not forming a homogeneous mixture when mixed

V. Final tasks

Task 19. Discuss the following ideas with your group-mates:

- 1. The role of lipids in living organisms.
- 2. The starting substances in biosynthesis of lipids.
- 3. The importance of the membrane in a living cell?

Task 20. Use the phrases given below to retell the text in your words:

Naturally occurring molecules, fats, waxes, sterols, fat-soluble monoglycerides, diglycerides, triglycerides, vitamins. phospholipids, storing structural components, energy, hydrophobic or amphiphilic small molecules, liposomes, "building blocks", saccharolipids, cellular plasma membrane, sphingomyelin, lipid bilayer, hydrophobic effect, dipose tissue, oxidative phosphorylation, steroid hormones.

VI. Individual reading: supplementary text

Task 21. Read the text and summaries it:

Wax

Waxes are a class of chemical compounds that are malleable near ambient temperatures. They are also a type of lipids. Characteristically, they melt at above 45°C (113°F) to give a low viscosity liquid. Waxes are insoluble in water but soluble in organic, non-polar solvents. All waxes are organic compounds, both synthetically and naturally occurring.

Waxes are organic compounds that characteristically consist of long alkyl chains. Natural waxes may contain esters of carboxylic acids and long chain alcohols or mixtures of substituted hydrocarbons, such as long chain fatty acids and primary alcohols. Synthetic waxes are long-chain hydrocarbons lacking functional groups.

Waxes are synthesized by many plants and animals. Those of animal origin typically consist of wax esters derived from a variety of carboxylic acids and fatty alcohols. In waxes of plant origin characteristic mixtures of unesterified hydrocarbons may predominate over esters. The composition depends not only on species, but also on geographic location of the organism. Because they are mixtures, naturally produced waxes are softer and melt at lower temperatures than the pure components. The most commonly known animal wax is beeswax, but other insects secrete waxes, too. A major component of the beeswax used in constructing honeycombs is ester myricyl palmitate which is an ester of triacontanol and palmitic acid. Its melting point is 62-65°C. Spermaceti occurs in large amounts in the head oil of the sperm whale. One of its main constituents is cetyl palmitate, another ester of a fatty acid and a fatty alcohol. Lanolin is a wax obtained from wool, consisting of esters of sterols.

Plants secrete waxes into and on the surface of their cuticles as a way to control evaporation, wettability and hydration. The epicuticular waxes of plants are mixtures of substituted long-chain aliphatic hydrocarbons, containing alkanes, alkyl esters, fatty acids, primary and secondary alcohols, diols, ketones, aldehydes. From the commercial perspective, the most important plant wax is Carnauba wax, a hard wax obtained from the Brazilian palm Copernicia prunifera. Containing the ester myricyl cerotate, it has many applications, such as confectionery and other food coatings, car and furniture polish, floss coating, surfboard wax, and other uses. Other more specialized vegetable waxes include candelilla wax and ouricury wax.

Although many natural waxes contain esters, paraffin waxes are hydrocarbons, mixtures of alkanes usually in a homologous series of chain lengths. These materials represent a significant fraction of petroleum. They are refined by vacuum distillation. Paraffin waxes are mixtures of saturated n- and iso- alkanes, naphthenes, and alkyl- and naphthene-substituted aromatic compounds. The degree of branching has an important influence on the properties. Millions of tons of paraffin waxes are produced annually. They are used in foods (such as chewing gum and cheese wrapping), in candles and cosmetics, as nonstick and waterproofing coatings and in polishes.

Waxes are mainly consumed industrially as components of complex formulations, often for coatings. The main use of polyethylene and polypropylene waxes is in the formulation of colourants for plastics. Waxes confer matting effects and wear resistance to paints. Polyethylene waxes are incorporated into inks in the form of dispersions to decrease friction. They are employed as release agents. They are also used as slip agents, e.g. in furniture, and corrosion resistance.

(From: <u>https://en.wikipedia.org/wiki/wax</u>).

VII. Additional texts

Did you know that liposomes have been used to improve the therapeutic index of new or established drugs by modifying drug absorption, reducing metabolism, prolonging biological half-life or reducing toxicity? To be a commercial product the liposome-drug formulation must have well-defined stability and a shelf life over a year.

Task 22: Read the text and make your questions to cover its content:

Liposome preparation methods

Lipids forming liposomes may be natural or synthetic, and liposome constituents are not exclusive of lipids; new generation liposomes can also be formed from polymers (sometimes referred to as polymersomes). Whether composed of natural or synthetic lipids or polymers, liposomes are biocompatible and biodegradable, which makes them suitable for biomedical research. Liposomes' ability to compartmentalize and solubilize both hydrophilic and hydrophobic materials, coupled with their biocompatibility and biodegradability, makes liposomes very attractive as drug delivery vehicles.

The manufactured liposome features are directly related to the preparation method. Although liposome formation may be spontaneous, often some mechanical agitation is required. In order to have control over the size and structure of the liposomes that are formed, increase the efficiency of entrapment of the desired molecules, and prevent subsequent leakage from the liposomes, different preparation methods have been devised.

There are a few parameters that should be considered during the method selection: 1) the physicochemical characteristics of the material to be entrapped and those of the liposomal ingredients, 2) the nature of the medium in which the liposomes are dispersed, 3) the effective concentration of the encapsulated material and its potential toxicity, 4) additional processes involved during application (delivery of the liposomes), 5) optimum size, polydispersity and shelf-life of the liposomes for the intended application and 6) batch-to-batch reproducibility and possibility of large-scale production of safe and efficient liposomal products.

Liposome size is a crucial parameter in determining the circulation half-life of liposomes in drug delivery. The amount of encapsulated drug is also related with the size and the number of bilayers of the prepared liposome. According to the desired formulation, different liposome preparation methods can be employed. The main difference in these methods is their approach to overcome the low solubility of lipids in water. Accordingly, these methods can be classified as mechanical agitation, solvent evaporation, solvent injection, and detergent solubilization.

In mechanical agitation method, lipids are directly solubilized in water upon application of high mechanical agitation, through the use of probe sonication, i.e. ultrasonic vibration to fragment the cells, macromolecules, and membranes. It is one of the simplest methods of liposome preparation, however, yields small liposomes that are highly unstable in terms of their size and suffers from the drawback that it is impossible to remove completely the risk of lipid degradation by contact with the hot probe, and contamination with titanium from the probe. Its advantage is the exclusion of use of organic solvents as described in the following methods. However, for drug delivery applications, liposomes prepared with mechanical agitation are not suitable due to their size instability and high leakage of encapsulated drugs.

Solvent evaporation method consists of four major steps; first is the solubilization of the lipid (and a hydrophobic compound) in an organic solvent; second is solvent evaporation; third is hydration with a buffer (and the hydrophilic compound) and if need the fourth often involves obtaining unilamellar liposomes from the obtained multilamellar ones.

In solvent injection method, lipids are first dissolved in an organic solvent and then brought into contact with the aqueous phase containing the materials to be encapsulated within the liposome. The lipids align themselves into a monolayer at the interface between the organic and aqueous phase which is an important step to form the bilayer of the liposome. There are three categories in solvent dispersion method including; (i) a miscible organic solvent with the aqueous phase, (ii) an immiscible organic solvent with the aqueous phase that is used in excess, and (iii) an immiscible organic solvent used in excess with the aqueous phase.

In surfactant (detergent) solubilization method, the phospholipids are brought into contact with the aqueous phase via the intermediary of surfactants. Phospholipid molecules associate with surfactants and form mixed micelles. The basic feature of this method is the removal of the surfactant from pre-formed mixed micelles containing phospholipids, whereupon unilamellar liposomes form spontaneously. However, removal of surfactants is carried out using techniques, such as dialysis and column chromatography, inevitably removes other small watersoluble molecules, making this method not very efficient in terms of percentage encapsulation values attainable for water soluble compounds. On the other hand, surfactant solubilization method has the ability to vary the size of the liposomes by precise control of the conditions of surfactant removal and to obtain liposomes of very high size homogeneity.

The transfer from laboratory to industry was very important for liposomes, as it is for any biotechnological discipline. The first liposomal drug delivery experiments in humans were carried out by freshly prepared liposomes but in order to be a commercial product the liposome-drug formulation must have well-defined stability and a shelf life over a year. Of the several preparation methods described in the literature, only a few of them have the potential to be used in the large scale liposome manufacturing. The crucial problem is the presence of organic solvent residues, pyrogen control, stability, sterility, size and size distribution as well as batch-to-batch reproducibility.

(From: https://www.intechopen.com/books/application-of-

<u>nanotechnology-in-drug-delivery/liposomes-as-potential-drug-carrier-</u> <u>systems-for-drug-delivery</u>).

Task 23. Analyze the text for the key phrases to be used in the following-up discussion. Write down the phrases in your exercise-book.

Task 24. Read the text again for more details and put 5-7 questions (wh-questions / open-end questions).

Task 25. Pair-work. Ask your partner the questions you have made up. Check if the answers are correct.

Task 26. Team-work. Divide into two teams and discuss the text during 5-7 minutes. Choose a presenter in each team to present the main ideas of the text in front of the class. Which of the teams presents best?

Unit 5

ASYMMETRIC SYNTHESIS

I. Pre-reading activities

Task 1. Discuss the following questions:

1) What do you know about asymmetric synthesis?

- 2) Do you know anything about asymmetric induction?
- 3) What is chirality?
- 4) What have you heard about diastereomers?
- 5) What kinds of compounds are called racemic?

Task 2. Pronounce the following international words and guess what they mean:

Asymmetric(al) [eIsI'metrIk((ə)l)]	Diastereomer [dıə'steriəmər]
Chirality [kaı'rælıtı]	Selectivity [sı,lɛ'ktıvıtı]
Induction [ın'd∧k∫ən]	Catalysis [kə'tæləsıs]
Racemic [rə'si:mɪk, rə'sɛmɪk]	Specificity [spesə'fIsətI]
Reaction [rı'æk∫ən]	Ligand ['ligənd]
Enantiomer [I'nantIə(ʊ)mə, ε-]	Hydrogenation [haɪdrədʒə'neɪ∫(ə)n]
Synthesis ['sɪnθɪsɪs]	Exploit [Ik'spl) It, Ek-]

Task 3. Match the synonyms:

1. Render	1) supplementary
2. Auxiliary	2) utilize
3. Promote	3) combination
4. Exploit	4) level
5. Encounter	5) provide
6. Scale	6) experience / be subjected to
7. Undergo	7) load
8. Weight	8) support
9. Synthesis	9) meet

Task 4. Match the opposites:

- 1. Intramolecularly
- 2. Specific
- 3. Versatile
- 4. Consecutive

9) immune response

- a) indefinite
- b) alternate
- c) inappropriate
- d) limited
- 5. Well-suited e) intermolecularly

Task 5. Guess from the context what the underlined words mean:

- 1) Certain expressions in other languages cannot be properly <u>rendered</u> into English.
- 2) Hackers often try breaking into corporate systems for fun and to <u>exploit</u> the vulnerabilities of wireless networks.
- 3) Every year thousands <u>undergo</u> this operation.
- 4) The proposed film material with a wide range of electrophysical properties is intended to be used in microelectronics and radio engineering versatile as constructional material.
- 5) The identity of tumor and vaccine antigens secures the <u>specificity</u> of the anti-tumor immune response induced with the vaccine.
- 6) China has been actively <u>promoting</u> the international nuclear disarmament process.
- 7) You must get a doctor's certificate if you're off work sick for more than three <u>consecutive</u> days.

equivalents on the right.	
1) reaction sequence	а) асиметрична індукція
2) the field of pharmaceuticals	b) різні енантіомери
3) asymmetric induction	с) часто зустрічається
4) various enantiomers	d синтез промислового
	масштабу
5) commonly encountered	е) галузь медичних препаратів
6) undirected process	f) імунна відповідь
7) industrial scale synthesis	g) послідовність реакцій
8) undergo an operation	h) неспрямований процес

Task 6. Match the English phrases on the left with their Ukrainian equivalents on the right:

і) перенести операцію

<u>II. While-reading activities</u>

Task 7. Read the text and answer the questions:

- 1) What can you say about chirality?
- 2) What is the difference between enantiomer and diastereomer?
- 3) What are the types of selectivity in organic reactions?

Asymmetric Synthesis

Asymmetric synthesis, also called chiral synthesis or enantioselective synthesis, is defined by IUPAC (International Union of Pure and Applied Chemistry) as: a chemical reaction (or reaction sequence) in which one or more new elements of chirality are formed in a substrate molecule and which produces the stereoisomeric (enantiomeric or diastereoisomeric) products in unequal amounts. To put it more simply: it is the synthesis of a compound by a method that favors the formation of a specific enantiomer or diastereomer.

Enantioselective synthesis is a key process in modern chemistry and is particularly important in the field of pharmaceuticals, as the different enantiomers or diastereomers of a molecule often have different biological activity.

Many of the building blocks of biological systems, such as sugars and amino acids, are produced exclusively as one enantiomer. As a result of this, living systems possess a high degree of chemical chirality and will often react differently with the various enantiomers of a given compound. Examples of this selectivity include:

• Flavour: the artificial sweetener aspartame has two enantiomers. L-aspartame tastes sweet, yet D-aspartame is tasteless.

• Odor: R-(–)-carvone smells like spearmint yet S-(+)-carvone, smells like caraway.

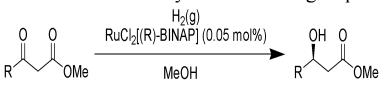
• Drug effectiveness: the antidepressant drug Citalopram is sold as a racemic mixture. However, studies have shown that only the (S)-(+) enantiomer is responsible for the drug's beneficial effects.

• Drug safety: D-penicillamine is used in chelation therapy and for the treatment of rheumatoid arthritis. However Lpenicillamine is toxic as it inhibits the action of pyridoxine, an essential B vitamin.

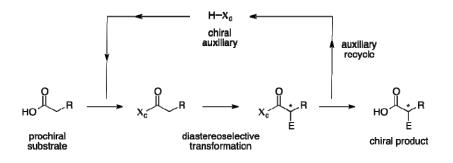
As such enantioselective synthesis is of great importance, but it can also be difficult to achieve. Enantiomers possess identical enthalpies and entropies, and hence should be produced in equal amounts by an undirected process - leading to a racemic mixture. The solution is to introduce a chiral feature which will promote the formation of one enantiomer over another via interactions at the transition state. This is known as asymmetric induction and can involve chiral features in the substrate, reagent, catalyst or environment and works by making the activation energy required to form one enantiomer lower than that of the opposing enantiomer.

Asymmetric induction can occur intramolecularly when given a chiral starting material. This behaviour can be exploited, especially when the goal is to make several consecutive chiral centres to give a specific enantiomer or a specific diastereomer. An aldol reaction, for example, is inherently diastereoselective; if the aldehyde is enantiopure, the resulting aldol adduct is diastereomerically and enantiomerically pure.

Enantioselective catalysis (known traditionally as asymmetric catalysis) refers to the use of chiral coordination complexes as catalysts. This approach is very commonly encountered, as it is effective for a broader range of transformations than any other method of enantioselective synthesis. The catalysts are typically rendered chiral by using chiral ligands, however it is also possible to generate chiral-at-metal complexes using simpler achiral ligands. Most enantioselective catalysts are effective at low concentrations making them well suited to industrial scale synthesis, so even exotic and expensive catalysts can be used affordably. Perhaps the most versatile example of enantioselective synthesis is asymmetric hydrogenation, which is able to reduce a wide variety of functional groups.



A chiral auxiliary is an organic compound which couples to the starting material to form new compound which can then undergo enantioselective reactions via intramolecular asymmetric induction. At the end of the reaction the auxiliary is removed, under conditions that will not cause racemization of the product. It is typically then recovered for future use.



Biocatalysis makes use of biological compounds, ranging from isolated enzymes to living cells, to perform chemical transformations. The advantages of these reagents include very high eneantiomeric excess and reagent specificity, as well as mild operating conditions and low environmental impact. Biocatalysts are more commonly used in industry than in academic research, for example in the production of statins. The high reagent specificity can be a problem, however, as it often requires that a wide range of biocatalysts be screened before an effective reagent is found.

(From: https://en.wikipedia.org/wiki/Enantioselective_synthesis)

III. Post-reading activities

Task 8. Complete the following sentences using the text:

- 1) _____ is the synthesis of a compound by a method that favors the formation of a specific _____ or ____.
- 2) _____ possess a high degree of chemical ____
- 3) Enantiomers possess identical _____ and ____
- 4) The solution is to introduce a chiral _____ which will _____ the formation of one _____.
- 5) At the end of the reaction the auxiliary is _____, under conditions that will not cause ____ of the product.
- 6) Biocatalysts are more commonly used in _____ than in _____.

Task 9. Read and analyze all the definitions given in the text.

Task 10. Answer the questions about the text:

- 1) What is an enantiomer?
- 2) What are the examples of selectivity between enantiomers in living organisms?
- 3) What is racemic mixture?
- 4) What is asymmetric induction?
- 5) How does asymmetric induction work?

- 6) How can you describe enantioselective catalysis?
- 7) What are the concepts of chiral auxiliaries?

Task 11. Are the following statements true or false? Say why:

- 1) Different enantiomers or diastereomers of a molecule have the same biological activity.
- 2) Introduction of a chiral feature will promote the formation of one enantiomer over another.
- 3) Catalysts are typically rendered chiral by using chiral ligands.
- 4) Enantiomers possess different enthalpies and entropies.
- 5) Enantioselective catalysts are effective at high concentrations making them unsuitable for industrial scale synthesis.
- 6) Asymmetric induction can occur intramolecularly when given a chiral starting material.

IV. Focus on grammar and lexis

Task 12. Here are the answers to some questions about the text. Write the questions:

- 1) They are different odour, flavour, drug effectiveness and safety for different stereoisomers.
- 2) The most versatile example of enantioselective synthesis is asymmetric hydrogenation.
- 3) The advantages include very high eneantiomeric excess and reagent specificity.
- 4) Because many of the building blocks of biological systems, such as sugars and amino acids, are produced exclusively as one enantiomer.

Task 13. Put the words in the right order to make correct sentences:

- 1) in a key chemistry enantioselective is process modern synthesis.
- 2) catalysts use refers complexes to catalysis coordination the chiral as of asymmetric.
- 3) when starting intramolecularly asymmetric given occur a chiral can induction material.
- 4) specificity be reagent a problem high can.
- 5) synthesis example enantioselective the asymmetric versatile is most of hydrogenation

Task 14. Correct the mistakes. There is one mistake in each of the following sentences. Find it and write the corrected sentences:

- 1) In the result of this, living systems possess a high degree of chemical chirality
- 2) A chiral auxiliary is an organic compound which couple to the starting material.
- 3) This approach is very commonly encounter.
- 4) Catalysts are effective by low concentrations.
- 5) It is typically then recovered for future using.

Task 15. Fill in the gaps with the suitable prepositions:

- 1) Many of the building blocks of biological systems are produced exclusively ____ one enantiomer.
- 2) Studies have shown that only the (S)-enantiomer is responsible _____ the drug's beneficial effects.
- 3) Biocatalysis makes use <u>biological compounds</u>.
- 4) Most enantioselective catalysts are highly effective ____ low concentrations.
- 5) L-penicillamine is toxic _____ it inhibits the action of pyridoxine.

Task 16. Translate from Ukrainian into English:

- Асиметричний синтез це хімічна реакція, результатом якої є утворення в молекулі субстрату нового елемента хіральності, у якому стереоізомери утворюються в нерівних кількостях.
- 2) Енантіомери мають однакові ентальпії та ентропії і, таким чином, у неспрямованому процесі вони повинні утворюватись у рівних кількостях.
- 3) Переваги біокаталізаторів включають високу специфічність та енантіомерні надлишки, а також сприятливі умови використання і низький вплив на навколишнє середовище.
- 4) Наприкінці реакції допоміжна група видаляється в умовах, які не спричиняють рацемізації продукту.
- 5) Енантіоселективний каталіз є ефективним для більшої кількості різноманітних перетворень, ніж будь-який інший метод асиметричного синтезу.
- 6) Асиметрична індукція може відбутися внутрішньомолекулярно, коли наявна хіральна вихідна речовина.

V. Final tasks

Task 17. Discuss the following ideas with your group-mates:

- 1. Is it possible to produce enantiomerically pure compounds without using asymmetric synthesis?
- 2. Are living systems chiral? What are the examples of selectivity in living organisms?
- 3. What is asymmetric induction? How does it work?
- 4. What are the advantages and disadvantages of asymmetric catalysis for industrial scale synthesis?
- 5. What is chiral auxiliary?
- 6. What are the advantages of biocatalysis?

Task 18. Use the phrases below to retell the text in your own words:

Asymmetric synthesis, chemical reaction, new elements of chirality, stereoisomeric products, building blocks of biological systems, react differently with the various enantiomers, identical enthalpies and entropies, racemic mixture, asymmetric induction, chiral features, chiral starting material, chiral ligands.

VI. Individual reading: supplementary text

Task 19: Read the text and answer the following questions:

- 1. What is the main feature of organocatalysis?
- 2. What advantages does organocatalysis offer?
- 3. Can organocatalysis be used for asymmetric synthesis? Why?

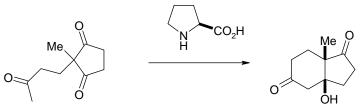
Organocatalysis

In organic chemistry, the term "organocatalysis" refers to a form of catalysis, whereby the rate of a chemical reaction is increased by an organic catalyst referred to as an "organocatalyst" consisting of carbon, hydrogen, sulfur and other nonmetal elements found in organic compounds. Because of their similarity in composition and description, they are often mistaken as a misnomer for enzymes due to their comparable effects on reaction rates and forms of catalysis involved.

Organocatalysts which display secondary amine functionality can be described as performing either enamine catalysis (by forming catalytic quantities of an active enamine nucleophile) or iminium catalysis (by forming catalytic quantities of an activated iminium electrophile). This mechanism is typical for covalent organocatalysis. Covalent binding of substrate normally requires high catalyst loading (for proline-catalysis typically 20-30 mol%). Noncovalent interactions such as hydrogen-bonding facilitates low catalyst loadings (down to 0.001 mol%).

Organocatalysis offers several advantages. There is no need for metal-based catalysis thus making a contribution to green chemistry. In this context, simple organic acids have been used as catalyst for the modification of cellulose in water on multi-ton scale. When the organocatalyst is chiral an avenue is opened to asymmetric catalysis, for example the use of proline in aldol reactions is an example of chirality and green chemistry.

Regular achiral organocatalysts are based on nitrogen such as piperidine used in the Knoevenagel condensation. DMAP used in esterfications and DABCO used in the Baylis-Hillman reaction. Thiazolium salts are employed in the Stetter reaction. These catalysts a long history but current interest and reactions have in organocatalysis is focused on asymmetric catalysis with chiral catalysts, called asymmetric organocatalysis or enantioselective organocatalysis. A pioneering reaction developed in the 1970s is called the Hajos-Parrish-Eder-Sauer-Wiechert reaction. Between 1968 and 1997, there were only a few reports of the use of small organic molecules as catalysts for asymmetric reactions (the Hajos-Parrish reaction probably being the most famous), but these chemical studies were viewed more as unique chemical reactions than as integral parts of a larger, interconnected field.



In this reaction, naturally occurring chiral proline is the chiral catalyst in an Aldol reaction. The starting material is an achiral triketone and it requires just 3% of proline to obtain the reaction product, a ketol in 93% enantiomeric excess. This is the first example of an amino acid-catalyzed asymmetric aldol reaction.

Many chiral organocatalysts are an adaptation of chiral ligands (which together with a metal center also catalyze asymmetric reactions) and both concepts overlap to some degree.

(From: <u>https://en.wikipedia.org/wiki/Organocatalysis</u>)

VII. Additional texts

Did you know that if two molecules are stereoisomers (same molecular formula, same connectivity, different arrangement of atoms in space) but are *not* enantiomers, then they are diastereomers by default? In practical terms, this means that at least one – but not all – of the chiral centers are opposite in a pair of diastereomers. By definition, two molecules that are diastereomers are *not* mirror images of each other.

Task 21: Read the text and make your questions to cover its content:

Chirality and Stereoisomers

Stereoisomers are isomers that differ in spatial arrangement of atoms, rather than order of atomic connectivity. One of the most interesting types of isomer is the mirror-image stereoisomer, a nonsuperimposable set of two molecules that are mirror image of one another. The existence of these molecules is determined by the concept known as chirality.

Organic compounds, molecules created around a chain of carbon atom (more commonly known as carbon backbone), play an essential role in the chemistry of life. These molecules derive their importance from the energy they carry, mainly in a form of potential energy between atomic molecules. Since such potential force can be widely affected due to changes in atomic placement, it is important to understand the concept of an isomer, a molecule sharing the same atomic make up as another but differing in structural arrangements.

The concepts of steroisomerism and chirality command great deal of importance in modern organic chemistry, as these ideas help to understand the physical and theoretical reasons behind the formation and structures of numerous organic molecules, the main reason behind the energy embedded in these essential chemicals. In contrast to more well-known constitutional isomerism, which develops isotopic compounds simply by different atomic connectivity, stereoisomerism generally maintains equal atomic connections and orders of building blocks as well as having same numbers of atoms and types of elements. What, then, makes stereoisomers so unique? To answer this question, the learner must be able to think and imagine in not just twodimensional images, but also three-dimensional space. This is due to the fact that stereoisomers are isomers because their atoms are different from others in terms of spatial arrangement.

First and foremost, one must understand the concept of spatial arrangement in order to understand stereoisomerism and chirality. Spatial arrangement of atoms concern how different atomic particles and molecules are situated about in the space around the organic compound, namely its carbon chain. In this sense, spatial arrangement of an organic molecule is different from another if an atom is shifted in any three-dimensional direction by even one degree. This opens up a very broad possibility of different molecules, each with their unique placement of atoms in three-dimensional space.

Stereoisomers, as mentioned above, contain different types of isomers within themselves, each with distinct characteristics that further separate each other as different chemical entities having different properties.

mirror-image, enantiomer the An is essential nonsuperimposable type of stereoisomer. Note that even if one were to flip over the left molecule over to the right, the atomic spatial arrangement will not be equal. This is equivalent to the left hand right hand relationship, and is aptly referred to as 'handedness' in molecules. This can be somewhat counter-intuitive, so you should try the 'hand' example. Place both palm facing up, and hands next to each other. Now flip either side over to the other. One hand should be showing the back of the hand, while the other one is showing the palm. They are not same and non-superimposable. This is where the concept of chirality comes in as one of the most essential and defining idea of stereoisomerism.

Chirality essentially means 'mirror-image, non-superimposable molecules', and to say that a molecule is chiral is to say that its mirror image (it must have one) is not the same as it self. Whether a molecule is chiral or achiral depends upon a certain set of overlapping conditions. The distinct characteristic of the achiral molecule is that it possesses two atoms of the same element. In theory and reality, if one were to create a plane that runs through the other two atoms, they will be able to create what is known as bisecting plane: The images on either side of the plane is the same as the other. In this case, the molecule is considered 'achiral'. In other words, to distinguish a chiral molecule from an achiral molecule, one must search for the existence of the bisecting plane in a molecule. All chiral molecules are deprived of bisecting plane, whether simple or complex.

As a universal rule, no molecule with different surrounding atoms is achiral. Chirality is a simple but essential idea to support the concept of stereoisomerism, being used to explain one type of its kind. The chemical properties of the chiral molecule differ from its mirror image, and in this lies the significance of chilarity in relation to modern organic chemistry.

The definition of diastereomers is simple: if two molecules are stereoisomers (same molecular formula, same connectivity, different arrangement of atoms in space) but are *not* enantiomers, then they are diastereomers by default. In practical terms, this means that at least one – but not all – of the chiral centers is opposite in a pair of diastereomers. By definition, two molecules that are diastereomers are *not* mirror images of each other.

(From: <u>https://chem.libretexts.org/Core/Organic_Chemistry/Chirality/</u> Chirality and Stereoisomers)

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Task 23. Read the text again for more details and put 5-7 questions (wh-questions / open-end questions).

Task 24. Pair-work. Ask your partner the questions you have made up. Check if the answers are correct.

Task 25. Team-work. Divide into two teams and discuss the text during 5-7 minutes. Choose a presenter in each team to present the main ideas of the text in front of the class. Which of the teams presents best?

Unit 6

NANOPORES

I. Pre-reading activities

Task 1. Discuss the following questions:

- 1) What do you know about nanotechnologies? What nanomaterials could be used in everyday life?
- 2) Have you ever tasted very salty water, for example from the Dead Sea? Can you quench your thirst with salty water?
- 3) What methods of water filtration do you know? Which of them do you use at home? Why?

Task 2. Pronounce the following international words after your treacher and guess what they mean:

nanopore (n)	polysaccharide
membrane	dioxide
crisis	collaboration
osmosis	functionalize
efficient	protein
filtration	contamination

Task 3. Match the synonyms:

1) issue	a) purification
2) rebuttal	b) blockage
3) withstand	c) pollute
4) filtration	d) resist, endure
5) film	e) contradiction
6) clogging	f) membrane
7) contaminate	g) problem

Task 4. Match the opposites:

1. foul (v)	a) mildly
2. complex	b) pour (v)
3. dramatically	c) put in
4. sought-after	d) evident
5. trickle (v)	e) unpopular
6. remove	f) purify (v)

Task 5. Guess from the context what the underlined words mean:

- 1) The optical and electronic properties of nanomaterials which depend on their size and shape can <u>be tuned</u> via synthetic techniques.
- 2) Nanomaterials research takes a materials science-based approach to nanotechnology, <u>leveraging advances</u> in materials metrology and synthesis which have been developed in support of <u>microfabrication</u> research.
- 3) In general, boilogical membranes are <u>impermeable</u> to large and polar molecules, such as ions, proteins, and polysaccharides, while being <u>permeable</u> to non-polar and/or hydrophobic molecules like lipids as well as to small molecules like oxygen, carbon dioxide, nitrogen, and nitric oxide.
- 4) <u>Reverse osmosis</u> is a separation process that uses pressure to force a solvent through <u>a semi-permeable membrane</u> that <u>retains</u> the solute on one side and allows the pure solvent to pass to the other side, forcing it from a region of <u>high solute concentration</u> through a membrane to a region of low solute concentration by applying a pressure in excess of the osmotic pressure.

Task 6. Match the English phrases on the left with their Ukrainian equivalents on the right:

1) osmotic pressure	а) потік іонного струму
2) to move by diffusion	b) мати успіх
3) down the concentration gradient	с) рухатися за рахунок дифузії
4) single-layer sheets	d) осмотичний тиск
5) to make good strides in	е) одношарові пластини
6) pore-forming proteins	f) по градієнту концентрації
7) the flow of ionic current	g) пороформуючі білки

<u>II. While-reading activities</u>

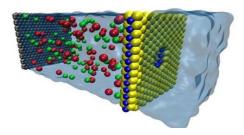
Task 7. Read the article and answer the questions:

- 1) How did the Illinois team discover that MoS₂ shows great efficiency in filtering water?
- 2) What are the drawbacks of reverse osmosis?
- 3) What chemical substances are used to filter water?
- 4) How can the water crisis be solved?
- 5) What are the benefits of the MoS_2 membrane?

MoS₂ Nanopores for Desalination

University of Illinois engineers have found an energy-efficient material for removing salt from seawater.

The material, a nanometer-thick sheet of molybdenum disulfide (MoS_2) riddled with tiny holes called nanopores,



is specially designed to let high volumes of water through but keep salt and other contaminates out, a process called desalination. In a study published in the journal Nature Communications, the Illinois team modeled various thin-film membranes and found that MoS_2 showed the greatest efficiency, filtering through up to 70 percent more water than graphene membranes.

"Even though we have a lot of water on this planet, there is very little that is drinkable," said study leader Narayana Aluru, a professor of mechanical science and engineering at University of Illinois. "If we could find a low-cost, efficient way to purify sea water, we would be making good strides in solving the water crisis".

"Finding materials for efficient desalination has been a big issue, and I think this work lays the foundation for next-generation materials. These materials are efficient in terms of energy usage and fouling, which are issues that have plagued desalination technology for a long time," said Aluru, who also is affiliated with the Beckman Institute for Advanced Science and Technology at the University of Illinois.

Most available desalination technologies rely on a process called reverse osmosis to push seawater through a thin plastic membrane to make fresh water. The membrane has holes in it small enough to not let salt or dirt through, but large enough to let water through. They are very good at filtering out salt, but yield only a trickle of fresh water. Although thin to the eye, these membranes are still relatively thick for filtering on the molecular level, so a lot of pressure has to be applied to push the water through.

"Reverse osmosis is a very expensive process," Aluru said. "It's very energy intensive. A lot of power is required to do this process, and it's not very efficient. In addition, the membranes fail because of clogging. So we'd like to make it cheaper and make the membranes more efficient so they don't fail as often. We also don't want to have to use a lot of pressure to get a high flow rate of water."

Aluru's group found that a single-layer sheet of MoS_2 outperformed its competitors thanks to a combination of thinness, pore geometry and chemical properties.

"MoS₂ has inherent advantages in that the molybdenum in the center attracts water, then the sulfur on the other side pushes it away, so we have much higher rate of water going through the pore," said graduate student Mohammad Heiranian, the first author of the study. "It's inherent in the chemistry of MoS_2 and the geometry of the pore, so we don't have to functionalize the pore, which is a very complex process with graphene."

In addition to the chemical properties, the single-layer sheets of MoS_2 have the advantages of thinness, requiring much less energy, which in turn dramatically reduces operating costs. MoS_2 also is a robust material, so even such a thin sheet is able to withstand the necessary pressures and water volumes.

The Illinois researchers are establishing collaborations to experimentally test MoS_2 for water desalination and to test its rate of fouling, or clogging of the pores, a major problem for plastic membranes. MoS_2 is a relatively new material, but the researchers believe that manufacturing techniques will improve as its high performance becomes more sought-after for various applications. Nanotechnology could play a great role in reducing the cost of desalination plants and making them energy efficient.

(From: <u>https://news.illinois.edu/blog/view/6367/276449</u>)

<u>III. Post-reading activities</u>

Task 8. Complete the following sentences using the text:

- 1) MoS₂ has inherent advantages in that the molybdenum in the center _____ water, then the sulfur on the other side _____, so we have much higher rate of water going through the pore.
- 2) The material, a nanometer-thick sheet of molybdenum disulfide (MoS₂) _____ with tiny holes called nanopores, is specially designed to let high volumes of water through but keep ______ out, a process called desalination.
- 3) It's inherent in the chemistry of MoS₂ and _____ of the pore, so we don't have to _____ the pore, which is a very complex process with graphene.
- 4) The membrane has holes in it _____ to not let salt or dirt through, but _____ to let water through.

Task 9. Read and analyze all the definitions given in the text.

Task 10. Are the following statements about the text true or false? Say why?

- 1) Most available desalination technologies rely on the process called osmosis.
- 2) The single-layer sheets of MoS_2 have the advantages of thickness, requiring much less energy, which, in turn, dramatically reduces operating costs.
- 3) The study leader Narayana Aluru is a professor of mechanical science and engineering at the University of Illinois.

IV. Focus on grammar and lexis

Task 11. Here are the answers to some questions about the text. Write the questions:

- 1) Because of the chemistry of MoS_2 and the geometry of the pore this is not needed.
- 2) This will reduce the operating costs.
- 3) They have the advantages of thinness, which requirs much less energy.

4) The molybdenum in the center attracts water, then the sulfur on the other side pushes it away.

Task 12. Put the words in the right order (the first and the last words are underlined):

- 1) we find a <u>crisis</u> could way to we sea water, would be purify making strides <u>If</u> good in solving the efficient water.
- 2) lot of is very required \underline{A} to it's do this process, power and not <u>efficient</u>.
- 3) <u>Even</u> this that there a of water on planet, is very we little lot is <u>drinkable</u> have though.
- Task F3n Ging neathernistorken Theredisannanistorkevin beech a orgenserie, and I think this work lays the foundation for next-generation materials.
 - 2) MoS_2 is a relatively new material, but the researchers believe that manufacturing techniques will improve as it's high performance becomes more sought-after for various applications.
 - 3) The membran has holes in it small enough to not let salt or dirt through, but large enough to let water through.

Task 14. Fill in the gaps with a suitable preposition:

- 1) Most available desalination technologies rely ____ a process called reverse osmosis to push seawater _____ a thin plastic membrane to make fresh water.
- 2) These materials are efficient in terms _____ energy usage and fouling, which are issues that have plagued desalination technology _____ a long time.
- 3) The Illinois researchers are establishing collaborations to experimentally test MoS₂ water desalination and to test its rate fouling, or clogging the pores, a major problem for plastic membranes.

Task 15. Translate into English:

1) Нанотехнології як перспективний напрямок природничих наук найближчим часом забезпечать людство революційними матеріалами нового покоління.

- Фільтри з сульфіду молібдену мають більше переваг порівняно з іншими відомими системами зворотного осмосу.
- 3) Однак говорити про стовідсоткове застосування молібденсульфідних фільтрів зарано, бо вони мають бути протестовані на швидкість забивання пор.
- 4) Молібденовий фільтр на 70% ефективніший, ніж графеновий, адже відомо, що основним недоліком графену є його взаємодії з водою та розчиненими в ній речовинами.
- 5) Дослідники вважають, що після певних технічних модифікацій фільтр знайде своє застосування у різноманітних сферах людського життя.

V. Final tasks

Task 16. Discuss the following ideas with your group-mates:

- 1) What do you know the procedure of getting funds for scientific research in the USA and Europe?
- 2) Do you believe that MoS_2 will be marketed successfully? Why?
- 3) How do you understand poet Samuel Taylor Coleridge's words: "Water, water, everywhere, nor any drop to drink?"
- 4) Do you know any other ways of water desalination? What do you know about Bear Grylls's recommendations?

Task 17. Use the phrases below to retell the text in your own words:

To remove salt from seawater nanometer-thick sheet of molybdenum disulfide nanopores materials for efficient desalination reverse osmosis disadvantages of common filtration systems inherent advantages of MoS_2 testing of MoS_2

VI. Individual reading: supplementary text

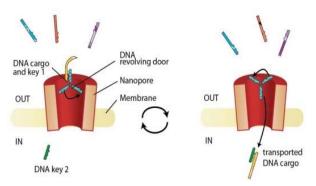
Task 18: Read the text and answer the following questions:

1. What is the name of the membrane proteins that act as specific doorways for the trafficking of ions and nutrients?

- 2. Do you know how these proteins actually act?
- 3. Have you got enough information from the text to understand what was actually done? Make your predictions and describe in detail the mechanism of DNA-assisted membrane transport.
- 4. What other opportunities of these nanopores can you see?
- 5. How can people apply this direct molecule transport?

Nanopore opens new cellular doorway for drug transport

A living cell is built with barriers to keep things out - and researchers are constantly trying to find ways smuggle to molecules in. Professor Giovanni Maglia (Biochemistry, Molecular Structural and Biology, KU his team Leuven) and have



engineered a biological nanopore that acts as a selective revolving door through a cell's lipid membrane. The nanopore could potentially be used in gene therapy and targeted drug delivery.

All living cells are enclosed by a lipid membrane that separates the interior of the cell from the outside environment. The influx of molecules through the cell membrane is tightly regulated by membrane proteins that act as specific doorways for the trafficking of ions and nutrients. Membrane proteins can also be used by cells as weapons. Such proteins attack a cell by making holes – nanopores – in 'enemy' cell membranes. Ions and molecules leak from the holes, eventually causing cell death.

Researchers are now trying to use nanopores to smuggle DNA or proteins across membranes. Once inside a cell, the DNA molecule could re-programme the cell for a particular action. Professor Maglia explains: "We are now able to engineer biological nanopores, but the difficult part is to precisely control the passage of molecules through the nanopores' doorways. We do not want the nanopore to let everything in. Rather, we want to limit entry to specific genetic information in specific cells."

Professor Maglia and his team succeeded in engineering a nanopore that works like a revolving door for DNA molecules. "We have introduced a selective DNA revolving door atop of the nanopore.

Specific DNA keys in solution hybridise to the DNA door and are transported across the nanopore. A second DNA key on the other side of the nanopore then releases the desired genetic information. A new cycle can then begin with another piece of DNA – as long as it has the correct key. In this way, the nanopore acts simultaneously as a filter and a conveyor belt."

"In other words, we have engineered a selective transport system that can be used in the future to deliver medication into the cell. This could be of particular use in gene therapy, which involves introducing genetic material into degenerated cells in order to disable or reprogramme them. It could also be used in targeted drug delivery, which involves administering medication directly into the cell. The possibilities are promising."

(From: <u>https://nieuws.kuleuven.be/en/content/2013/nanopore-opens-new-cellular-doorway-for-drug-transport</u>)

Task 19: Write a short summary of the text.

VII. Additional texts

Did you know that by nanopore sequencing methods, a single molecule of DNA or RNA can be sequenced with no need for polymerase chain reaction amplification or chemical labeling of the sample?

Task 20: Read the text and put your questions to cover its content:

Nanopore Sequencing

Nanopore sequencing is a fourth generation approach used in the sequencing of biopolymers – specifically, polynucleotides in the form of DNA or RNA.

Using nanopore sequencing, a single molecule of DNA or RNA can be sequenced without the need for PCR (polymerase chain reaction) amplification or chemical labeling of the sample. At least one of these afore-mentioned steps is necessary in the procedure of any previously developed sequencing approach. Nanopore sequencing has the potential to offer relatively low-cost genotyping, high mobility for testing, and rapid processing of samples with the ability to display results in real time. Publications on the method outline its use in rapid identification of viral pathogens, monitoring ebola, environmental monitoring, food safety monitoring, human genome sequencing, plant genome sequencing, monitoring of antibiotic resistance, haplotyping[,] and other applications.

What are the principles for detection and base identification? Nanopore sequencing uses electrophoresis to transport an unknown sample through an orifice of diameter 10^{-9} meters, in magnitude. A nanopore system always contains an electrolytic solution – when a constant electric field is applied, an electric current can be observed in the system. The magnitude of the electric current density across a nanopore surface depends on the nanopore's dimensions and the composition of DNA or RNA that is occupying the nanopore. Sequencing is made possible because, when close enough to nanopores, samples cause characteristic changes in electric current density across nanopore surfaces. The total charge flowing through a nanopore channel is equal to the surface integral of electric current density flux across the nanopore unit normal surfaces between times t₁ and t₂.

There are several types of sequencing, such as: biological, alpha hemolysin, MspA, solid state, tunneling current, and fluorescence.

nanopore sequencing relies Biological on the use of transmembrane proteins, called porins, which are embedded in lipid membranes so as to create size-dependent porous surfaces - with scale across "holes" distributed membranes. nanometer the Sufficiently low translocation velocity can be attained through the incorporation of various proteins that facilitate the movement of DNA or RNA through the pores of the lipid membranes.

Alpha hemolysin (α HL) is a nanopore from bacteria that causes lysis of red blood cells. Studies have shown that all four bases can be identified using ionic current measured across the α HL pore. The structure of α HL is advantageous to identify specific bases moving through the pore. The α HL pore is ~10 nm long, with two distinct 5 nm sections. The upper section consists of a larger, vestibule-like structure and the lower section consists of three possible recognition sites (R1, R2, R3), and is able to discriminate between each base.

There has been proved the ability of α HL to detect nucleotides at two separate sites in the lower half of the pore. The R1 and R2 sites enable each base to be monitored twice as it moves through the pore, creating 16 different measurable ionic current values instead of 4.

<u>Mycobacterium smegmatis porin A</u> (MspA) is the second biological nanopore currently being investigated for DNA sequencing.

The MspA pore has been identified as a potential improvement over α HL due to a more favorable structure. The pore is described as a goblet with a thick rim and a diameter of 1.2 nm at the bottom of the pore. A natural MspA, while favorable for DNA sequencing because of shape and diameter, has a negative core that prohibits single stranded DNA (ssDNA) translocation. The natural nanopore can be modified to improve translocation by replacing three negatively charged aspartic acids with neutral asparagines.

<u>The electric current detection</u> of nucleotides across the membrane has been shown to be tenfold more specific than α HL for identifying bases. Utilizing this improved specificity, a group at the University of Washington has proposed using double stranded DNA (dsDNA) between each single stranded molecule to hold the base in the reading section of the pore. The dsDNA would halt the base in the correct section of the pore and enable identification of the nucleotide.

Solid state nanopore sequencing approaches, unlike biological nanopore sequencing, do not incorporate proteins into their systems. Instead, solid state nanopore technology uses various metal or metal alloy substrates with nanometer sized pores that allow DNA or RNA to pass through. Additionally, these substrates most often serve integral roles in the sequence recognition of nucleic acids as they translocate through the channels along the substrates.

In <u>tunneling the electric current</u>, detection is made possible by the incorporation of electrodes along the nanopore channel walls – perpendicular to the ssDNA's velocity vector.

Measurement of electron tunneling through bases as ssDNA translocates through the nanopore is an improved solid state nanopore sequencing method. Most research has focused on proving that bases could be determined using electron tunneling. These studies were conducted using a scanning probe microscope as the sensing electrode, and have proved that bases can be identified by specific tunneling currents. After the proof of principle research, a functional system must be created to couple the solid state pore and sensing devices.

Researchers at the Harvard Nanopore group have engineered solid state pores with single walled carbon nanotubes across the diameter of the pore. Arrays of pores are created and chemical vapor deposition is used to create nanotubes that grow across the array. Once a nanotube has grown across a pore, the diameter of the pore is adjusted to the desired size. Successful creation of a nanotube coupled with a pore is an important step towards identifying bases as the ssDNA translocates through the solid state pore.

Another method is the use of nanoelectrodes on either side of a pore. The electrodes are specifically created to enable a solid state nanopore's formation between the two electrodes. This technology could be used to not only sense the bases but to help control base translocation speed and orientation.

<u>The fluorescence sequencing method</u> is an effective technique to determine a DNA sequence by converting each base into a characteristic representation of multiple nucleotides which bind to a fluorescent probe strand-forming dsDNA. With the two color system proposed, each base is identified by two separate fluorescences, and will therefore be converted into two specific sequences. Probes consist of a fluorophore and quencher at the start and end of each sequence, respectively. Each fluorophore will be extinguished by the quencher at the end of the preceding sequence. When the dsDNA is translocating through a solid state nanopore, the probe strand will be stripped off, and the upstream fluorophore will fluoresce.

This sequencing method has a capacity of 50-250 bases per second per pore, and a four-color fluorophore system (each base could be converted to one sequence instead of two), will sequence over 500 bases per second. Advantages of this method are based on the clear sequencing readout – using a camera instead of noisy current methods. However, the method does require sample preparation to convert each base into an expanded binary code before sequencing. Instead of one base being identified as it translocates through the pore, ~12 bases are required to find the sequence of one base.

Biological: Pros and Cons

Biological sequencing systems nanopore have several fundamental characteristics that make them advantageous as compared with solid state systems - with each advantageous design approach stemming this characteristic of from the incorporation of proteins into their technology. Uniform pore structure, the precise control of sample translocation through pore channels, and even the detection of individual nucleotides in samples can be facilitated by unique proteins from a variety of organism types.

The use of proteins in biological nanopore sequencing systems, despite the various benefits, also brings with it some negative characteristics. The sensitivity of the proteins in these systems to local environmental stress has a large impact on the longevity of the units, overall. One example is that a motor protein may only unzip samples with sufficient speed at a certain pH range while not operating fast enough outside of the range- this constraint impacts the functionality of the whole sequencing unit. Another example is that a transmembrane porin may only operate reliably for a certain number of runs before it breaks down. Both of these examples would have to be controlled for in the design of any viable biological nanopore system- something that may be difficult to achieve while keeping the costs of such a technology as low and as competitive, to other systems, as possible.

(From: <u>https://en.wikipedia.org/wiki/Nanopore_sequencing</u>)

Task 21. Analyze the text for the key phrases to be used in the following-up discussion. Write down the phrases in your exercise-book.

Task 22. Read the text again for more details and put 5-7 questions (wh-questions / open-end questions).

Task 23. Pair-work. Ask your partner the questions you have made up. Check if the answers are correct.

Task 24. Team-work. Divide into two teams and discuss the text during 5-7 minutes. Choose a presenter in each team to present the main ideas of the text in front of the class. Which of the teams presents best?

Unit 7

MOLECULAR IMPRINTING TECHNOLOGY

I. Pre-reading activities

Task 1. Discuss the following questions:

- 1) What do you know about molecular imprinting technology?
- 2) Where is it employed? What for?
- 3) What are the benefits of such a technology?

Task 2. Pronounce the following international words and guess what they mean:

molecular [mə'lekjulə]	polymerization [pɔlɪm(ə)raɪ'zeɪʃ(ə)n]
technology [tek'nɔlədʒɪ]	analogue ['ænəl ɔ g]
synthesis ['sɪnθəsɪs]	complementary [komplI'ment(ə)rI]
procedure [prə'si:dʒə]	template ['templeIt], [-lIt]
monomer ['mɔnəmə]	mimic ['mɪmɪk]

Task 3. Match the synonyms:

1) counterpart	a) stencil
2) configuration	b) aggressive
3) template	c) stability
4) durability	d) arrangement
5) recognition	e) crater
6) harsh	f) analogue
7) cavity	g) identification

Task 4. Match the opposites:

1) essential	a) derivative
2) permanent	b) unreliability
3) original	c) temporary
4) removal	d) natural
5) durability	e) worst
6) artificial	f) unimportant
7) optimal	g) intercalation

Task 5. Guess from the context what the underlined words mean:

- 1. The development of the biosensors depends on the <u>immobilization</u> methods of the biological macromolecules for solving several problems such as their loss, <u>preservation</u> of their stability and <u>shelf life</u>.
- 2. The direct and rapid <u>determination</u> of an interaction between the <u>recognition element</u> and the <u>target</u> analyte (<u>template</u>) was an encouraging factor for the development of such systems as alternatives to traditional bio-assay methods.
- 3. An important <u>challenge</u> for scientific research is the production of artificial systems able to <u>mimic</u> the recognition mechanisms occurring at the molecular level in living systems.
- 4. The potential applications of these systems include <u>affinity</u> <u>separations</u>, medical diagnostics, drug delivery, catalysis, etc.
- 5. Due to their high <u>stability</u>, <u>sensitivity</u> and <u>specificity</u>, <u>bio-</u> <u>mimetic</u> sensors-based membranes are used for environmental food, and, clinical uses.

Task 6. Match the English phrases on the left with their Ukrainian equivalents on the right:

1) biological counterparts	а) стійкість до високої
	температури і тиску
2) recognition properties	b) володіти молекулярною
	пам'яттю
3) possess the molecular memory	с) лінійні полімерні ланцюги
4) durability to heat and pressure	d) жорсткий полімер
5) linear polymer chains	е) зберегти розташування
6) to maintain the location	f) розпізнавальні властивості
7) rigid polymer	g) біологічні аналоги

II. While-reading activities

Task 7. Read the text and answer the questions:

- 1. What is the molecular imprinting polymer?
- 2. What is needed to create a molecular imprinting polymer?
- 3. How can you describe the stages of its synthesis?
- 4. Where is the molecular technology used?
- 5. What are the advantages of molecular imprinting technology?

Molecular Imprinting Technology

Molecular imprinting technology is a rapidly developing technique for the preparation of polymers having specific molecular recognition properties for a given compound, its analogues or for a single enantiomer. Synthesis of MIP is a relatively straightforward and inexpensive procedure.

To produce molecularly imprinted polymers (MIPs) three essential elements are required: the target molecule (or template) which is the substance that will be imprinted in the polymer; the functional monomer which is a compound having chemical and shape complementarity to the template and will polymerize in order to form polymer matrix; the cross-linking agent (or cross-linker) which is a multifunctional molecule containing two or more reactive split ends able to interact via substances chemical bound with specific functional groups present on other chemicals (e.g., linear polymer chains).

The synthesis entails the following steps: the template molecules form pre-polymerization complexes with polymerizable functional monomers capable of interacting with them. In this phase, the functional monomers arrange around the template in order to create the recognition sites. The pre-formed complexes are polymerized with the cross-linker molecules into a rigid polymer to maintain the location of the functional groups for binding the template. After the polymerization step, the template is removed from the polymeric matrix allowing for generating the specific recognition sites which possess the molecular memory of the template. In fact, they are capable to selectively rebind the template molecules with respect to other compounds, including their structural analogues.

After polymerization and extraction of a molecule out of the template, the resulting imprinted polymer possessing a permanent memory for the imprint species is formed, enabling the resultant polymer selectively to rebind the imprint molecule from a mixture of closely related compounds. The three-dimensional cavities that are complementary in both shape and chemical functionality arrangement to those of the template be left in the polymer matrix and the high degree of cross-linking enables the microcavities to maintain their shape after removal of the template, and thus the functional groups are held in an optimal configuration for rebinding the template, allowing the receptor to `recognize' the original substrate. Molecularly imprinted polymers demonstrate very good thermal and chemical stability and can be used in aggressive media. MIP possess several advantages over their biological counterparts including low cost, ease of preparation, storage stability, repeated operations without loss of activity, high mechanical strength, durability to heat and pressure, and applicability in harsh chemical media. As a technique for the creation of artificial receptor-like binding sites with a 'memory' for the shape and functional group positions of the template molecule, molecular imprinting has become increasingly attractive in many fields of chemistry and biology, particularly as an affinity material for sensors binding assays, artificial antibodies, adsorbents for solid phase extraction, and chromatographic stationary phases.

(From: Hongyuan Yan, Kyung Ho Row. Characteristic and Synthetic Approach of Molecularly Imprinted Polymer // *Int. J. Mol. Sci.* 2006, 7, 155-178).

III. Post-reading activities

Task 8. Complete the following sentences using the text:

- 1) Synthesis of MIP is a relatively _____ procedure.
- 3) After the ______, the template is removed from the polymeric matrix allowing for generating the specific recognition sites which ______ of the template.
- 4) The functional monomers arrange around the template in order to create _____.

Task 9. Read and analyze all the definitions given in the text.

Task 10. Answer the questions about the text:

- 1) What are the essential elements for the synthesis of molecular imprinting polymers?
- 2) Why do molecular imprinting polymers become attractive in many fields of chemistry and biology?
- 3) What is a cross-linker?
- 4) Why are MIPs called biomimetic polymers?
- 5) What are the steps of the synthesis of molecular imprinting polymers?
- 6) How have the specific recognition sites been formed?

Task 11. Are the following statements true or false? Say why:

- 1) Synthesis of molecular imprinted polymers is an extremely complex and expensive procedure.
- 2) To produce molecularly imprinted polymers, two essential elements are required: the target molecule (or template) and the functional monomer.
- 3) Imprinted polymers are well recognized today in many areas which exploit their molecular selectivity.
- 4) During the polymerization, the template is incorporated into the polymeric matrix and chemical groups of functional monomers will be arranged according to the shape and chemical properties of the template molecules.
- 5) The functional monomer is a multifunctional molecule containing two or more reactive split ends able to interact via substances chemically bound with specific functional groups present on other chemicals.
- 6) The imprinting technology is based on the synthesis of a polymeric material endowed with specific recognition sites towards the molecule which must be recognized (i.e. templates).
- 7) Molecular imprinting polymers were applied in infrared and Raman spectroscopy.

Task 12. Make a list of all the chemistry terms, procedures, experiments you can find in the text. Check all the examples in your class.

IV. Focus on grammar and lexis

Task 13. Put the verbs in brackets in the correct tense form:

- 1) The concept of specific recognition _____(pioneer) in 1955 by Dickey who _____(prepare) specific adsorbents of silica gel by simply _____(acidify) commercial silicate solutions containing methyl orange or one of its homologs.
- 2) In 1972, Wulff and Sarhan and Klots and Takagishi, in parallel, (report) the first examples of molecular imprinting of organic network polymers.
- 3) More recently, other studies _____(perform) to optimize the template removal from molecularly imprinted polymers.

- 4) The target analyte _____(immobilize) on the surface of a porous solid which _____(act) as molds to create a desired porosity.
- 5) In the last two decades, biosensors _____(become) very important tools for the detection of chemical and biological compounds for clinical, environmental and food monitoring.
- 6) The future of research in this area (have) a thriving development benefitting from the integration of different disciplines.
- 7) In particular, the requirement of novel testing approaches in substitution of the classical bio-recognition elements (determine) a rapid development of materials in biosensor technology.

Task 14. Put the words in the right order to make sentences:

- 1) polymers recognition are with a imprinted in bio-mimetic which elements component are these integrated transducer as systems used.
- 2) represents necessity specific level systems at key a living recognition a molecular of.
- 3) sensitive alterations of polymers polymerization small imprinted to also in the very is the conditions morphology.
- 4) today recognized many areas polymers their well exploit in molecular imprinted selectivity which are.
- 5) are recognition the classified and in biocatatalytic biological affinity elements.

Task 15. Fill in the gaps with the suitable prepositions:

- 1) The biosensors can be also classified _____ different types _____ relation to the transducers.
- 2) Biosensor technology is an area characterized _____ novel testing approaches.
- 3) Electrochemical approaches are extensively used ______ the development of these devices.
- 4) Traditional applications _____ imprinted materials _____ sensor technology involved the use of imprinted polymer particles.
- 5) MIPs can work _____ a continuous way and are therefore promising ______ an industrial application.

- 6) A considerable boost _____ this direction was given _____ the development of the molecular imprinting technology.
- 7) A great challenge ____ research ____ this field is the production of membranes imprinted ____ virus, which could be used _____ diagnosis and therapeutic treatments.

Task 16. Translate from Ukrainian into English:

- 1) Останнім часом значний інтерес дослідників привернули молекулярно-імпрінтовані полімери або так звані полімерибіоміметики.
- 2) Вони є привабливою альтернативою антитілам та іншим біорецепторам в імуноаналізі.
- Цей процес починається з утворення проміжного полімеризаційного комплексу між темплатом і функціональним мономером.
- 4) Подальше видалення темплату призводить до виникнення у структурі порожнин, які комплементарні матричним молекулам за розміром, формою та розміщенням функціональних груп.
- 5) Дуже перспективним напрямом є використання таких полімерів у сенсорній технології.
- 6) Отже, молекулярно-імпрінтовані полімери поєднують високу селективність біомолекул із надзвичайною стабільністю синтетичних полімерів за жорстких умов.
- 7) Молекулярно-імпрінтовані полімери імітують активні центри антитіл і біологічних рецепторів.

V. Final tasks

Task 17. Discuss the following ideas with your group-mates:

- 1. Do you agree that molecular imprinting technology is important in many fields of chemistry and biology? Give your reasons.
- 2. How do you understand the statement "Specific recognition at a molecular level represents a key necessity of living systems?"
- 3. What, in your opinion, are the typical and peculiar characteristics of molecular imprinting polymers?
- 4. What are the strong points of biosensors based on molecular imprinting polymers?

Task 18. Use the phrases below to retell the text in your own words:

Molecular imprinting technology; straightforward and inexpensive procedure; template, functional monomer and cross-linker; recognition sites; three-dimensional cavities; chemical and shape complementarity; durability to heat and pressure; artificial antibodies; chromatographic stationary phases.

VI. Individual reading: supplementary text

Task 19: Read the text and answer the following questions:

- 1. What is a membrane?
- 2. Where is the membrane used?
- 3. What are the benefits of molecular imprinting membrane?

Molecularly Imprinted Membranes

A membrane is defined as a selective barrier interposed between two neighboring phases and regulates the transport chemical species amongst the two phases. The development of membrane technology dates back to many years before the coming of the molecular imprinting technique and was applied in many research sectors. For instance, membranes were used in water treatment, enzymatic catalysis, controlled drug release, oil refinement and gas separations, for the development of biosensors and so much more.

Taking advantage of the "bio-inspired" molecular imprinting technique, numerous research efforts were devoted to the production of a new generation of highly selective membranes named – molecularly imprinted membranes (MIMs). Owing to the introduction of specific molecular recognition sites in its matrix, an imprinted membrane is able to discern between template and other analytes.

These novel systems made valuable contributions to the development of innovative bio-mimetic molecular recognition devices. In fact, MIMs marked a new path for the detection, transport or retention of targeted chemical and biological compounds. Membrane-based imprinting processes do not require additives and can be performed at low temperature, thus reducing the energy consumption costs.

In addition, compared to the traditional applications of imprinted polymers, MIMs can operate in a continuous mode by exploiting the characteristics of membrane and molecular imprinting technologies. In comparison with a traditional membrane, a MIM exhibits an improved specific selectivity maintaining at the same time the separation efficiency.

Two diverse transport mechanisms of target molecules can be distinguished in a molecularly imprinted membrane: the "retarded permeation" and the "facilitated permeation." The ability of MIMs to produce a selective transport or retention of specific molecules makes them good candidates for the development of highly innovative membrane processes. A wide variety of MIMs have been successfully exploiting the main following approaches: (1) the prepared contemporary production of recognition sites and membrane structure of a self-supported membrane; (2) the synthesis of a tailored imprinted polymer to use in successive membrane preparation step; (3) the preparation of a composite imprinted membrane (by surface thermal/photo-copolymerization imprinting, of pre-existing a membrane).

(From: <u>http://www.mdpi.com/1424-8220/14/8/13863/htm</u>)

VII. Additional texts

Did you know that in a perfect molecular memory device each molecule contains data leading to massive data capacity?

Task 20: Read the text and make your questions to cover its content:

The Memory of Water?

Molecular memory is a term for data storage technologies that use molecular species as the data storage element, rather than e.g. circuits, magnetics, inorganic materials or physical shapes. The molecular component can be described as a molecular switch, and may perform this function by any of several mechanisms, including charge storage, photochromism, or changes in capacitance. In a perfect molecular memory device, each individual molecule contains a bit of data, leading to massive data capacity. However, practical devices are more likely to use large numbers of molecules for each bit, in the manner of 3D optical data storage (many examples of which can be considered molecular memory devices). The term "molecular memory" is most often used to indicate very fast, electronically addressed solid-state data storage, as is the term computer memory. As of 2017, molecular memories are still found only in laboratories. One approach to molecular memories is based on special compounds such as porphyrin-based polymers which are capable of storing electric charge. Once a certain voltage threshold is achieved the material oxidizes, releasing an electric charge. The process is reversible, in effect creating an electric capacitor. The properties of the material allow for a much greater capacitance per unit area than with conventional DRAM memory, thus potentially leading to smaller and cheaper integrated circuits.

Several universities and a number of companies (Hewlett Packard, ZettaCore) have announced work on molecular memories, which some hope will supplant DRAM memory (Dynamic Random Access Memory) as the lowest cost technology for high-speed computer memory. NASA is also supporting research on non-volatile molecular memories.

At the same time, the life and work of Jacques Benveniste taught us valuable lessons about how to deal with fringe science, says journalist Philip Ball in his on-line publication of October 8, 2004 at Nature.News.com.

Jacques Benveniste, who gave the world the 'memory of water', died in Paris on 3 October, 2004. He will certainly be remembered for the phrase his work inspired, which has become the title of a play and a rock song, as well as a figure of everyday speech.But his controversial career also highlighted the tricky issue of how to deal with research on the fringes of science.

Back in 1988, Jacques Benveniste was the senior director of the French medical research organization INSERM's Unit 200, in Clamart, which studied the immunology of allergy and inflammation.

In 2003, he sent his notorious paper to Nature. In it, he reported that white blood cells called basophils, which control the body's reaction to allergens, can be activated to produce an immune response by solutions of antibodies that have been diluted so far that they contain none of these biomolecules at all.

It was as though the water molecules somehow retained a memory of the antibodies that they had previously been in contact with, so that a biological effect remained when the antibodies were no longer present. This, it seemed, validated the claims made for highly diluted homeopathic medicines.

After a lengthy review process, in which the referees insisted on seeing evidence that the effect could be duplicated in three other independent laboratories, Nature published the paper. The editor, John Maddox, prefaced it with an editorial comment entitled 'When to believe the unbelievable', which admitted: "There is no objective explanation of these observations."

Naturally, the paper caused a sensation. "Homeopathy finds scientific support," claimed Newsweek. But no one, including Benveniste, gave much attention to the critical question of how such a 'memory' effect could be produced. The paper itself offered only the suggestion, at face value almost meaningless, that "Water could act as a 'template' for the [antibody] molecule, for example by an infinite hydrogen-bonded network, or electric and magnetic fields."

The idea that water molecules, connected by hydrogen bonds that last for only about a picosecond $(10^{-12} \text{ seconds})$ before breaking and reforming, could somehow cluster into long-lived mimics of the antibody seemed absurd.

Other teams were subsequently unable to repeat the effect, and the independent results that the reviewers had asked for were never published. Further experiments carried out by Benveniste's team, in double-blind conditions overseen by Maddox, magician and pseudoscience debunker James Randi and fraud investigator Walter Stewart, failed to verify the original results.

The Nature paper was never retracted, but Maddox subsequently commented, "My own conviction is that it remains to be shown there is a phenomenon to be explained."

Benveniste was unmoved by the wave of skepticism; he devised another explanation for his strange results. Biomolecules, he said, communicate with their receptor molecules by sending out lowfrequency electromagnetic signals, which the receptors pick up like radios tuned to a specific wavelength.

Benveniste claimed that he was able to record these signals digitally, and that by playing them back to cells in the absence of the molecules themselves he could reproduce their biochemical effect, including triggering a defence response in neutrophils, which kill invading cells.

The questions this raises are, of course, endless. Why, if this is the way biomolecules work, do they bother with shape complementarity at all? (When Benveniste was asked about this, he said something about audio earpieces being shaped to fit the ear.) How could a molecule act as an antenna for electromagnetic wavelengths of several kilometres? And how does the memory of water fit into all of this? Benveniste proposes that transmission of the signal somehow involves the 'quantum-coherent domains' proposed in a paper – that now seems to be invoked whenever water's 'weirdness' is at issue - for example, to explain cold fusion.

The details were not, Benveniste said, his responsibility. He was an immunologist, not a physicist. But his failure to simplify his experimental system so that he could clarify the precise nature of the effects he claimed to see, or the mechanisms behind them, fell short of rigorous science. Benveniste could surely have tested his radiotransmission theory at the level of simple, cell-free molecular systems.

No evidence has been found that he ever devised such experiments: he stayed at the level of cells, tissues or whole organisms, where direct cause-and-effect is hard to track and statistical tests are needed to cope with the significant responses from control samples.

There can be no doubt that Benveniste was genuinely convinced he had chanced upon something revolutionary. It is a shame that he became isolated. But the fact that it is the 'memory of water', not 'digital biology', that he will be remembered for illustrates a point that Jacques failed to appreciate: his work tapped into a potent and persistent cultural myth about the miraculous properties of water. And under the influence of myth, it can be hard to keep a level head.

(From: <u>https://en.wikipedia.org/wiki/Molecular_memory</u> and <u>https://www.nature.com/news/2004/041004/full/news041004-19.html</u>)

Task 21. Analyze the text for the key phrases to be used in the following-up discussion. Write down the phrases in your exercise-book.

Task 22. Read the text again for more details and put 5-7 questions (wh-questions / open-end questions).

Task 23. Pair-work. Ask your partner the questions you have made up. Check if the answers are correct.

Task 24. Team-work. Divide into two teams and discuss the text during 5-7 minutes. Choose a presenter in each team to present the main ideas of the text in front of the class. Which of the teams presents best?

Unit 8

DYE-SENSITIZED SOLAR CELLS

I. Pre-reading activities

Task 1. Discuss the following questions:

1) What types of conductivity do you know?

2) How can you explain the differences between them?

3) What is an elementary electrochemical cell?

4) What processes could be initiated by energy of light?

Task 2. Pronounce the following international words and guess what they mean:

dye-sensitized [daI'sensItaIzd]	potential [pə'ten∫(ə)l]
photoelectrochemical	barrier ['bær 1 ə]
['fəutəuI'lektrəu'kemIk(ə)l]	
photoexcitation	efficiency [I'fI∫(ə)n(t)sI], [ə-]
['fəutəueks ı 'te ı∫ (ə)n], ['sa ı]	
re-combine [r 1 kəm'ba 1 n]	multi-junction ['m∧ltɪ'ʤʌŋk∫(ə)n]
chlorophyll ['klɔːrəfɪl]	titanium [tI'teInIəm], [taI-]
cathode ['kæθəud]	dioxide [daɪ'ɔksaɪd]
anode ['ænəud]	valence ['veIl(ə)n(t)s]
semiconductor [semIkən'dAktə]	solid ['sɔlɪd]
electrolyte [I'lektrəlaIt]	molecule ['mɔlɪkju:l]

Task 3. Match the synonyms:

1) emit	a) electrolyte
2) liquid conductor	b) energize
3) efficient	c) divided
4) sensitized	d) alteration
5) separated	e) doped
6) excite	f) absorb
7) conversion	g) effectual

1) solida) desorption2) anodeb) unsteadiness3) reductionc) parse4) absorptiond) cathode5) stabilitye) liquid6) generatef) oxidation

Task 4. Match the opposites:

Task 5. Match the English phrases on the left with their Ukrainian equivalents on the right:

1) valence band	а) платиновий каталізатор
2) conduction band	b) світлочутливий барвник
3) porous layer	с) валентна зона
4) electrolyte solution	d) зона провідності
5) photosensitive dye	е) перенесення заряду
6) titanium dioxide	f) пористий шар
7) platinum-based catalyst	g) двоокис титану
8) charge transport	h) розчин електроліту

Task 6. Guess from the context what the underlined words mean:

- 1. When placed in the sun, <u>photons</u> of the sunlight can <u>excite</u> electrons on the p-type side of the semiconductor, a process known as <u>photoexcitation</u>.
- 2. In contrast to the <u>conventional</u> systems where the <u>semiconductor</u> <u>assumes</u> both the task of light absorption and charge carrier transport the two functions are separated here.
- 3. <u>Charge separation</u> takes place at the interface via photo-induced electron <u>injection</u> from the dye into the conduction band of the solid.
- 4. The <u>valence band</u> is the highest range of electron energies in which electrons are normally present at absolute zero temperature, while the <u>conduction band</u> is the lowest range of vacant electronic states.
- 5. As such, the <u>electrical conductivity</u> of a <u>solid</u> depends on its capability to flow electrons from <u>valence band</u> to <u>conduction</u> <u>band</u>.

<u>II. While-reading activities</u>

Task 7. Read the text and answer the questions:

- 1. What is the main challenge of DSSC?
- 2. Where does the charge separation occur?
- 3. What is the difference between the functional principles of traditional silicon-based solar cells and DSSC?

Dye-sensitized Solar Cells

In the late 1960s it was discovered that illuminated organic dyes can generate electricity at oxide electrodes in electrochemical cells. In an effort to understand and simulate the primary processes in photosynthesis the phenomenon was studied at the University of California at Berkeley with chlorophyll extracted from spinach (using bio-mimetic or bionic approach). On the basis of such experiments electric power generation via the dye sensitization solar cell (DSSC) principle was demonstrated and discussed in 1972. The instability of the dye solar cell was identified as a main challenge. Its efficiency could, during the following two decades, be improved by optimizing the porosity of the electrode prepared from fine oxide powder, but the instability remained a problem. A modern DSSC is composed of a porous layer of titanium dioxide nanoparticles, covered with a molecular dye that absorbs sunlight, like the chlorophyll in green leaves. The titanium dioxide is immersed under an electrolyte solution, above which is a platinum-based catalyst. As in a conventional alkaline battery, an anode (the titanium dioxide) and a cathode (the platinum) are placed on either side of a liquid conductor (the electrolyte).

Sunlight passes through the transparent electrode into the dye layer where it can excite electrons that then flow into the titanium dioxide. The electrons flow toward the transparent electrode where they are collected for powering a load. After flowing through the external circuit, they are re-introduced into the cell on a metal electrode on the back, flowing into the electrolyte. The electrolyte then transports the electrons back to the dye molecules.

Dye-sensitized solar cells separate the two functions provided by silicon in a traditional cell design. Normally the silicon acts as both the source of photoelectrons, as well as providing the electric field to separate the charges and create a current. In the dye-sensitized solar cell, the bulk of the semiconductor is used solely for charge transport, the photoelectrons are provided from a separate photosensitive dye. Charge separation occurs at the surfaces between the dye, semiconductor and electrolyte.

The dye molecules are quite small (nanometer sized), so in order to capture a reasonable amount of the incoming light, the layer of dye molecules needs to be made fairly thick, much thicker than the molecules themselves. To address this problem, a nanomaterial is used as a scaffold to hold large numbers of the dye molecules in a 3-D matrix, increasing the number of molecules for any given surface area of a cell. In existing designs, this scaffolding is provided by the semiconductor material, which serves double-duty.

The dye-sensitized nanocrystalline electrochemical photovoltaic system has become a validated and credible competitor to solid-state junction devices for the conversion of solar energy into electricity. It is the prototype of a series of optoelectronic and energy technology devices exploiting the specific characteristics of this innovative structure for oxide and ceramic semiconductor films. Recent developments in the area of sensitizers for these devices have led to dyes which absorb across the visible spectrum leading to higher efficiencies. The recent development of an all solid-state heterojunction dye solar cell holds additional potential for further cost reduction and simplification of the manufacturing of dye solar cells.

(From: <u>https://en.wikipedia.org/wiki/Dye-sensitized_solar_cell</u>)

III. Post-reading activities

Task 8. Complete the following sentences using the text:

- 1) Modern DSSC is composed of a porous layer of _____
 - nanoparticles, covered with a molecular dye that absorbs sunlight, like the _____ in green leaves.
- 2) Dye-sensitized solar cells separate the _____ functions provided by silicon in a ______ design.
- 3) In the _____-sensitized solar cell, the bulk of the ______ is used solely for charge transport, the photoelectrons are provided from a separate ______ dye.
- 4) The dye molecules are quite _____ (_____ sized).

5) Recent developments in the area of ______ for these devices have led to dyes which ______ across the visible spectrum leading to ______ efficiencies.

Task 9. Answer the questions about the text:

- 1) What material is used for the anode and for the cathode?
- 2) What is the size of dye molecules?
- 3) What is the main problem of dye solar cells?
- 4) What are the main components of photoelectrochemical cells?

Task 10. Are the following statements true or false? Explain why:

- 1) Low efficiency is the main problem of energy conversion in DSSC.
- 2) The dye catches photons of incoming light, e.g. sunlight and ambient artificial light, and uses their energy to excite electrons, behaving like chlorophyll in photosynthesis.
- 3) The electron is conducted away by a dye molecule.
- 4) The dye is the photoactive material of DSSC, and it can produce electricity once it is sensitized by light.
- 5) A modern DSSC is composed of a solid layer of titanium dioxide nanoparticles.

IV. Focus on grammar and lexis

Task 11. Match the beginning of the sentence in the first column with an end in the second column:

1) DSSCs have a lot of potential because they	a) can work effectively in low light conditions and are less susceptible to losing energy to heat
2) The dye is	b) sensible to the visible light
3) The light creates an excitation	c) the surface of sintered TiO_2
in the dye that consists in	nanoparticles
4) Unlike traditional solar cells,	d) can be made and manufactured
dye-sensitized cells	with low-cost materials
5) The dye molecules are	e) reaches the counter electrode
adsorbed onto	
6) The electron reaches the	f) a highly energetic electron,
conductive electrode, travels	which is rapidly injected to the
through the wire, and	TiO ₂ particles

Task 12. Put the words in the right order to make sentences:

- 1) based solar although the silicon cells are more the dye-sensitized solar cells are considerably currently efficient to manufacture cheaper.
- 2) environment researchers processes where irradiation explored used to create an solar many ecologically have healthy can be.
- 3) collectors most photovoltaics and used solar are thermal widely.
- 4) electrolyte charge the surfaces occurs between separation the and at dye semiconductor.
- 5) functions traditional solar dye-sensitized separate the cell two provided silicon in a design cells by.

Task 13. The following words are borrowed from the text. Fill in the columns in the table by forming all possible parts of speech:

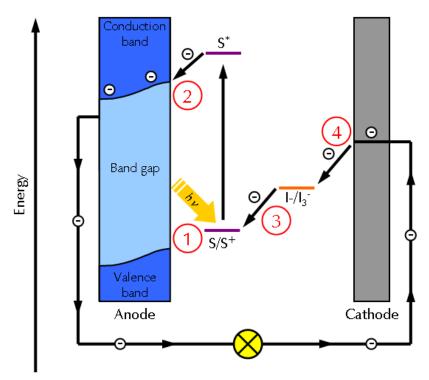
Noun	Verb	Adjective	Adverb	Gerund	Part. II
transport	transport	transportable		transporting	transported
	synthesize				
				flowing	
			separately		
	process				
validity					
					immersed
		cellular			
	increase				
					charged

Task 14. Match the definitions in A with the terms in B:

Α	В
caused to respond to certain stimuli, made susceptible	photovoltaic
relating to the production of electric current at the	silicon
junction of two substances exposed to light	
the process or fact of light beaming or raying	sensitized
a device containing electrodes immersed in an	irradiation
electrolyte, used for current generation or electrolysis	
a hard silver-gray metal of the transition series, used in	cell
strong, light, corrosion-resistant alloys	
a nonmetal with semiconducting properties, used in	titanium
making electronic circuits	

V. Final tasks

Task 15. Look at the energy diagram. Discuss the process depicted in it with your groupmates:



Task 16. Fill in gaps in the text below using the words from the box:

Band gap, semiconductor, conductive, excited, anode, electrolyte, current, energy, diffusion, load, semiconductor, regenerated, reduction, injected, dye, oxidized

Principles of a Dye Solar Cell

As the name implies, the mechanism of dye solar cells is based on the photoelectrochemical processes. The figure from task 15 depicts an energy diagram of a dye solar cell. The following section describes all relevant electrochemical processes.

STEP 1: The (1) ____ molecule is initially in its ground state (S). The semiconductor material of the (2) ____ is at this energy level (near the valence band) non-(3) ____.

When light shines on the cell, dye molecules get (4) _____ from their ground state to a higher (5) _____ state (S^*), see equation 1:

 $S \xrightarrow{h\nu} S^*$ Eq. 1

The excited dye molecule has now a higher energy content and overcomes the (6) ______ of the semiconductor.

STEP 2: The excited dye molecule (S^*) is (7) _____ (see equation 2) and an electron is (8) _____ into the conduction band of the (9) _____. Electrons can now move freely as the (10) _____ is conductive at this energy level.

 $S^* \longrightarrow S^+ + e^-$

Eq. 2

Eq. 3

Eq. 4

Electrons are then transported to the (11) _____ collector of the anode via (12) _____ processes. An electrical (13) _____ can be powered if connected.

STEP 3: The oxidized dye molecule (S^+) is again (14) _____ by electron donation from the iodide in the (15) _____ (see equation 3):

$$S^{+} + \frac{3}{2}I^{-} \longrightarrow S + \frac{1}{2}I_{3}^{-}$$

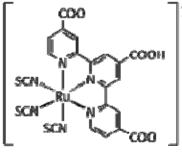
STEP 4: In return, iodide is regenerated by (16) ______ of triiodide on the cathode (see equation 4):

$$\frac{1}{2}I_3^- + e^- \longrightarrow \frac{3}{2}I^-$$

(From: <u>https://www.gamry.com/application-notes/physechem/dssc-</u> <u>dye-sensitized-solar-cells/</u>)

VI. Individual reading: supplementary text

Task 17. Read the text and write a summary.



3- The dyes used in early experimental cells (circa 1995) were sensitive only in the highfrequency end of the solar spectrum, in the UV and blue. Newer versions were quickly introduced (circa 1999) that had much wider frequency response, notably "triscarboxy-

ruthenium terpyridine" [Ru $(4,4',4''-(COOH)_3$ -terpy) (NCS)₃], which is

efficient right into the low-frequency range of red and IR light. The wide spectral response results in the dye having a deep brown-black color, and is referred to simply as "black dye". The dyes have an excellent chance of converting a photon into an electron, originally around 80% but improving to almost perfect conversion in more recent dyes, the overall efficiency is about 90%, with the "lost" 10% being largely accounted for by the optical losses in top electrode.

A solar cell must be capable of producing electricity for at least twenty years, without a significant decrease in efficiency. The "black dye" system was subjected to 50 million cycles, the equivalent of ten years' exposure to the sun in Switzerland. No discernible performance decrease was observed. However the dye is subject to breakdown in high-light situations. Over the last decade an extensive research program has been carried out to address these concerns. The newer dyes included 1-ethyl-3 methylimidazolium tetrocyanoborate [EMIB (CN)₄] which is extremely light- and temperature-stable, copper-diselenium [Cu (In, GA) Se₂] which offers higher conversion efficiencies, and others with varying special-purpose properties.

DSSCs are still at the start of their development cycle. Efficiency gains are possible and have recently started more widespread study. These include the use of quantum dots for conversion of higher-energy (higher frequency) light into multiple electrons, using solid-state electrolytes for better temperature response, and changing the doping of the TiO_2 to better match it with the electrolyte being used.

(From: <u>https://en.wikipedia.org/wiki/Dye-sensitized_solar_cell</u>)

VII. Additional texts

Did you know that in the 1950s, the first solar cells could convert 6% of the sun's energy into electricity, in 2012 - 15%, and in 2017 solar cell efficiency was about 20%?

Task 18: Read the text and make your questions to cover its content:

How much electricity does a solar panel produce?

by Ben Zientara

The amount of electricity a solar panel produces depends on three main things: the size of the panel, the efficiency of the solar cells inside, and the amount of sunlight the panel gets. We'll break down what you can expect from a typical solar panel, and how that power output compares to the power you need for the gadgets and appliances you use inside your home.

How big are solar panels?

When we say "solar panel," what we're talking about is a typical silicon photovoltaic panel. These days, most solar panels are about 5 and a half feet tall and a little more than 3 feet wide. If you look closely at a solar panel, you'll notice some 60 little squares. These squares are actually individual solar "cells," which are linked together by wires. The cells are where electricity is made, and the wires carry the electricity to a junction box where the panel is hooked into a larger array.

Why does solar panel size matter?

The more solar cells working in tandem, the more power they'll create. That's why the size of the panel matters if you're trying to calculate how much electricity a panel makes. Solar panels have been about this size for decades, but modern panels make more electricity than in the past. That's because panel manufacturers have found ways to improve cell efficiency over time.

How efficient are solar panels?

Solar efficiency relates to the amount of available energy from the sun that gets converted into electricity. Back in the 1950s, the first solar cells were capable of taking 6% of the energy from the sun and converting it into electricity. If they were configured to be the same array of 60 cells, that would have created a current of about 20 watts electricity, about a third of what would be needed to light up a 60 watt incandescent bulb. In 2012, solar cells could convert 15% of the energy heating them from the sun into power. As of 2017, solar cell efficiency is closer to 20%.

What's the power rating for an average solar panel?

If you combine the efficiency of the cells with the size of the panel, you get a number called the "power rating." In the solar industry, we say "that panel is rated to produce X watts."As of 2017, a typical solar panel produced around 265 watts of power. That can vary based on the size and efficiency of the solar panel you choose; you'll see panels that produce 210, 280, even 320 watts. More efficient panels are a little more expensive, and are usually only needed if you

have limited space on your roof. It generally matters less how much each panel can produce than how well the whole array performs.

How is a solar panel's rating calculated?

Your solar panels will have a number listed on the back that indicates how much power they will pump out during ideal conditions. This is called the Standard Test Condition rating (STC for short). To determine an STC rating, solar labs test the panels under ideal conditions called "peak sun," or 1,000 watts of sunlight per square meter of surface. That's approximately equal to the power of the sun at noon, on a sunny day, at the equator.

Even if you live at or near the equator, you can't expect to replicate these ideal conditions. The amount of electricity solar panels produce depends on average sunlight over the course of a year. If it's historically cloudier in your area, there's less available energy from the sun to convert into electricity.

The first step to figuring out how much electricity your solar panel can produce in a year is to find your place on the globe. If you live in the United States, you can figure out how to calculate the amount of electricity a solar panel produces and how much you can save using a simple solar calculator. In one year, the panels can produce enough to reduce your energy bills by \$1,198!

Using an example of a 250-watt STC rated panel, if you multiply the 250 watts the panel produces by the number of hours of full sun you get in a day, you'll get the amount of kwh that panel produces per day. Multiply by 30 days and you'll get mothly kWh output for the panel. The average roof in the United States gets about 4 hours of usable sun per day. We know the sun shines more than 4 hours, but "full sun" is a measurement that combines all the parts of the day when the sun is lower in the sky into one number.

Using 4 hours of full sun, gives you this equation: 250 watts x 4 hours. That's 1 kWh (1,000 watts) in a day per 250-watt panel.

If you multiply 1kWh per panel by 30 days in a month, you'll find that each 250 watt rated panel will produce about 30 kWh in an average month.

How much energy does a solar panel produce per square foot?

The average-sized solar panel takes up an area of 17.6 square feet and produces 265 watts under direct sunlight. That translates to just over 15 watts per square foot.

How many solar panels are needed to power an average house?

Sizing a solar panel system to your home's electric usage can be done by taking look at your energy bills over a year. Most utility companies provide information about your last few months of usage on your bill, Typically, homeowners in the United States use about 900 kWh a month on average. So, take 900 kWh and divide by the amount of kWh one solar panel produces over the course of a month (30kWh), and you get a 30 panel installation. 30 panels x 250 watts per panel equals a 7,500 watt system (7.5kW).

How much power do home devices use?

There's huge variation in power use between households depending on what you own and how often you use everything. People in the South and West United States tend to use more electricity for heating and air conditioning, whereas people in the North and East tend to heat with gas or fuel oil.

One basic old-fashioned light-bulb uses 60 watts of electricity; a CFL uses 18 watts. Laptops often use about 45 watts, and desktops can run between 150-300 watts. Window air conditioning can range between 500 and 1500 watts, and central air conditioning can use 3500 watts. The average home in the US uses about 1,000 kWh of electricity per month. All those little devices add up to big usage, with variations by season. Usage also varies between day and night. Unless you work at home, most of your electricity usage probably happens at night.

On or off the grid?

Since solar panels only generate power as the sun shines, you'll need a way to store the energy. Though it's possible to use a battery for storage, the easiest (and cheapest) solution for most people is to stay connected to the grid. If your solar panels are producing more energy than you're using – when you're at work, on vacation, or just not running many devices – excess power will flow back into the grid. In many locations, utility companies offer a program called "net metering" that can compensate you for extra power you produce.

At night, or anytime you need extra power, you'll pull it from the grid. With a grid-connected system, you'll never need to worry if you happen to need more power than your solar system has been sized to provide. You may also choose to supply only part of your average electricity bill with solar, and use the grid for the rest. Solar power is cheap. The generators and solar modules promise at least 20 years of low-costs electricity and energy storage sytems are getting more and more cost-effective. But at the beginning of such lucrative self-reliance there is a price that has to be paid: The technician has to buy in the components for you, in effect giving you an advance. He then installs them as well, which creates labour costs. All of that adds up to a few thousand euros, which begs the question how you can secure such an investment against interruptions, faults, damages or wear and tear. Law courts may help to settle disputes, but that cannot make up for the pleasure of an efficiently working solar installation.

(From: <u>https://solarpowerrocks.com/solar-basics/how-much-electricity-does-a-solar-panel-produce/; http://www.pveurope.eu/News/Planning-Operation/Solar-Saturday-Club-12-useful-tips-how-to-secure-your-PV-investment?</u>)

Task 19. Analyze the text for the key phrases to be used in the following-up discussion. Write down the phrases in your exercise-book.

Task 20. Read the text again for more details and put 5-7 questions (wh-questions / open-end questions).

Task 21. Pair-work. Ask your partner the questions you have made up. Check if the answers are correct.

Task 22. Team-work. Divide into two teams and discuss the text during 5-7 minutes. Choose a presenter in each team to present the main ideas of the text in front of the class. Which of the teams presents best?

Unit 9

CATALYSIS

I. Pre-reading activities

Task 1. Discuss the following questions:

- 1) What do we call catalysis?
- 2) What is another name for biological catalysts?
- 3) Why do we use inhibitors in catalytic reactions?
- 4) What chemical substances can be used as catalysts?

Task 2. The following English words sound similar to the Ukrainian ones. Pronounce them after your teacher and guess what they mean:

modification [m⊃dIfI'keI∫(ə)n]	mechanism ['mɛkənɪzm]
phenomenon [fI'n ɔ mInən]	generalization [$d3en(a)ralaI'zeI f(a)n$]
combination [kɔmbɪ'neɪ∫(ə)n]	inhibitor [In'hIbItə]
molecule ['mɔlɪkju:l]	concentration $[k \Im n(t) s(\vartheta) n' trei \int (\vartheta) n]$
transformation [trænsfə'meɪ∫(ə)n]	stability [stə'b1lət1]
platinum ['plætɪnəm]	hydrogen ['haɪdrədʒən]
manganese ['mæŋgəni:z]	alcohol ['ælkəhɔl]

Task 3. Match the English phrases on the left with their Ukrainian equivalents on the right:

1) catalytic force	а) інгібіювання, уповільнення
2) simultaneous reactions	b) ланцюгова реакція
3) reacting species	с) зовнішні умови
4) inhibition or retardation	d) одночасні реакції
5) complex formation	е) промислові процеси
6) appropriate catalyst	f) утворення комплексу

7) external conditions	g) каталітична сила
8) industrial processes	h) відповідний каталізатор
9) chain reaction	і) реагуючі частинки

Task 4. Guess from the contexts what the underlined words mean:

- 1) The importance of the concept of adsorption of reactants on the surface of <u>catalysts</u> has been greatly increased by the development of stereoregular <u>polymerization</u> processes, i.e. methods that <u>yield</u> polymers whose <u>molecules</u> have definite three-dimensional <u>patterns</u>.
- 2) In this case many thousands of molecules of <u>sodium</u> sulfite can be <u>oxidized</u> to <u>sulfate</u> if the initial activation process is produced by <u>absorption</u> of a limited number of <u>quanta</u> of light.
- 3) The best example of a <u>light-initiated</u> <u>chain reaction</u> is the <u>photocombination</u> of <u>hydrogen</u> (H₂) and <u>chlorine</u> (Cl₂).
- 4) Although earlier discoveries of enzymes had been made, a significant <u>confirmation</u> of their importance in living systems was found in 1897.
- 5) The properties of <u>dilute</u> concentrations of <u>platinum</u> metals in <u>oxide matrices</u>, such as <u>silica</u> and <u>alumina</u>, as well as on <u>carbon</u> <u>carriers</u> have been studied by Russian and American scientists.
- 6) Catalysis is the <u>modification</u> of the rate of a chemical reaction, usually an <u>acceleration</u>, by <u>addition</u> of a substance not consumed during the reaction.

<u>II. While-reading activities</u>

Task 5. Read the text and answer the following questions:

- 1) What is known about the history of catalysis discovery?
- 2) What are the reasons for theoretical and practical interest in the study of catalysis?
- 3) How do catalsysts affect chemical reactions?
- 4) What do we call autocatalytic reactions?
- 5) What is an anhibitor? How can it affect a chemical reaction?
- 6) What factors influence the rate of chemical reactions?
- 7) In what cases may the concentrations of an inhibitor be much lower than those of the reactants? Give your reasons.

The term *catalysis* was first employed by the great Swedish chemist Jons Jacob Berzelius in 1835 to correlate a group of observations made by other chemists in the late 18th and early 19th centuries. These included the enhanced conversion of starch to sugar by acids, first observed by Gottlieb Sigismund Constantin Kirchhoff, Sir Humphry Davy's observations that platinum hastens the combustion of a variety of gases; the discovery of the stability of hydrogen peroxide in acid solution but its decomposition in the presence of alkali and such metals as manganese, silver, platinum, and gold; and the observation that the oxidation of alcohol to acetic acid is accomplished in the presence of finely divided platinum. The agents promoting these various reactions were termed *catalysts*, and Berzelius postulated a special unknown catalytic force to be operating in such processes.

Catalysis, in chemistry, is the modification of the rate of a chemical reaction, usually an acceleration, by addition of a substance not consumed during the reaction. The rates of chemical reactions, that is, the velocities at which they occur, depend upon a number of factors, including the chemical nature of the reacting species and the external conditions to which they are exposed. A particular phenomenon associated with the rates of chemical reactions, which is of great theoretical and practical interest, is catalysis, the acceleration of chemical reactions by substances not consumed in the reactions themselves, substances known as catalysts. The study of catalysis is of interest theoretically because of what it reveals about the fundamental nature of chemical reactions. In practice, the study of catalysis is important because many industrial processes depend upon catalysts for their success. Fundamentally, the peculiar phenomenon of life would hardly be possible without the biological catalysts termed enzymes.

In a catalyzed reaction, the catalyst generally enters into chemical combination with the reactants but is ultimately regenerated, so the amount of catalyst remains unchanged. Since the catalyst is not consumed, each catalyst molecule may induce the transformation of many molecules of a reactant. For an active catalyst, the number of molecules transformed per minute by one molecule of catalyst may be as large as several million. Where a given substance or a combination of substances undergoes two or more simultaneous reactions that yield different products, the distribution of products may be influenced by the use of a catalyst that selectively accelerates one reaction relative to the other. By choosing the appropriate catalyst, a particular reaction can be made to occur to the extent of practically excluding another. Many important applications of catalysis are based on selectivity of this kind.

Since a reverse chemical reaction may proceed by reversal of the steps constituting the mechanism of the forward reaction, the catalyst for a given reaction accelerates the reaction in both directions equally. Therefore, a catalyst does not affect the position of equilibrium of a chemical reaction; it affects only the rate at which equilibrium is attained. Apparent exceptions to this generalization are those reactions in which one of the products is also a catalyst for the reaction. Such reactions are termed autocatalytic.

Cases are also known in which the addition of a foreign substance, called aninhibitor, decreases the rate of a chemical reaction. This phenomenon, properly termed inhibition or retardation, is sometimes called negative catalysis. Concentrations of the inhibitor may in some cases be much lower than those of the reactants. Inhibition may result from a decrease in the concentration of one of the reactants because of complex formation between the reactant and the inhibitor, a decrease in the concentration of an active catalyst ("poisoning" of the catalyst) because of complex formation between the catalyst and the inhibitor, or a termination of a chain reaction because of destruction of the chain carriers by the inhibitor. (From: https://www.britanniag.com/soigneg/actalysig)

(From: <u>https://www.britannica.com/science/catalysis</u>)

III. Post-reading actitvities

Task 6. Read the text again and complete the following sentences using the information you need:

- 1) The agents promoting various reactions were termed ______, and Berzelius postulated a special unknown catalytic ______ to be operating in such processes.
- 2) Catalysis is the ______ of the rate of a chemical reaction, usually an acceleration, by ______ of a substance not consumed during the reaction.

- 3) Fundamentally, the peculiar phenomenon of life would hardly be possible without the biological catalysts termed _____.
- 4) In a catalyzed reaction, the catalyst generally ______ into chemical combination with the reactants but is ultimately _____, so the amount of catalyst remains _____.
- 5) Cases are known in which the ______ of a foreign substance, called ______, decreases the rate of a chemical reaction.

Task 7. Are the statements about the text true or false? Explain why:

- 1) The term catalysis was first employed by the great Swedish chemist Jons Jacob Berzelius in 1837.
- 2) Catalysis is the modification of a chemical reaction rate, usually an acceleration, by adding a substance that is consumed during the reaction.
- 3) The peculiar phenomenon of life would be possible without the biological catalysts referred to as enzymes.
- 4) Concentrations of the inhibitor may, in some cases, be much higher than those of the reactants.
- 5) Cases are known in which the addition of a foreign substance, called aninhibitor, decreases the rate of a chemical reaction.

Task 8. Answer the questions about the text:

- 1) Who was the term "catalysis" introduced by and when?
- 2) What is inhibition or retardation? When and how can it occur?
- 3) How many molecules can be transformed per minute by one molecule of a catalyst?

Task 9. Make a list of all the chemicals / chemistry terms / procedures / experiments etc. you can find in the text. Check all the examples in the class.

IV. Focus on grammar and lexis

Task 10. Here are the answers to some questions about the text. Write the questions:

- 1) A catalyst affects only the rate at which equilibrium is attained, but not the position of equilibrium of a chemical reaction.
- 2) Each catalyst molecule may induce the transformation of many molecules of a reactant because the catalyst is not consumed.
- 3) An unknown catalytic force to be operating in such processes.

- 4) It decreases the rate of a chemical reaction.
- 5) It is known as "poisoning" of the catalyst.
- 6) It may occur when substances undergo two or more simultaneous reactions yielding different products.

Task 11. Match the beginning of the sentence in the first column with its end in the second column:

1) The agents promoting various reactions	a) aninhibitor, decreases the rate of a chemical reaction
2) The phenomenon of inhibition or retardation	b) much lower than those of a reactant
3) There are cases in which the addition of a foreign substance,	c) are known as catalysts
4) Concentrations of the inhibitor may be	d) are based on selectivity of this kind
5) Many important applications of catalysis	e) is sometimes called negative catalysis

Task 12. Put the words in the right order to make sentences:

- 1) without the biological catalysts fundamentally the peculiar phenomenon of life would hardly be possible termed enzymes;
- 2) many molecules of reactant since the catalyst the transformation of each catalyst molecule may induce is not consumed;
- 3) of this kind based on selectivity applications of catalysis are many important;
- 4) properly termed inhibition this phenomenon or retardation called negative catalysis is sometimes;
- 5) are termed such reactions autocatalytic.

Task 13. Fill in the gaps with a suitable preposition:

- 1) The term catalysis was first employed ____ the great Swedish chemist Jons Jacob Berzelius ____ 1835 to correlate a group ____ observations made by other chemists ____ the late 18th and early 19th centuries.
- 2) Cases are known _____ which the addition ____ a foreign substance, called aninhibitor, decreases the rate ____ a chemical reaction.

- 3) Since a reverse chemical reaction may proceed _____ reversal _____ the steps constituting the mechanism of the forward reaction, the catalyst _____ a given reaction accelerates the reaction _____ both directions equally.
- 4) The study of catalysis is _____ interest theoretically because of what it reveals _____ the fundamental nature ___ chemical reactions; _____ practice, the study ____ catalysis is important because many industrial processes depend ____ catalysts ____ their success.
- 5) _____a catalyzed reaction, the catalyst generally enters ______ chemical combination ______the reactants but is ultimately regenerated, so the amount _____catalyst remains unchanged.

Task 14. Translate from Ukrainian into English:

Реагенти, реагуючі частинки, каталітична сила, прискорення хімічної реакції, одночасні реакції, відповідний каталізатор, пряма реакція, зворотна реакція рівновага хімічної реакції, концентрація інгібітора, кількість молекул, залишатися незмінним, важливі застосування, зменшення швидкості реакції, припинення ланцюгової реакції.

V. Final tasks

Task 15. Discuss the following issues with your group-mates:

- 1) Enzymes as biological catalysts are highly important for human life? Give your reasons to prove this idea.
- 2) What could our world be like if there were no catalysis?
- 3) Provide a detailed explanation of the phenomenon of catalysis.
- 4) What industrial applications of catalysis can you mention?

Task 16. Use the phrases below to retell the text in your own words:

Chemical reaction, chemical nature of the reacting species, theoretical and practical interest, biological catalysts, simultaneous reactions, the mechanism of the forward reaction, concentrations of the inhibitor, complex formation between the catalyst and the inhibitor.

VI. Individual reading: supplementary text

Task 17: Read the text and answer the questions:

- 1. What catalysts are employed in reforming of gasoline?
- 2. Why are titration and adsorption procedures with hydrogen and oxygen used? Give your examples.
- 3. In what reactions the selectivity for isomerization varies by a factor of 100 for different catalysts? What are the examples of such reactions?

Determining Catalyst Structure and Properties

The nature of the active centres in catalytic material is further demonstrated by the enhancement of the catalytic activity of relatively inactive materials when they are subjected to intense radiation. Silica gel bombarded by gamma rays from cobalt-60 turns purplish in colour and becomes capable of inducing the reaction $H_2 + D_2 \rightarrow 2HD$ at liquid-nitrogen temperatures. The colour centres, which are positive "holes" (deficiencies) trapped in the vicinity of an oxygen ion next to an aluminum impurity, are bleached in vacua above 200 °C (400 °F) and are destroyed by hydrogen even at room temperature.

The properties of dilute concentrations of platinum metals in oxide matrices, such assilica and alumina, as well as on carbon carriers have been studied by Russian and American scientists. Such catalysts have technical significance in processes for the reforming of gasoline. In such catalysts containing about 0.5 percent by weight of platinum or palladium the degree of dispersion of the metal (that is, the ratio of the number of surface metal atoms to the total number present) is close to one. By contrast, on platinum foil the dispersion is only about 4×10^{-3} . The titration and adsorption procedures with hydrogen and oxygen are employed to evaluate these dispersions.

From these studies it becomes clear that there are two types of behaviour resulting from dispersion. For numerous catalytic processes, ranging from hydrogen-deuteriumex change to the hydrogenation of benzene and the hydrogenolysis of cyclopentane, the reactions are independent of dispersion in the critical region with catalystparticle size of 5 nm or less. Such structure-insensitive processes have been termed facile reactions. On the other hand, there are reactions such as the isomerization of neopentane to isopentane and simultaneous cracking of the latter to isobutane andmethane on platinum-alumina catalysts, where the selectivity for isomerization varies by a factor of 100 for the various catalysts studied (when the hydrogen-neopentane ratio is 10).

Since 1940 various instrumental techniques have been developed to explore the structure of catalytic materials and the character of the adsorbed species, even during the reaction itself. Among these techniques are: electron microscopy, field emission microscopy, electron microprobe methods, magnetic measurements, infrared spectroscopy, Mossbauer spectroscopy, measurements of heats of immersion, flash desorption procedures, low-energy electron diffraction studies, andnuclear magnetic resonance and electron spin resonance techniques.

(From: <u>https://www.britannica.com/science/catalysis/Determination-of-the-structure-and-properties-of-catalysts</u>)

VII. Additional texts

Did you know that zeolites – natural crystalline aluminosilicates with a porous structure – are described as "molecular sieves" because they contain cations that can be exchanged reversibly with other metal ions without destroying the aluminosilicate structure, and thus they rapidly adsorb certain molecules and exclude others?

Task 18: Read the text and make your questions to cover its content:

Other Catalytic Compounds

Polyfunctional heterogeneous catalysis is applied to a group of catalysts in which more than one component of the surface is active in processes under study. One example of a bifunctional the heterogeneous catalyst is the catalyst of metal (platinum or nickel) deposited on a silica-alumina "acidic" base. Such dual functional of are involved in the interconversions catalysts saturated hydrocarbons (paraffins) and unsaturated hydrocarbons (olefins) and normal (straight-chain) and iso (branched-chain) hydrocarbons, as well as in the splitting (cracking) of the hydrocarbon molecules. The interrelations involve metal-catalyzed and acid-catalyzed processes. Operating conditions can be altered to maximize the hydrocracking reactions relative to hydrogenolysis.

A variety of catalysts with "acidic" sites have been found to be active in the dehydration of alcohols and in the cracking and isomerization of hydrocarbons. Among these are silica, obtained by calcination (heating) of silica gel; high-purity alumina, prepared by the calcining of specially prepared aluminum hydroxide; and silicaalumina mixtures. The catalytic sites have been found to have varying degrees of acidity; their exact nature, as well as their characterization in terms of the atomic architecture of the solid catalyst, is still under discussion. In the case of silica-alumina, the sites are ascribed to the presence of trivalent aluminum ions, Al³⁺, in a matrix of quadrivalent silicon ions, Si⁴⁺, which gives rise to charge differences in the neighbourhood of the aluminum ions. These acidic sites can be poisoned by ammonia and amines, a finding that confirms their acidic nature. When these catalysts are treated with alkalies, their catalytic character is greatly modified. On the other hand, treatment with halogen elements, especially fluorine and chlorine, enhances the acidic properties of these oxide materials.

Zeolites are naturally occurring crystalline aluminosilicates that have a porous structure and contain cations, generally of the alkali or alkaline earth metals. The cations can be exchanged reversibly with other metal ions without destroying the aluminosilicate structure. Because the zeolites rapidly adsorb certain molecules and exclude others, they have been given the name "molecular sieves." The adsorption characteristics of natural and synthetic zeolites have been studied since the 1930s. Manufactured zeolites, some of which have structures not found in nature, are employed as dehydrating agents but also may be used for the production of catalytic materials by exchange with cationic elements or by impregnation of metal salt solutions into the pores of the zeolite; a large number of zeolitic catalysts have been developed.

A class of compounds termed electron donor-acceptor complexes has also been studied for its catalytic activity. The class may be exemplified by a complex between metallic sodium (the donor) and anthracene, $C_{14}H_{10}$, a tricyclic hydrocarbon (the acceptor). The complex can be visualized as an anthracene anion and a sodium cation. Such complexes can exchange the hydrogen of the anion with molecular hydrogen that has been brought into contact with the complex. A complex represented by ZH (in which Z represents all of the molecules except for the exchangeable hydrogen) could undergo an exchange with deuterium as follows: $ZH + D_2 \rightarrow ZD + HD$. It could also take part in corresponding exchanges with hydrocarbons or bring about hydrogenation of hydrocarbons. Among other electron-acceptor catalysts are the metal phthalocyanines (compounds related to certain biological catalysts) and activated charcoal. Some donor-acceptor complexes synthesize ammonia from nitrogen-hydrogen mixtures. This reaction represents a close approach to the activity of biological and bacterial catalysts.

(From: <u>https://www.britannica.com/science/catalysis/Determination-of-the-structure-and-properties-of-catalysts</u>)

Task 19. Analyze the text for the key phrases to be used in the following-up discussion. Write down the phrases in your exercise-book.

Task 20. Read the text again for more details and put 5-7 questions (wh-questions / open-end questions).

Task 21. Pair-work. Ask your partner the questions you have made up. Check if the answers are correct.

Task 22. Team-work. Divide into two teams and discuss the text during 5-7 minutes. Choose a presenter in each team to present the main ideas of the text in front of the class. Which of the teams presents best?

Unit 10

AMINO ACIDS

I. Pre-reading activities

Task 1. Discuss the following questions:

- 1) What do we call amino acids?
- 2) What do amino acids deal with?
- 3) What is the name for amino acids' chain?
- 4) Why are amino acids important?
- 5) Where are amino acids located in the human body?
- 6) How many amino acids do you know?

Task 2. Pronounce the following international words after your teacher and guess what they mean:

specific [spə'sifik]	polarity [pəu'lærItI]
nitrogen ['naItrIdʒ(ə)n]	aliphatic [ələ'fætik]
carbon ['kaːbən]	aromatic [ærəu'mæt 1 k]
hydrogen ['haIdrədʒ(ə)n]	protein ['prəuti:n]
oxygen ['vksId3ən]	category ['kætəg(ə)rI]
abiotic [eIbaI'DtIk]	decomposition [dik⊃mpə'zI∫(ə)n]

Task 3. Match the synonyms:

1) envelope	a) proceed
2) significance	b) cover
3) directly	c) immediately
4) occur	d) multitude
5) array	e) value
6) attach	f) circumstance
7) condition	g) afford

Task 4. Match the opposites:

1) importance	a) conceal
2) create	b) mixture
3) present (v)	c) abiotic
4) synthesize	d) insignificant
5) component	e) outdated
6) biodegradable	f) destroy
7) novel	g) decompose

Task 5. Guess from the contents what the underlined words mean:

- 1. Some important elements are found in the <u>side-chains</u> of certain amino acids.
- 2. A <u>substituent</u> is an <u>atom</u> or group of atoms substituted in place of a <u>hydrogen</u> atom on the <u>parent chain</u> of a <u>hydrocarbon</u>.
- 3. A polypeptide is a long, continuous, and unbranched <u>peptide</u> <u>chain.</u>
- 4. An <u>inhibitor</u> can reduce the effectiveness of a <u>catalyst</u> in a catalysed reaction (either a non-biological catalyst or an <u>enzyme</u>).
- 5. Fertilizers enhance the growth of plants.

Task 6. Match the English phrases	on the left with their Ukrainian
equivalents on the right:	

1) neurotransmitter transport	а) друга за величиною складова
2) side-chain group	b) умовно важливо
3) organic substituent	с) харчова добавка
4) conditionally essential	d) органічний замісник
5) nutritional supplement	е) група бічного ланцюга
6) biodegradable plastics	f) нейротрансмісійний транспорт
7) second-largest component	g) пластик, що розкладається під дією мікроорганізмів

<u>II. While-reading activities</u>

Task 7. Read the text and answer the questions:

- 1. What are the defining functional groups of amino acids?
- 2. Why are amino acids important in nutrition?
- 3. What is the basic principle for classification of amino acids?

Amino Acids

Amino acids are biologically important organic compounds containing amine (-NH₂) and carboxylic acid (-COOH) functional groups, usually along with a side-chain specific to each amino acid. The key elements of an amino acid are carbon, hydrogen, oxygen, and nitrogen, though other elements are found in the side-chains of certain amino acids. About 500 amino acids are known and can be classified in many ways. They can be classified according to the core structural functional groups' locations as alpha- (α -), beta- (β -), gamma- (γ -) or delta-(δ -) amino acids; other categories relate to polarity, pH level, and side-chain group type (aliphatic, acyclic, aromatic, containing hydroxyl or sulfur, etc.). In the form of proteins, amino acids comprise the second-largest component (water is the largest) of human muscles, cells and other tissues. Outside proteins, amino acids perform critical roles in processes such as neurotransmitter transport and biosynthesis.

In biochemistry, amino acids having both the amine and the carboxylic acid groups attached to the first (alpha-) carbon atom have particular importance. They are known as 2-, alpha-, or α -amino acids (generic formula H₂NCHRCOOH in most cases, where R is an organic substituent known as a "side-chain"); often the term "amino acid" is used to refer specifically to these. They include the 23 proteinogenic ("protein-building") amino acids, which combine into peptide chains ("polypeptides") to form the building-blocks of a vast array of proteins. These are all L-stereoisomers ("left-handed" isomers), although a few D-amino acids ("right-handed") occur in bacterial envelopes and some antibiotics. Twenty of the proteinogenic amino acids are encoded directly by triplet codons in the genetic code and are known as "standard" amino acids. The other three ("nonstandard" or "non-canonical") are selenocystein (present in many noneukaryotes as well as most eukaryotes, but not coded directly by DNA), pyrrolysine (found only in some archea and one bacterium) and N-formylmethionine (which is often the initial amino acid of proteins in bacteria, mitochondria, and chloroplasts). Pyrrolysine and selenocysteine are encoded via variant codons.

Many important proteinogenic and non-proteinogenic amino acids also play critical non-protein roles within the body. For example, in the human brain, glutamate (standard glutamic acid) and gammaamino-butyric acid ("GABA", non-standard gamma-amino acid) are, respectively, the main excitatory and inhibitory neurotransmitters; hydroxyproline (a major component of the connective tissue collagen) is synthesized from proline; the standard amino acid glycine is used to synthesize porphyrins used in red blood cells; and the non-standard carnitine is used in lipid transport.

Nine proteinogenic amino acids are called "essential" for humans because they cannot be created from other compounds by the human body and, so, must be taken in as food. Others may be conditionally essential for certain ages or medical conditions. Essential amino acids may also differ between species.

Because of their biological significance, amino acids are important in nutrition and are commonly used in nutritional supplements, fertilizers, and food technology. Industrial uses include the production of drugs, biodegradable plastics, and chiral catalysts. (From: https://en.wikipedia.org/wiki/Amino acid)

<u>III. Post-reading activities</u>

Task 8. Complete the following sentences using the text:

- 1) The key elements of an amino acid are _____
- 2) They can be classified according _____ as alpha- (α -), beta- (β -), gamma- (γ -) or delta-(δ -) amino acids.
- 3) Outside proteins, amino acids perform critical roles in processes such as _____.
- 4) Nine proteinogenic amino acids are called ______ for humans because they ______ and, so, must be taken in as food.

Task 9. Read and analyze the definitions given in the text.

Task 10. Answer the questions about the text:

- 1) What are the key elements of amino acids?
- 2) How many amino acids are known?
- 3) What kind of stereoisomers are almost all amino acids?

- 4) What substance do biochemists use for synthesis porphyrins?
- 5) What are the basic ways for classifications of amino acids?
- 6) How many proteinogenic amino acids are essential for humans?
- 7) Which amino acids play non-protein roles within the body?
- 8) How are amino acids used for industrial purposes?

Task 11. Are the following statements about the text true or false? Say why?

- 1) Amino acids contain amine (-NH₂) and carboxylic acid (-COOH) functional groups.
- 2) About 190 amino acids are known and can be classified in many ways.
- 3) Outside proteins, amino acids perform critical roles in processes such as neurotransmitter transport and biosynthesis.
- 4) Thirty of the proteinogenic amino acids are encoded directly by triplet codons in the genetic code and are known as "standard" amino acids.
- 5) Pyrrolysine and selenocysteine are encoded via variant codons.
- 6) Amino acids are insignificant in nutrition.
- 7) Twenty proteinogenic amino acids are called "essential" for humans.

Task 12. Make the list of all the chemicals/ chemistry terms/ procedures/ experiments/ pieces of equipment (glassware) you can find in the text. Check all the examples in your class.

IV. Focus on grammar and lexis

Task 13. Here are the answers to some questions about the text. Write the questions:

- 1) There are two main functional groups.
- 2) The key elements of amino acids are carbon, hydrogen, oxygen, and nitrogen.
- 3) They include 23 proteinogenic ("protein-building") amino acids.
- 4) Nine proteinogenic amino acids are called essential for humans.
- 5) Carnitine is used in lipid transport.
- 6) They are encoded directly by triplet codons in the genetic code. and are known as "standard" amino acids.
- 7) It is often the initial amino acid of proteins in bacteria, mitochondria, and chloroplasts

Task 14. Put the words in the right order to make correct sentences:

- 1) About can 500 acids are ways known and be amino classified in many.
- 2) In biochemistry, amino atom acids both the amine and the carboxylic acid groups attached importance to the first (alpha-) carbon having have particular.
- 3) Pyrrolysine encoded and selenocysteine codons are via variant.
- 4) Essential amino acids differ may species also between.
- 5) Industrial include plastics uses the production of catalysts, biodegradable, and chiral drugs.

Task 15. There is one mistake in each of the following sentences. Find it and write the corrected sentences:

- 1) Twenty of the proteinogenic amino acids encodes directly by triplet codons in the genetic code and are known as "standard" amino acids.
- 2) Amino acids are biologically important organic compounds are contained amine (-NH₂) and carboxylic acid (-COOH) functional groups, usually along with a side-chain specific to each amino acid.
- They known as 2-, alpha-, or α-amino acids (generic formula H₂NCHRCOOH in most cases, where R is an organic substituent known as a "side-chain").
- 4) Often the term "amino acid" used to refer specifically to these.
- 5) Pyrrolysine and selenocysteine are encodes via variant codons.
- 6) They includes 23 proteinogenic ("protein-building") amino acids, which combine into peptide chains ("polypeptides") to form the building-blocks of a vast array of proteins.

Task 16. Translate from Ukrainian into English:

З'єднані пептидними зв'язками; містити первинну аміногрупу; аспарагін виділений зі спаржі; позначати трибуквенним кодом; відповідні перетворюватися y кислоти; амінокислотні послідовності; утворювати ковалентні зв'язки: позначення конфігурації; поліпротеїнові абсолютної амінокислоти. розкладатися під дією мікроорганізмів, велика кількість білків, частини ліпідних мембран.

V. Final tasks

Task 17. Discuss the following ideas with your group-mates:

- 1. You have probably had some experience of making experiments with proteins. How can you describe your experience?
- 2. Say what similarities and differences you have found between alpha-, beta-, gamma- or delta- amino acids.
- 3. What, in your opinion, are the typical characteristics of all amino acids? Give your reasons.

Task 18. Use the phrases given below to retell the text:

The key elements of an amino acid are / proteinogenic amino acids / to be encoded directly by / triplet codons in the genetic code / to be classified according to the core structural functional groups' locations / to play critical non-protein roles within the body / nine proteinogenic amino acids / to be called "essential" for humans / to be important in nutrition / to be commonly used in nutritional supplements.

VI. Individual reading: supplementary text

Task 19. Read the following text and write a summary:

Essential Amino Acids

As we learn about amino acids, it is important to keep in mind that one of the most important reasons to understand amino acid structure and properties is to be able to understand protein structure and properties. We will see that the vastly complex characteristics of even a small, relatively simple, protein are a composite of the properties of the amino acids which comprise the protein.

Humans can produce 10 of the 20 amino acids. The others must be supplied in the food. Failure to obtain enough of even 1 of the 10 essential amino acids, those that we cannot make, results in degradation of the body's proteins – muscle and so forth – to obtain the one amino acid that is needed. Unlike fat and starch, the human body does not store excess amino acids for later use – the amino acids must be in the food every day.

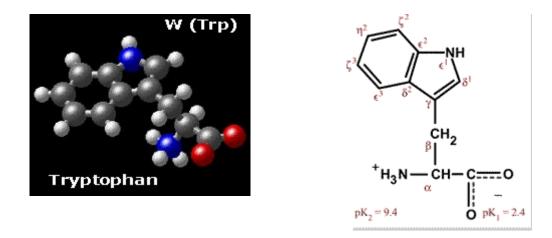
The 10 amino acids that we can produce are alanine, asparagine, aspartic acid, cysteine, glutamic acid, glutamine, glycine, proline, serine and tyrosine. Tyrosine is produced from phenylalanine, so if the diet is deficient in phenylalanine, tyrosine will be required as well.

The essential amino acids are arginine (required for the young, but not for adults), histidine, isoleucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan, and valine. These amino acids are required in the diet. Plants, of course, must be able to make all the amino acids. Humans, on the other hand, do not have all the the enzymes required for the biosynthesis of all of the amino acids. (From: http://www.biology.arizona.edu/biochemistry/problem sets/aa/

aa.html)

VII. Additional texts

Did you know that Tryptophan W (Trp), an essential amino acid, is the largest of the amino acids? It belongs to aromatic R-group, and, according to physical properties, it is nonpolar. It is a derivative of alanine, having an indole substituent on the β carbon. The indole functional group absorbs strongly in the near ultraviolet part of the spectrum. The indole nitrogen can hydrogen bond donate, and as a result, tryptophan, or at least the nitrogen, is often in contact with solvent in folded proteins.



Task 20: Read the text and put your questions to cover its content:

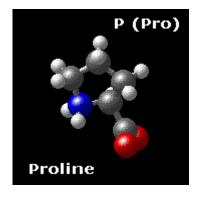
The Chemistry of Amino acids

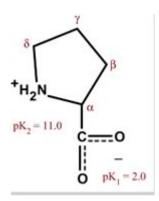
Aromatic amino acids are relatively nonpolar. To different degrees, all aromatic amino acids absorb ultraviolet light. Tyrosine and tryptophan absorb more than phenylalanine; tryptophan is responsible for most of the absorbance of ultraviolet light (ca. 280 nm) by proteins. Tyrosine is the only one of the aromatic amino acids with an ionizable side chain. Tyrosine is one of three hydroxyl containing amino acids.

Acidic amino acids are polar and negatively charged at physiological pH. Both acidic amino acids have a second carboxyl group.

Amides are polar and uncharged, and not ionizable. All are very hydrophilic. Acidic amino acids are polar and negatively charged at physiological pH. Both acidic amino acids have a second carboxyl group.

Proline is the only cyclic amino acid. It is nonpolar and shares many properties with the aliphatic group. Proline is one of the ambivalent amino acids, meaning that it can be inside or outside of a protein molecule. Due to its unique structure, proline occurs in proteins frequently in turns or bends, which are often on the surface.





Hydroxyl amino acids are polar, uncharged at physiological pH, and hydrophilic. The phenolic hydroxyl ionizes with a pKa of 10 to yield the phenolate anion. The hydroxyl groups of serine and threonine are so high that they are generally regarded as nonionizing.

Basic amino acids are polar and positively charged at pH values below their pK_a 's, and are very hydrophilic. Even though the basic amino acids are almost always in contact with the solvent, the side chain of lysine has a marked hydrocarbon character, so it is often found near the surface, with the amino group of the side chain in contact with solvent.

The sulfur-containing amino acids (cysteine and methionine) are generally considered to be nonpolar and hydrophobic. In fact, methionine is one of the most hydrophobic amino acids and is almost always found on the interior of proteins. Cysteine, on the other hand, does ionize to yield the thiolate anion. Even so, it is uncommon to find cysteine on the surface of a protein. There are several reasons. First, sulfur has a low propensity to hydrogen bond, unlike oxygen. A consequence of this fact is that H2S is a gas under conditions that H2O is a liquid. Second, the thiol group of cysteine can react with other thiol groups in an oxidation reaction that yields a disulfide bond. Perhaps, as a consequence, cysteine residues are most frequently buried inside proteins.

(From: <u>http://www.biology.arizona.edu/biochemistry/problem_sets/aa/a</u> <u>a.html</u>)

Task 21. Analyze the text for the key phrases to be used in the following-up discussion. Write down the phrases in your exercise-book.

Task 22. Read the text again for more details and put 5-7 questions (wh-questions / open-end questions).

Task 23. Pair-work. Ask your partner the questions you have made up. Check if the answers are correct.

Task 24. Team-work. Divide into two teams and discuss the text during 5-7 minutes. Choose a presenter in each team to present the main ideas of the text in front of the class. Which of the teams presents best?

Unit 11

THE MASS SPECTRUM

I. Pre-reading activities

Task 1. Discuss the following questions:

1) What is mass spectrum?

2) Where are mass spectra used?

3) Which of the mass spectra features do you know?

Task 2. Pronounce the following international words after your teacher and guess their meaning:

mass [mæs]	detector [dI'tektə]
spectrometer [spek'tr>mItə]	spectrum ['spektrəm]
organic [JI'gænIk]	intense [In'tens]
vacuum ['vækju:m], [-juəm]	process ['prəuses](n), [prə(u)'ses] (v)
electron [I'lektron]	base [beis]
molecule ['mɔlɪkju:l]	peak [pi:k]
ion ['aɪən]	characteristic [kærəktə'rIstIk]
isotope ['aIsətəup]	group [gru:p]
monoisotopic [monovaisə'topik]	spectra ['spektrə]
fragmentation [frægmən'te I ʃ(ə)n]	form [fɔːm]
instrument ['In(t)strəmənt]	method ['meθəd]

Task 3. Match the opposites:

- 1) intense a) blunt
- 2) output b) uniform
- 3) sharp c) input
- 4) accurate d) mild
- 5) various e) inexact

Task 4. Match the synonyms:

- 1) variousa) emanate2) fissionb) exclusion3) resolvedc) different4) doublyd) decided5) exceptione) goal6) arisef) come7) appearg) dissociation
- 8) purpose h) twofold

Task 5. Guess from the context what the underlined words mean:

- 1) The intensity of a peak in the spectrum is thus an indication of <u>the relative number</u> of ions.
- 2) Since the majority of ions are singly charged, the scale is often thought of as a <u>mass scale</u>.
- 3) The base peak is given the <u>arbitrary</u> value of 100 per cent.
- 4) An alternative method of representation is to <u>tabulate</u>.

Task 6. Match the English phrases on the left with their Ukrainian equivalents on the right.

- 1. Fission process
- 2. Ionization chamber
- 3. Electric field
- 4. Charge ratio
- 5. The precise mass

- а) відношення заряду
- b) точна маса
- с) процес ділення
- d) електричне поле
- е) іонізаційна камера

II. While-reading activities

Task 7. Read the text and answer the questions:

- 1. How does a typical mass spectrometer function?
- 2. How can mass spectra be represented?
- 3. What instruments are used in spectrometry?

The Mass Spectrum

In a typical mass spectrometer, an organic compound under high vacuum is bombarded with electrons (of about 70 eV energy). Loss of an electron from the molecule followed by various fission processes gives rise to ions and neutral fragments. The positive ions are expelled from the ionization chamber and resolved by means of a magnetic or an electric field.

The mass spectrum is a record of the current produced by these ions as they arrive at a detector. The intensity of a peak in the spectrum is thus an indication of the relative number of ions; the larger the peak the more abundant the ion producing it. Many mass spectrometers produce up to five traces simultaneously of differing sensitivity to allow weaker peaks to be studied, while also allowing intense peaks to be recorded on the chart. The most intense peak in the spectrum is known as the base peak. Ions produced in the fragmentation of the organic compound are separated according to their mass: charge ratio (m/z) (formerly m/e). Since the majority of ions are singly charged the scale is often thought of as a mass scale; however, doubly charged ions are not uncommon and these appear at half their mass value on the m/z scale. Many compounds give rise to an ion which corresponds to the removal of a single electron from the molecule; this is known as the molecular ion (M) and usually has the highest m/z value in the spectrum, with the exception of a characteristic group of peaks at m/z values of M + 1, M + 2, M + 3, ... etc. The latter are isotope peaks which arise from the fact that many of the elements normally present in organic molecules are not monoisotopic. Peaks in the mass spectrum are usually sharp and appear at integral mass values (with the exception of those arising from some doubly charged ions). Occasionally peaks are observed which are broad, spread over several mass units and of low intensity; these are called metastable peaks and give valuable information about the mode of fragmentation.

Spectra produced by most spectrometers are not in a suitable form for reproduction and cannot easily be compared with spectra from other instruments. Magnetic focusing instruments give spectra with non-linear m/z scales whereas those from quadruple or timeof-flight instruments are linear. It is common practice to represent spectra in the form of a bar graph with a linear m/z scale. The base peak is given the arbitrary value of 100 per cent and the height of each other peak is measured relative to that value. An alternative method of representation is to tabulate the intensity of the current arising from each ion relative to the total ion current. The output from many mass spectrometers can now be handled by computers which allow considerable flexibility in the form of presentation of the spectra. Bar graphs can be produced directly, and a large reference collection has been produced in this way. Instruments vary considerably in the extent to which they can separate ions of closely related m/z values. In the vast majority of routine uses the organic chemist requires only the separation of ions having nominal unit masses of up to molecular weights of about 500-600, which can be achieved using an instrument of low resolution. Occasionally, however, it is of value to determine the precise mass of particular ions accurately (up to six places of decimals) and for this purpose, an instrument of high resolution is required.

(From: <u>https://archive.org/stream/TextbookOfPracticalOrganicChemistry5thEd/VogelPracticalOrganicChemistry5thEditionnewfound</u> <u>V_djvu.txt</u>)

III. Post-reading activities

Task 8. Complete the following sentences using the text:

- 1) The mass ______is a record of the current produced by the _____ as they arrive at detector.
- 2) Ions produced in _____ of the organic compound are separated according to their mass _____.
- 3) Many _____ give rise to an ion which corresponds to _____ of a single electron from the molecule.
- 4) Peaks in the mass spectrum are usually _____ and _____ at integral mass values.
- 5) It is common practice to represent spectra in the form of _________ with a linear ______.

Task 9. Read and analyze the definitions given in the text.

Task 10. Answer the questions about the text:

- 1)What processes take place in a mass spectrometer?
- 2) What is the most intense peak in the spectrum?
- 3)Does the molecular ion have the highest m/z value in the spectrum?
- 4)How can we represent spectra in practice?
- 5)What is an alternative method of representing the intensity of current arising from each ion relative to the total ion current?

Task 11. Are the following statements about the text true or false? Say why.

- 1) The positive ions are expelled from the ionization chamber.
- 2) The smaller the peak the more abundant the ion producing it.
- 3) Many compounds give rise to an ion which does not correspond to the removal of a single electron from the molecule.
- 4) Magnetic focusing instruments give spectra with linear m/z scales whereas those from quadruple or time-of-flight instruments are non-inear.
- 5) The input from many mass spectrometers can now be handled by computers.

IV. Focus on grammar and lexis

Task 12. Here are the answers to some questions about the text. Write the questions:

- 1) The isotope peaks arise from the fact that many of the elements normally present in organic molecules are not monoisotope.
- 2) Because computers allow considerable flexibility in the form of presentation of the spectra.
- 3) The organic chemist requires only the separation of ions having nominal unit masses of up to molecular weights of about 500-600.

Task 13. Put the words in the right order to make correct sentences:

- 1) under is electrons vacuum in an organic with a typical compound high mass spectrometer;
- 2) the relative number of a peak is thus of the intensity an indication of ions in spectrum the;
- 3) the usually in molecular highest the ion the value spectrum has m/z;
- 4) 100 base arbitrary the is value peak given the per cent.

Task 14. Correct the mistakes. There is one mistake in each of the following sentences. Find it and write the corrected sentences:

- 1) The positive ions been expelled from the ionisation chamber and resolved by means of a magnetic or an electric field.
- 2) The base peak is given the arbitrary value by 100 per cent.

- **3)** Occasionally peaks are observed which is broad, spread over several mass units and of low intensity.
- 4) Bar graphs could be producing directly.
- 5) Those isotope peaks arise from the fact that many of the elements normally present in organic molecular are not monoisotopic.
- 6) Occasionally, it is of value to determine the precise mass of particularity ions accurately (up to six places of decimals).

Task 15. Fill in the gaps with suitable prepositions:

- 1) The intensity ____ a peak ____ the spectrum is an indication ____ the relative number ____ ions.
- 2) The most intense peak _ the spectrum is known __ the base peak
- 3) Ions produced _____ the fragmentation ____ the organic compound are separated according ____ their mass.
- 4) A mass spectrum will usually be presented _ a vertical bar graph,
- 5) The mass spectrum is a record _____ the current produced _____ ions as they arrive ____ a detector.
- 6) Even with simple compounds, it is rarely possible to explain the origin ____ all the fragment ions ____ a spectrum.

Task 16. Translate from Ukrainian into English:

- 1) Мас-спектроскопія належить до найінформативніших методів і відрізняється високими аналітичними характеристиками.
- 2) Піки в мас-спектрі, як правило, виразні і з'являються на інтегральних значеннях маси.
- Природа аналізованої речовини, особливості методу іонізації, і вторинні процеси в мас-спектрометрі можуть залишати свій слід у мас-спектрі.
- 4) В органічних речовинах молекули являють собою певні структури, утворені атомами.
- 5) Іони бувають однозарядні і багатозарядні, причому як органічні, так і неорганічні.
- 6) Інструменти значно розрізняються за ступенем, за яким вони можуть відокремити іони, тісно пов'язані зі значеннями m/z.

V. Final tasks

Task 17. Discuss the following ideas with your group-mates:

- 1. Do you agree that mass spectrometry is an analytical chemistry technique? Give your reasons.
- 2. How, in your opinion, can mass spectrometry help biochemists? Give your reasons.
- 3. What is the main purpose of laboratory practice with a mass spectrometer? Provide some evidence to support your viewpoint.

Task 18. Use the phrases below to retell the text in your own words:

A typical mass spectrometer, the positive ions, a detector, intense peaks, charge ratio (m/z), the molecular ion, m/z scale, isotope peaks, metastable peaks, most spectrometers, quadruple, a bar graph, the base peak, an alternative method, computers, instruments, the separation of ions, the precise mass.

VI. Individual reading: supplementary text

Task 19: Read the text and answer the following questions:

- 1. What is the most useful piece of information that can be derived from the mass spectrum?
- 2. How many ways are used to represent the data of isotope peaks?
- 3. What is necessary to determine the molecular formula?

Molecular Formulae

Probably the most useful single piece of information for the organic chemist which can be derived from the mass spectrum is the molecular formula. Provided that the molecular ion can be identified, there are in principle two methods for deriving the molecular formula, using either high or low resolution. The most reliable method, sophisticated the although requiring more high-resolution instrumentation, is the accurate mass measurement of the molecular ion. Since atomic masses are not exact integers, each combination of atoms will have a unique non-integral value. For example, CH₂O and C₂H₆ both have an integral mass of 30 but the accurate masses are 30.010565 and 30.046950 respectively. Accurate mass measurement will therefore distinguish between these two molecules. Tables are available which reduce the problem of relating accurate masses to possible molecular formulae. Accurate mass determination is most

useful to the organic chemist in confirming the identity of a specific molecular ion rather than in suggesting possible formulae for completely unknown molecules.

An alternative method of determination of the molecular formula which utilises low-resolution spectra is based on the measurement of the intensities of the isotope peaks. The data are presented in two ways, firstly as a percentage of the total isotopes present, and secondly as a percentage of the most abundant isotope. Each combination of atoms will thus give rise to a group of isotope peaks of predictable intensities. Taking methane as an example, the ratio is ¹²CH₄: ¹³CH₄. = 100 : 1.08. Thus the intensity of the M + 1 peak will be 1.08 per cent of the intensity of the molecular peak, although there will also be a very small contribution from ¹²C¹H₃³H. Extensive compilations of data are available: they can easily be modified to include elements other than C, H, O and N.

One limitation on the use of isotope peak intensities to determine the molecular formula is that the molecular ion must be relatively intense; otherwise the isotope peaks will be too weak to be measured with the necessary accuracy. Difficulty may also arise from spurious contributions to the isotope peak intensities from the protonated molecular ion, from weak background peaks or from impurities in the sample. In any event, the method is only reliable for molecules having molecular weights up to about 250-300.

(From: <u>https://archive.org/stream/TextbookOfPracticalOrganicChemis</u> <u>try5thEd/VogelPracticalOrganicChemistry5thEditionnewfoundV_djvu</u> .txt)

VII. Additional texts

Did you know that there are two main types of molecular vibrations: stretching and bending? A stretching vibration is a vibration along a bond axis such that the distance between the two atoms is decreased or increased. A bending vibration involves a change in bond angles.

For a diatomic molecule A—B, the only vibration that can occur is a periodic stretching along the A—B bond. The masses of the two atoms and of their connecting bond may be treated, to a first approximation, as two masses joined by a spring, and Hooke's law may be applied. This leads to the expression for the frequency of vibration v in wavenumbers (cm -1).

Infrared Spectroscopy

The light our eyes see is but a small part of a broad spectrum of electromagnetic radiation. On the immediate high energy side of the visible spectrum lies the ultraviolet, and on the low energy side is the infrared. The portion of the infrared region most useful for analysis of organic compounds is not immediately adjacent to the visible spectrum, but is that having a wavelength range from 2,500 to 16,000 nm, with a corresponding frequency range from $1.9*10^{13}$ to $1.2*10^{14}$ Hz.

Photon energies associated with this part of the infrared light (from 1 to 15 kcal / mole) are not large enough to excite electrons, but may induce vibrational excitation of covalently bonded atoms and groups. The covalent bonds in molecules are not rigid sticks or rods, such as found in molecular model kits, but are more like stiff springs that can be stretched and bent. The mobile nature of organic molecules was noted in the chapter concerning conformational isomers. We must now recognize that, in addition to the facile rotation of groups about single bonds, molecules experience a wide variety of vibrational motions, characteristic of their component atoms. Consequently, virtually all organic compounds will absorb infrared radiation that corresponds in energy to these vibrations. Infrared spectrometers, similar in principle to the UV-Visible spectrometer described elsewhere, permit chemists to obtain absorption spectra of compounds that are a unique reflection of their molecular structure.

The complexity of this spectrum is typical of most infrared spectra, and illustrates their use in identifying substances. The gap in the spectrum between 700 & 800 cm⁻¹ is due to solvent (CCl₄) absorption. Further analysis will show that this spectrum also indicates the presence of an aldehyde function, a phenolic hydroxyl and a substituted benzene ring.

Infrared spectra may be obtained from samples in all phases (liquid, solid and gaseous). Liquids are usually examined as a thin film sandwiched between two polished salt plates (note that glass absorbs infrared radiation, whereas NaCl is transparent). If solvents are used to dissolve solids, care must be taken to avoid obscuring important spectral regions by solvent absorption. Perchlorinated solvents such as carbon tetrachloride, chloroform and tetrachloroethene are commonly used. Alternatively, solids may either be incorporated in a thin KBr disk, prepared under high pressure, or mixed with a little non-volatile liquid and ground to a paste (or mull) that is smeared between salt plates.

As far as vibrational spectroscopy, it should be noted that a molecule composed of n-atoms has 3n degrees of freedom, six of which are translations and rotations of the molecule itself. This leaves 3n-6 degrees of vibrational freedom (3n-5 if the molecule is linear). Vibrational modes are often given descriptive names, such as stretching, bending, scissoring, rocking and twisting. The four-atom molecule of formaldehyde, for instance, in its gas phase spectrum provides an example of these terms.

The exact frequency at which a given vibration occurs is determined by the strengths of the bonds involved and the mass of the component atoms. In practice, infrared spectra do not normally display separate absorption signals for each of the 3n-6 fundamental vibrational modes of a molecule. The number of observed absorptions may be increased by additive and subtractive interactions leading to combination tones and overtones of the fundamental vibrations, in much the same way that sound vibrations from a musical instrument interact. Furthermore, the number of observed absorptions may be decreased by molecular symmetry, spectrometer limitations, and spectroscopic selection rules.

(From: <u>https://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Sp</u> ectrpy/Infrared/infrared.htm).

Task 21. Analyze the text for the key phrases to be used in the following-up discussion. Write down the phrases in your exercise-book.

Task 22. Read the text again for more details and put 5-7 questions (wh-questions / open-end questions).

Task 23. Pair-work. Ask your partner the questions you have made up. Check if the answers are correct.

Task 24. Team-work. Divide into two teams and discuss the text during 5-7 minutes. Choose a presenter in each team to present the main ideas of the text in front of the class. Which of the teams presents best?

Unit 12

X-RAY CRYSTALLOGRAPHY

I. Pre-reading activities

Task 1. Discuss the following questions:

- 1) Would visible light be a good choice to diffract in a molecule? Why or why not?
- 2) If you had to choose one of the following to diffract in a molecule: radio waves, microwaves, infrared, visible, ultraviolet or X-ray, which would you choose and why?
- 3) What is the source of X-rays?
- 4) What are the main materials for the anode of an X-ray tube?

Task 2. Pronounce the following international words after your teacher and guess what they mean:

coherent [kə(u)'hIər(ə)nt] (a)	radiation [reIdI'eI∫(ə)n]
incoherent [Inkəu'hIər(ə)nt] (a)	crystallography [krIst(ə)'l>grəfI]
electromagnetic [I,lektrə(u)mæg'netIk]	crystalline ['krIst(ə)laIn]
electron [i'lektrən]	intensity [in'tensiti]
proton ['prəut ɔ n]	fundamental [fAndə'ment(ə)l]
neutron ['nju:tr ɔ n]	vitamin ['vItəmIn], ['vaI-]
constructive [kən'strAktIv]	protein ['prəuti:n]
destructive [dI'strAktIv]	pharmaceutical [faːmə'sju:tɪk(ə)l]
diffraction [d I 'fræk∫(ə)n]	goniometer [gəunI'>mItə]
interference [Intə'fIər(ə)ns]	orientation [⊃:riən'tei∫(ə)n]
monochromatic [monəkrə'mætik]	illuminate [I'l(j)u:mIneIt] (v)

Task 3. Match the opposites:

- 1) constructive
- 2) stronger
- 3) totality
- 4) scatter
- 5) conductor

- a) part
- b) insulator
- c) gather
- d) destructive
- e) weaker

Task 4. Match the synonyms:

1) equal ['i:kwəl] (v)	a) ray
2) angle	b) basic
3) successive [sək'sesiv]	c) amount to
4) beam	d) detect
5) disorder	e) corner
6) fundamental	f) mess
7) reveal	g) consecutive [kən'sekjutiv]

Task 5. Guess from the contents what the underlined words mean:

- 1) In a single-crystal X-ray diffraction measurement, a crystal is mounted on a goniometer.
- 2) The crystalline atoms cause a beam of incident X-rays to diffract into many specific directions.
- 3) By measuring the angles and intensities of these <u>diffracted</u> <u>beams</u>, a crystallographer can produce a three-dimensional picture of the <u>density of electrons</u> within the crystal.
- 4) The <u>scattered</u> waves can themselves be scattered, but this secondary scattering is assumed to be <u>negligible</u>.

Task 6. Match the English phrases on the left with their Ukrainian equivalents on the right:

- 1) tree-dimensional picture
- 2) interplanar distance
- 3) path difference
- 4) crystalline lattice
- 5) small-angle scattering
- 6) diffraction pattern
- 7) finely focused

- а) кристалічна решітка
- b) тонко сфокусований
- с) міжплощинна відстань
- d) малокутове розсіювання
- е) тривимірна картина
- f) різниця ходу
- g) дифракційна картина

II. While-reading activities

Task 7. Read the text and answer the questions:

- 1) What is X-ray crystallography?
- 2) What information can be obtained by this method?
- 3) What is the role of X-ray crystallography in other scientific fields? Give your reasons.

X-ray crystallography is a tool used for identifying the atomic and molecular structure of a crystal, in which the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystal. From this electron density, the mean positions of the atoms in the crystal can be determined, as well as their chemical bonds, their disorder and various other information.

Since many materials can form crystals – such as salts, metals, minerals, semiconductors, as well as various inorganic, organic and biological molecules – X-ray crystallography has been fundamental in the development of many scientific fields. In its first decades of use, this method determined the size of atoms, the lengths and types of chemical bonds, and the atomic-scale differences among various materials, especially minerals and alloys. The method also revealed the structure and function of many biological molecules, including vitamins, drugs, proteins and nucleic acids such as DNA. X-ray crystallography is still the chief method for characterizing the atomic structure of new materials and in discerning materials that appear similar by other experiments. X-ray crystal structures can also account for unusual electronic or elastic properties of a material, shed light on chemical interactions and processes, or serve as the basis for designing pharmaceuticals against diseases.

In a single-crystal X-ray diffraction measurement, a crystal is mounted on a goniometer. The goniometer is used to position the crystal at selected orientations. The crystal is illuminated with a finely focused monochromatic beam of X-rays, producing a diffraction pattern of regularly spaced spots known as reflections. The twodimensional images taken at different orientations are converted into a three-dimensional model of the density of electrons within the crystal using the mathematical method of Fourier transforms, combined with chemical data known for the sample. Poor resolution (fuzziness) or even errors may result if the crystals are too small, or not uniform enough in their internal makeup.

X-ray crystallography is related to several other methods for determining atomic structures. Similar diffraction patterns can be produced by scattering electrons or neutrons, which are likewise interpreted by Fourier transformation. If single crystals of sufficient size cannot be obtained, various other X-ray methods can be applied to obtain less detailed information; such methods include fiber diffraction, powder diffraction and (if the sample is not crystallized) small-angle X-ray scattering (SAXS). If the material under investigation is only available in the form of nanocrystalline powders or suffers from poor crystallinity, the methods of electron crystallography can be applied for determining the atomic structure.

For all above mentioned X-ray diffraction methods, the scattering is elastic; the scattered X-rays have the same wavelength as the incoming X-ray. By contrast, inelastic X-ray scattering methods are useful in studying excitations of the sample, rather than the distribution of its atoms.

(From: https://www.researchgate.net/...crystals.../X-ray+crystallograp X-ray crystallography - ResearchGate)

III. Post-reading activities

Task 8. Complete the following sentences using the text:

- 1) X-ray crystallography is a tool used for identifying the atomic
- and molecular structure of a _____.2) A crystallographer can produce a _____ picture of the density of electrons within the crystal.
- 3) The method also revealed the structure and _____ of many biological molecules, including vitamins, drugs, proteins and nucleic acids such as .
- 4) In a -crystal X-ray diffraction measurement, a crystal is mounted on a _____.
- 5) For all above mentioned X-ray diffraction methods, the scattering is _____; the scattered X-rays have the same as the incoming X-ray.

Task 9. Read and analyze the definitions given in the text.

Task 10. Answer the questions about the text:

- 1) What can be measured by X-ray crystallography?
- 2) Can the method be used to study any biological molecules?
- 3) What types of materials can form crystals?
- 4) Which form has a diffraction pattern?

- 5) Are there any requirements for the formation of a beam of X-rays?
- 6) What different modifications of the method do you know?
- 7) What is a goniometer? How does it function?

Task 11. Are the following statements about the text true or false? *Explain why:*

- 1) The crystalline atoms cause a beam of incident X-rays to diffract into a single specific direction.
- 2) X-ray crystallography determines the size of atoms, the lengths and types of chemical bonds, and the atomic-scale differences among various materials.
- 3) A crystal is mounted on a plate in a single-crystal X-ray diffraction measurement.
- 4) Similar diffraction patterns can't be produced by scattering electrons or neutrons.
- 5) X-ray crystallography can be used to identify the atomic and molecular structure of a liquid.

Task 12. Make a list of all the chemistry terms/ procedures/ experiments etc. you can find in the text. Check the examples in class:

IV. Focus on grammar and lexis

Task 13. Put the words in the right order to make correct sentences:

- 1) with spots crystal as the X-rays spaced a finely known of producing is monochromatic a reflections beam of illuminated diffraction regularly focused pattern;
- 2) atoms X-ray of useful the in elastic are distribution methods its studying of sample scattering the rather in than excitations;
- 3) characterizing for experiments still materials by crystallography and similar X-ray in other chief new appear is materials materials the of the method discerning atomic that structure;
- 4) at chemical method into images crystal the electrons twodimensional sample the trans forms a different known model are Fourier of orientations using data three-dimensional of with combined the within for converted of density the mathematical taken the;

5) incident directions the X-rays specific atoms to cause crystalline into of a diffract many beam.

Task 14. Translate from Ukrainian into English:

- 1) Визначення середніх положень атомів в кристалі є одним із ключових етапів у цьому дослідженні.
- 2) Це засвідчує користь методу непружного розсіювання рентгенівських променів при дослідженні зразків.
- 3) Двовимірні зображення перетворюють у тривимірну модель електронної густини кристалу.
- 4) Необхідним є вимірювання кутів та інтенсивності дифрагованих променів.
- 5) Для позиціювання кристалу використовується гоніометр.
- 6) Застосування методів електронної кристалографії має важливе значення у мінералогії та металургії.
- 7) Рентгенівські кристалічні структури можуть пояснити незвичайні електронні або пружні властивості матеріалу, пролити світло на хімічні взаємодії та процеси.

Task 15. Put it the verbs in brackets in the correct tense form:

- 1) The initial studies _____(reveal) the typical radii of atoms, and _____(confirm) many theoretical models of chemical bonding.
- 2) The crystal is illuminated with a finely _____(focus) monochromatic beam of X-rays, _____(produce) a diffraction pattern of regularly spaced spots known as reflections.
- 3) A systematic X-ray crystallographic study of the silicates _____(to be) _____(undertake) in the 1920s.
- 4) The outgoing X-rays have the same energy, and thus same wavelength, as the incoming X-rays, only with _____(alter) direction.
- 5) The technique of single-crystal X-ray crystallography _____ (have) three basic steps.

Task 16. Correct the mistakes. There is one mistake in each of the following sentences. Find it and write the corrected sentences:

1) The first – and often most difficult – step are to obtain an adequate crystal of the material under study.

- 2) If single crystals of sufficient size cannot be obtain, various other X-ray methods can be applied.
- 3) A crystal is mounted in a goniometer.
- 4) X-ray crystallography is related by several other methods for determining atomic structures.
- 5) When a crystal is mounted and expose to an intense beam of Xrays, it scatters the X-rays into a pattern of spots or reflections that can be observed on a screen behind the crystal.

V. Final tasks

Task 17. Discuss the following ideas with your group-mates:

- 1) Suppose you have to give a lecture on "X-ray crystallography". What points are you going to emphasize in the lecture?
- 2) Do you agree that visible light is a bad choice to diffract in a molecule, unlike X-rays? Explain your choice.
- 3) How can you account for the fact that the directions of possible diffractions depend on the size and shape of the unit cell of the material? Illustrate your ideas with examples.

VI. Individual reading: supplementary text

Task 18: Read the text and answer the following questions:

- 1) What does Bragg's law explain?
- 2) What happens when X-rays are incident on an atom?
- 3) When does the Bragg's diffraction occur?
- 4) What measurements can lead to obtaining a diffraction pattern?

Bragg's Law

Bragg's law gives the angles for coherent and incoherent scattering from a crystal lattice. When X-rays are incident on an atom, they make the electronic cloud move as does any electromagnetic wave. The movement of these charges re-radiates waves with the same frequency, blurred slightly due to a variety of effects; this phenomenon is known as Rayleigh scattering (or elastic scattering). The scattered waves can themselves be scattered but this secondary scattering is assumed to be negligible.

A similar process occurs upon scattering neutron waves from the nuclei or by a coherent spin interaction with an unpaired electron. These re-emitted wave fields interfere with each other either constructively or destructively (overlapping waves either add up together to produce stronger peaks or are subtracted from each other to some degree), producing a diffraction pattern on a detector or film. The resulting wave interference pattern is the basis of diffraction analysis. This analysis is called Bragg diffraction.

Bragg diffraction occurs when radiation, with wavelength comparable to atomic spacings, is scattered in a specular fashion by the atoms of a crystalline system, and undergoes constructive interference. For a crystalline solid, the waves are scattered from lattice planes separated by the interplanar distance d. When the scattered waves interfere constructively, they remain in phase since the path length of each wave is equal to an integer multiple of the wavelength. The path difference between two waves undergoing interference is given by $2dsin\theta$, where θ is the scattering angle. The effect of the constructive or destructive interference intensifies because of the cumulative effect of reflection in successive crystallographic planes of the crystalline lattice. This leads to Bragg's law, which describes the condition on θ for the constructive interference to be at its strongest:

$2d\sin\theta = n\lambda$

where *n* is a positive integer and λ is the wavelength of incident wave. Note that moving particles, including electrons, protons and neutrons, have an associated wavelength called de Broglie wavelength. A diffraction pattern is obtained by measuring the intensity of scattered waves as a function of scattering angle. Very strong intensities known as Bragg peaks are obtained in the diffraction pattern at the points where the scattering angles satisfy Bragg condition.

(From: <u>https://en.wikipedia.org/wiki/Bragg%27s_law</u>)

VII. Additional texts

Did you know that X-ray crystallography had a pioneering role in the development of supramolecular chemistry, particularly in clarifying the structures of the crown ethers and the principles of host–guest chemistry? The latter describes complexes that are composed of two or more molecules or ions that are held together in unique structural relationships by forces other than those of full covalent bonds.

Task 19: Read the text and put your questions to sum it up:

Contributions to Chemistry and Material Science

X-ray crystallography has led to a better understanding of chemical bonds and non-covalent interactions. The initial studies revealed the typical radii of atoms, and confirmed many theoretical models of chemical bonding, such as the tetrahedral bonding of carbon in the diamond structure, the octahedral bonding of metals observed in ammonium hexachloroplatinate, and the resonance observed in the planar carbonate group and in aromatic molecules.

Kathleen Lonsdale's 1928 structure of hexamethylbenzene established the hexagonal symmetry of benzene and showed a clear difference in bond length between the aliphatic C–C bonds and aromatic C–C bonds; this finding led to the idea of resonance between chemical bonds, which had profound consequences for the development of chemistry. Her conclusions were anticipated by William Henry Bragg, who published models of naphthalene and anthracene in 1921 based on other molecules, an early form of molecular replacement. Also in the 1920s, Victor Moritz Goldschmidt and later Linus Pauling developed rules for eliminating chemically unlikely structures and for determining the relative sizes of atoms.

These rules led to the structure of brookite (1928) and an understanding of the relative stability of the rutile, brookite and anatase forms of titanium dioxide. The distance between two bonded atoms is a sensitive measure of the bond strength and its bond order; thus, Xray crystallographic studies have led to the discovery of even more exotic types of bonding in inorganic chemistry, such as metalmetal double bonds, metal-metal quadruple bonds, and three-center, two-electron bonds.

X-ray crystallography – or, strictly speaking, an inelastic Compton scattering experiment – has also provided evidence for the partly covalent character of hydrogen bonds. In the field of organometallic chemistry, the X-ray structure of ferrocene initiated scientific studies of sandwich compounds, while that of Zeise's salt stimulated research into "back bonding" and metal-pi complexes.

Finally, X-ray crystallography had a pioneering role in the development of supramolecular chemistry, particularly in clarifying the structures of the crown ethers and the principles of hostguest chemistry. In material sciences, many complicated inorganic and

organometallic systems have been analyzed using single-crystal methods, such as fullerenes, metalloporphyrins, and other complicated compounds. Single-crystal diffraction is also used in the pharmaceutical industry, due to some problems with polymorphs. The major factors affecting the quality of single-crystal structures are the crystal's size and regularity. Recrystallization is a commonly used technique to improve these factors in smallmolecule crystals. The Cambridge Structural Database contains over 500,000 structures; over 99% of these structures were determined by X-ray diffraction.

(From: <u>https://www.researchgate.net/...crystals.../X-ray+crystallograp</u> X-ray crystallography - ResearchGate)

Task 20: Read the text:

Early Scientific History of Crystals and X-rays

Crystals, though long admired for their regularity and symmetry, were not investigated scientifically until the 17th century. Johannes Kepler hypothesized in his work Strena seu de Nive Sexangula (A New Year's Gift of Hexagonal Snow) (1611) that the hexagonal symmetry of snowflake crystals was due to a regular packing of spherical water particles. The Danish scientist Nicolas Steno (1669) pioneered experimental investigations of crystal symmetry. Steno showed that the angles between the faces are the same in every exemplar of a particular type of crystal, and René Just Haüy (1784) discovered that every face of a crystal can be described by simple stacking patterns of blocks of the same shape and size.

Hence, William Hallowes Miller in 1839 was able to give each face a unique label of three small integers, the Miller indices which remain in use today for identifying crystal faces. Haüy's study led to the correct idea that crystals are a regular three-dimensional array (a Bravais lattice) of atoms and molecules; a single unit cell is repeated indefinitely along three principal directions that are not necessarily perpendicular.

In the 19th century, a complete catalog of the possible symmetries of a crystal was worked out by Johan Hessel, Auguste Bravais, Evgraf Fedorov, Arthur Schön- flies and (belatedly) William Barlow (1894). From the available data and physical reasoning, Barlow proposed several crystal structures in the 1880s that were validated later by X-ray crystallography. However, the available data were too scarce in the 1880s to accept his models as conclusive.

Wilhelm Röntgen discovered X-rays in 1895, just as the studies of crystal symmetry were being concluded. Physicists were initially uncertain of the nature of X-rays, but soon suspected (correctly) that they were waves of electromagnetic radiation, in other words, another form of light. At that time, the wave model of light – specifically, the Maxwell theory of electromagnetic radiation - was well accepted among scientists, and experiments by Charles Glover Barkla showed that X-rays exhibited phenomena associated with electromagnetic waves, including transverse polarization and spectral lines akin to those observed in the visible wavelengths. Singleslit experiments in the laboratory of Arnold Sommerfeld suggested that X-rays had a wavelength of about 1 angstrom. However, X-rays are composed of photons, and thus are not only waves of electromagnetic radiation but also exhibit particle-like properties. Albert Einstein introduced the photon concept in 1905, but it was not broadly accepted until 1922, when Arthur Compton confirmed it by the scattering of X-rays from electrons.

Therefore, these particle-like properties of X-rays, such as their ionization of gases, caused William Henry Bragg to argue in 1907 that X-rays were not electromagnetic radiation. Nevertheless, Bragg's view was not broadly accepted and the observation of X-ray diffraction by Max von Laue in 1912 confirmed for most scientists that X-rays were a form of electromagnetic radiation.

(From: <u>https://www.researchgate.net/...crystals.../X-ray+crystallograp</u> <u>X-ray crystallography - ResearchGate</u>)

Task 21. Analyze the text for the key phrases to be used in the following-up discussion. Write down the phrases in your exercise-book.

Task 22. Read the text again for more details and put 5-7 questions (wh-questions / open-end questions).

Task 23. Pair-work. Ask your partner the questions you have made up. Check if the answers are correct.

Task 24. Team-work. Divide into two teams and discuss the text during 5-7 minutes. Choose a presenter in each team to present the main ideas of the text in front of the class. Which of the teams presents best?

Unit 13

THE NATURE OF PHYSICAL CHEMISTRY

I. Pre-reading activities

Task 1. Discuss the following questions:

- 1) What is the subject of physical chemistry?
- 2) What role does physical chemistry play in understanding of biological molecules?
- 3) What is the difference between physical chemistry and chemical physics?

Task 2. Pronounce the following international words after your teacher and guess what they mean:

phenomena [fI'nɔːmɪnə]	complex ['kɔmpleks]
quantum ['kwɔ:ntəm]	magnetic [mæg'net 1 k]
technique [tek'ni:k]	neutron ['nju:tr ɔ n]
system ['sIstəm]	scheme [ski:m]
material [mə'tIərIəl]	accompany [ə'k∧mpənɪ]
energy ['enədʒɪ]	calculate ['kælkjule I t]
atom ['ætəm]	quantitative ['kw>ntItətIv]
theory ['θ ι ər ι]	biology [baɪ'ɔlədʒɪ]
adsorption [æd'sɔːp∫(ə)n]	condensation [k⊃nden'seI∫(ə)n]

Task 3. Match the synonyms:

1) predict	a). results
2) proposed	b) complete
3) target	c) stuff
4) full	d) omnipresent
5) provide	e) forecast
6) findings	f) suggested
7) material	g) ensure
8) ubiquitous	h) goal

145

Task 4. Match the opposites:

 vaporization absorbed traditional justification distinction to reach 	 a) to avoid b) confutation c) unimportant d) adsorbed e) condensation f) unconventional
6. to reach7. essential	f) unconventional g) similarity

Task 5. Guess from the context what the underlined words mean:

- 1. Physical chemistry is the branch of chemistry <u>concerned</u> with the interpretation of chemistry <u>phenomena</u> in <u>terms</u> of the <u>underlying</u> principles of physics.
- 2. Chemical kinetics examines how <u>rates of reactions respond</u> to changes in <u>conditions</u> or the presence of a catalyst.
- 3. The enormously <u>powerful technique</u> of nuclear magnetic resonance is now <u>ubiquitous</u> in chemistry.
- 4. It provides a basis for understanding the thermodynamic influences that <u>drive</u> chemical reactions <u>forward</u>.
- 5. The <u>scattering</u> of neutrons gives detailed information on the <u>motion</u> of molecules in liquids.
- 6. Physical chemistry is traditionally divided into a <u>number</u> of disciplines, but the <u>boundaries</u> between them are <u>imprecise</u>.

Task 6. Match	the English phrases	on the l	left with	their	Ukrainian
equivaler	nts on the right:				

1) solid-state structure	а) наявність каталізатора
2) nature of the chemical bond	b) об'ємна система
3) x-ray diffraction studies	с) твердотільна структура
4) a bulk system	d) використовується для розрахунку властивостей
5) entropy changes	е) природа хімічного зв'язку
6) the presence of a catalyst	f) рентгенівські дифракційні дослідження
7) used to calculate properties	g) ентропійні зміни

<u>II. While-reading activities</u>

Task 7. Read the text and answer the questions:

- 1. How can you define physical chemistry?
- 2. What branches of science is it subdivided into?
- 3. How useful is physical chemistry in your sphere of studies?
- 4. What prospects of its development can you think of?

Physical Chemistry

Physical chemistry is the branch of chemistry concerned with the interpretation of the phenomena of chemistry in terms of the underlying principles of physics. It lies at the interface of chemistry and physics, inasmuch as it draws on the principles of physics (especially quantum mechanics) to account for the phenomena of chemistry. It is also an essential component of the interpretation of the techniques of investigation and their findings, particularly because these techniques are becoming ever more sophisticated and because their full potential can be realized only by strong theoretical backing. Physical chemistry also has an essential role to play in the understanding of the complex processes and molecules characteristic of biological systems and modern materials.

Physical chemistry is traditionally divided into a number of disciplines, but the boundaries between them are imprecise.

Thermodynamics is the study of transformations of energy. Thermodynamic techniques and analyses are also used to elucidate the tendency of physical processes, such as vaporization, and chemical reactions to reach equilibrium.

Spectroscopy is concerned with the experimental investigation of the structures of atoms and molecules, and the identification of substances by the observation of properties of the electromagnetic radiation absorbed, emitted, or scattered by samples. The enormously powerful technique of nuclear magnetic resonance is now ubiquitous in chemistry. The detailed, quantitative interpretation of molecular and solid-state structure is based in quantum theory and its use in the interpretation of the nature of the chemical bond.

Diffraction studies provide detailed information about the shapes of molecules, and x-ray diffraction studies are central to almost the whole of molecular biology. The scattering of neutrons gives detailed information about the motion of molecules in liquids. Another major component is chemical kinetics. It examines, for example, how rates of reactions respond to changes in conditions or the presence of a catalyst.

Theoretical chemistry is a branch of physical chemistry in which quantum mechanics and statistical mechanics are used to calculate properties of molecules and bulk systems.

Physical chemistry is essential to understanding the other branches of chemistry. It provides a basis for understanding the thermodynamic influences (principally, the entropy changes accompanying reactions) that drive chemical reactions forward. It provides justifications for the schemes proposed in organic chemistry to predict and account for the reactions of organic compounds.

There is a distinction between physical chemistry and chemical physics. In physical chemistry, the target of investigation is typically a bulk system. In chemical physics, the target is commonly an isolated, individual molecule.

(From: <u>http://www.chemistryexplained.com/Ny-Pi/Physical-</u> Chemistry.html)

<u>III. Post-reading activities</u>

Task 8. Complete the following statements using the text:

- 1. Quantum and statistical mechanics in theoretical chemistry are used to _____.
- 2. There are several disciplines of physical chemistry, such as: _____.
- 3. Detailed information about the motion of molecules in liquids can be obtained from _____, which is a part of _____.
- 4. In physical chemistry, the target of investigation is ______, while in chemical physics ______.

Task 9. Read and analyze all the definitions given in the text.

Task 10. Answer the questions based on the text:

- 1. What are the disciplines of physical chemistry?
- 2. What does thermodynamics study?
- 3. Which disciplines examine the connection between the rates of reactions and changes in the conditions?
- 4. What information do diffraction studies provide?
- 5. Which discipline uses quantum and statistical mechanics?
- 6. What research techniques are used in chemistry nowadays?

- 7. Why are the boundaries between the disciplines imprecise?
- 8. How do the targets of investigation of physical chemistry and chemical physics differ?

Task 11. Are the following statements true or false? Explain why:

- 1. Physical chemistry is divided into a number of disciplines, and the differences between them are great.
- 2. Thermodynamic techniques and analyses are used to elucidate the tendency of physical processes and chemical reactions to avoid equilibrium.
- 3. The only difference between physical chemistry and chemical physics is their names.
- 4. The scattering of neutrons gives detailed information about the motion of molecules in liquids, and it is part of x-ray diffraction.
- 5. Physical chemistry provides a basis for understanding the thermodynamic influences that drive chemical reactions backward.
- 6. Physical chemistry is concerned with interpreting chemistry phenomena in terms of the underlying principles of physics.
- 7. Due to physical chemistry we can understand complex processes and molecules characteristic of mechanic systems and wellknown materials.

Task 12. Make a list of all the chemicals/ chemistry terms/ procedures/ experiments/ pieces of equipment (glassware) you can find in the text. Check all the examples in your class.

IV. Focus on grammar and lexis

Task 13. Put in the verbs in brackets in the correct tense form:

- 1. The key concepts of physical chemistry are the ways in which pure physics is _____ (apply) to chemical problems.
- 2. The term "physical chemistry" _____ (coin) by Mikhail Lomonosov in 1752, when he _____ (present) a lecture course entitled "A Course in True Physical Chemistry."
- 3. Modern physical chemistry _____ (originate) in the 1860s to 1880s.
- 4. The technological benefits will follow, as history has _____ (teach) us, with many examples.

5. In a century from now, someone else _____ (write) about its transformative achievements and impact.

Task 14. Put the words in the right order to make correct sentences:

- 1) essential physical understanding chemistry is to the of chemistry branches other;
- 2) are disciplines imprecise between these boundaries;
- 3) about scattering of molecules gives liquids information the motion of neutrons in;
- 4) how chemical catalyst respond kinetics rates examines of reactions to conditions or the presence of a changes in;
- 5) The chemistry technique is enormously powerful now in magnetic ubiquitous resonance of nuclear.

Task 15. Fill the gaps with the suitable preposition:

- 1) It is concerned ______ the experimental investigation.
- 2) It is divided _____ a few parts.
- 3) It has a role to play _____ the understanding _____ complex processes.
- 4) It provides a basis ____ understanding thermodynamic influences.
- 5) The detailed, quantitative interpretation _____ molecular and solidstate structure is based _____ quantum theory.

Task 16. Translate from Ukrainian into English:

- 1) Фізична хімія пов'язана з інтерпретацією явищ хімії в термінах основних принципів фізики.
- 2) Методи фізичної хімії поступово ускладнюються.
- 3) Спостереження за властивостями електромагнітного випромінювання є дуже важливими.
- 4) Вони розділені на кілька дисциплін і межі між ними величезні.
- 5) Раніше ми не знали такої потужної техніки ядерного магнітного резонансу.
- 6) Як швидкість реакцій залежить від змін умов або наявності каталізатора?
- 7) Фізична хімія важлива для розуміння інших галузей хімії.
- Існує певна різниця між фізичною хімією і хімічною фізикою.

V. Final tasks

Task 17. Discuss the following ideas with your group-mates:

- 1. Why is the technique of nuclear magnetic resonance ubiquitous in chemistry now? Give some examples.
- 2. Do you agree that thermodynamics is a discipline of chemistry? Or is it a branch of physics? Explain your opinion.
- 3. How important is physical chemistry for the other branches of chemistry? How does it depend on them?

Task 18. Use the phrases below to retell the text in your own words:

- 1. To have an essential role to play in physics and biology;
- 2. to consist of a number of disciplines;
- 3. to deal with energy transformation;
- 4. to identify substances without spectroscopy;
- 5. to include x-ray diffraction and neutron diffraction studies;
- 6. the presence of a catalyst;
- 7. to affect a reaction;
- 8. to use quantum mechanics and statistical mechanics:
- 9. to be connected with organic chemistry;
- 10. a significant difference between

VI. Individual reading: supplementary text

Task 19: Read the text and answer the following questions:

- 1. What is another name for chemical kinetics?
- 2. What does chemical kinetics study?
- 3. What law describes the elementary reaction?
- 4. How is the energy of activation determined?
- 5. What determines the kinetics of consecutive reactions?
- 6. What are the main factors that influence the reaction rate?

Chemical Kinetics

Chemical kinetics, also known as reaction kinetics, is the study of rates of chemical processes. Chemical kinetics includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction. In 1864, Peter Waage and Cato Guldberg pioneered the development of chemical kinetics by formulating the law of mass action, which states that the speed of a chemical reaction is proportional to the quantity of the reacting substances.

Chemical kinetics deals with the experimental determination of reaction rates from which rate laws and rate constants are derived. Relatively simple rate laws exist for zero order reactions (for which reaction rates are independent of concentration), first order reactions, and second order reactions, and can be derived for others. Elementary reactions follow the law of mass action, but the rate law of stepwise reactions has to be derived by combining the rate laws of the various elementary steps, and can become rather complex. In consecutive reactions, the rate-determining step often determines the kinetics. In consecutive first order reactions, a steady state approximation can simplify the rate law. The activation energy for a reaction is experimentally determined through the Arrhenius equation and the Eyring equation. The main factors that influence the reaction rate include: the physical state of the reactants, the concentrations of the reactants, the temperature at which the reaction occurs, and whether or not any catalysts are present in the reaction.

(From: https://books.google.com.ua/books?id=TC6r1ho75jQC - <u>Chemical Kinetics and Catalysis</u>)

Task 20: Write a twenty-word abstract of the text.

VII. Additional texts

Did you know that kinetics gives information on the reaction rate and reaction mechanism; the balanced chemical equation gives only the stoichiometry of the reaction?

Reaction rates generally increase with increasing reactant concentration, increasing temperature, and the addition of a catalyst. Physical properties such as high solubility increase reaction rates. Solvent polarity can either increase or decrease the reaction rate of a reaction, but increasing solvent viscosity generally decreases reaction rates. Increasing the temperature increases the average kinetic energy of molecules and ions, causing them to collide more frequently and with greater energy, which increases the reaction rate. First dissolve sugar in the hot tea, and then add the ice. Task 21: Read the text and put your questions to cover its content:

Factors Affecting Reaction Rates

Although a balanced chemical equation for a reaction describes the quantitative relationships between the amounts of reactants present and the amounts of products that can be formed, it gives us no information about whether or how fast a given reaction will occur. This information is obtained by studying the chemical kinetics of a reaction, which depend on various factors: reactant concentrations, temperature, physical states and surface areas of reactants, and solvent and catalyst properties if either are present. By studying the kinetics of a reaction, chemists gain insights into how to control reaction conditions to achieve a desired outcome.

Concentration effects

Two substances cannot possibly react with each other unless their constituent particles (molecules, atoms, or ions) come into contact. If there is no contact, the reaction rate will be zero. Conversely, the more reactant particles that collide per unit time, the more often a reaction between them can occur. Consequently, the reaction rate usually increases as the concentration of the reactants increases.

Temperature effects

Increasing the temperature of a system increases the average kinetic energy of its constituent particles. As the average kinetic energy increases, the particles move faster and collide more frequently per unit time and possess greater energy when they collide. Both of these factors increase the reaction rate. Hence the reaction rate of virtually all reactions increases with increasing temperature. Conversely, the reaction rate of virtually all reactions decreases with decreasing temperature. For example, refrigeration retards the rate of growth of bacteria in foods by decreasing the reaction rates of biochemical reactions that enable bacteria to reproduce.

In systems where more than one reaction is possible, the same reactants can produce different products under different reaction conditions. For example, in the presence of dilute sulfuric acid and at temperatures around 100°C, ethanol is converted to diethyl ether:

H₂SO₄ 2CH₃CH₂OH \rightarrow CH₃CH₂OCH₂CH₃+H₂O At 180°C, however, a completely different reaction occurs, which produces ethylene as the major product:

Phase and Surface Area effects

When two reactants are in the same fluid phase, their particles collide more frequently than when one or both reactants are solids (or when they are in different fluids that do not mix). If the reactants are uniformly dispersed in a single homogeneous solution, then the number of collisions per unit time depends on concentration and temperature, as we have just seen. If the reaction is heterogeneous, however, the reactants are in two different phases, and collisions between the reactants can occur only at interfaces between phases. The number of collisions between reactants per unit time is substantially reduced relative to the homogeneous case, and, hence, so is the reaction rate. The reaction rate of a heterogeneous reaction depends on the surface area of the more condensed phase.

Automobile engines use surface area effects to increase reaction rates. Gasoline is injected into each cylinder, where it combusts on ignition by a spark from the spark plug. The gasoline is injected in the form of microscopic droplets because in that form it has a much larger surface area and can burn much more rapidly than if it were fed into the cylinder as a stream. Similarly, a pile of finely divided flour burns slowly (or not at all), but spraying finely divided flour into a flame produces a vigorous reaction.

Solvent effects

The nature of the solvent can also affect the reaction rates of solute particles. For example, a sodium acetate solution reacts with methyl iodide in an exchange reaction to give methyl acetate and sodium iodide:

 $CH_3CO_2Na(soln)+CH_3I(1)\rightarrow CH_3CO_2CH_3(soln)+NaI(soln)$

This reaction occurs 10 million times more rapidly in the organic solvent dimethylformamide [DMF; $(CH_3)_2NCHO$] than it does in methanol (CH₃OH). Although both are organic solvents with similar dielectric constants (36.7 for DMF versus 32.6 for methanol), methanol is able to hydrogen bond with acetate ions, whereas DMF cannot. Hydrogen bonding reduces the reactivity of the oxygen atoms in the acetate ion.

H2SO4 CH3CH2OH→C2H4+H2O

Solvent viscosity is also important in determining reaction rates. In highly viscous solvents, dissolved particles diffuse much more slowly than in less viscous solvents and can collide less frequently per unit time. Thus the reaction rates of most reactions decrease rapidly with increasing solvent viscosity.

Catalyst Effects

A catalyst is a substance that participates in a chemical reaction and increases the reaction rate without undergoing a net chemical change itself. Consider, for example, the decomposition of hydrogen peroxide in the presence and absence of different catalysts. Because most catalysts are highly selective, they often determine the product of a reaction by accelerating only one of several possible reactions that could occur.

Most of the bulk chemicals produced in industry are formed with catalyzed reactions. Recent estimates indicate that about 30% of the gross national product of the United States and other industrialized nations relies either directly or indirectly on the use of catalysts.

(From: <u>https://chem.libretexts.org/Core/Physical_and_Theoretical_Chemistry/Kinetics/Reaction_Rates/Factors_That_Affect_Reaction_Rates</u>)

Task 22. Analyze the text for the key phrases to be used in the following-up discussion. Write down the phrases in your exercise-book.

Task 23. Read the text again for more details and put 5-7 questions (wh-questions / open-end questions).

Task 24. Pair-work. Ask your partner the questions you have made up. Check if the answers are correct.

Task 25. Team-work. Divide into two teams and discuss the text during 5-7 minutes. Choose a presenter in each team to present the main ideas of the text in front of the class. Which of the teams presents best?

Task 26. Consider and discuss the following conceptual problems.

- 1. What information can you obtain by studying the chemical kinetics of a reaction? Does a balanced chemical equation provide the same information? Why or why not?
- 2. If you were tasked with determining whether to proceed with a particular reaction in an industrial facility, why would studying the chemical kinetics of the reaction be important to you?

- 3. What is the relationship between each of the following factors and the reaction rate: reactant concentration, temperature of the reaction, physical properties of the reactants, physical and chemical properties of the solvent, and the presence of a catalyst?
- 4. A slurry is a mixture of a finely divided solid with a liquid in which it is only sparingly soluble. As you prepare a reaction, you notice that one of your reactants forms a slurry with the solvent, rather than a solution. What effect will this have on the reaction rate? What steps can you take to try to solve the problem?
- 5. Why does the reaction rate of virtually all reactions increase with an increase in temperature? If you were to make a glass of sweetened iced tea the old-fashioned way, by adding sugar and ice cubes to a glass of hot tea, which would you add first?
- 6. In a typical laboratory setting, a reaction is carried out in a ventilated hood with air circulation provided by outside air. A student noticed that a reaction that gave a high yield of a product in the winter gave a low yield of that same product in the summer, even though his technique did not change and the reagents and concentrations used were identical. What is a plausible explanation for the different yields?
- 7. A very active area of chemical research involves the development of solubilized catalysts that are not made inactive during the reaction process. Such catalysts are expected to increase reaction rates significantly relative to the same reaction run in the presence of a heterogeneous catalyst. What is the reason for anticipating that the relative rate will increase?
- 8. Water has a dielectric constant more than two times greater than that of methanol (80.1 for H_2O and 33.0 for CH_3OH). Which would be your solvent of choice for a substitution reaction between an ionic compound and a polar reagent, both of which are soluble in either methanol or water? Why?

(From: <u>https://chem.libretexts.org/Core/Physical_and_Theoretical_Chemistry/Kinetics/Reaction_Rates/Factors_That_Affect_Reaction_Rates</u>)

Unit 14

ACTIVATED CARBON

I. Pre-reading activities

Task 1. Discuss the following questions:

- 1) What do you know about activated carbon?
- 2) What is activated carbon used for? Give some examples.
- 3) What is physical adsorption?

Task 2. Pronounce the following international words after your teacher and guess what they mean:

activated ['æktIveItId] (adj)	chlorine ['klɔːrin] (n)
micropore ['maIkrəpJI(r)] (n)	chloride ['klJIraId] (n)
adsorption [æd'sɔːp∫(ə)n] (n)	chlorination [klɔːri'neɪ∫(ə)n] (n)
adsorbate [əd'zɔɪbɪt; -'sɔɪ-] (n)	iodine ['aIədi:n] (n)
migrate [maI'greIt] (v)	process ['prəuses] (n)
polar ['pəulə] (adj)	characterize ['kærəkt(ə)ra 1 z] (v)
atmosphere ['ætməsf 1 ə] (n)	characteristic [kærəktə'r 1 st 1 k (n)
chemical ['kemIk(ə)l] (adj)	product ['pr⊃d∧kt] (n)

Task 3. Match the opposites:

- a) insoluble
- 2) attractive force
- 3) dissolved

1) allow [ə'laʊ]

- 4) heavy
- 5) contaminant

- b) light
- c) cleaning agent
- d) disallow
- e) repulsive force

Task 4. Match the synonyms:

1) distribution	a) to follow
2) to contain	b) multitude
3) preference	c) division
4) to adhere	d) to include
5) variety	e) advantage
	1

Task 5. Guess from the contexts what the underlined words mean:

- 1. The large <u>internal surface</u> area of carbon has several <u>attractive</u> <u>forces</u> that work to attract other molecules.
- 2. A <u>polar</u> substance, i.e. a substance which is <u>soluble</u> in water, cannot or is badly <u>removed</u> by active carbon; while a <u>non-polar</u> substance can be removed totally by active carbon.
- 3. Activated carbon can remove and destroy <u>residual disinfectants</u> through a catalytic <u>reduction reaction</u> that involves a transfer of electrons from the activated carbon surface to the residual disinfectant.
- 4. <u>The abrasion resistance</u> of activated carbon can be important if the carbon is to be used in an <u>application</u> where frequent <u>back-washing</u> will be required.

<u>II. While-reading activities</u>

Task 6. Read the text and answer the questions:

- 1) What is activated carbon made from?
- 2) What are the properties of activated carbon?
- 3) How does activated carbon work?

Activated Carbon

Activated carbon is a material produced from carbonaceous source materials, such as coal, coconuts, nutshells, peat, wood, and lignite. The primary raw material used for activated carbon is any organic material with high carbon content. The carbon-based material is converted into activated carbon through physical modification and thermal decomposition in a furnace, under a controlled atmosphere and temperature. The finished product has a large surface area per unit volume and a network of submicroscopic pores where adsorption takes place.

An activated carbon product can be characterized by its activity and physical properties. Activity properties include pore size distribution that defines the available pore volume of a carbon over three pore size regions: the micropore, mesopore, and macropore regions:

- micropore region less than 100 angstroms
- mesopore region between 100 and 1,000 angstroms
- macropore region greater than 1,000 angstroms

Pore size distribution properties are key indicators of carbon's potential performance for removing contaminants (adsorbates) from water. The molecules encountered in the gas phase are generally smaller than those in the liquid phase applications; therefore, a gas phase carbon has the majority of its pores concentrated in the micropore region. A broad range of pore sizes must be available, both for ease of movement of adsorbates through the carbon pores and for the adsorption of particular molecular sizes. Liquid phase carbons often contain a broader pore size distribution to remove color bodies and larger organic materials, while maintaining some microporosity for the removal of taste and odor compounds. Physical properties include surface area, product density, mesh size, abrasion resistance, and ash content.

Physical adsorption is the primary means by which activated carbon works to remove contaminants from liquid or vapor streams. Carbon's large surface area per unit weight allows for contaminants to adhere to the activated carbon media. The large internal surface area of carbon has several attractive forces that work to attract other molecules. These forces manifest in a similar manner as gravitational force; therefore, contaminants in water are adsorbed (or adhered) to the surface of carbon from a solution as a result of differences in adsorbate concentration in the solution and in the carbon pores. Physical adsorption occurs because all molecules exert attractive forces, especially molecules at the surface of a solid (pore walls of carbon), and these surface molecules seek to adhere to other molecules. The dissolved adsorbate migrates from the solution through the pore channels to reach the area where the strongest attractive forces are located. Contaminants adsorb because the attraction of the carbon surface for them is stronger than the attractive forces that keep them dissolved in solution. Those compounds that exhibit this preference to adsorb are able to do so when there is enough energy on the surface of the carbon to overcome the energy needed to adsorb the contaminant. Contaminants that are organic have high molecular weights and are neutral or non-polar, and in their chemical nature are readily adsorbed on activated carbon. For water adsorbates to become physically adsorbed onto activated carbon, they must both be dissolved in water so that they are smaller than the size of the carbon pore openings and can pass through the carbon pores and accumulate. Besides physical adsorption, chemical reactions can

occur on a carbon surface. One such reaction is chlorine removal from water involving the chemical reaction of chlorine with carbon to form chloride ions.

Activated carbons are different because of the starting material and manufacturing methods. These raw materials establish general characteristics, and differences will exist in the finished product. Most carbons are manufactured from coals. The base raw material and pretreatment steps prior to activation can affect many of the physical and activity characteristics of activated carbon. These different properties make some carbons more suited than others for specific applications. Bituminous coal activated carbons have a broad range of pore diameters. Since these carbons have both a fine and wide pore diameter, they are well-suited for general dechlorination and the removal of a wider variety of organic chemical contaminants from water, including the larger color bodies. Coconut-based carbon tends to exhibit greater microporosity, which is more suited for removal of low concentrations of organics such as in drinking water applications. This property can be deduced when comparing iodine numbers on the activated carbons. Carbons with higher iodine numbers will tend to have larger surface area; therefore, they will have higher capacity for comparatively weakly adsorbed organics. On the other hand, carbons with lower iodine numbers may still have wider pores, which could be favored for removal of large organic molecules. There are some applications where color removal will be better facilitated by a reactivated carbon as opposed to a high iodine carbon.

Activated carbon is used to purify liquids and gases in a variety of applications, including municipal drinking water, food and beverage processing, odor removal, industrial pollution control, and point-of-use filters at home. Many of these home water filters use activated carbon to reliably remove dissolved impurities and disinfection byproducts that can make water taste bad.

(From: <u>http://tigg.com/wp-content/uploads/2017/11/What-is-Activated-</u> <u>Carbon.pdf</u>, by John Sherbondy)

III. Post-reading activities

Task 7. Answer the questions about the text:

- 1) What physical properties does activated carbon possess?
- 2) What are contaminants?

- 3) How can contaminants be described in terms of their chemical nature?
- 4) Why are activated carbons different?

Task 8. Read the text again and complete the following sentences using the information you need:

- 2) Activity properties include ______ that defines the available pore volume of a carbon over three pore size regions: the micropore, mesopore, and macropore regions.
- 3) _____ migrates from the solution through the pore channels to reach the area where the strongest attractive forces are located.
- d) Most carbons are manufactured from ______.
- 4) On the other hand, carbons with lower ______ may still have wider pores, which could be favored for removal of large organic molecules.
- 5) Coconut-based carbon tends to exhibit greater ______, which is more suited for ______ of organics such as in drinking water applications.

Task 9. Are the following statements about the text true or false? *Explain why.*

- 1) Activated carbons are different because of the starting material and manufacturing methods.
- 2) Physical properties include pore size distribution that defines the available pore volume of carbon over the micropore, mesopore, and macropore regions.
- 3) Carbon's large surface area per unit weight allows for contaminants to adhere to the activated carbon media.
- 4) The finished product has a large surface area per unit volume and a network of macroscopic pores where adsorption occurs.
- 5) Bituminous coal activated carbons have a broad range of pore diameters.

Task 10. Make a list of all the chemicals/ chemistry terms/ procedures/ experiments etc. you can find in the text. Check all the examples in your class.

IV. Focus on grammar and lexis

Task 11. Match the beginning of the sentence in the first column with its end in the second column:

1) The finished product has	a) exhibit greater microporosity
2) Besides physical adsorption,	b) a broader pore size distribution
3) Activated carbon is used to	c) the attraction of the carbon
	surface for them is stronger than
	the attractive forces
4) Coconut-based carbon tends to	d) a large surface area per unit
	volume
5) Contaminants adsorb because	e) purify liquids and gases
6) Liquid phase carbons often	f) chemical reactions can occur on
contain	a carbon surface

Task 12. Put the words in the right order to make sentences:

- 1) occurs all physical adsorption exert because molecules attractive forces;
- 2) the majority carbon a gas phase of its pores has in the concentrated micropore region;
- 3) surface area physical properties mesh size product density include abrasion resistance and ash content;
- 4) can product be characterized and physical properties an activated carbon by its activity;
- 5) may still with lower wider pores iodine numbers carbons have.

Task 13. Fill in the gaps with a suitable preposition:

- 1) Ash content can play an important role ____ applications____ water treatment.
- b) Activated carbon adsorption is an effective technology _____ environmental remediation, industrial processing and municipal water treatment.
- c) Activated carbon (activated charcoal) can be made ____ many substances containing high carbon content such __ coal, coconut shells and wood.
- d) Activated carbon has the strongest physical adsorption forces, or the highest volume _____ adsorbing porosity.
- e) This type is used _____ both liquid and gas phase applications.

f) The raw material has a very large influence _____ the characteristics and performance _____ the activated carbon.

Task 14. Translate from Ukrainian into English:

Вуглецевмісна сировина; забруднюючі речовини; розподіл пор за розмірами; мікропористість; макропора; сила тяжіння; фільтри для очистки води; зворотне промивання; велика площа поверхні.

V. Final tasks

Task 15. Discuss the following ideas with your group-mates:

- 1. Explain in your own words how activated carbon works.
- 2. Describe physical and chemical properties of activated carbon.
- 3. How useful and important is activated carbon in human life? Give your reasons.

Task 16. Use the phrases below to retell the text in your own words:

Carbonaceous source materials; activity properties; pore size distribution properties; physical adsorption; the dissolved adsorbate; chloride ions; bituminous coal activated carbons; coconut-based carbon; microporosity.

VI. Individual reading: supplementary text

Task 17: Read the text and answer the questions:

- 1. How can you describe the method of carbon filtering?
- 2. Where is carbon filtering used?
- 3. What types of carbon filters do you know?
- 4. How efficient are they?
- 5. What is known about the history of carbon filtering?

Carbon Filtering

Carbon filtering is a method of filtering that uses a bed of activated carbon to remove contaminants and impurities, using chemical adsorption. Each particle / granule of carbon provides a large surface area/pore structure, allowing contaminants the maximum possible exposure to the active sites within the filter media. One pound (450 g) of activated carbon contains a surface area of approximately 100 acres (40 Hectares).

Activated carbon works via a process called adsorption, whereby pollutant molecules in the fluid to be treated are trapped inside the pore structure of the carbon substrate. Carbon filtering is commonly used for water purification, in air purifiers and industrial gas processing, for example the removal of siloxanes and hydrogen sulfide from biogas. It is used in a number of other applications, including respirator masks, the purification of sugarcane and in the recovery of precious metals, especially gold. It is also used in cigarette filters.

Active charcoal carbon filters are most effective at removing chlorine, sediment, volatile organic compounds (VOCs), taste and odor from water. They are not effective at removing minerals, salts, and dissolved inorganic compounds.

The sizes of typical particles that can be removed by carbon filters range from 0.5 to 50 micrometres. The particle size will be used as part of the filter description. The efficacy of a carbon filter is also based upon the flow rate regulation. When the water is allowed to flow through the filter at a slower rate, the contaminants are exposed to the filter media for a longer amount of time.

There are two predominant types of carbon filters used in the filtration industry: powdered block filters and granular activated filters. In general, carbon block filters are more effective at removing a larger number of contaminants, based upon the increased surface area of carbon. Many carbon filters also use secondary media such as silver to prevent bacteria growth within the filter. Alternatively, the activated carbon itself may be impregnated with silver to provide this bacteriostatic property.

Carbon filters have been used for several hundred years and are considered one of the oldest means of water purification. Historians have shown evidence that carbon filtration may have been used in ancient Egyptian cultures for medical purposes and as a purifying agent. 2000 B.C. A Sanskrit text refers to filtering water through charcoal (1905 translation of "Sushruta Samhita" by Francis Evelyn Place). The first recorded use of a carbon filter to purify potable water on a large scale occurred in 19th century England. Currently, carbon filters are used in individual homes as point-of-use water filters, groundwater remediation, landfill leachate (water that carries salts dissolved out of materials through which it has percolated, especially polluted water from a refuse tip), industrial wastewater and, occasionally, in municipal water treatment facilities. They are also used as pre-treatment devices for reverse osmosis systems and as specialized filters designed to remove chlorine-resistant cysts, such as giardia (which cause an infection of the intestine with a flagellate protozoan, leading to diarrhea and other symptoms) and cryptosporidium (a parasitic coccidian protozoan found in the intestinal tract of many vertebrates, where it sometimes causes disease).

(From: <u>https://en.wikipedia.org/wiki/Carbon_filtering</u> and <u>https://ipfs.io/ipfs/QmXoypizjW3WknFiJnKLwHCnL72vedxjQkDDP</u> <u>1mXWo6uco/wiki/Carbon_filtering.html</u>).

VII. Additional texts

Did you know that the higher the internal surface area, the higher the effectiveness of carbon? The surface area of activated carbon is impressive: 500 to 1,500 m2/g or even more; a spoonful of activated carbon easily equates the surface area of a soccer field. It is in the activation process that this vast surface area is created. The most common process is steam activation; at around 1,000°C steam molecules selectively burn holes into the carbonized raw material, thus creating a multitude of pores inside the carbonaceous matrix. In chemical activation, phosphoric acid is used to build up such a porous system at a lower temperature.

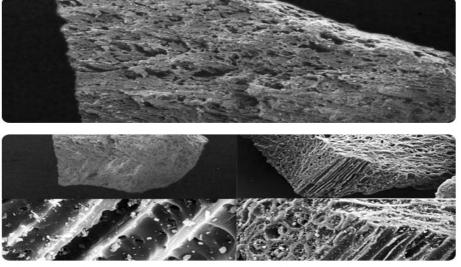
Task 18: Read the text and put your questions to cover its content:

Manufacturing Activated Carbon

Carbonaceous materials are activated using two methods: steam activation and chemical activation.

Steam activation is the most widely used process because it is generally used to activate both coconut shell and coal-based carbons. Steam activated carbons are produced in a two-stage process. Firstly the raw material, in the form of lumps, pre-sized material, briquettes or extrudates, is carbonized by heating in an inert atmosphere such as flue gas, so that dehydration and devolatilization of the carbon occur. For this stage temperatures usually do not exceed 700 C. Carbonization reduces the volatile content of the source material to below 20 %. A coke is produced which has pores that are either small or too restricted to be used as an adsorbent. The second stage is the activation stage which enlarges the pore structure, increases the internal surface area and makes it more accessible. The carbonized product is activated with steam at a temperature between 900 C and 1,100 C. The chemical reaction between the carbon and steam takes place at the internal surface of the carbon, removing carbon from the pore walls and thereby enlarging the pores. The steam activation process allows the pore size to be readily altered and carbons can be produced to suit specific end-sues. For an example, the pore structure has to be opened up more for the adsorption of small molecules from a solution, as in water purification, than for the adsorption of large colour molecules in sugar decolorization.

Steam activation produces activated carbon in the form of 1mm to 3mm pieces, which are crushed and screened to remove fines and dust to meet the specifications for granular activated carbons. To produce powdered activated carbons, the carbon pieces are further ground using a gentle pulverizing action.



Chemical activation is generally used for the production of activated carbon from sawdust, wood or peat. Chemical activation involves mixing the raw material with an activating agent, usually phosphoric acid, to swell the wood and open up the cellulose structure. The paste of raw material and phosphoric acid is dried and then carbonized, usually in a rotary kiln (a furnace or oven for burning, baking, or drying), at a relatively low temperature of 400 C to 500 C. On carbonization, the chemical acts as a support and does not allow the char produced to shrink. It dehydrates the raw material resulting in the charring and amortization of the carbon, creating a porous structure and an extended surface area. Activity is controlled by altering the proportions of raw material to reagent used. For phosphoric acid the ratio is usually between 1: 0.5 and 1: 4; activity increases with higher reagent concentration and is also affected by the temperature and residence time in the kiln.

Activated carbons produced by this method have a suitable pore distribution to be used as an adsorbent without further treatment. This is because the process involves an "acid wash" as a purifying step in steam activated carbons – post activation. Chemically activated carbons, however, have a lower purity than specifically acid-washed steam activated carbons as they contain a small amount of residual phosphate.

This chemical activation process mostly yields a powdered activated carbon. If granular material is required, granular raw materials are impregnated with the activating agent and the same method is used. The granular activated carbons produced have a low mechanical strength, however, and are not suitable for many gas phase uses. In some cases, chemically activated carbon is given a second activation with steam to impart additional physical properties.

(From: <u>http://www.haycarb.com/activated-carbon</u>)

Task 19. Analyze the text for the key phrases to be used in the following-up discussion. Write down the phrases in your exercise-book.

Task 20. Read the text again for more details and put 5-7 questions (wh-questions / open-end questions).

Task 21. Pair-work. Ask your partner the questions you have made up. Check if the answers are correct.

Task 22. Team-work. Divide into two teams and discuss the text during 5-7 minutes. Choose a presenter in each team to present the main ideas of the text in front of the class. Which of the teams presents best?

Unit 15

BIODEGRADABLE DRUG DELIVERY SYSTEMS

I. Pre-reading activities

Task 1. Discuss the following questions:

- 1) What do you know about biodegradable polymers?
- 2) What ways of delivering drugs do you know?
- 3) Why are polymers used for drug delivery?
- 4) What is biodegradation?
- 5) What negative effects may polymers have on a human body?

Task 2. Pronounce the following international words after your teacher and guess what they mean:

osmosis [Jz'məusIs]	microscopy [maɪ'krɔskəp1]
accumulation [əkju:mjə'leɪʃ(ə)n]	parenteral [pæ'rent(ə)r(ə)l]
degradation [degrə'de $I \int (\partial n)$]	behavior [bI'heIvjər], [bə-]
morphology [mɔː'fɔlədʒɪ]	hydrolysis [haɪ'drɔləsɪs]
barrier ['bær 1 ə]	irradiation [I,reIdI'eI∫(ə)n]
molecular [mə'lekjulə]	ingredient [In'gridIənt]
diffusion [dɪ'fju:ʒ(ə)n]	decomposition [dik⊃mpə'zɪʃ(ə)n]
synthetic [sIn'θetIk]	cohesion [kəu'hi:3(ə)n]
adhesion [əd'hi:3ən]	metabolic [metə'bɔlɪk]

Task 3. Match the synonyms:

a) decomposition
b) constancy
c) balm
d) processing
e)) innate
f) unity
g) feature

Task 4. Match the opposites:

1) diffusion	a) hydration
2) hydrolysis	b) absorption
3) adhesion	c) osmosis
4) synthetic	d) cohesion
5) irradiation	e) natural

Task 5. Guess from the context what the underlined words mean:

- 1. <u>Biodegradable polymers</u> are a specific type of polymers that break down after their <u>intended</u> purpose to result in natural byproducts such as gases (CO₂, N₂), water, biomass, and inorganic salts.
- 2. These polymers are found both <u>naturally</u> and <u>synthetically</u> made, and largely consist of <u>ester</u>, <u>amide</u>, and <u>ether</u> functional groups.
- 3. The structure of biodegradable polymers is instrumental in its <u>properties</u>.
- 4. One of the most active areas of research in biodegradable polymers is controlled <u>drug delivery</u> and <u>release</u>.
- 5. The great <u>benefit</u> of a biodegradable drug delivery system is the ability of the <u>drug carrier</u> to target the release of its <u>payload</u> to a specific <u>site</u> in the body and then degrade into nontoxic materials that are then <u>eliminated</u> from the body via natural <u>metabolic pathways</u>.
- 6. The polymer slowly <u>degrades</u> into smaller fragments, releasing a natural product, and there is controlled ability <u>to release</u> a drug. The drug slowly releases as polymer degrades.

Task 6. Match the English phrases on the left with their Ukrainian equivalents on the right:

1) drug delivery	а) низькомолекулярні
	фрагменти
2) low molecular weight	b) площа поверхні
fragments	
3) parenteral administration	с) доставка ліків
4) ion exchange	d) виведення з організму
5) surface area	е) іонний обмін
6) elimination from the body	f) парентеральне введення

<u>II. While-reading activities</u>

Task 7. Read the text and answer the questions:

- 1. Why are biodegradable polymers interesting for investigation?
- 2. How can we control the release of drugs?
- 3. Which polymers are best suited to deliver drugs? Why?

Biodegradable Drug Delivery Systems

During the last two decades, significant advances have been made in the controlled release drug delivery of therapeutic agents. Drug release can be controlled by several means, such as diffusion through a rate-controlling membrane or a matrix, osmosis, ion exchange, or degradation of a matrix or a part of a matrix.

Biodegradation for controlling drug delivery has the advantage that the drug delivery device may not have to be removed from the site of action after drug delivery is completed and the accumulation of polymers in the body during prolonged applications is avoided.

Polymers have been used extensively in controlled drug delivery systems. There are non-degradable polymers, those which are not hydrolytically or enzymatically cleaved in vivo and biodegradable systems available.

Biodegradable polymers have been studied extensively for their biomedical applications, such as temporary scaffold, temporary barrier for surgical adhesion, and matrices for drug delivery systems. Bioresorbable polymers, which degrade to low molecular weight fragments and are eliminated from the body, are preferred for systemic applications.

A wide variety of natural and synthetic biodegradable polymers have been investigated for prolonged drug release. However, only a few have reached the stage of clinical experimentations due to the fact that being biodegradable is not sufficient. Many other prerequisites must be fulfilled for clinical use and commercialization as biocompatibility, biofunctionality and stability. Synthetic polymers offer more advantages than natural materials, since they can be tailored to give a wider range of properties and more predictable lotto-lot uniformity. The most popular and well understood class is the polyesters. Their commercial availability in a variety of polymer ratios and molecular weights, make them desirable candidates for product development. When the polymers are fabricated into controlled drug delivery systems, additional qualities such as surface area, bulk density, surface morphology and particle size are introduced, and many affect both degradation and drug release from the polymeric system. Hausberger and DeLuca described a characterization program consisting of techniques that include DSC for thermal analysis; 13C nuclear magnetic resonance spectroscopy (NMR) to determine the comonomer ratio and sequence distribution of copolymers; size exclusion chromatography (SEC) for molecular weight; scanning electron microscopy (SEM) for surface morphology; gas adsorption for determination of specific surface area; tapped bulk volume measurements to determine bulk density of the microspheres; and in vitro analysis of degradation behavior.

When the polymers are intended for parenteral administration, the final polymeric devices should meet the pharmacopoeial requirements of sterility. However, the physicochemical liability of the polymers limits most conventional methods to sterilize. Since sterilization by autoclaving induces a degradation of PLGA by hydrolysis and ethylene oxide leads to toxic residues, ionizing irradiation is the most used method. Nevertheless, the effects of γ irradiation on PLGA showed controversial results, depending on the active ingredient used. Montanari et. al compared the effect obtained by β - and γ - irradiation performed on bupivacaine loaded PLGA microspheres. They found that the microspheres were more sensitive to γ -irradiation, which caused an increase of the in vitro drug release. (From: <u>http://www.diss.fuberlin.de/diss/servlets/MCRFileNodeServlet</u> /FUDISS_derivate_00000002179/1_introduction.pdf?hosts=)

III. Post-reading activities

Task 8. *Complete the following sentences using the text:*

- 1) Drug _____ can be controlled by several means, such as diffusion through a rate-controlling membrane or a matrix.
- 2) There are non-degradable polymers, those which are not hydrolytically or enzymatically _____ in vivo, and biodegradable systems available.
- 3) Polymers have been used _____ in controlled drug _____
 systems.

- 4) Biodegradable polymers have been studied ______ for their applications such as temporary scaffold, temporary barrier for surgical _____, and matrices for drug delivery systems.
 5) When the polymers are intended for ______ administration, the
- final polymeric devices should meet the pharmacopoeial requirements of ______.

Task 9. Read and analyze all the definitions given in the text.

Task 10. Are the following statements about the text true or false? Say why:

- 1) Polymers have been used extensively in controlled drug delivery systems.
- 2) All biodegradable polymers have reached the stage of clinical experiments.
- 3) Synthetic polymers offer more advantages than natural materials, since they can be tailored to give a wider range of properties and more predictable lot-to-lot uniformity.
- 4) The most popular and well understood class is polyketones.
- 5) Sterilization by autoclaving induces a degradation of PLGA by hydrolysis.
- 6) When the polymers are intended for rectal administration, the final polymeric devices should meet the pharmacopoeial requirements of sterility.
- 7) Biodegradable polymers have been studied extensively for their biomedical applications.

Task 11. Make a list of all the chemical/ chemistry terms/ procedures/ experiments/ pieces of equipment (glassware) you can find in the text. Check all the examples in your class.

IV. Focus on Grammar and Lexis

Task 12. Put in the verbs in brackets in the correct form:

In recent years there _____ (to be) an increase in interest in biodegradable polymers. Two classes of biodegradable polymers can ______ (distinguish): synthetic or natural polymers. Biodegradable polymers have been widely _____ (use) in biomedical applications because of their known biocompatibility and biodegradability. Degradable polymeric biomaterials ____ (to be) preferred candidates for _____ (develop) therapeutic devices such as temporary prostheses, three dimensional porous structures as scaffolds for tissue engineering and as controlled/ (sustain) release drug delivery vehicles. Biodegradable materials _____ (use) in packaging, agriculture, medicine and other areas. In the biomedical area, polymers are generally _____ (use) as implants and are ______ (expect) to perform long term service. These improvements contribute to _____ (make) medical treatment more efficient and to _____ (minimize) side effects and other types of inconveniences for patients.

Task 13. Here are the answers to some questions about the text. Write the questions:

- 1) Biodegradation is the chemical dissolution of materials by bacteria, fungi, or other biological means.
- 2) These polymers are often synthesized by condensation reactions, ring opening polymerization, and metal catalysts.
- 3) Polymers have been used extensively in controlled drug delivery systems.
- 4) The benefit of a biodegradable drug delivery system is the ability of the drug carrier to target the release of its payload to a specific site in the body and then degrade into nontoxic materials that are then eliminated from the body via natural metabolic pathways.
- 5) In order to achieve efficient targeted delivery, the designed system must avoid the host's defense mechanisms and circulate to its intended site of action.
- 6) The types of sustained release formulations include liposomes, drug loaded biodegradable microspheres and drug polymer conjugates.

Task 14. Put the words in the right order to make correct sentences:

- 1) popular is polyesters well the class and understood the understood is most;
- 2) last technology the decades controlled six over progressed delivery drug has;

- 3) biodegradable have to not the clinical that stage of being fact due few is the a experimentations only sufficient reached;
- 4) by PLGA a degradation the hydrolysis of by induces sterilization autoclaving;
- 5) biofunctionality commercialization must as be clinical use biocompatibility other for fulfilled many stability and prerequisites and.

Task 15. Translate from Ukrainian into English:

- Біоруйнування це хімічне розщеплення, що спричиняється біохімічними реакціями, у першу чергу, каталізується ферментами, які синтезують мікроорганізми.
- 2) Окрім того, покращується біодоступність і стає можливим контрольоване вивільнення ліків.
- 3) Спрямована доставка дозволяє значно зменшити токсичність лікарських препаратів і економно їх витрачати.
- Полімери дуже широко використовуються для контрольованої доставки ліків.
- 5) Біодеградуючі полімери та біоматеріали також представляють значний інтерес для тканинної інженерії.
- 6) Біодеградуючі полімери для контрольованої доставки ліків мають відповідати певним вимогам, а саме: бути нетоксичними, легко стерилізуватися, і продукти їх розпаду мають легко виводитися з організму.
- 7) Для контрольованої доставки лікарських препаратів краще використовувати синтетичні полімери.
- 8) Швидкість вивільнення ліків, насамперед, залежить від в'язкості препарату.

V. Final tasks

Task 16. Discuss the following ideas with your group-mates:

- 1) Do you agree that biodegradable drug delivery systems are a promising area of research at present? Give your reasons.
- 2) How do you understand the expression "controlled drug delivery systems?"
- 3) Suppose you have to deliver a lecture on "Biodegradable Drug Delivery Systems". What points would you emphasize in the lecture and why?

Task 17. Use the phrases below to retell the text in your own words:

Drug release can be controlled; to have the advantage; studied extensively for their biomedical applications; to degrade to low molecular weight fragments; being biodegradable is not sufficient; can be tailored; additional qualities; surface area; bulk density; surface morphology; the final polymeric devices; to meet requirements; ionizing irradiation; the most widely used method.

VI. Individual reading: supplementary text

Task 18: Read the text and answer the following questions:

- 1) Why are polyesters best studied for controlled drug delivery?
- 2) What determines the degradation and bioresorption characteristics of polymers?
- 3) What is the main route of polyester degradation?

PLA and PLGA

Aliphatic polyesters, such as poly(D,L-lactide) (PLA) and poly(D,L-lactide -coglycolide) (PLGA), belong to the most widely investigated polymers because of their biocompatibility, predictability of degradation kinetics, ease of fabrication and regulatory approval by the FDA (Food and Drug Administration). They are synthesized by ring opening polymerization of corresponding cyclic dimmers, namely lactide diastereomers and glycolide, using Sn octanoate or Sn chloride as the initiator. Since degradation and bioresorption characteristics are very much dependent on chain characteristics and solid morphology, it is important to produce polymers with identical characteristics from batch to batch. Vert et. al founded that polymers initiated by Zn metal and Sn octanoate are different insofar as water uptake, degradation and fate of initiator residues are concerned.

The commercially available PLGA polymers are usually characterized in terms of intrinsic viscosity, which is directly related to their molecular weights. A broad spectrum of performance characteristics of these polymers can by obtained by careful manipulation of four key variables: monomer stereochemistry, comonomer ratio, polymer chain linearity and polymer molecular weight.

The racemic poly(DL-lactide) DL-PLA is less crystalline and lower melting than the two stereoregular polymers, D-PLA and L-

PLA. Further, the copolymers of lactide and glycolide are less crystalline than the two homopolymers of the two monomers. In addition, the lactic acid polymer, because of the methyl group, is more hydrophobic than the glycolide polymer. The Tg (glass transition temperature) values range from 40 to 65°C. Poly(L-lactide) has the highest value and the Tg of PLGAs decrease with decrease of lactide content in the copolymer composition and with decrease in their molecular weight.

Their primary degradation route is hydrolysis. Degradation proceeds first by diffusion of water into the material (initially into the more amorphous zones) followed by random hydrolysis, fragmentation of the material, and finally a more extensive hydrolysis accompanied by phagocytosis, diffusion and metabolism. The hydrolysis is affected by the size and hydrophilicity of the particular polymer implant, the cristallinity of the polymer and the pH and temperature of the environment.

(From: <u>http://www.diss.fuberlin.de/diss/servlets/MCRFileNodeServlet</u> /FUDISS_derivate_00000002179/1_introduction.pdf?hosts=)

VII. Additional texts

Did you know that The field of "biomimetics" may be described as the "abstraction of good design from nature" or, plainly put, the "stealing of ideas from nature". The goal is to make materials for nonbiological uses under inspiration from the natural world by combining them with man-made, non-biological devices or processes.

In the biomedical field, the goal is to develop and characterize artificial materials or, in other words, "spare parts" for use in the human body to measure, restore, and improve physiologic function, and enhance survival and quality of life. Typically, inorganic (metals, ceramics, and glasses) and polymeric (synthetic and natural) materials have been used for such items as artificial heart-valves, (polymeric or carbon-based), synthetic blood-vessels, artificial hips (metallic or ceramic), medical adhesives, sutures, dental composites, and polymers for controlled slow drug delivery. The development of new biocompatible materials includes considerations that go beyond nontoxicity to bioactivity as it relates to interacting with and, in time, being integrated into the biological environment as well as other tailored properties depending on the specific "in vivo" application. Task 19: Read the text and put your questions to cover its content:

Biocompatible and Biodegradable Polymers

One area of intense research activity has been the use of biocompatible polymers for controlled drug delivery. It has evolved from the need for prolonged and better control of drug administration. The goal of the controlled release devices is to maintain the drug in the desired therapeutic range with just a single dose. Localized delivery of the drug to a particular body compartment lowers the systemic drug level, reduces the need for follow-up care, preserves medications that are rapidly destroyed by the body, and increases patient comfort and/or improves compliance. In general, release rates are determined by the design of the system and are nearly independent of environmental conditions.

A convenient classification of controlled-release systems is based on the mechanism that controls the release of the substance in question. The most common mechanism is diffusion. Two types of diffusion-controlled systems have been developed; the first is a reservoir device in which the bioactive agent (drug) forms a core surrounded by an inert diffusion barrier. These systems include membranes, capsules, microcapsules, liposomes, and hollow fibers. The second type is a monolithic device in which the active agent is dispersed or dissolved in an inert polymer. As in reservoir systems, drug diffusion through the polymer matrix is the rate-limiting step, and release rates are determined by the choice of polymer and its consequent effect on the diffusion and partition coefficient of the drug to be released.

In chemically controlled systems, chemical control can be achieved using bioerodible or pendant chains. The rationale for using bioerodible (or biodegradable) systems is that the bioerodible devices are eventually absorbed by the body and thus need not be removed surgically. Polymer bioerosion can be defined as the conversion of a material that is insoluble in water into one that is water-soluble. In a bioerodible system the drug is ideally distributed uniformly throughout a polymer in the same way as in monolithic systems. As the polymer surrounding the drug is eroded, the drug escapes. In a pendant chain system, the drug is covalently bound to the polymer and is released by bond scission owing to water or enzymes. In solventactivated controlled systems, the active agent is dissolved or dispersed within a polymeric matrix and is not able to diffuse through that matrix. In one type of solvent-controlled system, as the environmental fluid (e.g., water) penetrates the matrix, the polymer swells and its glass transition temperature is lowered below the environmental (host) temperature. Thus, the swollen polymer is in a rubbery state and allows the drug contained within to diffuse through the encapsulant.

A variety of natural, synthetic, and biosynthetic polymers are bio- and environmentally degradable. A polymer based on the C-C backbone tends to be non-biodegradable, whereas heteroatomcontaining polymer backbones confer biodegradability. Biodegradability can therefore be engineered into polymers by the judicious addition of chemical linkages such as anhydride, ester, or amide bonds, among others. The mechanism for degradation is by hydrolysis or enzymatic cleavage resulting in a scission of the polymer backbone. Macro-organisms can eat and, sometimes, digest polymers, and initiate a mechanical, chemical, or enzymatic aging.

To be used in medical devices and controlled-drug-release applications, the biodegradable polymer must be biocompatible and meet other criteria to be qualified as a biomaterial-processable, sterilizable, and capable of controlled stability or degradation in response to biological conditions. Polyesters based on polylactide (PLA), polyglycolide (PGA), polycaprolactone (PCL), and their copolymers have been extensively employed as biomaterials. Other biodegradable polymers include poly(hydroxyalkanoate)s of the PHB-PHV class, additional poly(ester)s, and natural polymers, particularly, modified poly(saccharide)s, e.g., starch, cellulose, and chitosan.

(From: <u>https://www.sigmaaldrich.com/technicaldocuments/articles/ma</u> <u>terials-science/biomaterials/tutorial.html</u>)

Task 20. Analyze the text for the key phrases to be used in the following-up discussion. Write down the phrases in your exercise-book.

Task 21. Read the text again for more details and put 5-7 questions (wh-questions / open-end questions).

Task 22. Pair-work. Ask your partner the questions you have made up. Check if the answers are correct.

Task 23. Team-work. Divide into two teams and discuss the text during 5-7 minutes. Choose a presenter in each team to present the main ideas of the text in front of the class. Which of the teams presents best?

Unit 16

PLASTIC RECYCLING

I. Pre-reading activities

Task 1. Discuss the following questions:

- 1) How do you reduce waste, reuse and recycle it at home?
- 2) How can different materials be recycled?
- 3) What information does the triangle recycling symbol with a special accompanying number contain?

Task 2. Pronounce the following international words after your teacher and guess what they mean:

polymer ['pɔlɪmə]	polyethylene [pɔlɪ'eθɪliːn]
plastic ['plæst 1 k]	production [prə'd∧k∫(ə)n]
material [mə'tIərIəl]	minimize ['mInImaIz]
container [kən'teInə]	operation [⊃ p(ə)'re I ∫(ə)n]
biodegradable [baIəudI'greIdəbəl]	process ['prəuses] (n)
original [ə'r ɪdʒ (ə)n(ə)l]	numerous ['nju:m(ə)rəs]
percentage [pə'sent1d3]	bottle ['bɔtl]
manufacture [mænju'fæktʃə]	pigment ['pIgmənt]

Task 3. Match the synonyms:

1) manufacture	a) convert
2) density	b) pigment
3) reprocess	c) fabricate
4) dye	d) thickness

Task 4. Match the opposites:

1) transparent	a) hard
2) biodegradable	b) natural
3) synthetic	c) non-biodegradable
4) soft	e) opaque

Task 5. Guess from the context what the underlined words mean:

- 1) <u>Plastics</u> are typically <u>organic polymers</u> of high <u>molecular mass</u>, but they often contain other substances.
- 2) <u>Recycling</u> is a process of <u>converting</u> <u>waste</u> materials into <u>reusable</u> materials to <u>prevent</u> waste of potentially useful materials.
- 3) <u>Pollution</u> is the presence in or <u>introduction</u> into the environment of a substance which has <u>harmful</u> or <u>poisonous effects</u>.
- 4) Recycling is a <u>viable</u> <u>alternative</u> in getting back some of this <u>energy</u> in the case of some polymers.

Task 6. Match the English phrases on the left with their Ukrainian equivalents on the right:

- 1) oil derivatives
- 2) feedstock recycling
- 3) transparent bottle
- 4) additive

а) прозора пляшка b) нафиотролицити

- b) нафтопродукти
- с) переробка сировини
- d) нафтопродукти

II. While-reading activities

Task 7. Read the text and answer the questions:

- 1. What kinds of non-biodegradable polymers exist?
- 2. Which methods are used to recycle materials?
- 3. Are there any barriers to recycling nowadays? What are they?

Plastic Recycling

Waste is now a global problem, and one that must be addressed in order to solve the world's resource and energy challenges. Plastics are made from limited resources such as petroleum, and huge advances are being made in the development of technologies to recycle plastic waste among other resources.

Plastics are non-biodegradable, synthetic polymers derived primarily from petro-fossil feedstock and made-up of long chain hydrocarbons with additives and can be moulded into finished products. These polymers are broken in the presence of a suitable catalyst into monomers such as ethylene, propylene, vinyl, styrene and benzene. These monomers are then chemically polymerized into different categories of plastics. There are about 50 different types of plastic. The main types include the following:

- HDPE – opaque bottles;

- PVC – transparent bottles, with a seam running across the base;

- PET – transparent bottles, with a hard moulded spot in the centre of the base.

Plastic recycling is the process of recovering scrap or waste plastic and reprocessing the material into useful products, sometimes completely different in form from their original state. Since plastic is not normally biodegradable, its recycling is part of global efforts to reduce plastic in the waste stream, especially the approximately eight million metric tonnes of waste plastic that enter the earth's ocean every year. This helps to reduce the high rates of plastic pollution.

Plastic recycling includes melting down soft-drink bottles and then casting them as plastic chairs and tables. However, this kind of "recycling" is rather a misnomer (a wrong or inaccurate use of a name or term) since plastic beverage bottles (soda, juice, milk) are never truly reformed into new beverage bottles, as this requires virgin plastic. So there is actually no true cycle in the "recycling" of plastic beverage containers, which actually and more precisely should be referred to as "downcycling". Plastics are also recycled during the manufacturing process of plastic goods such as polyethylene film and bags. A percentage of the recycled pellets are then re-introduced into the main production operation. This closed-loop operation has taken place since the 1970s and has made the production of some plastic products amongst the most efficient operations today.

Currently only about 3.5 % of all plastics generated is recycled, compared to 34 % of paper, 22 % of glass and 30 % of metals. At this time, plastic recycling only minimally reduces the amount of virgin resources used to make plastics. Recycling papers, glass and metal materials that are easily recycled more than once, saves far more energy and resources than are saved with plastic recycling.

Mechanical recycling methods to make plastic products and feedstock recycling methods that use plastic as a raw material in the chemical industry have been widely adopted, and awareness has also grown recently of the importance of thermal recycling as a means of using plastics as an energy source to conserve petroleum resources.

Compared with lucrative recycling of metal and similar to low value of glass, plastic polymers recycling is often more challenging

because of low density and low value. There are also numerous technical hurdles to overcome when recycling plastic.

A macro molecule interacts with its environment along its entire length, so total energy involved in mixing it is largely due to the product side stoichiometry. Heating alone is not enough to dissolve such a large molecule, so plastics must often be of nearly identical composition to mix efficiently.

When different types of plastics are melted together, they tend to phase-separate, like oil and water, and set in these layers. The phase boundaries cause structural weakness in the resulting material, meaning that polymer blends are useful in only limited applications.

Another barrier to recycling is the widespread use of dyes, fillers, and other additives in plastics. The polymer is generally too viscous to economically remove fillers, and would be damaged by many of the processes that could cheaply remove the added dyes. Additives are less widely used in beverage containers and plastic bags, allowing them to be recycled more often. Yet another barrier to removing large quantities of plastic from the waste stream and landfills is the fact that many common but small plastic items lack the universal triangle recycling symbol and accompanying number. An example is the billions of plastic utensils commonly distributed at fast food restaurants or sold for use at picnics.

The percentage of plastic that can be fully recycled, rather than downcycled or go to waste can be increased when manufacturers of packaged goods minimize mixing the packaging materials and eliminate contaminants. The Association of Plastics Recyclers has issued a Design Guide for Recyclability. The PIC (Plastic Identification Code), introduced by the Society of the Plastics Industry, Inc., provides a uniform system for the identification of various polymer types and helps recycling companies separate various plastics for reprocessing. Plastic product manufacturers are required to use PIC labels in some countries and can voluntarily mark their products with the PIC where there are no requirements. Consumers can identify the plastic types based on the codes usually found at the base or at the side of the plastic products, including food or chemical packaging and containers. (From: http://article.sapub.org/10.5923.c.jmea.201502.08.html http://www.recycling-guide.org.uk/materials/plastic.html https://www.pwmi.or.jp/ei/plastic recycling 2009.pdf https://en.wikipedia.org/wiki/Plastic recycling)

III. Post-reading activities

Task 8. Complete the following sentences using the text:

- 1). ______ is the process of recovering scrap or waste plastic and reprocessing the material into useful products.
- 2) Plastics are _____, synthetic polymers derived primarily from ______ and made-up of long chain hydrocarbons with additives.
- 3). A ______ interacts with its environment along its entire length.
- 4) Recycling _____, glass and _____ materials that are easily recycled more than once, saves ______ energy and resources than are saved with plastic recycling.
- 5). When different types of plastics are _____, they tend to phase-separate, like oil and water.
- 6). Additives are less widely used in ______ and plastic bags, allowing them to be ______ more often.
- 7) The ______, introduced by the Society of the Plastics Industry, Inc., provides a ______ system for the identification of various polymer types.

Task 9. Are the following statements true or false? Say why:

- 1). HDPE, PVC, PET are biodegradable plastics.
- 2). Mechanical recycling methods to make plastic products and feedstock recycling methods use plastics as an energy source to conserve petroleum resources.
- 3). Billions of plastic utensils are commonly distributed at fast food restaurants or sold for use at picnics.
- 4). Plastic doesn't contain any additives.
- 5) Plastic polymer recycling is often more challenging because of high content of carbon.
- 6) Consumers can identify the plastic types based on the codes at the base or at the side of the plastic products.

Task 10. Find and analyze all the definitions given in the text.

Task 11. Make a list of all chemical/ chemistry terms/ procedures/ experiments/ pieces of equipment etc. you can find in the text. Check all the examples in your class.

IV. Focus on grammar and lexis

Task 12. Put in the verbs in brackets in the correct form:

- 1). UK households _____ (produce) 30.5 million tonnes of waste in 2003/04, of which 17 % ____(collect) for recycling. 2). Today up to 60 % of the rubbish that ends up in the dustbin can
- _____ (recycle).
- 3). Plastic can _____ (take) up to 500 years to decompose.
 4). Carriers can _____ (reuse) next time you're at the shops, or _____ (deposit) at collection points _____ (provide) by some supermarkets.

Task 13. Here are the answers to some questions. Write the questions:

- 1) Plastic is a versatile and inexpensive material with thousands of uses, but it is also a significant source of pollution.
- 2) There are about 50 different types of plastic.
- 3) The average content of additives is 20 % of the polymer weight.
- 4) Currently only about 3.5 % of all plastics generated is recycled.
- 5) It helps recycling companies separate plastics for reprocessing.

Task 14. Put the words in the right order to make correct sentences: .

- 1) are reaching / the end of their lifecycle / mountains of waste plastic / Many plastic products / forming non-biodegradable;
- 2) Many / cannot currently / be recycled / plastic items;
- 3) is an excellent way / of saving energy / the environment / Recycling / and conserving;
- 4) are used / different materials / to recycle / Different processes.

Task 15. Fill in the gaps with the suitable preposition:

- 1) Plastics are made ____ limited resources such ___ petroleum.
- 2) Synthetic polymers are derived primarily ____ petro-fossil feedstock and made-up __long chain hydrocarbons __ additives.
- 3) These monomers are then chemically polymerized _____ different categories ____plastics.
- 4) There is actually no true cycle the "recycling" plastic beverage containers.
- 5) Plastics are also recycled _____ the manufacturing process ____ plastic goods such as polyethylene film and bags.

Task 16. Translate from Ukrainian into English:

- 1) Утилізація це доцільне використання відходів або залишків виробництва для отримання корисної продукції.
- 2) Основною сировиною для пластмас є нафта та газ.
- 3) Спалюваня досить поширений метод утилізації ПЕТ.
- Період розпаду пластикової пляшки становить близько 200 років.
- 5) Виробники пластмасової продукції мають зазначати на ній ідентифікаційний код пластмаси.

V. Final tasks

Task 17. Discuss the following ideas with your group-mates:

- 1) Plastic recycling is one of the urgent problems to be solved to ensure proper environmemntal protection. Give your reasons.
- 2) What measures would you suggest taking to reduce the amount of household waste?
- 3) How is the issue of recycling plastic tackled in Ukraine? What has to be done and how?

Task 18. Use the phrases below to retell the text in your own words:

Limited resources; mechanical recycling; thermal recycling; waste plastic; not normally biodegradable; reprocessing; melting down; polyethylene; triangle recycling symbol; petroleum; additives; dyes, fillers, PET; PVC, PIC.

VI. Individual reading: supplementary text

Task 19: Read the text and answer the following questions:

- 1) What is the chemical nature of plastics?
- 2) What are the main properties of plastics?
- 3) What was the world's first synthetic plastic?

Plastic

Plastic is a material consisting of any of a wide range of synthetic or semi-synthetic organics that are malleable and can be molded into solid objects of diverse shapes. Plastics are typically organic polymers of high molecular mass, but they often contain other substances. They are usually synthetic, most commonly derived from petrochemicals, but many are partially natural. Plasticity is the general property of all materials that are able to irreversibly deform without breaking, but this occurs to such a degree with this class of moldable polymers that their name is an emphasis on this ability.

Due to their relatively low cost, ease of manufacture, versatility, and imperviousness to water, plastics are used in an enormous and expanding range of products from paper clips to spaceships. They have already displaced many traditional materials, such as wood, stone, horn and bone, leather, paper, metal, glass, and ceramic, in most of their former uses. In developed countries, about a third of plastic is used in packaging and another third in buildings such as piping used in plumbing or vinyl siding. Other uses include automobiles (up to 20 % plastic), furniture, and toys. In the developing world, the ratios may be different – for example, reportedly 42 % of India's consumption is used in packaging. Plastics have many uses in the medical field as well, to include polymer implants, however the field of plastic surgery is not named for use of plastic material, but rather the more generic meaning of the word plasticity in regards to the reshaping of flesh.

The world's first fully synthetic plastic was bakelite, invented in New York in 1907 by Leo Baekeland, who coined the term 'plastics'. Many chemists contributed to the materials science of plastics, including Nobel laureate Hermann Staudinger who has been called "the father of polymer chemistry" and Herman Mark, known as "the father of polymer physics". The success and dominance of plastics starting in the early 20th century led to environmental concerns regarding its slow decomposition rate after being discarded as trash due to its composition of very large molecules. Toward the end of the century, one approach to this problem was met with wide efforts toward recycling.

(From: <u>https://en.wikipedia.org/wiki/Plastic</u>)

VII. Additional texts

Did you know that the word *plastic* is in a sense the antonym of the word *elastic*? An elastic material regains its original shape on being stretched or elongated. The plastic nature of the material does not permit the body to come back to its original phase once it has been deformed. All materials show both elastic and plastic properties. The difference arises in the application of the material and the amount of loads it can withstand within the limits of the two properties.

Recycling Options

A growing recycling option which will hopefully become more and more widespread in the UK are Reverse Vending Machines (RVMs), which collect plastics for recycling. The Reverse Vending Corporation provide fully automated reverse vending machines which utilise advanced technology to identify, sort, collect, process and recycle used beverage containers including cans, glass bottles, PET (plastic) bottles and vending cups. These machines have been used in Europe for many years, often as part of a 'refund for your empties' scheme, encouraging people to put their bottles in to get money back. The RVC hope to have over 300 RVMs operating in schools by the end of this year. Placed in offices, shops and schools, these machines could make recycling a lot easier.

Another option is manufacturing bioplastics, also called PLA (PolyLactic Acid) that are derived from renewable biomass sources, such as cereals (corn, wheat, peas), tubers (sugar beets, sweet potatoes), oleaginous plants (castor oil), sugar production plants (sugar canes), or protein rich plants. Most of these plant-based plastics can replace petrochemical processes or be associated with petroleum based polymers (a bioplastic can contain as little as 40 % organic plant material); they are biodegradable, do not use limited resources (as well as costly ones, due to market fluctuations), and help lower CO₂ emissions. However, using a biomass source consumes a lot of water, and research is now looking for processes that would be drier, more cost effective, and thus more environmentally friendly. Consequently, generation bioplastics are biodegradable second and some compostable, created from food or wood waste, and leave an almost invisible carbon footprint. At this time, some common household products are made with bioplastics (packaging, bags, kitchen ware, water bottles, razors, cling film), but the use of this type of plastic is still too negligible.

Recycling of non-biodegradable bioplastics, i.e. biomass sourced PET, ET, or PE for example, is increasing, and, if pre-existing plastic recycling industries continue to process these materials, it could slowly reconcile plastic and environment. On the other hand, the sorting of some biodegradable polymers such as PLA and PHA is not sufficiently carried out to avoid upsetting the general plastic recycling process.

The world's annual consumption of plastic materials has increased from around 5 million tons in the 1950s to nearly 100 million tons today. Plastics constitute approximately 3-7% of municipal waste. Presently, municipal garbage disposal departments burry the plastics along with other materials in landfill without even recognizing its ill effects. It is an improper way of disposing plastics and is identified as the cause of manifold ecological problems. Extrusion plays a prominent part in the plastics industry. It is a highvolume manufacturing process in which raw plastic is melted and formed into a continuous profile. Plastics extrusion is a continuous process, as opposed to moulding, which is a cyclic process.

In recent times, a number of companies are selling composite railroad ties manufactured from recycled plastic resins, and recycled rubber. Plastic / composite ties (P/C ties) can be made of recycled plastics, generally polyethylene, but often include other materials such as steel fibre, steel reinforcing bar, shredded used tires, mineral filler, virgin plastic, or concrete. The modelled representative P/C tie is assumed to be 8 % virgin HDPE (high-density polyethylene) plastic, 7 % talc (mineral filler), and the balance a mixture of post-consumer recycled milk bottles, grocery bags, and tires.

(From: <u>http://www.recycling-guide.org.uk/materials/plastic.html</u> and <u>https://www.paprec.com/en/understanding-recycling/recycling-</u> plastic/making-plastic-extracting-raw-material)

Task 21. Analyze the text for the key phrases to be used in the following-up discussion. Write down the phrases in your exercise-book.

Task 22. Read the text again for more details and put 5-7 questions (wh-questions / open-end questions).

Task 23. Pair-work. Ask your partner the questions you have made up. Check if the answers are correct.

Task 24. Team-work. Divide into two teams and discuss the text during 5-7 minutes. Choose a presenter in each team to present the main ideas of the text in front of the class. Which of the teams presents best?

Unit 17

ALDEHYDES AND KETONES

I. Pre-reading activities

Task 1. Discuss the following questions:

- 1. What do you know about aldehydes and ketones?
- 2. What is the structural difference between an aldehyde and a ketone?
- 3. Which important reactions of the carbonyl group do you know?

Task 2. Pronounce the following international words and guess what they mean:

carbonyl ['kaːbənaɪl, -nɪl]	indicate ['IndIkeIt]
group [gru:p]	position [pə'z ı∫ (ə)n]
characteristic [kærIktə'rIstIk]	medical ['medikəl]
aldehyde ['ældIhaId]	symptom ['sImptəm]
ketone ['kiːtəʊn]	laboratory [lə'b ɔ rət(ə)r 1]
nomenclature [nəu'meŋkləʧə]	atom ['ætəm]
polar ['pəʊlə]	alcohol ['ælkəhɔl]
system [sIstəm]	condition [kən'dɪ∫(ə)n]
final ['faIn(ə)l]	basis ['beIsIs]
suffix ['s∧f ı ks]	mixture ['mɪkstʃə]

Task 3. Match the synonyms:

 common position readily 	a) significantb) differentiatec) location
4) important5) fragrance	d) yield e) ordinary
6) produce7) distinguish	f) perfumeg) easily

Task 4. Match the opposites:

1) readily	a) special
2) oxidation	b) take
3) equilibrium	c) low
4) high	d) initial
5) final	e) unwillingly
6) give	f) reduction
7) versatile	g) imbalance

Task 5. Guess from the context what the underlined words mean:

- 1) The carbonyl group and the two groups <u>attached</u> to it are <u>coplanar</u>.
- 2) <u>Owing</u> to the <u>polar</u> carbonyl group, aldehydes and ketones are polar <u>compounds</u>.
- 3) Propanone is a useful and <u>versatile</u> solvent for organic compounds.
- 4) Ketones do not <u>undergo</u> further oxidation reactions.
- 5) Aldehydes and ketones may exist as <u>an equilibrium mixture</u> of keto and enol <u>tautomers</u>.

Task 6. Mach the English phrases on the left with their Ukrainian equivalents on the right:

1) polar compound	а) температура кипіння
2) boiling point	b) напівацеталь
3) ability	с) полярна сполука
4) fragrance chemicals	d) альдольна конденсація
5) primary alcohol	е) здатність
6) hemiacetal	f) ароматичні хімічні препарати
7) aldol condensation	g) первинний спирт

Task 7. Mach the terms on the left with their definitions on the right:

1) aldol	a) a colourless volatile liquid ketone made by
	oxidizing isopropanol CH3COCH3
2) carbonyl	b) another term for acetone
3) propanone	c) having a valency of two
4) acetone	d) a viscous liquid obtained when acetaldehyde dimerizes
	in dilute alkali or acid – CH ₃ CH(OH)CH ₂ CHO
5) divalent	e) denoting the divalent radical =C=O

<u>II. While-reading activities</u>

Task 8. Read the text and answer the questions:

- 1) What are the typical characteristics of aldehydes and ketones?
- 2) Which members of the aldehyde and ketone families can you name? What are their applications?
- 3) Which main reactions of aldehydes and ketones can you identify?

Aldehydes and Ketones

Both aldehydes and ketones contain a carbonyl group (=C=O), a functional group with a carbon-oxygen double bond. The names for aldehyde and ketone compounds are derived using similar nomenclature rules as for alkanes and alcohols, and include the class-identifying suffixes -al and -one, respectively.

In an aldehyde, the carbonyl group is bonded to at least one hydrogen atom. In a ketone, the carbonyl group is bonded to two carbon atoms. As text, an aldehyde group is represented as -CHO; a ketone is represented as -C(O)- or -CO-.

R____H Aldehydes

R_____R' Ketones

In aldehydes and ketones the carbonyl group =C=O and the two groups attached to it are coplanar. In ketones the carbonyl carbon is attached to two carbon-containing groups, whereas in aldehydes the carbonyl carbon is attached to at least one hydrogen; the second group attached to the carbonyl carbon in aldehydes may be another hydrogen or carbon atom. Owing to the polar carbonyl group, aldehydes and ketones are polar compounds. Their boiling points are higher than those of comparable hydrocarbons but lower than those of comparable alcohols. Small aldehydes and ketones are reasonably soluble in water because of the hydrogen bonding between the carbonyl group and water molecules. Larger carbonyl-containing compounds are less polar and thus more soluble in nonpolar organic solvents.

In the I.U.P.A.C. Nomenclature System, aldehydes are named by determining the parent compound and replacing the final -e of the parent alkane with -al, as mentioned above. The chain is numbered beginning with the carbonyl carbon as carbon-1. Ketones are named

by determining the parent compound and replacing the *-e* ending of the parent alkane with the *-one* suffix of the ketone family. The longest carbon chain is numbered to give the carbonyl carbon the lowest possible number. In the common system of nomenclature, substituted aldehydes are named as derivatives of the parent compound. Greek letters indicate the position of substituents. Common names of ketones are derived by naming the alkyl groups bonded to the carbonyl carbon. These names are followed by the word "ketone."

Many members of the aldehyde and ketone families are important as food and fragrance chemicals, medical substances, and agricultural chemicals. Methanal (formaldehyde) is used to preserve tissue. Ethanal causes the symptoms of a hangover and is oxidized to produce acetic acid commercially. Propanone is a useful and versatile solvent for organic compounds.

In the laboratory, aldehydes and ketones are prepared by the oxidation of alcohols. Oxidation of a primary alcohol produces an aldehyde; oxidation of a secondary alcohol yields a ketone. Tertiary alcohols do not react under these conditions. Aldehydes and ketones can be distinguished from one another on the basis of their ability to undergo oxidation reactions. The Tollens'test and Benedict's test are the most common such tests. Aldehydes are easily oxidized to carboxylic acids. Ketones do not undergo further oxidation reactions. Aldehydes and ketones are readily reduced to alcohols bv hydrogenation. The most common reaction of the carbonyl group is addition across the highly polar carbon-oxygen double bond. The addition of an alcohol to an aldehyde produces a hemiacetal. The hemiacetal reacts with a second alcohol molecule to form an acetal. The reaction of a ketone with an alcohol produces a hemiketal. A hemiketal reacts with a second alcohol molecule to form a ketal. Hemiacetals and hemiketals are readily formed in carbohydrates. Aldol condensation is a reaction in which aldehydes and ketones form larger molecules. Aldehydes and ketones may exist as an equilibrium mixture of keto and enol tautomers.

(From: <u>https://opentextbc.ca/chemistry/chapter/20-3-aldehydes-</u> <u>ketones-</u> and <u>http://www.wou.edu/chemistry/courses/online-</u> <u>chemistry-textbooks/ch105-consumer-chemistry/ch105-chapter-9-</u> <u>organic-compounds-oxygen/#ch105-9.4.1</u>)

III. Post-reading activities

Task 9. Complete the following sentences using the text:

- The carbonyl group =C=O is characteristic of _____.
 The names for aldehyde and ketone compounds are derived using similar nomenclature rules as for _____
- 3. In the I.U.P.A.C. Nomenclature System, the chain is numbered
- beginning with the carbonyl carbon as _____.4. Ethanal causes the symptoms of ______ and is oxidized to produce commercially.
- 5. Aldehydes are easily oxidized to _____.6. Hemiacetals and hemiketals are readily formed in _____.

Task 10. Are the following statements about the text true or false? Say why:

- 1) In ketones the carbonyl carbon is attached to two carboncontaining groups.
- 2) Larger carbonyl-containing compounds are less polar and thus reasonably soluble in nonpolar organic solvents.
- 3) The chain is numbered beginning with the carbonyl carbon as carbon-2.
- 4) Propanone is a versatile solvent for organic compounds.
- 5) In the laboratory, aldehydes and ketones are prepared by the oxidation of alcohols.
- 6) The reaction of a ketone with an alcohol produces a hemiacetal.

Task 11. Answer the questions about the text:

- 1) How are the names for aldehyde and ketone compounds derived? What do Greek letters indicate?
- 2) What makes aldehydes and ketones polar compounds?
- 3) What can you say about their boiling points?
- 4) Why are small aldehydes and ketones soluble in water?
- 5) Why are larger carbonyl-containing compounds more soluble in nonpolar organic solvents?
- 6) How can aldehydes and ketones be distinguished from one another?
- 7) What does the reaction of a ketone with an alcohol produce?
- 8) How can aldehydes and ketones be reduced to alcohols?

IV. Focus on grammar and lexis

Task 13. Put the words in the right order to make sentences:

- 1) the carbonyl carbon at least one hydrogen In aldehydes is attached to.
- 2) in water are reasonably soluble Small aldehydes and ketones.
- 3) indicate Greek letters of substituents the position.
- 4) (formaldehyde) to preserve tissue is used Methanal.
- 5) test and Benedict's are the most common The Tollens'test such tests.
- 6) in which aldehydes and ketones is a reaction Aldol condensation form larger molecules.

Task 14. Fill in the gaps with the suitable preposition:

- 1) The second group attached _____ the carbonyl carbon _____ aldehydes may be another hydrogen or carbon atom.
- 2) Small aldehydes and ketones are reasonably soluble _____ water because of the hydrogen bonding _____ the carbonyl group and water molecules.
- 3) _____ the I.U.P.A.C. Nomenclature System, aldehydes are named _____ determining the parent compound.
- 4) Tertiary alcohols do not react _____ these conditions.
- 5) Aldehydes and ketones can be distinguished from one another _____ the basis of their ability to undergo oxidation reactions.
- 6) _____ the laboratory, aldehydes and ketones are prepared ____ the oxidation of alcohols.

Task 15. Correct the mistakes. There is one mistake in each of the following sentences. Find it and write the corrected sentences:

- 1) Larger carbonyl-containing compounds is less polar and thus more soluble in nonpolar organic solvents.
- 2) Common names of ketones is derived by naming the alkyl groups bonded to the carbonyl carbon.
- 3) Aldehydes and ketones are readily reduce to alcohols by hydrogenation.
- 4) A hemiacetal react with a second alcohol molecule to form an acetal.

- 5) A hemiketal reacts with a second alcohol molecule to formed a ketal.
- 6) Aldol condensation is a reaction in which aldehydes and ketones forms larger molecules.

Task 16. Translate from Ukrainian into English:

- 1) За науковою номенклатурою назви альдегідів складаються з назв відповідних вуглеводнів з додаванням закінчення *-аль*.
- 2) При окисленні альдегідів утворюються карбонові кислоти.
- 3) Із первинних спиртів отримують альдегіди, із вторинних кетони.
- 4) Альдегіди є активнішиими, ніж кетони.
- 5) Мурашиний альдегід це газ, інші нижчі альдегіди і кетони є рідинами, які легко розчиняються у воді.
- 6) Карбонільна група =C=O є носієм запаху, тому альдегіди і кетони застосовуються в парфумерній промисловості.
- 7) Температура кипіння альдегідів і кетонів зростає в міру збільшення їхньої молекулярної маси.

V. Final tasks

Task 17. Discuss the following ideas with your group-mates:

- 1) Do you agree that the applications of aldehydes as food are more useful than others? Explain your choice.
- 2) How can you prove the statement that many members of the aldehyde and ketone families are important as food and fragrance chemicals, medical substances, and agricultural chemicals? Share your points of view in pairs.
- 3) Suppose you have to give a lecture on "Aldehydes and Ketones." What would you emphasize in the lecture?

Task 18. Use the phrases below to retell the text in your own words:

Carbonyl group, aldehydes, ketones, carbonyl carbon, polar compounds, boiling points, hydrogen bonding, to determine the parent compound and replace, I.U.P.A.C. Nomenclature System, the longest carbon chain, the lowest possible number, to be important as, to preserve tissue, to cause a hangover, versatile solvent, oxidation of alcohols, distinguish from one another, readily reduced to, the addition of an alcohol, carbohydrates, aldol condensation, tautomers.

VI. Individual reading: supplementary text

Task 19: Read the text and answer the following questions:

- 1) Where is formaldehyde used?
- 2) Which medical applications of aldehydes can you name?
- 3) Do you agree that medical applications of aldehydes as body fluids are more useful than others? Give your reasons.

Medical Applications of Aldehydes

Most aldehydes have irritating, unpleasant odors, and formaldehyde is no exception. Formaldehyde (with the formula HCHO is a colorless gas with a pungent and irritating odor. It is sold in an aqueous solution called formalin, which contains about 37 % formaldehyde by weight. Formaldehyde causes coagulation of proteins, so it kills bacteria and any other living organisms, and stops many of the biological processes that cause tissue to decay. It is an extremely toxic substance. As an aqueous solution, it has been used to preserve biological tissues and for embalming. It has also been used to disinfect environmental surfaces, body fluids, and feces. Under no circumstances is it used as an antiseptic on human tissue because of its toxic fumes and the skin irritations that it causes.

Formaldehyde is useful in the production of killed virus vaccines. A deadly virus, such as polio virus, can be treated with heat and formaldehyde. Formaldehyde reacts with the genetic information (RNA) of the virus, damaging it irreparably. It also reacts with the virus proteins but does not change their shape. Thus, when you are injected with the Salk polio vaccine, the virus cannot replicate and harm you. However, it will be recognized by your immune system, which will produce antibodies that will protect you against polio virus infection.

Formaldehyde can also be produced in the body! Drinking wood alcohol (methanol) causes blindness, respiratory failure, convulsions, and death. The liver enzyme alcohol dehydrogenase, whose function is to detoxify alcohols, catalyzes the conversion of methanol to formaldehyde (methanal). The formaldehyde produced reacts with cellular proteins, causing the range of symptoms mentioned above.

Acetaldehyde (ethanal) is produced from ethanol by the liver enzymes and is largely responsible for the symptoms of hangover experienced after a night of too much partying. This aldehyde is useful in treating alcoholics because of the unpleasant symptoms that it causes. When taken orally, in combination with alcohol, acetaldehyde quickly produces symptoms of a violent hangover with none of the perceived benefits of drinking alcohol.

The liver enzymes that oxidize ethanol to acetaldehyde are the same as those that oxidize methanol to formaldehyde. Physicians take advantage of this in the treatment of wood alcohol poisoning by trying to keep those enzymes busy with a reaction that produces a less toxic (not nontoxic) by-product. In cases of methanol poisoning, the patient receives ethanol intravenously. The ethanol should then be in greater concentration than methanol and should compete successfully for the liver enzymes and be converted to acetaldehyde. This gives the body time to excrete the methanol before it is oxidized to the potentially deadly formaldehyde.

(From: <u>https://opentextbc.ca/chemistry/chapter/20-3-aldehydes-ketones-carboxylic-acids-and-esters/</u>)

VII. Additional texts

Did you know that ketones are formed in the human body: in blood, urine and breath as a by-product of lipid metabolism? The two common metabolites produced in humans are the ketone-containing, acetoacetic acid and the alcohol metabolite, β -hydroxybutyrate. Acetone is also produced as a breakdown product of acetoacetic acid. Acetone can then be excreted from the body through the urine or as a volatile product through the lungs.

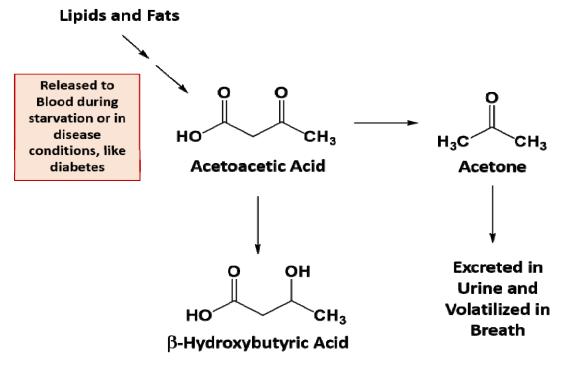
Task 20: Read the text and put your questions to cover its content:

Aldehydes and Ketones in Nature

Similar to the other oxygen-containing functional groups, aldehydes and ketones are also widespread in nature and are often combined with other functional groups. Naturally occurring molecules which contain an aldehyde or ketone functional group found in plants, microorganisms and animals. Many of these molecular structures are chiral and have distinct stereochemistry.

When chiral compounds are found in nature they are usually enantiomerically pure, although different sources may yield different enantiomers. For example, carvone is found as its levorotatory (R)enantiomer in spearmint oil, whereas, caraway seeds contain the dextrorotatory (S)-enantiomer. In this case the change of the stereochemistry causes a drastic change in the perceived scent. Aldehydes and ketones are known for their sweet and sometimes pungent odors. The odor from vanilla extract comes from the molecule vanillin. Likewise, benzaldehyde provides a strong scent of almonds. Due to their pleasant fragrances aldehyde and ketone containing molecules are often found in perfumes. However, not all of the fragrances are pleasing. In particular, 2-Heptanone provides part of the sharp scent from blue cheese and (R)-Muscone is part of the musky smell from the Himalayan musk deer. Lastly, ketones show up in many important hormones such as progesterone (a female sex hormone) and testosterone (a male sex hormone). Notice how subtle differences in structure can cause drastic changes in biological activity. The ketone functionality also shows up in the anti-inflammatory steroid, Cortisone.

In the human body ketones are formed as a by-product of lipid metabolism.



Normally, ketones are not released into the bloodstream in appreciable amounts. For example, the normal concentration of acetone in the human body is less than 1 mg/100 mL of blood. Instead, ketones that are produced during lipid metabolism inside cells are usually fully oxidized and broken down to carbon dioxide and water. This is because glucose is the primary energy source for the body, especially for the brain. Glucose is released in controlled

amounts into the bloodstream by the liver, where it travels throughout the body to provide energy. For the brain, this is the primary energy source, as the blood-brain barrier blocks the transport of large lipid molecules. However, during times of starvation, when glucose is unavailable, or in certain disease states where glucose metabolism is disregulated, like uncontrolled diabetes mellitus. the ketone concentrations within blood rises to higher levels to provide an alternative energy source for the brain. However, since acetoacetic acid and β -hydroxybutyrate contain carboxylic acid functional groups, the addition of these molecules to the blood cause acidification which if left unchecked can cause a dangerous condition called ketoacidosis that can be a life threatening event. Ketones can be easily detected, as acetone is excreted in the urine. In severe cases, the odor of acetone can also be noted on the breath (see the figure above that describes the formation of ketones in the human body).

(From: <u>http://www.wou.edu/chemistry/courses/online-chemistry-</u> textbooks/ch105-consumer-chemistry/ch105-chapter-9-organiccompounds-oxygen/#ch105-9.4.1)

Task 21. Analyze the text for the key phrases to be used in the following-up discussion. Write down the phrases in your exercise-book.

Task 22. Read the text again for more details and put 5-7 questions (wh-questions / open-end questions).

Task 23. Pair-work. Ask your partner the questions you have made up. Check if the answers are correct.

Task 24. Team-work. Divide into two teams and discuss the text during 5-7 minutes. Choose a presenter in each team to present the main ideas of the text in front of the class. Which of the teams presents best?

Unit 18

FULLERENES

I. Pre-reading activities

Task 1. Discuss the following questions:

- 1) What do you know about fullerenes? Where are they used?
- 2) How are fullerenes produced?
- 3) What is buckminsterfullerene?

Task 2. Pronounce the following international words after your teacher and guess what they mean:

fullerene ['fʊləriːn]	nanostructure ['nænə'str∧kt∫ə]
nano tube ['nænət(j)u:b], [-tʃu:b]	hexagon ['heksəgən]
graphite ['græfa 1 t]	pentagon ['pentagon]
liquid ['l 1 kw 1 d]	pyrolysis [paɪ'rɔːlɪsɪs]
crystal ['krIst(ə)l	polymer ['pɔlɪmə]
association [əsəusɪ'eɪ∫(ə)n], [-∫ɪeɪ-]	ferrocene['ferəsi:n]

Task 3. Match the synonyms:

1) fullerene

- 2) to discover
- 3) cage
- 4) to interlock
- 5) variety
- 6) soot

Task 4. Match the opposites:

- 1) full
- 2) association
- 3) dirty
- 4) inaccessible
- 5) far
- 6) to exclude
- 7) condensation

- a) to find
- b) frame
- c) to connect
- d) diversity
- e) grime
- f) buckyball
- a) close
- b) evaporation
- c) to insert
- d) hollow
- e) available
- f) pure
- g) separation

Task 5. Guess from the context what the underlined words mean:

- 1) <u>Evaporation</u> is the process by which water changes from a liquid to a gas or vapor.
- 2) <u>Diamond</u> and <u>graphite</u> are the only two naturally formed polymers of carbon.
- 3) <u>Liquid crystals</u> are matter in a state that has properties between those of <u>conventional</u> liquid and those of <u>solid</u> crystal.
- 4) Fullerenes are produced in small amounts naturally, in fires and <u>lightning strikes.</u>

Task 6. Match the English phrases on the left with their Ukrainian equivalents on the right:

1) buckminsterfullerene	а) везикула
2) vaporizing graphite	b) зшиті полімери
3) lightning strikes	с) делокалізовані електрони
4) electron beam evaporation	d) випаровування графіту
5)cross-linked polymers	е) дуговий розряд
6) arc discharge	f) доставка ліків
7) graphite electrodes	g) електронно-променеве
	випаровування
8) vesicle	h)графітовий електрод
9) drug delivery	і) фулерен
10) delocalized electrons	j) удари блискавки

II. While-reading activities

Task 7. Read the text and answer the questions:

- 1) What was the name of the first fullerene?
- 2) Which electrodes are used in the arc discharge?
- 3) What research on functionalization has been done? Why?

Fullerenes

A fullerene is a molecule of carbon in the form of a hollow sphere, ellipsoid, tube, and many other shapes. Spherical fullerenes, also referred to as Buckminsterfullerenes or buckyballs, resemble the ball used in association football. Cylindrical fullerenes are also called carbon nanotubes (buckytubes). Fullerenes are similar in structure to graphite, which is composed of stacked graphenesheets of linked hexagonal rings. Unless they are cylindrical, they must also contain pentagonal (or sometimes heptagonal) rings.

The first fullerene discovered was the buckyball. Also known as buckminsterfullerene, after the architect Buckminster Fuller, whose geodesic dome it resembles, it was discovered in 1985 at Rice University in Houston by Richard Smalley, Robert Curl and Harry Kroto, who shared a Nobel Prize in 1996 for the discovery. Buckminsterfullerene, or buckyball, molecules are roughly spherical cages of 60 carbon atoms (C_{60}) arranged in interlocking hexagons and pentagons, like the patches on a soccer ball.

Other fullerenes were discovered shortly afterwards with more and fewer carbon atoms, ranging from 28 up to hundreds, though C_{60} remains the easiest to produce, and cheapest, with prices rising rapidly for the larger fullerenes. The word 'fullerene' covers this collection of hollow carbon molecules made of a cage of interlocking pentagons and hexagons. Carbon nanotubes, made of graphite sheets of hexagonal arrays of carbon rolled into tubes, are close cousins in terms of production methods and some of their properties, and can be included in the fullerene family if their ends are closed, in which case they are like a buckyball extended into a tube by the insertion of carbons along its midriff.

Fullerenes are in fact produced in small amounts naturally, in fires and lightning strikes, and there is some evidence that the massive Permian extinction of 250 million years ago was caused by the impact of an object containing buckyballs. However, they were first produced by man (at least knowingly) in the soot resulting from vaporizing graphite with a laser. The earliest bulk production process is the arc discharge (or Kritschmer-Huffman) method, using graphite electrodes, developed in 1990. This produces predominantly C_{60} and C_{70} but can be made to produce higher fullerenes, for instance by having more porous electrodes. Separation with solvents, such as toluene, can achieve near 100 % purity for C_{60} .

A little later, a group at MIT started producing C_{60} in a benzene flame. And pyrolysis (transformation of a compound by heat, without burning) of a variety of aromatic compounds has also been used to produce fullerenes. As is known, aromatic compounds have benzenederived ring structures. A typical attribute of aromatics is that they have bonding electrons free to move around, so-called delocalized electrons. Thus fullerenes themselves are aromatic. Methods such as sputtering (covering a surface with metal by using fast ions) and electron beam evaporation (with a graphite precursor) have been shown to preferentially produce higher fullerenes, such as C_{70} , C_{76} , C_{78} , and C_{84} .

Chemical groups can be attached to a fullerene's carbon atoms, a process called functionalization, modifying their properties. The number of carbon atoms available to do this has led to the epithet "molecular pincushion" (a small cushion into which pins are stuck for convenient storage), especially within the context of medical applications such as those being developed by the company C Sixty. Research on functionalization of fullerenes has been aimed at varying from the creation of polymers to biologically active variants.

A nice illustration of the lengths to which functionalization can be taken comes from a group at the University of Tokyo and their creation of molecular 'shuttlecocks'. These have potential in liquid crystal applications, which goes beyond liquid-crystal displays as there is growing interest in their use in areas such as non-linear optics, photonics and molecular electronics. The University of Tokyo has also done some interesting work on creating hybrids of ferrocenes and fullerenes.

Ferrocenes are compounds containing iron and organic groups that have attracted much interest in the decades since their discovery. The hybrids might create vesicles for drug delivery or be the basis of nanostructures with useful electronic or photonic properties. Vesicles have also been created at the university using the potassium salt of pentaphenylfullerene, each composed of about 13,000 modified C_{60} molecules. Polyfullerenes are much more stable than organic polymers like polyethylene, polypropylene or nylon, and the addition of fluorine to the polyfullerenes could make it easier for chemists to use them in subsequent chemical reactions.

Researchers at SRI International have also done work on creating fullerene-based polymers, starting with attaching amines to C_{60} . The result was a variety of highly cross-linked polymers suitable for spray-, dip-, or spin-coating which are very hard and show high thermal stability.

(From: <u>https://en.wikipedia.org/wiki/Fullerene;</u>

http://www.clubofamsterdam.com/contentarticles/01%20Nanotechnol ogy/Fullerenes.pdf)

III. Post-reading activities

Task 8. *Complete the following sentences using the text:*

- 1) The first fullerene discovered was _____.
- 2) The word 'fullerene' covers a collection of _____ carbon molecules made of a cage of _____ pentagons and _____.
- 3) Fullerenes are produced in _____ amounts naturally, in fires and _____.
- 4) A typical attribute of aromatics is that they have bonding electrons free to move around, so-called _______ electrons.
- 5) Ferrocenes are compounds containing _____ and _____ groups.
- 6) ______ are much more stable than organic polymers like polyethylene, polypropylene or nylon.

Task 9. Answer the questions about the text:

- 1) What is the formula and structure of Buckminsterfullerene?
- 2) What's the difference between nanotubes and fullerenes?
- 3) Why are fullerenes aromatic?
- 4) In what way can fullerenes be manufactured?
- 5) How are fullarenes produced in nature?
- 6) Where are fullerenes applied?
- 7) Why are hybrid fullerenes created?

Task 10. Are the following statements about the text true or false? *Explain why:*

- 1) Buckminsterfullerene, or buckyball, molecules are roughly spherical cages of 60 carbon atoms (C_{60}) arranged in interlocking hexagons and pentagons.
- 2) Carbon nanotubes are made of graphite sheets of pentagonal arrays of carbon rolled into tubes.
- 3) They were first produced by man in the soot resulting from vaporizing graphite with a laser.
- 4) The earliest bulk production process is the arc discharge method, using fullerenes electrodes, developed in 1990.
- 5) Chemical groups can be attached to a fullerene's carbon atoms, a process called functionalization, modifying their properties.
- 6) Ferrocenes are compounds containing iron and inorganic groups that have attracted much interest in the decades since their discovery.

Task 11. Find and analyze all the definitions given in the text.

Task 12. Make a list of all the chemicals/ chemistry terms/ procedures/ experiments etc. you can find in the text. Check all the examples in your class.

IV. Focus on grammar and lexis

Task 13. Put in the verbs in brackets in the correct tense form:

Amorphous carbon is the name _____ (use) for carbon that _____ (not have) any crystalline structure. As with all glassy materials, some short-range order can ____ (observe), but there _____ (not be) long-range pattern of atomic positions. While entirely amorphous carbon can ______ (produce), most amorphous carbon actually contains microscopic crystals of graphite-like, or even diamond-like carbon. Coal and soot, or black carbon, _____ (be) informally ______ (call) amorphous carbon. However, they _____ (be) products of pyrolysis (the process of decomposing a substance by the action of heat), which _____ not produce) true amorphous carbon under normal conditions.

Task 14. Put the words in the right order to make sentences:

- 1) used, the name, Amorphous carbon, does not have, crystallinestructure, any, for, carbon, that, is.
- 2) fullerene, was, The first, the buckyball, discovered.
- 3) of 250 million years ago, the impact, buckyballs, Permian extinction, caused, was, by, of an object.
- 4) attribute, A typical, is that, bonding electrons, delocalization electrons, free to move around, have, they, so-called, of aromatics.
- 5) interlocking pentagons and hexagons, carbon molecules, made of cage, The word "fullerene", this collection, hollow, covers, of.

Task 15. Fill in the gaps with a suitable preposition:

- 1) Carbon nanotubes are allotropes _____ carbon ____ a cylindrical nanostructure.
- 2) Fullerenes are similar _____ structure to graphite, which is composed _____ stacked graphenesheets _____ linked hexagonal rings.

- 3) Carbon nanotubes, made ____ graphite sheets of hexagonal arrays of carbon rolled _____ tubes, are close cousins ___ terms of production methods and some ____ their properties.
- 4) ______ particular, owing _____ their extraordinary thermal conductivity and mechanical and electrical properties, carbon nanotubes find applications as additives ______ various structural materials.
- 5) Separation _____ solvents, such ____ toluene, can achieve near 100 % purity ____ C₆₀.
- 6) Hybrids might create vesicles ____ drug delivery or be the basis _____ nanostructures _____ useful electronic or photonic properties.
- 7) They are like a buckyball extended _____ a tube _____ the insertion of carbons ______ its midriff.

Task 16. Translate from Ukrainian into English:

- 1) Найвідоміший фулерен С₆₀ має ідеальну форму футбольного м'яча.
- 2) Фулерени формуються шляхом конденсації атомів вуглецю, які утворюються при випаровуванні графіту.
- 3) Природні фулерени можна знайти в сажі.
- 4) Фулерен є яскраво вираженим акцептором електронів, Крім того, він легко приєднує нуклеофіли і вільні радикали.
- 5) Наявність у молекулі фулерену великої кількості атомів вуглецю дозволяє синтезувати безліч сполук із новими властивостями.
- 6) Хоча теоретично фулерени не токсичні, їхня безпечність для людей все ще широко обговорюється.

V. Final tasks

Task 17. Discuss the following ideas with your group-mates:

- 1) Which forms of carbon do you know? What are the differences between them?
- 2) Fullerenes are nanoparticles. How can you prove it?
- 3) Carbon nanotubes are essentially long cylindrical fullerenes.
- 4) Do you agree that fullerene molecules can be used for drug delivery into the body?
- 5) Carbon nanotubes have very high tensile strength, very good electrical conductivity and relatively high thermal conductivity. What are the benefits of these properties?

Task 18. Use the phrases below to retell the text in your own words:

Roughly spherical cages, interlocking hexagons and pentagons, carbon nanotubes, to be made of, graphite sheets, vaporizing graphite, to be produced naturally, in small amounts, hybrids, functionalization, ferrocenes, stable compounds, polyfullerenes.

VI. Individual reading: supplementary text

Task 19: Read the text and answer the questions:

- 1) What are endohedral fullerenes?
- 2) Which symbols are used to describe them?
- 3) What are the disadvantages of creating fullerenes in the presence of the elements to be encapsulated?
- 4) What are the possible applications of endofullerenes in medicine?

Endohedral Fullerene

An area of research that has been at least as active as functionalization of fullerenes is that of putting atoms inside them. The results are called endohedral fullerenes, which are described with the notation $X@C_{60}$, where X is the trapped atom (or atoms) and C_{60} could be any fullerene. Reactive elements can be stabilized inside the fullerene cage. The contained element can also change the electronic and magnetic properties of the fullerene (the caged atom can contribute electrons to the fullerene molecule). The creation of endohedral fullerenes has proved challenging. Simple approaches involve creating the fullerenes in the presence of the element to be encapsulated, but this produces a low yield, typically less than 1 %.

However, some researchers, such as Lothar Dunsch, have claimed that it is possible, by adjusting reaction conditions, to get certain endohedral fullerenes as the main product of a reaction. Alternatively, fullerenes can be mixed with the substance to be encapsulated and subjected to high temperatures and pressures, or a chemical approach can be taken to open up the fullerene to let the other substance in.

Researchers at UCLA (University of California, Los Angeles) have managed to open quite large holes, although closing them again remains elusive. A huge number of elements have been encapsulated in fullerenes, including the noble gases, which have no desire to bond with the surrounding carbon atoms but can be used in applications such as magnetic resonance imaging (MRI). Using endohedral fullerenes for medical imaging applications requires them to be water soluble. The higher fullerenes (above C_{60}) have derivatives that are generally more soluble, but they are more expensive to produce. C_{60} endohedral fullerenes are generally less soluble and air-sensitive, but relatively cheap to produce. Functionalization has managed to improve solubility and also stability in the air. Additionally, C_{60} derivatives appear to be efficiently excreted while higher fullerenes, such as C_{82} , have shown a tendency to accumulate in the lungs, liver and bones. The relatively high tolerance of biological systems to carbon is one of the reasons for the potential of buckyballs in medical applications, from delivery of radioisotopes to cancer cells, to MRI. Anything included in the buckyball is effectively shielded from the body. Importantly, buckyballs are small enough to pass through the kidneys and be excreted. Biological systems can be sensitized to buckyballs, however, as has been demonstrated by the development of antibodies to them (useful for monitoring the presence of buckyballs in tissue and biological fluids).

Researchers at Rice University (Houston, Texas) have designed C_{60} and other fullerene molecules with an atom of gadolinium inside and with chemical appendages that make them water-soluble. In typical MRI contrast agents, the metal gadolinium is linked to a non-fullerene molecule, which is normally excreted quickly from the body. Fullerene-encapsulated gadolinium might allow the contrast agent to remain in the body longer.

(From: <u>http://www.clubofamsterdam.com/contentarticles/01%20Nano</u> technology/Fullerenes.pdf)

VII. Additional texts

Did you know that the discovery of fullerenes has implications for all the natural sciences and was born of astronomy by the wish to grasp the behavior of carbon in red giant stars in interstellar gas clouds? The discovery, for which Richard Smalley, Harry Kroto and Robert Curl who vaporized the graphite to produce C_{60} and won the Nobel Prize in Chemistry in 1996, has expanded knowledge of chemistry and physics. Fullerenes have been found in geological formations and in sooty flames. Research on fullerenes has resulted in the synthesis of a steadily increasing number of new compounds, already more than a thousand, and it still provides abundant opportunities for scientists.

Five Surprising Uses for Carbon Nanotubes

By Chris Jablonski for Emerging Tech July 22, 2011

Carbon nanotubes are quickly becoming the building blocks of innovation across most industries. Here are five potential applications that underscore the wide impact of these tiny tubes.

First discovered under an electron microscope over a half a century ago, carbon nanotubes are among the most sought-after materials today. The tiny structures are used in dozens of applications that touch nearly every industry, including aerospace, electronics, medicine, defense, automotive, energy, construction, and even fashion. Carbon nanotubes (aka CNTs) are made from graphene sheets consisting of a single atomic layer of carbon atoms in a honeycomb framework that can be rolled into a tube measuring about a nanometer, or one billionth of a meter, in diameter. At this scale, these cylindrical molecules defy the classic laws of physics with exceptional properties. Carbon nanotubes have excellent electrical conductivity, the ability to withstand high working temperatures, and the highest strength-to-weight ratio of any known material.

Scientists are developing new applications using these nanomaterials at a staggering clip. Below are five notable research areas that demonstrate the sweeping impact of CNTs:

1) Carbon nanotube "cupcakes" to help measure terahertz laser light

Unlike the tasty cupcakes your grandmother makes, these are made up of vertically aligned carbon nanotube arrays (VANTAs) that are grown on silicon. Using a razor blade, visible chunks of these densely packed arrays can be sliced off and placed on top of a laser power detector to detect terahertz radiation. Terahertz radiation can penetrate materials like plastic, clothing, paper and some biological tissues, making it an attractive candidate for applications, such as concealed weapons detection, package inspection and imaging skin tumors. Until 2011, there wasn't a standard method for measuring the output power of terahertz lasers, but researchers at the National Institute of Standards and Technology (NIST) have found that dense arrays of extra-long carbon nanotubes absorb nearly all light of long wavelengths, and thus are promising coatings for prototype detectors intended to measure terahertz laser power.

2. Carbon nanotubes for cleaning polluted water

Scientists from Department of Environmental Geosciences, University of Vienna, found that by using filters made of carbon nanotubes, pollutants could be removed more effectively from contaminated water as compared to common charcoal filters. CNTs have a very large surface area (e.g., 500 m2 per gram of nanotube) that gives them a high capacity to retain pollutants, such as water soluble drugs. A team at the University of Vienna found that at concentrations likely to occur in the environment, the tubes removed Polycyclic Aromatic Hydrocarbons 13 (PAHs) tested from contaminated water. The results are published in the journal Environmental Science and Technology. However, there are still many health and environmental questions to answer before such filters find their way into municipal water treatment plants.

3. Boosting solar energy storage by a factor of 10,000

The business of storing solar energy in molecules that change state in response to light could be entirely transformed by carbon nanotubes. Researchers at the Massachusetts Institute of technology (MIT) have announced a new solar thermal fuel that could store up to 10,000 times more energy than previous systems. The fuel consists of carbon nanotubes modified with azobenzene, a mix that is expected to provide the same energy storage per volume as lithium-ion batteries and can store solar energy almost indefinitely. It can also be recharged by simply exposing it to sunlight – no electricity required. There are studied some catches, however. The fuel has been using computational chemistry but not yet fully tested in the lab (as of 2011), so commercialization is still far off. Another limitation is that to produce electricity would require another conversion step, using thermoelectric devices or producing steam to run a generator.

4. Tubes by the ton for more efficient electrical transmission lines

Pure metallic carbon nanotubes could be the key to overhauling the electrical power grid with more efficient transmission lines – but only if they could be made in huge quantities and uniformly. Through a refined version of a technique called "amplification," researchers at Rice University plan to make long and highly conductive nanotube fibers they dubbed "armchair quantum wire" that could be woven into more efficient electrical transmission lines. They eagerly plan to generate a large quantity of this material by the end of summer. Aaron Franklin, a researcher at IBM's Watson Research Center says that the update Rice study probably doesn't reveal "the golden ticket for achieving high volumes of metallic-only tubes," reports MIT Technology Review. We'll just have to wait and see."

5. Molecular syringes, probes, and bioelectronic noses

Medical researchers are eying carbon nanotubes as well, such as needles for injecting drugs or genes into sick cells. Size and shape are only half the reason why. As probes, their physical properties, including their great electrical and thermal conductivity, make them particularly suited for exchanging information between the inside and outside of the cell. Nanotube probes may be used to test for certain substances and test certain processes beyond cell membranes. Besides, researchers at University of Pennsylvania are developing a carbon nanotube transistor that can "smell" by integrating a CNT transistor with olfactory receptor proteins taken from mice. The goal of this type of research, Nanowerk reports, is to transfer the sensing properties of biological molecular systems to artificial electronic devices.

Carbon nanotubes and the broader field of nanotechnology have the potential to transform our lives, but it could be decades before that potential is fully developed.

(From: <u>http://www.zdnet.com/article/5-surprising-uses-for-carbon-nanotubes/</u>)

Task 21. Analyze the text for the key phrases to be used in the following-up discussion. Write down the phrases in your exercise-book.

Task 22. Read the text again for more details and put 5-7 questions (wh-questions / open-end questions).

Task 23. Pair-work. Ask your partner the questions you have made up. Check if the answers are correct.

Task 24. Team-work. Divide into two teams and discuss the text during 5-7 minutes. Choose a presenter in each team to present the main ideas of the text in front of the class. Which of the teams presents best?

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