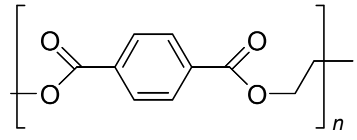
Problem 1

"I'll be back"
Terminator T-800

Paying tribute to my constant co-author

Plastic pollution is defined as accumulation of plastic products in the environment producing a negative impact on animal and human habitats. This problem is among the most vital challenges facing humanity nowadays. Surprisingly, sometimes nature itself offers assistance, such as bioremediation. Thus, Japanese researchers have recently discovered that the bacterium *Ideonella sakaiensis* can use polyethylene terephthalate (PET), a polymer with an extremely high resistance towards biodegradation, as the major source of carbon and energy.

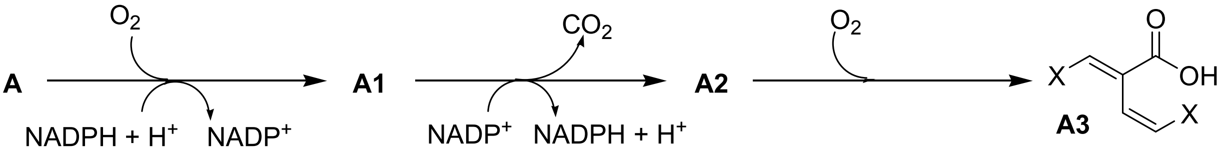


PET biodegradation involves two enzymatic steps catalyzed by hydrolases and leading to three low molecular weight (M<600 g/mole) aromatic products **A**, **B**, and **C** with the number of types of hydrogens of 2, 4, and 6, respectively. After penetration inside *Ideonella sakaiensis* cells, **C** is metabolized into **A**, which turns out to be the only source of carbon for the bacterium.

1. Show the chemical bonds (use arrows) in the PET formula that are cleaved in the process of its hydrolase-catalyzed biodegradation.

2. Draw all possible structures of **A**, **B**, and **C**, which are in agreement with the given data.

A undergoes a three-step enzyme catalyzed metabolic transformation (all chemical equations):



X is a functional group in **A3**, $NADP^+$ and NADPH are oxidized and reduced co-enzyme forms, respectively.

3. Deduce the structural formula of **A3** if its molar fractions of oxygen and hydrogen are equal and lower than that of carbon.

4. Draw the structural formulae of **A1** and **A2**.

5. Choose the correct statement concerning *Ideonella sakaiensis* in the Answer Sheet.

It was reported that the rate of the PET-based film biodegradation by an established bacterial colony with a constant number of cells is of 0.13 $mg\cdot cm^{-2}\cdot days^{-1}$.

6. Calculate how many days the colony would need to degrade 1 mass% of spherical PET granules with the diameter of 1 cm and density of 1.45 $g\cdot cm^{-3}$.

The possibility of PET hydrolysis was previously shown for cutinase, the enzyme involved in nature in a similar process of degradation of the biopolymer cutin, which is the major component of cuticle covering plant leaves. The compound **D** (70.54% C, 11.84% H, and 17.62% O by mass) is the major monomer in cutin biosynthesis.

7. Deduce the structure of **D** (M < 300 g/mole) if it is an unbranched compound free of chiral carbon atoms.

8. Draw the monomer unit of the polymer composed solely of **D**.

Problem 2

Proteins are composed of α-amino acid residues linked together by peptide bonds between carboxylic and amino groups. Alongside such canonical (proteinogenic) α-amino acids, there are other natural compounds containing amino and acidic groups. Being involved in metabolic processes, the latter substances are not found in proteins. Thus, the compound **A** with the molar mass of 125 g/mole is used as a drug and nutritional supplement. It reveals much more pronounced acidic properties than those of α-amino acids.

1. Give one example of each of optically inactive and optically active canonical α-amino acids. Draw the latter as a Fischer projection of the isomer incorporated into proteins during biosynthesis. Indicate the absolute configuration (*R*/*S*) of the asymmetric center.

A is a white crystalline powder readily soluble in water and poorly in most organic solvents. Values of the acidity constants pK_a of the acidic and ammonium groups in **A** equals 1.50 and 8.74, respectively, whereas there are no other ionogenic groups in **A**.

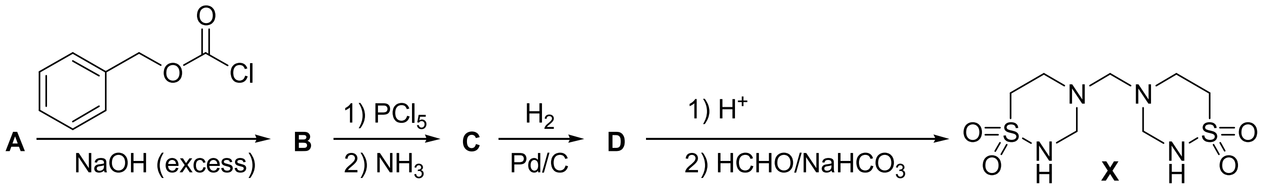
2. Write down expressions for the acidity constants. Denote the neutral form of **A** as HA, and the acidity constants as $K_1 = K_a(H_2A^+)$ and $K_2 = K_a(HA)$.

3. Show the prevailing form of an amino acid at its isoelectric point (the total charge of all the amino acid forms equals zero) using alanine (2-aminopropionic acid) as an example.

4. Calculate the pH value of the **A** solution at its isoelectric point.

5. What is the molar fraction of the completely uncharged form of **A** in the above solution if ionization of the ionogenic groups in **A** occurs independently?

The antimicrobial compound **X** was first synthesized from **A** according to the hereunder scheme:



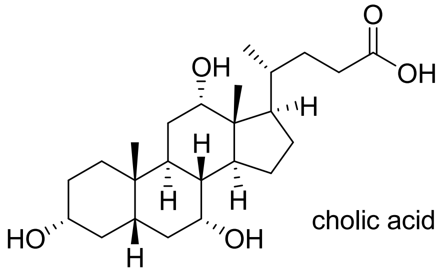
6. Draw the structural formulae of **A** – **D**.

A is very important for mammals. Most of them are capable of biosynthesizing it form an α-amino acid **E** in three consecutive enzymatic steps (enzymes $E_1 – E_3$) given hereunder. The process includes only decarboxylation and two-electron oxidation reactions. Still, **A** is an indispensible substance for some mammals because of low decarbolylase activity, which terminates the synthesis at the second step and makes the presence of **A** in the diet obligatory.

$$\mathbf{E} \xrightarrow{E_1} \mathbf{F} \xrightarrow{E_2} \mathbf{G} \xrightarrow{E_3} \mathbf{A}$$

7. Write down the three-step scheme of the **A** biosynthesis showing the structures of the intermediates and starting amino acid **E**.

A was first time isolated as its sodium salt from bovine bile. **A** interacts with bile acids (cholic, in particular) providing conjugates, which act as surfactants facilitating emulsification of fats in intestinal track. In liver, cholic acid combines with glycine and **A** affording **H** and **I**, respectively.

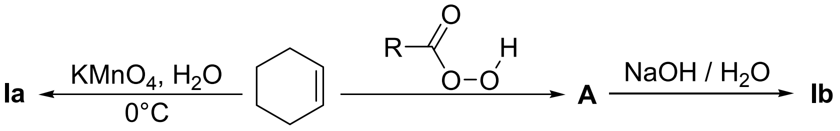


cholic acid

8. Draw the structural formulae of **H** and **I**. Which of these is a more potent emulsifier of fats? Choose the molecule and encircle the functional group responsible for the enhanced emulsifying ability.

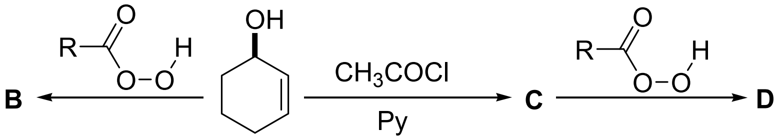
Problem 3

Alkene oxidation reactions belong to the most widespread methods of C–C double bond functionalization in the organic synthesis.



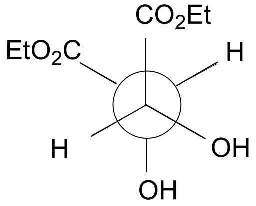
1. Write down structural formulae of compound **A** and stereoisomers **Ia** and **Ib** if both **Ia** and **A** has a plane of symmetry but compound **Ib** has not.

Stereoselectivity of epoxidation of cyclohexenes bearing a substituent at the allylic position depends on the nature of this substituent.



2. Write down structural formulae of compounds **B** – **D** if epoxidation is determined by either steric factor (for one transformation) of intermolecular hydrogen bond formation wherein substituent in the cyclohexene moiety is a hydrogen bond donor (for another one).

Sharpless developed an enantioselective epoxidation of allylic alcohols based on the use of *t*-BuOOH as an oxidant and **Me**(OR)$_n$ as a catalyst. Here, **Me** is a transition metal and OR is a chiral ligand. Namely, this ligand is either (+)- or (–)-diethyl tartrate ((+)-DET and (-)-DET, respectively). The stereochemical formula of (–)-DET is given below as a Newman projection.



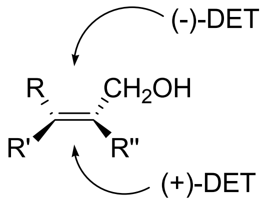
3. Write down structural formula of (–)-DET using the Fischer projection. Belong this molecule to *D*- or *L*-hydroxyacids?

Racemic mixture of (+)- and (–)-DET is synthesized from but-2-enedioic acid (**II**) by reaction with RCO_3H followed by treatment of product with aq. NaOH.

4. Write down structural formula of compound **II**.

5. Determine the formula of alcoholate **Me**(OR)$_n$ if spectrum ^{1}H NMR contains two signals (doublet and septet with the relative intensity of 6:1), and ω_C = 50.7%.

To determine a major enantiomer of oxirane, formed in the above reaction, the Sharpless rule is applied. According to this rule, molecule of allyl alcohol derivative is presented by way given below. If (–)-DET is using for epoxidation, epoxide ring is formed above the alkene plane. If (+)-DET is using, a new ring is formed below this plane.

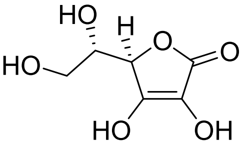


The oxidation of (*Z*)-tridec-2-en-1-ol (**E**) using *t*-BuOOH/**Me**(OR)$_n$/(-)-DET system into compound **F** is the key step in one of the synthesis of disparlure (pheromone of gypsy moth *Lymantria dispar*).

6. Write down structural formulae of compounds **E** and **F**. Point out the absolute configuration (R/S) for the chiral centers in molecule of **F**.

Problem 4

Oxidation of iodide ion with hydrogen peroxide in acidic medium occurs slowly. When we add a compound instantly binding molecular iodine, the iodine color does not appear for a certain time (lag period). When 0.125 M H_2O_2 and 0.05 M KI (concentrations are given in the reaction mixture at the start of the reaction) and ascorbic acid (AA, see Fig.; its concentrations at the start of the reaction were $1.25 \cdot 10^{-4}$, $5 \cdot 10^{-4}$ and $1.25 \cdot 10^{-3}$ M) were mixed at pH 4.5, the iodine color appeared after τ = 4, 16 and 40 s, respectively.



1. Write down:

a) Slow reaction (1) of oxidation of iodide ion with hydrogen peroxide in acidic medium;

b) Fast reaction (2) that retards the appearance of molecular iodine color (denote dehydroascorbic acid as $C_6H_6O_6$);

c) Equation relating the time of appearance of color τ with the concentration of ascorbic acid in solution (calculate the numerical value of the coefficient of proportionality);

d) Kinetic equation of the rate of consumption of H_2O_2 according to reaction (1) at a constant pH, taking into account that it has the first order in iodide ion (denote the rate constant as k_1).

2. Given that the rates of consumption of AA and reaction (1) are equal, calculate:

a) The rate of consumption of AA by reaction (2) in mol/(L·s);

b) The value of the rate constant k_1 of reaction (1), taking the current concentrations of the components equal to the original ones;

c) The duration of the lag period τ for 0.05 M H_2O_2, 0.05 M KI and $1.25 \cdot 10^{-3}$ M AA at pH 4.5, assuming current concentrations of the components are equal to their initial concentrations.

3. Molybdate ion catalyzes the oxidation of iodide with peroxide, since supramolybdic acid H_2MoO_5 and its anions oxidize iodide faster than H_2O_2 does.

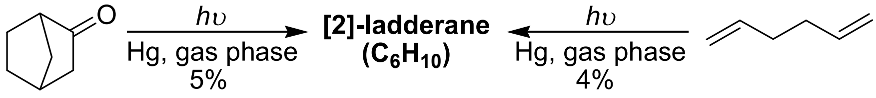
a) Assuming that molybdate is present only in the form of H_2MoO_5, write down the kinetic equation for this reaction in its general form (denote the rate constant as k_{Mo}).

b) Estimate the value of the constant k_{Mo} in presence of $1 \cdot 10^{-4}$ M MoO_4^{2-}, if the lag period was 50 s for the conditions specified in point 2c.

c) Calculate the duration of the lag period for $3 \cdot 10^{-4}$ M molybdate.

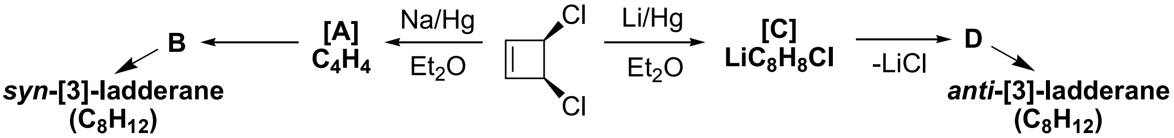
Problem 5

Ladderanes form very interesting class of hydrocarbons, unusual structural fragment of which is present in the Nature in lipids of planctomycetes that realize anammox, i.e. ANaerobic AMMonium OXidation. The molecular formula of [2]-ladderane, the simplest representative of this class, is C_6H_{10}. This compound can be produced in low yield by photolysis of norbornan-2-one or 1,5-hexadiene.



1. Write down structural formula of [2]-ladderane if it is known that: a) it has no free rotating bonds; b) its ^{1}H NMR spectrum consists of 3 signals, c) two signals are present in its ^{13}C NMR spectrum. Write name of [2]-ladderane using IUPAC nomenclature.

Molecular formula of [3]-ladderane is C_8H_{12}; it has two stereoisomers: *anti*-[3]-ladderane, having one plane of symmetry, and *syn*-[3]-ladderane, having two planes of symmetry. Both isomers were synthesized from *cis*-3,4-dichlorocyclobut-1-ene. Its treatment with sodium amalgam produces very active intermediate **A** (C_4H_4) which dimerizes immediately affording compound **B**. The catalytic hydrogenation of **B** yields *syn*-[3]-ladderane. On the another hand, treatment of *cis*-3,4-dichlorocyclobut-1-ene with lithium amalgam gives rise to organolithium compound **C** (LiC_8H_8Cl) which spontaneously eliminate lithium chloride with formation of hydrocarbon **D**, the catalytic hydrogenation of which accomplishes synthesis of *anti*-[3]-ladderane.



2. Decipher structures of [3]-ladderanes. Write down structural formulae of compounds **B**, **D** as well as reactive intermediates **A** and **C**.

3. Write down the general structural formula of [*n*]-ladderanes no accounting for stereochemistry of these compounds.

Anaerobic bacteria *Candidatus Brocadia anammoxidans* use the transformation of NO_2^- and NH_4^+ into N_2 and H_2O as the source of energy. This process proceeds in organelle that has very unusual membrane: 90% of lipid component of this membrane is formed by **pentacycloanammoxic** acid, $C_{20}H_{30}O_2$. The key structural element of this acid is [5]-ladderane which has only *anti*-arrangement of rings. It is also known that this acid has 9 tertiary carbon atoms, has no quaternary carbons; carbon atom of the ladderane scaffold, bearing a substituent, has (*S*)-configuration.

4. Write down structural formula of **pentacycloanammoxic acid**.

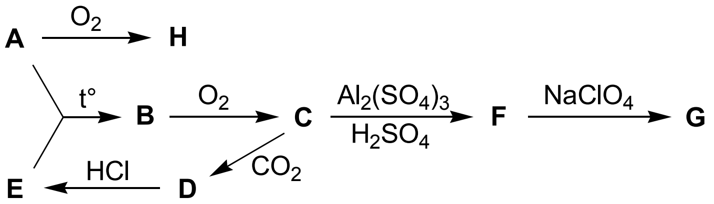
Problem 6

H. Davy (1778 – 1829)

It was a serious breakthrough in chemistry with the discovery of electricity: the birth of electrochemistry, the discovery of new elements, etc. In 1807 Humphry Davy obtained the metals **A** and **B** by electrolysis of their molten compounds. The reactivity of these elements is incomparable, thus, being on the air, they quickly turn into a mixture of oxides, peroxides, nitrides, carbonates and others.

During the combustion of **B** on the air the orange substance **C** (ω (O) = 45%) is formed, the combustion of **A** causes the formation of other oxygen-compound **H** (ω (O) = 41%) of pale yellow colour. Both **C** and **H** compounds are used for the regeneration of oxygen in submarines and spacecraft. This process is based on the interaction between **C** and carbon dioxide, which leads to the formation of **D** and oxygen. Evaporating of the solution obtained by reacting of **D** with hydrochloric acid, the compound **E** may be prepared, which is the starting material for obtaining **B** by the reaction with **A** in industry. The latter reaction of obtaining **B** is used even more in industry than electrolysis. This process takes place in a stainless steel column: the melt of **E** moves downwards and the vapour of **A** moves down up. The vapour of **B** sublimes and condenses in the refrigerator. Upon cooling the solution obtained by adding **C** to the acidified by sulfuric acid solution of aluminum sulfate is obtained well-faceted colorless crystals **F**. At the reaction of the solution of **F** with sodium perchlorate, a white precipitate **G** is obtained, which is one of the few poorly soluble metal compounds of **B**.

1. Determine the **A** – **H** formulae, write the equations according to the scheme:



2. What is the reason of the equilibrium shift towards producing products in the reaction of obtaining metal **B** from the melt of **E** and the vapour of **A**? Specify true in the answer sheet.

Typically, **A** and **B** in all the compounds exhibit a positive oxidation state, however, there are examples of complex compounds in which these metals are present in a negative oxidation state.

3. Among the above ligands in the answer sheet, select those in the complex compounds of which **A** has a negative oxidation state.

It is known that **A** and **B** form an intermetallic compound. The mole fraction of **B** is 33.3%.

4. Identify the composition of intermetallic compound.

Problem 7

There are many types of cement, but the most widespread one is Portland cement. It is mostly (more than 90%) composed of ground clinker, whose approximate composition is given in the table below. The properties of Portland cement are commonly defined by two calcium silicates, **X** and **Y**, in the clinker. The mass fractions of calcium in **X** and **Y** are 52.66% and 46.54% respectively. The first row of the table below contains the international designations (in cement chemistry) of various components of the clinker. In reality, clinker comprises approximately 2–3% mass. of minor components (oxides of potassium, sodium, phosphorus, manganese, sulfur, hydrogen, etc. in bound states, which come from the source materials), but we will not consider them in this problem.

Designation			**C_4AF**	**C_3A**	**M**
Composition	**X**	**Y**	$Ca_4Al_2Fe_2O_{10}$	$Ca_3Al_2O_6$	MgO
ω,%	62.0	16.0	8.50	12.0	1.50

The raw materials used in making the clinker are various natural minerals: limestone (calcite), clay (kaolinite $Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$), periclase (MgO), iron ore (Fe_2O_3) and quartz sand. All the aforementioned minerals contain SiO_2 as an impurity, which is 8.50% of the minerals by mass. In addition to SiO_2, iron ore also contains 4.10% of Al_2O_3, and clay contains 4.60% of Fe_2O_3. All the starting materials are mixed together in required proportions and calcined (heated when exposed to air) at 1500 °C in special rotating furnaces to obtain clinker. After cooling and grinding, the clinker is mixed with gypsum (under these conditions, it partially dehydrates to form gypsum plaster, also known as plaster of Paris) to produce Portland cement. The amount of gypsum added must be so that the mass fraction of sulfur oxide (VI) in the final product is 3.00%.

Because the compositions of natural raw materials used in the process are not constant in a real industrial process, the ratios of the components used in making clinker must constantly be adjusted. The properties of Portland cement are most affected by the ratio of **X** and **Y**, which depends on the ratio of SiO_2, Al_2O_3 and Fe_2O_3 in the clinker. In order to control this ratio, the Lime Saturation Factor (LSF) is used, which is computed by using the mass fractions of the aforementioned oxides in the clinker. The Lime Saturation Factor is computed as follows:

$$\mathrm{LSF} = \frac{\omega(\mathrm{CaO})}{2.80\cdot\omega(\mathrm{SiO_2})+1.18\cdot\omega(\mathrm{Al_2O_3})+0.650\cdot\omega(\mathrm{Fe_2O_3})}$$

The LSF characterizes the ratio between quantities of **X** and **Y**, as well as the degree of binding of CaO in the clinker. If LSF = 1, then only **X** is present and there is no **Y**, and if LSF>1, then **X** and unbound CaO are present. The magnitude of LSF is used to confirm that the composition of cement is standardized, and will behave in a predictable manner.

1. Determine the chemical formulas of X and Y and give their international designations.

2. Calculate the masses of all components needed to produce 100 tons of Portland cement.

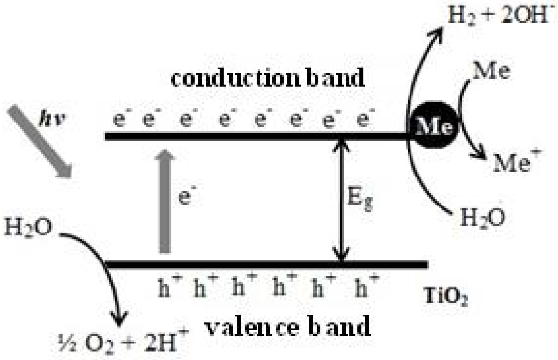
3. Calculate the mass fractions of all oxides in Portland cement.

4. Calculate LSF for Portland cement of the above composition. Show your calculations.

In all calculations, use atomic masses rounded to the nearest integer. The final answers should have at least three significant figures.

Problem 8

Hydrogen is a promising renewable energy source. One of the ways of production of hydrogen is photocatalytic decomposition of water. The mechanism of the process is presented in figure. Titanium dioxide can serve as an example of such a photo-catalyst. Under light excitation with photon energy, greater than the band gap of the semiconductor (E_g) electrons transfer to the conduction band, leaving holes (h+) in the valence band. The efficiency of the process decreases because of rapid recombination of the pairs e^-–h^+. For charge separation the catalyst is doped by transition metals.



1. Choose the metals in the table, addition of which can improve the efficiency of photo-catalytic decomposition of water.

Ion	$E^0(Me^{n+}/Me)$, V
Fe^{3+}	–0.037
Mn^{2+}	–1.19
Co^{2+}	–0.28
Ce^{3+}	–2.34

Ion	$E^0(Me^{n+}/Me)$, V
Pt^{2+}	1.12
Ru^{2+}	0.445
Cu^{2+}	0.521
Ag^+	0.7996

In the systems, having particles smaller than 100 nm, size effects are often observed – dependence of physical-chemical properties of substances from the size of the particles. Dependence of the band gap on the size of nanoparticles for an oxide semiconductor is expressed by the formula

$$E_g(R) = E_{g0} + \frac{a}{R^2} - \frac{b}{R},$$

where E_{g0} – band gap of the bulk phase, $\mu = m_e^* \cdot m_h^* / (m_e^* + m_h^*)$ – reduced mass of the effective masses of electron (m_e^*) and a hole (m_h^*), ε_0 – electric constant, ε – dielectric permittivity, e – electron charge, R – radius of the particle, $a = h^2/8\mu$, $b = 1.8e^2/4\pi\varepsilon\varepsilon_0$.

2. a) Calculate the band gap energy value for TiO_2 nanoparticles with $R = 2$ nm, if $E_{g0} = 3.0$ eV, $\varepsilon = 184$, $\mu = 0.74\ m_e$; b) In what direction shifts the wavelength of radiation which initiates conductivity, in case of nanoparticles, compared with bulk phase? c) Calculate the effective mass of electrons and holes if $m_e^* = 12.5\ m_h^*$.

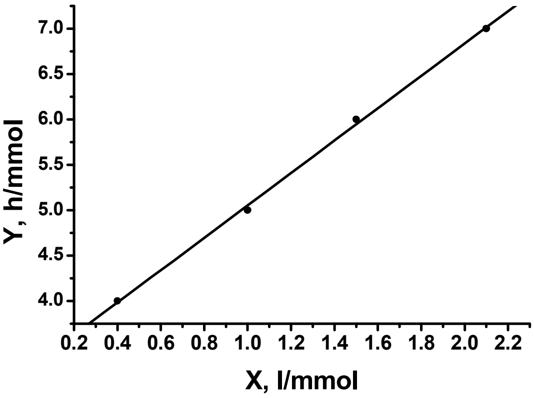
Efficiency of photocatalytic hydrogen production can be estimated with the quantum yield φ – ratio of the number of the "effective" electrons (n_e) to the number of photons (n_p) generated by a light source per time unit.

3. Calculate the quantum yield n_e/n_p (%). The maximum rate of hydrogen formation for this catalyst $V_{max} = 5.6$ μmol/min, light source power $P = 67$ mW, light wavelength 421 nm.

Kinetics of the reactions, occurring on the photocatalyst surface, can be described using Langmuir – Hinshelwood model:

$$\mathrm{A + Z} \overset{K_A}{\longleftrightarrow} \mathrm{AZ} \xrightarrow{k} \mathrm{P + Z}$$

where Z – adsorption centers, A – organic substrate, P – product of the reaction, K_A – adsorption constant, k – reaction rate constant. The rate of hydrogen in this reaction is defined as $W(H_2) = kn_A$, where $n_A = \dfrac{K_A C_{0A}}{1 + K_A C_{0A}}$ – degree of surface coverage. After linearization of the curve $W(H_2)$ the equation $y = 3.27 + 1.78x$ was obtained (see figure).



4. a) Determine, to what variables correspond x and y on the graph; b) calculate k and K_A.

Physical constants: $h = 6.63 \cdot 10^{-34}$ J·s, $N_A = 6.02 \cdot 10^{23}$ mol^{-1}, $c = 3 \cdot 10^8$ m·s^{-1}, 1 eV = $1.6 \cdot 10^{-19}$ J, $m_e = 9.1 \cdot 10^{-31}$ kg, $\varepsilon_0 = 8.85 \cdot 10^{-12}$ F/m, $e = 1.6 \cdot 10^{-19}$ C.