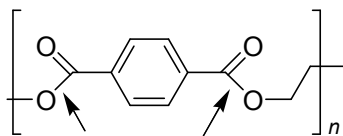# Problem 1 (author Garifullin B.N.)

**1.** The ester bond is only one hydrolase target in the PET structure (0.5 point):

2. Only ester bonds being hydrolyzed, either hydroxyl or carboxylic groups are found as the terminal ones in **A**, **B**, and **C**. The ratio of the total number of hydrogen atoms and their types in the products allow concluding that these are compounds with high symmetry. With due account for the molecular mass limit one gets only one variant for **A** (terephthalic acid), two structures for **B** and three options for **C**.
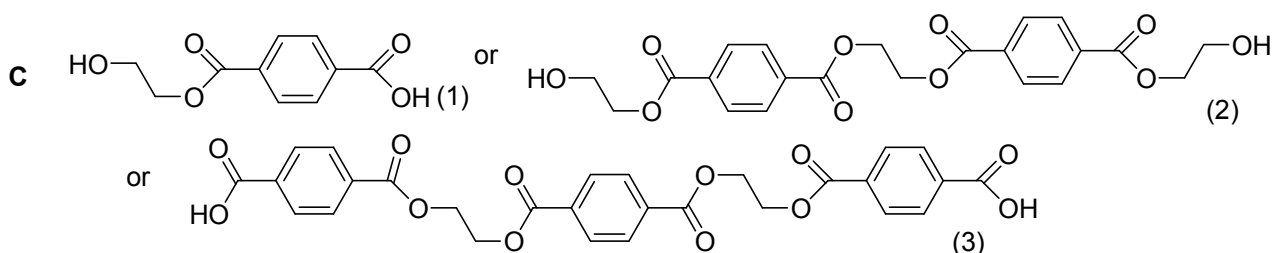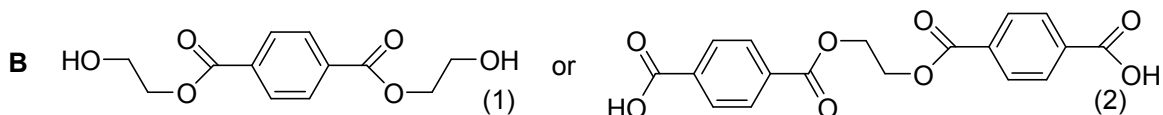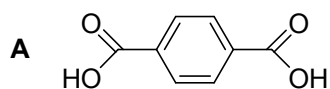

Actually, **B** and **C** are found as the products labeled (1) (0.5 point for each structure, 3 points in total).

3. The numbers of O and H atoms is equal in **A3** because of equality of the corresponding molar fractions. The fragment of **A3** (the residue lacking two functional groups X) contains 2 O and 4 H atoms. Supposed X has x O and y H atoms, one gets: $2x + 2 = 2y + 4$, and $x = y + 1$. The molar fraction of C dictates the presence of carbon in X. Combining all the above data, one gets that X is the carboxylic group (-COOH). Finally, the structural formula of **A3** is (0.25 point for the calculations, 0.5 point for the structure, 0.75 points in total):
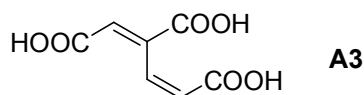

4. The **A** → **A3** transfer can be represented as:
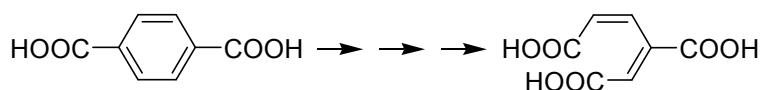
All steps in the scheme being the reaction equations, the molecular formulae of the intermediates are as follows: **A1** ($C_8H_8O_6$) and **A2** ($C_7H_6O_4$). The corresponding structural formulae can be determined based on the reaction mechanisms (1 point for each structure, 2 points in total):
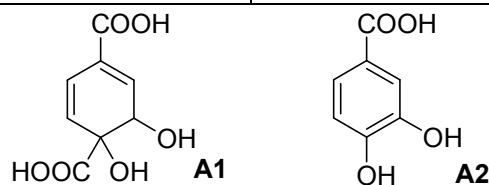
Another theoretically possible metabolic pathway is in disagreement with the final product:
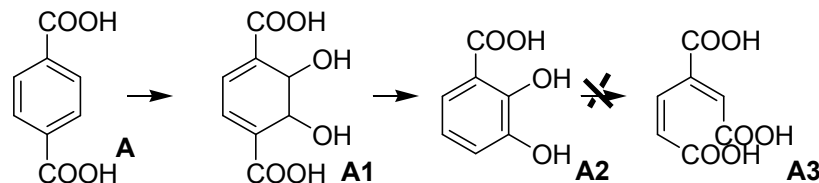

5. *Ideonella sakaiensis* uses molecular oxygen at least at two steps of terephthalic acid metabolism, which demonstrates it aerobic character. Penetration of **C** inside the cell from the extracellular space suggests the initial PET hydrolysis catalyzed by an enzyme secreted by *Ideonella sakaiensis* outside the cell (0.75 point).

6. The area of an individual PET granule surface is $S = 4 \cdot \pi \cdot r^2 = 3.14$ cm^2. The *Ideonella sakaiensis* colony decreases the granule mass by 3.14 cm$^{-2} \cdot 0.13$ mg$\cdot$cm$^{-2} \cdot$day$^{-1} \cdot 1$ day = 0.41 mg. The initial mass of the PET granule is = 754 mg, and 1% of it is 7.54 mg. Neglecting the change of the granule surface area as a result of 1% mass decrease (i.e. considering the process rate constant), one gets that the colony needs 7.54 / 0.41 ≈ 18 days (1 point).

7. The net formula of **D** is:

$$n(\text{C}) : n(\text{H}) : n(\text{O}) = \frac{70.54}{12.01} : \frac{11.84}{1.008} : \frac{17.62}{16.00} = 16 : 32 : 3,$$

which turns out to be the empirical one ($C_{16}H_{32}O_3$) with due respect to the molar mass limit. Cutinase hydrolyses the ester bonds in PET. Thus, one can suppose that cutin also contains ester bonds. Since **D** affords cutin if used as the only monomer, it should contain both carboxylic and hydroxyl groups. With due account of other information about **D**, the only possible structure is (0.5 point for the calculations, 0.75 point for the structure, 1.25 points in total):
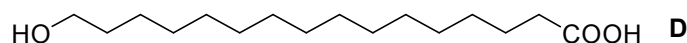
8. The monomer unit of the 16-hydroxypalmatic acid polymer (0.75 point):
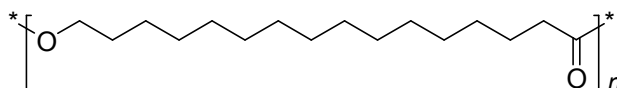
Problem 2 (authors Shved A.M., Gladilin A.K.)

1. Glycine (aminoacetic acid) is the only optically inactive canonical α-amino acid. Other amino acids like alanine (2-aminoprpanoic acid) are optically active containing at least one chiral center. Proteins are synthesized only from *L*-amino acids, which corresponds to *S*-configuration of the α-carbon atom, except for *L*-cysteine with *R*-configuration of the α-carbon atom and glycine as an achiral compound (0.5 point for each example, 0.25 point for each of the configuration indication and Fischer projection, 1.5 points in total)
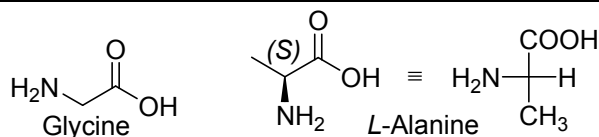
2. Acid-base equilibria in an amino acid solutions can be considered as a sequence of dissociation steps of a polyprotic acid. The amine group being protonated in strongly acidic solutions, the positively charged particles H_2A^+ is the prevailing form of the amino acid under such conditions. The amino acid exists in its neutral form HA in neutral solutions and is deprotonated affording the negatively charged form A^- in basic solutions (0.5 points for each expression, 1 point in total):

$$H_2A^+ \rightleftharpoons HA + H^+ \qquad K_1 = \frac{[H^+][HA]}{[H_2A^+]} = 10^{-8.74}$$

$$HA \rightleftharpoons A^- + H^+ \qquad K_2 = \frac{[H^+][A^-]}{[HA]} = 10^{-1.50}$$
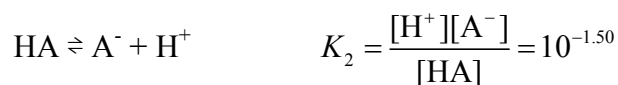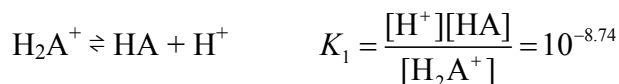
3. Amino acids are amphoteric electrolytes due to the presence of both basic amine and acidic carboxylic groups. Zwitterion (inner salt) with zero net charge is the prevailing form of any amino acid at its isoelectric point (0.25 point for alanine structure (stereochemistry not necessary), 0.25 point for zwitterionic form, 0.5 point in total).
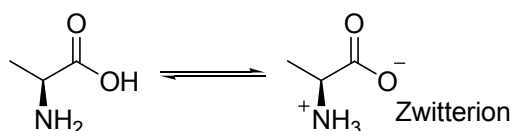
4. The net charge of an amino acid at its isoelectric point is zero. Thus, concentrations of H_2A^+ and A^- are equal, whereas that of the neutral zwitterion form is maximal. Using the expressions for K_1 and K_2, one gets:

$$[H_2A^+] = [A^-] \Rightarrow \frac{[H^+][HA]}{K_1} = \frac{K_2[HA]}{[H^+]} \Rightarrow \frac{[H^+]}{K_1} = \frac{K_2}{[H^+]} \Rightarrow [H^+]^2 = K_1 \cdot K_2 \Rightarrow [H^+] = \sqrt{K_1 \cdot K_2}$$

pI (pH at the isoelectric point) (0.5 point):

$$pI = -\log[H^+] = -\log(\sqrt{K_1 \cdot K_2}) = \frac{1}{2}(-\log K_1 - \log K_2) = \frac{pK_1 + pK_2}{2} = \frac{8.74 + 1.50}{2} = 5.12$$

5. Given protonation of the amino (–NH₂) and deprotonation of the acidic (–AH) groups occur independently, the molar fractions of neutral forms of these groups are:

$$\alpha(-NH_2) = \frac{[-NH_2]}{[-NH_2] + [-NH_3^+]} = \frac{[-NH_2]}{[-NH_2] + [-NH_2]\frac{[H^+]}{K_1}} = \frac{K_1}{K_1 + [H^+]} = \frac{10^{-8.74}}{10^{-8.74} + 10^{-5.12}} = 2.40 \cdot 10^{-4}$$

$$\alpha(-AH) = \frac{[-AH]}{[-AH] + [-A^-]} = \frac{[-AH]}{[-AH] + [-AH]\frac{K_2}{[H^+]}} = \frac{[H^+]}{[H^+] + K_2} = \frac{10^{-5.12}}{10^{-5.12} + 10^{-1.50}} = 2.40 \cdot 10^{-4}$$

Then the molar fraction of the completely uncharged form of **A** is (0.5 point for each calculation of the molar fractions, 1.5 points in total):

$$\alpha(-NH_2, -AH) = \alpha(-NH_2) \cdot \alpha(-AH) = (2.40 \cdot 10^{-4})^2 = 5.76 \cdot 10^{-8} (5.76 \cdot 10^{-6}\%)$$

**6.**   **A** contains both amino and acidic groups, which strongly suggests the amino group protection at the first step, and formation of the acyl chloride with its subsequent transformation into the amide **C** as the second one. This is followed by deprotection resulting in **D**, containing amide and amino groups. Then **D** is treated with an acid providing the corresponding salt. Finally, formaldehyde is added to the neutralized solution of **D** leading to taurolidine **X** containing aminal (aminoacetal) groups. Thus, **A** is 2-aminoethanesulfonic acid or taurine. $M(A) = M(NH_2–CH_2–CH_2–SO_3H) = 125$ g/mole, whereas the acidic properties of **A** are due to the sulfo group. The scheme of taurolidine synthesis is (0.5 point for each of **A** – **D**, 2 points in total):
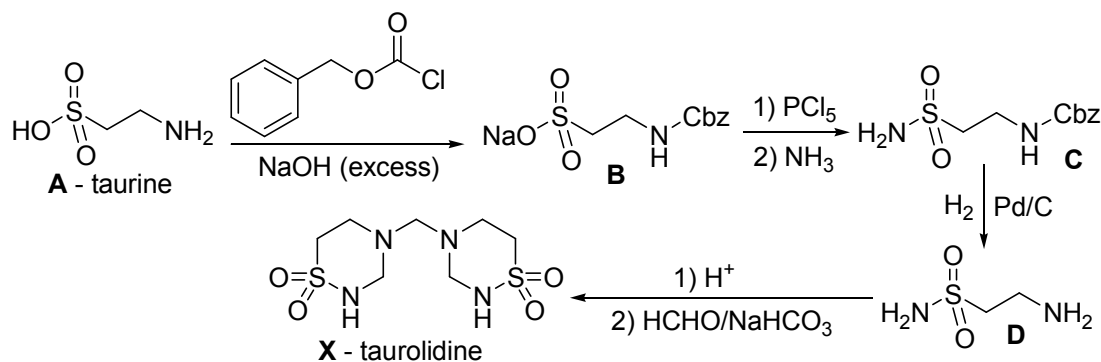
7.   With due account for the steps of **A** biosynthesis, the amino acid **E** should have a sulfur-containing group subjected to oxidation and 3 carbon atoms. Cysteine is the only amino acid meeting the criteria. The metabolic pathway should include two oxidations (S(II) to S(IV) and S(IV) to S(VI)) and decarboxylation Some mammals (e.g. cats) are not capable of the decarboxylation, while the biosynthesis is blocked at the second step. Then the sequence of reactions is as follows (0.5 point for each structure, 0.5 point for the correct sequence of steps, 2 points in total):
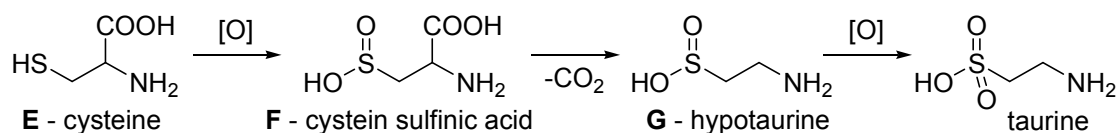

8.   Glyco- and taurocholic acids are amides formed by corresponding amino acids and cholic acid. Bile acids and conjugates participate in the formation of micelles with food lipids. In this case, the non-polar fragments of the conjugates are oriented inside the micelles and contact with triacylglycerides, and the ionogenic groups are exposed towards intestinal lumen, leading to fat droplets emulsification. The form of emulsion is necessary for effective fat splitting, which is carried out by lipase enzyme. Since the conjugates have identical non-polar moiety, the effectiveness of fat absorption is determined by dissociation degree of the corresponding acidic group. Taurocholic acid possesses a much stronger acidic group, thus being a better fat emulsifier (0.25 point for each structure, 0.25 for choosing the compound, 0.25 point for the functional group, 1 point in total).

H - glycocholic acid   **I** - taurocholic acid
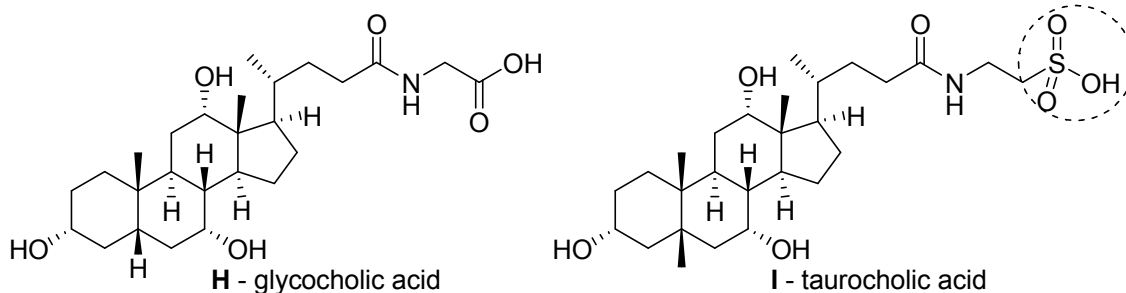
Problem 3 (author Bahtin S.G.)

1. Accounting for elements of symmetry, compound **Ia** is *cis*-diol and compound **Ib** is its *trans*-isomer. Compound **A** is, evidently, cyclohexene oxide (three structural formulae, 0.5 points for each, 1.5 points in total)
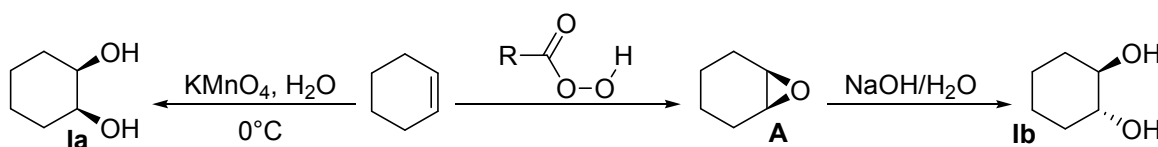
2. Acetoxy group cannot be a hydrogen bond donor. So, this donor is OH-group. Therefore, cyclohexenol oxidation should proceed *via* approach of oxidant from the side occupied by hydroxyl-group (*syn* addition). Oppositely, oxidation of its acetate is controlled by steric factors, therefore, oxidant approaches to C–C double bond from the opposite side (*anti* against bulky acetoxy-group) (three structural formulae, 1 point for each, 3 points in total).
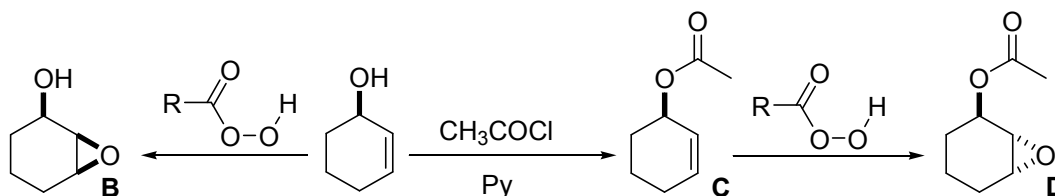
3. In the Fischer projection the carbon skeleton of the main chain is arranged in a vertical direction. Vertical substituents are located below plane of paper, horizontal substituents are located above this plane. Knowledge of these rules allows one to present (-)-DET in the Fischer projection (fischer projection for (–)-DET – 0.5 point, the identification of molecule as derivative of *L*-aldaric acid – 0.5 point, 1 point in total).
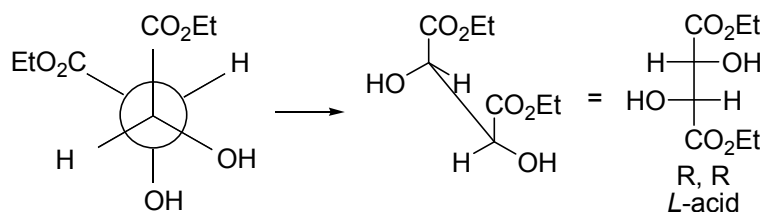
4. From question 1 we can conclude that the consecutive treatment of alkenes with peracid and aqueous alkali solution affords *trans*-dihydroxylation products. So, we can re-write structure of

DET as a conformation wherein OH groups have *trans*-arrangement. This allows to understand that the starting alkene had *Z*-configuration (1 point for the structural formula of II).
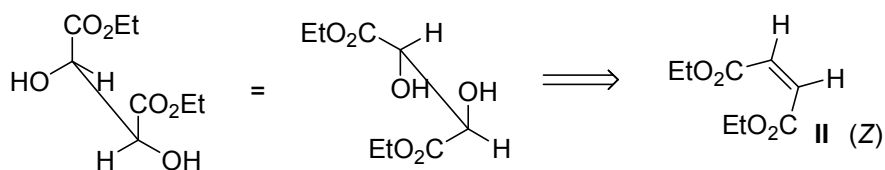
5. The multiplicities and relative intensities of signals in ^1H NMR spectrum are indicative of isopropyl group $(CH_3)_2CH$. Therefore, metal alcoholate is – **Me**$(O-i-C_3H_7)_n$. If $n = 2$, **Me** is Mg. However, magnesium is not transition metal. However, if $n = 4$, **Me** – Ti, alcoholate is $Ti(O-i-C_3H_7)_4$ (1 point for formula).

6. Let us write down structure of **E** from its name using the Sharpless rule. This allows to predict the stereochemical result of the epoxidation (compound **F**). In compound **F** atom C(2) has (*R*)-configuration, атом C(3) has (*S*)-configuration (structural formula of E – 0.5 points, structural formula of F – 1 point; right indication of the absolute configuration of two chiral centers – 0.5 points for both centers, 2.5 points in total).
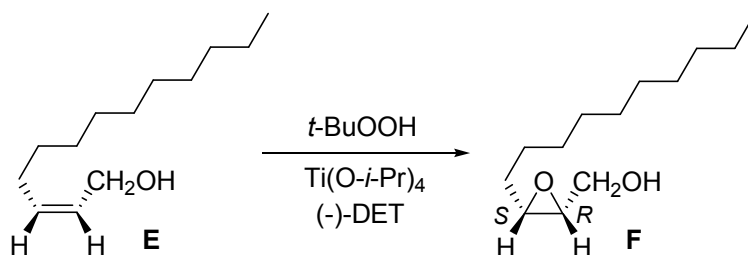
Problem 4 (author Beklemishev M.K.)

The described reactions with "retardants" are called Landolt type reactions.

1. a) $H_2O_2 + 2I^- + 2H^+ = I_2 + 2H_2O$ (1 point)   (1)

b) $C_6H_8O_6 + I_2 = C_6H_6O_6 + 2I^- + 2H^+$ (1 point)   (2)

c) Judging by the times of appearance of molecular iodine and the concentrations of AA, these values are proportional to each other ($\tau = y[AK]$) with the proportionality coefficient $y = 3.1 \cdot 10^4$ (0.5 points).

d) The rate of reaction (1) at a constant pH is written as follows, taking into account its first order in iodide ion specified by the problem situation: $-d[H_2O_2]/dt = k_1[H_2O_2][I^-]$ (1 point, 3.5 points in total).

2. The rate of reaction (1) is substantially lower than that of reaction (2), therefore, all iodine evolved reacts instantly with AA. For that reason, the rate of consumption of AA is equal to the rate of iodine production, i. e. reaction rate (1): $-d[AK]/dt = -d[H_2O_2]/dt$, as noted in point 2 of the problem specification. The remaining calculations follow from that.

a) The average consuming rate of AA can be assessed as follows: $-d[AK]/dt = 1.25 \cdot 10^{-3}$ M/40 s $= 5 \cdot 10^{-4}$ M/16 s $= 1.25 \cdot 10^{-4}$ M/4 s $= 3.1 \cdot 10^{-5}$ M/s (1 point).

b)   From $-d[AK]/dt = k_1[H_2O_2][I^-]$ we find $k_1 = 3.1 \cdot 10^{-5}/(0.125 \cdot 0.05) = 0.0050$ M^{-1}·s^{-1} (**1 point**).

c)   Let us evaluate the rate of reaction **1** in terms of question 2d, knowing the value of k_1: $d[I_2]/dt$ = $k_1[H_2O_2][I^-] = 0.005 \cdot 0.05 \cdot 0.05 = 1.25 \cdot 10^{-5}$ M/s. On account that reaction (2) is fast and $d[I_2]/dt =$ $-d[AK]/dt$, we can find the time necessary to work out the iodine concentration corresponding to the concentration of AA given in the question: $\tau = [AA]/k_1[H_2O_2][I^-] = 1.25 \cdot 10^{-3}$ M$/1.25 \cdot 10^{-5}$ M/s = 100 s (2 points).

3.   a) $-d[H_2O_2]/dt = k_1[H_2O_2][I^-] + k_{Mo}[H_2MoO_5][I^-]$ (1 point).

b)   In the expression derived under 2c, an <u>additional summand</u> ($k_{Mo}[H_2MoO_5][I^-]$) will appear due to the catalytic action of molybdate: $\tau = [AA] / (k_1[H_2O_2][I^-] + k_{Mo}[H_2MoO_5][I^-]) =$ $= 1.25 \cdot 10^{-3} / (1.25 \cdot 10^{-5} + k_{Mo} \cdot 1 \cdot 10^{-4} \cdot 0.05) = 50$ s, wherefrom $k_{Mo} = 2.5$ M^{-1}·s^{-1} (1 point).

c) $\tau = [AA]/(k_1[H_2O_2][I^-] + k_{Mo}[H_2MoO_5][I^-]) = 1.25 \cdot 10^{-3}/(1.25 \cdot 10^{-5} + 2.5 \cdot 3 \cdot 10^{-4} \cdot 0.05) = 25$ s (0.5 points).

Problem 5 (author Volochnyuk D.M.)

1.   The solution below is not the most efficient but demonstrates the general principles allowing for solve this problem using knowledge typical for the most participants of Olympiad. So, from the molecular formula of [2]-ladderane we can conclude that this may be alkyne, diene, cycloalkene or bicycloalkane. Evidently, it is possible to write down all possible isomers and select compounds with symmetry pointed out in the problem. However, this approach is time-consuming. We know that ^{13}C NMR spectrum contains two signals only demonstrating high symmetry of [2]-ladderane. Only two compounds meet this requirement.
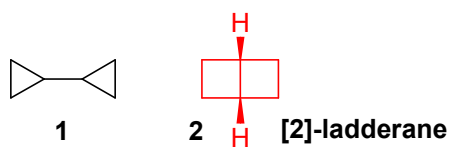
Both structures have also 3 signals in their ^{1}H NMR spectra. Only compound **2** has no free rotating bonds. So, it is [2]-ladderane. Two rings in this molecule have *cis*-annulation as *trans*-connection is impossible due to vast steric strain. The nomenclature name of this compound is bicycle[2.2.0]hexane (1 point for structural formula, 1 point for name; 2 points in total).

2.   To answer this question, we can consider topology of molecule or analyze chemical data. It is possible to suppose that intermediate **A** is antiaromatic cyclobutadiene (other possible isomers, such as methylenecyclopropene or butatriene do not meet the requirements of problem). Therefore, compound **B** is the product of the Diels-Alder dimerization of cyclobutadiene, i.e. *syn*-annulated tricyclic diene hydrogenation of which produces *syn*-[3]-ladderane. To determine this structure, we can write down structural formula of *anti*-[3]-ladderane even considering no the transformation

leading to it. Moreover, knowledge of structure of *anti*-[3]-ladderane allows to write down the second part of the scheme (structural formulae of two ladderanes, compounds **B** and **D** – 1 point for each, structural formula of **A** and **C** – 0.5 points for each; 5 points in total).
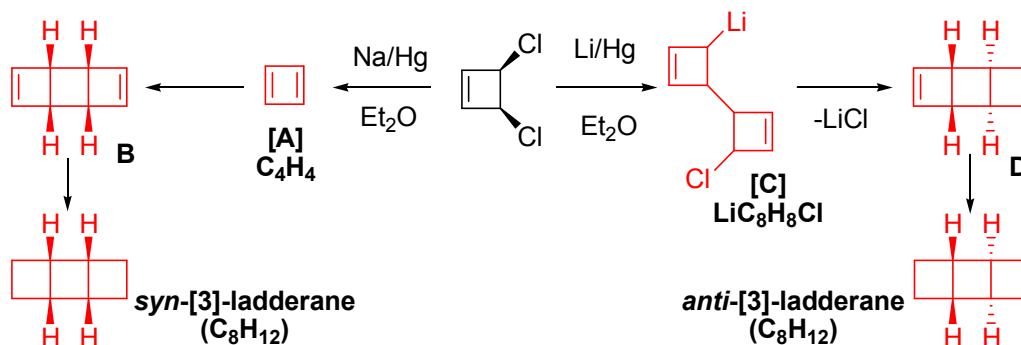
3. Analysis of the determined structures of [2]- and [3]-ladderanes allows for determining the general structural formula of [n]-ladderane (1 point).
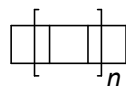
4. Analysis of data given in the problem allows for determining umambiguously the structure of pentacycloanammoxic acid (2 points including 1 point for scaffold, 0.5 point for the relative configuration of the substituent and rings, 0.5 point for the absolute configuration)
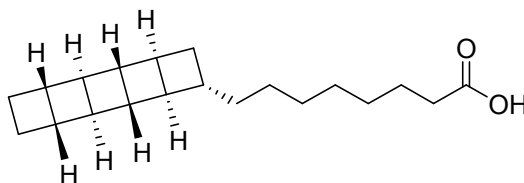
Problem 6 (author Likhanov M.S.)

1. During the combustion metals can be oxidized to oxides, suboxides, peroxides, superoxides. Examining the possible oxidation states for metals and types of their oxygen compounds, we get the following variants: M_2O, MO, M_2O_3, MO_2, M_2O_2, where M is the unknown metal. Then, based on the mass fraction of oxygen 10 equations can be obtained:

$$\text{in case of } M_2O: \frac{16}{16 + 2x} = 0.45 \text{ and } \frac{16}{16 + 2x} = 0.41$$

$$MO: \frac{16}{16 + x} = 0.45 \text{ and } \frac{16}{16 + x} = 0.41$$

$$M_2O_3: \frac{48}{48 + 2x} = 0.45 \text{ and } \frac{48}{48 + 2x} = 0.41$$

$$MO_2: \frac{32}{32 + x} = 0.45 \text{ and } \frac{32}{32 + x} = 0.41$$

$$M_2O_2: \frac{32}{32 + 2x} = 0.45 \text{ and } \frac{32}{32 + 2x} = 0.41$$

In all cases, x is a mass of unknown metal. Solving the equations, we find that in the case of MO_2 with $\omega(O) = 45\%$ $x = 39.1$, this is potassium. And for the case of M_2O_2 and $\omega(O) = 41\%$ $x = 23.0$, this is sodium (1 point for the calculation).

Thus, A and B - is the alkali metals sodium and potassium, respectively. Combustion of sodium leads to the formation of sodium peroxide and in case of potassium a superoxide is formed:
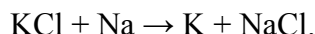
$$2Na + O_2 \rightarrow Na_2O_2, \ K + O_2 \rightarrow KO_2; \ \textbf{H} - Na_2O_2, \ \textbf{C} - KO_2.$$
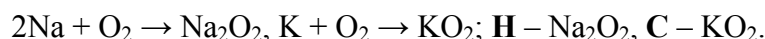
KO_2 absorbs carbon dioxide with the formation of carbonate and oxygen:

$$4KO_2 + 2CO_2 \rightarrow 2K_2CO_3 + 3O_2\uparrow; \ \textbf{D} - K_2CO_3.$$

The reaction of potassium carbonate with hydrochloric acid is a simple metathesis reaction:

$$K_2CO_3 + 2HCl \rightarrow 2KCl + H_2O + CO_2\uparrow; \ \textbf{E} - KCl.$$
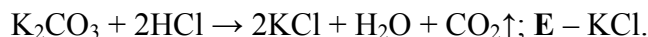
Preparation of potassium from the melt of its chloride with sodium vapour:
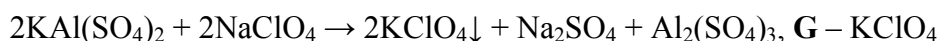
$$KCl + Na \rightarrow K + NaCl.$$

The addition of potassium superoxide to an acidified solution of aluminum sulfate with the following cooling is the way to grow the beautiful faceted clear crystals of potash alum. At the same time a controlled and slow addition of KO_2 to the solution causes the formation of oxygen and H_2O_2:

$$2KO_2 + Al_2(SO_4)_3 + H_2SO_4 + 24H_2O \rightarrow 2KAl(SO_4)_2 \cdot 12H_2O\downarrow + H_2O_2 + O_2\uparrow,$$
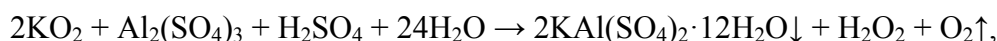
Uncontrolled rapid addition of KO_2 causes the decomposition of hydrogen peroxide with the formation of oxygen:

$$4KO_2 + 2Al_2(SO_4)_3 + 2H_2SO_4 + 46H_2O \rightarrow 4KAl(SO_4)_2 \cdot 12H_2O\downarrow + 3O_2\uparrow,$$

$\textbf{F} - KAl(SO_4)_2 \cdot 12H_2O.$ (any of the written reactions considered true)
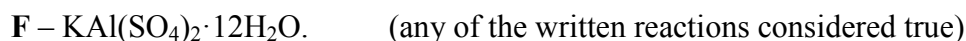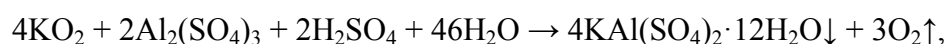
Potash alum solution reacts with a solution of sodium perchlorate with the formation of poorly soluble potassium perchlorate:

$$2KAl(SO_4)_2 + 2NaClO_4 \rightarrow 2KClO_4\downarrow + Na_2SO_4 + Al_2(SO_4)_3, \ \textbf{G} - KClO_4$$

(0.5 points for each compound and equation, 8.5 points in total)

2. The shift of the equilibrium in the reaction $KCl + Na \rightarrow K + NaCl$ is associated with a greater volatility of potassium in comparison with sodium (0.5 points).

3. It is known the example of a complex of sodium with cryptand, sodium cryptate, in which sodium is divided on Na^+ and Na^-, a similar situation is observed in the sodium complex with 15-crown-5 ether (0.25 points for each complex, 0.5 points in total).

4. The intermetallic compound – Na_2K (0.5 points).

Problem 7 (author Khvalyuk V.N.)

1. The formula of **X** is Ca_3SiO_5 (or $3CaO·SiO_2$), the formula of **Y** is Ca_2SiO_4 (or $2CaO·SiO_2$).

The compositions could be write down as simple oxides. The designation system can be determined from this writing: $Ca_4Al_2Fe_2O_{10}$ (or $4CaO·Al_2O_3·Fe_2O_3$) is C$_4$AF, while $Ca_3Al_2O_6$ (or $3CaO·Al_2O_3$) is C$_3$A. This means that **C** is used to designate calcium oxide CaO, while **A** is used to designate aluminum oxide Al_2O_3. Likewise, **F** is iron oxide Fe_2O_3, **M** is magnesium oxide MgO. Therefore silicon dioxide should be designated by **S**. The subscript determines the number of oxide formula units in the compound. From this information, it is evident that the international designation of **X** is C$_3$S and of **Y** is C$_2$S (0.25 points for formula and designation of **X** and **Y**, total 1 point).

2. We shall compute the masses required to produce 100 grams of Portland cement, and then multiply the obtained values by 10^6 to obtain the masses required to produce 100 tons.

100 grams of cement should contain 3.00% by mass, or 3.00 g, of SO_3, which means that $\dfrac{3.00}{M(SO_3)} \cdot M(CaSO_4 \cdot 2H_2O) = 6.45$ g of gypsum should be added to the clinker, which will partially dehydrate and form $\dfrac{6.45}{M(CaSO_4 \cdot 2H_2O)} \cdot M(CaSO_4 \cdot 0.5H_2O) = 5.44$ g of gypsum plaster (0.5 points). This means that 100 g of cement should contain (100 – 5.44) = 94.56 g of clinker. The clinker must contain 94.56·0.015 = 1.418 g MgO. The mass fraction of MgO in periclase is (1.00 – $\omega(SiO_2)$) = 0.915, so $\dfrac{1.418}{0.915}$ =1.55 g of periclase are needed to make the clinker (0.5 points).

Taking into account the mass fractions of the components of clinker, the mass of CaO in it should be:

$$M(CaO) \cdot [3 \cdot \frac{94.56 \cdot \omega(C_3S)}{M(C_3S)} + 2 \cdot \frac{94.56 \cdot \omega(C_2S)}{M(C_2S)} + 4 \cdot \frac{94.56 \cdot \omega(C_4AF)}{M(C_4AF)} + 3 \cdot \frac{94.56 \cdot \omega(C_3A)}{M(C_3A)} = 63.82g$$

In order to form this amount of CaO, one must have $M(CaCO_3) \cdot \dfrac{63.82}{M(CaO)} = 114.0$ g of $CaCO_3$.

The mass fraction of $CaCO_3$ in calcite is (1.00 – $\omega(SiO_2)$) = 0.915, and so $\dfrac{114.0}{0.915} = 124.6$ g of limestone are needed (0.5 points).

The amounts of Fe_2O_3 and Al_2O_3 needed in the clinker are $\dfrac{94.56 \cdot \omega(C_4AF)}{M(C_4AF)} = 0.0165$ mol and $\dfrac{94.56 \cdot \omega(C_4AF)}{M(C_4AF)} + \dfrac{94.56 \cdot \omega(C_3A)}{M(C_3A)} = 0.0586$ mol respectively.

Let us assume that the masses of clay (contains $Al_2O_3·2SiO_2·2H_2O$, SiO_2 and Fe_2O_3) and iron ore (contains Fe_2O_3, SiO_2 and Al_2O_3) are **a** and **b** respectively. Because both of these minerals contain both Al_2O_3 and Fe_2O_3, at the same time we can write down and solve the follow system of equations:

$$0.0586 = \frac{a \cdot (1.00 - \omega(SiO_2) - \omega(Fe_2O_3))}{M(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O)} + \frac{b \cdot \omega(Al_2O_3)}{M(Al_2O_3)}$$

$$0.0165 = \frac{b \cdot (1.00 - \omega(SiO_2) - \omega(Al_2O_3))}{M(Fe_2O_3)} + \frac{a \cdot \omega(Fe_2O_3)}{M(Fe_2O_3)}$$

Solving this system of equations, one obtains a = 17.12 and b = 2.12, which means 17.12 g of clay (1 points) and 2.12 g of iron ore (1 point) are required.

The clinker should contain $\dfrac{94.56 \cdot \omega(C_3S)}{M(C_3S)} + \dfrac{94.56 \cdot \omega(C_2S)}{M(C_2S)} = 0.3451$ mol of SiO₂, which is

equivalent to $0.3451 \cdot M(SiO_2) = 20,71$ g. The periclase contains $1.55 \cdot 0.085 = 0.132$ g of SiO₂, the limestone contains $124.6 \cdot 0.085 = 10.59$ g of SiO₂, the clay contains $17.12 \cdot 0.085 +$

$+ 2 \cdot M(SiO_2) \cdot \dfrac{17.12 \cdot (1.00 - \omega(SiO_2) - \omega(Fe_2O_3))}{M(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O)} = 8.375$ g of SiO₂, and the iron ore contains

$2.12 \cdot 0.085 = 0.180$ g of SiO₂. This means that an additional $(20.71 - 0.132 - 10.59 - 8.375 - 0.180) =$ $= 1.43$ g of quartz sand are needed (1 point). Therefore to make 100 tons of Portland cement, one needs 6.45 tons of gypsum, 1.55 tons of periclase, 124.6 tons of limestone, 17.12 tons of clay, 2.12 tons of iron ore, and 1.43 tons of quartz sand (4.5 points in total).

3. 100 grams of Portland cement contain: 3.00 g of SO₃,

$\dfrac{3.00}{M(SO_3)} \cdot M(CaO) = 2.10$ g CaO, and $0.5 \cdot \dfrac{3.00}{M(SO_3)} \cdot M(H_2O) = 0.3375$ g ≈ 0.34 g H₂O from the

gypsum plaster; the clinker contains 1.418 g $\approx$ 1.42 g of MgO, 63.82 g of CaO, $0.0586 \cdot M(Al_2O_3) = 5.98$ g of Al₂O₃, $0.0165 \cdot M(Fe_2O_3) = 2.64$ g of Fe₂O₃ and 20.71 g of SiO₂. Therefore, the mass fractions of all oxides in Portland cement are:

Oxide	SO₃	H₂O	CaO	SiO₂	Al₂O₃	Fe₂O₃	MgO
ω,%	3.00	0.340	65.92	20.71	5.98	2.64	1.42

(0.5 point for each oxide, total 3.5 points)

4. In order to calculate the LSF, one should use the mass fraction of the CaO that is a part of clinker, which is equal to 63.82%.

$$LSF = \frac{63.82}{2.80 \cdot 20.71 + 1.18 \cdot 5.98 + 0.650 \cdot 2.64} = 0.956, \text{ or } 95.6\% \text{ (1 point)}$$

It is interesting to note that in reality, LSF usually lies between 92% and 98%.

Problem 8 (author Gulevich D.G.)

1. The table shows two groups of metal ions, which reduction potential is either greater or less than 0 V. Addition of metal ions which electrode potential is higher than the standard hydrogen electrode leads to competition reaction of the metal phase formation. If the value of the electrode

potential of metal ion is less than this value, then in the system there are reactions of ions with h$^+$, therefore, increases the separation of the charge and rate of the target process. Thus, for doping of platinum, silver, copper and ruthenium can be used (each metal 0.25 points, 1 point in total).

2. a) The gap for TiO_2 particle:

$$E_g = 3.0 \cdot 1.6 \cdot 10^{-19} + \frac{\left(6.63 \cdot 10^{-34}\right)^2}{8 \cdot \left(2 \cdot 10^{-9}\right)^2 \cdot 0.74 \cdot 9.1 \cdot 10^{-31}} - \frac{1.8 \cdot \left(1.6 \cdot 10^{-19}\right)^2}{4 \cdot 3.14 \cdot 8.85 \cdot 10^{-12} \cdot 184 \cdot 2 \cdot 10^{-9}} =$$
$$= 4.98 \cdot 10^{-19} + 1.67 \cdot 10^{-21} - 3.22 \cdot 10^{-22} = 4.99 \cdot 10^{-19} \, J = 3.13 \, eV.$$

Thus, the band gap increases by 0.12 eV (calculation of E_g 0.5 points).

b) As $E_g(R) > E^0$, the wavelength of the absorbed radiation decreases (0.25 points).

c) $\mu = \dfrac{m_e^* \cdot m_h^*}{m_e^* + m_h^*} = 0.74 m_e$, since $m_e^* = 12.5 m_h^*$, $\dfrac{12.5 m_h^* \cdot m_h^*}{12.5 m_h^* + m_h^*} = 0.74 m_e$. Therefore $m_h^* = 0.8 m_e$, m_e^*

$= 12.5 \times 0.8 m_e = 10 m_e$. (calculation of m_e^* and m_h^* 1 point, 2.75 points in total).

3. Given the reduction of the hydrogen needs two electrons we obtain $n_e = 2 V_{max} N_A / 60 \, s =$
$= 2 \cdot 5.6 \cdot 10^{-6} \cdot 6.02 \cdot 10^{23} / 60 = 1.1 \cdot 10^{17}$ electrons/s. The specific power of the light source

$$\frac{P}{n_p} = h\nu = \frac{hc}{\lambda}$$

Therefore

$$\frac{n_p}{t} = \frac{\lambda \cdot P}{h \cdot c} = \frac{421 \cdot 10^{-9} \cdot 0.067}{6.63 \cdot 10^{-34} \cdot 3 \cdot 10^8} = 1.4 \cdot 10^{17} \text{ photons/s.}$$

The quantum yield $\varphi = (1.1 \cdot 10^{17} / 1.4 \cdot 10^{17}) \cdot 100\% = 78.6\%$, i. e. every 100 photons generate 79 electrons involved in the reaction for producing hydrogen. In the case of molecular hydrogen $\varphi(H_2) =$
$= \varphi/2 = 39.3\%$ (calculation of n_e 1 point, n_p 2 points, φ 0.25 points, $\varphi(H_2)$ 0.25 points, 3.5 points in total).

4. a) The units x and y shown in the graph, indicate that it was plotted in the coordinates $y = 1/W(H_2)$, $x = 1/C_A$ (determination x and y axes by 0.5 points);

b) For plotting an expression for the rate of hydrogen producing was rewritten in the form

$$\frac{1}{W_{H_2}} = \frac{1}{k} + \frac{1}{kK_A} \cdot \frac{1}{C_{0A}}$$

In the equation $y = 3.27 + 1.78x$, $3.27 = 1/k$ the tangent of the inclination angle is equal $1.78 = 1/kK_A$. Therefore $k = 0.306$ mmol/h, $K_A = 1.84$ l/mmol (calculation of k − 0.75 points, K_A − 1 point, 2.75 points in total).