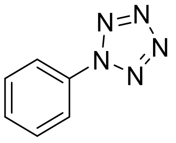
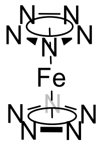
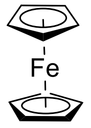
Problem 1 (author Trushkov I.V.)

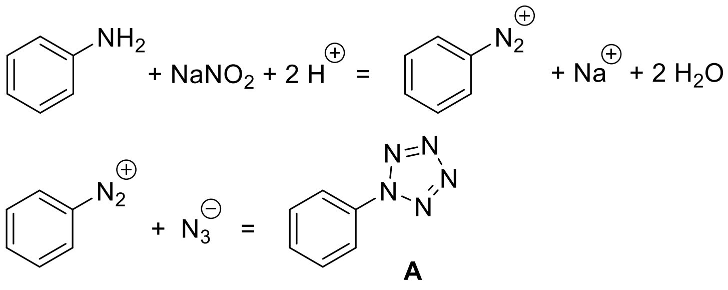
1. From the zinc content in the salt $Zn(Q)(NO_3)$ one can calculate its molecular weight as $65.38 / 0.03859 = 169.42$ amu. Q accounts for $169.42 - 65.38 - (14.01 + 48.00) = 42.03$ amu. Therefore, Q is the azide ion, N_3^-, which is in agreement with the fact that $Zn(Q)(NO_3)$ is formed from $Zn(X)(NO_3)$ accompanied by gas evolution, whereas both salts contain the same elements. Then the released gas is either nitrogen (N_2) or its oxide, and X is an anion formed only by nitrogen or nitrogen and oxygen atoms.

The conclusion about the structure of the anion X and acid HX can be drawn based on the following. FeX_2 (**B**) is isoelectronic to FeY_2 (**C**), which was discovered in 1951 to pioneer a new field of chemistry. The compound has properties unusual for typical inorganic compounds and is included in textbooks on both inorganic and organic chemistry. Combining all the facts, one can deduce that FeY_2 (**C**) is ferrocene. Then, FeX_2 (**B**) is its analogue, in which the pentazolate anion (i.e., that composed by five nitrogen atoms forming an aromatic six-electron ring) is present instead of the cyclopentadienyl one.

HX	**D**	**E**
HN_5	$Zn(N_5)(NO_3)$	$Zn(N_3)(NO_3)$
A	**B**	**C**
		

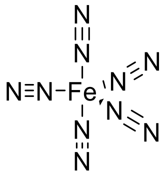
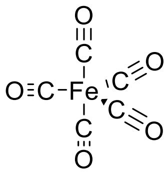
(1 point for molecular formulas of each of **HX**, **D**, **E**; 1 point for each of the structures of **A**–**C**, **6 points** in total)

2. The zinc salt was obtained by the method of Huisgen and Ugi from *para*-anisidine using sodium azide (NaQ). PhN_5 was prepared from a derivative of the PhY type (derived from aniline) and sodium azide. Subtracting the N_3^- ion from PhN_5, one gets that $PhY = PhN_2^+$. Thus, this is the transformation of aniline into a diazonium salt (any correct equation accepted, *i.e.* the reaction with sodium nitrite in an acidic medium) followed by the reaction with sodium azide at low temperatures (reaction conditions not graded).



(0.5 points for each equation, even if described in a single equation; **1 point** in total)

3. B, as well as isomeric **F**, has the composition of FeN_{10}. Then, $Fe(N_2)_5$ is the only possible option for **F** (this compound was obtained cryochemically by capturing the iron atoms into a nitrogen matrix). Iron pentacarbonyl $Fe(CO)_5$ is its isoelectronic analogue **G**.

F	**G**
	

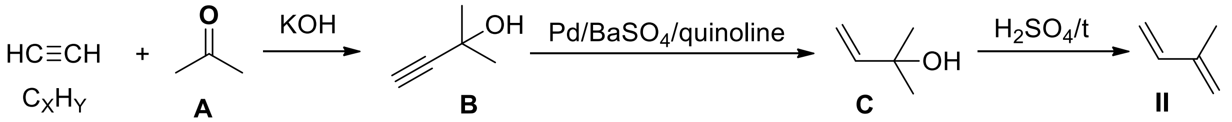
(1 point for each of the structures of **F** and **G**; **2 points** in total)

4. The above conclusion about the molecular formula and structure of HX can be confirmed by analyzing the data for the salt **H**. Assuming that it contains one chlorine atom, the molecular weight is 35.453 / 0.0606 = 584.885. Then **H** contains 584.885 · 0.0431 = = 25 H, 584.885 · 0.08142 / 14.007 = 34 N and 584.885 · 0.0821 / 16 = 3 O atoms. Therefore, one **H** molecule contains three H_3O^+ cations. There are still 16 protons left found in 4 ammonium cations. In total, one gets 7 single-charged cations. There is also 1 chloride ion, thus 6 single-charged X anions remain (the composition of **D** and **E** suggest that the anions are single-charged), which account for 34 − 4 = 30 N atoms. As a result, the molecular formula of X is confirmed as N_5^-, and that of HX as HN_5. **H** has the composition of $(H_3O)_3(NH_4)_4(N_5)_6Cl$, and its molecular formula is $ClH_{25}N_{34}O_3$.

(**1 point** in total)

Problem 2 (author Bakhtin S.G.)

1. C_XH_Y, giving precipitate with the ammonia solution of silver oxide is terminal alkyne. Since **B** contains 5 carbon atoms, the alkyne can be acetylene, propyne, or butyne-1. If C_XH_Y is acetylene, then **A** must contain 3 carbon atoms, i.e., it is acetone (propanal would give a silver mirror reaction). The variants with propyne and butyne are also invalid, since otherwise **A** would be an aldehyde (ethanal or methanal, respectively). **II** is 2-methylbuta-1,3-diene (isoprene).



(0.5 points for each structure; **2.5 points** in total)

2. The addition of acetylene to acetone occurs under conditions of base catalysis in the presence of KOH, which generates a reactive acetylenide anion. LDA, which is a very strong base, is used in stoichiometric rather than catalytic amounts; the basicity of triethylamine is insufficient to deprotonate acetylene.

(**0.5 points** in total)

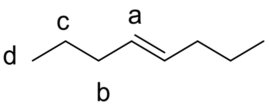
3. Let's denote **I** as an isoprene oligomer, i.e. as $(C_5H_8)_n$. $M = (12 \cdot 5 + 8) \cdot n = 272$; $n = 4$ (diterpene) (0.25 point), **I** – $C_{20}H_{32}$ (0.25 point).

(**0.5 points** in total)

4. $n(\mathbf{I}) = m/M = 16.32/272 = 0.06$ mol; $n(H_2) = pV/(RT) = 2.3 \cdot 2.764 / (0.082 \cdot 323) =$ $= 0.24$ mol; $n(H_2)/n(\mathbf{I}) = 0.24 / 0.06 = 4$, i.e. one molecule of cembrene contains 4 double bonds. On the other hand, its degree of unsaturation ($n_{\text{ring}} + n_{C=C}$) equals 5 from the molecular formula of **I**; so n_{ring} equals 1.

(0.5 points for the number of double bonds and rings; **1 point** in total)

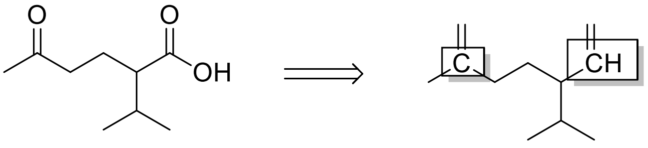
5. In the spectrum *of trans*-4-octene, the signal with $\delta > 5$ ppm with the lowest intensity corresponds to 2 olefinic protons (***a***). The signals ***b*** and ***c*** have equal intensities and belong to the protons of allylic and homoallylic positions, respectively (the chemical shift of the signal ***b*** is greater due to the fact that the acceptor C=C bond is located closer to these protons). The most intense signal is due to the protons of two CH_3 groups.

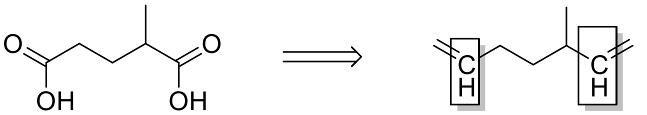


Dihydrocembrene is obtained from cembrene by the addition of two H atoms, i.e. it has the molecular formula of $C_{20}H_{34}$. It can be seen that the total intensity of the signals in both spectra (the height of the jumps in the integral curve) coincides with the total number of protons in each of the compounds: 16 protons for *trans*-4-octene and 34 protons for **III**. This means that the number of H atoms in each signal is equal to the jump height of the curve. The signal located about 5 ppm is due to the olefinic protons in *trans*-4-octene; the total intensity of this range for **III** is 4. So $n_H\text{-}sp^2 = 4H$; $n_H\text{-}sp^3 = 34H - 4H = 30H$.

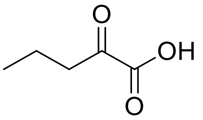
(0.25 points for each group ***a–d*** and for each number of hydrogen atoms; **1.5 points** in total)

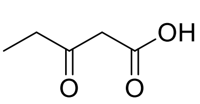
6. Let us consider the structures of 2-isopropyl-5-oxohexanoic and 2-methylpentanedioic acids.

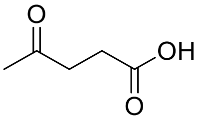


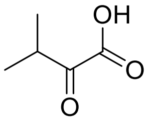


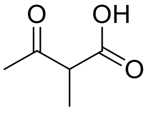
The fragments of these compounds contribute in total three olefinic protons in the case of **III** (since the ketone group is formed during ozonolysis from −C=, and the carboxyl one from −CH=). In the previous question, we found that the molecule of **III** has four olefinic protons, which means that there is one olefinic H atom for **X**. Since there are no carbon-containing products but those indicated in the task text, all the C=C double bonds are found in the ring. Then **X** is a ketoacid containing $20 - 9 - 6 = 5$ C atoms with the molecular formula of $C_5H_8O_3$. One can propose five ketoacids of this composition:











The second and fifth acids are unstable β-oxoacids, spontaneously undergoing decarboxylation, therefore they cannot be obtained as a result of oxidative ozonolysis. Of the remaining options, the first and fourth ketoacids contain a ketone group in the α-position to the carboxyl one; such fragment is formed as a result of ozonolysis of the conjugated diene fragment, but dihydrocembrene **III** cannot contain it, since it is obtained by the reduction of 1,3-dienes with hydrogen from Li/NH_3. Then 4-oxopentanoic acid (levulinic) is the only option left for **X**.

(1.5 points for molecular formula of **X** (0.5 points for the correct number of carbons with an incorrect molecular formula), 2 points for the structure of **X**; **3.5 points** in total)

7. The carbon skeleton is not destroyed during the reduction of **I** to **III**. This means that the ring size in cembrene is equal to the sum of the distances (expressed in the number of atoms) between the carbon atoms bonded to oxygen for all three ozonolysis products of **III**. It equals to: 5 [2-isopropyl-5-oxocaproic acid] + 5 [2-methylglutaric acid] + 4 [levulinic acid] = 14. (0.5 points **in total**)

Problem 3 (author Garifullin B.N.)

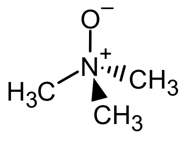
1. Due to the fact that the atomic masses of carbon, nitrogen, and oxygen rounded to the nearest integer are divisible by two without a remainder, their products by the number of atoms are even numbers. Also note that all numbers in the series 3^m, where m is a natural number or zero, are odd numbers. Let's take into account that zero is also an integer, like negative numbers, but the latter give fractional coefficients with a value less than one.
Hydrogen has an odd relative atomic mass. Multiplied by an odd number of atoms, it would give an odd molar mass. The sum of an odd and several even numbers is always odd, which is what needed to be proven. The following equation holds for the compound $C_kH_nN_lO_m$:

$$M(\mathbf{X}) = 2 \cdot (6 \cdot k + 7 \cdot l + 8 \cdot m) + n, \text{with } n \in \{1,3,9,27 \ldots\}$$

Any reasonable work will be graded. (**1 point** in total)

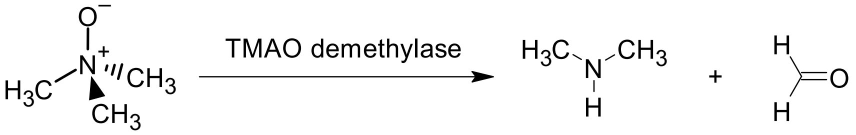
2. The coefficients of atoms in the molecule **X** are 1 (3^0), 3 or 9 (i.e. $m \leq 2$); the number of atoms equal to 27 (3^3), even if it is attributed to hydrogen, looks clearly excessive for a low-molecular substance (remember the definition of osmolyte).
Let's move from the mass ratio of elements to the molar one: there are three times more carbon (3 atoms) than nitrogen (1 atom) in the molecule X - do not forget about the virtual limitation of the molecular weight (keep in mind the formulas of glycine and glycerol).
Note that the molecular weight of **X** relates to those of **X1** and **X2** as 5:3:2, respectively. Then, due to its integer value, the molecular weight of **X** must be a multiple of 5. The C_3N fragment has the molecular weight of 50 g/mol, which means that the remaining part of the molecule containing H and O atoms must also have the molar mass that is a multiple of 5. Search for the number of hydrogen (1, 3 or 9) and oxygen atoms (1 or 3) atoms leads to the only option, H_9O (25 g/mol). Hence the molecular formula of **X** is C_3H_9NO.
The molecular masses of gaseous substances **X1** and **X2** are 45 and 30 g/mol, respectively. The formulas of nitrogen(II) oxide NO and formaldehyde (CH_2O) can be proposed for **X2** from the available set of elements. However, in the case of NO, C_3H_9 is left as the formula of the gas **X1** (we are dealing with the reaction equation!), which is impossible. Hence **X2** has the formula of CH_2O, and X1 of C_2H_7N (dimethylamine or ethylamine).
(0.75 points for each of **X**, **X1**, and **X2**; **2.25 points** in total)

3. Of the substances with the composition C_3H_9NO, only trimethylamine-*N*-oxide (TMAO) has the structural formula, in which all carbon atoms are equivalent:



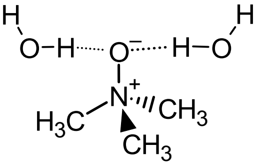
X

Enzymatic degradation of **X** leads to the formation of an equimolar mixture of dimethylamine and formaldehyde:



Interestingly, TMAO, which is also formed in the human body, is considered as an independent factor in the development of cardiovascular accidents.
(**1 point** in total)

4. The ratio of carbon and nitrogen atoms in the **Y** molecule is the same (3:1). If we assume that there is a C_6N_2 fragment in the formula of **Y**, then the molar mass balance is only 11 g/mol. Mathematically, this corresponds to 11 hydrogen atoms, which makes no chemical sense (in addition, **Y** must contain oxygen). Then **Y** contains the C_3N group of atoms, and the balance accounts for 61 g/mol, which unambiguously corresponds to 3 O and 13 H atoms. The excessive hydrogen content can only be attributed to crystallization water. Then the molecular formula of **Y** is $C_3H_9NO{\cdot}2H_2O$. In other words, taking into account the equivalence of carbon atoms, we have trimethylamine-*N*-oxide dihydrate, produced industrially in the form of a laboratory reagent.


Y

Unlike van der Waals interaction, hydrogen bonding is very direction sensitive. Typically, the donor valence bond (O–H) faces directly toward the acceptor (oxygen atom) with which the hydrogen bond is formed. Actually, it is due to building such a system of hydrogen bonds that TMAO acts as a piesolite.
(0.5 points for the molecular formula of **X**; 1 point for the structure of **X**; **1.5 points** in total)

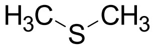
5. Of the three elements that are definitely present in **Z** (see the acrylic acid formula), only hydrogen has an odd valence. Therefore, the question can be reworded into a more convenient format: we need to prove that the fourth, yet unknown element, cannot exhibit an odd valence. If N_H is an odd number, then all three different factors must be odd, and the minimum value of N_H is $1 \cdot 3 \cdot 5 = 15$, which contradicts the condition. Then N_H is an even number, and 3 combinations of 4 different numbers are possible: {1; 2; 3; 6}, {1; 2; 4; 8} and {1; 2; 5; 10}. Let us look at the molecular formula of acrylic acid, $C_3H_4O_2$. It is clear that the second largest figure in any quartet is the number of carbon atoms (there must be at least 3 of these). In any case, there should be 2 oxygen atoms in **Z** (and both proceed to acrylic acid!). This means that the target element (hereinafter referred to as **E**) is present in Z as one atom (the formula of Z is $(CH_2)_nO_2$**E**, where $n = 2, 3,$ or 4), but with an even number of hydrogen atoms it cannot exhibit an odd valence. The statement is proven. Any reasonable consideration is accepted.
(**1.5 points** in total)

6. Z has one of three possible formulas: $C_3H_6O_2$**E**, $C_4H_8O_2$**E**, or $C_5H_{10}O_2$**E**. The possible molecular formulas of **Z1** can be obtained by subtracting the formula of acrylic acid from all three molecular formulas of **Z**. These are H_2**E**, CH_4**E**, or C_2H_6**E**. Taking into account the even valence of **E** and the obtained formulas, it is logical to assume that we are dealing with a chalcogen. One can calculate the relative atomic masses of **E** for the **Z2** variants containing one or two oxygen atoms (a larger number is not compatible with the equivalence of O atoms):

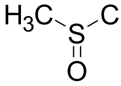
N_{atoms}(O) in **Z2**	A_r(**E**)		
	H_2**E**	CH_4**E**	C_2H_6**E**
1	60	46	32
2	44	30	16

Thus, **E** is sulfur, and the molecular formulas are: $C_5H_{10}O_2S$ (**Z**), C_2H_6S (**Z1**) and C_2H_6SO (**Z2**).

Since **Z2** is a molecule with high symmetry, the structures of **Z1** (dimethyl sulfide) and **Z2** (dimethyl sulfoxide) are:

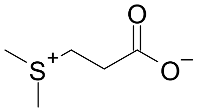


Z1



Z2

Taking into account the mechanism of the osmolyte destruction, the presence of similar structural motifs with TMAO (zwitterion), as well as the understanding of the presence in biological systems of compounds like *S*-adenosylmethionine containing the sulfonium ion, the structure of **Z** corresponds to dimethylsulfoniopropionate:

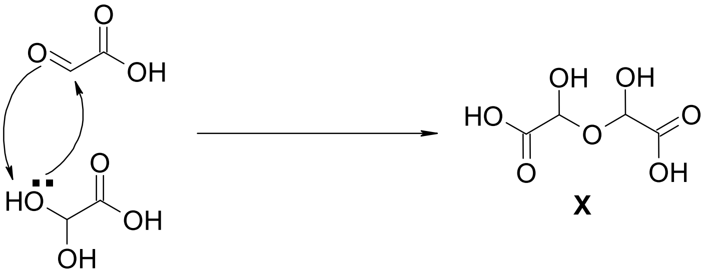


Z

(0.25 points for the molecular formulas of each of **Z**, **Z1**, and **Z2**; 0.5 points for the structures of each of **Z1** and **Z2**; 1 point for the structure of **Z**; **2.75 points** in total)

Problem 4 (authors Ilievski Ph., Gladilin A.K.)

1. Hemiacetals are formed by the reaction of a carbonyl and a hydroxyl groups. Thus, the only possible symmetrical structure of **X** is (**1 point** in total):



X

2. This part can be approached differently. One of these is as follows. Glyoxylate is composed of 3 elements (C, H, and O), thus all the metabolites of the cycle have the general formula $C_xH_yO_z$, with the charge(s) being due to the presence of carboxylate anion(s).

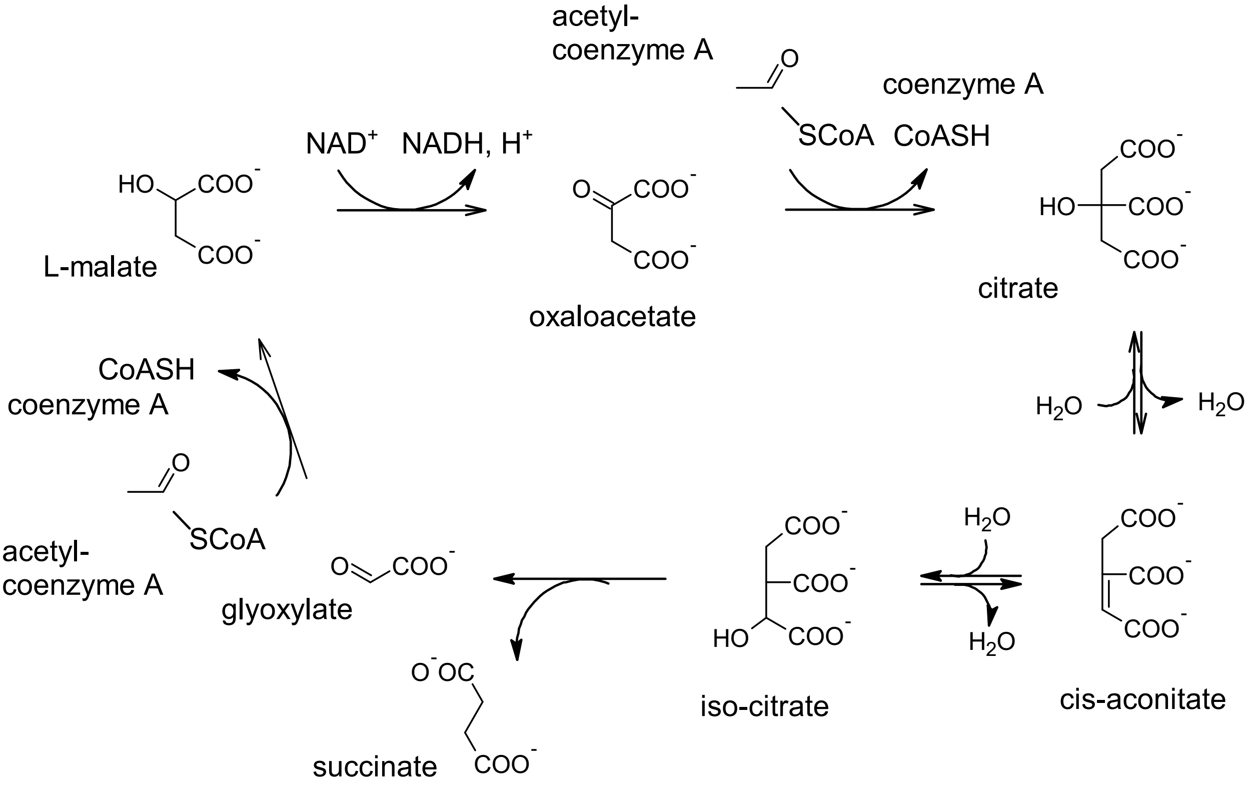
The **A1** → **A2** transformation is accompanied by the loss of two H atoms, whereas the number of C and O atoms in the cycle intermediates is unchanged. Then, the following system of two equations is valid:

$$\frac{12.01\cdot n}{M(\mathbf{A1})} = 0.3637\ (1);\ \frac{12.01\cdot n}{M(\mathbf{A1})-2.016} = 0.3694\ (2).$$

Then $n = 4$, whereas M(**A1**) rounded to the integer equals 132 g/mol. The molecular formulae of **A1** and **A2** are unambiguously found as $C_4H_4O_5$ and $C_4H_2O_5$, respectively. Thus, **Y** contains acetyl (the 2C acyl) residue.

A1 gets an extra charge as compared to glyoxylate, which can be only due to the moiety liberated from **Y**. Thus, **Y** is acetyl coenzyme A. **A2** has the same charge as **A1**, which is true only if the hydroxyl group is oxidized to the carbonyl one. Thus, **A2** is oxaloacetate, further condensation of which with another acetyl fragment produces citrate **A3**. The latter gives **A5**

due to the dehydration/hydration, which suggests that these metabolites are isomers. The conclusion is supported by the same mass fraction of C in **A3** and **A5** (*iso*-citrate). **A4** is aconitate. Though it is actually the *cis*-isomer, both *cis*- and *trans*- isomers are accepted, since the data given is insufficient for unambiguous choice between isomer options. The aldol lyase regenerates glyoxylate due to retro-aldol condensation, giving succinate (**A6**) as the other reaction product. The mass fractions given in the table corroborate the found structures.

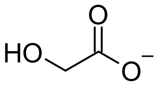


(0.5 points for each of **A1**–**A6** and **Y**, **3.5 points** in total)

3. $2CH_3C(O)-SCoA + NAD^+ + 2H_2O \rightarrow (CH_2-COO^-)_2 + 2CoA-SH + NADH + 3H^+$

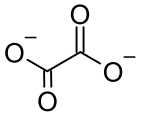
(**0.5 points** in total)

4. The molar ratios of the products of **X1**, **X2**, and **X3** combustion suggests hydrocarbon fragments of their non-ionized molecular formulae as C_2H_4, C_2H_2, C_2H_5, respectively. The odd number of H atoms in **X3** means that there is an element of odd valence and in odd quantity in its structure. There are two options of biogenic elements meeting the above requirements, nitrogen and phosphorus. Still, the latter does not suit because it forms phosphoesters bearing charges at physiological pH values. Then **X3** is glycine, an amino acid prevailingly existing as a zwitterion at pH about 7. With due account for the data given in the Table, the molecular masses of **X1** and **X2** are found as 76 and 90 g/mol, respectively, and the corresponding molecular formulae are $C_2H_4O_3$ (**X1**) and $C_2H_2O_4$ (**X2**). With an account for the charges, the structures of **X1**, **X2**, and **X3** are (0.5 points for each of **A1**−**A6** and **Y**, **3.5 points** in total):



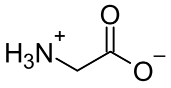
Glycolate

X1



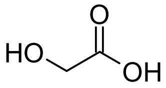
Oxalate

X2

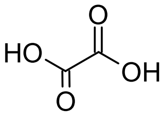


Glycine

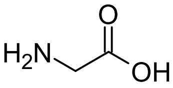
X3



Glycolic acid



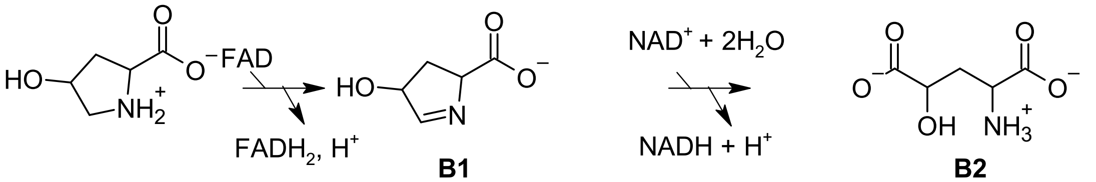
Oxalic acid



Glycine

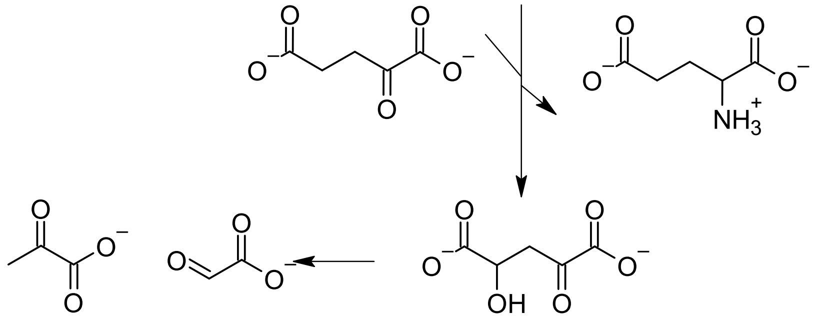
5. X1 → glyoxylate: oxidase; glyoxylate → **X3**: transaminase
(0.5 points for each enzyme, **1 point in total**)

6. B3 undergoes retro-aldol condensation, and only 4-hydroxyketoglutarate can give such pattern of the products. It should be mentioned that the 4-OH group present in **B3** originates from the starting 4-hydroxyproline. The transformation of **B2** to **B3** involves the transamination reaction with α-ketoglutarate, suggesting **B2** as 4-hydroxyglutamate. **B2** is formed from **B1** because of oxidation by NAD^+ requiring 2 molecules of water. 4-Hydroxyproline is oxidized to **B1** with retention of the OH-group, thus oxidation should result in a double bond appearance. Its position can be deduced with an account for the product of the subsequent ring opening reaction affording 4-hydroxyglutamate.



B1 Δ¹-pyrroline-3-hydroxy-5-carboxylate

B2 4-hydroxyglutamate



B3

pyruvate glyoxylate 4-hydroxyketoglutarate

(0.5 points for each of **B1** to **B3**, **1.5 points** in total)

7. Pyruvate is the acetyl-CoA precursor, the latter entering the glyoxylate cycle affording succinate and glyoxylate, see the solution of scheme in Fig. 1.
(**1 point** in total).

Problem 5 (author Karpushkin E.A.)

1. Substitution of the available data in the equation (with the numeric values converted to the International System of Units):

$$1.093c_0 = c_0 e^{\frac{2\cdot 0.45\cdot V_\mathrm{m}}{1\cdot 10^{-7}\cdot 8.314\cdot(25+273)}},$$

gives $V_\mathrm{m} = 2.45\cdot10^{-5}$ m^3/mol. (**1 point** in total).

2. The molar mass can be calculated from the density and the molar volume: $M = V_\mathrm{m}\cdot d = 24.5$ cm^3/mol $\cdot 3.18$ g/cm^3 = 77.9 g/mol. This value, accounting for the accuracy of the data in the task, corresponds to the only reasonable halide: calcium fluoride. *The alternative value given in the task text ($2.95\cdot10^{-5}$ m^3/mol) corresponds to FeF_2.*

(1 point for calculation of the molar mass, 1 point for determination of the formula; **2 points** in total).

3. Let's calculate the mass of a particle with the edge length of r nm and density $d = 3.18$ g/cm^3, $m_0 = (3.18\cdot10^{-21})\cdot r^3$ g. Then the number of the particles in the specimen $N = 10$ g/m_0 (see the table below). The average size of the particles $r_\mathrm{av} = \frac{\sum r_i N_i}{\sum N_i} = $
$= \frac{40\cdot4.91\cdot10^{16}+60\cdot1.46\cdot10^{16}+80\cdot0.61\cdot10^{16}}{4.91\cdot10^{16}+1.46\cdot10^{16}+0.61\cdot10^{16}} = 47.7$ nm. (**2 points** in total).

4. The increase in solubility depending on the particle size (c/c_0) can be obtained by substituting the known values in the Gibbs–Freundlich–Ostwald equation. The absolute solubilities of the particles of each size are found from the macroscopic phase solubility, derived in its turn from the solubility product: $K_\mathrm{sp} = [Ca^{2+}][F^-]^2 = c_0(2c_0)^2$ and $c_0 = \sqrt[3]{K_\mathrm{sp}/4} = 1.96\cdot10^{-4}$ mol/L.

(1 point for c_0, 1point for the rest calculations; **2 points** in total)

r, nm	m_0, g	N, pc.	c/c_0	c, mol/L
40	$2.04\cdot10^{-16}$	$4.91\cdot10^{16}$	1.25	$2.45\cdot10^{-4}$
60	$6.87\cdot10^{-16}$	$1.46\cdot10^{16}$	1.16	$2.27\cdot10^{-4}$
80	$16.3\cdot10^{-16}$	$0.61\cdot10^{16}$	1.12	$2.20\cdot10^{-4}$

5. Solubility of each of the three fractions exceeds 10^{-5} mol/L, hence they all can be involved in ripening. However, the difference in the solubility of the particles with sizes of 60 and 80 nm is as low as 3.5%. Thus, these two types of the particles will grow due to dissolution of the finest fraction, solubility of which is significantly higher.

Mass of the dissolving fraction is 10 g; let's calculate the proportion in which it is redistributed between the growing particles. The surface area of a particle with the edge length of 60 nm is $2.16\cdot10^{-14}$ nm^2, the total surface area being $1.46\cdot10^{16}\cdot2.16\cdot10^{-14} = 314$ m^2; for the 80 nm particles the total surface area is 236 m^2. Hence, $10\cdot314/(314+236) = 5.7$ g is precipitated at the particles with the initial size of 60 nm, whereas the increase in mass of the 80 nm particles is $10 - 5.7 = 4.2$ g.

Once the precipitation is complete, mass of the particles with the initial size of 60 nm is 15.7 g. Since their number is constant ($N = 1.46\cdot10^{16}$), the new mass of a single particle is $1.08\cdot10^{-15}$ g with the edge length of 69.7 nm. Similarly, for the particles with initial size of 80 nm the new mass of a single particle is $2.33\cdot10^{-15}$ g with the new edge length of 90.1 nm. Average size of the particles after ripening is $r_\mathrm{av} = \frac{69.7\cdot1.47\cdot10^{11}+90.1\cdot0.62\cdot10^{11}}{1.47\cdot10^{11}+0.62\cdot10^{11}} = 75.8$ nm.

(0.5 points for the choice of the remaining fractions, 0.5 points for account for different surface areas, 2 points for major calculations; **3 points** in total).

Problem 6 (author Khvalyuk V.N.)

1. Since the aqueous solution of **D** is titrated with an alkali, we conclude that it is acidic in nature (with an account for its binary nature, it can be, for example, an acidic oxide or an oxygen-free acid). Then the reaction between **X** and **B** could be like hereunder:

salt(**X**) + acid(**B**) = new salt + new acid(**D**).

Based on this hypothesis, let us find a solution which is in agreement with the task text. (You can check another hypothesis of the formation of an acidic oxide and water instead of an (unstable) acid.)

Since **B** contains 65% of oxygen by mass, its molar mass *M*(**B**) with different numbers of oxygen atoms (*x* from 1 to 6) in the molecule equals 16*x*/0.65:

Number of O atoms in the molecule of **B**, *x*	1	2	3	4	5	6
Molar mass, *M*(**B**)	25	49	74	98	123	148

At $x = 4$ the molar mass is approximately 98 g/mol, which corresponds to at least two known acids solid at 0°C: H_2SO_4, H_3PO_4. The osmotic pressure data allows choosing between them. The solution contains approximately (677 mg / 98 g/mol) = 6.9 mmol of an acid. The mass of the resulting solution (0.677 g + 15.3 g) = 16.0 g and (taking into account the dilution) its volume is approximately 16 cm^3. Then the molar concentration of an acid in the solution approximately equals ($6.9\cdot10^{-3}$ mol / $16\cdot10^{-3}$ dm^3) = 0.43 mol/dm^3. Sulfuric acid is a strong with respect to the first dissociation constant and weak with respect to the second one. Thus, the total concentration of all particles (H^+, HSO_4^-, and SO_4^{2-}) in the solution is slightly higher than $0.43 \cdot 2 = 0.86$ M. Phosphoric acid is weak with respect to all dissociation constants, thus the total concentration of all particles (H_3PO_4, H^+, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}) in the solution is slightly higher than 0.43 M. Accordingly, the osmotic pressure at 298 K in these solutions approximately equals:

$$\pi(H_2SO_4) = 0.86 \cdot 8.314 \cdot 298 = 2130 \text{ kPa};$$
$$\pi(H_3PO_4) = 0.43 \cdot 8.314 \cdot 298 = 1065 \text{ kPa}.$$

Comparing the obtained values with those specified in the task text, we conclude that **B** is H_3PO_4.

Of the widely used substances, HCl, HBr and HI satisfy the properties of **D** given in the task text (HF (liquid) and H_2S (slightly soluble in water) do not match). We exclude HI from the list, since storage of its saturated solution in air leads to rapid darkening (formation of iodine due to oxidation by atmospheric oxygen). The titration results allow choosing between HCl and HBr.

In a saturated solution, the molar concentration of HCl is $0.418 \cdot 1202$ g/dm^3 / 36.5 g/mol = = 13.77 mol/dm^3. To standardize the alkali, it was diluted 250.0 cm^3 / 10.00 cm^3 = 25 times and therefore the molar concentration of hydrochloric acid used for standardization was equal to 13.77 mol/dm^3 / 25 = 0.551 mol/dm^3. Due to the equality of volumes during standardization (10.00 cm^3 each), the molar concentration of the alkali solution also equals 0.551 mol/dm^3.

It is seen from the results of titration of **D** that its molar concentration in a solution saturated at 20°C is $0.551 \cdot 26.13 = 14.4$ mol/dm^3. Let's compare this value with the molar concentration of HCl in its saturated solution calculated above (13.77 mol/dm^3). This is less than the molar concentration in a saturated solution of **D**, so **D** is not hydrogen chloride. Then **D** is HBr, and the salt **X** is a bromide.

In the experiment with the reactor, the pressure decrease to almost zero is due to formation of products in a condensed (liquid or solid) state. In the case of an acid-base reaction, the substance **C** must be basic. With respect to its properties, NH_3 is an ideal option (binary substance, gas at 0°C and 100 kPa, very soluble in water, reaction with HBr gives a solid product). Thus, **C** is NH_3, and the salt **X** is ammonium bromide NH_4Br.
A base or basic oxide is required to obtain NH_3 from NH_4Br. Since **A** contains 43% of oxygen by mass, its molar mass M(**A**) with different numbers of oxygen atoms (y from 1 to 6) in the molecule equals $16y/0.43$:

Number of O atoms in the molecule **A**, y	1	2	3	4	5	6
Molar mass, M(**A**)	37	74	111	149	186	223

Approximately 74 g/mol are found at $y = 2$, which corresponds to calcium hydroxide. Thus **A** is $Ca(OH)_2$.
(1 point each for each of **A**, **B**, **C**, **D**, **X** (0.2 points per substance without calculations); **5 points** in total)
2.

$$NH_4Br + H_3PO_4 = NH_4H_2PO_4 + HBr \text{ (excess } H_3PO_4)$$
$$2NH_4Br + Ca(OH)_2 = CaBr_2 + 2H_2O + 2NH_3$$
$$NH_3 + HBr = NH_4Br$$
$$HCl + NaOH = NaCl + H_2O$$
$$HBr + NaOH = NaBr + H_2O$$

(1 point for the first reaction, 0.5 points for each of the rest reactions, **3 points** in total)
3. Various methods are known for obtaining small quantities of HBr in laboratory conditions, for instance reduction of bromine with a suitable reducing agent as:
hydrazine

$$2Br_2 + N_2H_4 = 4HBr + N_2$$

red phosphorus

$$3Br_2 + 2P + 6H_2O = 6HBr + 2H_3PO_3 \text{ and then } Br_2 + H_3PO_3 + H_2O = 2HBr + H_3PO_4$$

tetrahydronaphthalene

$$C_{10}H_{12} + 4Br_2 = C_{10}H_8Br_4 + 4HBr \text{ (in the presence of Fe).}$$

and other substances.
Small amounts of HBr can be easily obtained by hydrolysis of bromides of some non-metals, for example, PBr_3, PBr_5, $SiBr_4$.

$$SiBr_4 + (2+x)H_2O = SiO_2{\cdot}xH_2O + 4HBr$$

The choice of a method depends on the required quantity and purity of the product, availability and cost of the reagents and other factors (any reasonable and easily feasible laboratory preparation method is accepted).
(**1 point** in total)
4. The medium of an aqueous solution of NH_4Br is acidic due to hydrolysis of the cation. In such an environment, magnesium reduces H^+ to hydrogen H_2, turning into the Mg^{2+} cation. Ammonia is the other product of this reaction:

$$2NH_4Br + Mg = MgBr_2 + H_2 + 2NH_3.$$

(**1 point** in total)

Problem 7 (author Khvalyuk V.N.)

1. For $R = 5.00$ a.u. $E_1 = 6.55\exp(-2.10 \cdot 5.00) - {}^{2.39}/_{(5.00)^6} = 2.74 \cdot 10^{-5}$.

For $R = 7.00$ a.u. $E_1 = 6.55\exp(-2.10 \cdot 7.00) - {}^{2.39}/_{(7.00)^6} = -1.76 \cdot 10^{-5}$.

The positive sign of E_1 in the first case indicates that repulsion predominates at the distance of 5.00 a.u. between the atoms, and the negative sign of E_1 indicates that attraction predominates at the distance of 7.00 a.u.

(1 point for each calculation; 0.5 points penalty for calculation error(s); **2 points** in total)

2. The maximum value by which the energy of the system of two He atoms can decrease due to intermolecular interaction corresponds to the minimum value of E_1.

From the values obtained in i. 1, we can conclude that the minimum value of E_1 is observed at the distances greater than 5.00 a.u. On the other, the minimum value of E_1 can be observed both at a distance greater than 7.00 a.u. and within the range of 5.00 a.u. – 7.00 a.u. To check it, additional calculations should be performed for the R values both inside and outside this range. Let us carry out the calculation for R equal to 6.00 a.u. and 8.00 a.u.

$$E_1(6.00) = 6.55\exp(-2.10 \cdot 6.00) - {}^{2.39}/_{(6.00)^6} = -2.91 \cdot 10^{-5}.$$

$$E_1(8.00) = 6.55\exp(-2.10 \cdot 8.00) - {}^{2.39}/_{(8.00)^6} = -0.879 \cdot 10^{-5}$$

Comparing the obtained values with the data from i. 1, we conclude that the minimum value of E_1 corresponds to an R value inside the range of 5.00 a.u. – 7.00 a.u. As the first approximation, we can take the middle of the range ($R = 6.00$ a.u.). Then the obtained value of E_1 is $-2.91 \cdot 10^{-5}$ a.u., which is $-2.91 \cdot 10^{-5} \cdot 27.21 \cdot 1.60 \cdot 10^{-19}$ J $= -1.27 \cdot 10^{-22}$ J. To get more precise values we need to consider the middle values of the subranges of 5–6 a.u. and 6–7 a.u. (5.50 a.u. and 6.50 a.u.). By successively repeating the procedure described above, it is possible to come to a narrow range of R and obtain the minimum value of E_1 with the desired accuracy. This is the essence of the method of successive approximations.

The minimum value of E_1 can be determined mathematically by finding the first derivative of E_1 on R, equating the resulting expression to zero, and solving it by numerical methods. The exact values obtained mathematically are as follows: $R = 5.89$ a.u. and $E_1 = -2.94 \cdot 10^{-5}$ a.u., which corresponds to $-1.28 \cdot 10^{-22}$ J. The negative sign means that the energy of the system of two helium atoms can decrease by $1.28 \cdot 10^{-22}$ J at most.

(3 points for calculating the minimum value of E_1; 0.5 points penalty for calculation error(s); **3 points** in total).

3. If the particles are charged, then the Coulomb energy E_2 is added to E_1:

$$E_3 = E_2 + E_1$$

The coefficients that determine E_1 depend on the electronic structure of the particles. The Li^+ and F^- ions are isoelectronic to the He and Ne atoms, respectively. Therefore, to calculate the energy of intermolecular interaction (E_1) between Li^+ and F^-, we use the coefficients for the He–Ne pair given in the task text. The bond length in LiF is 152 pm, which gives $R = 152 / 52.9 = 2.87$ a.u. The charges of Li^+ and F^- in atomic units are +1 and −1, respectively. Then the binding energy (E_3) between Li^+ and F^- in atomic units equals to:

$$E_3 = E_2 + E_1 = \frac{(+1)\cdot(-1)}{2.87} + 33.0 \cdot \exp(-2.27 \cdot 2.87) - \frac{4.65}{(2.87)^6} = -0.308.$$

The value corresponds to $-0.308 \cdot 27.21 = -8.38$ eV $= -8.38 \cdot 1.60 \cdot 10^{-19}$ J $= -13.4 \cdot 10^{-19}$ J. It is necessary to spend $13.4 \cdot 10^{-19}$ J to convert one LiF molecule into Li^+ and F^- ions.

(1 point for calculating only the Coulomb energy; 2 points for taking into account the intermolecular interaction between ions; 0.5 points penalty for calculation error(s); **3 points** in total).

4. The bond energy (E_4) corresponds to the transformation of a molecule into atoms:

$$LiF(g) = Li(g) + F(g).$$

It is necessary to spend 8.38 eV to convert a LiF molecule into Li^+ and F^- ions (see i. 3). The transformation of a Li^+ ion into the Li atom (addition of an electron) is accompanied by the release of 5.39 eV (the ionization energy), and the transformation of a F^- ion into the F atom (removal of an electron) is accompanied by the consumption of 3.45 eV (the affinity energy). Therefore, to transform a LiF molecule into the Li and F atoms it is necessary to spend: $E_4 = 8.38 - 5.39 + 3.45 = 6.44$ eV or $6.44 \cdot 1.60{\cdot}10^{-19} = 1.03{\cdot}10^{-18}$ J, or $1.03{\cdot}10^{-18} \cdot 6.02{\cdot}10^{23} = 620.3$ kJ/mol, if recalculated per 1 mole of bonds.

(2 points for calculating the molar binding energy; 0.5 points penalty for calculation error(s); **2 points** in total).

Problem 8 (author Shved A.M.)

1. Decoded signals:

A	**B**	**C**	**D**	**E**	**F**
$^{14}N^+$, $^{14}N_2^{2+}$	$^{16}O^+$, $^{16}O_2^{2+}$	$^{1}H^{16}O^+$	$^{1}H_2{}^{16}O^+$	$^{40}Ar^{2+}$	$^{14}N_2^+$
G	**H**	**I**	**J**	**K**	**L**
$^{14}N^{15}N^+$	$^{15}N_2^+$	$^{16}O_2^+$	$^{16}O^{18}O^+$	$^{40}Ar^+$	$^{12}C^{16}O_2^+$

(0.25 points per signal; **3 points** in total)

2. Reaction equations:

1) human respiration (on the example of glucose): $C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O$

2) photosynthesis of a plant: $6CO_2 + 6H_2O = C_6H_{12}O_6 + 6O_2$

3) rusting of iron: $4Fe + 2H_2O + 3O_2 = 4FeOOH$ (other hydrated iron(III) oxides are also accepted)

4) combustion of octane: $2C_8H_{18} + 25O_2 = 16CO_2 + 18H_2O$

5) decomposition of hydrogen peroxide under the action of baker's yeast: $2H_2O_2 = 2H_2O + O_2$

(0.5 points per reaction; **2.5 points** in total)

3. Let us find the ratio between the signal intensities of N_2 and Ar:

$$I(N_2)/I(Ar) = I(O_2)/I(Ar) : I(O_2)/I(N_2) = 14.4 : 0.214 = 67.3$$

The ratio of the signal intensities of all substances divided by the signal intensity of argon is equal to the ratio of the mole fractions of the substances:

$$x(N_2) : x(O_2) : x(Ar) : x(CO_2) : x(H_2O) = 67.3 : 14.4 : 1 : 0.23 : 3.2$$

The sum of all mole fractions equals 1 or 100%:

$$x(N_2) + x(O_2) + x(Ar) + x(CO_2) + x(H_2O) = 1\ (100\%)$$

The mole fractions of all the substances:

$$x(N_2) = 67.3/86.13 = 0.781\ (78.1\%)$$
$$x(O_2) = 14.4/86.13 = 0.167\ (16.7\%)$$
$$x(Ar) = 1/86.13 = 0.0116\ (1.16\%)$$
$$x(CO_2) = 0.23/86.13 = 0.00267\ (0.267\%)$$
$$x(H_2O) = 3.2/86.13 = 0.0372\ (3.72\%)$$

(0.25 points for the workflow, 0.25 points per a molar fraction, total **1.5 points**)

4. Let us analyze the change in the quantities of gases in the experiments:
1) 4 human inhalations–exhalations: slight decrease in O_2, slight increase in CO_2
2) photosynthesis of a plant (1 day): slight decrease in CO_2, slight increase in O_2
3) rusting of iron (30 min): slight decrease in O_2
4) combustion of octane (5 min): strong decrease in O_2, strong increase in CO_2
5) decomposition of hydrogen peroxide under the action of *baker's* yeast (5 min): strong increase in O_2

The change in the amount of H_2O serves as a less reliable factor, as can be seen from the relatively little differences in the values. Water content depends on the experimental conditions and is related to condensation and evaporation processes.

Let us consider the percentage change (Δ) in the amounts of O_2 and CO_2, which can be calculated using the formula:

$$\Delta = \frac{I(\mathrm{O_2}\text{ или }\mathrm{CO_2/Ar})_{\text{sample}} - I(\mathrm{O_2}\text{ или }\mathrm{CO_2/Ar})_{\text{initial}}}{I(\mathrm{O_2}\text{ или }\mathrm{CO_2/Ar})_{\text{initial}}} \cdot 100\%$$

The intensities relative to N_2 presented in the table can also be used to calculate the change in the O_2 content.

The obtained values:

Sample	$\Delta(O_2/N_2)$	$\Delta(O_2/Ar)$	$\Delta(CO_2/Ar)$
Sample **I**	−16%	−16%	52%
Sample **II**	821%	803%	1161%
Sample **III**	−15%	−19%	5204%
Sample **IV**	6%	12%	−100%
Sample **V**	−75%	−77%	15117%

It is also allowed to use direct comparison of the values using inequality symbols. Thus, with respect to the initial air:

Sample	Amount of O_2	Amount of CO_2
Sample **I**	$<$	$\approx$
Sample **II**	$\gg$	$>$
Sample **III**	$<$	$>$
Sample **IV**	$>$	$<$
Sample **V**	$<$	$\gg$

The assignment, consistent with the analysis of the reactions:
Sample **I** – 3) rusting of iron (30 min)
Sample **II** – 5) decomposition of hydrogen peroxide under the action of *baker's* yeast (5 min)
Sample **III** – 1) 4 human inhalations–exhalations
Sample **IV** – 2) photosynthesis of a plant (1 day)
Sample **V** – 4) combustion of octane (5 min)
(Fully correct assignment – 2 points, 3 correct assignments – 1.5 points, 2 correct assignments – 1 point, 1 correct assignment – 0.5 points; 0.5 points for confirmation; **2.5 points** in total)

5. The possibilities are, for example, enzymatic fermentation in the presence of residual sugars in baker's yeast or yeast's respiration:

$$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2 \text{ or } C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O$$

(**0.5 points** in total)