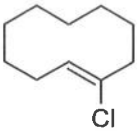
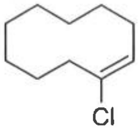
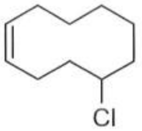
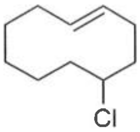
Problem I-1 (author Bakhtin S.G.)

I-1.1 Structures of the isomers specified in the statement:

a) 

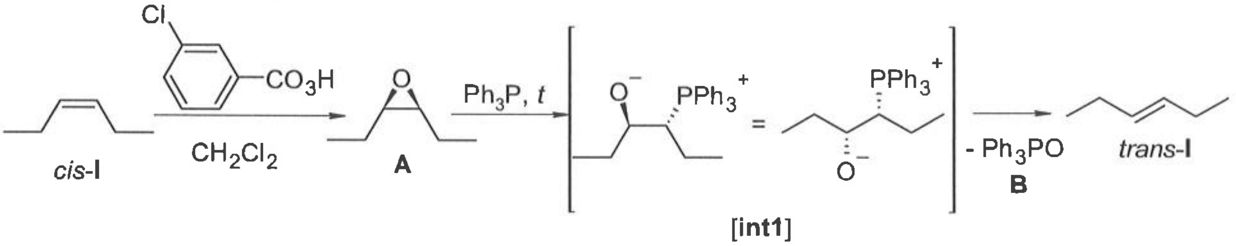
b) 

c) 

d) 

(0.25 points per structure; total **1 point**)

I-1.2 The small number of signals in the spectrum of *cis*-**I** indicates that the starting alkene is symmetric. The signal with a relative intensity of 1 belongs to the proton of the double bond −CH=; given the intensities of the two remaining signals (2 : 3), CH_2 and CH_3 groups are also present; thus, it is *cis*-hexene-3. The first step is the epoxidation of the alkene with retention of the double bond configuration. The final product is an isomer of the starting alkene. Thus, the epoxide **A** should "get rid" of the oxygen during the reaction with Ph_3P: nucleophilic attacks of one of the carbon atoms of the oxirane by triphenylphosphine from the back side (S_N2) affords the phosphonium alkoxide that eliminates triphenylphosphine oxide. If so, the Ph_3P group and the oxygen atom must be on the same side (this is achieved by rotation about the C−C single bond).



(0.25 points for each of *cis*-**I**, **A**, **B**, and *trans*-**I**, 0.5 points for [**int1**]; total **1.5 points**)

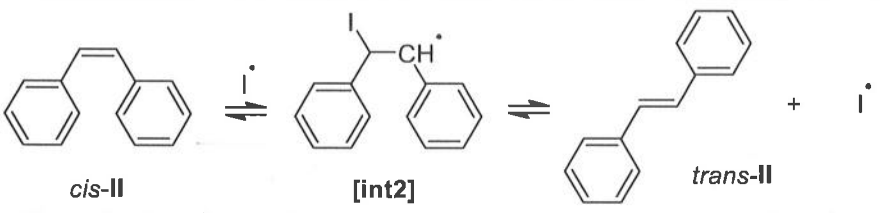
I-1.3 For the reaction *cis*-**II** ⇄ *trans*-**II** $\Delta_rG = -15.5$ kJ/mol, from which:

$$K = e^{-\Delta_r G/RT} = e^{15500/8.314\cdot 411} = 93.3.$$

Let x be the mole fraction of *trans*-**II**; then $x / (1 - x) = 93.3$; $x = 0.989$ (98.9%), hence the mole fraction of *cis*-**II** is 1.1%. Considering the mole fraction of *trans*-**II**, the initial amount of hydrocarbon **II** is 0.0356 / 0.989 = 0.0360 mol; M_r(**II**) = 6.48 / 0.0360 = 180. **II** is C_nH_m; $12n + m = 180$; since n and m are even, $n = 14$ and $m = 12$ is the only valid option. If two carbon and two hydrogen atoms are allocated to the CH=CH fragment in the hydrocarbon $C_{14}H_{12}$, the remaining fragment $C_{12}H_{10}$ corresponds to two phenyl substituents C_6H_5. Therefore, **II** is 1,2-diphenylethylene (stilbene).

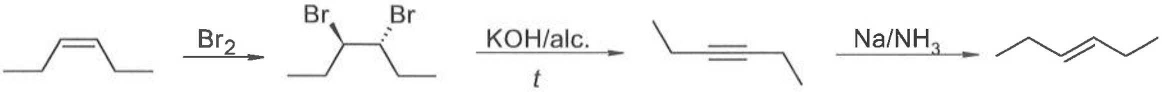
The catalytic action of I_2 is due to an iodine atom addition at the C=C bond, resulting in the formation of a radical and a single C−C bond with conformational rotation about it possible:

$$I_2 \rightleftharpoons 2\,I^{\bullet}$$



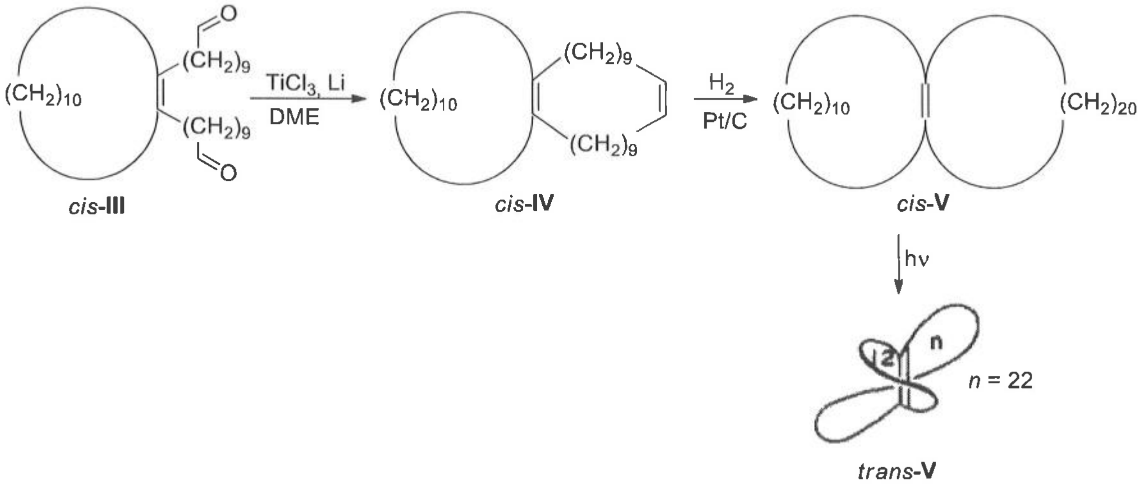
(0.5 points for K, mole fractions of stereoisomers, M_r(**II**), and the molecular formula of **II**; 0.25 points for each structure of the stereoisomers of **II**; 0.5 points for [**int2**]; total **3.5 points**)

I-1.4 The use of excess KOH, alcohol, and heat at one of the steps of ***Method 3*** indicates that the starting *cis*-alkene was converted into an alkyne. It is necessary to reduce the triple bond using Na/NH_3 to obtain the *trans*-alkene from the latter:



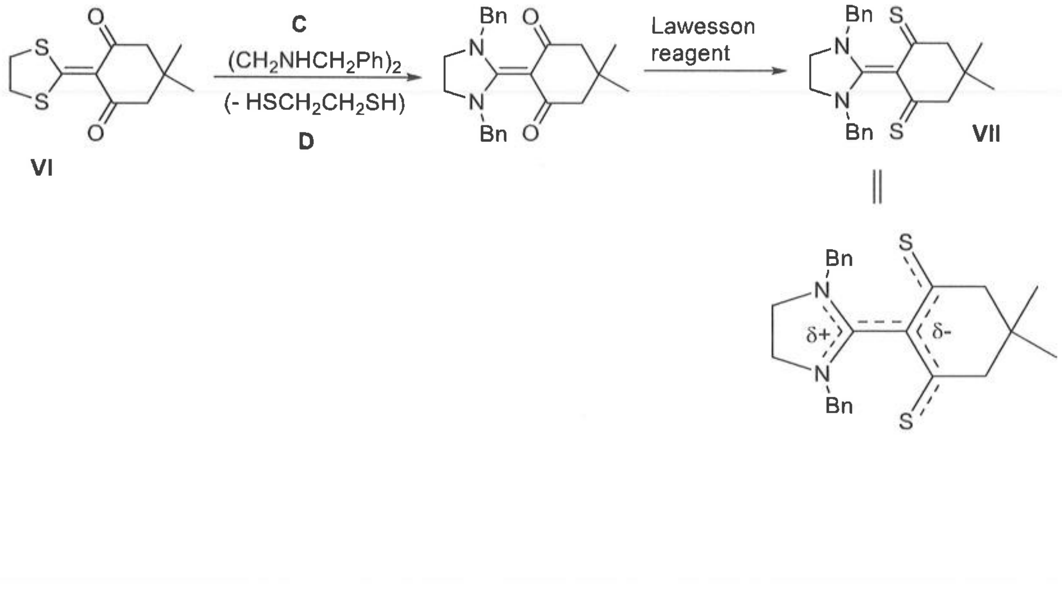
(total **0.5 points**)

I-1.5 There are no reactions changing the total number of carbon atoms in the synthesis of *trans*-**V** from *cis*-**III**. One of the rings contains 12 carbon atoms in *trans*-**V**, thus 32 − 12 = 20 are left. Two carbon atoms from the double bond also belong to the second ring, then $n = 20 + 2 = 22$. Since the last two steps of the synthesis do not affect heteroatoms and there are none of those in *trans*-**V**, *cis*-**IV** does not contain any oxygen atoms. Its formation involves the coupling of the carbon atoms of the aldehyde groups resulting in the formation of a double bond between them. During hydrogenation, only one C=C bond is cleaved, as the other remains in *trans*-**V**.



(0.25 points for each of *n*, *cis*-**III**, *cis*-**IV**, and *cis*-**V**; total **1 point**)

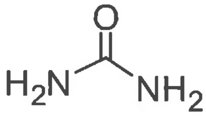
I-1.6, I-1.7 One can see a fragment of the substance **C** with the formula $C_{16}H_{20}N_2$ in the provided structure of the intermediate compound. Thus, it is an amine $(CH_2NHCH_2Ph)_2$. Summing up the molecular formulae of **VI** and **C** and subtracting that of the intermediate compound gives the eliminated compound **D** ($C_2H_6S_2$), which corresponds to ethan-1,2-dithiol. This also allows deduction of the structure of **VI**. Then, the Lawesson reagent replaces oxygen atoms with sulfur.



The sulfur atoms of the thioketone groups in **VII** are conjugated through the C=C bond with the nitrogen atoms, which imparts a partially single-bond character to the bond (for **VII**, one may also provide resonance structures instead of the delocalized bonds).
(0.5 points for each of **VI**, **C**, **D**, and **VII**; 0.5 points for electronic effects; total **2.5 points**)

Problem I-2 (author Khvalyuk V.N.)

I-2.1 The sum of the mass fractions of carbon, nitrogen, and oxygen in **A** is $(20.00 + 46.65 + 26.64) = 93.29\%$. Therefore, **A** contains at least other element besides C, N, and O. Since the substance is organic, it is reasonable to assume that the missing element may be hydrogen. Then its mass fraction in **A** is $(100.00 - 93.29) = 6.71\ \%$. This composition corresponds to the formula CH_4ON_2 – that is, urea, $CO(NH_2)_2$. In fact, the date of Friedrich Wöhler's laboratory synthesis of urea is considered as the beginning of the rapid development of organic chemistry. The structure of urea is:



(total **0.5 points**)

I-2.2 Urea was obtained by the isomerization of ammonium cyanate

$$NH_4^+ \quad {}^-O-C\equiv N$$

upon heating.
(total **0.5 points**)

I-2.3 In industry, urea is produced from ammonia and carbon dioxide at high temperature and pressure. In the first step, ammonium carbamate is formed, which then decomposes into urea and water:

$$CO_2 + 2NH_3 = NH_2COONH_4;$$
$$NH_2COONH_4 = NH_2CONH_2 + H_2O.$$

(0.25 points for each reaction; total **0.5 points**)

I-2.4 Among the given substances, ammonia is the strongest and urea is the weakest base in aqueous solution:

$$CO(NH_2)_2 < N_2H_4 < NH_3.$$

(total **1 point**)

I-2.5 By analogy with ammonia, which reacts with nitric acid to form a salt of composition $NH_3{\cdot}HNO_3$, it can be assumed that urea, as a base, also forms a salt of composition $CO(NH_2)_2{\cdot}xHNO_3$. Using the value of the mass fraction of nitrogen in **B**, one can determine that $x = 1$. Thus, **B** is urea nitrate, $CO(NH_2)_2{\cdot}HNO_3$ (or $CH_5N_3O_4$). (calculations 0.5 points; total **1 point**)

I-2.6 The amount of unabsorbed gas is:

$$\frac{34.12\cdot100}{8.314\cdot(273.15+20.0)} = 1.40\text{ mol}$$

Among the decomposition products listed, only NH_3 is present in the unabsorbed residue after passing through the NaOH column. Then, the amount of the other gases in the residue is:

$$(1.40 - n(NH_3)) = (1.40 - 0.78) = 0.62\text{ mol,}$$

and their mass is:

$$(36.37 - 0.78{\cdot}M(NH_3)) = (36.37 - 0.78{\cdot}17.03) = 23.09\text{ g.}$$

The average molar mass of the gaseous mixture of the two substances is:

$$\frac{23.09}{0.62} = 37.24\ \text{g/mol}.$$

C, N, H, and O are present in **B**. NO, N_2O, and CO could be the binary gaseous decomposition products (containing these elements) that are not absorbed by the NaOH column (apart from NH_3) and are gaseous at 20°C (formation of gaseous hydrocarbons C_xH_y is considered unlikely). The value of the average molar mass of the mixture suggests that a substance with a molar mass greater than 37.24 g/mol must be one of its components. This is N_2O; the third component can be either NO or CO.

Thus, two variants of the mixture composition ($NH_3 + N_2O + NO$) and ($NH_3 + N_2O + CO$) are possible. Upon exposure to air, only the mixture ($NH_3 + N_2O + NO$) will change its color due to the conversion of colorless NO into brown NO_2.

If 0.62 mol of the mixture ($N_2O + NO$) contains x mol of NO, then the amount of N_2O is $(0.62 - x)$ mol. Setting up the equation for the mass of this mixture:

$$23.09 = 44.01 \cdot (0.62 - x) + 30.01x$$

one obtains $x = 0.30$ mol.

Thus, there are: 0.78 mol of NH_3, 0.30 mol of NO, and $(0.62 - 0.30) = 0.32$ mol of N_2O in the unabsorbed residue after the NaOH column. The volume fractions of the components in the mixture are: $\varphi(NH_3) = 0.78 / 1.40 = 55.7\%$, $\varphi(N_2O) = 0.32 / 1.40 = 22.9\ \%$, and $\varphi(NO) = 0.30 / 1.40 = 21.4\ \%$.

(0.75 points for each of N_2O and NO, 0.5 points for the volume fraction of each of the three substances; total **3 points)**

I-2.7 There are 1 mol of [C], 4 mol of [O], 3 mol of [N], and 5 moles of [H] in 1 mol of $CO(NH_2)_2{\cdot}HNO_3$. The following amounts are present in the known decomposition products:

	n(N), mol	n(H), mol	n(C), mol	n(O), mol
0.78 mol of NH_3	0.78	$3 \cdot 0.78$		
0.49 mol of HNO_3	0.49	0.49		$3 \cdot 0.49$
0.69 mol of H_2O		$2 \cdot 0.69$		0.69
0.22 mol of CO_2			0.22	$2 \cdot 0.22$
0.32 mol of N_2O	$2 \cdot 0.32$			0.32
0.30 mol of NO	0.30			0.30
Total	2.21	4.21	0.22	3.22

There is a deficiency of: $(3 - 2.21) = 0.78$ mol [N], $(5 - 4.21) = 0.79$ mol [H], $(1 - 0.22) =$ $= 0.78$ mol [C], and $(4 - 3.22) = 0.78$ mol [O] relative to the initial quantities of each element (1 mol [C], 4 mol [O], 3 mol [N], and 5 mol [H]). It can be concluded that the last decomposition product has the composition of $H_{0.79}O_{0.78}C_{0.78}N_{0.78}$ or HOCN. Four isomers of this compound are known.

$H{-}O{-}C{\equiv}N$

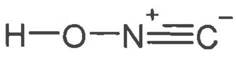
(1)

$H{-}N{=}C{=}O$

(2)


$H{-}C{\equiv}\overset{+}{N}{-}O^{-}$

(3)


$H{-}O{-}\overset{+}{N}{\equiv}C^{-}$

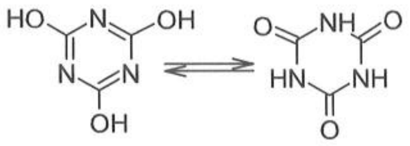
(4)

(1 point for the formula HOCN, 0.25 points for the structural formula of each of the four isomers; **total 2 points)**

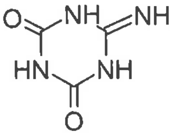
I-2.8 The mixture contains isocyanic acid (HNCO, structure 2).

(total **0.5 points)**

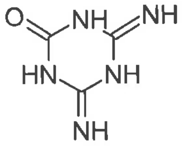
I-2.9 Since HNO_3 is among the decomposition products of **B**, it can be assumed that urea may be formed as an intermediate product upon its cleavage, while **D1–D4** may be the products of the thermal decomposition of $CO(NH_2)_2$. Indeed, various cyclic structures (**D1–D4**) can be formed during the thermal decomposition of urea, cyanuric (isocyanuric) acid **D1** is the most known of which:



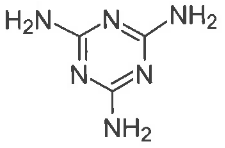
D1



D2



D3



D4

Any of the structures is accepted.
(total **1 point**)

Problem I-3 (author Garifullin B.N.)

I-3.1 Take, for example, the homologous difference in the form of the methylene group ($-CH_2-$) and write the formal equation for its complete combustion:

$$CH_2 + 1.5O_2 \rightarrow CO_2 + H_2O$$

The sum of all coefficients in this equation is $1 + 1.5 + 1 + 1 = 4.5$, which serves as the step of an arithmetic progression.

In general, for an arbitrary binary homologous increment $\mathbf{X}_n\mathbf{Y}_m$ one can write the following equation (where k and p are the oxidation states of elements **X** and **Y** in their oxides):

$$\mathbf{X}_n\mathbf{Y}_m + \tfrac{1}{4}(kn + pm)\ O_2 \rightarrow n/2\ \mathbf{X}_2O_k + m/2\ \mathbf{Y}_2O_p$$

In this case, the increment of the progression will be $1 + \tfrac{1}{4}(kn + pm) + \tfrac{1}{2}(n + m)$.

The formation of substances other than oxides (in particular, molecular nitrogen) is invalid because of complete absorption of the combustion products by the $Ca(OH)_2$ solution; hydrogen halides or molecular halogens are also excluded from consideration.

Any reasonable homologous differences presented in a general form are accepted.
(total **1 point**; 0.5 points if only a particular case is discussed)

I-3.2 It is clear that water, which is absorbed in the second series of experiments by the well-known drying agent phosphorus(V) oxide ($P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$), is among the combustion products of the organic substances **X1–X5**.

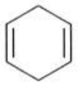
However – and this is strange! – the removal of water from the gas mixture does not change the difference in masses of the supernatant solutions compared to the first series of experiments, in which the vapor, upon condensation, mixes with the aqueous solution of calcium hydroxide, thereby increasing its mass. This can occur only if, during the combustion of equimolar amounts of the starting substances, an equimolar amount of water is formed. In other words, the number of hydrogen atoms in the molecules of **X1–X5** is identical; that is, the required ratio N_H(**X1**) : N_H(**X2**) : N_H(**X3**) : N_H(**X4**) : N_H(**X5**) is 1 : 1 : 1 : 1 : 1.

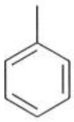
Note that such a ratio of the number of hydrogen atoms does not correspond to the familiar homologous difference in the form of a methylene group (i.e. the stepwise increase in the number of hydrogen atoms by two).
(total **1.5 points**; any other ratio: 0 points)

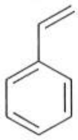
I-3.3 X1–X5 are organic compounds that necessarily contain carbon. Upon complete combustion, carbon forms carbon dioxide, which, when absorbed by an excess of a $Ca(OH)_2$ solution, produces insoluble calcium carbonate:

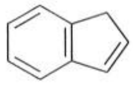
$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3\downarrow + H_2O$$

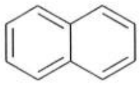
Let us calculate the ratio of the number of carbon atoms in the molecules of **X1–X5** by analogy with the previous question:
N_H(**X1**) : N_H(**X2**) : N_H(**X3**) : N_H(**X4**) : N_H(**X5**) = 72.1 : 84.1 : 96.1 :108.1 : 120.1 =
= 6 : 7 : 8 : 9 : 10.
Note that the molecules of compounds **X1–X5** can be exclusively hydrocarbons containing an identical number of hydrogen atoms. One should understand that even a slight increase in the number of hydrogen atoms in the molecules of the compounds in the C_9–C_{10} series (for example, as in naphthalene or azulene, $C_{10}H_8$, which are solids at standard conditions) is associated with an increase in melting temperature.


X1 (C_6H_8)


X2 (C_7H_8)

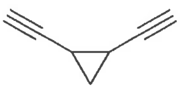

X3 (C_8H_8)

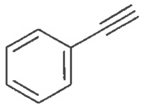

X4 (C_9H_8)

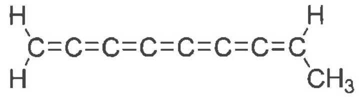

X5 ($C_{10}H_8$)

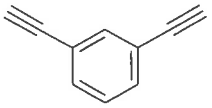
Hence, the optimal strategy in solving this question is to present hydrocarbons with a relatively small number of hydrogen atoms. The possible formulae for **X1–X5** (for convenience, the author has chosen six hydrogen atoms) are:


X1 (C_6H_6)


X2 (C_7H_6)


X3 (C_8H_6)


X4 (C_9H_6)


X5 ($C_{10}H_6$)

(0.5 points per a formula; total **2.5 points**; −0.25 points penalty for incorrect physical state)

I-3.4 Taking into account the range of biogenic elements, calcium sulfite is the only suitable candidate for the second component of the precipitate (calcium fluoride is not acceptable since **X1–X5** do not contain halogen atoms).

Note that the reactions of carbon(IV) and sulfur(IV) oxides with calcium hydroxide can be described by the general equation:

$$Ca(OH)_2 + \mathbf{Z}O_2 \rightarrow Ca\mathbf{Z}O_3 + H_2O$$

The difference in the masses of the supernatant solutions for $\mathbf{X}_{i+1}$ and $\mathbf{X}_i$ (8.4 g) formally corresponds to the mass of calcium oxide (CaO) that precipitates from the solution. Then, $n(CaO) = 8.4 / 56 = 0.15$ mol, which is equivalent to the same amount of $Ca\mathbf{Z}O_3$ with the mass of 18 g (the difference between the masses of the precipitates of adjacent homologs). A simple calculation ($M_r(Ca\mathbf{Z}O_3) = 18 / 0.15 = 120$) shows that the differences in the masses of the precipitates in the series **X1–X5** are exclusively due to calcium sulfite. Consequently, the molecules of **X1–X5** contain the same number of carbon atoms, differing only in the number of sulfur atoms. Then the molecule of **X1**, which is the starting member of the homologous series, should contain one sulfur atom. Hence, the composition of the precipitate in experiments with this compound is: 90.2 g of $CaCO_3$ and 18 g $CaSO_3$, and the required molar ratio is $n(CaCO_3) : n(CaSO_3) = n(C) : n(S) = 6 : 1$.
(calculation 0.75 points, ratio 0.75 points; total **1.5 points**)

I-3.5 Taking into account the molar ratio of carbon and sulfur, one can write the formulae of all five compounds: C_6SH_x (**X1**), $C_6S_2H_x$ (**X2**), $C_6S_3H_x$ (**X3**), $C_6S_4H_x$ (**X4**), $C_6S_5H_x$ (**X5**), where $x \in \mathbb{N}$. The sum of numbers of C and H atoms is constant in this set. On chemical grounds, $x \vdots 2$; therefore, only compounds **X2** and **X4** yield even sums of the pairwise number of atoms (sulfur should contribute to at least one of them) with a value ≥12 (the sum of the sulfur and carbon atoms even for **X5** is only 11). At the same time, *x*, a summand in both totals (12 and 16), can only be equal to 10. Hence, the molecular formulae are:

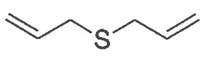
C_6SH_{10} (**X1**), $C_6S_2H_{10}$ (**X2**), $C_6S_3H_{10}$ (**X3**), $C_6S_4H_{10}$ (**X4**), $C_6S_5H_{10}$ (**X5**).

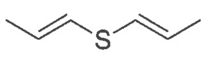
(0.2 points for each formula; total **1 point**)

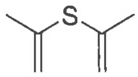
I-3.6 Since the number of types of carbon atoms in the molecules of **X1–X5** is three, which is half the total number of carbon atoms, it is logical to propose a generalized symmetric structure of the following type, where $n = 1–5$:

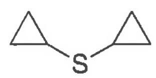
$$C_3H_5–(S)_n–C_3H_5$$

Note that heterocyclic structures are not considered, according to the stipulation in the task. By varying the structure of the C_3H_5 substituent, four possible structures for **X1** can be obtained (without specifying the stereochemistry):

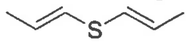

(1)

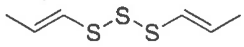

(2)

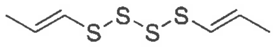

(3)

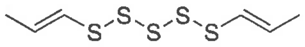

(4)

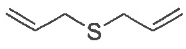
It turns out that molecule (4) does not meet the requirement regarding the number of types of carbon and hydrogen atoms, while structure (3) is unsuitable due to the number of types of hydrogen atoms. We cannot distinguish between structures (1) and (2) based on the given data. Therefore, the structural formulae of the two series of polysulfides (with a homologous difference equal to one sulfur atom) are as follows:

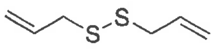


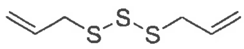


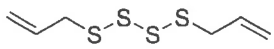


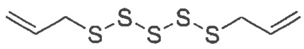



X1


X2


X3


X4


X5

The substances forming the lower series are produced by plants of the genus *Allium*, most for example, by garlic (*Allium sativum*), whose characteristic odor is largely determines by them. (0.5 points per a formula; total **2.5 points**; −0.5 points penalty for the absence of the second series of compounds)

Problem I-4 (author Karpushkin E.A.)

I-4.1 The scheme of synthesis of **X** suggests that it can consist of atoms of N, P, Sb, F, Cl, or Na. Sodium is the only element from its group of the periodic table, and no reasonable compositions are possible for halogens. In view of the explosion hazard and the fact that the product of combustion corresponding to **B** is an elementary compound (cf. i. **I-4.6**), **B** is nitrogen. The composition of **X** for **A** = P is PN_{23}. No reasonable composition is available for **A** = Sb.

(0.5 points for each element; total **1 point**)

I-4.2 The scheme describes the preparation of the pentazenium salt:

$N_2F_2 + SbF_5 \longrightarrow (N_2F)SbF_6$ (**P**)

$(N_2F)SbF_6 + HN_3 \longrightarrow N_5SbF_6$ (**Q**) + HF

$PCl_5 + 6NaN_3 \longrightarrow NaP(N_3)_6$ (**R**) + 5NaCl

$N_5SbF_6 + NaP(N_3)_6 \longrightarrow N_5P(N_3)_6$ (**X**) + $NaSbF_6$ (**S**)

(0.25 points for each compound and equation, 0.15 points for a gross formula instead of structure; total **2.25 points**)

I-4.3 Equations of combustion of the considered compounds:
$C_3H_5N_3O_9 \rightarrow 3CO_2 + 2.5H_2O + 1.5N_2 + 0.25O_2$
$C_7H_5N_5O_8 + 4.25O_2 \rightarrow 7CO_2 + 2.5H_2O + 2.5N_2$
$PN_{23} + 1.25O_2 \rightarrow 0.25P_4O_{10} + 11.5N_2$
Decomposition of 1 mol of trinitroglycerin (227.11 g) gives 0.25 mol of O_2 (8 g), which is 3.52 wt%. Hence, $\Omega = +3.52\%$. Similarly, Ω equals -47.36% for tetryl and -11.33% for **X**.
(total **1.25 points** for correct calculations; penalty −0.25 points per an arithmetic error or incorrect equation coefficients)

I-4.4 Direct proportionality between the said values means that $Q = a\Omega + b$. From the data given in the problem and the values of Ω obtained in i. **I-4.3**, one gets $a = 37.1$ kJ/(kg·%), $b = 6097$ kJ/kg. Then $Q(\mathbf{X}) = 5677$ kJ/kg.
(total **1 point**)

I-4.5 Let us write a set of thermochemical equations:
$PN_{23} + 1.25O_2 \rightarrow 0.25P_4O_{10} + 11.5N_2 + 5677$ kJ/kg (= 2005 kJ/mol)
$P + 1.25O_2 \rightarrow 0.25P_4O_{10} + 746$ kJ/mol
Subtracting the former equation from the latter, one gets
$P + 11.5N_2 \rightarrow PN_{23} - 1259$ kJ/mol
Hence, $\Delta_fH(\mathbf{X}) = 1259$ kJ/mol.
(total **1 point**)

I-4.6 An explosion of 35 g of **X** yields $35 / 353.2 \cdot 11.5 = 1.140$ mol of the gaseous product (nitrogen) and consumes $35 / 353.21 \cdot 1.25 = 0.124$ mol of oxygen. Hence, the starting amount of oxygen, $10^5 \cdot 0.01 / 8.314 / 263.15 = 0.457$ mol, decreases to 0.333 mol, and the total amount of the gases in the mixture upon the explosion is 1.473 mol.
An explosion of 35 g of **X** yields $35 \cdot 5677 / 1000 = 198.7$ kJ of heat. Heating of the mixture of ice and gases to 0°C consumes $10 \cdot (1.473 \cdot 12.5 + 100 \cdot 2) / 1000 = 2.184$ kJ of heat, melting of ice consumes $100 \cdot 332 / 1000 = 33.2$ kJ, and heating of the mixture of liquid water and gases to 100°C takes $100 \cdot (1.473 \cdot 12.5 + 100 \cdot 4.2) / 1000 = 43.84$ kJ. The total sum of these values is 79.2 kJ, and the remaining $198.7 - 79.2 = 119.5$ kJ are consumed for partial evaporation of water; the amount of the evaporated water is $119.5 \cdot 1000 / 2256 = 53.0$ g (2.944 mol). The equilibrium mixture contains $2.944 + 1.473 = 4.42$ mol of gases at 100°C. Thus, pressure in the 10 L vessel is $4.42 \cdot 8.314 \cdot 373.15 / 0.01 = 1.4 \cdot 10^6$ Pa.
(1 point for the amount of gases, 1 point for temperature (including the heat balance), 1 point for pressure; total **3 points**)

I-4.7 Calculation of the heat of explosion of **X** above considered its transformation into P_4O_{10} and N_2. However, the hydration of phosphorous oxide occurs in the presence of water, $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$, along with dissociation of the formed phosphoric acid, which affects the heat effect of the process.
(the hydration equation with the acid dissociation is accepted; total **0.5 points**)

Problem I-5 (author Shved A.M.)

I-5.1 **A** – $NaHSO_4$, **B** – Na_2SO_4, **C** – $NaHCO_3$, **D** – Na_2CO_3.
(0.5 points per a compound; total **2 points**)

I-5.2. Reaction equations:
A + **C**: $NaHSO_4 + NaHCO_3 \rightarrow Na_2SO_4 + CO_2\uparrow + H_2O$
A + **D**: $2NaHSO_4 + Na_2CO_3 \rightarrow 2Na_2SO_4 + CO_2\uparrow + H_2O$
$BaCl_2$ + **A**: $BaCl_2 + NaHSO_4 \rightarrow BaSO_4\downarrow + NaCl + HCl$
$BaCl_2$ + **B**: $BaCl_2 + Na_2SO_4 \rightarrow BaSO_4\downarrow + 2NaCl$
$CaCl_2$ + **C**: $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaCl$
(0.2 points per a reaction; total **1 point**)

I-5.3 Even if the identity of the anions has not been determined, it is still possible to calculate the acidity constants of the corresponding acids. Based on the pH increase, the salts have the following formulae: **A** – $Na\mathbf{HX}$, **B** – $Na_2\mathbf{X}$, **C** – $Na\mathbf{HY}$, **D** – $Na_2\mathbf{Y}$.

For the salt **B**, one can consider hydrolysis only at the first step:

$$\mathbf{X}^{2-} + H_2O \rightleftarrows H\mathbf{X}^- + OH^-$$

$$K_{a,2}(H_2\mathbf{X}) = \frac{[H^+][\mathbf{X}^{2-}]}{[H\mathbf{X}^-]} \approx \frac{[H^+](c - [OH^-])}{[OH^-]} \approx \frac{[H^+]^2 c}{K_w}$$

$$pK_{a,2}(H_2\mathbf{X}) = 2pH - \lg c - pK_w = 2 \cdot 7.52 - \lg 0.1 - 14 = 2.04$$

Since the pH of the solution is close to 7, the autoprotolysis of water can additionally be taken into account. This results in a slightly more accurate value of the acidity constant:

$$H_2O \rightleftarrows H^+ + OH^-$$

$$[OH^-] = [H^+] + [H\mathbf{X}^-] \Rightarrow [H\mathbf{X}^-] = [OH^-] - [H^+] = \frac{K_w}{[H^+]} - [H^+]$$

$$K_{a,2}(H_2\mathbf{X}) = \frac{[H^+][\mathbf{X}^{2-}]}{[H\mathbf{X}^-]} = \frac{[H^+](c - [H\mathbf{X}^-])}{[H\mathbf{X}^-]} \approx \frac{[H^+]c}{\frac{K_w}{[H^+]} - [H^+]} = \frac{[H^+]^2 c}{K_w - [H^+]^2}$$

$$pK_{a,2}(H_2\mathbf{X}) = 2pH - \lg c + \lg(K_w - [H^+]^2) = 2.00$$

A similar calculation for **D**:

$$pK_{a,2}(H_2\mathbf{Y}) = 2pH - \lg c - pK_w = 2 \cdot 11.65 - \lg 0.1 - 14 = 10.3$$

For the solution of the salt **C**, it is important to note that only its pH does not change upon dilution. This indicates that **C** can be considered amphoteric, and the corresponding formula independent of concentration can be used to calculate pH:

$$K_{a,1}(H_2\mathbf{Y}) \cdot K_{a,2}(H_2\mathbf{Y}) = \frac{[H^+][H\mathbf{Y}^-]}{[H_2\mathbf{Y}]} \cdot \frac{[H^+][\mathbf{Y}^{2-}]}{[H\mathbf{Y}^-]} = [H^+]^2 \cdot \frac{[\mathbf{Y}^{2-}]}{[H_2\mathbf{Y}]} \approx [H^+]^2$$

$$[H^+] = \sqrt{K_{a,1}(H_2\mathbf{Y}) \cdot K_{a,2}(H_2\mathbf{Y})}$$

$$pH = \frac{pK_{a,1}(H_2\mathbf{Y}) + pK_{a,2}(H_2\mathbf{Y})}{2}$$

$$pK_{a,1}(H_2\mathbf{Y}) = 2pH - pK_{a,2}(H_2\mathbf{Y}) = 2 \cdot 8.34 - 10.3 = 6.38$$

This property is not observed for the solution of the salt **A**. This may indicate that the acid $H_2\mathbf{X}$ is strong at the first dissociation step. Therefore, $H\mathbf{X}^-$ in solution of **A** is practically non-hydrolyzed, but behaves like a weak acid:

$$H\mathbf{X}^- \rightleftarrows H^+ + \mathbf{X}^{2-}$$

$$K_{a,2}(H_2\mathbf{X}) = \frac{[H^+][\mathbf{X}^{2-}]}{[H\mathbf{X}^-]} \approx \frac{[H^+]^2}{c - [H^+]}$$

$$\mathrm{p}K_{\mathrm{a},2}(\mathrm{H_2}\mathbf{X}) = 2\mathrm{pH} + \lg(c - [\mathrm{H}^+]) = 2 \cdot 1.57 + \lg(0.100 - 10^{-1.57}) = 2.00$$

The same result is obtained as before (using the pH of the solution **B**). Therefore, the assumption that the acid H_2**X** is strong at the first step was valid and it is rather impossible to reliably estimate its value using the available data. If the composition of the salts was determined earlier in the problem, this conclusion correlates with the properties of sulfuric acid H_2SO_4.

(1 point per the value of each acidity constant; total **4 points**)

I-5.4 The given values of acidity constants correspond to an acid dissociating completely at the first step and partially at the second step:

$$\mathrm{H_2}\mathbf{Z} \rightarrow \mathrm{H}^+ + \mathrm{H}\mathbf{Z}^-$$
$$\mathrm{H}\mathbf{Z}^- \rightleftarrows \mathrm{H}^+ + \mathbf{Z}^{2-}$$

The mass balance based on the initial acid concentration c:

$$c = [\mathrm{H}\mathbf{Z}^-] + [\mathbf{Z}^{2-}]$$

Water autoprotolysis can be neglected, thus the total concentration of H^+ is equal to the sum of the concentration of protons released at the first step ($[H^+]_1 = c$ because of complete dissociation) and at the second step ($[H^+]_2 = [\mathbf{Z}^{2-}]$):

$$[\mathrm{H}^+] = [\mathrm{H}^+]_1 + [\mathrm{H}^+]_2 = c + [\mathbf{Z}^{2-}]$$

$$K_{\mathrm{a},2}(\mathrm{H_2}\mathbf{Z}) = \frac{[\mathrm{H}^+][\mathbf{Z}^{2-}]}{[\mathrm{H}\mathbf{Z}^-]} = \frac{[\mathrm{H}^+][\mathbf{Z}^{2-}]}{c - [\mathbf{Z}^{2-}]} = \frac{[\mathrm{H}^+]([\mathrm{H}^+] - c)}{2c - [\mathrm{H}^+]}$$

$$[\mathrm{H}^+]^2 + \left(K_{\mathrm{a},2}(\mathrm{H_2}\mathbf{Z}) - c\right)[\mathrm{H}^+] - 2K_{\mathrm{a},2}(\mathrm{H_2}\mathbf{Z})c = 0$$

$$[\mathrm{H}^+] = \frac{c - K_{\mathrm{a},2}(\mathrm{H_2}\mathbf{Z}) + \sqrt{\left(K_{\mathrm{a},2}(\mathrm{H_2}\mathbf{Z}) - c\right)^2 + 8K_{\mathrm{a},2}(\mathrm{H_2}\mathbf{Z})c}}{2} = 0.141\ \mathrm{M}$$

Another root of the quadratic equation turns out to be negative. Therefore,

$$\mathrm{pH} = -\lg(0.141) = 0.85$$

(total **1 point**)

I-5.5 The acid **E** can be determined either from the description or from calculations. Let us assume that the monoprotic acid **E** has the composition H**L**. To form a salt with a hydrogen-containing anion, it is necessary to have several protons, which is only possible in the case of oligomerization of the acid. For example, in the case of dimerization, the following reaction equation with ammonia is possible:

$$2\mathrm{NH_3} + 3\mathrm{H}\mathbf{L} \longrightarrow \mathrm{NH_4}\mathbf{L} + \mathrm{NH_4}[\mathrm{H}\mathbf{L}_2]$$

From the masses of the reacting substances, the molecular mass of H**L** can be determined as:

$$M_r(\mathrm{H}\mathbf{L}) = \frac{120}{68} \cdot \frac{2}{3} \cdot 17.0 = 20.0$$

This corresponds to the acid HF, which is known to form intermolecular hydrogen bonds, explaining the existence of the anion $[HF_2]^-$. The mass fraction of hydrogen in the salt **G** confirms the validity of the solution and allows us to unambiguously identify **E** as HF, **F** as NH_4F, and **G** as $NH_4[HF_2]$.

(0.5 points per compound; total **1.5 points**)

I-5.6 When equal amounts of a weak base and a weak acid are mixed, a solution of a salt is formed, exhibiting amphoteric properties. The pH of such solutions (NH_4F in this case) can be calculated using the formula:

$$\mathrm{pH} = \frac{\mathrm{p}K_\mathrm{a}(\mathrm{NH_4}^+) + \mathrm{p}K_\mathrm{a}(\mathrm{HF})}{2} = \frac{(14 - 4.79) + 3.17}{2} = 6.19$$

(total **0.5 points**)

Problem I-6 (author Kozlov M.I.)

> "But I don't want to go among mad people," Alice remarked.
> "Oh, you ca'n't help that," said the Cat: "we're all mad here. I'm mad. You are mad."
> "How do you know I'm mad?" said Alice.
> "You must be," said the Cat, "or you wouldn't have come here."
> Lewis Carroll, *Alice's Adventures in Wonderland*

I-6.1 Based on the mass fractions, **E** contains only **X** and Cl. Consequently, **E** is the chloride of **X** with the general formula XCl_n. Thus, one can write the equation:

$$30.98 = \frac{100 \cdot n \cdot M(\mathrm{Cl})}{M(\mathbf{X}) + n \cdot M(\mathrm{Cl})} = \frac{3545n}{M(\mathbf{X}) + 35.45n}.$$

For $n = 1$, $M(\mathbf{X}) = 78.97$ g/mol, which corresponds to selenium. For $n = 2$, the value is approximately of 158 g/mol, which is close to gadolinium and terbium; however, they do not satisfy the given data. Further trials are pointless as the masses would exceed 230 g/mol. Thus, **X** is Se, and **E** is selenium(I) chloride. There is an indication that **E** contains a Se–Se bond; therefore, compound **E** is Se_2Cl_2. From the mass fractions, one can calculate the composition of **D** and **I**: there is an equal number of atoms of all elements in these compounds. **D** is KSeCN, and there is a Se–Se bond in **I**; thus, **I** is Na_2Se_2.

According to the mass fractions, copper and selenium are present in a 1 : 2 molar ratio in **A**, and there is also a third element, the mass of which calculated per one atom of copper is:

$$m = \frac{M(\mathrm{Cu}) \cdot (100 - \omega_{\mathrm{Cu}} - \omega_{\mathrm{Se}})}{\omega_{\mathrm{Cu}}} = 55.85\ \mathrm{g/mol},$$

which corresponds to iron. Thus, **A** is $CuFeSe_2$, known as eskebornite (a mineral, the selenium analog of chalcopyrite). Upon its calcination, selenium is converted into **B** (SeO_2). **C** (Na_2SeO_3) is formed in the reaction of SeO_2 with NaOH.

In the formation of **G**, one equivalent of Se_2Cl_2 reacts with six equivalents of Se; consequently, **G** contains a ring of eight selenium atoms. Aluminum chloride acts as a Lewis acid, binding the chlorine atoms into the complex ion $[AlCl_4]^-$. Then, **G** is $Se_8[AlCl_4]_2$. **G** disproportionates into **E** and **H** according to the equation:

$$x\mathrm{Se_8[AlCl_4]_2} = \mathrm{Se_2Cl_2} + 3\mathrm{Se}_n\mathrm{[AlCl_4]}_m + y\mathrm{AlCl_3}.$$

The material balance condition for Se, Al, and Cl leads to the following equations:

$$\begin{cases} 8x = 2 + 3n \\ 2x = 3m + y \\ 8x = 2 + 12m + 3y \end{cases}$$

One obtains that $y = 2$ from the second and third equations Thus:

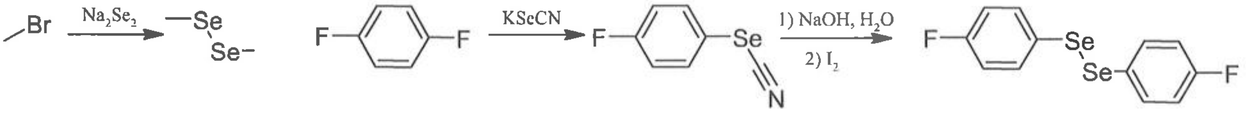
$$\begin{cases} n = \dfrac{8x - 2}{3} \\ m = \dfrac{2x - 2}{3} \end{cases}$$

For $x = 1$ one gets $n = 2$ and $m = 0$, that is, compound Se_2, which does not contain a polycation; therefore, it is invalid. For $x = 2$ and 3, fractional n values are obtained. For $x = 4$, $n = 10$ and $m = 2$. Thus, **H** is $Se_{10}[AlCl_4]_2$.

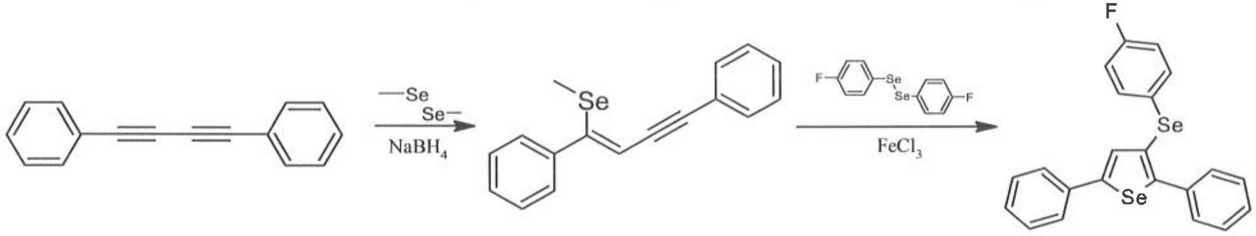
A – $CuFeSe_2$; **B** – SeO_2; **C** – Na_2SeO_3; **D** – KSeCN; **E** – Se_2Cl_2; **G** – $Se_8[AlCl_4]_2$; **H** – $Se_{10}[AlCl_4]_2$; **I** – Na_2Se_2.

(0.3 points for **X**, 0.35 points for each of **G** and **H**, and 0.25 points for each of the remaining compounds; total **2.5 points**; 0 points if **X, A, D, E, G, H, I** are given without calculations)

I-6.2 In the first step, nucleophilic substitution of bromine by diselenide occurs with the formation of **L**; similarly, nucleophilic substitution of fluorine by selenocyanide leads to the formation of **M**. **N** contains two selenium atoms; hence, cyanide is eliminated and a diselenide bridge is formed upon hydrolysis and oxidation of **M**.



Selenophene is the selenium-containing heterocyclic aromatic compound. Diphenylbutadiyne is used for its synthesis. Methylselenide (formed by the reduction of dimethyl diselenide) is nucleophilically added at the first atom. Then, arylselenide is added at the third atom under the action of the Lewis acid. Finally, the resulting carbocation closes the ring with selenium.



(0.5 points for each structure; total **2.5 points**; analogous structures with sulfur give full mark, other heterocyclic compounds are not accepted)

I-6.3 Since **Y(N)** is a series of fused selenium-containing heterocyclic compounds, **Y(1)** is the selenophene, and **Y(2)** is selenolo[3,2-b]selenophene; accordingly, they contain 6 and 10 π-electrons. These electrons occupy the lowest three orbitals in **Y(1)** ($n = 0$ and ± 1) and five orbitals in **Y(2)** ($n = 0, \pm 1$ and ± 2).

Thus, the transition to the first excited state in the case of **Y(1)** corresponds to an electron transition from the orbital with $n = 1$ to that with $n = 2$, and in the case of **Y(2)**, to a transition from $n = 2$ to $n = 3$:

$$\Delta E(\mathbf{Y(1)}) = E_2(\mathbf{Y(1)}) - E_1(\mathbf{Y(1)}) = (q_e \cdot 4.989)\ \mathrm{J};$$

$$\Delta E(\mathbf{Y(2)}) = E_3(\mathbf{Y(2)}) - E_2(\mathbf{Y(2)}) = (q_e \cdot 4.106)\ \mathrm{J}.$$

In the equations above, the electron charge is needed to convert eV to J.

Y(1) can be considered a circle, i.e., an ellipse with equal semiaxes, while **Y(2)** is an ellipse with semiaxes r_1 and r_2:

$$S(\mathbf{Y(1)}) = 2\pi\sqrt{\frac{r_1^2+r_1^2}{2}}; \qquad S(\mathbf{Y(2)}) = 2\pi\sqrt{\frac{r_1^2+r_2^2}{2}}.$$

Substituting S into the equation for the energy levels of a "particle on an ellipse," one obtains:

$$\Delta E(\mathbf{Y(1)}) = E_2(\mathbf{Y(1)}) - E_1(\mathbf{Y(1)}) = \frac{h^2 2^2}{2m_e S(\mathbf{Y(1)})^2} - \frac{h^2 1^2}{2m_e S(\mathbf{Y(1)})^2} = (q_e \cdot 4.989)\ \mathrm{J};$$

$$\frac{3h^2}{2m_e(2\pi r_1)^2} = \frac{3h^2}{8\pi^2 m_e r_1^2} = (q_e \cdot 4.989)\ \mathrm{J}; \qquad r_1 = \sqrt{\frac{3h^2}{8\pi^2 m_e q_e \cdot 4.989}} = 1.514\ \text{Å}.$$

$$\Delta E(\mathbf{Y(2)}) = E_3(\mathbf{Y(2)}) - E_2(\mathbf{Y(2)}) = \frac{h^2 3^2}{2m_e S(\mathbf{Y(2)})^2} - \frac{h^2 2^2}{2m_e S(\mathbf{Y(2)})^2} = (q_e \cdot 4.106)\ \mathrm{J};$$

$$\frac{5h^2}{2m_e \cdot 2\pi^2 \cdot (r_1^2+r_2^2)} = \frac{35}{4\pi^2 m_e (r_1^2+r_2^2)} = (q_e \cdot 4.106)\ \mathrm{J};$$

$$r_2 = \sqrt{\frac{5h^2}{4\pi^2 m_e q_e \cdot 4.106} - \frac{3h^2}{8\pi^2 m_e q_e \cdot 4.989}} = 2.643\ \text{Å}.$$

(0.5 points for each value; total **1 point**)

I-6.4 It is stated in the task that r_N depends linearly on N. The parameters of this dependence can be determined based on r_1 and r_2: $r_N = (1.130\mathrm{N} + 0.383)$ Å.

Molecule **Y(N)** contains $4N + 2$ electrons in the π-system. They occupy $(2N + 1)$ orbitals with $n = 0, \pm1, \pm2, \dots \pm N$; hence, the transition to the first excited state corresponds to an electron transition from the N-th orbital to the $(N + 1)$-th one.

$$\Delta E(\mathbf{Y}(\boldsymbol{N})) = E_{N+1}(\mathbf{Y}(\boldsymbol{N})) - E_N(\mathbf{Y}(\boldsymbol{N})) = \frac{hc}{\lambda};$$

$$\frac{h^2(N+1)^2}{2m_eS(\mathbf{Y}(N))^2} - \frac{h^2N^2}{2m_eS(\mathbf{Y}(N))^2} = \frac{h^2(2N+1)}{4\pi^2m_e(r_1^2+r_N^2)} = \frac{hc}{\lambda}.$$

Substituting $\lambda = 380$ nm, one obtains $N = 2.95$, and $N = 7.09$ for $\lambda = 780$ nm. Thus, $2.95 < N < 7.09$; that is, the transition to the first excited state will fall in the visible region for molecules **Y(N)** containing from three to seven cycles.

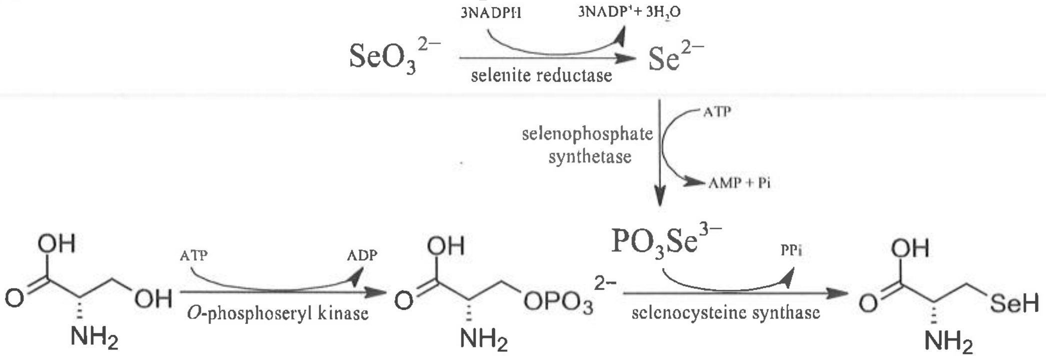
(0.2 points for the r_N dependence parameters, 0.4 points for the calculation for each wavelength; **total 1 point**)

I-6.5 The proteinogenic amino acid containing selenium is selenocysteine (see the list in the Reference Data section); it can be either **Z2** or **Z3**. The mass fraction of selenium in selenocysteine is $\omega_{Se} = 46.99\%$. Therefore, that in the second amino acid can be $\omega_{Se} = 46.99 - 6.72 = 40.27\%$ or $\omega_{Se} = 46.99 + 6.72 = 53.71\%$. Presumably, the amino acid contains one selenium atom; then, the mass of the second amino acid could be 196.10 g/mol or 147.03 g/mol. Obviously, this amino acid contains selenium and $H_2N{-}CH{-}COOH$ as the common fragment for all amino acids. Thus, the mass of the amino acid cannot be less than 153.03 g/mol. Therefore, the mass of 147.03 g/mol is not acceptable. The mass of the remaining fragments of the amino acid is 196.10 − 153.03 = 43.07 g/mol, which corresponds to three carbon and seven hydrogen atoms. The only amino acid that contains three carbons in its side chain as well as oxygen or sulfur (which can be replaced by selenium), is methionine (structural similarity of methionine and selenomethionine leads to erroneous introduction of the residues of the latter in the propagating polypeptide chain). Thus, selenomethionine is the second amino acid in the pair of **Z2** and **Z3**. In the biosynthesis scheme, **Z2** does not undergo methylation or demethylation, moreover, sulfur is not removed. Therefore, **Z2** is selenocysteine, which is obtained from **Z1** (serine), and **Z3** is selenomethionine.

(0.75 points for each compound; total **2.25 points**)

I-6.6 **C** is Na_2SeO_3. It is reduced by three equivalents of NADPH; hence, selenium gains six electrons and is converted into Se^{2-} (**V**). At the next step, ATP is converted to AMP and phosphate. One more phosphorus atom, evidently, reacted with selenium, resulting in the formation of selenophosphate PO_3Se^{3-} (**W**).

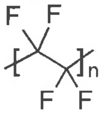
Similarly, in the formation of **U**, ATP loses one phosphorus atom; thus, it is attached to serine, yielding phosphoserine (**U**). The described processes are shown in the scheme below.



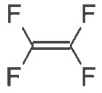
(0.25 points for each of **U**, **V**, **W**; total **0.75 points**)

Problem I-7 (author Trushkov I.V.)

I-7.1 From the problem statement, one can easily deduce that polymer **A** is Teflon (the IUPAC name: poly(tetrafluoroethylene)), formed by polymerization of tetrafluoroethylene **B**.



A



B

(0.5 points for each of the two structural formulae; total **1 point**)

I-7.2 The decomposition of tetrafluoroethylene with the formation of an elementary substance can formally lead to the formation of either carbon or fluorine. However, fluorine is the most reactive element, which interacts with unsaturated compounds and even with hydrocarbons, so its formation due to the decomposition of tetrafluoroethylene is impossible. Thus, **D** is carbon. **C** contains only carbon and fluorine, with the carbon content in it being lower than that in C_2F_4. An explosive decomposition cannot lead to the formation of compounds with a greater molecular mass compared to that of the decomposing compound. Consequently, **C** is tetrafluoroethane, CF_4.

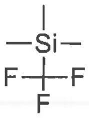
Industrial production of tetrafluoroethylene **B** is based on the reaction of chloroform with HF (**E**), involving the substitution of chlorine by fluorine. Clearly, the introduction of only one fluorine atom will not lead to the formation of tetrafluoroethylene due to the pyrolysis of $CHFCl_2$. Therefore, **F** and **G** are CHF_3 and CHF_2Cl. The formation of tetrafluoroethylene due to the pyrolysis of CHF_3 is accompanied by the elimination of HF. Thus, **G** is CHF_3, and **F** is CHF_2Cl.

(the structures of **C** and **E–G**, 0.5 points for each; total **2 points**)

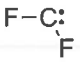
I-7.3. Deprotonation of **G** gives the anion CF_3^-, which acts as a nucleophile toward the electrophilic species present in the reaction medium. The product of nucleophilic addition to the carbonyl group is formed when it attacks benzophenone; subsequent neutralization affords the alcohol $Ph_2C(OH)CF_3$ (**H**). In the reaction with trimethylchlorosilane, chlorine is replaced by the CF_3 group due to the nucleophilic substitution, to afford $(CH_3)_3SiCF_3$ (**I**) known as the Ruppert–Prakash reagent. When one attempts to generate the trifluoromethyl anion in the form of a lithium or magnesium derivative, the corresponding metal halide readily eliminates with the formation of difluorocarbene, CF_2 (**J**). The reaction of the latter with alkenes gives the corresponding cyclopropane as the main or sole product.

(four structural formulae, 0.5 points each; **total 2 points**)

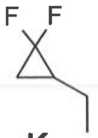
H



I



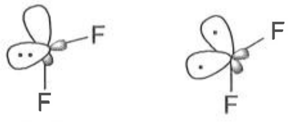
J



K

I-7.4. Regardless of the answer to the previous question, mentioning of the two forms and one bond angle for each form allows concluding that **J** is a carbene, namely difluorocarbene. It is known that the singlet form of difluorocarbene is more stable. The singlet form (one orbital contains a pair of electrons, the other orbital is empty) has a bond angle of approximately 105°; the triplet form (both orbitals contain one electron with the same spin) has a bond angle of approximately 120°.

(0.5 points for each of singlet and triplet forms of difluorocarbene, 0.5 points for the choice of the more stable form, 0.25 points for correct choice of each bond angle; total **2 points**)



singlet triplet

I-7.5 When treated with tetrabutylammonium fluoride, the Ruppert–Prakash reagent (**I**) is converted into the trifluoromethyl anion (its tetrabutylammonium salt). As discussed above, it is a nucleophile. In its reaction with benzaldehyde, the corresponding alkoxide is formed, which gives the silyl ether, $PhCH(OSiMe_3)CF_3$ in the reaction with trimethylsilyl fluoride. The treatment of $PhCH(OSiMe_3)CF_3$ with dilute acid leads to the removal of the silyl group with the formation of the secondary alcohol $PhCH(OH)CF_3$. This alcohol is also obtained by the reduction of the corresponding ketone with sodium borohydride, whereas this ketone is formed by the attack of the trifluoromethyl anion on methyl benzoate.

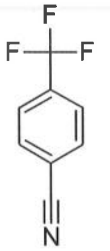
(0.5 points for each of three structural formulae; total **1.5 points**)

L

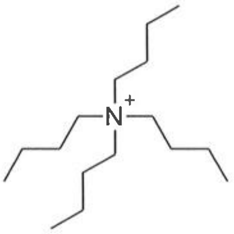
M

N

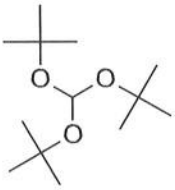
I-7.6. First, let us determine the molecular mass of **Q**. It contains 22.09% of silver, so $M(\mathbf{Q}) = 107.87 / 0.2209 = 488.3n_{Ag}$. If **Q** contains one silver atom, the remaining atoms account for $488.3 - 107.87 = 380.43$ g/mol. **Q** is a salt. One can assume that tetrabutylammonium (the mass of 242.47 g/mol) is the cation in this salt. Thus, the remaining atoms account for 138 g/mol. Since **Q** was obtained from trifluoromethane, one can assume that it contains the CF_3 fragment (69 g/mol). Then one can conclude that **Q** contains the tetrabutylammonium cation, the silver cation, and two trifluoromethyl anions. In view of the ionic structure, its formula is $(Bu_4N)[Ag(CF_3)_2]$. Its reaction with 4-cyanophenyldiazonium tetrafluoroborate gives the same product **P** that was formed from 4-bromobenzonitrile. Thus, this product is 4-(trifluoromethyl)benzonitrile, $4\text{-}NCC_6H_4CF_3$. The reaction of trifluoromethane with sodium *tert*-butylate gives the product that contains three types of carbon atoms and two types of hydrogen atoms. There are one type of hydrogen atoms and two types of carbon atoms in the *tert*-butyl group. It can be assumed that **R** is formed by the substitution of one or more fluorine atoms with a *tert*-butoxy group. The mass fraction of carbon suggests that it is tris(*tert*-butyl) orthocarbonate.



P



Q



R

(0.5 points for each of three structures; total **1.5 points**)

Problem I-8 (author Garifullin B.N.)

I-8.1 The fundamental first-order pharmacokinetic equation as applied to the case:

$$\ln\frac{0.1N_0}{N_0} = -\lambda t = -\frac{\ln 2}{T_{1/2}}t$$

Solving for t, one obtains $t = 33$ days.

(total **0.75 points**)

I-8.2 Notice that the ratio of the densities of the gaseous products is equivalent to that of their molar masses. Also, note that two products of the enzymatic reaction, in terms of their molar masses, are members of an arithmetic progression. By taking the progression increment as d and the molar mass of **B3** as M, one can write the equation:

$$\frac{M+2d}{M} = 1.12$$

and $M = 16.7d$. Rounding the molar masses to obtain an arithmetic progression of natural numbers, one can arrange the following table (with $d \le 2$, since the substances are gaseous):

d	M(**B1**)	M(**B2**)	M(**B3**)	M(**Z**)	M(**X**)	M(**A**)
1	44	19	17	18	20	60
2	85.5	37	33	35	39	116.5

Considering that the process described is biochemical (enzymatic), **B1** is CO_2, **B3** is NH_3, and **A** is urea (i.e., the progression increment equals one).

Based on the suggested set of reagents and products, we are dealing with hydrolysis of urea. The only explanation for the observed discrepancies with the conventional reaction (namely, that the molar mass of water is 20 g/mol and that three hydrolysis products are produced instead of two) is an unusual isotopic composition of water.

Water labeled with the stable ^{18}O isotope is excluded based on the molecular mass of CO_2. Thus, **X** must contain heavy isotopes of hydrogen and can be either D_2O or THO. However, in the case of deuterated water (D_2O), urea hydrolysis cannot yield three products in equimolar ratio: first, isotope exchange processes are negligible due to the extremely high rate of the enzymatic process; second, the mechanism of urea hydrolysis in heavy water (with an intermediate formation of carbamic acid) implies the formation of only one isotopolog of ammonia:

$$CO(NH_2)_2 + D_2O \rightarrow CO_2 + 2NDH_2$$

Hence, **X** is tritium-protium water (THO), which reacts with urea in the presence of urease giving an equimolar mixture of CO_2, NH_3, and the tritium-labeled isotopolog of ammonia (NTH_2):

$$CO(NH_2)_2 + THO \rightarrow CO_2 + NH_3 + NTH_2$$

Note that measuring the content of D_2O in drinking water sources is unnecessary because no natural or anthropogenic mechanism significantly alters the proportions of water isotopologs. By contrast, anthropogenic tritium-labeled water may be present in surface waters near nuclear fuel-cycle facilities, leading to radioactive contamination (the THO content is estimated indirectly by the activity of tritium itself).

A compound similar to **X** in chemical properties, **Z**, with a molar mass of 18 g/mol, is ordinary water (H_2O). Overconsumption of H_2O is known to cause intoxication.

Compound **Y** exhibits pronounced toxicity; therefore, it must contain tritium (heavy water D_2O or its isotopomer HDO, which are widely present on our planet, are expectedly low-toxic due to their abundance and lack of radioactivity). Consequently, **Y** is likely to be either tritium water (T_2O) or tritium-deuterium water (TDO). The differences between these cannot be distinguished based on the given data; any water isotopolog containing tritium along with a secondary stable oxygen isotope – ^{17}O or ^{18}O – is accepted for **Y**.

X	**Y**	**Z**	**B1**	**B2**	**B3**	**A**
THO	T_2O or TDO	H_2O	CO_2	NTH_2	NH_3	$CO(NH_2)_2$

(0.75 points for molecular formulae of **X**, **Z**, **A**, **B1–B3**, 0.5 points for each of two possible formulae for **Y**; total **5.5 points**)

I-8.3 Tritium-protium water is expected to mix with ordinary water in any ratio.

(total **0.75 points**)

I-8.4 The use of tritium-labeled urea is the simplest modification of the reaction deciphered above (case a, *variant 1*):

$$CO(NH_2)(NTH) + H_2O \rightarrow CO_2 + NH_3 + NTH_2$$

Theoretically, one might consider the use of urea labeled with the ^{16}N isotope in the following process (case a, *variant 2*):

$$CO(NH_2)(^{16}NH_2) + H_2O \rightarrow CO_2 + NH_3 + {}^{16}NH_3$$

However, the nitrogen isotope ^{16}N is extremely unstable (the half-life of≈7 s), which limits the possibility of an experiment similar to that described in the problem. As the participants are not required to know nitrogen isotope half-lives, this answer is also accepted as correct. For case b it is worth noting that if we choose one reactant from the $CO(NH_2)_2$/THO pair, the other one must be an isomer of the remaining species. Clearly, one must consider the isomers of urea. Ammonium isocyanate is extremely unstable; therefore, case b) corresponds to the hydrolysis of ammonium cyanate at moderate heating (60°C):

$$NH_4OCN + THO \rightarrow CO_2 + NH_3 + NTH_2$$

(1 point for each of a) and b); total **2 points**)

I-8.5 Corrosion of metals upon prolonged contact with tritium-protium water is due to the radiolysis of water initiated by the radioactive decay of tritium (having an excess of neutrons, it undergoes β^- decay):

$$^3_1H \rightarrow {}^3_2He + e^-$$

Subsequently, water ions (H_2O^+ and H_2O^-) are formed, which decompose to yield, among other products, the hydroxyl radical, which then reacts with an electron to form the hydroxide ion:

$$OH^{\cdot} + e^- \rightarrow OH^-$$

An increase in the solution pH promotes the corrosion of aluminum, an amphoteric metal. Note that D_2O, like ordinary water, can be stored in aluminum containers for extended periods without adverse effects.

(total **1 point**)