SECTION I. PHYSICAL CHEMISTRY

Problem 1 (author Gulevich D.G.)

1. Since K_α-radiation corresponds to the transition of an electron from the energy level $m = 2$ to $n = 1$, then $\frac{1}{\lambda} = R(Z-\sigma)^2\left(1-\frac{1}{4}\right)$ and $C(\alpha) = 3/4R$. For K_β-radiation $m = 3$, $n = 1$ and $\frac{1}{\lambda} = R(Z-\sigma)^2\left(1-\frac{1}{9}\right)$, $C(\beta) = 8/9R$ (1 point for each constant, total 2 points).

2. We obtained that $\lambda_\alpha > \lambda_\beta$. The transition from the L-shell to K is energetically more favorable than the transition M → K. Hence, peak 2 corresponds to K_α-radiation, and peak 1 corresponds to K^β-radiation (0.5 points for each peak, total 1 point).

3. a) By the transition from wavelength to energy, the expression for Moseley's law will be rewritten as $E = 0.75hcR(Z-\sigma)^2$ or $\sqrt{E} = \sqrt{0.75hcR}(Z-\sigma)$, where h – Planck's constant, c – is the speed of light in vacuum (0.5 points). $\sigma = -a/b = -(-3.74)/3.22 = 1.16$ (1 points).

b) Rydberg constant will be equal to (1.5 points, 3 points in total)

$$R = \frac{4b^2\cdot1.6\cdot10^{-19}}{3hc} = \frac{4\cdot3.22^2\cdot1.6\cdot10^{-19}}{3\cdot6.63\cdot10^{-34}\cdot2.998\cdot10^8} = 1.12\cdot10^7\ \text{м}^{-1}.$$

4. According to the graph we determine the energy of X-ray radiation corresponding to the element **A**: $E(\mathbf{A}) = 80^2 = 6.4$ keV $= 1.024\cdot10^{-15}$ J. From the expression for the Moseley law we get

$$Z = \sqrt{\frac{E}{0.75hcR}} + \sigma = \sqrt{\frac{1.024\cdot10^{-15}}{0.75\cdot6.63\cdot10^{-34}\cdot2.998\cdot10^8\cdot1.12\cdot10^7}} + 1.16 = 24.8 + 1.16 = 25.96 \approx 26.$$

In this way **A** – Fe (3 points).

5. Considering that $eU = h\nu_{max} = hc/\lambda_{min}$, we have (1 point)

$$U = \frac{hc}{e\lambda_{min}} = \frac{6.63\cdot10^{-34}\cdot2.998\cdot10^8}{1.6\cdot10^{-19}\cdot0.31\cdot10^{-10}} = 40\ \text{kV}$$

6. a) Electron remove from the inner shell can be described as a transition from $n = 1$ to $m = \infty$.Then the energy to be spent is equal to $\Delta E = -hcR(Z-\sigma)^2 \approx -11.3$ keV.

b) For elements with a smaller atomic number, the corresponding energy will be even less. This means that all the radioisotopes listed in the table can be used to generate X-rays in a selected series of elements ($Z = 21 - 30$).

c) Electron capture: ${}^{26}_{13}\text{Al} + {}^{0}_{-1}\text{e} \rightarrow {}^{26}_{12}\text{Mg}$; β^+-decay: ${}^{26}_{13}\text{Al} \rightarrow {}^{26}_{12}\text{Mg} + {}^{0}_{+}\text{e} + \nu_e$.

(Calculation of ΔE - 2 points, determination of the radioisotopes - 0.5 points, each nuclear reaction equation - 1 point, total 4.5 points)

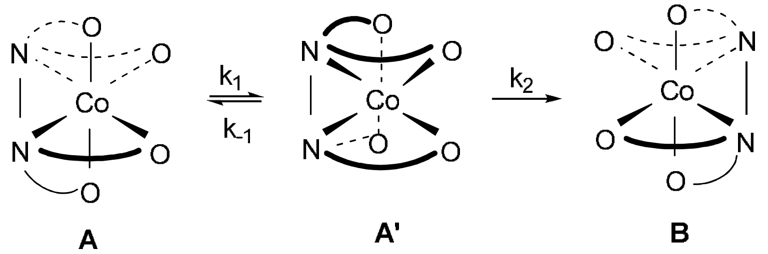
7. ^{18}Ar(39.95), ^{19}K(39.10), ^{27}Co(58.98), ^{28}Ni(58.71), ^{52}Te(127.6), ^{53}I(126.9) (0.5 points).

Problem 2 (authors Rozantsev G.M., Shved E.N.)

1. For the first-order reaction $\ln(C^o/C) = kt$, at $t_{1/2}$ $C = C^0/2$, $k = (\ln2)/t_{1/2}$. Then k_{obs} = $(\ln2)/(170·60) = 6.80·10^{-5}$ s^{-1} (0.5 points). On the assumption of $\mathbf{A} \leftrightarrows \mathbf{A'}$ (k_1; k_{-1}), $\mathbf{A'}H \leftrightarrows \mathbf{A'} + H^+$ (K_a) and material balance $C_\mathbf{A} = [\mathbf{A}] + [\mathbf{A'}] + [\mathbf{A'}H] = [\mathbf{A}] + k_1[\mathbf{A}]/k_{-1} + (k_1[\mathbf{A}][H^+])/K_ak_{-1}$; $[\mathbf{A}] = C_\mathbf{A}K_ak_{-1}/(K_ak_{-1} + K_ak_1 + k_1[H^+])$; $k_{obs} = K_ak_{-1}/(K_ak_{-1} + K_ak_1 + k_1[H^+])$ (1 point), *i. e.* reaction rate depends on pH. (1.5 points).

2. By the equation $\ln(k_2/k_1) = E_a(1/T_1 – 1/T_2)/R$, $E_a = RT_1T_2\ln(k_2/k_1)/(T_2 - T_1)$ = $8.314·373·318·(\ln(4.018·10^{-6}/3.110·10^{-10}))/(373 – 318)$ = 169736 J/mol. $\Delta H^\# = E_a - nRT$ = $169736 – 8.314·373 = 166635$ J/mol. From the Arrhenius equation $k = Ae^{–Ea/RT}$ $\ln A = \ln k + E_a/RT$ = $\ln(4.018·10^{-6}) + 169736/(8.314·373) = 42.31$. The entropy of the intermediate formation $\Delta S^\#$ = $R(\ln A – \ln T – \ln(k_B/h) – 1) = 8.314(42.31 – \ln373 – \ln(1.381·10^{-23}/6.626·10^{-34}) – 1)$ = 96.69 J/mol·K. The Gibbs energy $\Delta G^\# = \Delta H^\# - T\Delta S^\# = -RT\ln K^\#$; $373·96.69 – 166635 = 8.314·373·\ln K^\#$; $K^\# = 5.18·10^{-19}$ (2 points).

3. Two-stage mechanism:



$r = k_2C_{\mathbf{A'}}$; $dC_{\mathbf{A'}}/dt = 0$; $k_1C_\mathbf{A}=(k_{-1} + k_2)C_{\mathbf{A'}}$; then rate $r = [k_1k_2/(k_{-1} + k_2)]C_\mathbf{A}$ $r = k_{obs}C_\mathbf{A}$, where k_{obs} = $k_1k_2/(k_{-1} + k_2)$ (2 points).

4. In alkaline medium $\mathbf{A} + OH^- \leftrightarrows \mathbf{A'}OH^-$ (k_3; k_{-3}), $\mathbf{A'}OH^- \rightarrow \mathbf{B} + OH^-$ (k_4), $r = k_4C_{\mathbf{A'}OH}$ $dC_{\mathbf{A'}OH}/dt = 0$, $k_3C_\mathbf{A}·C_{OH}^- = (k_{-3} + k_4)C_{\mathbf{A'}OH-}$. Rate $r = [k_3k_4/(k_{-3} + k_4)]C_\mathbf{A}C_{OH^-} = k_{obs}C_\mathbf{A}C_{OH^-}$. Hence $k_{obs} = r/(C_\mathbf{A}C_{OH}^-) = r/(0.01C_{OH^-})$. At any pH from the table k_{obs} = 0.54 L/mol·s (2 points)

5. Rate $r = k_{obs}C_\mathbf{A}C_{OH}^- = 0.54·0.01·10^{-9} = 5.40·10^{-12}$ mol/L·s (3 points)

The two-stage mechanism considers both acidic and alkaline medium data.

6. I stage: $\mathbf{A} + H_2O \leftrightarrows \mathbf{A'}H_2O$ (k_1; k_{-1}); $\mathbf{A'}H_2O \rightarrow \mathbf{B} + H_2O$ (k_2), considering pseudo-order ($C_{H2O} >> C_\mathbf{A}$), $r = kC_\mathbf{A}$. II stage: $\mathbf{A} + OH^- \leftrightarrows \mathbf{A'}OH^-$ (k_3; k_{-3}), $\mathbf{A'}OH^- \rightarrow \mathbf{B} + OH^-$ (k_4), $r = k'C_\mathbf{A}C_{OH^-}$. Total equation: $r = kC_\mathbf{A} + k'C_\mathbf{A}C_{OH^-} = (k + k'C_{OH^-})C_\mathbf{A} = k_{obs}C_\mathbf{A}$ (Total 2 points)

7. For 45°C, the rate constant k is found from the equation: $r = (3.11·10^{-10} + 0.54·10^{-9})·0.01$ = $8.51·10^{-10}$ mol/L·s, which coincides with the experimental value $8.50·10^{-10}$ mol/L·s (2 points)

Problem 3 (author Borschevsky A.Ya.)

1. By convention, the water (product of combustion) must be in a liquid state. Combustion equation (1 point):

$$C_3H_8(g) + 5O_2(g) = 3CO_2(g) + 4H_2O(l).$$

2. According to the law of uniform distribution, each translational and rotational degree of freedom of a molecule contributes to the molar heat capacity $C_{V,\mathrm{m}}$ contribution equal $R/2$. Molecules O_2 и N_2 have three translational and two rotational degrees of freedom, therefore $C_{V,\mathrm{m}}(\mathrm{air}) = 2.5\,R = \underline{20.8\ \mathrm{J/mol{\cdot}K}}$ (1.5 points)

3. At constant pressure, the heat of the process coincides with the change in enthalpy. From the data of the table on the enthalpies of formation of participants in the combustion reaction we find:

$$\Delta_r H^\circ = 4 \cdot (-285.8) + 3 \cdot (-393.5) - (-103.85) - 1 \cdot 0 = -2219.8\ \mathrm{kJ/mol}.$$

The standard enthalpy of formation of oxygen as an element is zero. The molar mass of propane is roundly equal to 44 g/mol, hence the specific calorific value of propane $q_c = 2219.8/44 = \underline{50.45\ \mathrm{kJ/g}}$ (1 point)

4. Calculate the amount of heat Q required to heat the room. Heating occurs at constant pressure, therefore $Q = \Delta H = n_0 C_{P,\mathrm{m}} \Delta T$, where n_0 – the number of moles of air in the room before heating. According to the ideal gas state equation $n_0 = PV/RT_0$, where P и V – pressure in the room and volume of the room, respectively, T_0 - initial temperature. Molar heat capacity of air $C_{P,\mathrm{m}} = C_{V,\mathrm{m}} + R$. In this way,

$$Q = \frac{PV}{RT_0} C_{P,\mathrm{m}} \Delta T = 3.5 \frac{PV}{T_0} \Delta T = \frac{3.5 \times 101325 \times 50 \times 30}{263} = 2022.6\ \mathrm{kJ}.$$

From here we find that heating is required $m(C_3H_8) = (2022.6/2219.8) \cdot 44 = \underline{40.1\ \mathrm{g}}$ of propane (2 points)

5. Propane saturated vapor pressure is the equilibrium constant for the “reaction” $C_3H_8(l) = C_3H_8(g)$. Calculate the enthalpy and entropy of propane vaporization: $\Delta_v H = (-103.9) - (-120.9) = 17.0\ \mathrm{kJ/mol}$, $\Delta_v S = 269.9 - 195.2 = 74.7\ \mathrm{J/(mol{\cdot}K)}$. According to the well-known formula $\Delta_r G^\circ = -RT \ln K_P$ we have (2 points)

$$\ln P_{\text{нас}} = \frac{1}{R}\left(-\frac{\Delta_v H}{T} + \Delta_v S\right) = \frac{1}{8.314}\left(-\frac{17000}{263} + 74.7\right) = 1.21, \qquad P_{\text{нас}} = \underline{3.35\ \text{атм}}.$$

6. In the equilibrium between saturated vapor and liquid, the number of molecules hitting the surface of the liquid, and "sticking" to it, is equal to the number of molecules that pass into the gas phase. Consequently, the number of molecules evaporating from the open surface (the conditions set in the problem are equivalent to evaporation from the open surface) and entering the burner can be calculated by the formula (1). Multiplying this expression by the evaporation area $S = \pi(d/2)^2$, we get (3.5 points)

$$I = \nu S = \frac{PS}{\sqrt{2\pi m k_\mathrm{B} T}} = \frac{3.35 \times 101325 \times \pi \times (0.2/2)^2}{\sqrt{2\cdot\pi\cdot 44\cdot 1.66\cdot 10^{-27}\cdot 1.38\cdot 10^{-23}\cdot 263}} = \underline{19.1\,\mathrm{g/s}}.$$

7. Living quarters are never hermetic, so heating the air in the room does not change the pressure in it. It follows that the amount of air in the volume of the room when heated decreases, as its excess goes through the cracks to the outside. The initial thermal energy of the air was equal to $U_0 = n_0C_{V,\mathrm{m}}T_0$, where n_0 – number of moles of air in a cold room. In the heated room $U = nC_{V,\mathrm{m}}T$. From these equalities we find:

$$\frac{U}{U_0} = \frac{n}{n_0}\frac{T}{T_0}.$$

On the other hand $PV = n_0RT_0 = nRT$, from where $n/n_0 = T_0/T$. Finally

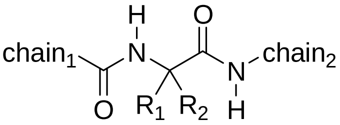
$$\frac{U}{U_0} = \frac{T_0}{T}\frac{T}{T_0} = 1.$$

In this way, $U = U_0$ and $\underline{\Delta U = 0}$, that is, the internal energy of the air in the room will not change. The heat released during the combustion of propane was spent on increasing the internal energy of all the air released through the gaps and to work W to expand the air against atmospheric pressure: $Q = \Delta U_0 + W$ (4 points)

SECTION II. LIFE SCIENCES AND POLYMERS

Problem 1 (author Garifullin B.N.)

1. Singlets with chemical shifts of 9.24 and 9.74 ppm can only correspond to the hydrogen atoms of the amide groups of the peptide bonds. However, a dublet should typically be observed, since hydrogen atom is found at α-carbon atom of nearly all amino acids (note that all atoms of the peptide chain are involved in the multiplet splitting according to the given conditions). This is not true for the **A** and **B** residues, leading to the hereunder peptide chain fragment (R_1, $R_2 \neq H$) (1 point for the fragment, 0.5 point for the signal, 1.5 point in total):

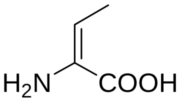


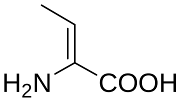
2. The C to H molar ratio in **C** is:

$$n(C):n(H) = \frac{C(C)}{A_r(C)} : \frac{C(H)}{A_r(H)} = 1:1.75 = 4:7$$

The sum of atoms 1 N + 2O typical of amino acids (**C** is found in a cyclic heptapeptide) accounts for the rest 45.51 % of the mass fraction. Close inspection of the ^{1}H-NMR spectrum of the amino acid A (three H atoms with the chemical shift of 1.83 ppm and one H atom with the chemical shift of 6.26 ppm) isomeric to **C** suggests that the elementary formula coincides with the true one. Thus, the molecular formula of **C** is $C_4H_7NO_2$ (1.5 points, including 0.5 point for calculation of the C to H ratio, and 0.75 point for calculation of the group of atoms 1 N + 2O).

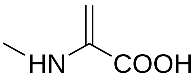
3. α-Amino acids **A** and **B** also have the molecular formula of $C_4H_7NO_2$. Representing the amino acids as it was done in i. 1, one concludes that substituents R_1 and R_2 contain 2 C + 4 H in total. With due account of the ^{1}H-NMR spectroscopy data, only the hereunder structures are valid for **A** and **B**:





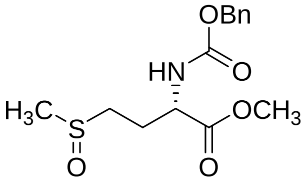
You have been provided with the spectra of **A** and **B** residues incorporated into cyclic peptides. Differing in the amino acid composition and geometry, the latter can alter the theoretical values of chemical shifts calculated for individual **A** and **B**. Thus, it is impossible to unambiguously attribute E- and Z-isomers to **A** and **B** (1.5 points for each structure, 3 points in total, 1 point penalty for unambiguously attributed structure of **A** and/or **B**).

4. The following ratios of integral intensities of signals in the ^{1}H-NMR spectrum are possible for **C**: 3:3:1 (variant 1) or 3:1:1:1:1 (variant 2). Information about the properties of **C** allows making the final choice in favor of variant 2 (note that H atoms at the methylene group are not equal) (2 points):

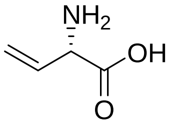


C

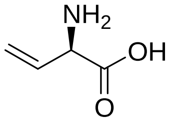
5. The first step of *L*-methionine methyl ester modification includes protection of the amino group with subsequent oxidation of sulfur affording D1:


D1

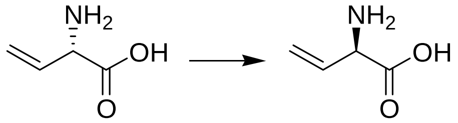
Pyrolysis followed by treatment with acid results in **D1** transformation into *L*-vinylglycine isomeric to the compounds **A – C** (1.25 points for each structure, 2.5 points in total):


D

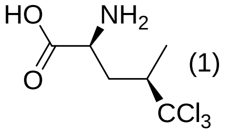
6. **E** is an α-amino acid, which can be formed in one step (note that only one enzyme is needed, whereas the substrate does not leave the active site) from one of **A**, **B**, **C**, or **D**. Thus, **E** is undoubtedly *D*-vinylglycine (1 point):

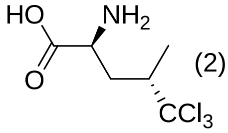

E

7. (1 point)



8. Carbon dioxide and nitrogen are very realistic candidates for the combustion products present in the molar ration of 12:1, since that of C to N atoms in leucine equals 6:1. Then, the molar ratio of the unknown combustion product to nitrogen (6:1) is transformed into that of 3:1 with due account for triple substitution of the hydrogen atoms in leucine by an unknown particle. Hydrogen halide turns out to be the only option. Molecular halogens are formed upon burning of bromine - and iodne-containing compounds, leaving only chlorine and fluorine under consideration. However, hydrogen fluoride does not meet the molar mass lower limit. Any of two equivalent methyl groups of leucine are the only targets of triple hydrogen substitution by chlorine. Since the enzyme stereospecificity is not known, there are two possible variants of the structure of F (1.25 points for each structure, 2.5 points in total):


(1)

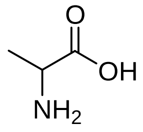
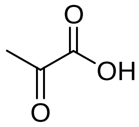
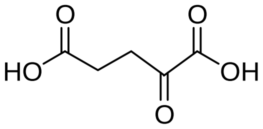
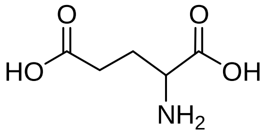

(2)

Problem 2 (author Larionov K.V.)

1. An α-keto acid formed as a result of a canonical α-amino acid transamination contains 3 to 5 oxygen atoms. In the case of 3 atoms: 16·3/(0.5454)=88.008. Subtracting masses of the carboxylic and keto groups one gets: 88–45–28=15, which corresponds to the methyl group. There is no α-amino acid suitable for the cases of 4 and 5 oxygen atoms. Thus, **B** is pyruvic acid, and **A** is *L*-alanine.

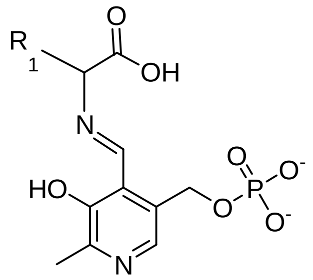
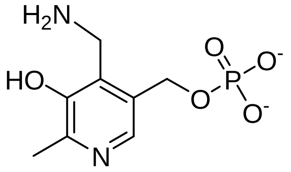
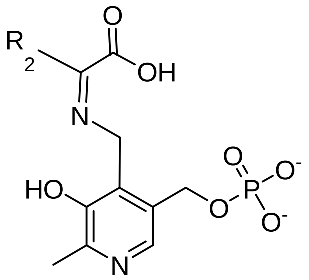
The total negative charge at pH 7 strongly suggests that a carboxylic group is present in the side substituent of **D**. Then, **C** contains more than 3 carbon atoms.

In the case of 4 carbon atoms: 12·4/0.4109=116.81. Subtracting masses of 4 carbon and 2+1+2=5 oxygen atoms, one gets –11.81. In the case of 5 carbon atoms: 12·5/(0.4109)–16·5–12·5=6, which corresponds to 6 hydrogen atoms. Then, **C** is α-keto glutaric acid, and **D** is *L*-glutamic acid (0.5 point for each calculation, 0.75 point for each structure, 4 points in total)

			
A	**B**	**C**	**D**

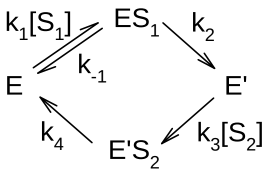
2. S_1 is the amino group donor, ES_1 and ES_2 are enzyme-substrate complexes, S_2 is the amino group acceptor (0.5 point for the attribution of each form, 2 points in total).

3. Of the PLP groups potentially available for interaction, only carbonyl one can enter the reaction with the amino group of S_1. As a result, a Schiff base is formed, which is followed by tautomerization, ketamine formation and hydrolysis. The subsequent steps are just reverse reactions of those considered above (0.5 point for each structure, 1.5 point in total).

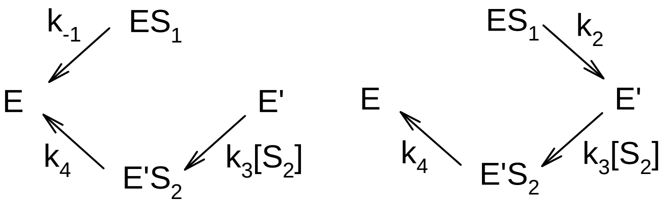
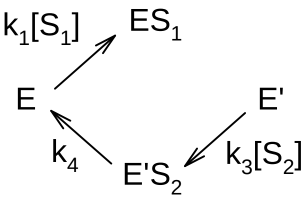
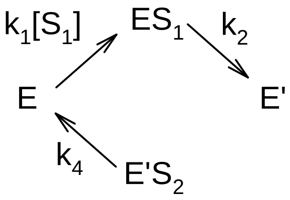
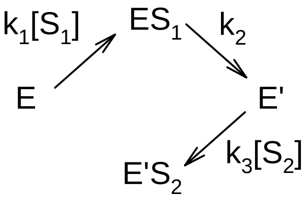
		
ES1	E'	E'S2

Note. In real systems, PLP in its initial state exists in the form of a Schiff base with the lysine residue of the active site, the bond being cleaved upon the attack of an α-amino acid substrate.

4. The directed graph for the "ping-pong" mechanism (1 point)



5. (0.5 point for each spanning tree, 2.5 points in total)

 E	 ES1
 E'	 E'S2

6. (0.5 point for each determinant, 2 points in total)

$w(E) = k_{-1}k_3k_4[S_2] + k_2k_3k_4[S_2]$ $w(ES_1) = k_1k_3k_4[S_1][S_2]$

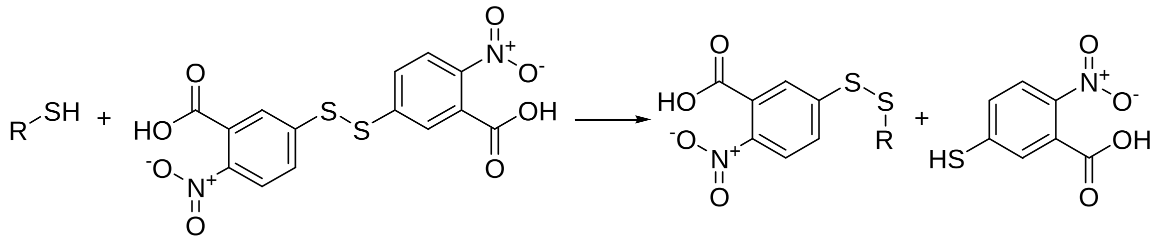
$w(E') = k_1k_2k_4[S_1]$ $w(E'S_2)= k_1k_2k_3[S_1][S_2]$

7. (1 point for each of the numerator and denominator, 2 points in total):

$$\nu = \frac{k_4k_3k_2k_1[S_1][S_2][E_0]}{k_1k_3(k_2 + k_4)[S_1][S_2] + k_3k_4(k_{-1} + k_2)[S_2] + k_1k_2k_4[S_1]}$$

Problem 3 (authors Karpushkin E.A., Lukyanova M.A.)

1.

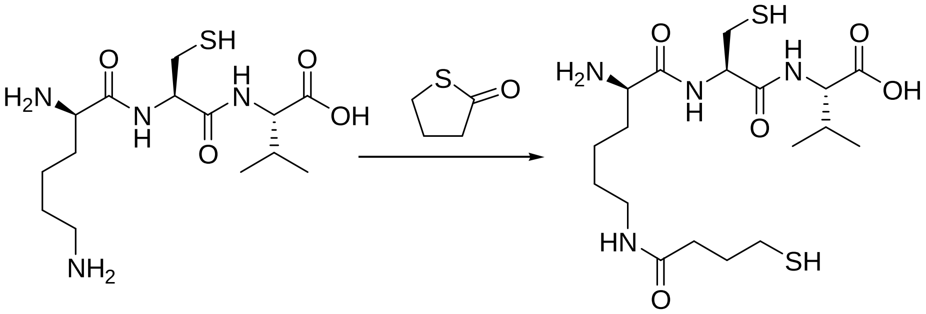


The colored product is 2-nitro-5-thiobenzoic acid (actually, its dianion formed via deprotonation). The concentration of the colored product formed as a result of the reaction with the Ellman's reagent is $0.815/14150 = 5.76\cdot10^{-5}$ mol/L. The concentration of the thiol groups is equal to that of the colored product; therefore, 0.0146 mg = $1.46\cdot10^{-5}$ g of the polymer **P1** contains $5.76\cdot10^{-8}$ mol of the thiol groups. Finally, the content of the thiol groups in **P1** equals $3.95\cdot10^{-3}$ mol/g (0.5 point for the reaction equation, 0.5 point for the colored product, 1 point for the calculation, 2 points in total).

2. $RSH + CH_3HgOD \rightarrow RSHgCH_3 + HOD$

$0.15\cdot1.600\cdot10^{-5} = 2.40\cdot10^{-6}$ mol of CH_3HgOD was consumed for the titration, hence, the concentration of the thiol groups is $2.40\cdot10^{-7}$ mol per 1 mL of the titrated solution. With a due account for its concentration, the content of the thiol groups in polymer **P** is $1.08\cdot10^{-3}$ mol/g (0.5 point for the reaction, 1 point for calculation, 1.5 points in total).

3. The calculations in i. 1 and 2 show that the modification of the peptide **P** leads to a significant increase in the content of the thiol groups, which is only possible due to the ring-opening addition of thiobutyrolactone. As stated in the task, the ring opening is nucleophilic, ε-amino groups of lysine acting as the nucleophile:



It is incorrect to determine the ratio of the amino acid units by simply dividing the values obtained in i. 1 and 2 ($(3.95\cdot10^{-3} - 1.08\cdot10^{-3})/1.08\cdot10^{-3} = 2.66$), since the lysine and cysteine content is expressed reduced to 1 g of the peptide, and the molar masses of **P** and **P1** are different. Thus, the above determined (specific) contents of the thiol groups should be expressed using the molar masses of the amino acid residues and amounts of the latter in the peptides. If *a*, *b*, and *c* are the amounts of valine, lysine, and cysteine units in the molecule of **P**, respectively, then (the molar masses of the amino acids calculated with due account for the loss of water upon condensation):

$$1.08\cdot10^{-3} = c\ /\ (99.13a + 128.17b + 103.13c + 18.02)$$

$$3.95\cdot10^{-3} = (b + c)\ /\ (99.13a + 230.32b + 103.13c + 18.02)$$

Expressing *a* from both equations:

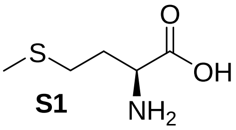
$$a = –0.181 – 1.290b + 8.308c$$

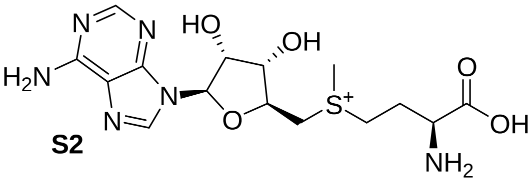
$$a = –0.181 + 0.230b + 1.513c$$

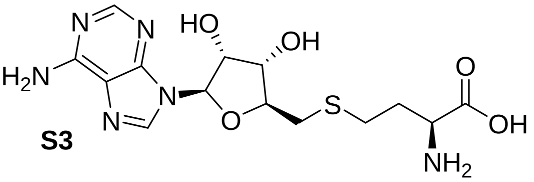
and equating: $–0.181 – 1.290b + 8.308c = –0.181 + 0.230b + 1.513c$ one gets: $1.52b = 6.80c \rightarrow b/c = 4.47 \approx 4.5$ (1 point for the reaction, 2 points for the calculation of the ratio, 3 points in total).

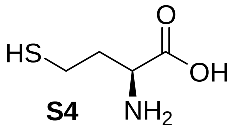
4. Adenosine triphosphate enters the **S1**→**S2** reaction in the form of tetraanion, whereas the products are inorganic phosphate (charge −2) and pyrophosphate (charge −3). The **S2** charge should be +1 to balance the overall charge.

It is convenient to start deciphering the scheme from the best described transformation, **S1**→**S2**. Gross formulae of the starting compounds (besides **S1**) are $C_{10}H_{12}N_5O_{13}P_3$ ($ATP^{4–}$) and H_2O (with due account for the hydrolysis of triphosphate into phosphate and pyrophosphate). Gross formulas of the products are HPO_4 (phosphate), HP_2O_7 (pyrophosphate), and $C_{15}H_{23}N_6O_5S$ (**S2**). Thus, **S1** has the gross formula of $C_5H_{11}NO_2S$. Since **S1** should contain a labile methyl group, be a natural compound, and exist in the zwitter ion form at pH 7, it is the amino acid methionine. **S2** is S-adenosyl methionine, the product of the adenosyl fragment addition (note that the reaction is catalyzed by a transferase). **S3** is S–adenosylhomocysteine, the product of **S2** demethylation (consider **Y** transformation into **Y**–CH_3). Hence, **S4** is homocysteine, the compound formed because of adenosine elimination from **S3** and affording methionine upon methylation (consider the formulae of the second substrate and the second product of the **S4**→**S1** step.


S1

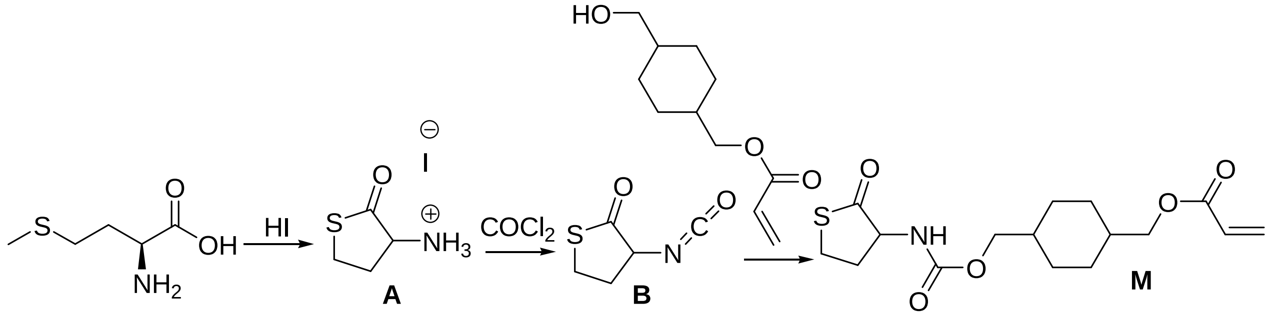

S2


S3


S4

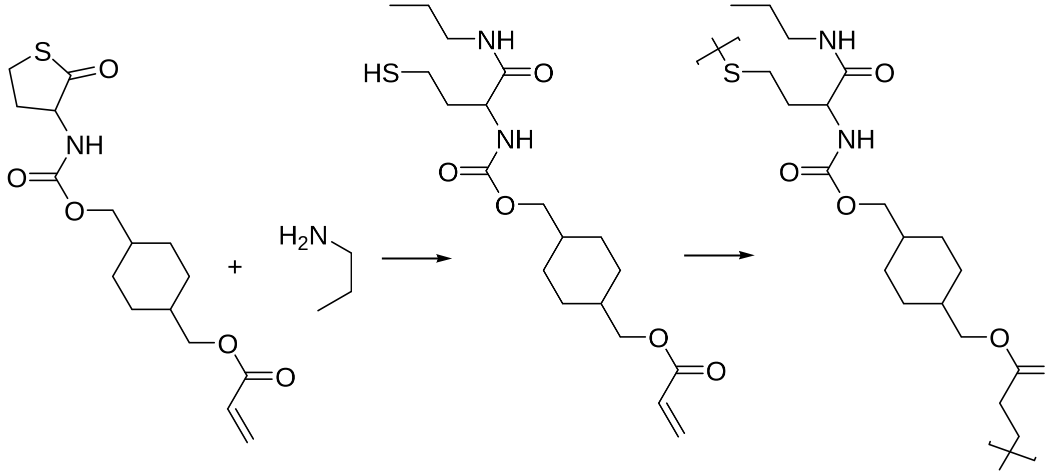
Two compounds of the four above can be the precursor of **A** (C_4H_8NIOS). Since the **X**→**A** transformation (the acid-catalyzed cyclization) requires HI known to readily eliminate a methyl group from thiomethyl moiety, both R–SH and R–SCH_3 can be equivalently involved into the transformation. Of two potentially available pairs (**S1**+**S4** and **S2**+**S3**), the latter is rejected because of the gross formula of **A**. If elimination of adenosine moiety was possible under the conditions of the **X** → **A** transformation, all four substances would be suitable for that reaction rather than only two (0.5 point for the charge of **S2** and each of **S1** – **S4** structures, 0.25 point for each choice of **S1** and **S4**, 3 points in total).

5. The first step towards **M** consists in the homocysteine (either starting **X** or formed from methionine under HI action) ring closing affording amino thiolactone (due account for the gross formula of **A**). Subsequent treatment with phosgene converts the amino group into the isocyanate one (**B**), which is further esterified with the alcohol:



The above conclusions are confirmed by the alternative synthetic route. First, the alcohol group of the acrylate derivative is converted into chloroformate upon the reaction with an excess of phosgene. Finally, chloroformate is transformed into the carbamate group of **M** due to reaction with the amine **A** (1 point for each structure, 3 points in total).

6. The chain growth during polymerization of **M** consists in the opening of the thiolactone cycle under the action of propylamine, giving a reactive thiol group. In contrast to the example reaction leading to the dicarboxylic acid, the interacting thiol and acrylate groups are parts of the same molecule in the case of monomer **M**, the interaction yielding a polymeric product:



According to the reaction mechanism, the monomer should have been completely consumed in the presence of the equivalent amount of propylamine if the yield at the first step had been quantitative. Since the monomer conversion was of 90%, the yield at the first step equals 90%. Then, if the yield at the second step (monomer addition) was quantitative, the product would be a single cyclic macromolecule with the polymerization degree of $0.9 \cdot 0.001 \cdot 6.02 \cdot 10^{23} = 5.4 \cdot 10^{20}$. That of the actually formed product with the molar mass of 36050 is as low as 90 due to incomplete transformation at the second step. The product with the polymerization degree of 90 is formed as a result of exactly 89 sequential Michael reactions, followed by a process leading to the loss of reactivity at the 90th step. Hence, the yield at the second stage can be estimated as 89/90 = 98.9% (0.5 point for each step and the yield at the first step, 1 point for the yield at the second step, 2.5 points in total).

SECTION III. INORGANIC CHEMISTRY

Problem 1 (authors Rozantsev G.M., Shvartsman V.E.)

1. Based on stoichiometry $\mathbf{YNX}_3$, $w_\mathbf{X}/A_\mathbf{X}$: 42.42/14 = 3. The value $w_\mathbf{X} = 9.10\ A_\mathbf{X}$ is substituted in the equation $w_\mathbf{X}/A_\mathbf{X} : (57.58 - w_\mathbf{X})/A_\mathbf{Y} = 3$, obtaining $A_\mathbf{Y} = 19 - 3\ A_\mathbf{X}$ and $A_\mathbf{X}$ should be 19/3≤6.33. Helium does not match, then $A_\mathbf{X} = 1$, and $A_\mathbf{Y} = 19\text{-}3 = 16$ (g/mol) (0.5 points). Hence, **X** – H, **Y** – O, $\mathbf{YNX}_3$ – NH_2OH (hydroxylamine) (3 points). Total equation: $HNO_2 + 2HSO_3^- + H_2O = NH_2OH + 2HSO_4^-$ (0.5 points, 4 points in total)

2. $NH_2OH + H_2O \leftrightarrows NH_3OH^+ + OH^-$ $K_B = [NH_3OH^+][OH^-]/[NH_2OH]$.

$C=[NH_3OH^+]+[NH_2OH]=[NH_3OH^+]+[NH_3OH^+][OH^-]/K_B=[NH_3OH^+](K_B+[OH^-])/K_B$

$\alpha=[NH_3OH^+]/C=K_B/(K_B+[OH^-])$ $\alpha=6.6\cdot10^{-9}/(6.6\cdot10^{-9}+1\cdot10^{-11})=0.9985$ (99.85%) (3 points)

3. $\nu_{NO2-}=0.08500/85=0.001$; $\nu_{SO2(1)}=0.0224/22.4=0.001$; $\nu_{OH-}=0.1\cdot0.01=0.001$(mol). In the solution there are $SO_2+OH^-=HSO_3^-$ and NO_2^-. Then one added $\nu_{SO2(2)} = 0.0224/22.4=0.001$(mol): Reaction $NO_2^-+HSO_3^-+SO_2=[HON(SO_3)_2]^{2-}$ or $NO_2^-+HSO_3^-+SO_2=[ON(SO_3)_2]^{3-}+H^+$ (1 point) $\nu_{NO2-}=\nu_A$ and $M_A= m_A/\nu_A=0.1292/(0.48\cdot0.001)=269$ (g/mol) (0.5 points). This corresponds to the salt **A** – $K_2[HON(SO_3)_2]$ (0.5 points).

At the hydrolysis $[HON(SO_3)_2]^{2-}+H_2O=[HONH(SO_3)]^-+HSO_4^-$.

The salt **B** – $K[HONH(SO_3)]$ (0.5 points, 2.5 points in total).

4. $HNO_2+2HSO_3^- = [HON(SO_3)_2]^{2-}$ $[HON(SO_3)_2]^{2-}+H_2O = [HONH(SO_3)]^- +HSO_4^-$. $[HONH(SO_3)]^- +H^++H_2O=NH_3OH^++HSO_4^-$. $NH_3OH^++NaOBu = NH_2OH+Na^++BuOH$.

(0.25 points for each reaction, 1 point in total).

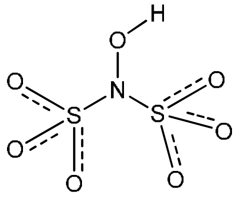
5. $\nu_N:\nu_S:\nu_H=2.80/14:12.79/32:1.20/1=1:2:6$. Because of the bond lengths are the same as in the $[HON(SO_3)_2]^{2-}$, but there is no H, then anion in **E** is $[ON(SO_3)_2]^{3-}$, and the salt **E** – $Rb_3[ON(SO_3)_2]$ $3H_2O$ (1 point). Using the principle of electroneutrality for **I**

$w_N(-1)/M_N+ (1)\ w_H/M_H + (1)\ w_{Rb} / M_{Rb} +w_S(6)/M_S + (-2)\ w_S /=0$, we obtain the equation:

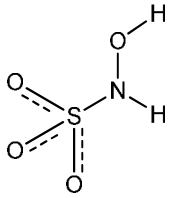
$3.25(-1)/14+0/81(1)/1+49.57(1)/85.5+w_S(6)/32+ (-2)\ w_O / M_O =0$, of which the content of sulfur and oxygen is equal to: $w_S=14.79\%$ and $w_O=31.66\%$ (0.5 points). Then

$\nu_N:\nu_S:\nu_O:\nu_{Rb}:\nu_H=3.25/14:14.84/32:31.66/16:49.51/85.5:0.81/1=2:4:17:5:7$. Since **I** has twice as many N – S bonds then **E**, and there is a three-center O – H – O bond (0.241 nm), then in the salt **I** the anion is $[(SO_3)_2NOHON(SO_3)_2]^{5-}$, and salt **I** – $K_5\{[ON(SO_3)_2]_2H\}\cdot3H_2O$ (1 point). It was shown in the section **3** that in the solution anions $[HON(SO_3)_2]^{2-}$ and $[ON(SO_3)_2]^{3-}$ are possible, which can form a dimer with each other due to the hydrogen bond (2.5 points in total).

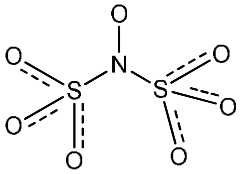
6. Using the data from the table, the structures of anions of salts can be represented as (0.5 points for each structure, 2 points in total):



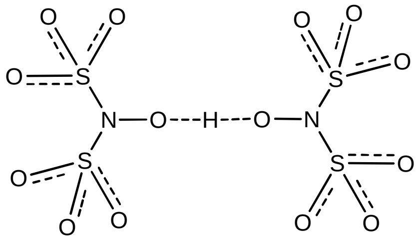
A



B



E



I

Problem 2 (author Karpushkin E.A.)

1. Molar mass of equivalent of the unknown element in oxide **B**: E = (100–43.98)/43.98·8 = 10.2 g/mol. The only possible oxide with the given fraction of oxygen is V_2O_5. Similarly, for oxide **C1**: E = (100–74.06)/74.06·8 = 2.80 g/mol, and the formula of the oxide is N_2O_5. Hence, compounds **C1 – C3** are nitrogen oxides, whereas compounds **A1 – A3** contain vanadium, nitrogen, and oxygen. Compound **A1** prepared from the highest oxides in the absence of any reducing agent is a vanadium(V) nitrate. However, $V(NO_3)_5$ does not exist; moreover, stoichiometry of a hypothetic equation of its formation $V_2O_5 + 5N_2O_5 \rightarrow 2V(NO_3)_5$ does not correspond to the data in the task. If the V:N stoichiometry is 1:3, V(V) should be assumed in the oxocation form VO^{3+}, and **A1** is oxovanadium(V) nitrate (another cationic form VO_2^+ is not also suitable to the given stoichiometry too)

$$(1)\ 3N_2O_5 + V_2O_5 \rightarrow 2VO(NO_3)_3$$

Compound **A2** is obtained under reducing conditions and, in view of the color, should be oxovanadium(IV) (or vanadyl) nitrate:

$$(2)\ V_2O_5 + 4HNO_3 + H_2C_2O_4 \rightarrow 2VO(NO_3)_2 + 3H_2O + 2CO_2$$

The following exchange reaction is a possible route to vanadyl nitrate:

$$(3)\ VOSO_4 + Ba(NO_3)_2 \rightarrow VO(NO_3)_2 + BaSO_4\downarrow$$

A mixture of highest vanadium and nitrogen oxides can be obtained (in the absence of other reagents) from another possible form of vanadium(V) nitrate: **A3**, dioxovanadium(V) nitrate:

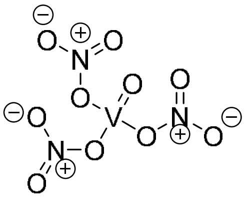
$$(5)\ 2VO_2NO_3 \rightarrow V_2O_5 + N_2O_5.$$

Since N_2O_5 is thermally unstable, the decomposition results in the formation of the solid residue V_2O_5 and mixture of N_2O_5, NO_2, and O_2. (decomposition to both N_2O_5 or NO_2+O_2 is considered correct)

Elementary compound **D** is vanadium (since the reaction of vanadium oxide with nitrogen is hardly possible). The interaction of vanadium with nitrogen oxide in the intermediate oxidation state (**C2**) yielding to the formation of a compound of nitrogen(V) and vanadium(V) (**A3**) must be accompanied by the evolution of nitrogen oxide (**C3**) with lower oxidation state of nitrogen as compared with **C2** (0.5 point for each compound, 0.75 point for each reaction = 7.25 points):

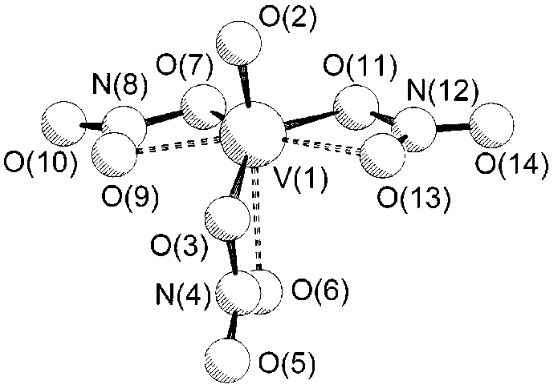
$$(4)\ V + 2N_2O_4 \rightarrow VO_2NO_3 + 3NO\uparrow$$

2. Molecular structure of **A1** is as follows:



Depending on the path of heterolytic cleavage of the covalent fragment V–O–N (at the V–O or O–N bond), this structure can be represented as the following forms differing, according to the task, in the nature of the central atom in the cation (and, respectively, anion): $(VO^{3+})(NO_3^-)_3$ (oxovanadium(V) nitrate) and $(NO_2^+)_3(VO_4^{3-})$ (nitronium orthovanadate) (0.5 point for molecular form, 0.25 point for each ionic form, 1 point in total).

3. Since vanadium is bound only to oxygen in the structure of $VO(NO_3)_3$ and nitrate is a bidentate ligand the coordination number of vanadium in **A1** is seven. The only possibility of existence of a mirror plane in such structure is the location of the oxygen atom in the plane of one of the nitrates and symmetrical location of the other two nitrates with respect to that plane:



The polyhedron which is the closest to this structure is pentagonal bipyramid. (0.75 point for coordination number, 0.5 point for polyhedron, 1.25 point in total)

4. Compound **F** contains fluorine and vanadium (since vanadium is contained in the product of the **F** + **G** interaction, and it can hardly be contained in the silane derivative **G**). If a molecule of **F** contained fluorine atom. its molar mass would be 19.00/0.4598 = 41.3 g/mol and it could not contain vanadium. If a molecule of **F** contained two fluorine atoms, its molar mass would be 38.00/0.4598 = 82.6 g/mol, with no reasonable solution. Finally, with three fluorine atoms per an **F** molecule, its molar mass is 57.00/0.4598 = 124.0 g/mol, corresponding to VOF_3. Evidently **E** = $VOCl_3$, and reactions 6 – 7 are as follows:

$$(6)\ V_2O_5 + 3SOCl_2 \rightarrow 2VOCl_3 + 3SO_2$$

$$(7)\ VOCl_3 + 3HF \rightarrow VOF_3 + 3HCl$$

Since **G** is a derivative of silane, it most likely contains one silicon atom. Then its molar mass is 28.09/0.2438 = 115.2 g/mol, with 87.1 g/mol available for the substituents. The substituents giving the singlet signal in ^1H NMR spectrum are methyl groups bonded to silicon (in view of the closeness of the spectrum signal to that of the $Si(CH_3)_4$ reference). Substituents other than CH_3 in the structure of **G** should be hydrogen-free, and at least one of them should contain nitrogen. Running over the number of methyl groups from 1 to 3, one can find a possible solution: $Si(CH_3)_3N_3$ (*M* 115.2 g/mol). Reaction 8 of formation of oxovanadium(V) azide (indeed, thermally unstable compound) becomes evident (0.5 point for each equation, 0.5 point for each compound, 3.5 points in total).

$$(8)\ VOF_3 + 3Si(CH_3)_3N_3 \rightarrow VO(N_3)_3 + 3Si(CH_3)_3F$$

5. Compound **J** is the easiest to be determined, in view of the ratio between the fused V_2O_5 and Cs_2CO_3: $V_2O_5 + 3Cs_2CO_3 \rightarrow 2Cs_3VO_4 + 3CO_2$

and **J** is cesium orthovanadate. The interaction of N_2F_2 with SbF_5 may give a hexafluorostibate(V) salt with N_2F^+ or N_2^{2+} as cation. The calculation of the mass fraction of fluorine in $(N_2F)SbF_6$ (**H**) supports the former possibility: $N_2F_2 + SbF_5 \rightarrow (N_2F)SbF_6$

Mass fraction of fluorine in **I** is significantly lower than in **H**. Hence, the **I** → **H** transformation should be either addition reaction (but mass fraction of fluorine in the hypothetic product N_5HSbF_7 is not equal to the given in the task) or substitution of a lighter fragment with a heavier one. A reasonable possibility considering that **I** should contain nitrogen (since it is contained in **A5**, a product of the **I** + Cs_3VO_4 interaction) is:

$$(N_2F)SbF_6 + HN_3 \rightarrow (N_5)SbF_6\ (\mathbf{I}) + HF$$

Correctness of this suggestion is confirmed by the calculation of the mass fraction of fluorine in **I** and the fact that the transformations have been started with *cis*-isomer of N_2F_2 (such orientation of the substituents facilitates the formation of cyclic cation N_5^+ in the interaction with linear azide ion). It is now evident that the preparation of **A5** was attempted via the following exchange reaction:

$$Cs_3VO_4 + (N_5)SbF_6 \rightarrow (N_5)_3VO_4 + 3CsSbF_6$$

(the substitution should be complete in view of the qualitative composition of **A5**) (0.5point for each compound, 2 points in total)

Problem 3 (author Likhanov M.S.)

1. Tetrahedrite is a complex sulfide, so when decomposed by nitric acid, copper turns into copper sulfate, and the unknown element falls as an insoluble precipitate. The reaction of the precipitate with zinc in hydrochloric acid with the emission of gas and its subsequent decomposition during heating and the formation of a metal mirror is a well-known Marsh test, which is a sensitive reaction for the detection of arsenic. However, arsenic is soluble in alkaline sodium hypochlorite solution, which does not satisfy the conditions of the problem. Another element that, like arsenic, behaves in the Marsh test is antimony. It is easy to distinguish arsenic from antimony by dissolving the antimony in a sodium hypochlorite solution or in an ammonia solution of hydrogen peroxide.

Therefore, the unknown element **X** in the composition of the tetrahedrite is antimony. The emitted gas **B** in the reaction with zinc in nitric acid is SbH_3 stibine, and since the oxidation state of antimony in **A** is more than in SbH_3, the precipitate is insoluble antimony oxide (V) – Sb_2O_5, which exists as hydrated form in solution.

Thus, the mineral tetrahedrite has the formula $Cu_{12}Sb_4S_{13}$, the reaction of its dissolution in nitric acid:

$$Cu_{12}Sb_4S_{13} + 122HNO_3 = 2Sb_2O_5 + 12CuSO_4 + 122NO_2 + H_2SO_4 + 60H_2O$$

$$\text{or } Cu_{12}Sb_4S_{13} + 122HNO_3 = 2Sb_2O_5 \cdot H_2O + 12CuSO_4 + 122NO_2 + H_2SO_4 + 58H_2O$$

Marsh test:

$$Sb_2O_5 + 8Zn + 16\,HCl = 2SbH_3 + 8ZnCl_2 + 5H_2O \qquad 2SbH_3 = 2Sb + 3H_2$$

(1 point for each compound and reactions, 5 points in total)

2. The number of formula units of a tetrahedrite is easy to determine by calculating the number of copper atoms in single unit cell:

on the edges: $24 \cdot 1/4 = 6$

on the faces: $24 \cdot 1/2 = 12$

inside the unit cell: $6 \cdot 1 = 6$

24 atoms in single unit cell. Hence the number of formula units is 2 (2 points for formula units).

Calculate the number of sulfur atoms in a single unit cell. It is known that there are two types of sulfur atoms: located at the vertices and inside the unit cell. Then, in a single cell: $8 \cdot 1/8 = 1$ atom at the vertices, and since the number of formula units is 2, there are $13 \cdot 2 - 1 = 25$ atoms inside the cell. (2 points for number of sulfur atoms, 4 points in total)

3. Theoretical density is the mass of the unit cell per volume of the unit cell (2 points for density):

$$\frac{2 \cdot (12 \cdot 63.55 + 4 \cdot 121.76 + 13 \cdot 32.07)}{N_A \cdot 10.33^3 \cdot (10^{-8})^3} = 5.023 \text{ g/cm}^3$$

4. To calculate the value of band gap, it is necessary to calculate the values of specific electrical conductivity at two temperatures from the available data. First, we calculate the electrical resistivity from the formula of figure of merit.

ρ is $3.2 \cdot 10^{-5}$ Ohm·m at the 300K

ρ is $2 \cdot 10^{-5}$ Ohm·m at the 600K

Specific electrical resistivity is the reciprocal of specific resistance:

σ is 31250 $(\text{Ohm} \cdot \text{m})^{-1}$ at the 300K

σ is 50000 $(\text{Ohm} \cdot \text{m})^{-1}$ at the 600K

Taking advantage of the Arrhenius equation and solving the system of equations, we obtain the value of E_g.

$31250 = \sigma_0 \cdot \exp(-E_g/600 \cdot k_B)$

$50000 = \sigma_0 \cdot \exp(-E_g/1200 \cdot k_B)$

Then $E_g \approx 0.049$ eV (2 points for the value of band gap)

5. Calculate the ratio of copper atoms in different oxidation states in unsubstituted $Cu_{12}Sb_4S_{13}$ tetrahedrite. Sb is in +3 oxidation state, and S is in -2 oxidation state, then from the principle of electroneutrality 12 copper atoms have a charge of +14, therefore, 10 copper atoms are in +1 oxidation state, and the remaining 2 atoms in +2 oxidation state. After substitution copper by iron: Cu^{2+} exactly 1 atom remained. Iron-substituted tetrahedrite has the formula $Cu_{12-x}Fe_xSb_4S_{13}$, copper and iron still have a charge of +14 together, given that all iron is in +3 oxidation state, it's not difficult to make the equation:

$$1 \cdot (+2) + (11 - x) \cdot (+1) + x \cdot (+3) = 14$$

$$x = 0.5$$

Then the formula of iron-substituted tetrahedrite is $Cu_{11.5}Fe_{0.5}Sb_4S_{13}$ (2 points for the composition)

SECTION IV. ORGANIC CHEMISTRY

Problem 1 (author Volochnyuk D.M.)

1. ***A.*** Obviously, only light elements can be present in interstellar space and m/z = 3 can only give C^{4+} or H_3^+. It is clear that it is impossible to apply the concept of aromaticity to a single atom or its ion, therefore, Particle **A** is the cation H_3^+. The catione structure is a regular triangle with a bond length of 0.90 Å, which is formed by a delocalized three-center 2-electron bond with an energy of about 104 kcal/mol.[1]

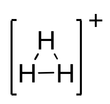
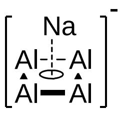
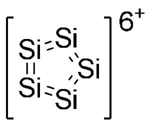
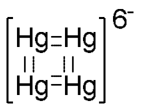
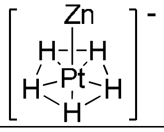
B. Based on the molecular weight of the ion, it can be calculated that it contains one Na atom and four Al atoms. Based on the symmetry of the particle, it can be assumed that it contains a cycle of 4 aluminum atoms with a charge of –2, if the sodium is positively charged. The number of electrons in the Al_4^{2-} cluster are $3 \cdot 4 + 2 = 14$, which satisfies the Hückel's rule. The structure of the anion $NaAl_4^-$ is shown in table 1.[2]

C. Based on the material balance, it is easy to calculate that particle **C** is a Si_5^{6+} cation. The number of electrons involved in the formation of particles is $5 \cdot 4 - 6 = 14$, therefore, it is aromatic.[3]

D. Similarly, in the case of the Na_3Hg_2 amalgam, the number of electrons for Hg_4^{6-} is $2 \cdot 4 + 6 = 14$, which means that it is isoelectronic with Al_4^{2-}.[4]

E. It is difficult to determine the composition of the ion without special modeling due to the presence a lot of isotopic peaks in the mass-spectrum.However, it can be accurately determined that it contains only one Zn atom and one Pt atom with composition $ZnPtH_n^-$, where n = 3-5. From the symmetry of the particle (5th order axis), it is unambiguously concluded that n = 5 and the structure that satisfies the condition is given in Table 1.5. The number of electrons in the σ-aromatic anion H_5^- is 6, which also satisfies the Hückel's rule (0.5 points for each structure and 0.5 points for the correct number of electrons, 5 points in total).

Table 1. The answer to the question №1.

Particle	A	B	C	D	E
Structure					
Number of e^-	2	14	14	14	6

2. The solution of the second question of the problem can be started with decoding the compounds **F** and **G**. First, we need to define the element **X**. Considering that this section of the problem deals with the synthesis and properties of compounds that are both π-and σ-aromatic, it is easy to assume that **X** is carbon. Moreover, π-aromatic cycles are most characteristic of carbon. In addition, the scale of chemical shifts from question 4 are also typical for carbon. From the binary compounds C_xY_y, which most likely already possesses π-aromaticity, with x = 6 and y = 6 we find that compound **F** is hexaiodobenzene. Obviously, when it is treated with a strong oxidizing agent CF_3SO_2–OOH (which is formed from H_2O_2 and $(CF_3SO_2)_2O$), hexaiodobenzene can be oxidized forming compounds $[C_6I_6]^{n+}(CF_3SO_3^-)_n$. Based on the carbon content in compound **G**, it is possible to determine unambiguously that $n = 2$, and compound **G** is $[C_6I_6]^{2+}(CF_3SO_3^-)_2$. The stability of such a dication can be explained by the formation of an additional σ-aromatic ring formed by the p-orbitals of 6 iodine atoms. In the case of the neutral molecule C_6I_6, the formation of the second aromatic system is impossible due to the Hückel's rule (contains 12 electrons). However, it becomes possible in the dication, because the number of electrons becomes 10, which corresponds to the Hückel rule.[6,7]

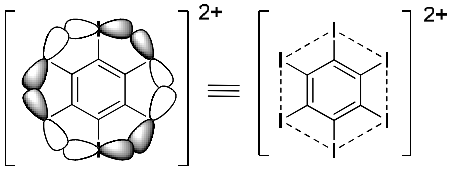
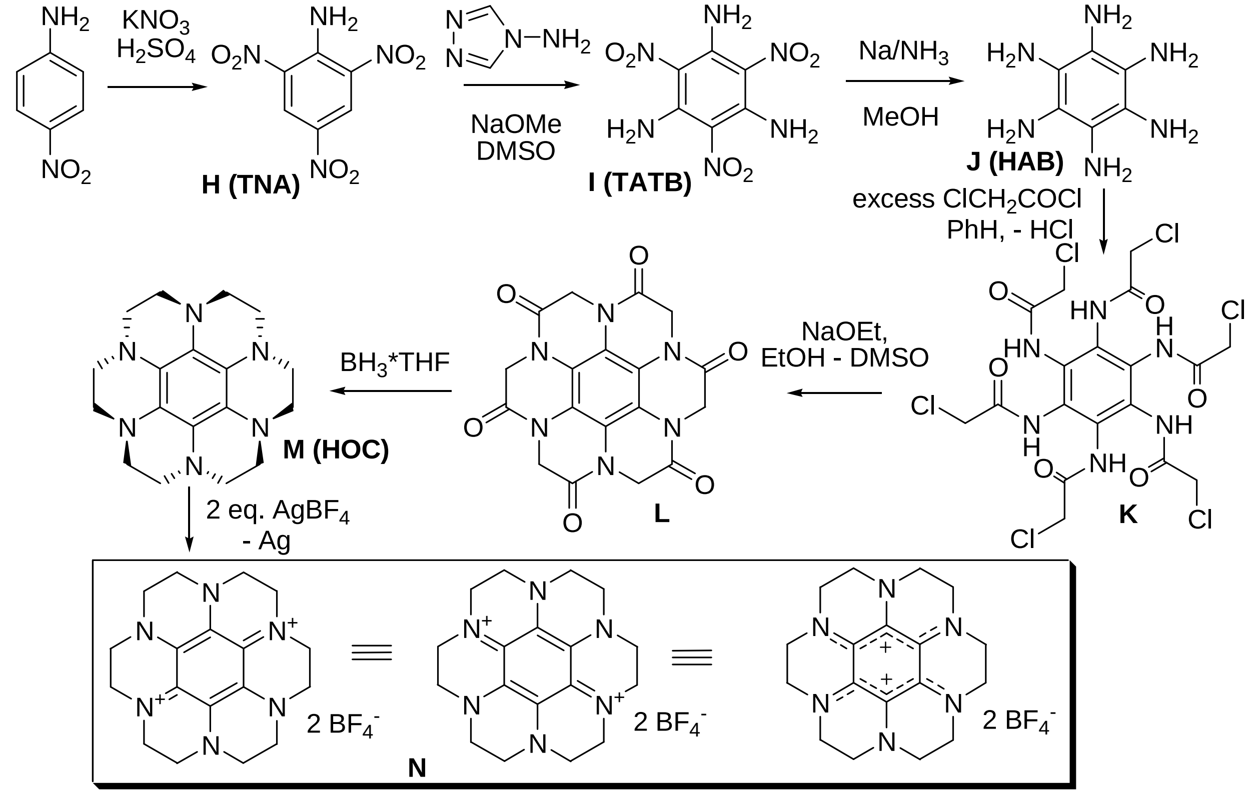


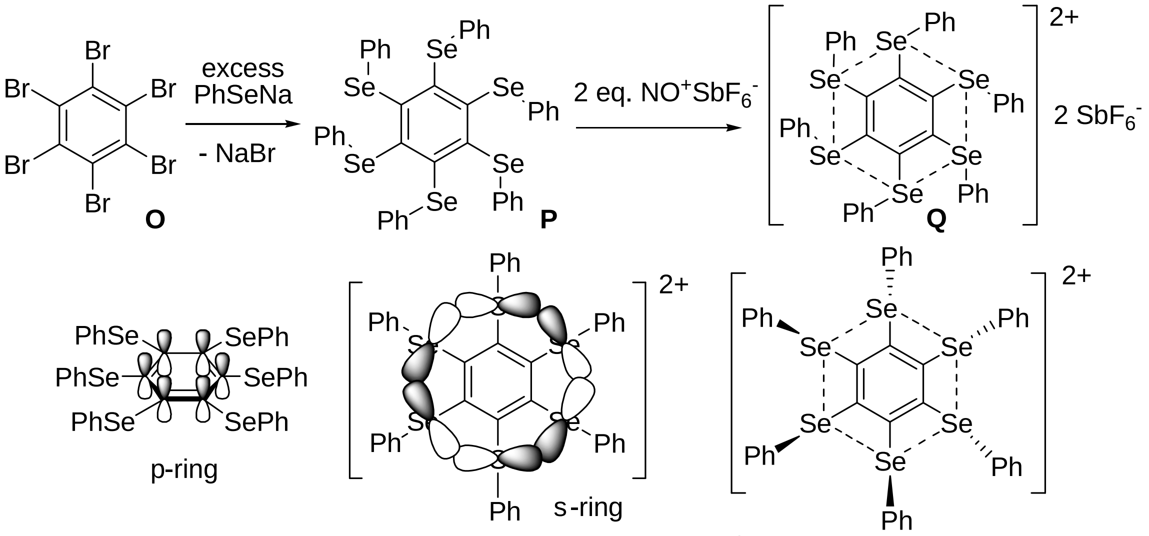
Fig. 1. Schematic view of σ-aromatic ring in $[C_6I_6]^{2+}$.

Next, it is possible to define scheme of synthesis of ionic compound **N** (Scheme 1). Based on the reagents, it can be assumed that the first stage of the synthesis is nitration, which leads to the formation of trinitroaniline (TNA) – compound **N**. Then, the unusual reagent N-aminotriazole can be considered as the donor "NH_2^+" particle that can be formed due to the fact that the starting triazole can play the role of a good leaving group. In this case, double amination occurs with the formation of a substance **I** – 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), which has a third-order symmetry axis. It is then reduced by sodium in liquid ammonia forming **J** – hexaaminobenzene (HAB) with 6th-order symmetry axis.[8] Acylation of an unstable **HAB** with excess of chloroacetyl chloride results in the corresponding hexa-acetyl derivative **K**. The addition of the base to **K** leads to its intramolecular cyclization with the formation of amide **L**. Reduction of this amide with borane results in formation of polycyclic hexaamine **M** – hexaazaoctahydrocoronene (**HOC**).[9] Oxidation of the compound **M** by Ag^+ ions gives dication **N**. However, conformational constraines created by methylene groups make impossible formation of σ-aromatic ring. Therefore, the compound exists as a conjugated dication, which has a second order symmetry axis.[10]



Scheme 1. Synthesis of hexaazaoctahydrocoronene (**HOC**).

Then based on the composition of the binary compound **O**, by analogy with compound **F**, one can easily determine that **O** is hexabromobenzene. Exhaustive replacement of bromine atoms by PhSe-substituent leads to compound **P**. Next, its oxidation leads to ionic compound **Q**.[11] (1 point for element and 0.75 points for each structure, 10 points in total).



Scheme 2. Synthesis of $[C_6(SePh)_6]^{2+}$ 2 SbF_6^{-}.

A dication in compound **Q** has two aromatic rings, one π-ring formed by the sp^2-electrons of the carbon atoms of the benzene and a σ-ring formed by p-orbitals of 6 selenium atoms (see Scheme 2). Evidence of this is the same distance between all selenium atoms in dication **Q**, and at the same time it is smaller than that in compound **P**.

According to the data on symmetry and general reasoning of steric hindrances, phenyl residues with Se atoms cannot be in the same plane. So, in order to fulfill the symmetry conditions, only one confirmation is possible in which, the Ph-substituents at Se(1), Se(2) and Se(3) are on one side of the σ-ring plane, and the rest – on the other (see scheme 2).

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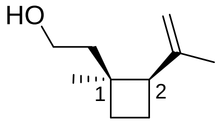
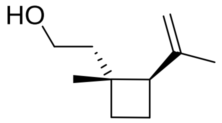
Problem 2 (author Kandaskalov D.V.)

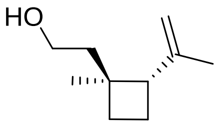
1. Grandisol has 2 chiral carbon atoms and realizes all 4 possible stereoisomers (0.25 points for each right structure and stereochemistry index, 1 point in total):



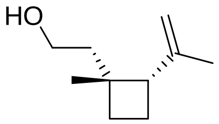
1S, 2R



1R, 2R

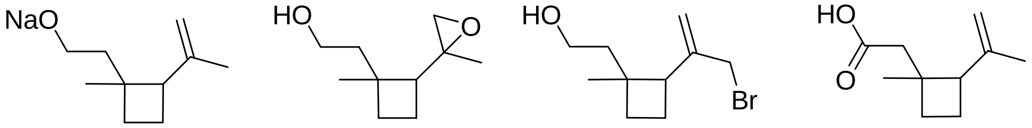


1S, 2S

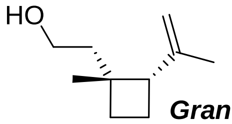


1R, 2S

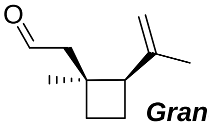
2. The mentioned reagents illustrate the various possible reactivity of Grandisol which contains an alcohol group that can oxidize as well as an unsaturated bond and allyl fragment (0.5 points for each right structure, 2 points in total).



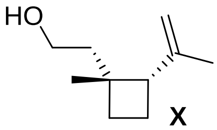
3. Having the stereochemical indices, it is possible to determine the structures of natural products, as well as to determine the correct diastereomer **X**, in which the methyl group with a proton are in the cis-position of the cyclobutane cycle (0.25 points for Grandisol, 0.25 points for X and 0.5 points for Grandisal, 1 point at all).



Grandisol

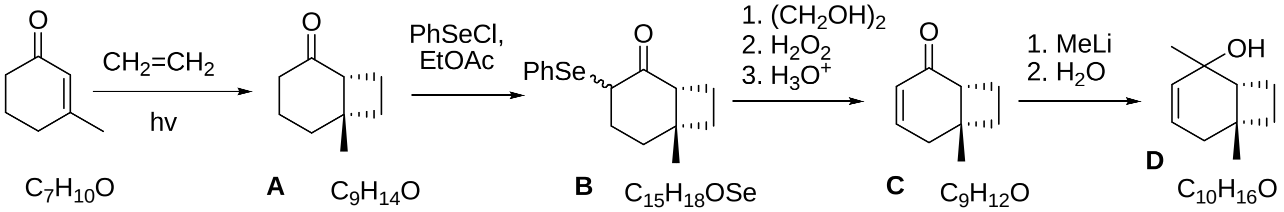


Grandisal



X

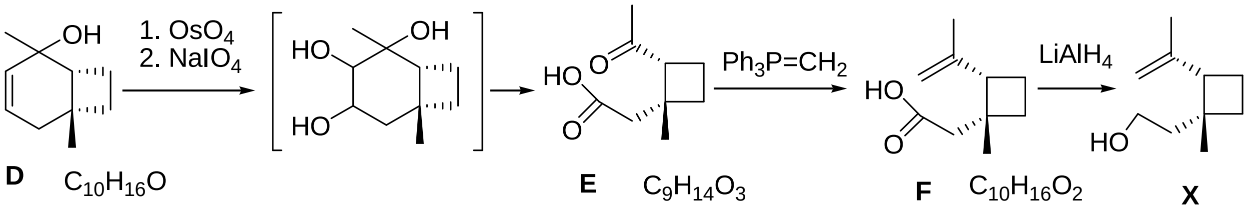
4. We start the resolution of the synthesis from ketone $C_7H_{10}O$. The compound **D** has the formula $C_{10}H_{16}O$, which is is larger than the original substance by C_3H_6 fragment. Based on the IR spectrum of substance **D**, it can be concluded that it is an alcohol. Then substance **C** must be a ketone which, interacting with MeLi reactif, gives the corresponding derivative. Based on this, the formula of substance **C** – $C_9H_{12}O$ and it differs from the initial substance by the C_2H_2 fragment, which can be interpreted as the addition of C_2H_4 with subsequent formal oxidation, i.e. an increase in the degree of unsaturation by 1. In the first reaction, since the keto group is remaining, the reaction center is alkene. This is the reaction of [2+2] -addition with the formation of a 4-membered cycle, the formation of which can be assumed by looking at the Grandisol formula, and also from the given condition that the key synthesis intermediates are condensed cyclobutanes. The next 2 stages of the synthesis are the selenization by the α-CH_2 group (the anion of the α-CH group is less stable due to the lack of complete coplanarity of the α-C p orbitals with π-orbitals of the C = O group, and is also more sterically difficult). Stage B → C is the protection of the carbonyl group, followed by oxidation of the selenium atom and selenoxide elimination and removal of the protective group from the ketone:



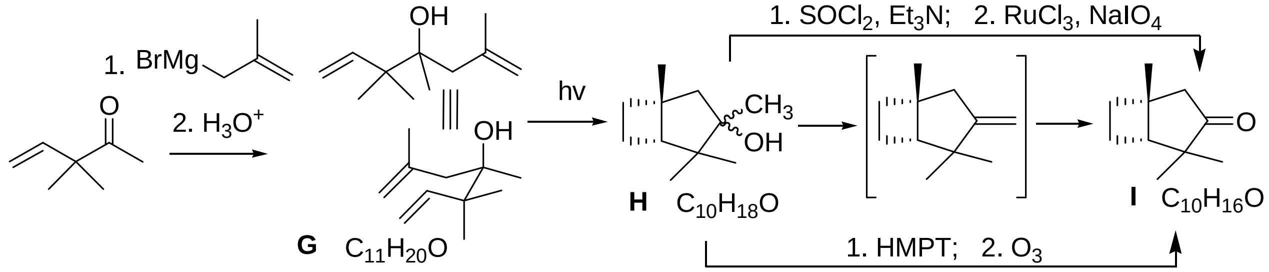
The NMR data of the **D** compound confirm its structure: two 3H singlets, 2 alkene signals, one OH group signal, which is exchanged with D_2O.

Next stage **D** → **E** is an oxidative opening of a six-membered cycle passing through the transformation of an alkene group into a diol and subsequent oxidation with a periodate of sodium.

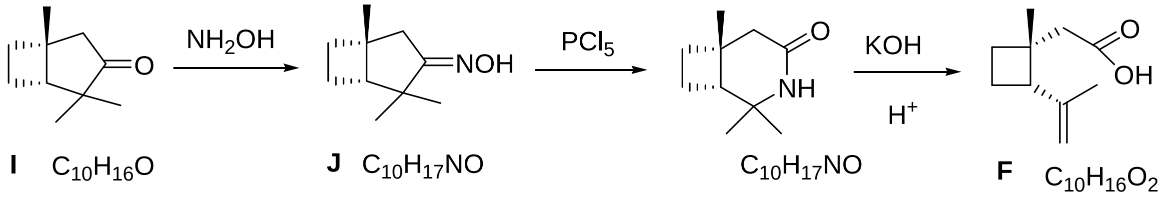
The obtained substance **E** ($C_9H_{14}O_3$) undergoes the Wittig reaction, in which the oxygen of the ketone group is replaced by the methylene group turning into **F** ($C_{10}H_{16}O_2$). At the last stage, the carboxyl group is reduced to alcohol under the action of $LiAlH_4$.



Let's begin with the second synthesis. The intermediate compound **I** is a ketone based on the IR spectrum. The NMR spectrum of **I** indicates the presence of three methyl groups and one diastereotopic methylene group, which has no spin-spin interaction with other protons of the molecule. Taking into account the fact that substance **I** also has a cyclobutane fragment, we unambiguously determine the structure of this compound (see diagram below). The first reaction is a classic reaction of the interaction of carbonyl compound with organomagnesium with the formation in this case of a secondary alcohol **G**. Based on the formula of substance **I**, it is clear that the organomagnesium reagent has the formula C_3H_5MgBr (if there is no loss of carbon atoms later) and must contain a methylene fragment. But, such a substance will not contain an unbranched carbon skeleton, which means that at least 4 carbon atoms are necessary to observe the branching of the carbon skeleton, this substance could be C_4H_7MgBr this substance has a uniquely defined structure $CH_2{=}C(CH_3)CH_2MgBr$. The second stage of the reaction is an internal [2+2]-addition with the formation of the bicyclic compound **H** ($C_{11}H_{20}O$), in which the tertiary alcohol group must be oxidized with the loss of the methyl group and form a ketone. To achieve the above mentioned transformation the sequence water elimination – oxidation of the methylene fragment needed. There are literature precedents for the preparative using of the sequence avoiding intermediate alkene isolation.



The following stages are the formation of oxime, Beckmann rearrangement with alkaline hydrolysis of cyclic amide, which leads to the additional elimination of ammonia (1 point for each right structure A – J and RMgBr. 11 points at all):



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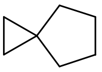
Problem 3 (author Shved E.N.)

1. Determination of the compound's **A** formula.

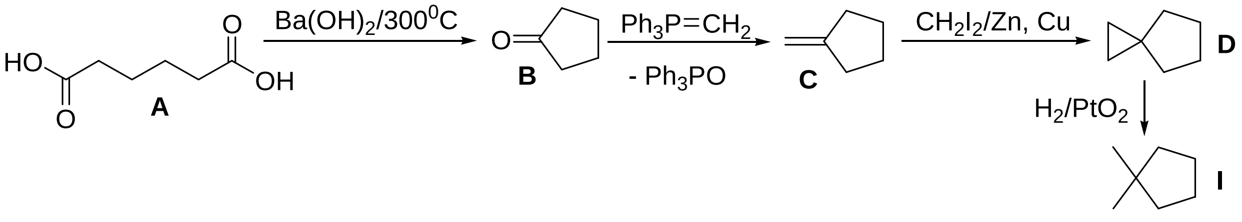
$M(C_xH_{x+y}O_y) = 12x + x + y + 16y = 13x + 17y$; $w(H) = (x + y)\cdot100\%/(13x + 17y) = 6.85\%$;

$x = 1.5y$, то есть $y = 2$, $x = 3$, the simplest formula of **A** is $C_3H_5O_2$. Since 2 equivalents of alkali are used for titration of **A** and the number of hydrogen atoms in $C_3H_5O_2$ is odd, the final formula of **A** is $C_6H_{10}O_4$. Structural formula – HOOC–(C_4H_8)–COOH. Taking into account the structure of **I** **A** is HOOC–(CH_2)$_4$–COOH. Stage **A** → **B** – cyclization. Stage **C** → **D** – formation of [2,4]spirocycle. Consequently, a [2+1]cycloaddition occurs leading to a structure that has three nonequivalent proton groups:



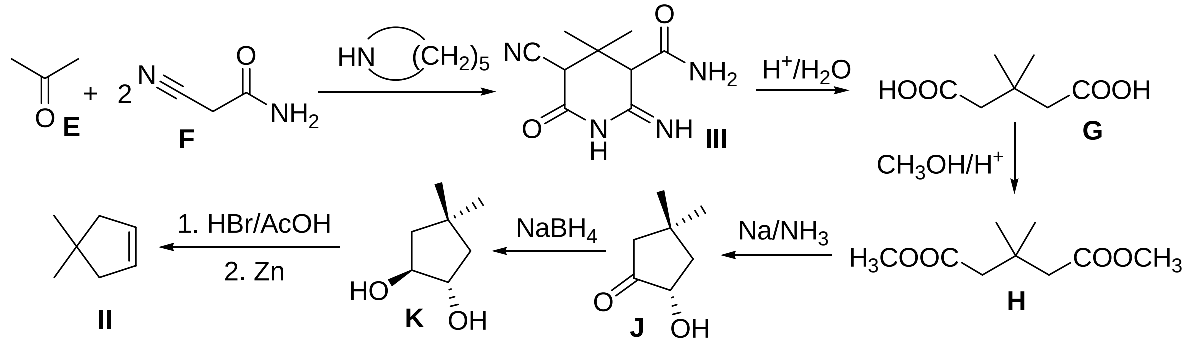
D

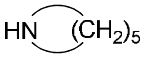
Scheme:



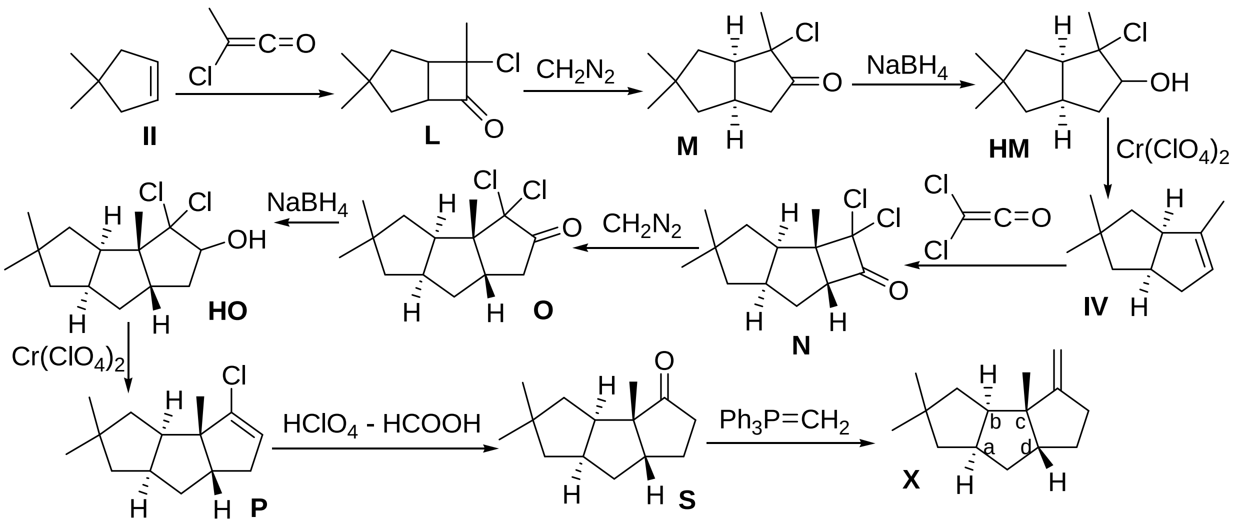
(1 point for formula and structure **A**, 0.5 point for each structure, 2.5 points in total)

2. Analysis of the structures **E** and **III** allows us to conclude that **E** contains CH_3–C–CH_3 fragment, therefore, **E** – CH_3–CO–CH_3. A comparison of structures **II** and **G** reveals that **G** contains 7 carbon atoms. Taking into account that **G** is a homologue of **A** and contains in the ^{1}H NMR spectrum three singlet (3 : 2 : 1), then **G** is HOOC–CH_2–C(CH_3)$_2$–CH_2–COOH. Structure **F** is determined by comparison with **III** and **E**. Since **III** is formed by condensation with carbonyl compound **E**, then **F** must contain an active methylene group. Therefore, **F** is NC–CH_2–$CONH_2$. The scheme of transformation of **E** into **II** (0.5 points for each structure, 3 points in total):

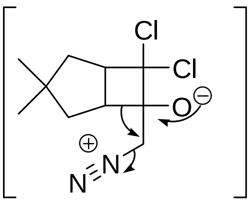


3. The reaction **E** + 2**F** occurs at room temperature in the presence of base, i.e. in the presence of b)  (0.5 points).

4. Compounds **M**, **N**, **O**, **S** contain a carbonyl group (ν = 1750 cm^{-1}). Taking into account structures **II** or **IV** and ketenes stages **II**→**L** and **IV**→**N** are [2+2]-cycloaddition. The formation of **M** and **O** occurs with the extension of the cycle, i.e. the formation of a five-membered cycle. **P** is formed in similar to **IV** reaction, i.e. contains a double bond in the five-membered cycle. Hence, the scheme of transformation is (1 point . for each structure **L**, **M**, **S**; 0.5 points for each structure **HM**, **N**, **O**, **HO**, **P**, 5.5 points in total):

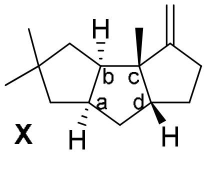


5. Since CH_2N_2 + **L** is a nucleophilic addition, the zwitterion **L'** is (0.5 points):



6. Due to the nature of cleavage, ketenes were obtained by the reactions (2 points):

7. The configuration of the atoms in hirsutene (1 point):



a – S; b – R; c – R; d – R.

SECTION V. ANALYTICAL CHEMISTRY

Problem 1 (author Dubenskiy A.S.)

1. When boiling a mixture of Reineke salt with alkali, ammonia will be released and then absorbed in the receiver by boric acid (reaction **1**):

$$2NH_3 + 4H_3BO_3 = (NH_4)_2B_4O_7 + 5H_2O \text{ (0.25 points).}$$

When the receiver content is titrated with hydrochloric acid in the presence of bromocresol green, reaction **2** occurs (0.25 points):

$$B_4O_7^{2-} + 2H^+ + 5H_2O = 4H_3BO_3 \text{ или } (NH_4)_2B_4O_7 + 5H_2O + 2HCl = 2NH_4Cl + 4H_3BO_3$$

2. Adding formaldehyde to a solution containing a weak acid (ammonium ions) produces an equivalent amount of a strong acid (reaction **3**), which can be titrated with an alkali solution (0.75 points):

$$4NH_4^+ + 6CH_2O = (CH_2)_6N_4 + 4H^+ + 6H_2O \text{ or } 4NH_4^+ + 6CH_2O = (CH_2)_6(NH)_4^{4+} + 6H_2O$$

3. Method ***1*** was used to determine the nitrogen content in the complex, both as an ammonium cation and as neutral ammonia molecules (0.25 points). According to the results of the titration by method ***1***:

$$n(NH_3)_{total} = 4n((CH_2)_6N_4) = n(H^+) = 14.13 / 1000 \cdot 0.0600 = 8.478 \cdot 10^{-4} \text{ mol (0.75 points).}$$

According to method ***2***, only the content of ammonium nitrogen was determined (0.25 points), therefore, based on the results of titration we can obtain:

$$n(NH_4^+) = n(H^+) = n(OH^-) = 5.65 / 1000 \cdot 0{,}0500 = 2.825 \cdot 10^{-4} \text{ mol (0.75 points).}$$

4. In the equivalence point the pH of the solution will be higher than 7 (0.5 points), since there is a weak base in the solution (hexamethylene tetramine). In this regard, the indicator bromocresol green with a pH of the color transition of 3.8–5.4 is not suitable for visual indication of the titration end point using method ***2*** (0.25 points).

5. In the Volhard method, silver nitrate is used as a titrant most frequently for the determination of halide or pseudohalide ions (thiocyanate, cyanate, cyanide). Since the addition of Fe^{3+} ions to the reaction mixture resulted in a red color of the solution, we are talking about determination of the thiocyanatate ion (SCN^-) (0.75 points).

6. According to the results of the determination by Folgard:

$$n(SCN^-) = n(Ag^+) = 22.60 / 1000 \cdot 0.0500 = 1.13 \cdot 10^{-3} \text{ mol (0.75 points).}$$

7. At a temperature of about 100°C, water evaporates, i.e., perhaps, salt **P** is a crystalline hydrate.

$m(H_2O) = 1.000 \cdot 0.05085 = 0.05085$ g

$n(H_2O) = 0.05085 / 18 = 2.825 \cdot 10^{-3}$ mol (0.5 points).

8. According to the difference of the data obtained by methods ***2*** and ***1*** (question **3**), it is possible to calculate the content of ammonia in the form of neutral molecules in the salt **P** (0.75 points):

$$n(NH_3) = n(NH_3)_{total} - n(NH_4^+) = 8.478\cdot10^{-4} - 2.825\cdot10^{4} = 5.653\cdot10^{-4}\text{ mol}$$

Note that the amount of water is obtained for the sample of 1.000 g, and the rest of the data is obtained based on a 0.1000 g sample. Therefore, to derive the formula, we have to use the following number of moles: $n(H_2O) = 2.825\cdot10^{-4}$ mol (0.75 points).

Then we can find the ratio:

$n(NH_4^+) : n(NH_3) : n(SCN^-) : n(H_2O) = 2.825\cdot10^{-4} : 5.653\cdot10^{-4}: 1.13\cdot10^{-3} : 2.825\cdot10^{-4}$, or

$n(NH_4^+) : n(NH_3) : n(SCN^-) : n(H_2O) = 1 : 2 : 4 : 1$ (0.75 points).

If the salt contains one Cr^{3+} ion, the resulting ratio agrees well with the total charges of the cation and complex anion:

$NH_4^+[Cr(NH_3)_2(SCN)_4]^- \cdot H_2O$, $M_P = 354$ g/mol;

If the salt contained two Cr^{3+} ions, the molar mass would exceed 600 g/mol (0.75 points).

9. The reaction of the salt decomposition with alkali in the ionic form (reaction **4**) (1 point):

$$NH_4[Cr(NH_3)_2(SCN)_4] + 4OH^- = Cr(OH)_3\downarrow + 4SCN^- + 3NH_3\uparrow + H_2O;$$

10. The reaction equation of salt **P** synthesis (reaction **5a**) in the melt in ionic form:

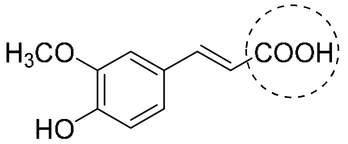
$4Cr_2O_7^{2-} + 3SCN^- + 26H^+ = 8Cr^{3+} + 3SO_4^{2-} + 3OCN^- + 13H_2O$ (reaction **5a**) (2 points)

The total equation for the synthesis of salt **P** in the melt in molecular form (reaction **5б**) (2.5 points):

$$4(NH_4)_2Cr_2O_7 + 35NH_4SCN = 8NH_4[Cr(NH_3)_2(SCN)_4] + 3(NH_4)_2SO_4 + 3NH_4OCN + 10NH_3 + 13H_2O$$

Problem 2 (author Shved A.M.)

1. Ferulic acid (*trans*-4-hydroxy-3-methoxycinnamic acid):



Formate buffer is composed of formic acid and its salt, so the buffer region is about $pK_a\pm1$, i.e. from 2.75 to 4.75 in our case. In that region the acidity is too high for deprotonation of phenol group (pK_a is about 9–10), while carboxylic acids dissociate much easier at this value of pH (pK_a is about 4–5) (1 point for a structural formula, 0.5 point for encircled carboxylic group, total 1.5 points).

2. The expression for *k* (total 1.5 points):

$$k = c_{HA}k_{HA} + c_{A^-}k_{A^-} = \frac{[HA]k_{HA} + [A^-]k_{A^-}}{[HA]+[A^-]} = \frac{k_{HA} + k_{A^-}\times\frac{K_a}{a_{H^+}g_{A^-}}}{1+\frac{K_a}{a_{H^+}g_{A^-}}}.$$

3. The filled table is as follows:

№	pH	c_{HCOONa}, M	c_{HCOOH}, M	I, M	γ_{A^-}
1	3.15	0.002	0.008	0.0027	0.93
2	3.93	0.006	0.004	0.0061	0.90
3	4.35	0.008	0.002	0.0080	0.89

The concentrations of sodium formate and formic acid can be estimated from the approximate equation for pH calculation of a buffer solution: $\mathrm{pH} = pK_\mathrm{a} + \lg\frac{c(HCOONa)}{c(HCOOH)}$ or from the expression $K_\mathrm{a} = \frac{[H^+][HCOO^-]}{[HCOOH]} \approx [H^+]\frac{c(HCOONa)}{c(HCOOH)}$. According to the problem situation, $c(HCOONa) + c(HCOOH) = 0.010M$, therefore this part of a question comes down to solving of a system of two equations, resulting, for example, in the following expressions

$$\begin{cases} c(HCOONa) = \dfrac{0.01\cdot K_\mathrm{a}}{[H^+]+K_\mathrm{a}} \\ c(HCOOH) = 0.01 - c(HCOONa) \end{cases}$$

In the expression for ionic strength all the ions presented in the solution are taken into account: H$^+$, Na$^+$, HCOO$^-$ (we can ignore OH$^-$ ions since their very little concentrations in acidic solutions). The concentrations of H$^+$ and Na$^+$ can be found from pH (approximation $\mathrm{pH} = -\lg a_{H^+} \approx -\lg[H^+]$) and HCOONa concentration. The concentration of HCOO$^-$ can be calculated as a total amount of initial sodium formate and dissociated acid, which to a first approximation equals the concentration of the formed H$^+$ ions, i.e. $[HCOO^-] = c(HCOONa) + [H^+]$. Then the ionic strength can be calculated using the equation:

$$I = 0.5\sum z_\mathrm{i}^2[X_\mathrm{i}] = 0.5\cdot((+1)^2\cdot 10^{-\mathrm{pH}} + (+1)^2\cdot c(HCOONa) + (-1)^2\cdot(c(HCOONa) + 10^{-\mathrm{pH}})) =$$
$$= 10^{-\mathrm{pH}} + c(HCOONa).$$

The found values of I now can be plugged into the Debye–Hückel equation for the calculation of activity coefficients:

$$-\lg\gamma = \frac{A\sqrt{I}}{1+a_0B\sqrt{I}} \quad \Rightarrow \quad \gamma_{A^-} = 10^{-\frac{A\sqrt{I}}{1+a_0B\sqrt{I}}}.$$

(0.4 point for each filled cell of a table, total 4.8 points)

4. The retention factors are calculated using the expression $k = \frac{t_\mathrm{r} - t_\mathrm{m}}{t_\mathrm{m}} = \frac{t_\mathrm{r} - 100.0}{100.0}$:

№	t_r, c	k
1	233.3	1.333
2	229.7	1.297
3	223.3	1.233

(0.4 point for each calculated value of *k*, total 1.2 points).

5. The expression from question 2 can be linearized with respect to the unknowns k_{HA}, $k_{A^-}K_\mathrm{a}$ and K_a:

$$k = k_{HA} + k_{A^-}K_\mathrm{a}\cdot\frac{1}{a_{H^+}\gamma_{A^-}} - K_\mathrm{a}\frac{k}{a_{H^+}\gamma_{A^-}}$$

Inserting k, a_{H^+} и γ_{A^-}, найденные для каждого уравнения, получаем систему из трёх уравнений с тремя неизвестными. Её решение позволяет найти искомые pK_a феруловой кислоты и соответствующие факторы удерживания k_{HA} и k_{A^-}.

$$\begin{cases} 1.333 = k_{HA} + k_{A^-}K_\mathrm{a}\cdot\dfrac{1}{10^{-3.15}\cdot 0.93} - K_\mathrm{a}\cdot\dfrac{1.333}{10^{-3.15}\cdot 0.93} \\ 1.297 = k_{HA} + k_{A^-}K_\mathrm{a}\cdot\dfrac{1}{10^{-3.93}\cdot 0.90} - K_\mathrm{a}\cdot\dfrac{1.297}{10^{-3.93}\cdot 0.90} \\ 1.233 = k_{HA} + k_{A^-}K_\mathrm{a}\cdot\dfrac{1}{10^{-4.35}\cdot 0.89} - K_\mathrm{a}\cdot\dfrac{1.233}{10^{-4.35}\cdot 0.89} \end{cases} \Rightarrow \begin{cases} k_{HA} = 1.34 \\ k_{A^-}K_\mathrm{a} = 1.64\cdot 10^{-6} \\ K_\mathrm{a} = 4.79\cdot 10^{-6} \end{cases}$$

$$pK_\mathrm{a} = 5.32;\quad k_{HA} = 1.34;\quad k_{A^-} = 0.34.$$

If suggested in the task values of γ_{A^-} and k were used, in similar way we would get: $pK_\mathrm{a} = 4.80$; $k_{HA} = 1.51$; $k_{A^-} = 0.35$ (2 points for composing a system of equations, 1 point for each parameter found, total 5 points).

6. In aqueous solution the polarity of the medium is higher, so the acid becomes stronger and therefore the pK_a will be lower (total 1 point).

Problem 3 (author Shved A.V.)

1. The values of p$K_\mathrm{a,1}$ and p$K_\mathrm{a,2}$ are calculated as decimal cologarithms of the corresponding values of acid dissociation constants (0.5 point for each expression, total 1 point):

$$pK_\mathrm{a,1} = -\lg(9.12\cdot 10^{-4}) = 3.04$$

$$pK_\mathrm{a,2} = -\lg(4.26\cdot 10^{-5}) = 4.37.$$

2. Acid salts of tartaric acid are classified as ampholytes, therefore the formula for calculation of pH of ampholytes can be used to find the required pH. This exactly corresponds to the maximum amount of hydrotartrate ions (HA^-) in the solution:

$$\mathrm{pH_{max}} = \frac{\mathrm{p}K_\mathrm{a,1} + \mathrm{p}K_\mathrm{a,2}}{2} = \frac{3.04 + 4.37}{2} = 3.71.$$

The same answer can be obtained by the analysis of the expression for mole fraction of HA^- dependence on the concentration of $[H^+]$ (total 1.5 points for calculation in every way):

$$\alpha(HA^-)=\frac{[H^+]K_{a,1}}{[H^+]^2+[H^+]K_{a,1}+K_{a,1}K_{a,2}},\ \alpha'(HA^-)=0\Rightarrow$$

$$K_{a,1}([H^+]^2_{max}+[H^+]_{max}K_{a,1}+K_{a,1}K_{a,2})-[H^+]_{max}K_{a,1}(2[H^+]_{max}+K_{a,1})=0$$

$$K_{a,1}K_{a,2}=[H^+]^2_{max}$$

$$[H^+]_{max}=\sqrt{K_{a,1}K_{a,2}}\Rightarrow\ \mathrm{pH}_{max}=\frac{\mathrm{p}K_{a,1}+\mathrm{p}K_{a,2}}{2}$$

3. The distribution diagram for a weak acid is a plot of the mole fractions of all the forms, in which it is presented in the solution, versus pH. The corresponding expressions are obtained from the material balance equation and acidity constants.

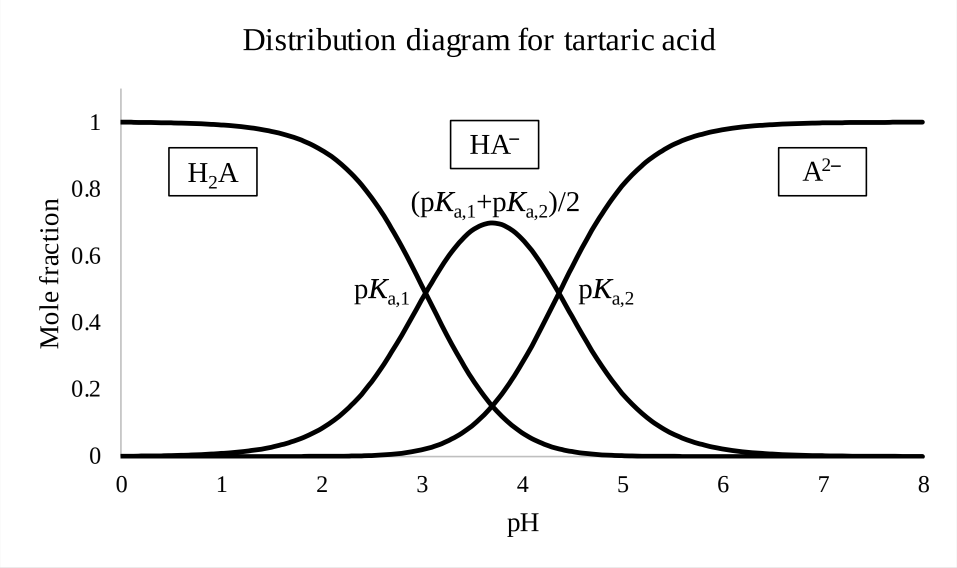
$$c_0=[H_2A]+[HA^-]+[A^{2-}],\quad K_{a,1}=\frac{[H^+][HA^-]}{[H_2A]},\quad K_{a,2}=\frac{[H^+][A^{2-}]}{[HA^-]}$$

$$\alpha(H_2A)=\frac{[H_2A]}{c_0}=\frac{[H^+]^2}{[H^+]^2+[H^+]K_{a,1}+K_{a,1}K_{a,2}}$$

$$\alpha(HA^-)=\frac{[HA^-]}{c_0}=\frac{[H^+]K_{a,1}}{[H^+]^2+[H^+]K_{a,1}+K_{a,1}K_{a,2}}$$

$$\alpha(A^{2-})=\frac{[A^{2-}]}{c_0}=\frac{K_{a,1}K_{a,2}}{[H^+]^2+[H^+]K_{a,1}+K_{a,1}K_{a,2}}$$

It therefore follows that when $[H_2A]=[HA^-]$ we obtain $[H^+]=K_{a,1}$ and when $[HA^-]=[A^{2-}]$ we have $[H^+]=K_{a,2}$, i.e. the pH is equal to p$K_{a,1}$ and p$K_{a,2}$ at the intersections of curves $\alpha(H_2A)$ – $\alpha(HA^-)$ and $\alpha(HA^-)$ – $\alpha(A^{2-})$, respectively. The calculated in question 2 pH_{max} corresponds to the maximum of the curve $\alpha(HA^-)$, which lies in the middle of p$K_{a,1}$ and p$K_{a,2}$ (0.5 point each for a general shape of the curves $\alpha(H_2A)$, $\alpha(HA^-)$ and $\alpha(A^{2-})$, 0.5 point each for the alignment of p$K_{a,1}$ and p$K_{a,2}$ with the points of intersection of two curves, 0.5 point for the alignment of pH_{max} with the maximum of the curve $\alpha(HA^-)$, total 3 points).



4. During the precipitation of potassium bitartrate, the hydrotartrate ions are removed from the system, resulting in the shifting of equilibria in which this ion is formed. These equilibria are the deprotonation of H_2A and protonation of A^{2-}:

$$H_2A \rightleftarrows HA^- + H^+$$

$$A^{2-} + H^+ \rightleftarrows HA^-$$

At pH < pH_{max} the concentration of H_2A is higher than of A^{2-}, therefore the main input in the formation of HA^- is provided by the first equilibrium, resulting in the decrease of pH. At pH > pH_{max}, on the contrary, there are more A^{2-} ions than H_2A in the solution, therefore during the precipitation of potassium bitartrate the second equilibrium is shifted to a greater extent and, consequently, the pH increases.

A similar conclusion may be reached if these systems with pH < pH_{max} and pH > pH_{max} are considered as buffer. In the first case it is a buffer solution H_2A/HA^-, where HA^- acts as a weak base. The decrease of its concentration will result in the decrease of pH. In the second case it is a buffer solution HA^-/A^{2-}, where HA^- acts now as a weak acid. Therefore, by the decrease of its concentration the pH will increase (1 point for the right alignment of the effects of pH changes with initial conditions, 1 point for equilibria equations and reasoning, total 2 points).

These considerations are confirmed by the experimental plots (*Journal of Chemical Education*, Vol. 81 No. 1, 2004, P. 94–96).

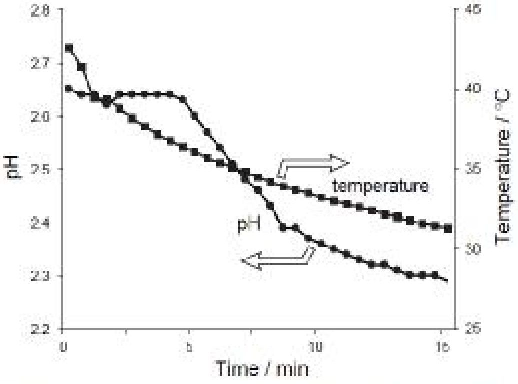


Figure 1. Variation of pH and temperature with time in an aqueous solution with an initial pH less than 3.7.

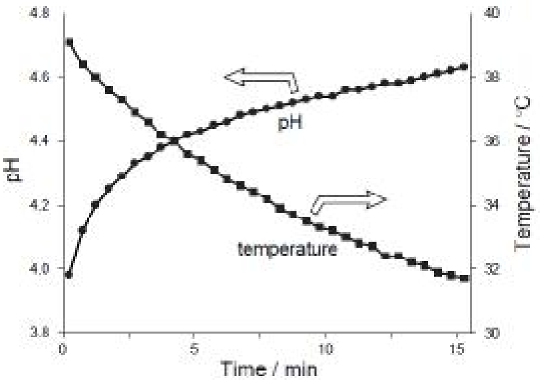


Figure 2. Variation of pH and temperature with time in an aqueous solution with the initial pH greater than 3.7.

5. Using the definition of solubility product, the concentration of HA^- ions can be found:

$$K_{sp} = [K^+][HA^-] \Rightarrow [HA^-] = \frac{K_{sp}}{[K^+]} = \frac{5.00\times10^{-5}}{1.0/39} = 1.95\times10^{-3}\,(M).$$

The percentage of free HA^- relative to the total amount of tartaric acid (total 2 points):

$$\alpha(HA^-) = \frac{[HA^-]}{c(H_2A)} = \frac{1.95\times10^{-3}}{1.4/150} = 0.209\,(20.9\%).$$

6. In wine tartaric acid presents in 4 forms: H_2A, HA^-, A^{2-} and complexed with other ions (not H^+) and organic compounds. The fraction for the last one can be found using the material balance equation (total 2.5 points).

$$c(H_2A) = [H_2A] + [HA^-] + [A^{2-}] + [H_2A]_{\text{complexed}} = \left(\frac{[H^+]}{K_{\text{a},1}} + 1 + \frac{K_{\text{a},2}}{[H^+]}\right)[HA^-] + \alpha_{\text{complexed}}\,c(H_2A) \Rightarrow$$

$$\alpha_{\text{complexed}} = 1 - \left(\frac{[H^+]}{K_{\text{a},1}} + 1 + \frac{K_{\text{a},2}}{[H^+]}\right)\frac{[HA^-]}{c(H_2A)} = 1 - \left(\frac{10^{-3.5}}{9.12\cdot 10^{-4}} + 1 + \frac{4.26\cdot 10^{-5}}{10^{-3.5}}\right)\frac{1.95\cdot 10^{-3}}{1.4/150} = 0.690\,(69.0\%)$$

7. The precipitate is formed when the product of equilibrium concentrations of K^+ и HA^- ions exceeds the value of K_{sp}.

$$[K^+][HA^-] > K_{\text{sp}} \Rightarrow [K^+]\cdot c(H_2A)\cdot\alpha(HA^-) > K_{\text{sp}}$$

$$\frac{1.0}{39}\cdot\frac{1.4}{150}\cdot\frac{[H^+]K_{\text{a},1}}{[H^+]^2 + [H^+]K_{\text{a},1} + K_{\text{a},1}K_{\text{a},2}} > 5.00\cdot 10^{-5}$$

$$\begin{cases}[H^+] = 1.13\cdot 10^{-5} \Rightarrow \text{pH} = 4.95\\ [H^+] = 3.44\cdot 10^{-3} \Rightarrow \text{pH} = 2.46\end{cases}$$

The pH range: 2.46 – 4.95 (1 point for the condition for precipitate formation, 1 point for the equation, 0.5 point each for upper and lower bounds of the range, total 3 points).