SECTION I. PHYSICAL CHEMISTRY

Problem 1

Diatomic are the simplest molecules. Accordingly, they have been investigated in detail both theoretically and experimentally. Rotational-vibrational spectroscopy is among the most important methods for studying diatomic molecules. The "Harmonic oscillator – rigid rotator" approximation is a basic model for the description of the vibrational-rotational spectra. Within this model, the types of intermolecular motion under discussion are independent, whereas their energy levels are as follows:

$$E_{\text{vib}} = \omega_e\left(n + \tfrac{1}{2}\right), \qquad E_{\text{rot}} = B_e J(J+1),$$

where $\omega_e = h\nu$ is the vibrational constant, ν is the frequency of vibrations, $n = 0, 1, 2, \ldots$ is the vibrational quantum number, $B_e = h^2/(8\pi^2\mu r_e^2)$ is the rotational constant, $\mu = m_A m_B/(m_A + m_B)$ is the reduced mass of the molecule, r_e is the equilibrium internuclear distance, $J = 0, 1, 2, \ldots.$ is the rotational quantum number. Only $(n, J) \rightarrow (n \pm 1, J \pm 1)$ transitions are allowed.

For the HF molecule, the energy of transition from the ground vibrational, ground rotational level to the first vibrational, first rotational level equals $\Delta E(0, 0 \rightarrow 1, 1) = 4180.23$ cm^{-1}; the energy of transition from the ground vibrational, first rotational level to the first vibrational, ground rotational level is $\Delta E(0, 1 \rightarrow 1, 0) = 4096.41$ cm^{-1}.

1. Calculate ω_e and B_e in cm^{-1}.
2. Calculate v in Hz and r_e in Å.

The model of anharmonic oscillator allows a more precise description of the molecular vibrations. In this model, the energy of the n^{th} vibrational level equals:

$$E_{\text{vib}} = \omega_e\left(n + \tfrac{1}{2}\right) - \omega_e x_e\left(n + \tfrac{1}{2}\right)^2,$$

where $\omega_e x_e$ is the anharmonicity constant. Decrease in the distance between the neighboring levels (n and $n + 1$) is a specific feature of the model. This leads to the equality of energies $E_{\text{vib}}(n)$ and $E_{\text{vib}}(n + 1)$ for a definite $n_{\max}$, which is due to the absence of the vibrational levels for $n > n_{\max}$, since the molecule dissociates into atoms above this level.

3. Express $n_{\max}$ in terms of ω_e and $\omega_e x_e$.
4. Express the dissociation energy in terms of ω_e and $\omega_e x_e$.

Beside this, the rotational-vibrational interaction can occur, due to which the rotational constant B_e depends on vibrational state n:

$$E_{\text{rot}} = B_n J(J+1), \qquad B_n = B_e - \alpha_e\left(n + \tfrac{1}{2}\right),$$

where α_e is the constant of the rotational-vibrational interaction.

5. From the following options, select those, which correctly explain why B_n depends on n:
the kinetic energy of rotation of the molecule increases with an increase of n;
the average bond length in the molecule changes with an increase of n;
due to the repulsion of the atoms, the molecule is rather stretched than compressed during oscillations;
due to the Heisenberg uncertainty principle, the bond length permanently changes.

Methylidyne CH is the smallest molecule, which can be notionally named organic. Though the radical its extremely unstable, it was detected spectroscopically in the so-called CH-stars. Also, it is involved in the Fischer–Tropsch process. Spectral properties of CH are well studied. The energies (cm^{-1}) of some rotational-vibrational transitions are given below.

	$n = 0 \rightarrow n = 1$	$n = 1 \rightarrow n = 2$
$J = 0 \rightarrow J = 1$	2759.77	2632.66
$J = 1 \rightarrow J = 2$	2785.97	2657.79

6. Using the data in the table, calculate ω_e, $\omega_e x_e$, B_e, and α_e in cm^{-1}.
7. Using the expression derived in i. **4**, calculate the dissociation energy of the C−H bond in cm^{-1}. *If you failed to answer i.* **4**, *use the approximate formula* $E \approx \omega_e^2/(4\omega_e x_e)$.
8. Calculate the length of the C−H bond in Å.

Reference materials:
Masses of isotopes (a.m.u.): m(F) = 18.9984, m(C) = 12.0000, m(H) = 1.0078.
Conversion of reciprocal centimeters to joules: E(J) = $100hcE$(cm^{-1}).
$h = 6.626 \cdot 10^{-34}$ J·s is the Planck constant, $c = 2.998 \cdot 10^{8}$ m/s is the speed of light, $N_A = 6.022 \cdot 10^{23}$ mol^{-1} is the Avogadro's number.

Problem 2

Despite its simplicity, the Ligand Field Theory (LFT) satisfactorily explains most of the magnetic and spectral properties of complex compounds of transition elements. Ligands are considered as a source of an electrostatic field with certain symmetry, acting on the electronic system of the central ion. The field shifts the energy levels (terms) of the free ion and splits them. The magnitude and nature of splitting depend on the field strength of the ligands and their location.

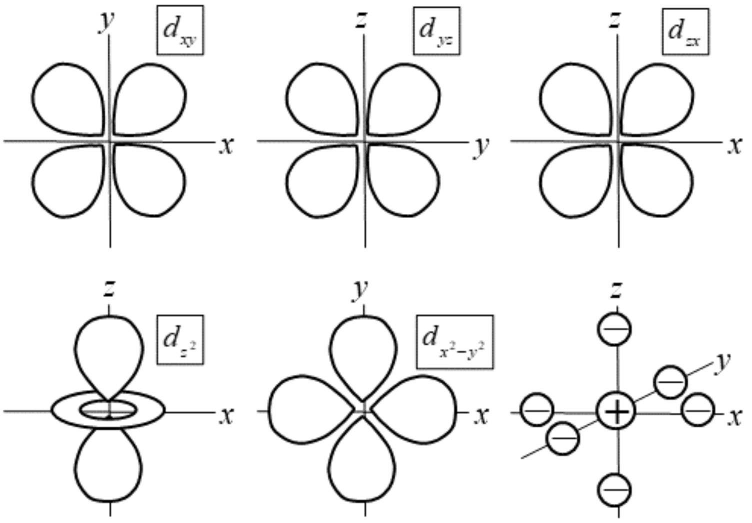


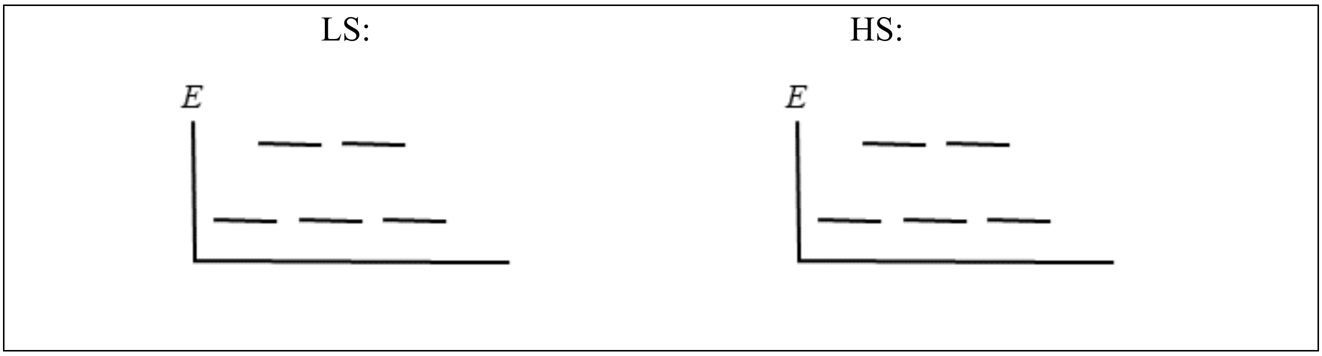
Figure 1

Fig. 1 shows the shape of the five *d*-orbitals of a free atom or ion and the arrangement of ligands in an octahedral environment. The three orbitals in the top row are geometrically equivalent. The two orbitals in the bottom row are also equivalent to each other, despite their different appearance.

1. What is the degeneracy factor (*g*) of the energy level of a free ion with a single *d*-electron over the closed shells?
2. Draw a diagram of the level splitting of the central ion in the octahedral complex $[Ti(H_2O)_6]^{3+}$. For split levels, give Mulliken notation based on the symbols for irreducible representations of group theory.

In an octahedral field, the levels are split in the proportion 3 : 2 (relative to the "center of gravity", i.e. the energy of an ion placed in a spherical shell with the charge equal to the sum of the ligand charges). Let us denote the energy interval between split levels as Δ_o, and the pairing energy of electrons in one orbital as *P*.

3. Distribute electrons onto the energy levels for the low-spin (LS) and high-spin (HS) the states of the complex with the Fe^{2+} ion. Indicate the total spin *S* of the complex and the type of magnetism (paramagnetic/diamagnetic).



4. Find the relationship between Δ_o and *P*, at which the energies of the LS and HS states of the octahedral complex formed by the Fe^{2+} ion are the same.

For the Fe^{2+} ion $P = 17600$ cm^{-1}, and for the complexes $[Fe(H_2O)_6]^{2+}$ and $[Fe(CN)_6]^{4-}$ $\Delta_o = 10400$ cm^{-1} and 33000 cm^{-1}, respectively.

5. Which one is high-spin and which one is low-spin?

Fig. 2 shows the dependence of the term energy of the Ni^{2+} ion in an octahedral field on the strength of the ligands. For $[Ni(NH_3)_6]^{2+}$ $\Delta_o = 10800$ cm^{-1}.

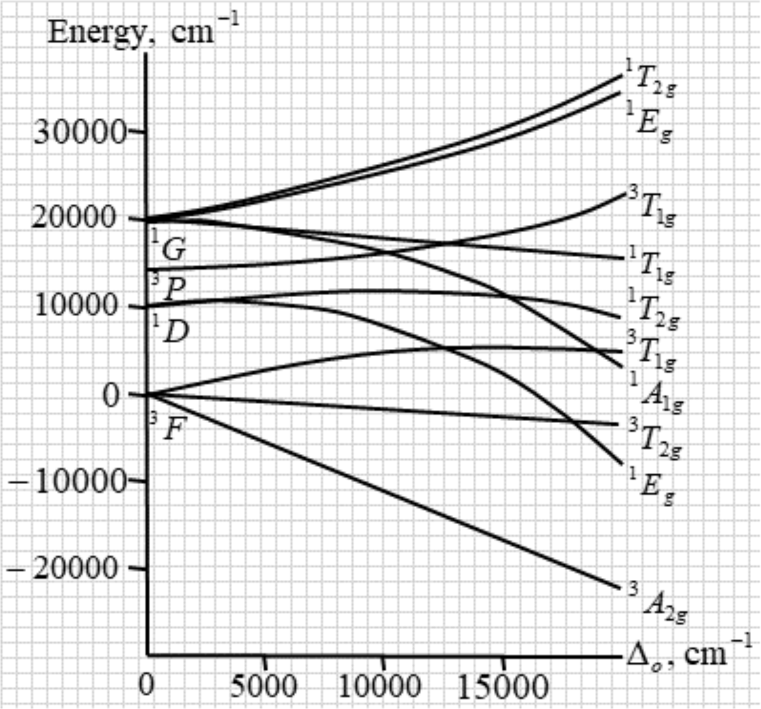


Figure 2

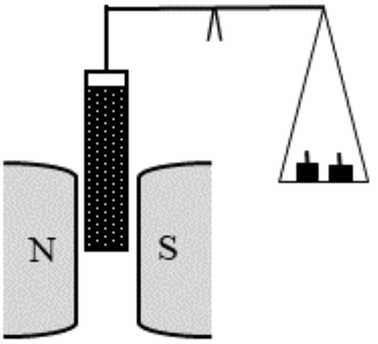


Figure 3

6. How many bands are there in the absorption spectrum associated with the *d–d* transitions from the ground electronic state of this complex (choose the correct answer: 3, 6 or 9)? Predict the frequencies (cm^{-1}) of the absorption band maxima.

The magnetic susceptibility of a unit volume of a substance χ_V (a dimensionless quantity) can be measured by the Gouy method following the apparent change in the mass of the sample in a non-uniform magnetic field (Fig. 3). The magnetic force acting on the sample is:

$$F = \frac{1}{2}\chi_V H^2 \sigma \text{ dyn}, \qquad (1)$$

where H is the field strength (Gauss, Gs) at the level of the ampoule bottom, σ is the ampoule cross section area (cm^2).

The empiric formula for calculating the specific susceptibility (per 1 g of substance) of Mohr's salt $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ is:

$$\chi_S = \frac{9.5}{T+1} \cdot 10^{-3} \text{ cm}^3\text{/g}, \qquad (2)$$

where T is the temperature in Kelvins. The salt crystals have a cubic structure with the lattice parameter $a = 1.2318$ nm, the unit cell contains $Z = 4$ formula units. The salt is placed in a cylindrical ampoule with the diameter $d = 1.4$ cm. At $H = 5000$ Gs, $\Delta m = 0.868$ g.

7. Determine the density ρ (g/cm^3) of the Mohr's salt crystals and calculate χ_S at 25°C. Assuming that the sample is tightly packed in the ampoule, calculate the χ_V of Mohr's salt.

On the other hand, the molar susceptibility can be expressed as

$$\chi_M = \frac{N_A \mu_{\text{eff}}^2}{3k_B T} \text{ cm}^3\cdot\text{mol}^{-1}, \qquad (3)$$

where N_A is the Avogadro's number, k_B is the Boltzmann constant, μ_{eff} is the effective magnetic moment of the central ion in Bohr magnetons $\mu_B = 0.917 \cdot 10^{-20}$ erg/Gs.

8. Find χ_M and determine μ_{eff} of Mohr's salt in Bohr magnetons at 25°C.

Expression (3) does not account for the constantly present diamagnetism reducing the susceptibility. The magnetic moment, which is due only to the spin of the central ion, is given as (in Bohr magnetons):

$$\mu_S = 2\sqrt{S(S+1)} = \sqrt{n(n+2)}, \tag{4}$$

where n is the number of unpaired electrons.

9. Assuming that the magnetic moment of Mohr's salt is determined only by the spin of the Fe^{2+} ion, use the expression (4) to estimate whether this complex is low-spin or high-spin.

Reference materials:
The degeneracy of an energy level is the number of different states corresponding to the given level.
In question **6**, in the symbols of the terms of the free ion (on the left) and the split terms (on the right), only the superscripts (multiplicities) are important. The latter are equal to $2S + 1$, where S is the total spin of the d-shell of the ion.
Acceleration of free fall near the earth's surface $g = 981$ cm/s^2; 1 N (Newton) = 10^5 dyn, 1 J (Joule) = 10^7 erg; $N_A = 6.022 \cdot 10^{23}$ mol^{-1}; $k_B = 1.38 \cdot 10^{-16}$ erg/K; 1 a.m.u. = $1.66 \cdot 10^{-24}$ g.

Problem 3

In H_2 + oxidant (Ox) reactions, metal cations are able to activate H_2 in a solution because of homo- or heterolytic cleavage of the H−H bond, whereas [Ox] is not included in the kinetic equation.

1. Illustrate both types of the H−H bond cleavage using Lewis formulas.
2. Derive the equation and calculate the enthalpies of the transitions $H_2(aq) = 2H(aq)$ and $H_2(aq) = H^+(aq) + H^-(aq)$, if the enthalpies of hydration are (kJ/mol): −1088 (H^+); −452 (H^-); −9 (H_2); −13 (H), and standard enthalpies of formation are (kJ/mol): 1536 (H^+); 140 (H^-); 0 (H_2); 218 (H).

Calvin showed that Cu^+ salts with organic anions catalyze the Cu^{2+} reduction with dissolved H_2, which dissociates homolytically according to the hereunder mechanism, the dissociation being the rate-limiting step:

$$2Cu^+ + H_2 \leftrightarrows (Cu^+\cdot H)_2 \qquad (k_1;\ k_{-1}),$$
$$(Cu^+H)_2 + 2Cu^{2+} \rightarrow 4Cu^+ + 2H^+ \qquad (k_2).$$

3. Derive the kinetic equation for the reaction.

Halpern and Peters showed that in the absence of Cu^+ activation of H_2 by Cu^{2+} cation in $HClO_4$ solution leads to the reaction order change from 2 to 3 with increasing $[H^+]$ according to the mechanism:

$$Cu^{2+} + H_2 \leftrightarrows Cu^+H + H^+ \qquad (k_3;\ k_{-3}),$$
$$CuH^+ + Cu^{2+} \rightarrow 2Cu^+ + H^+ \qquad (k_4),$$
$$2Cu^+ + \text{Cr(VI) substrate} \rightarrow \text{Cr(III) products} + 2Cu^{2+} \qquad (k_{ox},\ \text{fast}).$$

4. Derive the kinetic equation for the reaction and give the condition under which the change in the reaction order is possible.

A similar equation but with a more complex expression for the reaction rate was obtained by Halpern when studying the kinetics of Cr(VI) reduction with activation of H_2 by the Ag^+ cation:

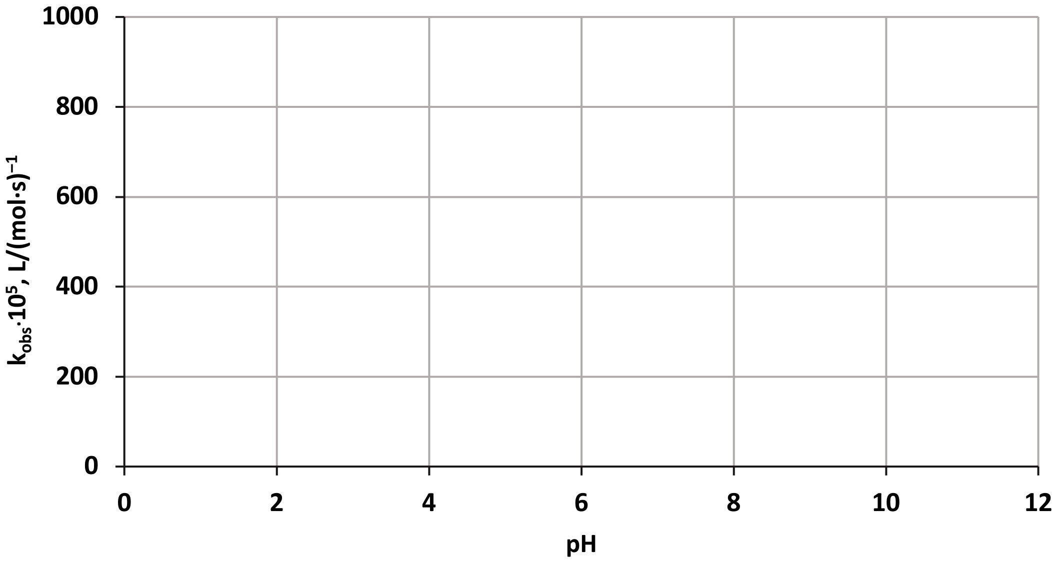
$$d[H_2]/d\tau = k[Ag^+]^2[H_2] + k_5[Ag^+]^2[H_2]/([Ag^+] + k_{-5}/k_6[H^+]).$$

5. Indicate whether this rate equation corresponds to homo- or heterolytic dissociation of H_2. Suggest the reaction mechanism and equation for k_{obs}, if a binuclear intermediate is formed at the second step.

For the reaction at 27°C and $[Ag^+]$ = 1 mol/L in the $HClO_4$ medium, Halpern obtained the data given in the table and the equation: $k = 6.8\cdot10^7\cdot e^{-14666/RT}$ (R = 8.314 J·mol^{-1}·K^{-1}).

pH	1	3	4	5	6	8	10
$k_{obs}\cdot10^5$, L/(mol·s)	1.995	11.31	87.01	436.7	739.9	801.2	801.9

6. Draw the $k_{obs} = f$(pH) plot and explain its S-shape, indicating the assumptions that must be made.



7. Specify the coordinates, which will allow rectilinear function for the data given in the table. Show how to calculate k_5 and $a = k_{-5}/k_6$ from it.

8. Calculate k, k_5 and $a = k_{-5}/k_6$, using the data for pH = 4 and pH = 5.

SECTION II. ANALYTICAL CHEMISTRY

Problem 1

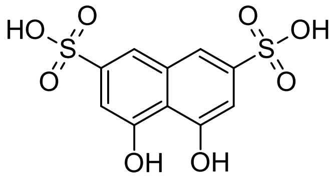
Monitoring the concentration of nitrogen oxides in the air of industrial premises is an important task for nitrogen industry enterprises. Development of optical chemical dosimeters that show excess concentrations of nitrogen oxides is one of approaches towards solving this problem. Determination of nitrogen dioxide concentration often involves disproportionation according to the reaction 1 (NO_2 dimerization is neglected due to low concentrations):

$$2NO_{2(g)} + H_2O = NO_2^-{}_{(aq)} + NO_3^-{}_{(aq)} + 2H^+_{(aq)} \qquad (1)$$

Colorimetric determination of the resulting nitrite can be achieved using the diazotization reaction with subsequent azo coupling.

1. Write down the equation for the reaction of 4-nitroaniline (4-NA) with nitrite ion in an acidic medium affording the 4-nitrophenyldiazonium salt (reaction 2).

The resulting diazonium salt enters an azo coupling reaction with chromotropic acid Chr (see the fig.), that reacts at one of the ortho (with respect to the OH group) positions to form the dye "Acid Red 176".



2. Write down the equation for the azo coupling (reaction 3) and the structure of the resulting dye.

3. Write down the expressions in accordance with the law of mass action (assume that the assay system contains a buffer medium and do not include the H^+ concentration in the expressions):

a) for the rate v_1 of the formation of nitrite ion by reaction 1, rate constant $k_1 = 1\cdot10^5$ L/(mol·s);

b) for the rate v_2 of the formation of 4-nitrophenyldiazonium according to reaction 2, the rate constant $k_2 = 1.0$ L/(mol·s);

c) for the rate v_3 of the formation of Acid Red according to reaction 3, rate constant $k_3 = 1\cdot10^2$ L/(mol·s).

4. Assume that all the reactions occur on an indicator paper in a film of adsorbed water with the total volume of 50 μL, the concentrations of 4-nitroaniline and chromotropic acid in which are 0.1 M each.

a) Calculate the rate of nitrite formation in such aqueous solution by reaction 1 if the concentration of NO_2 in air corresponds to the maximum permissible concentration (MPC) equal to 5 mg/m^3.

b) At what time will the rate of nitrite consumption by reaction 2 become equal to that of its formation by reaction 1? Take the concentration of 4-nitroaniline equal to 0.1 M.

c) What is the rate of formation of Acid Red (P) at a reaction time much higher than the value you found in i. *b*?

d) Draw qualitatively the dependences of the concentrations of the diazonium salt and Acid Red in the indicator paper on time at reaction times much higher than the value you found in i. *b*.

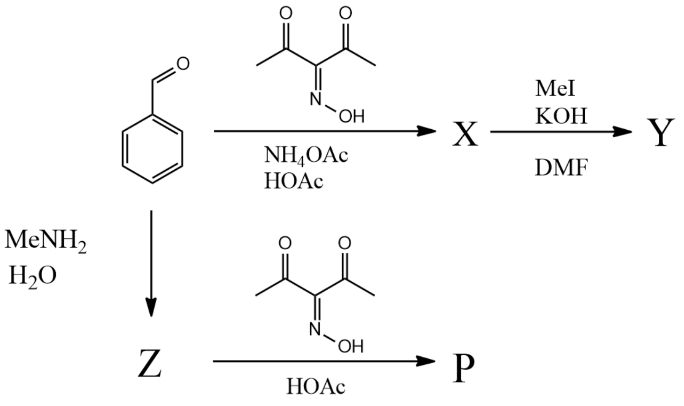
e) The color of the indicator paper becomes noticeable when it contains Acid Red in the amount of $5\cdot10^{-11}$ mol. What is the time of the color appearance after introducing the paper into the atmosphere of NO_2 with the concentration equal to the MPC?

5. a) Assume that if conducting an infinite number of experiments with concentrations of nitrogen oxides equal to the MPC, the signal (color) is observed in 90% of the experiments. Two similar experiments were carried out at the concentration equal to the MPC. What is the probability that nitrogen oxides will be detected ("Yes, the concentration of nitrogen oxides has reached the MPC")? In the case of one positive and one negative result, the answer will be uncertain.

b) How many parallel experiments must be carried out in order to judge that the MPC is exceeded with at least 95% probability?

Problem 2

On May 8, 1980, the World Health Organization declared the complete liquidation of smallpox, therefore, the universal vaccination of the population was stopped. For this reason, the number of people susceptible to this infection increases every year. In previously immunized populations, immunity against smallpox viruses weakens by half every ten years, so the number of human-to-human infections, such as monkeypox virus, is increasing. 1-Hydroxyimidazole derivatives inhibit the smallpox virus and at the same time have low cytotoxicity. The new 1-hydroxyimidazole derivatives were prepared according to the following scheme:



1. Determine the structures of **X–P,** if **Y** and **P** are isomers and **P** is a zwitter ion.

X is in a tautomer equilibrium with **A** in aqueous solution. The equilibrium constant of tautomerism is $K_{AX} = \frac{[X]}{[A]} = 0.09$.

2. Determine the molar fraction of **X** (%) in the aqueous solution after equilibrium has been established.

3. Determine the structure of **A**.

Twice the volume of aniline was added to the aqueous solution of **A**, and the mixture was shaken. The equilibrium of tautomerism in the organic phase is shifted toward **X**, as can be decided from the value of the equilibrium constant $K_{A_1X_1} = \frac{[X_1]}{[A_1]}$, which is 25 times higher than the tautomerism constant for the aqueous solution.

4. Determine the total yield of **X** (%) if isolation of this compound from the organic phase is being done after establishing the extraction and tautomerism equilibria; take $K_{AA_1} = \frac{[A_1]}{[A]} = 1$.

By adding hexane (C_6H_{14}), which is immiscible with water and aniline, a three-phase system can be obtained and described by the following equilibria:

$$\begin{tikzcd}
H_2O & PhNH_2 & C_6H_{14} \\
A \arrow[r, shift left, "K_{AA_1} = 1"] \arrow[r, leftarrow, shift right] \arrow[d, shift left] \arrow[d, leftarrow, shift right, "K_{AX} = 0.09"'] & A_1 \arrow[r, shift left, "K_{A_1A_2} = 4"] \arrow[r, leftarrow, shift right] \arrow[d, shift left] \arrow[d, leftarrow, shift right, "K_{A_1X_1}"'] & A_2 \arrow[d, shift left, "K_{A_2X_2}"] \arrow[d, leftarrow, shift right] \\
X \arrow[r, shift left] \arrow[r, leftarrow, shift right, "K_{XX_1}"'] & X_1 \arrow[r, shift left] \arrow[r, leftarrow, shift right, "K_{X_1X_2} = 16"'] & X_2
\end{tikzcd}$$

5. Determine the unknown equilibrium constants (write them for the "left-to-right" and "top-to-bottom" transitions).

6. Determine the total yield of **X** (%) that can be isolated from the organic phases, if 1 M aqueous solution of **A** is extracted with equal volumes of aniline and hexane added simultaneously ($V^{\text{aq}} = V_1^{\text{org}} = V_2^{\text{org}}$ = 1 L).

7. One volume of an aqueous solution of **X** was contacted with different volumes of other solvents and shaken (experiments a–d). Arrange the experiments in the increasing order of the yield of **X** when isolated from the organic phase(s).

a) Equal volume of aniline and hexane.

b) Equal volume of aniline.

c) Twice the volume of hexane.

d) Twice the volume of aniline.

Problem 3

Alcohol, depending on its content in the human body, leads to various negative effects. Blood alcohol content (BAC) is usually calculated as the mass of ethanol (g) in a unit volume of blood (L) or expressed as a percentage (BAC of 1% corresponds to 1 g of ethanol in 100 mL of blood). The Widmark formula can be used to estimate BAC (in g/L) from the amount of alcohol consumed:

$$\text{BAC} = \frac{a}{V_\text{d}} - \beta t = \frac{a}{m \cdot k_\text{d}} - \beta t,$$

where a is the mass of ethanol consumed (g); V_d is the volume of ethanol distribution in the body (L); m is the mass of a person (kg); k_d is the Widmark distribution coefficient, which is equal to 0.71 and 0.58 L/kg for males and females, respectively; β is the rate of ethanol elimination, averaging 0.15 g/(L·h); t is the time since alcohol consumption (h).

1. Calculate how many times the lethal dose of ethanol for a female weighing 60 kg is less than that for a male weighing 80 kg. Consider that the effect of alcohol is determined only by its concentration in the blood, regardless of gender.

The vast majority of countries have BAC limits for drivers. The maximum allowed BAC ranges from 0 (total ban) to 0.08%, e.g. in China the BAC limit is 0.02%.

2. Calculate the maximum volume V_max (mL) of the Chinese alcoholic beverage Huangjiu ("yellow wine") with the ethanol content (φ) of 10 vol.% that can be drunk by a male weighing 80 kg 30 min before driving. The density of pure ethanol (ρ) is 0.789 g/mL.

Note! Despite acceptable BAC values other than 0 (which is due to metabolic peculiarities in different people), drinking alcohol before driving is extremely unsafe!

The determination of BAC can be carried out using a variety of analytical methods. For quick analysis, such as when checking drivers on the road, breathalyzers are used to determine the amount of ethanol in one's breath. One of the first breathalyzers was developed by R.F. Borkenstein. Exhaled air was passed through a solution of $K_2Cr_2O_7$ in the presence of H_2SO_4 and small amounts of $AgNO_3$. The intensity of the color change from orange to blue-green was used to conclude the degree of intoxication of the person being tested.

3. Write down the reaction equation that underlies the Borkenstein breathalyzer.

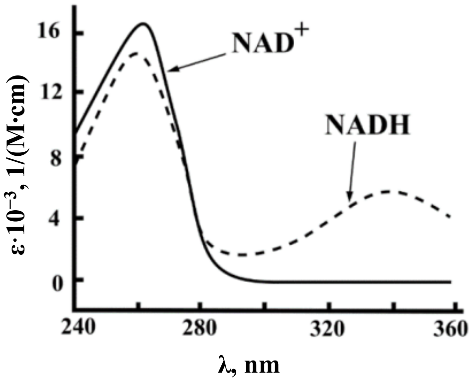
To find the amount of reacted $K_2Cr_2O_7$ and thus ethanol in the sample, it is possible to use the spectrophotometric method. The table summarizes the results of absorbance (A) measurements from testing people with different levels of BAC. Measurements were made at a wavelength at which absorbance by the reaction products can be neglected. The volume of solution in the breathalyzer is 3.0 mL and the volume of exhaled air is 1.0 L. Assume that 1 mL of blood contains on average the same amount of ethanol as 2100 mL of exhaled air.

BAC	0.000%	0.030%	0.060%	0.100%	0.150%
A	0.898	0.640	0.382	0.150	0.150

4. Calculate the maximum BAC_{max} value (%) that can be numerically determined with this breathalyzer.

5. Calculate the concentration $c(K_2Cr_2O_7)_0$ (mM) in the stock solution. Assume that the volume of the solution in the breathalyzer does not change when passing the analyzed breath.

In hospitals, an enzymatic assay (EA) is often used to determine *BAC*. For this, the enzyme alcohol dehydrogenase (ADH) is added to blood serum, resulting in the oxidation of ethanol with the coenzyme NAD^+. The *BAC* can be calculated by measuring the absorbance of the solution.



6. Write down the equation of the reaction occurring during the EA of ethanol in blood serum.

7. Using the given UV absorption spectrum of NAD^+ and NADH, give the value of wavelength λ (nm) that is optimal for measuring the absorbance for *BAC* calculation.

When analyzing samples with a complex matrix, such as blood serum, the method of standard additions is used. For this purpose, known amounts of the determined substance are introduced into the analyzed sample, and the EA of the resulting solutions is carried out. As a result of such analysis, the following calibration dependence of absorbance (A) on the concentration of added ethanol (c_{add}, μM) was obtained: $A = 6.20 \cdot 10^{-3} \cdot c_{add} + 0.155$. Calibration solutions were prepared by adding the calculated amounts of the standard ethanol solution to the 100 μL aliquots of blood serum followed by dilution with the physiological solution to 1.00 mL.

8. Calculate the concentration of ethanol c(EtOH) (μM) in the analyzed blood serum.

SECTION III. LIFE SCIENCES AND POLYMERS

Problem 1

A drug based on the compound **X** ($M = 696$ g/mol) is used to reduce pain in patients with malignant neoplasms complicated by tumor metastasis to the bones.

X is obtained from the organic acid **Y**, the non-ionized form of which has 3 types of H atoms, 2 types of each of C and O atoms, and 1 type of N atoms.

It is known that the fraction of protons (p, elementary particles) belonging to the carbon atoms from the number of protons of all atoms in the molecule of **Y** is 15.93%. Similar fractions for hydrogen and nitrogen atoms in **Y** are 8.85% and 6.19%, respectively. Assume that the molecule of **Y** is formed exclusively by atoms of the most common isotopes in nature of each of the five elements.

1. From the four elements mentioned above, select those for which the ratio of mass fractions and that of the sums of protons of all identical atoms in the molecule of **Y** numerically coincide pairwise [in other words, the equality $\omega(\mathrm{El}_1) : \omega(\mathrm{El}_2) = N_p(\mathrm{El}_1) : N_p(\mathrm{El}_2)$ is true].

The total number of atoms of the five elements that form the non-ionized form of **Y** is 44.

2. Find the total number of protons of all atoms in the molecule of **Y**. Prove by calculations.
3. Find the molecular formula of **Y**. Prove by calculations.

It is known that **Y** can be obtained by prolonged heating of ethylenediamine, formaldehyde and inorganic acid **A** in a strongly acidic medium.

4. Find the structure of **Y**.

X is a neutral double salt containing, among other things, the cation of an alkali metal (represented by the most abundant isotope) and the anion of the acid **Y**. The total number of atoms of all elements forming **X** is 42, and the total number of protons is 335

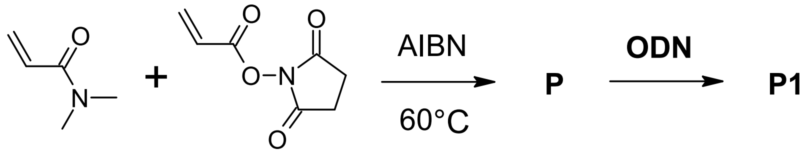
5. Deduce the structure of **X**.

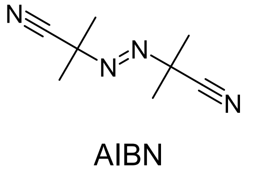
When a sealed ampoule containing an aqueous solution of **X** is left standing for a long time, the compound **Z** ($M = 696$ g/mol) is formed, which does not undergo further transformations. The reaction behind this process determines the therapeutic effect of the drug.

6. Deduce the structure of **Z**.
7. Write down the equation for the reaction underlying the mechanism of action of the pharmaceutical based on **X**.
8. Write down the equation for the reaction explaining how **X** predominantly accumulates in bone tissue.
9. Select the most rational way in clinical practice (peroral, intravenous, rectal or by inhalation) for administering the drug based on **X** into the human body.

Problem 2

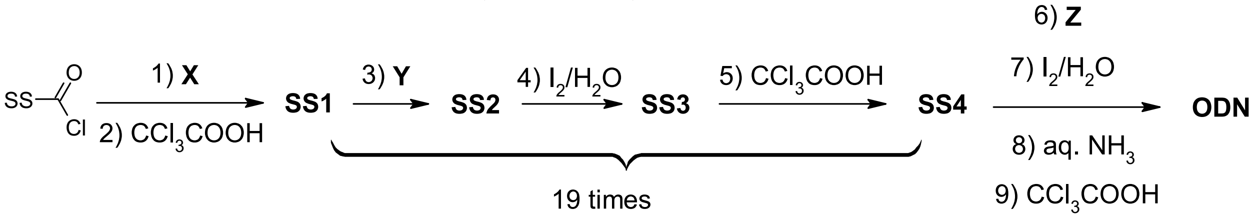
The interaction of complementary nucleobases (A–T and G–C) leads to the formation of reversible noncovalent crosslinks (double-helix fragments of DNA) between the chains of the polymer **P1**. This polymer was synthesized via AIBN-initiated radical copolymerization and then modified with oligonucleotide fragment **ODN**, which allowed transformation of an aqueous solution of the linear polymer into insoluble cross-linked gel by tuning the external conditions.

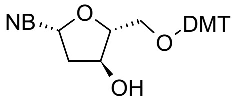




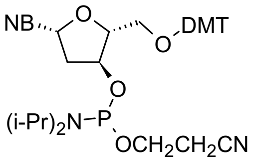
AIBN

ODN, a 20-unit oligonucleotide containing terminal *n*-dodecylamine moiety, was prepared via the synthesis on solid substrate **SS** bearing surface −COCl groups. In the structures of **X** and **Y**, **NB** stands for a nucleobase (A, C, G, T).

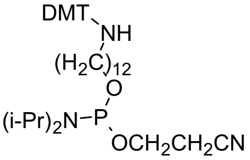




X

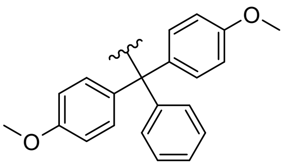


Y

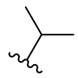


Z

DMT



i-Pr



1. **P** consists of two types of repeat units. A sample of **P** (mass of 2.00 g) was treated with 10.00 mL of NaOH (0.100 mol/L), and then excess of alkali was titrated with 1.60 mL of HCl (0.400 mol/L). Draw the structures of the repeat units in **P** and determine the molar fraction of the units containing the succinimide group.

2. Draw the structures of **SS1**–**SS4** formed after one cycle of steps 3–5. Draw the structure of **ODN** and denote the 3'- and 5'-ends of the oligonucleotide part of the molecules. *Use the **SS** and **NB** notation in the structures.*

3. Complete the partially deciphered nucleotide sequence of **ODN** to obtain the sequence affording the most efficient pairing with the **ODN** fragment of another polymer chain. Calculate the molar mass of **ODN**. *If you have failed to determine the sequence of **ODN**, consider its composition to be $A_4C_{10}T_6$.*

5'-A-☐-T-☐-C-☐-C-☐-C-☐-T-☐-C-☐-A-☐-C-☐-T-☐-3'

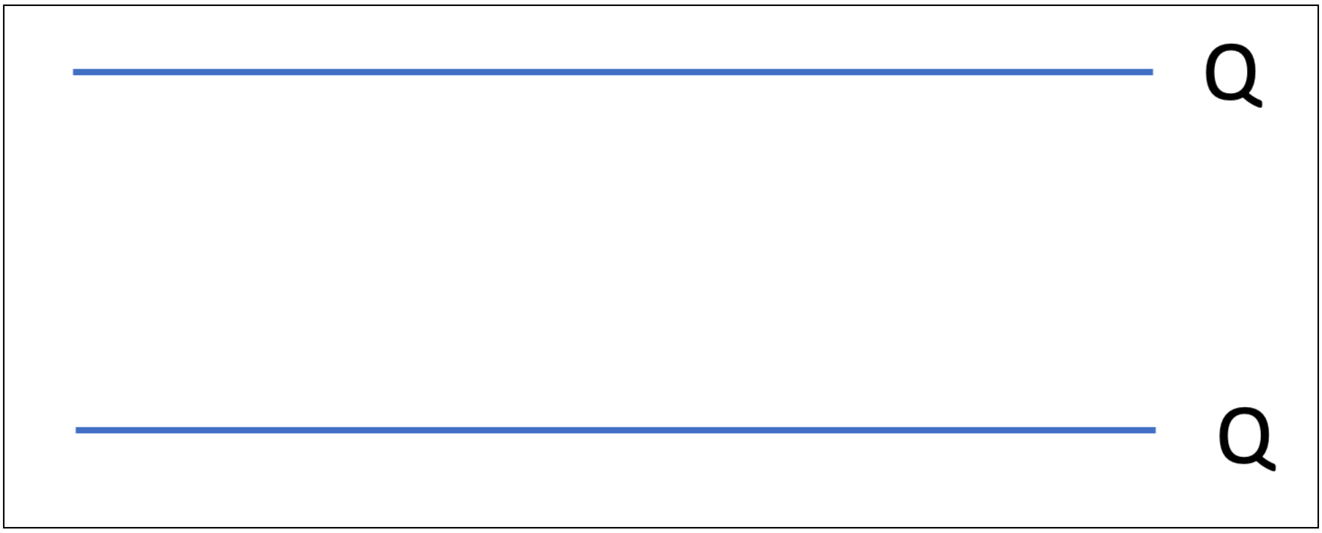
4. The interaction of **P** with **ODN** is accompanied by hydrolysis of the succinimide units, conversion of the latter being complete. Draw the structures of the repeat units in **P1** and calculate the molar fraction of the **ODN**-modified units to the hydrolyzed units in the product if the mass fraction of phosphorus in **P1** is 2.19% (consider the acidic groups to be in the protonated state).

5. Determine the lowest average molar mass of **P1**, macromolecules of which can be converted into a gel (completely cross-linked into a joint structure). Consider the complementary pairing of **ODN** to be quantitative.

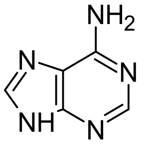
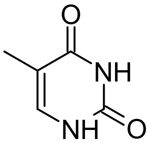
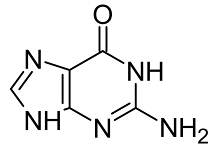
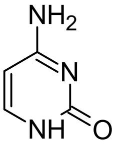
6. Give the range of acidity of the aqueous solution within which **P1** can form insoluble hydrogel via complementary pairing of the **ODN** fragments. Point at the pH value, at which the non-porous hydrogel of **P1** being at equilibrium with the aqueous medium absorbs the largest amount of water.

Hydrogels formed via self-assembly of DNA macromolecules avoiding the use of additional reagents are of special interest.

7. The structure of the DNA sample **Q** is formed via repetition of the 5'−CACAGTCGCGTTAGGTAAACGAAT−3' fragment. Suggest a sequence of the DNA molecule capable (upon interaction with two fragments of **Q**) of formation of an element of three-dimensional network with three DNA chains meeting at each node of it. There are no single-strand parts in the formed network, and the length of the linker between the macromolecules **Q** is 12 base pairs. Complete the scheme of the formation of the network element containing molecules of **Q** (already drawn as lines) and the molecule(s) suggested by you (complete the drawing). Assign the 3'- and 5'-ends of all chains.



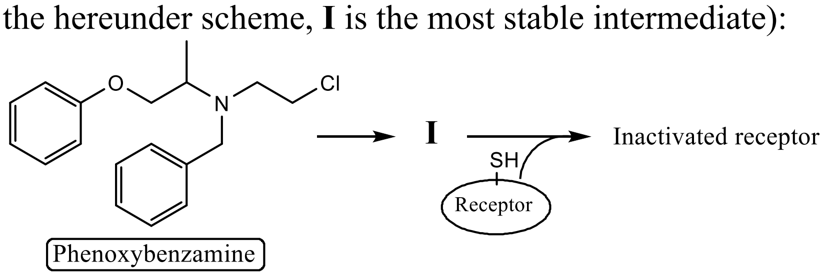
Reference materials:

Notation	Nucleobase	M of the nucleoside monophosphate (protonated form)
A		347.22
T		322.21
C		323.20
G		363.22

Problem 3

"Dark-cell" tumor

Pheochromocytoma (PCC) is a hormone-producing tumor causing periodic acute increase in blood pressure, phenoxybenzamine being the drug of choice for its reduction. It can block irreversibly the receptors covalently binding to a cysteine residue according to S_N1 mechanism (see the hereunder scheme, **I** is the most stable intermediate):



1. Draw the structures of **I** and the product of its interaction with the receptor.

The interaction of the hormone (L) produced by PCC with the receptor (R) can be described by a dynamic equilibrium with the dissociation constant K_d.

$$L + R \underset{K_d}{\rightleftharpoons} LR \qquad (1)$$

2. Derive the dependence of the fraction (θ) of the receptor bound to the hormone on the hormone concentration for scheme (1).

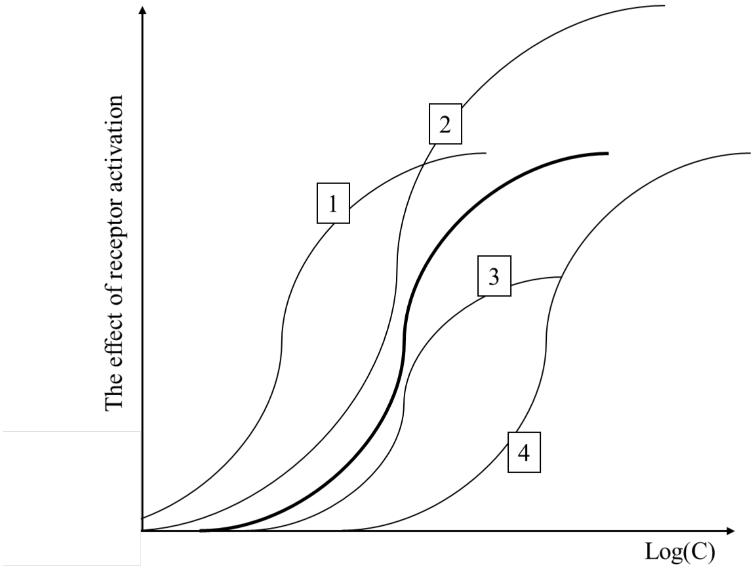
In some cases, more than one equivalent of a hormone can bind to its receptor:

$$nL + R \underset{K_d}{\rightleftharpoons} L_nR \qquad (2)$$

Then the dependence of the fraction of the receptor bound to the hormone (θ) on the hormone concentration is described by the Hill equation.
3. Derive the Hill equation.
4. Derive the linear form of the Hill equation.

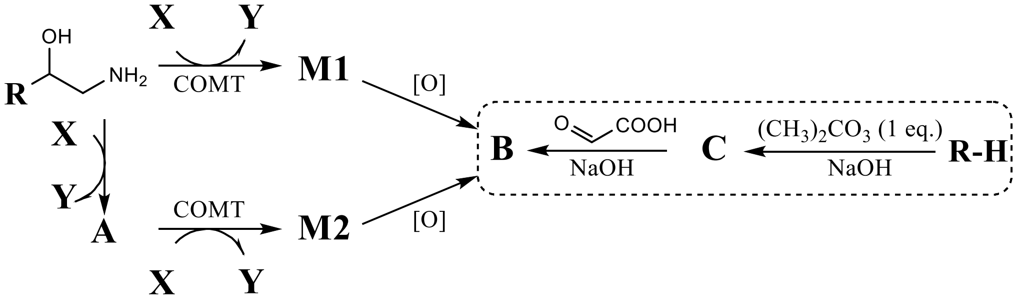
The Hill equation can be used to describe the dose–effect relationship (the dependence of the effect of the receptor stimulation on the hormone concentration).

5. Choose the graph of the dose–effect relationship describing the effect of phenoxybenzamine (the bold line corresponds to the graph before the drug administration).



6. What is the hormone concentration that corresponds to the half-maximal effect of the receptor stimulation?

Diagnostics of PCC begins with the laboratory analysis of the concentration of **M1** and **M2** (products of enzymatic breakdown of hormones) in urine. **M1** and **M2** are formed as a result of the reaction catalyzed by the enzyme COMT as shown in scheme (3). The final metabolite **B** is an intermediate in the organic synthesis of a well-known confectionery flavoring (part of this synthesis is shown framed).

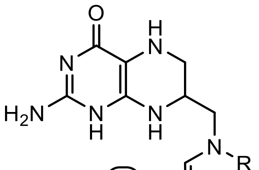


(3)

Addition of iron(III) chloride to the **R-H** solution results in an emerald-green coloration. When reacted with iron(III) chloride, the isomers **R'-H** and **R"-H** are colored dark purple and brown, respectively. The mass fraction of oxygen ω(O) in **M1** is by 1.0767 times higher than that in **M2**.

7. Draw the structures of **B**, **C**, **R-H**, **R'-H**, and **R"-H**.

8. From the options given below, choose the compound which is most suitable as **X**. Draw the structure of **Y** corresponding to your choice of **X**.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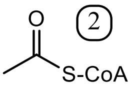
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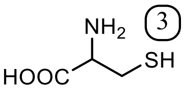
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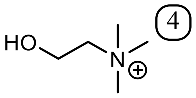
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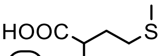
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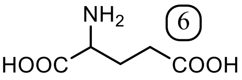
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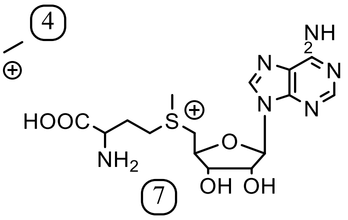
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9. Draw the structures of **A**, **M1**, and **M2**.

The content of **M1** and **M2** in urine is assayed by liquid chromatography with tandem mass spectrometry (LC–MS). The sample is first subjected to chromatography and the separated substances are analyzed in the multiple reaction monitoring mode. This method involves ionization of the initial metabolite and isolation of a single ion, which is further split into several new ions. Only one of these is subjected to further analysis. For example, in the case of **M1** the [**M1** $+H^+ -H_2O$] ion is first isolated, and only the [**M1** $+H^+ -H_2O -CH_3OH$] ion obtained after splitting is further analyzed. Finally, the intensity of the chromatogram peaks is used to determine the concentration of **M1**.

10. Draw the structures of the [**M1** $+H^+ -H_2O$] and [**M1** $+H^+ -H_2O -CH_3OH$] ions.

SECTION IV. INORGANIC CHEMISTRY

Problem 1

The phenomenon of superconductivity was discovered in 1911. Superconductors are substances with electrical resistance dropping down to zero below a certain critical temperature T_c. The transition to the superconducting (s) state from the normal (n) one is possible for many metals, alloys, intermetallic compounds, some hydrides, mixed oxides and other compounds. In Figure 1, the temperature dependences of the resistivity (ρ) of substances with semiconductor and metallic conductivity are shown, as well as of those having a transition to the superconducting state.

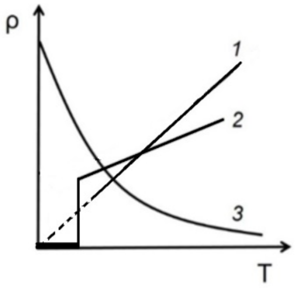


Fig. 1.

1. Indicate the type of conductivity for each of the dependences *1*, *2*, and *3* (semiconductor, metal or superconductor).

There are superconductors of two types (I and II). The magnetic field destroys superconductivity of all superconductors, when the value of critical strength (H_c) is reached. The temperature dependence of H_c for type I superconductors is described by the formula: $H_c = H_{c0} \cdot (1 - \frac{T^2}{T_c^2})$, where H_{c0} is the value of critical strength at $T = 0$ K.
Mercury with $T_c = 4.156$ K was the first metal for which superconductivity was discovered. The vast majority of metals having the transition to the superconducting state are classified as type I superconductors.

2. Calculate the value of critical strength H_c for mercury at the temperature $T = 3.00$ K, if $H_{c0} = 3.2627$ kA/m.

In 1950, samples of different isotopes of mercury were shown to have different T_c values. This dependence of T_c on the molar mass of an isotope is referred to as the isotopic effect; for many superconductors the dependence can be written as $T_c \sim \text{const}/M^{\zeta}$. The parameter ζ varies for different superconductors. M is the molar mass of an isotope or element with an account for the isotopic distribution.

3. Calculate the value of the parameter ζ for mercury, if $T_c = 4.177$ K for the monoisotopic sample ^{198}Hg ($M = 197.97$ g/mol).
4. Using the data presented in the table for stable isotopes, determine the range, in which the T_c values can vary for monoisotopic samples of mercury.

M, g/mol	195.97	197.97	198.97	199.97	200.97	201.97	203.97
A	196	198	199	200	201	202	204

Phase transitions for the type I superconductors between the n and s states are classified as the first-order phase transitions but one point, at which the phase transition is of the second order. During the transition to the superconducting state, the changes in specific entropy (S) and specific heat capacity (C) are described by the formulas:

$$\Delta S = S_s - S_n = \frac{H_c}{4\pi}\left(\frac{\partial H_c}{\partial T}\right)_P, \qquad \Delta C = C_s - C_n = \frac{H_{c0}^2 T}{\pi T_c^2}\left(3\frac{T^2}{T_c^2} - 1\right).$$

5. At what temperature (other than the absolute zero) is the $n \rightarrow s$ transition for mercury classified as the second-order phase transition, characterized by the absence of an entropy jump?
6. Calculate at what temperature (other than absolute zero) the heat capacities of the *s* and *n* states of Hg are equal.

One of the first intermetallic compounds with superconducting properties was discovered in 1929. This binary compound **X** had a low value of T_c = 1.8 K, but it was of interest, since none of its components was a superconductor in the form of a simple substance.

7. Determine the composition of **X**, if it is known that heating in air and subsequent interaction of the products with concentrated hydrochloric acid leads to the formation of a solution of a compound containing the metal **A** and a precipitate of the colored metal **B**, the mass of which accounts to 65.34% of that of **X**. When an excess of cesium iodide is added to the solution, an orange precipitate of a complex salt is formed, in which the mass fraction of the cation **A** is w(**A**) = 24.60%, and the mole fraction x(**A**) = 16.67%. Write the equations of the mentioned reactions.

Metals and intermetallic compounds have low T_c values. It became possible to obtain compounds with T_c close to room temperatures in the 21st century. The discovery of superconductivity at 260 K in hydrogen-rich compounds such as LaH_{10} has intensified the search for superconductivity among both well-known and new hydrides. At high pressures, decomposition of **T1**, which is stable under normal conditions, affords the compound **T2** and a simple substance. **T2** is stable at pressures up to 37 GPa. An increase in pressure above 110 GPa leads to the formation of **T3** with $T_c \approx 203$ K, which has the same quantitative composition as **T2**. The unit cells of **T2** and **T3** are shown in Figures 2 and 3, respectively. The unit cell parameter of **T3** is 0.2984 nm, d = 4.388 g/cm^3.

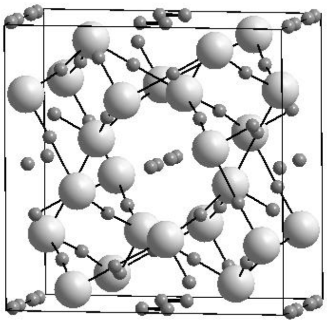


Fig. 2.

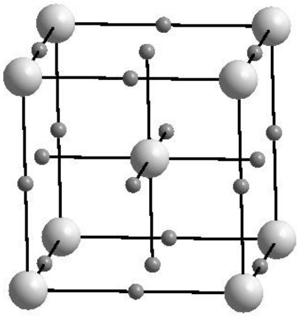


Fig. 3.

8. Determine quantitative composition of **T3** and **T1**.
9. Indicate the molecular structural fragments that are present in the **T2** structure. Write down the formula for **T2** representing these structural fragments. Write the reaction for obtaining **T2** from **T1**.

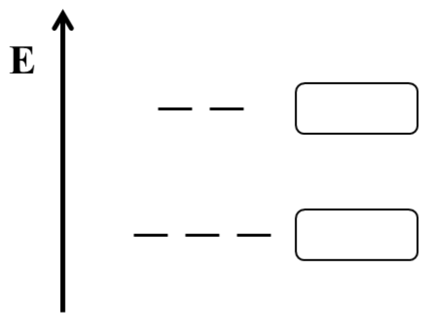
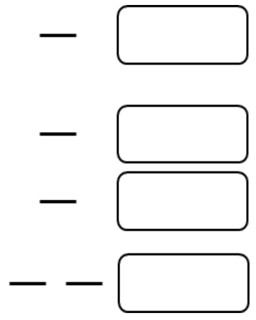
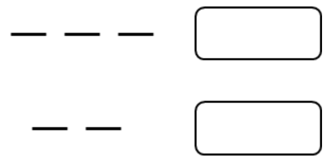
Problem 2

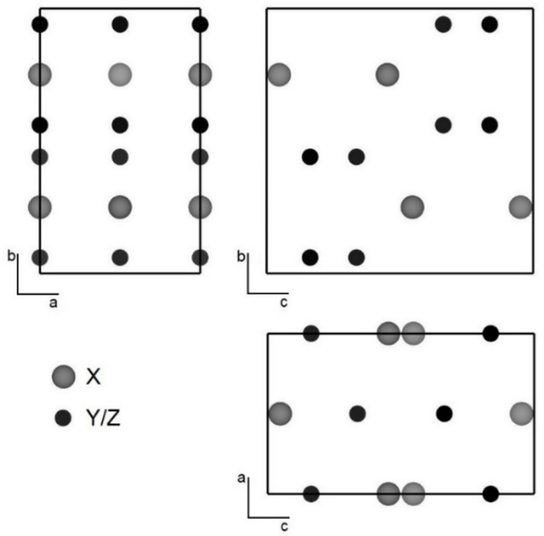
The metal **Y**, when alloyed with cesium, forms an intermetallic compound **M** (the molar fraction of cesium x(Cs) = 8/19). All the **Y** atoms form clusters with the cesium atoms located between them in the structure of **M**. Despite the large number of **Y** atoms forming the cluster, a trigonal prism $\mathbf{Y_6}$ with an equilateral triangle at the base is the structural basis. Other **Y** atoms are located at a distance of 2.68 Å or 2.64 Å to the nearest **Y** atoms of the trigonal prism. In this case, the cluster has the same symmetry as a trigonal prism.

1. Determine the quantitative composition of **M**. Draw the cluster fragment of **Y** atoms in its structure.

Elements **X**, **Y**, and **Z** are found in another intermetallic compound **N**. A sample of **N** weighing 42.60 g ($d = 6.864$ g/cm^3) was completely dissolved in concentrated nitric acid. An excess of concentrated sodium hydroxide solution was added to the obtained solution, as a result of which a mixture of **A** and **B** precipitated and the solution **C1** was formed. The precipitates were separated, kept in air for a long time, and then an excess of dilute sulfuric acid solution was added. A part of the precipitate dissolved to form a solution of the compound **D**. The undissolved brown precipitate weighing 8.545 g was isolated and slowly heated to 120°C. As a result, the substance **E** formed (with the mass loss 23.67 wt.%). **E** exhibits the properties of both an oxidizing agent and a reducing agent. When **E** is fused with sodium peroxide, a green substance **G** is formed, which is unstable in water. When **E** reacts with concentrated hydrochloric acid, a gas is released and a complex compound **H** is formed, the effective magnetic moment of which is $\mu_{eff} = 4.9\ \mu_B$. Metallic zinc was added to the solution of **D**, which led to the formation of a white precipitate **F** containing the element **X**. If sulfuric acid is added dropwise to the **C1** solution, a white precipitate first forms, which is readily dissolved in an acid excess, forming the **C2** solution. The metal **Y** can be obtained by electrolysis of the **C2** solution. When **Y** reacts with $HgCl_2$, a binary chloride **I** is formed (ω(Cl) = 50.4%).

2. Identify **A**–**I** and write down the reaction equations.
3. Indicate the oxidation states of the elements in **I**.
4. For **H**, choose the correct energy diagram in the Answer Sheet, label the atomic orbitals and place the electrons of the central atom on them.



The figure shows the projections of the **N** unit cell on the *ab*, *bc* and *ac* planes. It is known that the **Y** and **Z** atoms are in the same position, and their ratio can be different, which leads to the formation of the $\mathbf{XY_{a-\delta}Z_{\delta}}$ solid solution.

5. Determine the exact composition of **N** used in the experiments.
6. Determine the range of existence of the solid solution (δ_{min} and δ_{max}) of the $\mathbf{XY_{a-\delta}Z_{\delta}}$ intermetallic compound, if its density varies within the range of 6.847–7.118 g/cm^3. Consider the unit cell parameters to be constant for all the solid solution compositions.

Problem 3

For a long time, hydrogen was believed to form the H^+ and H^- ions in gaseous phase, and the H_2^+ particle under gas discharge at low pressure. Later, the molecular cation H_3^+ was discovered in gas discharges (Thomson) and in the atmosphere of hydrogen planets (Mac Nab). Relatively recently, it was shown that the H_2 molecules can attach to H_3^+ to form H_5^+, H_7^+, and H_9^+.

1. Draw the structure of the H_3^+ cation, if the hydrogen atoms are equidistant from each other. Draw the overlap of the *s*-orbitals of the atoms and choose what type of bond is formed in the H_3^+ cation. Draw the structures of the cations H_5^+, H_7^+ and H_9^+, in which 3 atoms form right triangle in the mirror symmetry plane, while other atoms are in the planes perpendicular to the latter and containing the medians of the triangle.

In an aqueous solution, the existence of bound H^+ and H^- as parts of compounds is possible.

2. Write the reactions that describe the behavior of unbound H^+ and H^- in an aqueous solution. By calculating $\Delta_r G° = -nFE°$ of the reaction $H_2O + H^- \rightarrow \ldots$ ($E°_{H_2/H^-} = -2.23$ V; $E°_{H_2O/H_2} = -0.83$ V) prove that the existence of an unbound H^- in the solution is impossible.

The H^- anion, which is unstable in solution, is stabilized in complexes with the formation of a M–H bond. Like H^+, it most often has the CN = 1. At the same time, it turned out that in hydrides H^- can form bridges and have the CN up to 6.

3. Draw the structures of HM_n fragments in the complexes: $[(CO)_5WHW(CO)_5]^+$ (angle MHM < 180°); $[HRh_3(C_5H_5)_4]$ (angle close to 109.5°); $[HCo_6(CO)_{15}]^-$ (angles of 90 and 180°).

Hydrides are often obtained by an oxidative addition reaction, which occurs with the oxidation of the M complex: *cis*-$[MClCO(PPh_3)_2] + nH_2 = $ **A**, Ph = C_6H_5. In the mechanism of oxidative addition, an intermediate formation precedes that of the hydride **A**. This is accompanied by the appearance of the band ν ~ 1500 cm^{-1} in the IR spectrum of the hydride **A** (in H_2

$\nu = 4160$ cm^{-1}), whereas the r_{H-H} distance changes from 0.074 nm in H_2 to ~0.170 nm in the hydride.

4. Decipher M, if $\omega_{Cl} = 4.53\%$, and $\omega_H = 4.13\%$ in **A**. Give the formula of **A**, the number of electrons around M, and the oxidation state of M in the original complex and in **A**. Draw the structure of **A**.

The researchers failed to synthesize the intermediate of the oxidative addition reaction until 1980, when Kubas managed to stop the reaction at the step of the intermediate formation. After passing hydrogen ($p = 1$ atm) for 20 min through a dark purple solution in toluene containing 4.1442 g of *trans*-[M'(CO)$_3$(PCy$_3$)$_2$], Cy = C_6H_{11}, he isolated 3.74 g of the yellow crystals **B** containing the ligand L (the reaction yield was of about 90%). The band appears at $\nu = 2690$ cm^{-1} in the IR spectrum of the complex **B**; the bond length $r_{H-H} = 0.084$ nm and $\omega_{M'} = 22.13\%$ in **B**.

5. Decipher M' and **B**. Draw its spatial structure.

It is rarely possible to stop the reaction at the intermediate step. Even if it looks like so, a mixture of the intermediate and hydride is usually formed, because their thermodynamic characteristics are close. Thus, Luo and Harbtree obtained a product as a result of the treatment of [$ReCl_3(CO)(PMe_2Ph)_3$] with $LiAlH_4$ in ether at 193.2 K. Addition of $HBF_4{\cdot}OEt_2$ in CD_2Cl_2 at 193.2 K to the product leads to an equilibrium mixture of **D**$^+$ and **E**$^+$ cations. For equilibrium **D**$^+$ $\rightleftarrows$ **E**$^+$, the enthalpy $\Delta_r H°$ is −4.6 kJ/mol, and the entropy $\Delta_r S°$ is −10 J/(mol·K).

6. Determine the formulas of **D**$^+$ and **E**$^+$, if there are two r_{H-H} distances (0.087 and 0.180 nm) in the structure of **E**$^+$ and only one r_{H-H} distance (0.176 nm) in that of **D**$^+$.

7. Calculate the equilibrium constant and the composition of the equilibrium mixture χ in mol%.

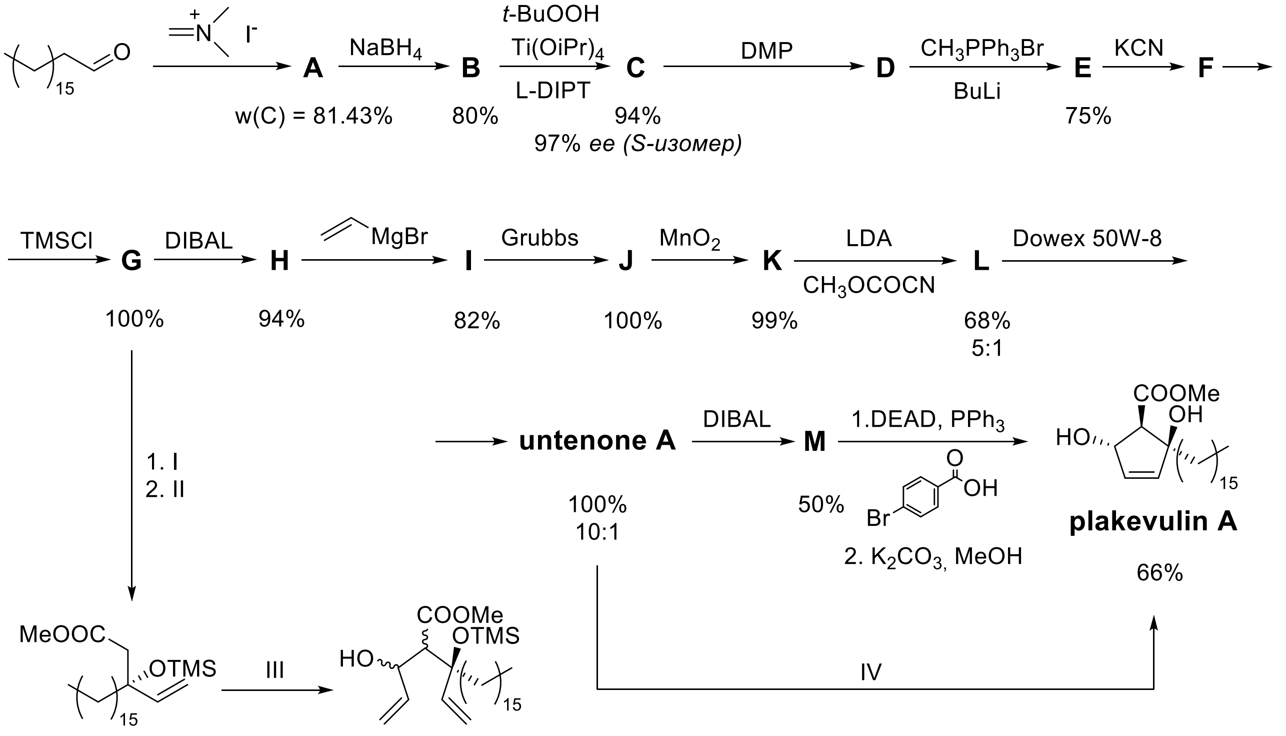
Analysis of the synthesized compounds showed that different ligands in the complex can contribute to the formation of either the intermediate or hydride.

8. Give the MO diagram for the ligand L and calculate the bond multiplicity in it. Indicate with an arrow the possible direction of the electron transfer between π_d-orbitals of M and molecular orbitals of L.

SECTION V. ORGANIC CHEMISTRY

Problem 1

In 2022, K.B. Sharpless became the second scientist in the history who has received two Nobel Prizes in chemistry. The first prize was awarded for the discovery of the enantioselective epoxidation of alkenes, which has preparative significance in the synthesis of various organic compounds. As an example of the use of this reaction, the total synthesis of the natural products **untenone A** and **plakevulin A** isolated from marine sponges and exhibiting inhibitory activity against mammalian DNA polymerases is given below.



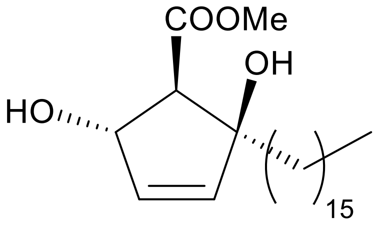
TMS = trimethylsilyl
L-DIPT = diisopropyl L-tartrate
DM periodinane = Dess-Martin periodinane
DIBAL = diisobutylaluminum hydride
Grubbs = Grubbs catalyst
LDA = lithium diisopropylamide
DEAD = diethyl azodicarboxylate
ee (*S*-isomer) = ([S] – [R])/([S] + [R])·100%

1. Give the structures of **A**–**M** and **untenone A**, taking into account stereochemistry. Note that Dowex 50W-8 is a strongly acidic cation-exchange resin in the H^+ form. After all reactions with organometallic reagents, the reaction mixture was treated with water before isolation.

In addition to the basic reaction scheme that leads to the desired products, the authors attempted to synthesize **untenone A** and **plakevulin A** using a different sequence of steps. However, it did not lead to success.

2. Which reagents (I, II, and III) could be used by the authors? Under what reaction conditions (IV) it could be possible to try obtaining **plakevulin A** from **untenone A** in one step?

3. Determine the absolute configuration of the stereocenters in **plakevulin A**.

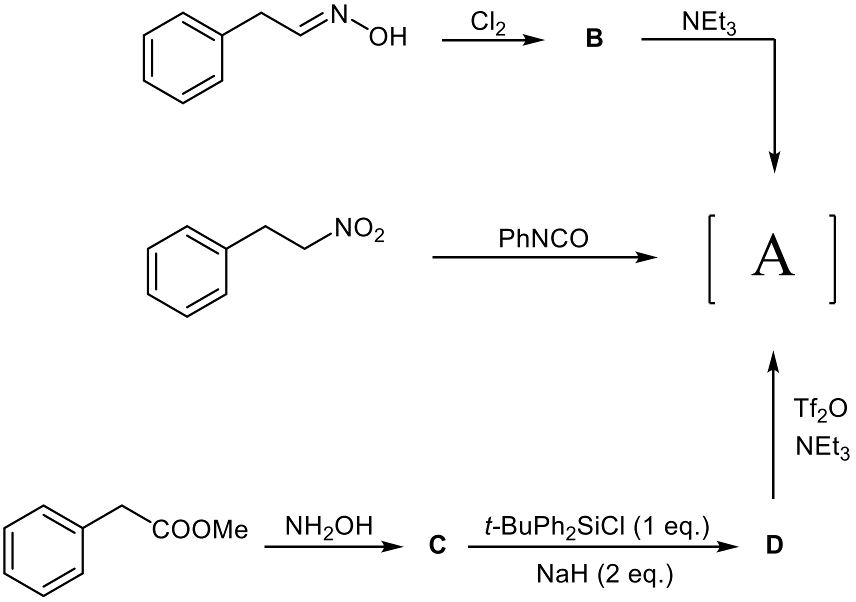


plakevulin A

Problem 2

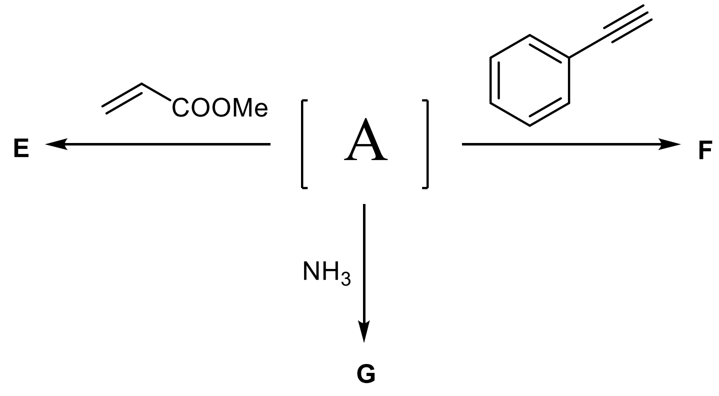
Short but bright life of intermediates

The higher is the energy of a particle, the higher is its reactivity. Usually, it is impossible to isolate high-energy particles in a free form, and they immediately enter into further transformations, so they are often reactive intermediates. Let's consider three ways to generate the intermediate **A**:



1. Write down the structures of **B**, **C**, **D**, and **A**.

A rapidly interacts with various reagents:

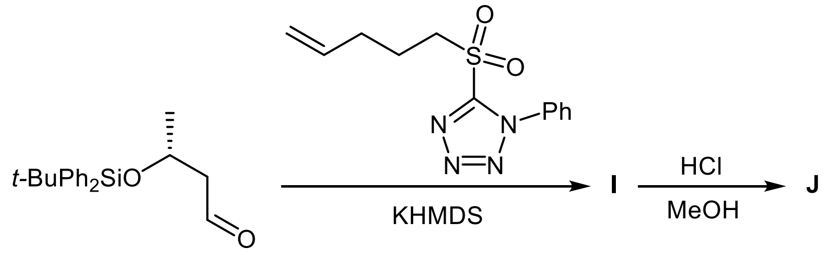


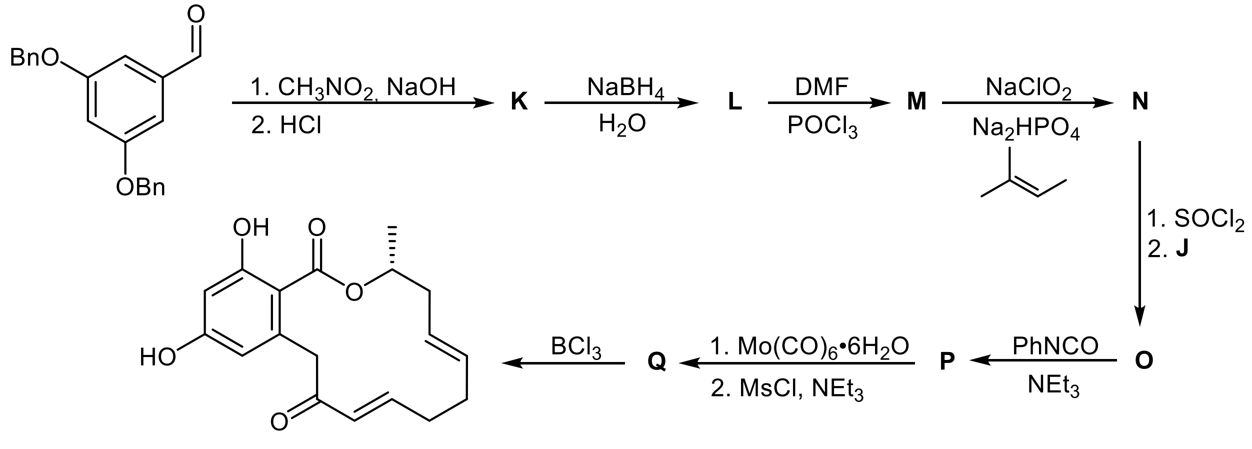
2. Write down structures of **E**, **F**, **G**.

If the reaction mixture does not contain a suitable partner to react with **A**, then **A** reacts with itself to form the aromatic compound **H**.

3. Write down the structure of **H**.

The reactivity of intermediates like **A** has been used in the total synthesis of natural compounds. A total synthesis of natural polyketide **(+)-Monocillin II** Is given below.



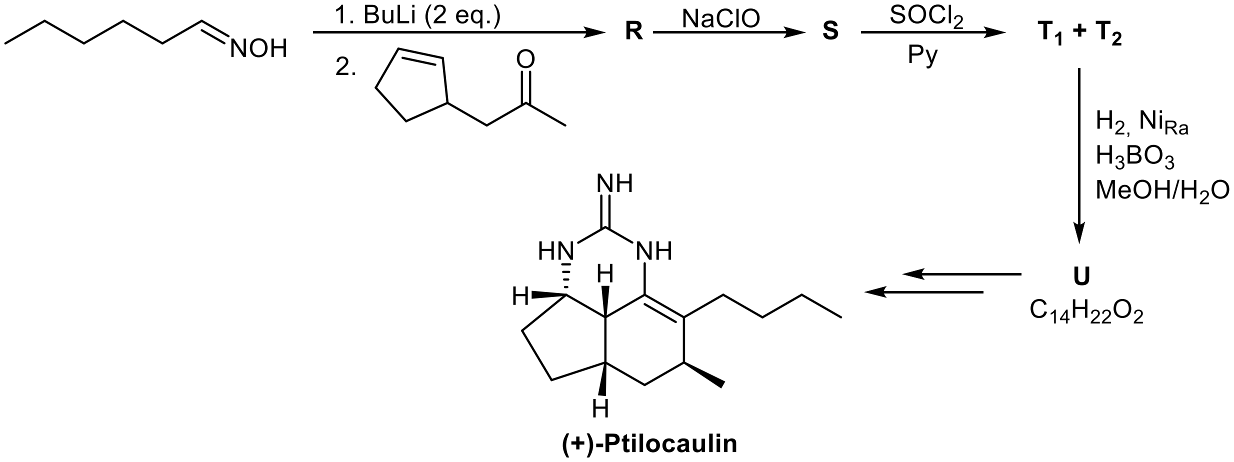


(+)-Monocillin II

KHMDS = potassium bis(trimethylsilyl)amide
Bn = benzyl
DMF = *N*,*N*-dimethylformamide
Ms = methanesulfonyl

4. Write down the structures of **I**–**Q**.

Another example of the use of intermediates like **A** is the synthesis of **(+)-Ptilocaulin**, isolated from the caribbean marine sponge *Ptilocaulis aff. P. spiculifer*. A fragment of the preparation of the key intermediate **U** in the synthesis of **(+)-Ptilocaulin** is shown below.



Py = pyridine
Ni_{Ra} = Raney nickel

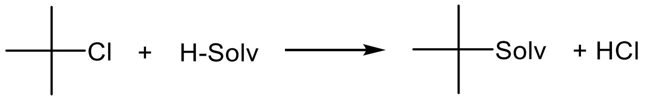
5. Write down the structures of **R**, **S**, **T$_1$**, **T$_2$**, **U**, if it is known that **T$_1$** and **T$_2$** are structural isomers, the reaction of a mixture of which with hydrogen on Raney nickel under slightly acidic conditions gives the only product **U**.

Problem 3

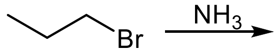
Nucleophilic substitution

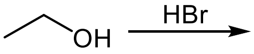
The properties of atoms, molecules, and ions in solutions are very different from those in the solid state or gas phase. The solvent can change the direction of the reaction, whereas the rates of the same reaction in different solvents can differ by the factor of millions. Reactions in which charges arise in the transition state or charges already present in the reagents are concentrated in a smaller space are accelerated with increasing polarity of the solvent. If the ionic charges of the reactants are neutralized in the transition state or distributed over a larger space, the reactions slow down as the polarity of the solvent increases. Let us consider the effect of a solvent polarity on the progress of nucleophilic substitution reactions.

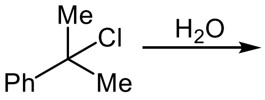
1. Match the solvents (Solv: H_2O, CH_3OH, C_2H_5OH, HCOOH) with the relative rate (1, 9, 12200, 335000) of solvolysis of *tert*-butyl chloride:

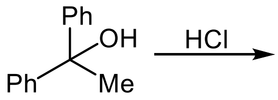


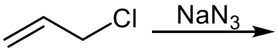
2. For the nucleophilic substitution reactions below, indicate the mechanism (S_N1/S_N2), the change in charge distribution in the transition state (charge neutralization/separation/distribution), and the effect of increasing solvent polarity on the reaction rate (acceleration/deceleration).

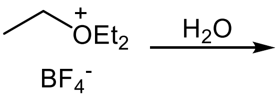
1)


2)


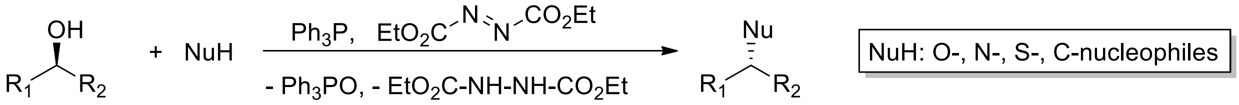
3)


4)


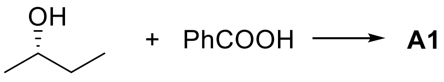
5)


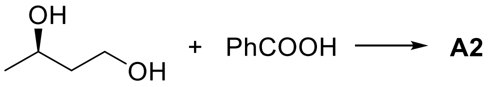
6)


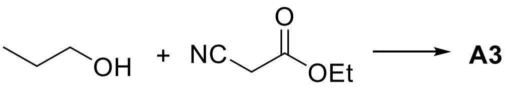
The hydroxyl group is a very poor nucleofuge, since in most cases its replacement is thermodynamically unfavorable. However, several approaches have been proposed for S_N2 processes in alcohols, the Mitsunobu reaction being among the most regio- and stereoselective:

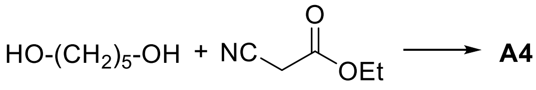


3. Write the products of reactions 7)–10) taking into account the stereochemistry of the Mitsunobu reaction. Indicate which reactions are regioselective and which are stereoselective.

7)


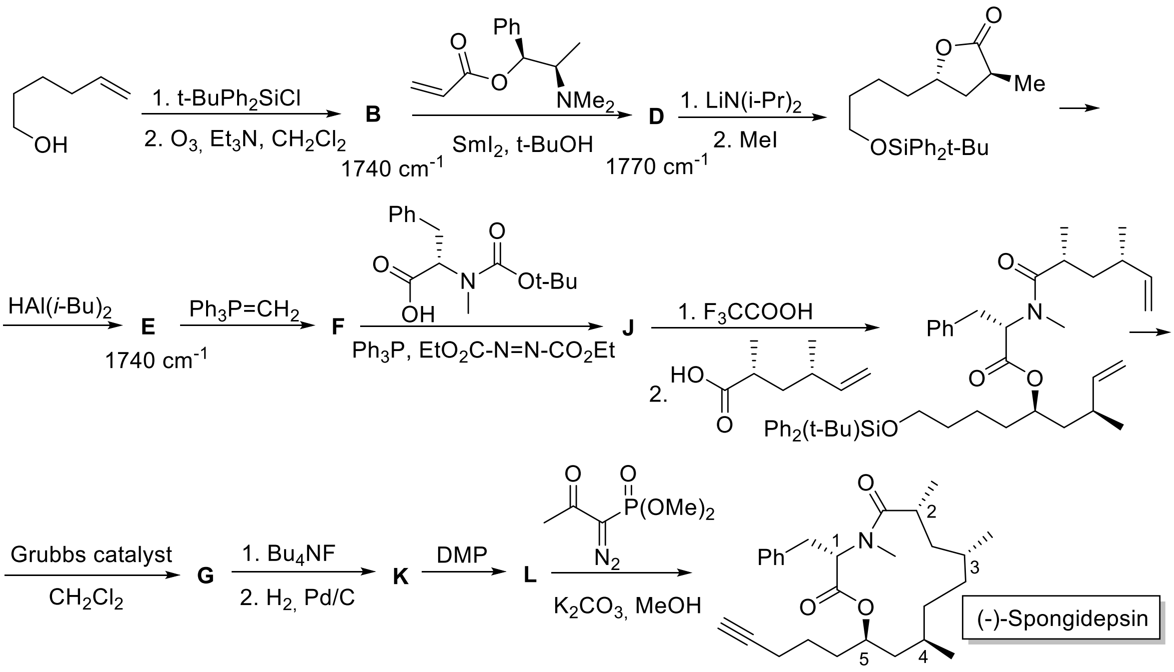
8)


9)


10)


Note that the stereocenter configuration has not changed in **A2**; **A3** has three triplets (1H, 3H, 3H), two quadruplets (2H, 2H), and a quintet (2H) in the ^{1}H NMR spectrum; there are no singlets in **A4**, compared to the signals of the starting substances. All reagents in reactions 7)–10) are taken in equimolar quantities.

The Mitsunobu reaction is effectively used in the synthesis of various biologically active compounds. Thus, in the synthesis of the tumor cell inhibitor (−)-Spongidepsin, the Mitsunobu reaction was applied for the convergent assembly of two fragments of the target molecule:

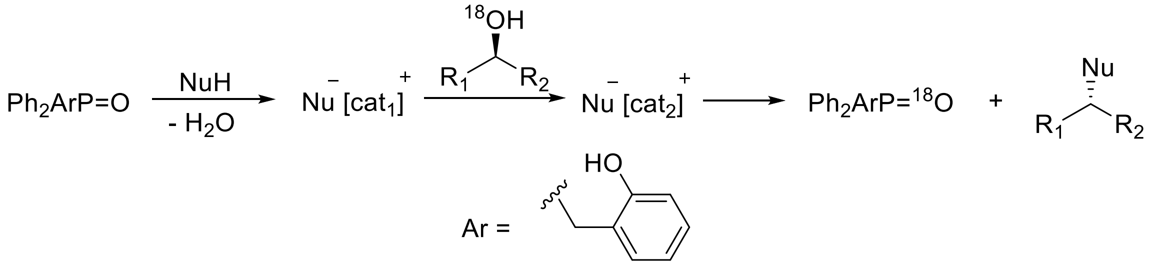


Grubbs catalyst – Ru-based alkene metathesis catalyst
DMP – Dess-Martin periodinane

4. Determine the structures of **B–L**. Use the following information: characteristic absorption frequencies of functional groups in IR spectra: (−CHO) = 1740 cm^{-1}; (C=O) = 1720 cm^{-1}; (lactone) = 1770 cm^{-1}.

5. Determine the absolute configurations of the stereocenters 1, 2, 3, 4, 5 in (–)-Spongidepsin.

Organocatalytic process in which phosphorus compounds are used in catalytic quantities due to their participation in the cycle is an alternative option for nucleophilic substitution of the hydroxyl group in alcohols. The mechanism of catalysis, each step of which can be described as a nucleophilic substitution, is presented in the scheme:



6. Suggest the structures of [cat$_1$]$^+$ and [cat$_2$]$^+$, if there is no signal of the OH group in the ^{1}H NMR spectrum of [cat$_1$]$^+$, but there is a signal of OH group in that of [cat$_2$]$^+$. Indicate the position of the isotopic label after the second cycle.