LIFE SCIENCES AND POLYMERS

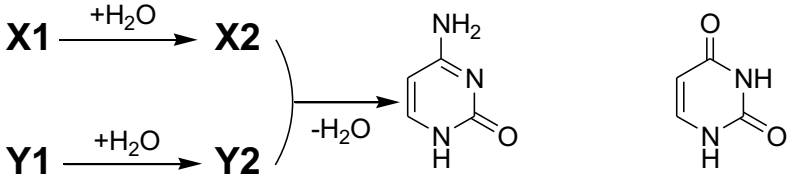
Problem II-1

Question	II-1.1	II-1.2	II-1.3	II-1.4	II-1.5	II-1.6	II-1.7
Points	1.5	4	1	1.5	1.5	2.5	3

Today a hypothetical stage in the origin of life on Earth is recognized: the RNA world, when this biopolymer performed the functions of genetic information storage and catalysis of biochemical processes in the earliest forms of living matter, instead of DNA and proteins in contemporary living things.

For the main nitrogenous bases inherited by extant organisms from the RNA world, a synthesis from prebiotic molecules (PM) has been modeled. These are compounds that, being present in proto-planetary gas-dust clouds, can participate in the formation of key biomonomers on recently formed celestial bodies. However, the probability of forming any significant molecules in outer space is low; therefore, species containing from three to five atoms inclusively are classified as simple PM, while those containing six or more atoms are considered complex.

Both constituent parts of cytidine can be formed from PM: the cytosine moiety from compounds **X1** and **Y1**, and the sugar moiety from acyclic compounds **Z1** and **Z2** (with only the precursors of ribose being complex PM). The synthesis scheme for cytosine, consisting of reaction equations, is given below:

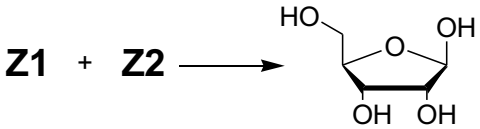


II-1.1 Based on general considerations, propose a set of three stable simple PM (each with a molecular mass not exceeding 30 a.m.u.), which together contain five π-bonds and a total of 11 atoms.

II-1.2 Determine the structural formulae of **X1**, **X2**, **Y1**, and **Y2**, given that **X1** and **Y1**, as non-ionized molecules and contain the same functional group. Note that M_r of **Y2** is the highest among the quartet under consideration. Prove your answer by the calculation or reasoning in commonly accepted chemical language.

II-1.3 Propose a scheme for the prebiotic synthesis of another pyrimidine base, uracil, using only the substances present in the cytosine synthesis scheme. You may use the **X1**, **X2**, **Y1**, and **Y2** to denote the respective compounds.

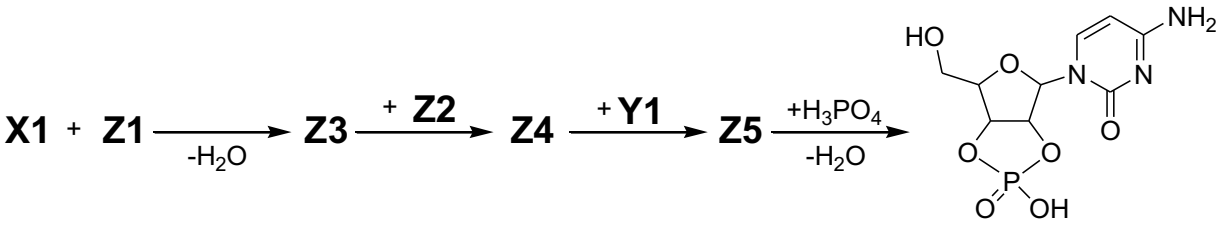
Analysis of an aqueous solution, originally containing **Z1** and **Z2**, shows the presence of four products including D-ribose after storage at room temperature for an extended period. Equation of the reaction of D-ribose synthesis is:



Molecular masses (g/mol) of **Z1** and **Z2**, rounded to whole numbers, are composite numbers that can be factored into similar sets of single-digit prime factors, differing only in one position (k in the case of **Z1** and m in the case of **Z2**, where $k < m$).

II-1.4 Without revealing the formulae of **Z1** and **Z2**, use mathematical considerations to determine the numerical value of the sum $k + m$. Prove by calculations.
II-1.5 Determine the structures of **Z1** and **Z2** (indicating stereochemistry where necessary), given that they contain identical functional groups.
II-1.6 Depict the structures of three products other than D-ribose that are found in the reaction mixture originally containing **Z1** and **Z2**. Encircle those that do not occur in living nature, at least on our planet.

A direct reaction between ribose and cytosine to form cytidine is impossible (primarily due to the delocalization of the lone electron pair on the N1 atom of cytosine). To resolve this contradiction, a mechanism for the synthesis of ribocytidine-2,3-cyclic phosphate involving the same PM in a phosphate buffer solution was proposed. The mechanism is given below as a set of reaction equations):

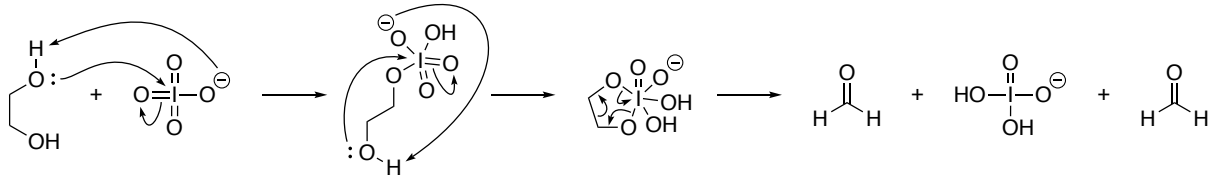


II-1.7 Depict the structures of **Z3**–**Z5** (without stereochemistry), considering that the number of heterocycles and the number of heteroatoms in them increase stepwise as the numerical index increases.

Problem II-2

Question	II-2.1	II-2.2	II-2.3	II-2.4	II-2.5	II-2.6	II-2.7	II-2.8
Points	1.5	1.5	1.5	2.5	3	1	0.75	3.25

The drug **X** (M = 2662.04 g/mol) was used in the early 21st century for the treatment of peptic ulcer disease due to its ability to increase the pH of gastric juice. Substance **A** is the starting material for the synthesis of **X**. In order to identify **A**, the Malaprade reaction was employed, which is an oxidative cleavage of vicinal diols by metaperiodate ion. The mechanism of this transformation, using ethylene glycol as an example, is shown below.

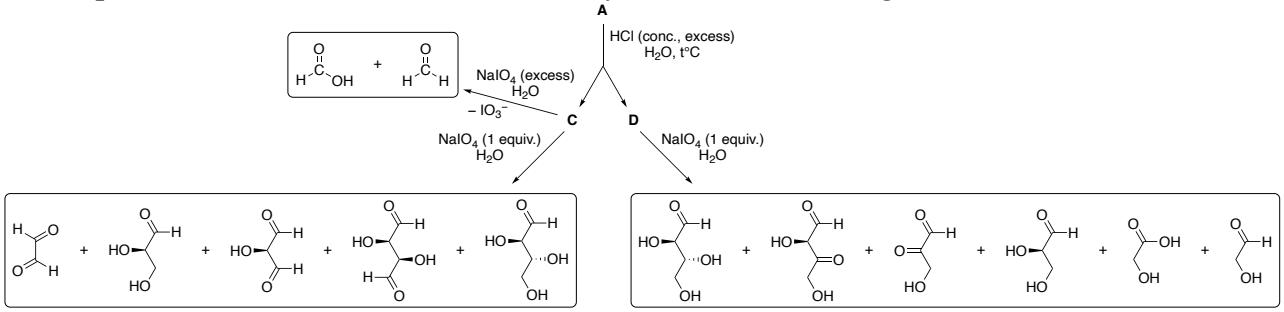


II-2.1 For the compounds provided in the Answer Sheet, write the products of the oxidative cleavage corresponding to the enframed fragments of the starting substrates.

It is known that **A** exists in solution as a single chiral isomer, the complete acidic hydrolysis of which produces isomeric compounds **C** and **D** in equimolar amounts. An excess of sodium metaperiodate (0.2139 g) was added to a solution containing 0.1 mmol of **C**. The volume of the resulting solution was adjusted to 100.0 mL. An excess of solution of potassium iodide in aqueous sulfuric acid was added to a 10.0 mL aliquot (***reactions 1*** and ***2***), and then the mixture

was titrated with a $Na_2S_2O_3$ solution (c = 0.0500 M) (***reaction 3***). The titration required 14.0 mL of titrant.

When each of **C** and **D** is treated with equivalent amount of sodium metaperiodate, mixtures of compounds are formed. Structures of only some of them are given in the scheme below.



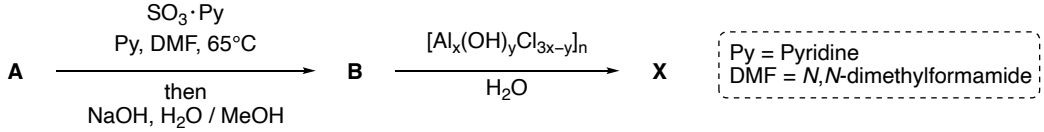
II-2.2 Combine in pairs the products of partial cleavage of **D** shown in the above scheme to obtain all theoretically possible products of the original unbranched compounds. How many of these fragments (N_{frag}) are there?

II-2.3 Write the equations of ***reactions 1–3***.

II-2.4 Determine the number of carbon atoms (N) in **C** and **D**; provide the corresponding calculations.

II-2.5 Give the structures of **A**, **C**, and **D**.

The synthesis of **X** is carried out according to the scheme:



To assess the efficacy of **X**, the patient's gastric contents (volume 0.973 L, pH = 1.12) were aspirated. After adding 4.660 g of **X** to the gastric juice, the pH increased to 2.41. Then, the solution was titrated with 13.2 mL of a KOH solution until the pH reached 4.00. The precipitate formed after titration was burnt in an excess of oxygen. The mass of the remaining aluminum oxide was found equal to 1.366 g. Assume the gastric juice is a solution of hydrochloric acid. Changes in volume upon addition of substance **X** can be neglected.

II-2.6 Calculate the ratio of the amount of aluminum atoms to the amount of substance **X**, n(Al) : n(**X**).

II-2.7 Calculate the ratio of the amount of basic groups in **X** to the amount of substance **X**, n(basic) : n(**X**).

II-2.8 Provide the structural formulae of **B** and **X**; be sure to depict the structure of the inner coordination sphere of aluminum. *If you failed to determine the structure of **A**, denote this substance here as R−OH.*

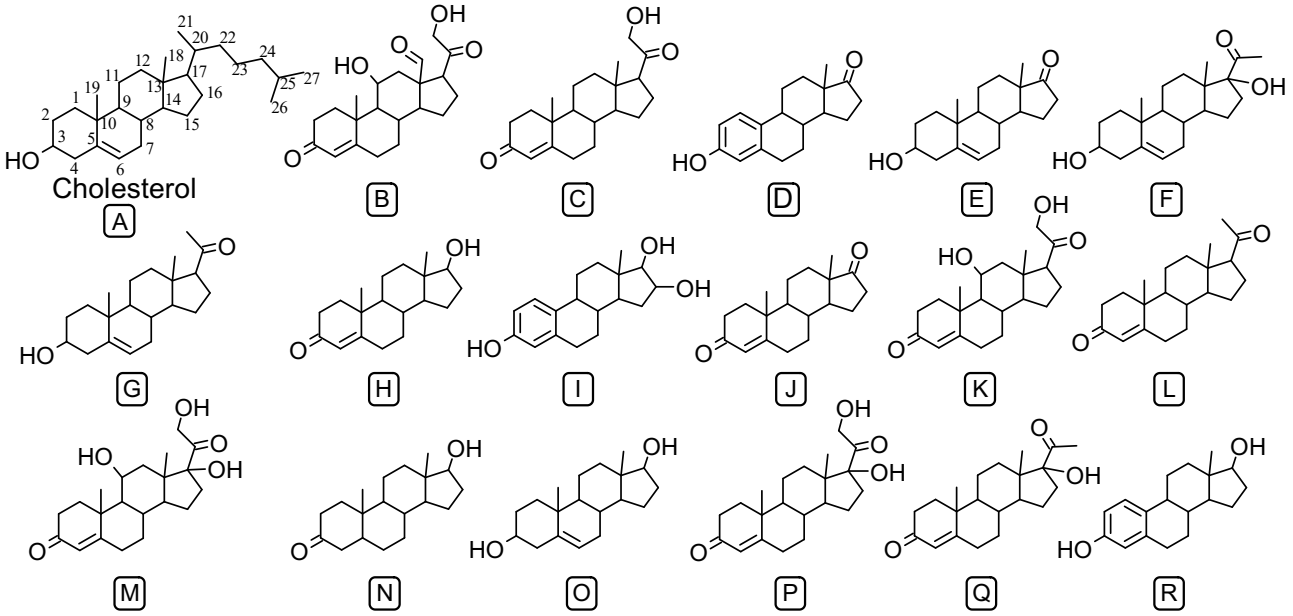
Note:

For $Al(OH)_3$: pK_{b1} = 8.08; pK_{b2} = 8.68; pK_{b3} = 8.86; $K_{sp} = 2 \cdot 10^{-33}$.

Problem II-3

Question	II-3.1	II-3.2	II-3.3	II-3.4
Points	1.75	1	11	1.25

Steroidogenesis is the process of the biosynthesis of steroid hormones from cholesterol. To study this process, several steroids shown below were isolated from the human adrenal cortex:



It is known about steroidogenesis in the human body that:

- all the metabolites isolated from the adrenal gland (and no others) are involved in it;
- it counts for 21 redox enzymatic reactions (12 of which involve molecular oxygen) and one hydration reaction;
- it involves co-enzymes NAD^+ (which acts as the main electron acceptor, being reduced to NADH) and NADPH (which acts as the main electron donor, being oxidized to $NADP^+$);
- cholesterol and 21-hydroxysteroids are substrates in only one enzymatic reaction each;
- the metabolite **E** is formed from cholesterol in three steps.

II-3.1 Which of the steroids considered in the task cannot be quantitatively isolated from the homogenate (finely chopped adrenal tissue) by extraction with a nonpolar solvent:
a) after treatment of the homogenate with an aqueous alkali solution;
b) one hour after treatment of the homogenate with a solution of silver oxide in aqueous ammonia?

II-3.2 Some metabolites are the products of two simultaneously (but no more than two) different reactions. Calculate the number (N) of such metabolites.

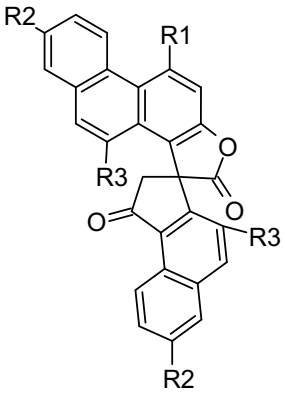
II-3.3 In the Answer Sheets, write down all a) redox and b) hydrolytic reactions of steroidogenesis by filling in the blanks in the schemes. *Be sure to include **all** the compounds participating in each reaction by providing the corresponding stoichiometric coefficients.*

II-3.4 Reconstruct the scheme of steroidogenesis by combining all the reactions recorded in the previous question into chains of sequential transformations (compounds other than **A**–**R** can be omitted).

ORGANIC CHEMISTRY

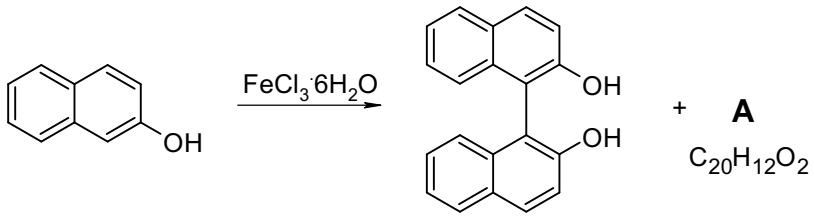
Problem II-4

Question	II-4.1	II-4.2	II-4.3	II-4.4	II-4.5
Points	0.5	6	6.5	1.5	0.5



X, **X1-X4**

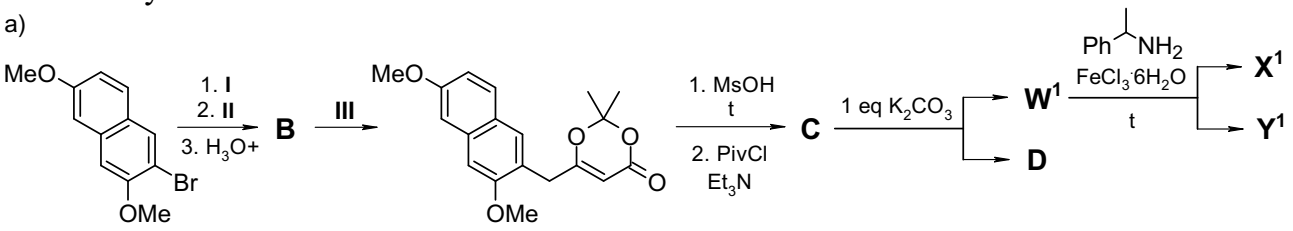
In 2017, Katsuki and co-authors published the first total synthesis of the natural product dendrochrysanene (**X**), which is found in plants of the orchid family. The structure of **X** had already been established earlier using X-ray crystallography, which revealed the presence of a spirolactone core. A similar framework fragment is also present in compound **A**, which can be obtained via a tandem reaction consisting of oxidative dimerization of 2-naphthol followed by a rearrangement of the carbon framework. Salts such as $FeCl_3 \cdot 6H_2O$ or $Cu(NO_3)_2 \cdot 3H_2O$ can be used as catalysts for these transformations.



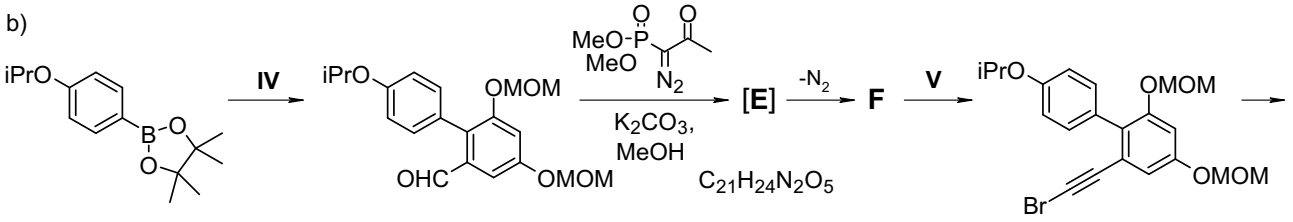
II-4.1 Determine the structure of **A**, if it is characterized by absorption at 1805 cm^{-1} in the IR spectrum, a signal at 175 ppm in the ^{13}C NMR spectrum, and a non-symmetrical structure according to ^1H NMR data.

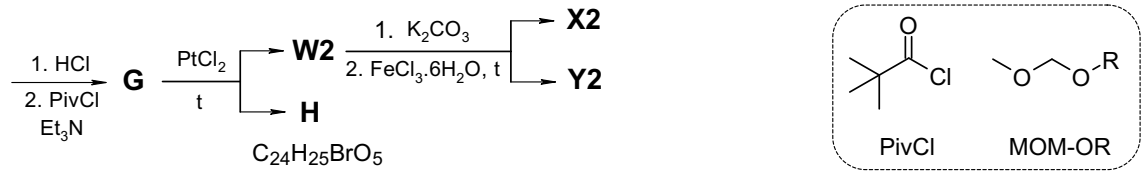
The researchers' path to the successful synthesis of **X** was not an easy one. You are now invited to decipher two synthetic schemes towards the compounds **X1** and **X2** related to dendrochrysanene.

a)



b)





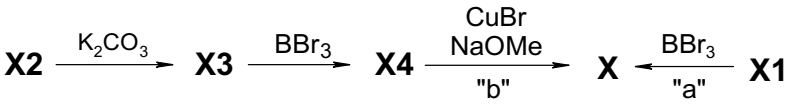
The following signals are observed in the ^1H NMR spectrum of **C** (400 MHz, $CDCl_3$): 8.87 (d, J = 9.2 Hz, 1H), 7.98 (d, J = 2.8 Hz, 1H), 7.13 (d, J = 2.8 Hz, 1H), 7.04−7.00 (m, 2H), 6.90 (s, 1H), 4.03 (s, 3H), 3.92 (s, 3H), 1.52 (s, 9H), 1.40 (s, 9H). The mechanism of formation of intermediate **E** is similar to the Wittig reaction and proceeds through a four-membered

transition state. Compounds **W1** and **W2, Y1** and **Y2** share identical structural fragments and differ only in substituents.

II-4.2 For synthetic scheme "a" determine:
a) structures of **B**–**D**, **W1**, **Y1**, and **X1**;
b) conditions for reactions **I**–**III**.

II-4.3 For synthetic scheme "b" determine:
a) structures of **E**–**H**, **W2**, **Y2**, and **X2**;
b) conditions for reactions **IV** and **V**.

From **X1** and **X2**, Katsuki and his team proposed variants of dendrochrysanene synthesis, as shown in the scheme below. However, only one of the schemes was implemented experimentally.



II-4.4 Determine the structures of **X3**, **X4**, and **X**, if **X4** and **X** differ by one type of substituent (**R1**, **R2**, or **R3**), and **X1** and **X** share one identical type of substituent (**R1**, **R2**, or **R3**).

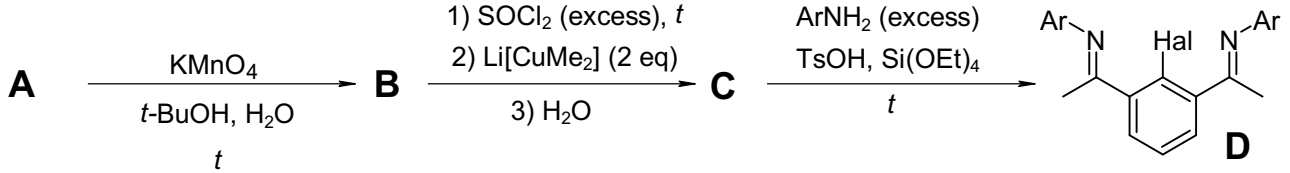
II-4.5 Hypothesize final step of which scheme ("a" or "b") could not be carried out by the researchers. Justify your answer by selecting the correct statements.

a	Scheme "a" is impossible, since substituent **R1** does not react with BBr_3
b	Scheme "a" is impossible, since substituent **R2** does not react with BBr_3
c	Scheme "b" is impossible, since substituent **R3** does not react with CuBr/NaOMe
d	Substituent **R3** reacts neither with CuBr/NaOMe nor with BBr_3, since it is sterically hindered
e	Substituents **R1** and **R2** do not react with BBr_3 because of their positions in the aromatic ring
f	Substituent **R3** reacts neither with CuBr/NaOMe nor with BBr_3, because of its position in the aromatic ring
g	Scheme "a" is impossible because of many side reactions
h	Scheme "b" is impossible because of many side reactions

Problem II-5

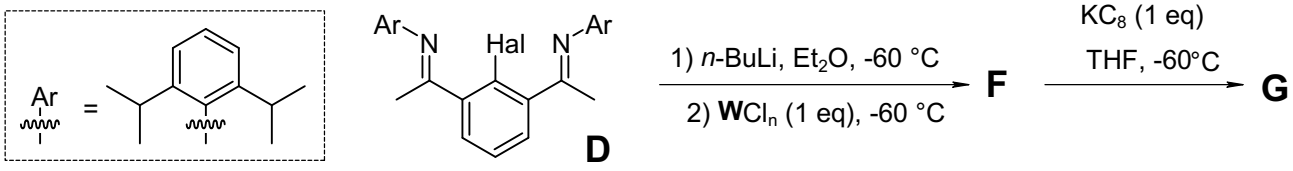
Question	II-5.1	II-5.2	II-5.3	II-5.4	II-5.5	II-5.6	II-5.7	II-5.8	II-5.9
Points	3	3	0.5	2	1	3	0.5	1	1

Many "unusual" chemical compounds may be synthesized if the right ligand environment is set around the reactive site of the molecule. One of such ligands is compound **D**, synthesis of which is presented below.



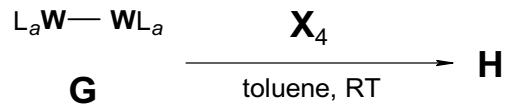
II-5.1 Draw the structures of **A**–**C**. **A** and **B** contain the same number of carbon atoms; in **A**, $\omega_C = 51.92\%$ and $\omega_{Hal} = 43.18\%$ (Hal = a halogen).

The ligand **D** was used to stabilize element **W** in the unusual oxidation state in compound **G**.



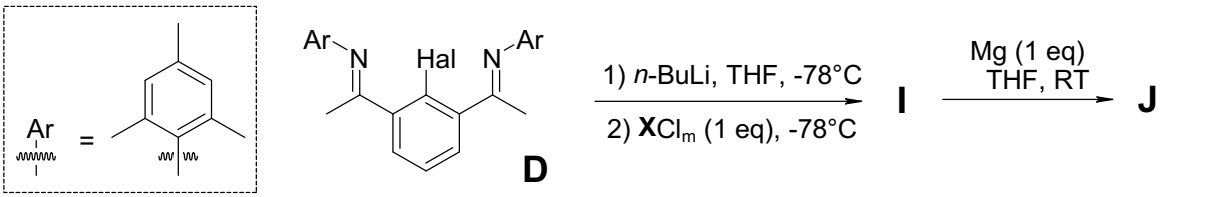
II-5.2 Decipher the formula of **W**Cl$_n$, draw the structures of **F** and **G**.
II-5.3 Write the oxidation state (OS) of the element **W** in **G**.

G is a reactive molecule containing a **W**–**W** bond. It produces **H** in the reaction with **X**$_4$.



II-5.4 Draw the structures of **X**$_4$ and **H**. Use the abbreviation of **G** presented in the scheme. Only one bond in **X**$_4$ is cleaved during the reaction.
II-5.5 H exhibits only two peaks in the **X**-NMR spectrum. From the list given hereunder, choose the multiplicity for a) peak 1, b) peak 2, if the spin of the NMR-active **X** nucleus is ½. Consider only the **X**–**X** coupling. *The peak numbering in the Answer Sheet is arbitrary.*
s – singlet, d – doublet, t – triplet, q – quartet, p – quintet, dd – doublet of doublets

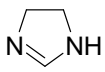
Similar reaction sequence may be set up for halide of the element **X** as presented below.



II-5.6 Decipher the formula of **X**Cl$_m$, draw the structures of **I** and **J**.
II-5.7 From the below list, choose heterocycle(s), which is/are isoelectronic and isostructural to the heterocyclic core of the compound **J**.

1

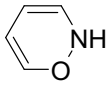
2



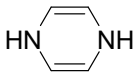
3

4

5



6



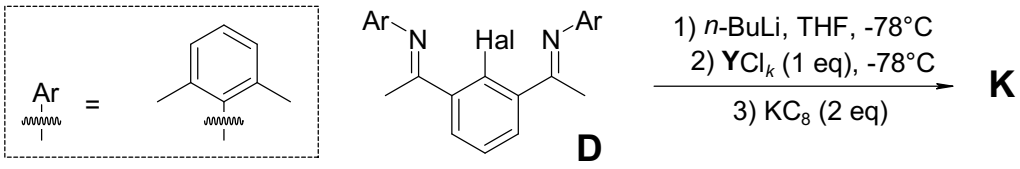
7

8

II-5.8 J has unsymmetrical structure in solid state, which is confirmed by X-ray crystallography. However, there are only 9 peaks in ^{13}C NMR instead of expected 16 peaks in the region above 100 ppm. Choose the reason(s) for this phenomenon.

a) Symmetry of **J**
b) Fast isomerism of a double bond
c) Fast rotation about a single bond
d) Monomer–oligomer equilibrium
e) Fast tautomerism

The compound **K** is obtained via the similar path from chloride of the element **Y**.



II-5.9 Draw the structure of **K**.

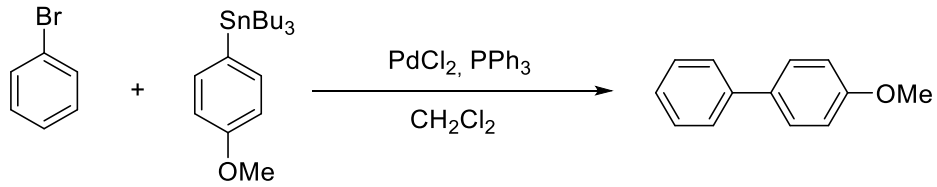
Notes:

- KC_8 is potassium metal intercalated in graphite.
- **W**−**W** bond may be hypothetically triple in **G** (however, it is not the case).
- **G**, **J**, and **K** give negative Beilstein test and are not isostructural.
- The element **X** has exactly 3.4 times less protons in the nucleus than **Y**.
- **Y** and **X** belong to the same group of the Periodic table.
- **W** and **Y** have difference in one proton in the nuclei.
- The elements **W**, **X**, and **Y** do not have their highest oxidation state in any of the compounds mentioned in the task; the described halides are stable at room temperature.
- Use "Ar" to represent the aryl group.

Problem II-6

Question	II-6.1	II-6.2	II-6.3	II-6.4	II-6.5	II-6.6	II-6.7	II-6.8	II-6.9
Points	2	1	1	1	0.5	3	1.5	3	2

Ligands surrounding the metal play a key role in metal complex catalysis. However, their effect on the course of the reaction is not always as straightforward as it may appear at first glance. Let us consider, as an example, the Pd-catalyzed Stille reaction:



It is known that the rate of this reaction decreases markedly both at excessively high and at excessively low concentrations of triphenylphosphine in the reaction mixture.

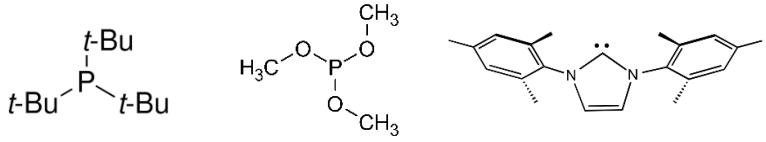
II-6.1 Provide the mechanism of the catalytic cycle of the Stille reaction that explains the decrease in the reaction rate at very high concentrations of triphenylphosphine. Encircle the step, the rate of which decreases with an increase in phosphine concentration.

II-6.2 At too low a concentration of triphenylphosphine in the reaction mixture, an elementary substance **Z** is formed, which noticeably reduces the reaction rate. Draw the formula of **Z**.

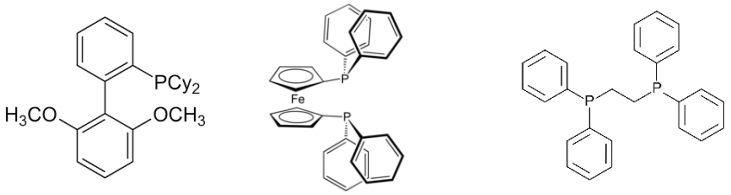
Oxidative addition is one of the main steps of Pd-catalyzed reactions. Aryl chlorides are much cheaper and more readily available than the corresponding bromides and iodides, thus activation of aryl chlorides is an important challenge in metal complex catalysis. However, the oxidative addition of aryl chlorides to standard triphenylphosphine palladium complexes is hindered due to the high strength of the carbon–chlorine bond; therefore, ligands that render

the complex more reactive by creating coordinatively unsaturated species are used to carry out reactions with aryl chlorides.

II-6.3 Which of the given ligands allow for the formation of coordinatively unsaturated complexes capable of undergoing oxidative addition with aryl chlorides?



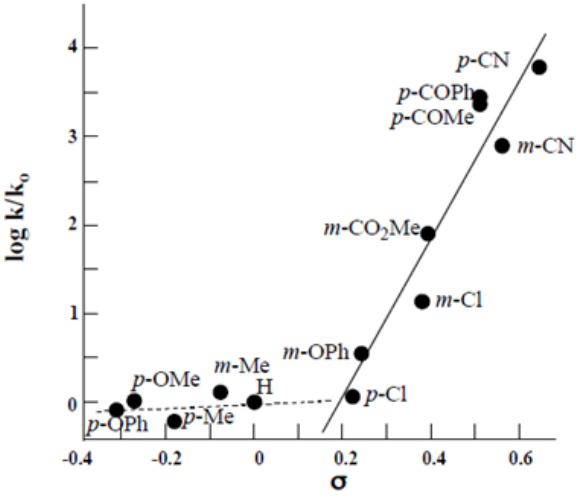
A **B** **C**



D **E** **F**

Oxidative addition is not an elementary step and can proceed via different mechanisms. a) Concerted three-center addition and b) nucleophilic aromatic substitution are the two most frequently encountered mechanisms. To determine which one is operative, one can assess the influence of the electronic effects of substituents in the aryl halide. For a quantitative assessment of the electronic effect of a substituent, it is convenient to use the Hammett constants σ, calculated from the acidity constants of substituted benzoic acids: $\sigma_X = \lg\left(\frac{K_X}{K_H}\right)$, where σ_X is the Hammett constant for substituent X, K_H is the acidity constant of unsubstituted benzoic acid, and K_X is the acidity constant of the benzoic acid containing substituent X in the ring.

The figure shows the dependence of the logarithm of the ratio of the rate constants for the oxidative addition of the triphenylphosphine nickel complex to aryl chlorides on the Hammett constant of the substituent in the aryl chloride (*m* – *meta*-position, *p* – *para*-position, *k* – rate constant for the reaction with the substituted aryl chloride, k_0 – rate constant for the reaction of chlorobenzene).

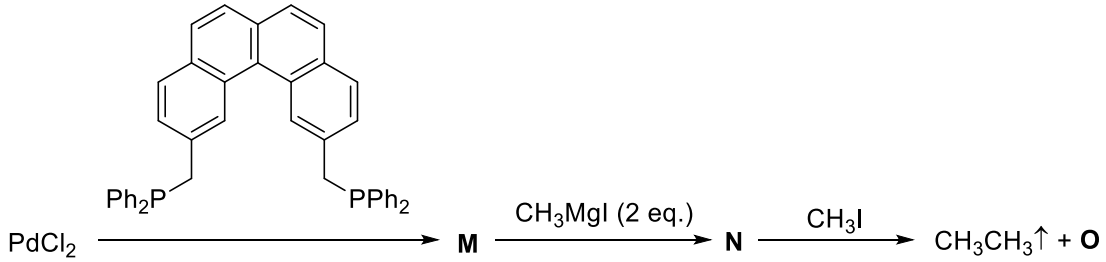


II-6.4 Match each substituent with the mechanism of oxidative addition to the corresponding aryl chloride. Complete the table in the Answer Sheet.

II-6.5 For which substituent is it impossible to unambiguously establish the mechanism of oxidative addition using this method?

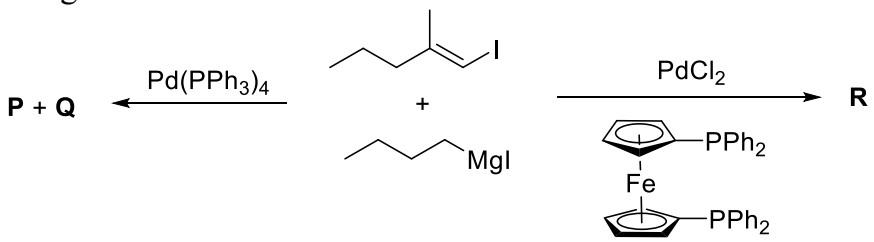
Reductive elimination, through which a new carbon–carbon bond is typically formed, is another key step in Pd-catalyzed reactions. In this case, the nature of the ligand can dramatically affect the course of the reaction. For example, the palladium complex **N**, whose

synthesis scheme is shown below, does not undergo reductive elimination even at high temperatures. However, **N** is observed to release ethane upon treatment with iodomethane.



II-6.6 Provide the structures of complexes **M**, **N**, and **O** that reflect their spatial arrangement.
II-6.7 a) Provide the mechanism for the formation of ethane in the final stage.
b) Encircle "Y" is this reaction is catalytic, encircle "N" is this reaction is not catalytic.

The choice of ligand for the palladium catalyst can influence the reaction pathway. The reaction between butylmagnesium iodide and vinyl iodide may lead to different products depending on the ligand chosen:



II-6.8 Draw the structures of the organic products **P**, **Q**, and **R**.
II-6.9 Provide the mechanism for the formation of **P** and **Q**.

PHYSICAL CHEMISTRY

Problem II-7

Question	II-7.1	II-7.2	II-7.3	II-7.4	II-7.5	II-7.6	II-7.7
Points	3	2	2	1	2	1	4

According to the Boltzmann distribution, the probability to find a molecule of an ideal gas in a state with energy E_n is given by the formula

$$\rho(E_n) = \frac{1}{Q}\exp\left(-\frac{E_n}{k_B T}\right),$$

where $k_B = 1.381 \cdot 10^{-23}$ J/K is the Boltzmann constant; Q is the molecular partition function (the sum over all states). The expression for Q follows from the normalization constraint (the sum of all probabilities equals one).

II-7.1 Derive the expression for the vibrational partition function Q_{vib}, assuming that the vibrational energy is measured from the ground (lowest, $n = 0$) state.

At high vibrational frequencies and room temperature, the overwhelming majority of particles is in the ground state ($n = 0$); therefore, the contributions of all other states can be neglected.

II-7.2 At what temperature (K) will 99.9% of all particles be in the zero (ground) vibrational state, if the vibrational frequency is 3000 cm^{-1}?

Knowledge of the partition function allows one to calculate any thermodynamic function of the harmonic oscillator, in particular the Gibbs free energy (per an oscillator):

$$G = G_0 + G_{vib} = G_0 - k_B T \ln Q_{vib},$$

where G_{vib} is the vibrational contribution to the Gibbs energy, and G_0 includes all other contributions, including the constant that defines the energy reference level.

II-7.3 Assuming now that the vibrational energy is measured from the bottom of the oscillator's potential well, obtain an expression for G_{vib} in two cases: a) all vibrational states are taken into account; b) all molecules are in the ground state.

The vibrational contribution to the Gibbs energy explains the isotope effect, that is the change in the equilibrium constant upon isotopic substitution, since the vibrational frequency (and, consequently, the Gibbs energy) changes.

II-7.4 Which types of energy of a gas will change upon isotopic substitution?

a. Electronic
b. Kinetic
c. Rotational
d. Intermolecular interaction

Table 1 lists the ionization constants of light and heavy water at different temperatures.

Table 1.

T, °C	10	15	20	25	30	35	40	45	50
$pK_w(H_2O)$	14.53	14.34	14.17	14.00	13.83	13.68	13.54	13.40	13.27
$pK_w(D_2O)$	15.50	15.30	15.12	14.95	14.78	14.63	14.48	14.33	14.20

II-7.5 Find the change in enthalpy (J/mol) and entropy (J/(mol·K)) upon the ionization of light and heavy water.
II-7.6 Estimate the neutral pH and pD values for light and heavy water at 100°C.

In Table 2 the vibrational frequencies (in cm^{-1}) for various species are given.

Table 2.

H_2O	D_2O	H_3O^+	D_3O^+
3755.79	2788.05	3463.34	2606.72
3656.65	2671.46	3421.13	2582.81
1594.59	1178.33	3408.18	2466.45
		1605.61	1184.99
		1602.56	1183.82
		567.04	504.46

II-7.7 Using the data from Table 2 and the previous parts of the task, estimate the vibrational frequencies (cm^{-1}) of the OH^- and OD^- ions. *If you failed to answer **II-7.5**, use the following values: for light water $\Delta H = 49210$ J/mol and $\Delta S = -77.15$ J/(mol·K); for heavy water $\Delta H = 50790$J/mol and $\Delta S = -90.07$ J/(mol·K).*

Notes:
a) Masses of isotopes (a.m.u.): m(H) = 1.0078, m(D) = 2.0141, m(O) = 15.9949.
b) The sum of a geometric progression with ratio $-1 < q < 1$:

$$\sum_{n=0}^{\infty} q^n = \frac{1}{1-q}.$$

c) The energy of the n-th level of an oscillator with frequency ν (n = 0, 1, 2, ...):

$$E_n = h\nu\left(n + \frac{1}{2}\right).$$

d) The vibrational frequency of the A–B bond:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}},$$

where k is the force constant and $\mu = m_A m_B / (m_A + m_B)$ is the reduced mass.
e) 1 $cm^{-1} = 2.9979 \cdot 10^{10}$ Hz $= 1.986 \cdot 10^{-23}$ J.
f) If a polyatomic molecule has several types of vibrations, then the contributions from each vibration are summed in the harmonic approximation.

Problem II-8

Question	II-8.1	II-8.2	II-8.3	II-8.4	II-8.5	II-8.6	II-8.7
Points	2	2	2	2	2	2	3

Dissociation is often the first step in substitution reactions in cyclic complexes. In the case of bidentate ligands, dissociation proceeds stepwise as $M(A_2)_n \rightleftarrows M(A_2)_{n-1} + A_2$ (k_1, k_2, …, k_n), is catalyzed by H^+, and the rates of the steps depend on the ligand field stabilization energy (LFSE, with values for the *d*-orbitals shown in the table).

Complex polyhedron	Energy of *d*-orbitals (in *Dq* units)				
	d_{x2-y2}	d_{z2}	d_{xy}	d_{yz}	d_{zx}
Octahedron	6.00	6.00	−4.00	−4.00	−4.00
Square	12.28	−4.28	2.28	−5.14	−5.14
Tetrahedron	−2.67	−2.67	1.78	1.78	1.78

II-8.1 a) Choose the CFT diagram for Fe^{2+} and Ni^{2+};
b) calculate the LFSE (*Dq*) in $M(A_2)_3$ and $M(A_2)_2$;
c) write the relationships between LFSE to explain why in the case of $Fe(A_2)_3$ $k_1 < k_2$, while in the case of $Ni(A_2)_3$ $k_1 > k_2$.

The dissociation steps are reversible. The reverse reaction (k_{-1}) can be prevented by using electrophilic or nucleophilic reagents to accelerate the dissociation (schemes):

$M(A{-}A) \rightleftarrows [{-}M{-}A{-}A{-}]$ (k_1, k_{-1});
$[{-}M{-}A{-}A{-}] + \mathbf{B} \rightarrow [B{-}M{-}A{-}A{-}]$ (k_2);
$[B{-}M{-}A{-}A{-}] \rightarrow MB + A{-}A$ (k_3) scheme 1;

$M(A{-}A) \rightleftarrows [{-}M{-}A{-}A{-}]$ (k_1, k_{-1});
$[{-}M{-}A{-}A{-}] + \mathbf{D} \rightarrow [{-}M{-}A{-}A{-}D]$ (k_2');
$[{-}M{-}A{-}A{-}D] \rightarrow M + D\,(A{-}A)$ (k_3') scheme 2.

II-8.2 Among H^+, OH^-, CN^-, Zn^{2+}, and Cu^{2+}, indicate which are a) electrophilic and b) nucleophilic reagents. State which type of reagents (a or b) **B** belongs to.

The substitution reactions $MY^{2-} + Me^{2+}$ (Y^{4-} is ethylenediaminetetraacetate) are not always catalyzed by H^+. For example, the reaction $PbY^{2-} + Zn^{2+}$ proceeds via two pathways. The first is catalyzed by an acid and includes the cleavage of the Pb−OCO bond (k_1, k_{-1}), protonation (k_2), and attack by Zn^{2+} (k_3). The second pathway is independent of $[H^+]$, and its rate is equal to $\frac{dc_{ZnY^{2-}}}{d\tau} = \frac{k_4 k_1 c_{PbY^{2-}} c_{Zn^{2+}}}{k_{-1} + k_4 c_{Zn^{2+}}}$.

II-8.3 Using the method of stationary approximations, derive the kinetic equation of the first reaction path of the reaction $PbY^{2-} + Zn^{2+}$:

Pb−OCO bond cleavage $PbY^{2-} \rightleftarrows (PbY{-})^{2-}$ (k_1, k_{-1});
protonation $(PbY{-})^{2-} + H^+ \rightarrow (PbY{-}H)^-$ (k_2);
attack by Zn^{2+} $(PbY{-}H)^- + Zn^{2+} \rightarrow ZnY^{2-} + Pb^{2+} + H^+$ (k_3).

II-8.4 Propose a mechanism for the other pathway.

For $NiY^{2-} + Zn^{2+}$ (Cu^{2+}) in the pH range 3–6 at 25°C, the data were obtained for the observed rate constant k_{obs}, (L/(mol·s)) as a function of pH: $1.56\cdot10^{-6}$ (3.00); $2.23\cdot10^{-6}$ (4.00); $2.40\cdot10^{-6}$ (5.00). An associative mechanism with the rate equation

$\frac{dc_{\mathrm{ZnY^{2-}}}}{d\tau} = (k_5[\mathrm{NiY^{2-}}] + k_6[\mathrm{NiHY^-}])c_{\mathrm{Zn^{2+}}}$ was proposed, which adequately explains the pH dependence of the rate.

II-8.5 a) Derive the equation for calculating and b) calculate the dissociation constant (K_a) for $NiHY^- \rightleftarrows NiY^{2-} + H^+$, if the formation constants for the complexes NiY^{2-} ($\beta_1 = 4.2\cdot10^{18}$) and $NiHY^-$ ($\beta_2 = 3.6\cdot10^{11}$), as well as the dissociation constant of the ligand HY^{3-} ($K_4 = 5.5\cdot10^{-11}$), are known.

II-8.6 Derive the equation for k_{obs} that depends solely on K_a and $[H^+]$, and calculate k_5 and k_6.

The intermediate is formed only in the pathway with k_5, in which first an associate is formed reversibly (K), and then the reaction product is formed (k). It turned out that for the reaction of NiY^{2-} with Me^{2+}, the relationship between K and k_5 is linear: $\lg k_5 = -12.35 + 1.01\cdot\lg K$.

II-8.7 Derive the kinetic equation, and calculate K and k.

Problem II-9

Question	II-9.1	II-9.2	II-9.3	II-9.4	II-9.5	II-9.6	II-9.7
Points	1	3	1.5	1.5	3	3	2

Chemical and physical properties of substances can depend significantly on the size of a sample. A decrease in the melting temperature has been observed for nanocrystals of Ag, Al, Au, Bi, Cu, Ga, In, Pb, and Sn. From a thermodynamic point of view, the transition from the solid to the liquid state with increasing temperature begins with the appearance of a thin liquid layer on the surface of a nanoparticle while its core remains solid. This phenomenon is caused by the surface tension at the solid phase/liquid interface, which alters the energy of the system. For spherical and cylindrical nanoparticles, the Gibbs energy is higher than that of the macrophase due to the excess surface pressure (p):

$$G_{\mathrm{solid}} = G^{\infty}_{\mathrm{solid}} + pV_{\mathrm{m}}$$

The excess pressure for spherical (p_1) and cylindrical (p_2) particles of radius r can be calculated using Laplace's equation:

$$p_1 = \frac{2\sigma}{r}, \qquad p_2 = \frac{\sigma}{r},$$

Here, σ is the surface tension at the solid phase/liquid phase interface.

II-9.1 Calculate the excess pressure (atm) at the specified interface at the melting temperature for a) a gold wire with the diameter of 0.5 mm; b) gold nanoparticles with the diameter of 15 nm. The surface tension of gold is 3 mN/cm.

The dependence of the melting temperature of gold nanoparticles on the radius r can be described by the Gibbs–Thomson equation:

$$T_{\mathrm{melt}} = T^{\infty}_{\mathrm{melt}}(1 - a/r),$$

where $T^{\infty}_{\mathrm{melt}}$ is the melting temperature of the macrophase, and a is a parameter that depends on V_{m}, σ, and ΔH_{melt} and is equal to $4.88\cdot10^{-10}$ m. Equilibrium between the two phases at constant pressure and temperature is achieved when the molar Gibbs energies of the substance in these phases are equal. For example, at a melting temperature

$$G_{\mathrm{solid}}(T_{\mathrm{melt}}) = G_{\mathrm{liq}}(T_{\mathrm{melt}}), \qquad \Delta S_{\mathrm{melt}} = \Delta H_{\mathrm{melt}}/T^{\infty}_{\mathrm{melt}}.$$

II-9.2 Determine the density of gold (kg/m^3), if $\Delta H^{\mathrm{Au}}_{\mathrm{melt}} = 12.55$ kJ/mol. Hint: derive the equation for the dependence of the melting temperature on the radius of the nanoparticles (the Gibbs–Thomson equation) and obtain an expression for the parameter *a*.

The melting temperatures of gold as nanoparticles with a radius of 6.5 nm and as the macrophase differ by 100°C.

II-9.3 Determine the standard entropy of melting of gold (J/(mol·K)).

II-9.4 Calculate the standard electrode potential (V) of the AuI_2^-/Au pair at 25°C, given that $E^0_{\mathrm{Au^+/Au}} = 1.69$ V and $\beta_{\mathrm{AuI_2^-}} = 5.6 \cdot 10^{18}$.

II-9.5 Write the ionic equation for the dissolution reaction of a gold nanowire with the diameter of 10 nm in a solution of KI_3 (1 M) + KI (1 M) and calculate its equilibrium constant at 25°C. The surface tension at the solid phase/water interface for gold is 0.55 N/m, $E^0_{\mathrm{I_2/2I^-}} = 0.536$ V, $\beta_{\mathrm{I_3^-}} \approx 1$. *If you failed to determine the density of gold in* ***II-9.2****, assume it to be 19000 kg/m*^{3}.

The electrical conductivity of nanofilms drops significantly with decreasing their thickness. The presence of lattice defects arising from an increased surface-to-volume ratio is one of the factors for the increase in the resistance. The classical theory of size effects in the electrical conductivity of thin films is known as the Fuchs–Sondheimer model. For the resistivity of a thin film with thickness *d* and an electron mean free path *l*, the following empirical equation has been obtained:

$$\rho = \rho_0 \cdot \left(1 + \frac{3l}{8d}\right).$$

The electron mean free path can be estimated by the formula:

$$l = k \cdot \sqrt[3]{\frac{3}{8\pi}} \cdot \frac{h}{e^2 \cdot \sqrt[3]{n^2}} \cdot \sigma_0,$$

where σ_0 is the electrical conductivity of the macrophase (in 1/(Ω·m)), *e* is the electron charge ($1.602 \cdot 10^{-19}$ C), *n* is the concentration of conduction electrons (1/m^3), *h* is Planck's constant ($6.626 \cdot 10^{-34}$ J·s), and *k* is a proportionality factor ($8.69 \cdot 10^5$).

Below are the values of the electrical conductivity of gold nanofilms of various thicknesses:

σ, 1/(Ω·m)	36.10	39.82	41.35	42.24	44.15	44.85
d, nm	40	60	80	100	140	180

II-9.6 Calculate the resistivity of the macrophase ρ_0 (in Ω·m) and the electron mean free path in gold (in nm).

II-9.7 Calculate the number of conduction electrons (N_e) per gold atom in the thin film. *If you failed to determine the resistivity of macrophase ρ_0 and the electron mean free path l, assume them as 0.0182 Ω·m and 40 nm, respectively, for further calculations.*

INORGANIC CHEMISTRY

Problem II-10

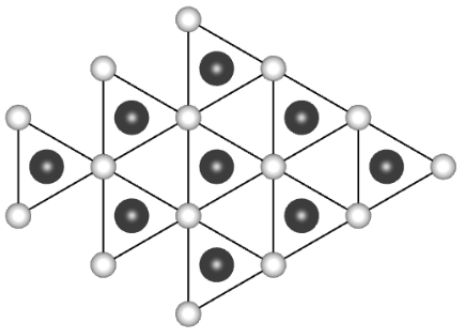
Question	II-10.1	II-10.2	II-10.3	II-10.4	II-10.5	II-10.6	II-10.7	II-10.8
Points	1	0.5	3.5	2.5	0.5	4.5	2	0.5

In 2025, the Division of Inorganic Chemistry at the Chemistry Department, Lomonosov Moscow State University celebrates its 150th anniversary. Let us consider several outstanding works done by the Division researchers.

The distinguished academician I.A. Kablukov was one of the first heads of the Division (1917–1926); some of his works were devoted to the theory of solutions. He investigated the electrical conductivity of electrolyte solutions in non-aqueous media and introduced the concept of ion solvation.

II-10.1 Arrange the following solutions in order of increasing their molar electrical conductivity: 0.01 M NaCl in water, 0.01 M NaCl in ethanol, 0.01 M $[PdCl_2(NH_3)_2]$ in water, 0.01 M $CaCl_2$ in water, 0.01 M H_2SO_4 in water.

Academician V.I. Spitsyn, the head of the Division (1942–1988), is the founder of the chemistry of rare and trace elements in Russia. Spitsyn's works made a background for production of metal **M1** from the binary mineral **A**, which has a layered structure with van der Waals interactions between the layers only. Each layer consists of trigonal prisms joined along common edges, with an **M1** atom located at the center of each prism. The figure shows a top view over such a layer.



II-10.2 Determine the ratio of atoms in **A**.

The technology of obtaining **M1** involves calcination of mineral **A** (which contains 60 wt% of **M1**) in oxygen to produce oxide **B**. To purify the oxide, **B** is dissolved in ammonia to yield the crystalline product **C**; **C** reverts to **B** upon thermal decomposition. Reduction of **B** with hydrogen at heating is the final production step.

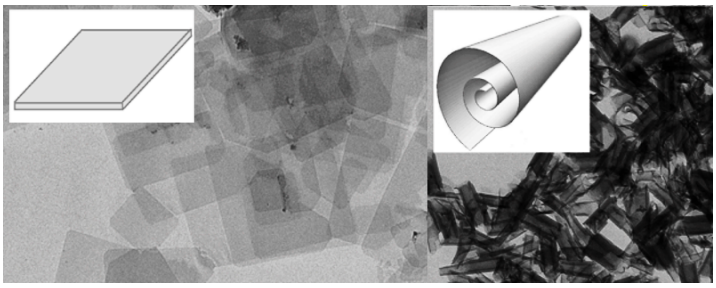
II-10.3 a) Decipher **M1** and write the formulae of **A**, **B**, and **C**; b) write the equations of the described reactions.

The works of academician A.V. Novoselova dated back to the 1930s–40s were devoted to the chemistry of rare metals and their compounds. She made a significant contribution to the study of the rare light metal **M2**, which does not react with water or steam but readily dissolves in a concentrated ammonium fluoride solution due to the formation of a stable water-soluble fluoride complex **X1**. **M2** is in tetrahedral environment of fluoride ions in the structure of **X1**. The problem of synthesizing the high-melting orthosilicate of **M2** from oxides was resolved by conducting the reaction under a gas-transport regime. The substance **X2**, a sodium analog of **X1**, was used as a transport agent. The formation of two main gaseous components **Y** and **Z**, from which the orthosilicate is produced, was proved by mass-spectrometry of this gas-transport reaction. The mass numbers of **Y** and **Z** are 89 and 82, respectively.

II-10.4 a) Determine **M2**, **X1**, **X2**, **Y**, and **Z**; b) write the equations for the dissolution of **M2** in NH_4F and the synthesis of the orthosilicate from **Y** and **Z**.
II-10.5 What is the structure of **Z** in the gas phase?
a) tetrahedron; b) trigonal planar; c) disphenoid; d) T-shape; e) octahedron; f) angular

The study of high-temperature superconductors is among the most important research directions at the Division since late 1980s. Thus, Corresponding Member of Russian Academy of Sciences E.V. Antipov and Dr. S.N. Putilin described a multi-step synthesis of compound **N**. Initially, compound **R** is obtained by sintering three salts, **S1**–**S3**, in a molar ratio of 2 : 1 : 2 at 925°C in an oxygen atmosphere; these salts contain identical anions. Subsequent sintering of **R** with the binary compound **T** in equimolar amounts at an oxygen pressure of 18 kbar and 880°C leads to the formation of **N**, which has a superconducting critical temperature T_C = 104 K. The mass fraction of the heaviest element in **N** is 26.97%. The ratio of the mass fractions of the cation and nitrogen in **S1** is 4.90. The mass fractions of cations in **S2** and **S3** are 16.97% and 26.30%, respectively. **T** cannot be obtained by the thermal decomposition of a salt containing the same anion as in **S1**–**S3**, but it can be prepared by treatment of that salt with an alkali. The mass percentage of the cation in **T** is 92.61%.

II-10.6 a) Write formulae of **N**, **S1**–**S3**, **R**, and **T**; provide your calculations. b) Write the reaction of the formation of **R**.



One of the most interesting works of recent years is devoted to nano-objects. Professor R.B. Vasiliev's research group obtained nanosheets and nanoscrolls of cadmium telluride with a sphalerite structure (a = 6.48 Å). The reaction proceeds between cadmium acetate and tellurium in trioctylphosphine, resulting in cadmium telluride nanosheets in which both surfaces consist solely of cadmium atoms. To stabilize the nanoparticles, each cadmium atom is coordinated by an anion of oleic (*cis*-9-octadecenoic) acid. A ligand exchange reaction with hexadecanethiol was performed to determine the thickness of the sheets. The mass loss of 4.148% was observed as a result of complete ligand replacement.

II-10.7 a) Write the ligand exchange reaction; b) calculate the thickness s of a single nanosheet (Å).
II-10.8 Production of which metals and their compounds:
a) **M1**, b) **M2**, c) metal in **T**, d) cadmium
requires specially strict safety measures to prevent their entry into the human body and the environment, which could lead to an ecological disaster?

Problem II-11

Question	II-11.1	II-11.2	II-11.3	II-11.4	II-11.5	II-11.6
Points	4	1	2	2	3	3

For a long time, chemists failed to obtain inorganic salts containing the anion **X**, an analog of a well-studied anion containing a neighboring element from the same group of the periodic table. The first reports on the synthesis of sodium salt **A** with this anion appeared as early as 1894. In this synthesis, the salt **B** (w(Na) = 41.07%) was used as the starting material. **B** was obtained by the reaction of sodium with the compound **C**, a gas (at 20.0°C, 100.0 kPa) with a characteristic odor. The authors assumed that **A** was formed as a result of the reaction between **B** and CO. In addition to **A**, water is produced in this reaction, which prevented the isolation of **A** from the reaction mixture, since water decomposes **A** into the salt **D** (w(Na) = 33.80%) and **C**. The authors considered the presence of **D** and **C** in the reaction products as indirect evidence for the formation of **A**.

II-11.1 Determine the formulae of **A**, **B**, **C**, and **D**. Give your calculations.
II-11.2 Write equations of the reactions that, according to the authors, occur during the synthesis of **A**.

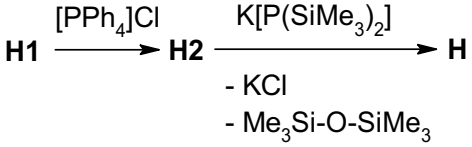
It took a very long time before the erroneous views of the authors reported the first synthesis of the salt **A** were disproved. Only in 2011 (117 years later!) the reaction between **B** and CO was re-investigated using modern analytical methods. It has been found that, instead of **A**, the salt **E** (w(Na) = 28.05%) is formed, along with trace amounts of the salt **F** (w(Na) = 27.37%).

II-11.3 Write a) the formulae of **E** and **F**; b) draw structural formulae of their anions. Give your calculations.

The acid **Y**, which contains the anion **X**, was more fortunate than **A**. The isolation of **Y** was reported for the first time in 1961. The composition and structure of **Y** were confirmed by IR spectroscopy, mass spectrometry, and elemental analysis. Moreover, the compound **G** was the sole product of the reaction of **Y** with an excess of hydrogen chloride at –110°C, which indirectly confirmed the composition and structure of **Y**.

II-11.4 Write a) equation of the reaction of **Y** with an excess of hydrogen chloride and b) draw the structural formula of **G**.

In 2004, the first successful two-step synthesis of the salt **H** was reported. The salt consists of a tetraphenylphosphonium cation (PPh_4^+) and an anion, which is an adduct of $B(CF_3)_3$ and **X**.



II-11.5 Draw the structures of **H**, **H1**, and **H2**.

Notably, **H** is stable for several days in moist acetonitrile. An attempt to obtain the potassium salt in the exchange reaction between **H** and $K[BPh_4]$ in the presence of moisture was unsuccessful and resulted in the formation of potassium salt **J** (w(K) = 11.64%) with a different anion.

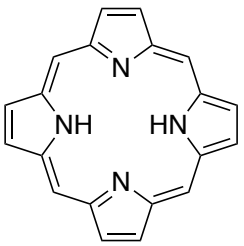
II-11.6 Draw the structure of the anion of salt **J**.

Problem II-12

Question	II-12.1	II-12.2	II-12.3	II-12.4	II-12.5
Points	2.25	2	8.25	1.5	1

The element **X** exhibits many allotropes; it forms one of the hardest and the most refractory elementary substances. Its chemistry is extremely complex and interesting from both practical and theoretical perspectives.

Hydrolysis-unstable needles **A** were obtained by fast heating of a mixture of **X** sulfide and S_8 (***reaction 1***). Although the substance is poorly studied and has found no practical application yet, it possesses a very interesting high-symmetry structure, somewhat like that of porphyrin. It contains no **X**−**X** bonds and no $-S_3-$ or $-S_4-$ fragments. The unit cell parameters of **A** are: $a = 12.158$ Å, $b = 4.089$ Å, $c = 21.961$ Å; angle = 107.65°, density $\rho = 1.9109$ g/cm³, number of formula units $Z = 2$.



porphyrin

II-12.1 a) Calculate the molar mass M (g/mol) of **A**;
b) decipher **X** and **A**;
c) draw structure of **A**;
d) write the equation of the ***reaction 1***.

The compound **B** is formed upon heating of stoichiometric amounts of Rb_2S, S_8, and **X** at 600°C (***reaction 2***). **B** consists of five-membered rings that are linked via common **X** atoms into polymer chains. The compound **C** is obtained in the case of heating of a mixture of Tl_2S, S_8, and **X** at 850°C (***reaction 3***). The structure of **C** is almost analogous to that of **B**: only an additional sulfur atom is incorporated in every third ring. There are no **X**−**X** bonds in **B**.

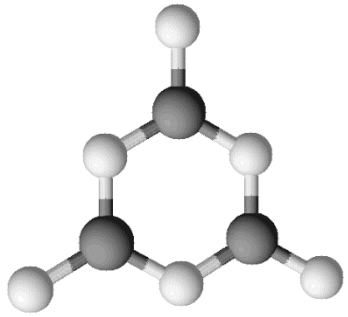
II-12.2 a) Determine **B** and **C**;
b) draw structure of the anion in **B**;
c) write equation of the ***reaction 2***;
d) write equation of the ***reaction 3***.

New compounds with anions containing the elements **X** and **Y** are intensively synthesized and investigated now, forming a rapidly developed branch of chemistry.

The compound **D** with the composition $Li_a\mathbf{X}_b\mathbf{Y}_c$ (where a, b, and c are natural numbers, they are consecutive terms of an arithmetic progression) is a well-known lithium-ion conductor, which can be used as electrolyte in lithium-ion batteries. This substance is obtained by heating a mixture of the binary compounds **E** and **F** to 750°C (***reaction 4***). Since **D** is the sole product in this reaction and is easily oxidized, its synthesis must be carried out under oxygen-free conditions. **F** hydrolyzes readily with the evolution of a gas.

Other compounds related to **D** are also actively studied due to their high mechanical strength and tunable transport properties, to be used as insulators, metallic conductors, or superconductors. The derivatives containing the element **Z** with the composition $\mathbf{Z}_m\mathbf{X}_n\mathbf{Y}_k$ (where m, n, and k are natural numbers) are of particular interest.

Z is a soft, silvery-white metal that exhibits two (besides 0) oxidation states in its compounds. **G** is often used at the first step of the synthesis of derivatives $\mathbf{Z}_m\mathbf{X}_n\mathbf{Y}_k$. **G** has a NaCl-type structure. Like **F**, **G** hydrolyzes easily with the evolution of a gas.



The compound **H** was obtained upon heating a mixture of **E** and **G** at 1273°C (***reaction 5***). In practice, **H** is used primarily as a precursor for obtaining other derivatives $\mathbf{Z}_m\mathbf{X}_n\mathbf{Y}_k$. For example, **H** is oxidized by bromine at 1073°C to form the compound **I** (***reaction 6***). The coefficient m is the same in the formulae of **H** and **I**, but they contain different anions. The structure of the anion in **I** is shown in the figure.

An attempt was made to obtain a non-stoichiometric compound **J** by reacting **H** with **F**, but the synthesis did not yield the expected result. **J** can be prepared theoretically by intercalation (insertion) of lithium into **I** by passing a 20.492 mAh of charge per 1000 mg of the final product. Ultimately, **J** was obtained by heating a mixture of **D** and the higher chloride of **Z** at 850°C (***reaction 7***).

The anion of **D** is linear; the product $A_r(\mathbf{Y}) \cdot A_r(\mathbf{X})$ is slightly lower than $A_r(\mathbf{Z})$, and the anions of **H** and **I** have the same simplest formula.

II-12.3 a) Calculate the molar mass M (g/mol) of **D**;
b) decipher the elements **Y** and **Z**, and the compounds **D**–**F**;
c) calculate the molar mass M (g/mol) of **J**
d) decipher **G**–**J**.

Reactions 5 and *7* are accompanied by the evolution of the same gas; **E** is formed in ***reaction 7***.

II-12.4 Write the equations of the ***reactions 4***–*7*.

II-12.5 a) Calculate the capacity (C, mAh/g) of LiC_6;
b) compare capacities of LiC_6 and **J** (choose among the options below).

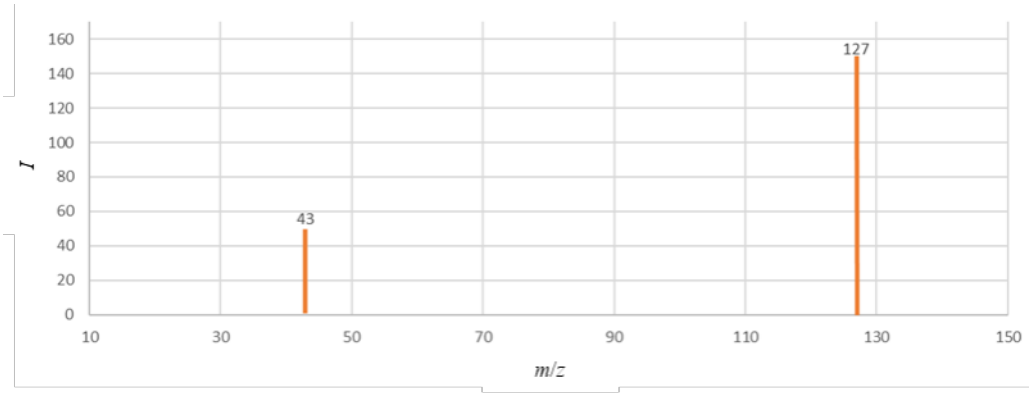
1) $C(LiC_6) > C(\mathbf{J})$
2) $C(LiC_6) < C(\mathbf{J})$
3) $C(LiC_6) = C(\mathbf{J})$
4) Insufficient data

ANALYTICAL CHEMISTRY

Problem II-13

Question	II-13.1	II-13.2	II-13.3	II-13.4	II-13.5	II-13.6	II-13.7
Points	3	2	2	2	3	1	2

An organic compound **A** is synthesized on an industrial scale and is mainly used in the production of polymer resins. This substance was also at the center of one of the largest food industry scandals that occurred in 2008. Investigations revealed that several manufacturers in one country were adding **A** to their dairy products to artificially increase the measured protein content. Unfortunately, this led to urinary system problems of thousands of children.
A contains three equivalent amino groups. The mass fraction of one of the elements in **A** is 66.67%. The mass spectrum of **A** (electrospray ionization, positive ion detection mode, *I* is relative intensity) is given below:



II-13.1 Determine the molecular formula of **A** and propose structures for the species corresponding to the *m*/*z* 43 and *m*/*z* 127 signals.

An analytical laboratory took milk samples containing **A** and conducted three analyses. In analysis No 1 based on the Kjeldahl method, a 2.00 g milk sample was heated with concentrated sulfuric acid. After treatment with a base, a gas **B** was released and absorbed by boric acid. The titration of the resulting tetraborate salt required 7.15 mL of 0.100 M HCl.

II-13.2 a) Provide the molecular formula of **B**.
b) Write the equation for its reaction with boric acid.
II-13.3 a) Write the equation for the titration reaction.
b) Calculate the nitrogen mass fraction (w(N), %) in the milk sample analyzed by the Kjeldahl method. *If you failed to obtain an answer, use the value of 1.00% in further calculations.*

Analysis No 2 was performed using the Sørensen method (formol titration), which allows determining the number of free amino groups ($R{-}NH_2$) in a protein. A 20.0 g milk sample was titrated with 0.100 M NaOH using phenolphthalein as an indicator until a faint pink color appeared, which required 9.60 mL of the titrant. Assume that at this point: all organic acids in the milk have been titrated; **A** is present in its neutral form; protein amino groups are protonated ($R{-}NH_3^+$). Then, 5.00 mL of an aqueous formaldehyde solution (37%, density 1.09 g/mL) was added, allowed to react for a few minutes, and titrated again until a faint pink color appeared. The total NaOH volume required for the first and second titrations was

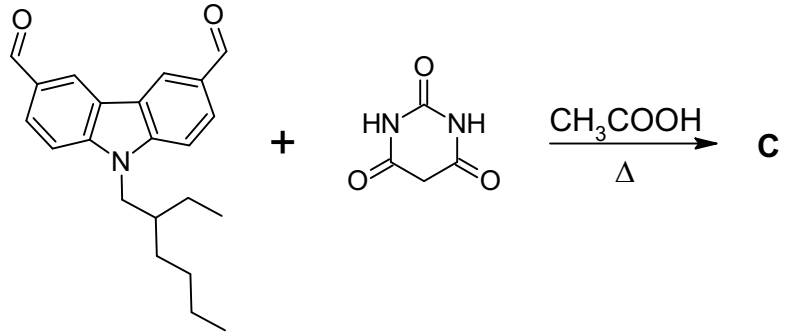
14.15 mL. To account for the neutralization of the formaldehyde solution, a control experiment was performed separately. The titration of 5.00 mL of the formaldehyde solution required 2.35 mL of 0.100 M NaOH.

II-13.4 Write the reaction equations that occur: a) upon the addition of formaldehyde; b) during subsequent titration with the base; c) in the control experiment.

A standard milk sample contains 3.20 g of protein per 100 g of milk. Free amino groups in proteins account for an average of 4.7% of the total nitrogen content, and the nitrogen mass fraction in protein is on average 15.7%.

II-13.5 a) Calculate the mass fraction of **A** (w(**A**), %) in the analyzed milk.
b) Determine the factor (x), by which the protein content in the analyzed milk is lower than the standard value.

Detecting compound **A** in various food matrices remains a challenging task requiring the development of cost-efficient and express methods. Fluorescent analysis is one of promising approaches, in which **A** binds to a sensor **C** via the formation of six hydrogen bonds. **C** is synthesized according to the following scheme:



II-13.6 Draw the structure of **C**.

The analytical laboratory performed analysis No 3 using the fluorescence method. For this, 200 μL of the milk sample was diluted with an organic solvent to a total volume of 5.00 mL. Then, 1.00 mL of the obtained solution was mixed with 1.00 mL of **C** solution to obtain ***solution 1***. In another 200 μL milk sample, 2.00 mL of a 500 ppm solution of **A** (1 ppm corresponds to 1 mg of a substance per 1 L of the solution) was added, followed by dilution to 5.00 mL. Then, 1.00 mL of the resulting solution was mixed with 1.00 mL of **C** solution to obtain ***solution 2***. The fluorescence intensity of ***solution 1*** was I_1 = 3.46 a. u. (arbitrary units), while ***solution 2*** had I_2 = 4.87 a. u. The fluorescence intensity of the control solution, i.e., without milk and **A**, was I_0 = 2.72 a. u.

II-13.7 Calculate the concentration of **A** (c(**A**), mg/mL) in the analyzed milk according to the fluorescence method.

Problem II-14

Question	II-14.1	II-14.2	II-14.3	II-14.4	II-14.5
Points	2	2	3	6	2

Answering all the questions in this problem, provide your calculations.

The necessary physical and chemical conditions for the formation of calcium phosphates occur near the bottom sediments of water reservoirs with high biological productivity. In these relatively shallow areas, phosphorus is bioconcentrated. The biogenic material formed by organisms contains a significant amount of phosphorus and due to shallow depths quickly reaches the bottom with minimal loss of phosphorus. As a result, concentrations of the dissolved mineral phosphorus of up to 5–10 mg/L are registered near the bottom sediments, which is sufficient to form even the most soluble (amorphous) apatite. Phosphate minerals also include monazite ($CePO_4$) and francolite, a carbonate-rich form of fluorapatite.

The solubility of salts containing anions of weak acids depends on pH. To calculate such solubilities, the protonation of anions of the weak acid must be taken into account, which shifts the dissolution equilibrium towards the products. The values of the mole fractions of anions at different pH values are given at the end of the problem. Ignore the change in pH of water during dissolution, the content of extraneous ions, and the hydrolysis of the cation in all subsequent parts of the problem, if not stated otherwise.

II-14.1 Monazite was discovered in the South Ural Mountains close to the city of Miass. 28.82 mg of monazite is dissolved in 1 m^3 of pore water with pH 7.46 initially containing 2 μg/L of the inorganic phosphorus. Calculate the solubility product of monazite $K_{sp}^{monazite}$.

II-14.2 Noting the molar solubility of francolite ($Ca_{9.54}Na_{0.33}Mg_{0.13}(PO_4)_{4.8}(CO_3)_{1.4}F_{2.48}$) by s, express the solubility product $K_{sp}^{francolite}$ in terms of s and the mole fractions of the anions $\alpha_{PO_4^{3-}}$, $\alpha_{CO_3^{2-}}$, and α_{F^-}.

II-14.3 Determine the total concentration (mg/L) of inorganic phosphorus formed by dissolution of francolite $Ca_{9.54}Na_{0.33}Mg_{0.13}(PO_4)_{4.8}(CO_3)_{1.4}F_{2.48}$:

a) in pore waters of Lake Turgoyak (Chelyabinsk region, Russia) with pH 7.46.

b) in acidic waters of the Leviathan mine (California, USA) with pH 3.83.

$K_{sp}^{francolite} = 10^{-94.7}$.

It is known that isomorphic substitution of PO_4^{3-} by CO_3^{2-} because of an increased carbonate alkalinity is accompanied by an increase in the solubility of apatites. For francolites ($Ca_{10}(PO_4)_{5.83-0.57x}(CO_3)_xF_{2.52-0.3x}$), the hereunder linear relationship between $\log_{10} K_{sp}$ of francolite and corresponding fluorapatite ($x = 0$) was found:

$$\log_{10} K_{sp}^{francolite} = \log_{10} K_{sp}^{fluorapatite} + kx,$$

where k is the proportionality factor.

To study the dependence of francolite solubility on the degree of isomorphic substitution of PO_4^{3-} by CO_3^{2-}, the composition of mine waters from the Lovozero alkaline massif (Kola Peninsula, Russia) with pH 11.74 was investigated (note that these waters can be considered as a saturated solution over francolites):

x	0.25	0.5	1	1.25
$[Ca^{2+}]$, M	$4.60 \cdot 10^{-7}$	$9.05 \cdot 10^{-7}$	$1.72 \cdot 10^{-6}$	$2.75 \cdot 10^{-6}$

Assume that the Ca^{2+}, PO_4^{3-}, CO_3^{2-}, and F^- ions are formed in solution only due to dissolution of francolite.

II-14.4 Determine $K_{\text{sp}}^{\text{fluorapatite}}$ and the proportionality factor *k*. *If you failed to determine* $K_{sp}^{fluorapatite}$ *and k, use* 10^{-130} *and 13.0, respectively, in subsequent calculations.*

The Leviathan Mine was reported to produce some few million liters of acidic water each year. During spring and fall, precipitation volumes increase significantly, which results in up to 15 million liters of acid mine waters generated annually.

II-14.5 Calculate K_{sp} for the francolite $Ca_{10}(PO_4)_{5.4}(CO_3)_{0.75}F_{2.3}$. How many years (*t*) are needed to have 50 tons of this mineral dissolved in the Leviathan mine?

Notes:
a) Mole fractions of anions at different pH values:

Mole fraction	pH 3.83	pH 7.46	pH 11.74
$\alpha_{PO_4^{3-}}$	$3.56\cdot10^{-12}$	$2.34\cdot10^{-5}$	0.41
$\alpha_{CO_3^{2-}}$	$9.52\cdot10^{-10}$	$1.25\cdot10^{-3}$	0.96
α_{F^-}	0.817	1	1

b) The mole fraction for the anion: $\alpha_{A^{n-}} = \frac{[A^{n-}]}{[A^{n-}]+\ldots+[H_nA]} = \frac{[A^{n-}]}{c_0^{A^{n-}}}$

Problem II-15

Question	II-15.1	II-15.2	II-15.3	II-15.4	II-15.5
Points	5.5	2	2	3	2.5

Hydrocyanic acid HCN and its salts (cyanides) are lethal poisons that, when ingested, inhibit the enzyme of the respiratory electron transport chain and lead to cellular hypoxia. The maximum permissible daily dose of HCN is 0.6 mg per 1 kg of human body weight.
Various detection reactions are used to identify cyanide in solutions, such as described in ***Experiments 1–3***:

Experiment	Procedure	Observations
1	CN^- + reagent **A**, then reagent **B**	dark blue precipitate
2	CN^- + reagent **C**, then reagent **B**	blood-red coloration of the solution
3	reagent **D** + reagent **E**, then CN^-	dissolution of black precipitate, release of gas with a pungent odor

II-15.1 Select the appropriate reagents **A**–**E** from the list below (all proposed reagents are aqueous solutions):

NaOH	HNO_3(conc.)	HCl	$FeSO_4$	$Fe_2(SO_4)_3$
$(NH_4)_2S$	$(NH_4)_2S_2$	$K_2Cr_2O_7$	$KMnO_4$	$CuSO_4$

Write the ionic equations for the chemical reactions described in a) ***Experiment 1***, b) ***Experiment 2***, and c) ***Experiment 3***.

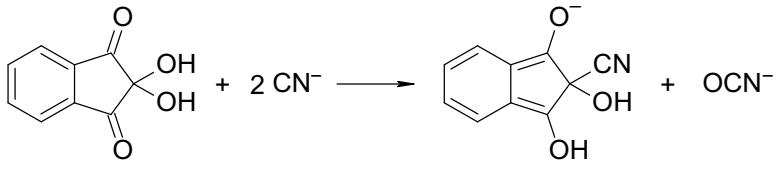
Cyanogenic substances that form HCN upon entering the body are present in the fruits of certain plants. For example, bitter almonds contain the cyanogenic compound amygdalin ($C_{20}H_{27}NO_{11}$), which is responsible for their bitterness and characteristic aroma. The average amygdalin content is 44 g per 1 kg of almonds, and the mass of a single almond kernel is approximately 3.2 g.

II-15.2 Calculate the maximum number of bitter almond kernels (N) that a 65 kg person can safely consume in one day. Assume the almond kernels are indivisible.

For the qualitative analysis of cyanogenic substances, the fruit is ground into a powder, placed in a flask with a gas outlet tube, mixed with water and NaOH, and thoroughly stirred. Then, 1 M H_2SO_4 is gradually added to the suspension while passing a stream of air through it. The outlet tube is placed into a solution of $[Cu(NH_3)_4]SO_4$ containing an excess of NH_3. If cyanides are present in the sample, the blue color of the solution changes to green due to the formation of a neutral complex **G**, which contains copper ions in different oxidation states and an equal number of NH_3 and CN^- ligands. The formation of **G** requires 5/3 mol of CN^- per 1 mol of $[Cu(NH_3)_4]^{2+}$, of which 1/3 mol undergoes a two-electron oxidation to the ion **F**.

II-15.3 Identify the ion **F** and determine the composition of the complex **G**.

Another source of HCN, along with dozens of other toxic substances, is smoking. About 10% of the HCN released during tobacco combustion passes through the filter and enters the cigarette smoke inhaled by a smoker. The amount of HCN in cigarette smoke can be estimated spectrophotometrically. For this, a cigarette is connected to the inlet tube of a gas wash bottle filled with 40.0 mL of a 2% Na_2CO_3 solution. The outlet tube is connected to a vacuum pump, and the cigarette is lit, causing all the cigarette smoke to pass through the Na_2CO_3 solution. A 1.00 mL aliquot of the resulting solution is mixed with 0.50 mL of a 0.5% ninhydrin (**X**) solution and left for 15 min to allow the following reaction to take place, during which the yellow color of the solution changes to red due to the formation of the compound **Y**.

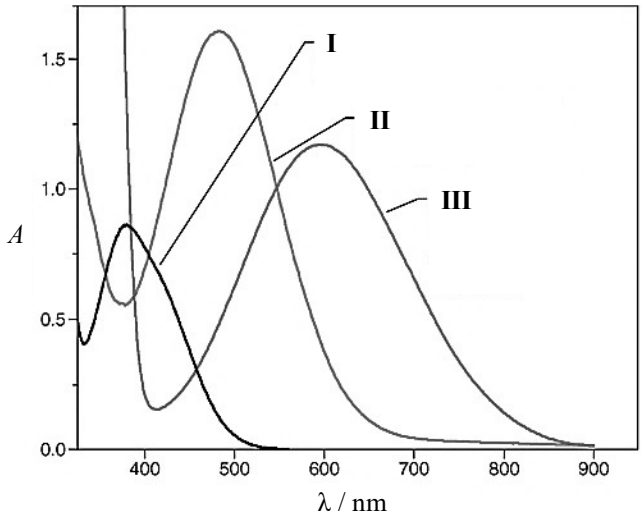


X **Y**

The experiment was repeated for two additional cigarettes using fresh Na_2CO_3 solutions. The absorbance (A) of all three solutions was measured at the maximum absorption wavelength of **Y** with a molar extinction coefficient of $\varepsilon = 1.40 \cdot 10^5$ L·mol^{-1}·cm^{-1}. The cuvette width was $l = 1$ cm. The absorbance values relative to the blank solution for the three aliquots were 0.277, 0.265 and 0.274.

II-15.4 Calculate the total mass of HCN ($m(HCN)_0$, μg) released during the combustion of one cigarette.

Addition of 1 M NaOH solution to **Y** results in the solution color change to blue due to the formation of substance **Z**. The absorption spectra of **X**–**Z** are given below:



II-15.5 Provide the structure of **Z** and match the spectra **I**–**III** to **X**–**Z**.