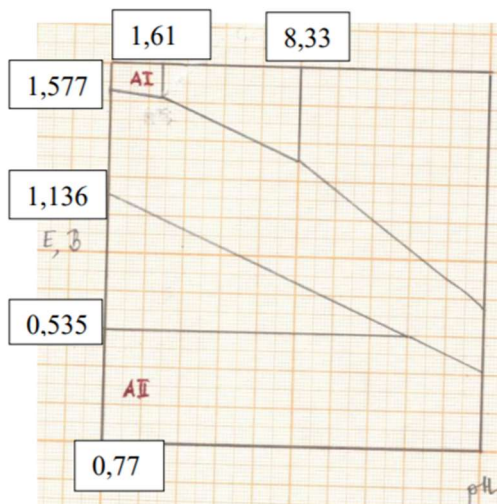**Task 1. Inorganic Chemistry (8 points)**

This is a Pourbaix Diagram of Iodine. [note: the x-axis is pH and the y-axis is the electrode potential, in volts]

1. Given that A^{II} is the most reduced form of iodine, fill in the Pourbaix diagram.

2. Find A^{I}.

3. Calculate the first two acidity constants for substance A^{I}.

4. Calculate the standard electrode potentials for the substances shown in the Pourbaix diagram, assuming that there are no other forms in the range pH 0-0.77.

5. Draw a Latimer diagram and calculate the value of the standard electrode potential $E(A^{I}/A^{II})$.

6. At pH 1, is it possible to oxidize chloride, bromide, or Fe^{3+} ions into chlorine, bromine, or ferrate ions with this (A^{I}/A^{II}) couple? If not, does there a specific pH at which it is possible? Data: $(E(Cl_2/Cl^-) = 1.538$ V, $E(Br_2/Br^-) = 1.065$ V, $E°(FeO4^{2-}/Fe^{3+}) = 1.9$ V)

7. Reacting sodium persulfate with Cu(OH)2 in the presence of the anion of the acid A^{I} at pH = 10 leads to a mononuclear complex in which the central atom is surrounded by two bidentate ligands. Draw the structure of this anion and draw its orbital splitting diagram.

8. State the formula of a Co(II) Complex that is labile, thermodynamically stable, and can reduce water. Write the expression for its Ligand Field Splitting Energy and the reaction between it and water.

9. Give an example of a diamagnetic transition metal complex that exists as hexa-aqua complex in an aqueous solution at pH 0, but is not able to form an ammonia complex even when an excess of ammonia is added.

Task 2. Organic Synthesis (9 points)

In 2018, a group of Japanese scientists from Nagoya university synthesized a common tricyclic core that is found in a family of alkaloids isolated from plants of the genus *Daphniphyllum*. Give the structural formulae of substances A-Z, including stereochemistry. Draw the final product with stereochemistry as well.
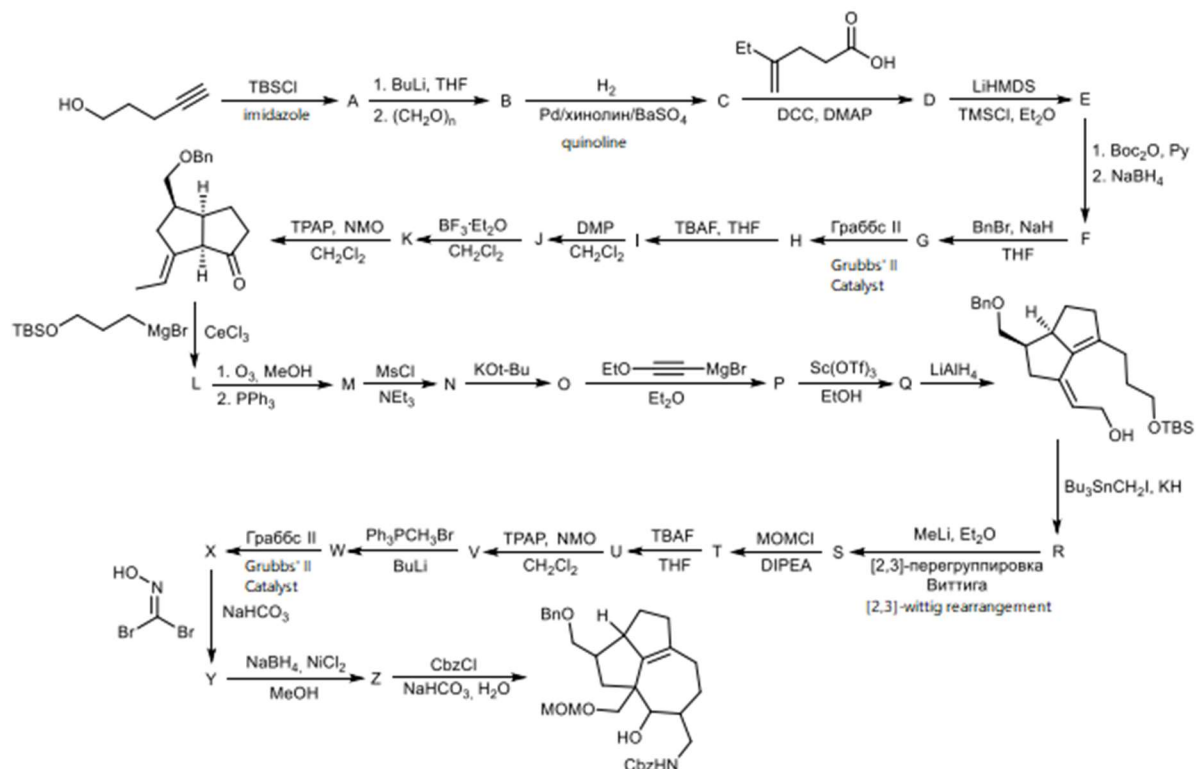
Task 3. Composition of the drink Kolokolchik (7 points)

This task is the same as tasks 1-4 of Problem 3 from the second theoretical tour of the 2001 Mendeleev Olympiad, which is already available in English, so it has been omitted from this translation.

Task 4. Enantioselective Epoxidation (8 points)

The Sharpless asymmetric epoxidation is an enantioselective reaction involving a chiral catalyst, which Sharpless received the 2001 Nobel Prize for. It epoxidates allyl alcohols with tert-butyl peroxide and a titanium complex. If a chiral ligand is used, one enantiomer is favored in the reaction. The classic ligand used is diethyl tartrate (DET).
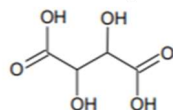

Structure of DET

When trying to prepare (+)-DET from (+)-tartaric acid, the chemists did not keep track of the amount of acid released, so the product underwent partial racemization (forming (-) and meso forms). A solution of this product with a concentration of 3.28 M in EtOH in a 6 cm cuvette has an optical rotation of 2.3 degrees. The specific rotation of (+)-DET (1g/mL in EtOH) is 7.5 degrees.

1. Draw the structural formulae of the DET forms present in the mixture, with stereochemistry. Find the absolute configurations of the stereocenters.

2. The Ti-(+)-DET catalyst is involved in the below reaction (CH_2Cl_2, ee = 0.92 at 0 ° C):
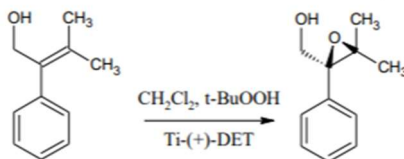
The activation energy for forming the R-isomer is 110.5 kJ/mol when using the Ti-(+)-DET catalyst. Determine the activation energy for forming the R-isomer when using the Ti-(-)-DET catalyst instead. Calculate the temperature required for which ee = 0.95 can be achieved. Assume that the preexponential factor is the same for both reactions.

A catalyst was prepared using the impure mixture from part 1, and was used to oxidize the above compound. The mixture of products formed has an ee = 0.72. Assume that the Ti-meso-DET S-epoxide is formed 9 times faster than with the Ti-(-)-DET catalyst.

3. Calculate the composition of the synthesized DET and its ee.

4. 20.0 g of the DET from part 1 was purified with recrystallization, resulting in the separation of 2.2 g of the mixture with zero specific rotation. Calculate the new optical rotation of the mixture (3.28 M in EtOH, cuvette length 6 cm)

5. The equilibrium between D-, L-, and meso forms of tartaric acid in aqueous HCl was studied with relaxation methods. Setting $x = [M] - [M]_{eq} = [D]_{eq} + [L]_{eq} - [D] - [L]$, an equation between dx/dt and x was written. The relaxation time was found to be 84 minutes. Calculate the rate constants for the conversion of the meso form into the optically active form and vice versa.

Task 5. Isotope Effects (7 points)

Thiocyanic acid (HSCN) exists in equilibrium with isothiocyanic acid, HNCS. At room temperature, the equilibrium constant K = 60400, so it is almost always found as HNCS. The vibrational frequencies of the H-S bond in HSCN is 2650 cm^{-1}, and that of the H-N bond in HNCS is 3528 cm^{-1}.

1. Calculate the vibrational frequencies of both bonds, if the H is replaced with deuterium.

2. Find the difference in the Gibbs Free Energy change of the reaction when H is replaced with deuterium. Calculate the new equilibrium constant using deuterium and find the ratio of the deuterated to undeuterated equilibrium constants.

3. Draw the state of the transition state for this reaction.

4. When there is isotopic substitution in the transition state, the frequency of one vibration changes significantly – from 2541 cm^{-1} to 1850 cm^{-1}. How much will the activation energies of the direct and reverse reactions change with isotopic substitution?

5. Find the ratio of the rate constants of the deuterated and non-deuterated reactions, for both forward and reverse reactions.

6. A similar reaction occurs in organic thiocyanates, for example, the equilibrium between PhSCN and PhNCS. Will there be an isotopic effect when replacing phenyl hydrogens with deuterium? Explain.

Task 6. Biochemistry (8 points)
Hint. Draw structures carefully - this will help you solve the problem.
Hoogsteen base pairs are an alternative base pair in DNA proposed by K. Hoogsteen 10 years after the double spiral model's publication by Watson and Crick. In Hoogsteen pairs, the purines are rotated 180 degrees from the normal orientation, and a hydrogen bond is formed instead from the 5-membered purine ring not involved with the N-glycosidic bond.

1. Draw Watson-Crick A-T and G-C base pairs with hydrogen bonds.

Note: For this problem, a pair is considered to exist if there are at least 2 hydrogen bonds between bases. Only consider base structures containing exocyclic C=O and NH2 groups, and designate the carbohydrate part of the base pairs as 'R.'

2. Depict all possible Hoogsteen pairs of DNA. Note that there must be one purine and one pyrimidine.

In both Watson-Crick and Hoogsteen pairs, the nitrogenous bases can be orientated relative to each other in two different ways, thereby creating direct and inverse pairs. In the first case, the angle between two N-glycosyl bonds is slightly less than 90 degrees, and in the second case, the angle is close to 180 degrees, which is achieved by rotating the pyrimidine unit.

3. Depict all possible inverse Watson-Crick and Hoogsteen pairs. Note that there must be one purine and one pyrimidine.

In the genetic code, 64 codons are possible. 3 are stop codons, and the other 61 encode amino acids. Each codon must individually pair with tRNA, but some tRNAs can pair with multiple codons. Crick put forth the Wobble hypothesis to explain this, which states that the 5'-terminal base of the anticodon is not as substantial as the other two, and it can participate in the formation of ambiguous base pairs. In non-standard pairs, there is geometric deviation from the canonical base pairs. The most common non-standard pairs are Watson-Crick analogues of G-C: G-U, I-C, I-U, and I-A, where I is hypoxanthine.

4. Depict the non-standard pairs mentioned above in which there are geometric deviations that cause the bases to deviate up or to the right of the standard G-C pair.

5. Aside from the double helix of DNA, scientists have also discovered triple spirals, in where a third strand uses Hoogsteen pairing (depicted as *) to pair to the traditional duplex. Draw a fragment of the triple helix TA*T and TA*A.

6. Recently, DNA quadruplexes have been discovered to occur in a region that contains repeating hexanucleotide sequences formed by only two major nitrogenous bases. The molecular weight of the corresponding fully protonated hexanucleotide is 1913 daltons. Determine its molecular formula.

7. Draw the structure of a quadruplex of DNA that forms due to 8 hydrogen bonds in a plane.

Task 7. Synthesis and modification of polymers (6 points)
Polymer **P** was prepared by the following procedure:
To a solution of 9-chloromethylanthracene (0.25 g), 2-ethyl-2-oxazoline (1.203 g), and 2-(dec-9-enyl)-2-oxazoline (0.461 g) in 3.15 g dichloromethane was added 0.165 g of sodium iodide. The reaction mixture was heated to 140 C and microwaved for 20 minutes. After cooling, a 5-fold molar excess (with respect to the initiator) of sodium azide was added, and the mixture was stirred at room temperature for 12 hours. The resulting white precipitate was separated by filtration, and the polymer solution was washed with water and dried over MgSO$_4$. After isolation, P was sequentially modified in three ways:
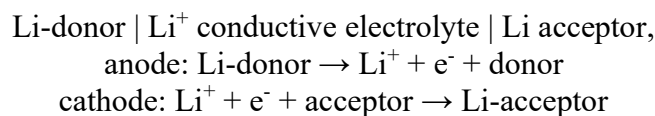   a) Mixing with dibenzocyclooctinol (**A**) in chloroform at room temperature
   b) Irradiation (356 nm) in a mixture of thiol (RSH) and 2,2-dimethoxy-2-phenylacetophenone in tetrahydrofuran
   c) Heating with maleimide (**B**) in dimethylformamide (120 C, 48 h)
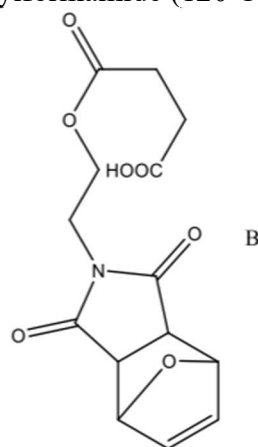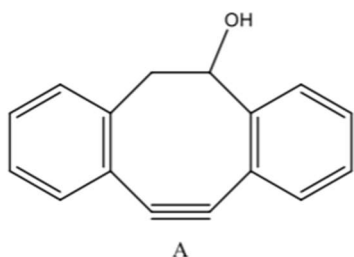
1. Assuming quantitative yield for all reactions, depict the structure of the polymer P, including end groups. Indicate the type of distribution of links in the polymer chains.

2. Depict the effects of each of the modifications mentioned above. You need not redraw the structure of the polymer that remains unchanged.

3. Indicate the order in which the modifications should be performed. Justify your answer.

4. Give examples for the R-group of the thiols used for modifications that would allow for inclusion of the following atoms into the polymer:
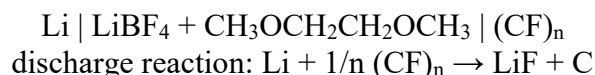a) potassium
b) iodine
c) copper.

Task 8. Lithium-ion batteries: cathodic and anodic materials (7 points)

At first glance, any lithium-ion battery and the reactions occurring within it seem simple, and can be represented as follows:

$$\text{Li-donor} \mid \text{Li}^+ \text{ conductive electrolyte} \mid \text{Li acceptor},$$
$$\text{anode: Li-donor} \rightarrow \text{Li}^+ + e^- + \text{donor}$$
$$\text{cathode: Li}^+ + e^- + \text{acceptor} \rightarrow \text{Li-acceptor}$$

However, the choice of cathodic and anodic materials, as well as the electrolyte, determine important properties such as capacitance, emf, maximum current, number of discharge-charge cycles, temperature range of use, safety, price, and ultimately determine the cell's suitability. In this problem we will focus on some cathode and anode materials used in these cells.

One interesting cathode material is carbon monofluoride $(CF)_n$ – a colorless crystalline substance obtained by direct fluorination of graphite. Like graphite, it has a layered structure (not a single covalent C — C bond is broken in the process its formation from graphite); however, it does not conduct electric current. Thus, many chemically inert conductive additives are added. An example of a galvanic cell with such a cathode is as follows:

$$\text{Li} \mid \text{LiBF}_4 + \text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3 \mid (CF)_n$$
$$\text{discharge reaction: Li} + 1/n \ (CF)_n \rightarrow \text{LiF} + \text{C}$$

The emf of this cell is 3.2 V at 25 ° C.
1. What is the hybridization of the orbitals in graphite and carbon monofluoride?

2. One important parameter in galvanic cells is the internal electrical resistance that occurs due to limited conductivity in both the electrolyte and electrodes. How will the internal electrical resistance change as the cell discharges? Explain your answer.

It is known that at 25 C, the electromotive potential of a $\text{Li} \mid \text{Li}^+$ - solid electrolyte $\mid \text{F}_2$ cell is 6.10 volts, the standard reduction potentials of the Li^+/Li pair and the F_2/F^- pair respectively are -3.04 and +2.87 volts, and the standard enthalpy and entropy of formation of gaseous carbon tetrafluoride are respectively -930 kJ/mol and -148 J/(mol K).

3. Calculate the equilibrium vapor pressure of carbon tetrafluoride over carbon monofluoride at 25 C.

4. Calculate the solubility product constant of LiF in water at 25 C.

Li-containing intermetallic compounds are used as anode materials, since they release lithium ions during discharge as follows:

$$Li_xM \rightarrow x\ Li^+ + x\ e^- + M$$

However, they have a disadvantage in that a significant volume change occurs when charging/discharging, resulting in reduced mechanical performance. As a result, significant research is being done into metal/intermetallic pairs in which another metal is capable of displacing lithium from intermetallic compounds. An example of such a pair is the Cu/Cu_2LiSb electrode, whose discharge can be represented as follows:

$$Cu + Cu_2SbLi \rightarrow Cu_3Sb + Li^+ + e^-$$
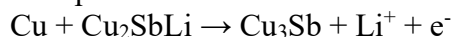
The unit cell of Cu_3Sb is composed of antimony atoms occupying a FCC lattice, with copper atoms at the centers centers of all edges, the center of the unit cell, and the centers of all octants. The substitution of Lithium for Copper does not change the crystal structure, though the lattice parameter does change. The unit cell is pictured below:
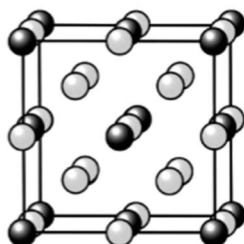
5. It is known that in an FCC lattice, there are holes. Determine the proportion of copper atoms that fill each type of holes (octahedral/tetrahedral/other) in the structure formed by the antimony atoms.

6. Crystalline copper has an FCC lattice, while crystalline lithium has a BCC lattice. The densities of copper and lithium are respectively 8.96 g/mL and 0.534 g/mL. Find the ratio of the atomic radii of copper and lithium.

7. The radius of antinomy is 1.09 times that of copper. Calculate the density of the intermetallic compound Cu_3Sb.