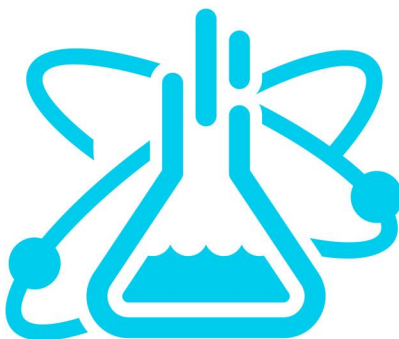


INTERNATIONAL AL-BERUNIY CHEMISTRY OLYMPIAD



ABU REIKHAN BERUNIY INTERNATIONAL CHEMISTRY OLYMPIAD

UZBEKISTAN 2023

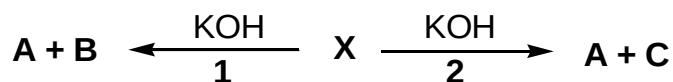
PREPARATORY PROBLEMS

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Problem 1. Inorganic puzzle

An elementary substance of element **X** reacts with alkali under two different conditions in different ways. In the first case, salts **A** and **B** are formed, and in the second, salts **A** and **C**.



	A	B	C
Mass fraction of element X , %	47,55	39,15	28,93

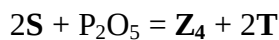
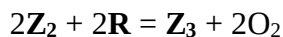
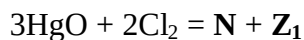
When heated, salts **B** and **C** decompose eventually forming only salt **A** and an elementary substance of element **Y**:



1. Determine the elements **X**, **Y** and salts **A-D**, if it is known that **B**, **C** and **D** consist of three chemical elements.
2. Define conditions **1** and **2**.

Problem 2. Chlorine oxides

Chlorine forms only four oxides **Z**₁ – **Z**₄. Methods of obtaining **Z**₁ – **Z**₄ (with coefficients) are given below:



1. Determine the formulas of substances **Z**₁ – **Z**₄ and **N-T**, if it is known that:
 - in compound **N**, ω(Hg)=85,4 %
 - compound **P** is gas at STP.
 - Mass fraction of chlorine in **Z**₄ is 1.098 times greater than in **S**
2. Which of **Z**₁ – **Z**₄ has the highest melting point? Explain your choice.

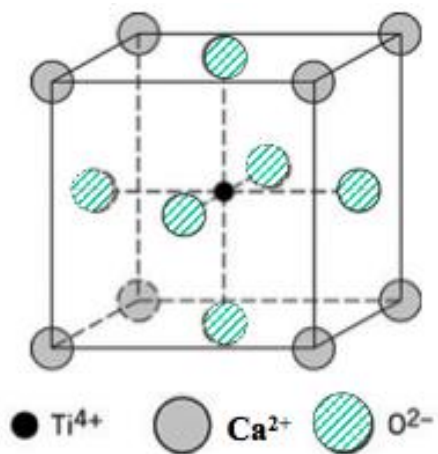
Problem 3. Useful inorganic salt.

After the electrolysis of saturated solution of $KHSO_4$, salt **A** is obtained, and gas **X** is released at the cathode (1-reaction). An excess of potassium iodide solution is added to the solution, obtained by dissolving 1.35 grams of salt **A** in water, in the presence of sulfuric acid (2-reaction). Released iodine was titrated with 0.500 M solution of sodium thiosulfate (3-reaction). It required 20.0 ml of sodium thiosulfate solution.

1. Determine the chemical formula of salt **A** and gas **X**.
2. Draw the Lewis structures for the anions of $KHSO_4$, sodium thiosulfate and salt **A**.
3. Write the reaction equations mentioned above. (3 reaction equations)
4. Salt **A** is used as an initiator for the polymerization of propylene. Write the reaction equations for initiation and chain growth steps with participation of anions of salt **A** in the process of obtaining polypropylene. (2 reaction equations)

Problem 4. Perovskite and its analogs.

One of the most common crystal structures of oxides containing transition metals is the mineral perovskite, whose cubic unit cell is given in the figure below:



1. Using given figure, determine the chemical formula of perovskite.
2. What is the coordination number of each atom in the structure of perovskite ?
3. Ionic radii of Ca^{2+} and O^{2-} in the perovskite are 1.34 Å and 1.40 Å respectively. Calculate the edge length of the cube (Å) for the perovskite unit cell.
4. Calculate ionic radius (Å) of Ti in this structure.
5. Calculate the density (g/cm^3) of the perovskite mineral.

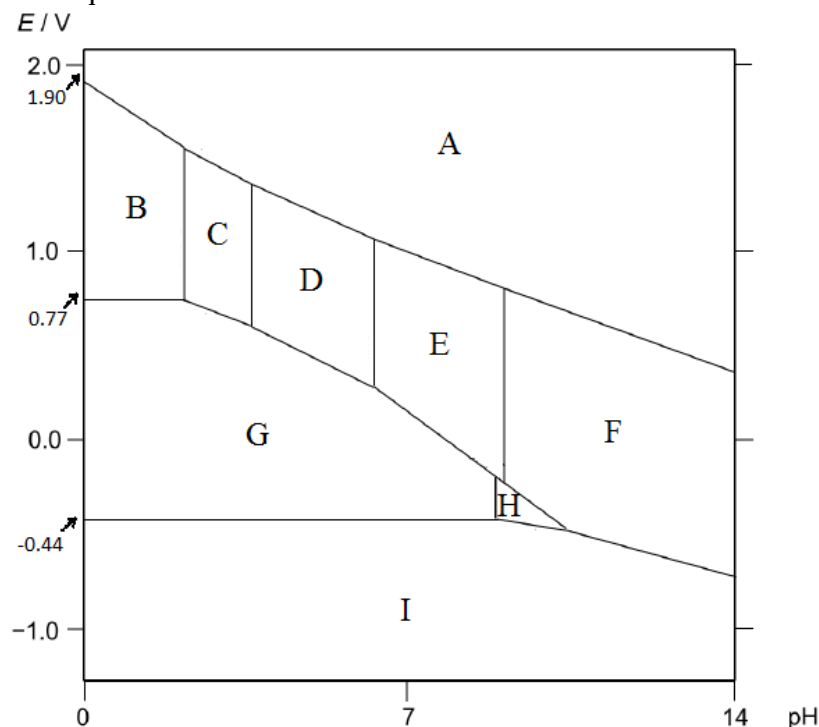
In 2018, scientists from Taiwan reported on the photocatalytic activity of perovskite-like compound **X**. In the experiment, 1 mmole of $Pb(NO_3)_2 \cdot H_2O$ and 1 mmole of $Bi(NO_3)_3 \cdot 5H_2O$ are dissolved in the glass with the help of 15ml of 1M HNO_3 solution in order to obtain **X**. After complete dissolution of the salts, the pH value of the solution was brought to 7 by using 5M

solution of NaOH. White precipitate has formed. After that, 1ml of 1M KBr solution was added to the solution. Obtained solution was stirred for 30 minutes. Then, it was dried for 12 hours at temperature of 150°C. The solid residue was washed first with deionized water, and then with ethanol. The precipitate was dried during one night at 60°C. The result was 528 mg (quantitative yield) of compound X.

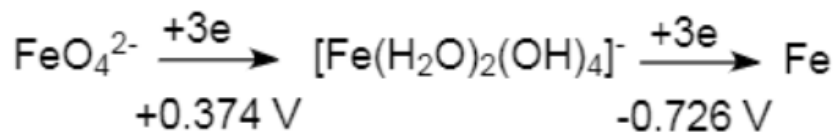
6. Determine the chemical formula of compound X.
7. Write the reaction equations for the forming of white precipitate and compound X.
8. Compound X exhibits the properties of a semiconductor when irradiated with visible light, absorbing most of the waves with a length of 512 nm. Calculate E_g (the energy difference between the conduction band and the valence band of a semiconductor, in eV) for compound X. $h = 6,626 \cdot 10^{-34} \text{ J}\cdot\text{s}$, $c = 2,998 \cdot 10^8 \text{ m/s}$, $1 \text{ eV} = 1,602 \cdot 10^{-19} \text{ J}$.
9. When compound X absorbs the wave with length of 512nm, following occurs: $X \rightarrow h^+$ («hole») + e^- («free electron»). Researchers from Taiwan have found that when X is emitted by visible light, the concentration of $O_2^{\bullet-}$ and $OH^\bullet$ particles increases. Propose the equations of reactions of the formation of particles $O_2^{\bullet-}$ and $OH^\bullet$.

Problem 5. Pourbaix diagram of iron-containing particles.

The Pourbaix diagram (dependence of equilibrium value of E pH of the solution) for the iron is given below under standard conditions and at 298K. Take into account that, each line on the diagram separates the stability zones of two different particles, and along the line, concentrations of these particles are equal.

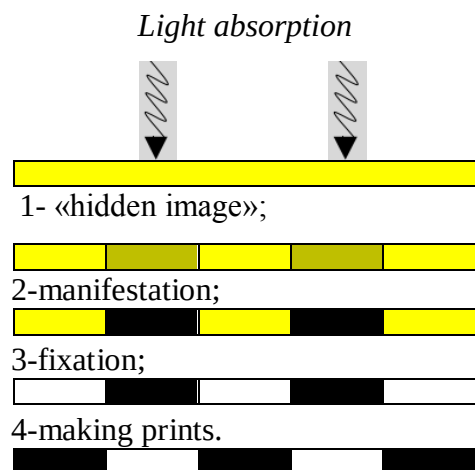


Based on the Pourbaix diagram, Latimer diagram for the iron can be created at pH=14:



- Determine unknown particles **A,B,C,D,E,F,G,H,I**.
- Using Latimer diagram for the iron at pH=14, calculate the standard electrode reduction potential of FeO_4^{2-} to Fe.
- Using the data from Pourbaix diagram, create a similar Latimer diagram for iron at pH = 0 as shown in the problem for pH =14.
- Why the line separating particles **B** and **C** is vertical? Choose one correct answer.
 - There is no protons exchange in the process of transforming $\text{B} \rightarrow \text{C}$.
 - There is no electrons exchange in the process of transforming $\text{B} \rightarrow \text{C}$.
 - During the transformation of $\text{B} \rightarrow \text{C}$, the exchange of the same number of protons and electrons occurs.
 - During the transformation of $\text{B} \rightarrow \text{C}$, an unequal number of protons and electrons are exchanged.
- Choose the strongest acid among the above:
 - $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
 - HFeO_4^-
 - $[\text{Fe}(\text{H}_2\text{O})_3(\text{OH})_3]$
 - H_2FeO_4
- The line separating particles **A** and **B** can be written as a function: $E = a + b \cdot \text{pH}$. Determine the values of a and b
- Considering the values of stability constants: $\lg\beta([\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}) = 11,8$; $\lg\beta([\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]^+) = 22,3$; $\lg\beta([\text{Fe}(\text{H}_2\text{O})_3(\text{OH})_3]) = 30,0$; $\lg\beta([\text{Fe}(\text{H}_2\text{O})_2(\text{OH})_4]^-) = 34,4$, calculate the similar values of a and b for the line separating particles **A** and **F**.
- When water is oxidized, oxygen is released, and when it is reduced, hydrogen is released. Draw the similar Pourbaix diagram for the water at standard conditions and 298K in the interval of pH=0-14, if it is known that $E^\circ(\text{O}_2, 4\text{H}^+/2\text{H}_2\text{O}) = 1,23 \text{ V}$, $E^\circ(2\text{H}^+/\text{H}_2) = 0 \text{ V}$.
- Which iron particles are stable in the neutral solution of water under standard conditions and 298K?

Problem 6. Chemical bases of black-white photography



Compound **A** is halide of metal **X**, in which mass fraction of the halogen is 42.55%, is used for the manufacture of photosensitive films in photography. The photographic process consists of four stages. At stage 1, substance **A** decomposes under the action of the light and clusters of metallic **X** are formed (1-reaction). However, their number is so small that they are invisible. In the 2nd stage, the "hidden image" is enhanced by treating the film with compound **B** (in the ^1H NMR spectrum of which there are signals from protons of the aromatic cycle and has 3 planes of symmetry; $\omega_{\text{O}} = 29.06\%$) (2-reaction). In this case, **X** metal clusters catalyze the reduction of the **X** metal cation and a drawing of the photographed object is formed in a "negative" form. In the 3rd stage, to protect against restoration and blackening, the undecomposed **A** remaining on the film is removed using compound **C** ($\omega_{\text{S}} = 40.48\%$; $\omega_{\text{O}} = 30.36\%$) (3-reaction). In this case, the residual metal **X** cations are washed off in the form of a complex **D** ($\omega_{\text{X}} = 26.90\%$). In stage 4, light is passed through the "negative" drawing, which falls on a new photographic film. Further, the operations of manifestation and fixation are repeated. In this way, "positive" black-white images are obtained. In the figure on the left, the yellow color indicates compound **A**, the black color is metal **X**, and the white color is an empty film.

1. Determine metal **X** and substances **A**, **B**, **C**, **D**, for **B**-draw a structural formula. Confirm the answer with calculations.

2. Write the equations of all reactions mentioned in the problem (3 reaction equations).

In the manufacture of photographic films, fine-grained granules (diameter of granules $\approx 1 \mu\text{m}$) of compound **A** are applied to a transparent film containing an adhesive substance.

3. Determine the number of **X** atoms in one granule. Consider that the granules have the shape of a sphere and $\rho_{\text{A}} = 6.47 \text{ gr/sm}^3$.

4. Why, despite the catalytic activity of metal **X**, at the stage of manifestation **B** does not restore the weight of **A** on the film? Remember that **A** on the film is in the form of separate granules.

Problem7. Vinegar.

There is always a place for vinegar in the Uzbek national cuisine. The main component of the vinegar is acetic acid. Vinegar contains 5% CH_3COOH by volume. $\rho(\text{anhydrous } \text{CH}_3\text{COOH}) = 1.05 \text{ gr/ml}$.

1. Calculate the molar concentration of CH_3COOH (M) in vinegar.

- Calculate the dissociation degree of CH_3COOH (α , %) in vinegar and the pH value of vinegar, if the acidity constant (K_a) of CH_3COOH is 1.75×10^{-5} .
- A 100.0 ml vinegar sample was diluted with water to a final volume of 250.0 ml. 10.0 ml aliquot of the obtained solution was titrated with 0.50 M NaOH solution. What volume (ml) of alkali will be consumed during titration?
- Which of the following indicators is most suitable for use in the above case of titration? Explain your choice.

Indicator:	pH range of the indicator color change:
Methyl orange	3,2-4,4
Methyl red	4,2-6,2
Phenol red	6,8-8,4
Phenolphthalein	8,2-10,0

Problem8. Factors affecting the solubility of a hardly soluble salt.

Silver chloride is extremely slightly soluble in water. The dissolution of silver chloride in water proceeds by the following reaction: $AgCl(s) \leftrightarrow Ag^+(aq) + Cl^-(aq)$. The equilibrium constant of this reaction at 298 K is $1.77 \cdot 10^{-10}$.

- Calculate the solubility (mol/l) of AgCl in water at 298 K.

The solubility of AgCl is affected by temperature and the presence of other ions in the solution.

- How does the solubility of AgCl change with increasing temperature? For the dissolution process, $AgCl \Delta_r H^\circ = +62.4 \text{ kJ/mol}$.
- Calculate the equilibrium constant of the AgCl dissolution process at 100°C.
- How does the solubility of AgCl change in the presence of NaCl in solution?
- Calculate the solubility of AgCl (mol/l) in 0.50M NaCl solution at 298K.
- How does the solubility of AgCl change in the presence of NH_3 in the solution?
- Calculate the solubility of AgCl (mol/l) in 0.50M solution of NH_3 at 298K. Consider that ammonia is completely converted into the $[Ag(NH_3)_2]^+$ complex.

Problem 9. Catalysts of hydrogen peroxide decomposition.

A catalyst is a chemical that accelerates the reaction, but is not consumed during the reaction. Manganese dioxide, iodide ions and various enzymes can be catalysts for the decomposition of hydrogen peroxide into water and oxygen

1. Write the equation of the reaction of decomposition of hydrogen peroxide into water and oxygen.
2. Iodide ions catalyze the decomposition of H_2O_2 in two stages. Write the reaction equation of the 1st stage of catalysis, if the 2nd stage proceeds as follows: $IO^- + H_2O_2 = I^- + O_2 + H_2O$.
3. Catalase is an enzyme that catalyzes the decomposition of H_2O_2 . The rate of oxygen formation (r , ml O_2 /min) depends on the concentration of H_2O_2 ($C\%(H_2O_2)$) as follows: $r = \frac{r_{max} * C\%(H_2O_2)}{K_M + C\%(H_2O_2)}$, here r_{max} and K_m are constant numbers. An experiment was conducted to study the rate of O_2 formation with a catalase sample, the results are shown in the table below:

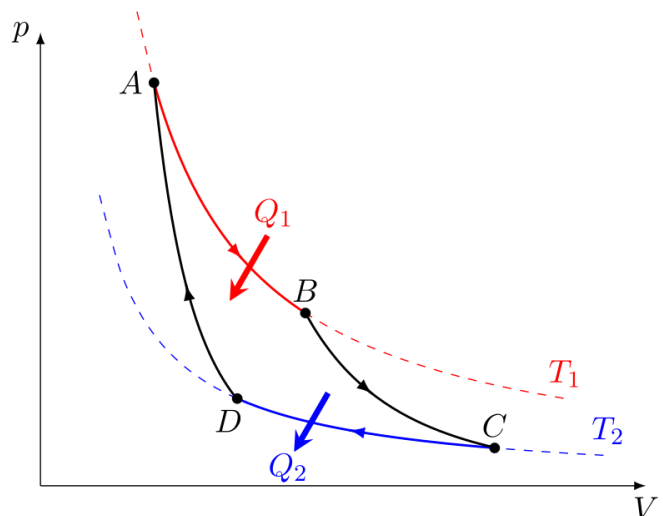
№ of experiment	$C\%(H_2O_2)$, %	r , ml O_2 /min
1	3	9,13
2	6	16,15
3	«?»	26,25

Determine the concentration "?" at which the rate of O_2 formation reaches 26.25 ml O_2 / min.

4. During the catalytic decomposition of H_2O_2 at 25 ° C in the presence of Pt, the activation energy of the reaction decreases by 25 kJ/mol. Considering that the pre-exponential multipliers of the catalytic and non-catalytic reactions are equal, calculate how many times the rate constant increases in the presence of Pt. Arrhenius equation: $k = A * \exp(-E_A/RT)$.

Problem 10. Carnot cycle

The Carnot cycle is an ideal circular process consisting of two adiabatic (BC and DA) and two isothermal (AB and CD) processes. In the Carnot process, the thermodynamic system performs mechanical work due to the exchange of heat (Q_1 and Q_2) with two heat reservoirs that have constant but different temperatures. A tank with a higher temperature (T_1) is called a *heater*, and a tank with a lower temperature (T_2) — *refrigerator*.



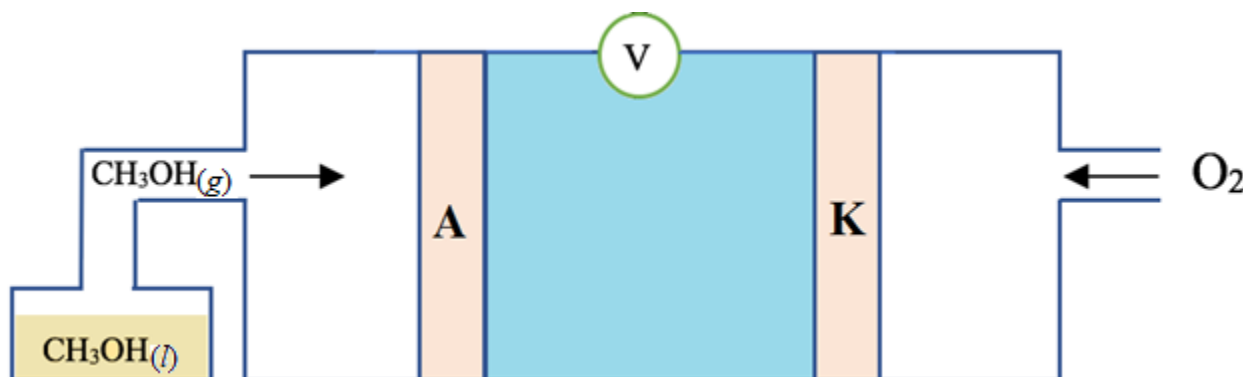
Note that the following equalities are observed in adiabatic processes: $pV^\gamma = \text{const}$, where $\gamma = C_p/C_v$; $dU = nC_vdT$.

70 g of gaseous nitrogen completes the Carnot cycle at temperatures of the heater and refrigerator, $T_1 = 400 \text{ K}$ and $T_2 = 300 \text{ K}$, respectively. The gas volumes at points A and C are $V_A = 10 \text{ dm}^3$ and $V_C = 50 \text{ dm}^3$, respectively.

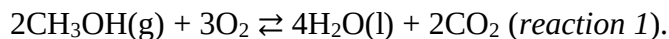
1. Calculate the coordinates of points (values of pressure (kPa) and volume (dm^3)) A, B, C and D.
2. Calculate the amount of heat Q_1 (J) received by nitrogen from the heater in 1 cycle.
3. Calculate the useful work (J) done by nitrogen in 1 cycle.
4. Using your answers to tasks 2-3, calculate the efficiency of the Carnot cycle involving nitrogen.
5. Qualitatively draw a Carnot cycle in T-S coordinates, as $T=f(S)$. Specify the position of points A, B, C, D and the direction of the cycle.
6. If the efficiency of the Carnot cycle can be calculated using the formula: $\eta = (Q_1 - Q_2)/Q_1$, using the graph you drew in task 5, derive the dependence $\eta = f(T_1, T_2)$. Use this formula to calculate the efficiency of the Carnot cycle with nitrogen.
7. Estimate when the efficiency of the Carnot cycle is 100%? And when is 0%?
8. What is the power of the heat engine (W) in the Carnot cycle, if all processes in it are carried out ideally without friction?

Problem 11. Methanol fuel cell

A methanol fuel cell is a type of fuel cell with a proton exchange membrane in which methanol is used as fuel. The scheme of operation of such a fuel cell is shown in the figure below:



where A- anode, K- cathode. Overall reaction for this fuel cell:



1. Write the equations of the half-reactions that occur at the electrodes (at the anode and at the cathode) of a methanol fuel cell.
2. Specify the direction (from the anode to the cathode or from the cathode to the anode) of the movement of electrons and protons in this fuel cell.
3. Using the thermodynamic data below, calculate the change in the standard Gibbs free energy of reaction 1 at a temperature of 298 K.

	$\Delta_f H^\circ(298 \text{ K}),$ kJ/mol	$S^\circ(298 \text{ K}),$ J/(mol·K)	$c_p,$ J/(mol·K)
CH ₃ OH(l)	-239,2	126,8	79,9
CH ₃ OH(g)	-201,0	239,9	52,3
O ₂	0	205,2	29,4
H ₂ O(l)	-285,8	69,9	75,4
CO ₂	-393,5	213,8	36,6
H ₂	0	130,6	28,5

4. The energy capacity (the amount of energy in a given volume, kJ/dm³) of methanol is higher than of hydrogen in the same volume. Modern high-pressure cylinders allow storing hydrogen in them at 800 atm. Considering that the reaction in a hydrogen fuel cell: $2\text{H}_2 + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$ (reaction 2), calculate the change in the standard Gibbs free energy of reaction 2 at a temperature of 298 K and calculate how many times the energy capacity of liquid methanol is higher than that of compressed hydrogen gas up to 800 atm. [density of liquid methanol] = 0.7918 g/cm³.

5. The methanolic fuel cell works effectively at a temperature closer to the boiling point of CH₃OH. Calculate the boiling point of CH₃OH at a pressure of 1 bar. What is the boiling point of CH₃OH at a pressure of 10 bar? At this point, consider that $\Delta_r H^\circ$ and $\Delta_r S^\circ$ do not depend on temperature.

6. Calculate $\Delta_r H^\circ$, $\Delta_r S^\circ$, $\Delta_r G^\circ$ for reaction 1 at a temperature of 60 °C. At this point, it should be assumed that $\Delta_r H^\circ$ and $\Delta_r S^\circ$ change with temperature changes. Use the Kirchhoff's equation and conclusions from the 2nd law of thermodynamics: $\Delta_r H^\circ(T_2) = \Delta_r H^\circ(T_1) + \Delta C_p(T_2 - T_1)$; $\Delta_r S^\circ(T_2) = \Delta_r S^\circ(T_1) + \Delta C_p \ln(T_2/T_1)$.

7. Calculate the standard EMF (V) of a methanol fuel cell at a temperature 60 °C.

8. What volume (dm³) of methanol will be required for this fuel cell to work non-stop for 24 hours with a power of 5 kW at 60 °C?

Problem 12. Nuclear fission.

On July 16, 1945, in the state of New Mexico (USA), scientists conducted the world's first test of nuclear weapons technology. The first atomic bomb was called "Trinity" and it was schematically built according to the following (Fig. 1):

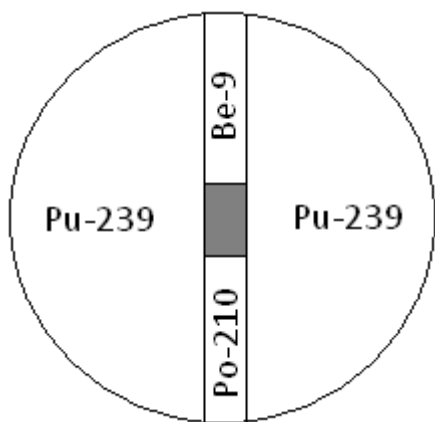


Fig. 1

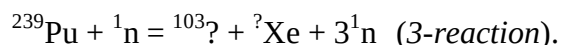


400 m
Fig. 2

2 hemispheres of isotopes of plutonium-239, each 2.95 kg, are separated by a septum. In the center of the sphere there are sufficient amounts of berellium-9 and polonium-210 isotopes to initiate the chain process of fission of plutonium-239 nuclei. The test was successful. Let's analyze how the "Trinity" explosion process occurred to develop our understanding about the chain reactions of nuclear fission.

1. Polonium-210 is a radioactive isotope and undergoes α -decay (1-reaction). When the partition between berellium-9 and polonium-210 is removed, α -particles begin bombarding berellium-9 nucleus and as a result a certain number of neutrons (2-reaction) are obtained, which are necessary to initiate the process of fission of 239-plutonium nuclei. Write the equations of nuclear reactions 1 and 2.

2. Under the action of neutrons, 2 interconnected hemispheres of plutonium-239 undergo a chain process of nuclear fission:



Find the chemical formula of isotope $^{103}\text{?}$ and relative mass of xenon isotope.

3. Which particle among the products of nuclear fission sustains the chain process?

4. Calculate the "mass defect" (a.m.u.) in the 3-reaction. Relative isotopic masses:

$^{239}\text{Pu} - 239,0521634 \text{ a.m.u.}$, $^{103}\text{?} - 102,9266012 \text{ a.m.u.}$, $^{\text{?}}\text{Xe} - 133,9053946 \text{ a.m.u.}$, $^1\text{n} - 1,0086649 \text{ a.m.u.}$.

5. Radiochemical analysis of the soil after the explosion showed that the energy release amounted to about 21 thousand tons of TNT equivalent. Calculate the maximum amount of energy (in tons of TNT equivalent) that is released during the fission of plutonium-239 nuclei weighing 5.9 kg.

Note: $E = \Delta mc^2$, where $c = 3 \cdot 10^8 \text{ m/s}$; 1 gram of TNT equivalent = 4184 J.

6. The growing fiery hemisphere captured in the photograph (fig. 2) after the explosion reached 400 meters in diameter, it melted the sand of the landfill, turning it into glass. Theoretically estimate the air temperature in this fiery hemisphere after the explosion. Consider air as an ideal gas, the initial temperature is 298 K, the isochoric heat capacity of diatomic gases is $5R/2 \text{ J / (mol} \cdot \text{K)}$. Consider that the energy released during the decay of ^{239}Pu is used only to heat the air in the fiery hemisphere.

7. In order to continue without stopping the chain process, it is necessary to have at least a certain minimum mass of the isotope ("critical mass"). For plutonium-239, the "critical mass" is 5.6 kg. If spherical plutonium-239 has a mass of less than 5.6 kg, then there will be no chain process of nuclear fission. Estimate how long (years) after its creation, the "Trinity" test would not have been successful, that is, there would have been no chain reaction of fission and explosion. $T_{1/2} (^{239}\text{Pu}) = 24\,110 \text{ years}$.

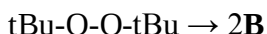
Problem 13. Production of PVC

According to statistics, Uzbekistan annually produces more than 100 thousand tons of **PVC**. The bulk of this substance is used for the production of pipes, fittings, plastics, and cables. In manufacturing, **PVC** is synthesized in 2 stages: 1 – synthesis of monomer **M**; 2 – polymerization of monomer **M** in **PVC**.

1. In the 1st stage, ethylene reacting with chlorine forms substance **A** (reaction 1), subsequently substance **A** undergoes pyrolysis in the presence of a catalyst and a monomer **M** (reaction 2) is obtained, while the resulting HCl is oxidized with oxygen and converted back into chlorine (reaction 3). Provide the noted 3 reaction equations and the general equation of the 1st stage reaction, if it is known that the most modern technologies require 460 kg of ethylene, 585 kg of chlorine, 139 kg of oxygen to produce 1 ton of monomer **M**.

2. With what yield (%) monomer **M** can be obtained from ethylene using modern technologies?

3. Polymerization of monomer **M** in PVC can be simplified as follows:

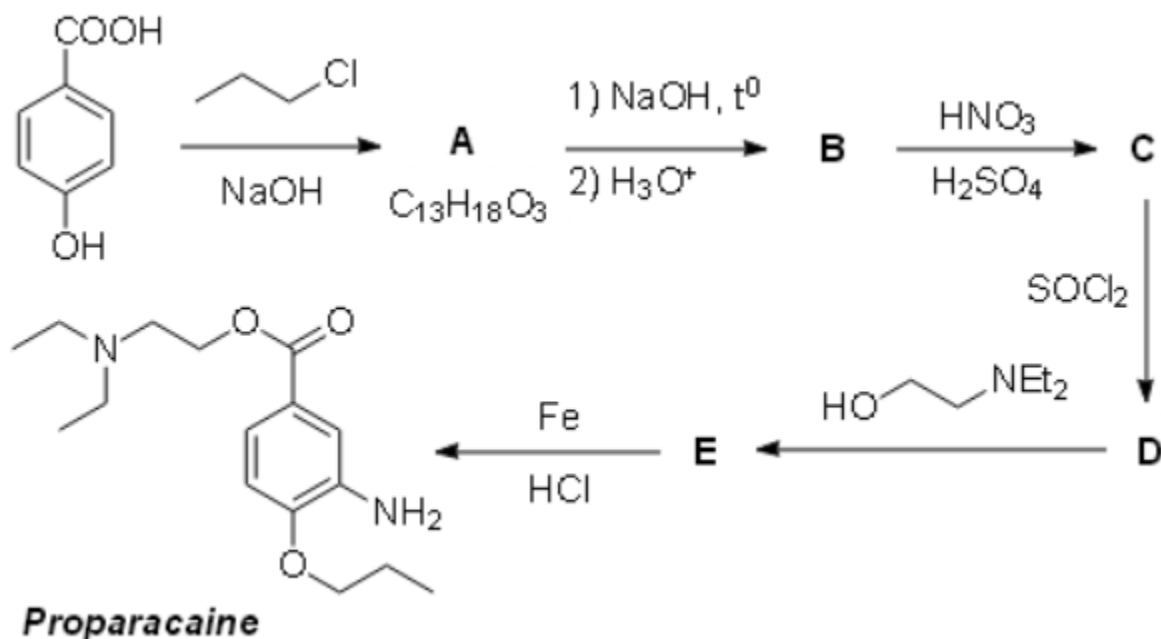


Identify the particles **B** and **C** in this scheme.

4. Determine the degree of polymerization of PVC, if it is known that 2.92 kg of ditertbutyl peroxide (tBu-O-O-tBu) was consumed during polymerization of 1 ton M.

Problem 14. Synthesis of Proparacaine.

Proparacaine is a representative of local anesthetics. It can be synthesized from 4-hydroxybenzoic acid according to the following scheme:

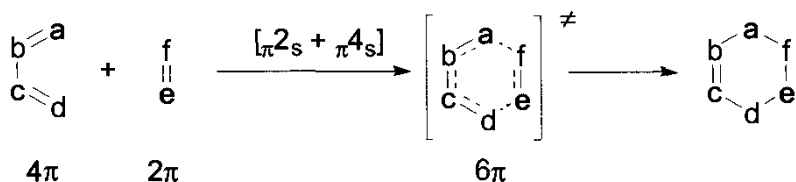


1. Draw the structures of **A**, **B**, **C**, **D** and **E**.

2. The reagent used in the conversion of **D** $\rightarrow$ **E** can be obtained by a one-step reaction between diethylamine and substance **X** (formula $\text{C}_2\text{H}_4\text{O}$). Draw the structure of **X**.

Problem 15. The Diels-Alder reaction.

The Diels-Alder reaction (diene synthesis) is a reaction of $[4+2]$ —cycloaddition of dienophiles and conjugated dienes to form a six-membered cycle. The authors of the discovery were awarded the Nobel Prize in Chemistry in 1950. The reaction mechanism is given below:



To engage in the [4+2]-cycloaddition reaction, the diene adopts a planar s-cis conformation in which both double bonds are on one side of the single C–C bond.

1. Draw the s-cis and s-trans conformations of butadiene-1,3. Calculate the quantitative ratio between the molecules of s-cis and s-trans conformations of butadiene-1,3 at 298 K, if it is known that $\Delta E = 9.6$ kJ/mol. Consider that the butadiene-1,3 molecules obey the Boltzmann distribution.
2. Arrange the molecules of butadiene-1,3, cyclopentadiene-1,3 and 2,3-di-tert-butyl-butadiene-1,3 in order of increasing reactivity in the reaction of diene synthesis.
3. From the point of view of the frontier molecular orbital theory, the reaction can be represented as the interaction of the highest occupied molecular orbital (HOMO) of an electron-donating diene and the lowest free molecular orbital (LUMO) of a dienophile:

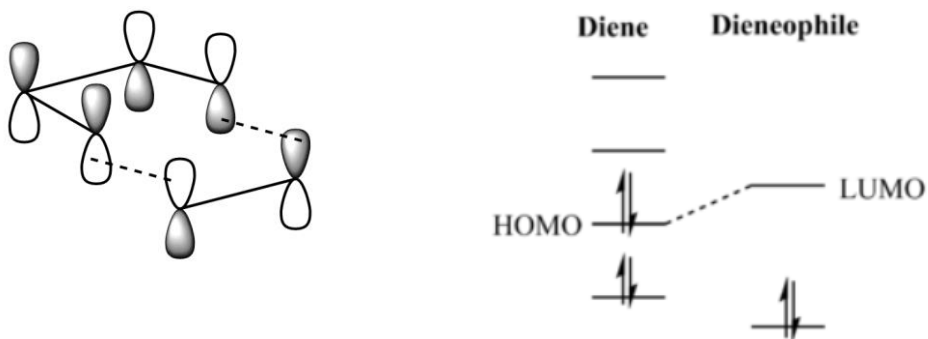


Fig. 1

Which of the following list of molecular orbitals corresponds to the HOMO of diene:

$$\Psi_1 = 0.3717 \varphi_1 + 0.6015 \varphi_2 + 0.6015 \varphi_3 + 0.3717 \varphi_4;$$

$$\Psi_2 = 0.6015 \varphi_1 + 0.3717 \varphi_2 - 0.3717 \varphi_3 - 0.6015 \varphi_4;$$

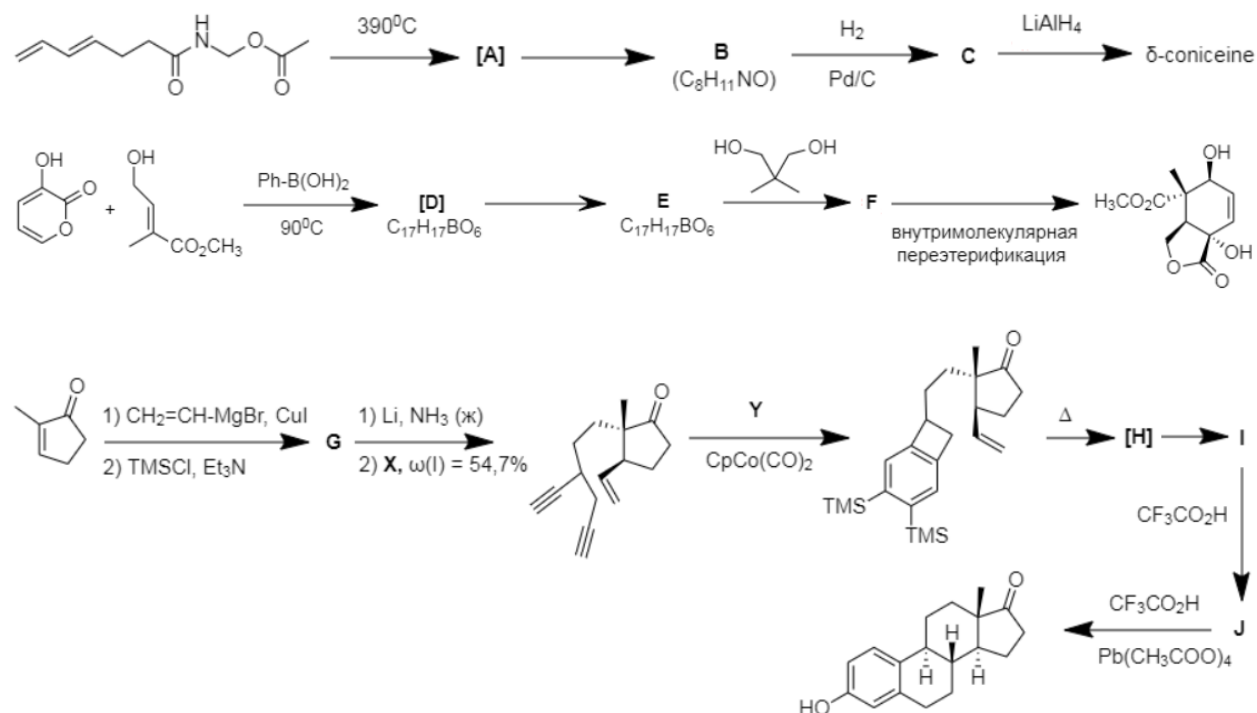
$$\Psi_3 = 0.6015 \varphi_1 - 0.3717 \varphi_2 - 0.3717 \varphi_3 + 0.6015 \varphi_4;$$

$$\Psi_4 = 0.3717 \varphi_1 - 0.6015 \varphi_2 + 0.6015 \varphi_3 - 0.3717 \varphi_4?$$

4. Schematically draw HOMO of a dienophile. Write an expression for HOMO and LUMO of dienophile, as it is done for diene in task 3, if all atomic p-orbitals make the same contribution to both HOMO and LUMO.
5. Which molecular orbitals interact in the case of the reversed variant (electron-deficient diene and electron-donor dienophile) of diene synthesis? Draw the interaction of these orbitals similarly to fig. 1 of paragraph 3.

6. How does the reaction rate between cyclopentadiene-1,3 and a number of cyanoethylenes change with an increase in the number of nitrile groups in the dienophile?

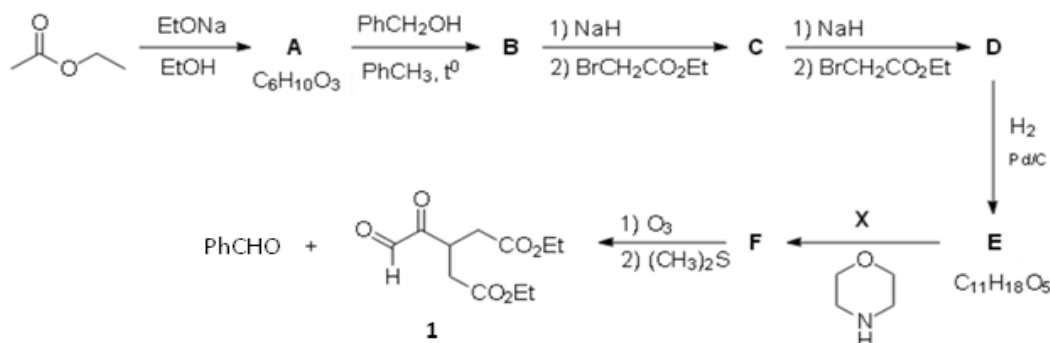
Below are some examples of the use of diene synthesis in the production of precious organic compounds:



7. Draw the structures of **[A]**, **B**, **C**, **[D]**, **E**, **F**, **G**, **[H]**, **I**, **J**, reagents **X**, **Y** and product δ -coniceine. Indicate stereochemistry where it's necessary.

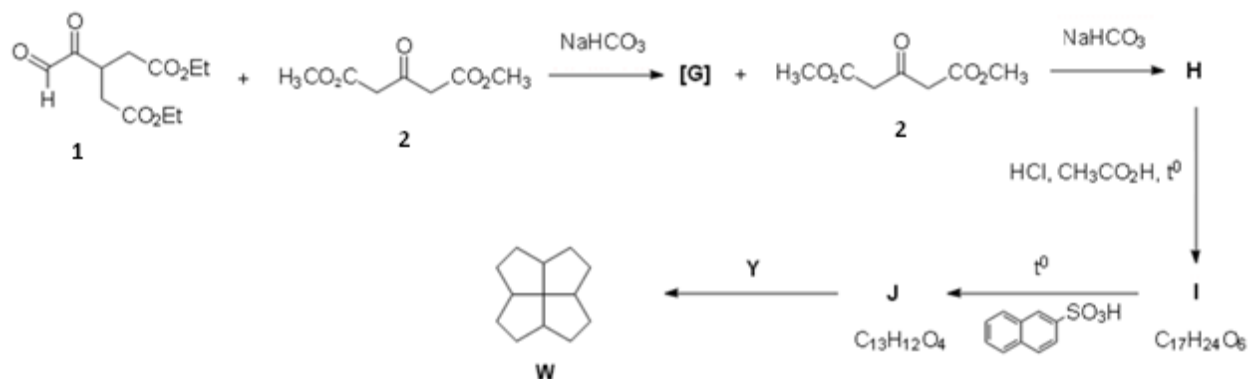
Problem 16. Cyclopentanoids.

Cyclopentanoids – contain several cyclopentane rings in their composition. The originator of this series is the substance **W**. In this problem, consider the chain of transformations of the synthesis of substance **W**. The first step is to obtain substance **1**:



1. Draw the structures of **A**, **B**, **C**, **D**, **E**, **F** and **X**.
2. How many signals should be expected in the ^1H NMR spectrum of compound **A**? Indicate the multiplicity of these signals.

At the second stage, substance **1** is converted into the target product **W** according to the following scheme:

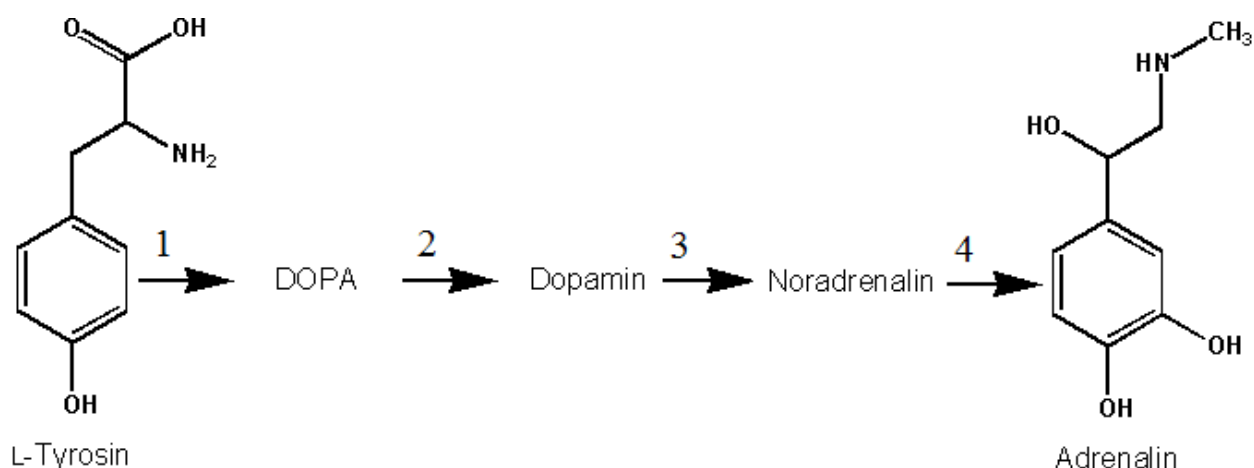


Substance **1** reacting with 1 equivalent of substance **2**, first forms an unstable intermediate **[G]**, which contains a cyclopentadienone cycle. And then the intermediate substance **[G]**, by adding the second equivalent of substance **2** according to the type of double Michael reaction, turns into a bicyclic compound **N**. At the last stage, substance **J** is reduced to product **W**.

3. The instability of cyclopentadienone derivatives lies in the fact that they dimerize rapidly at room temperature. Draw the structure of the cyclopentadiene dimer.
4. Draw the structures of compounds **[G]**, **H**, **I** and **J**.
5. Which of the following reducing agents performs the role of reducing agent **Y** better?
 - a) H_2 , Pd/C
 - b) LiAlH_4
 - c) N_2H_4 , KOH
 - d) DIBAL-H
6. How many cycles does the substance **W** contain?

Task 17. Epinephrine biosynthesis.

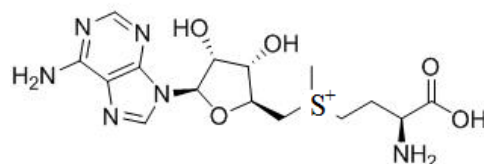
In the adrenal gland, epinephrine is synthesized from L-tyrosine in 4 stages:



The molecules added and detached at each stage together with the coefficients:

Step:	1	2	3	4
Added molecules:	$O_2 + H_4B$ (B-Biopterin)	-	$O_2 + C_6H_8O_6$	$SAM^+ + H_2O$
Detached molecules:	$H_2O + H_2B$ (B-Biopterin)	CO_2	$H_2O + C_6H_6O_6$	Homocysteine + Adenosine + H^+

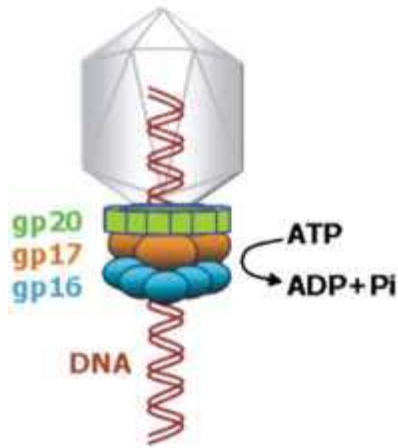
1. Determine the absolute configuration (*R/S*) of the asymmetric carbon atom in L-tyrosine.
2. Draw the DOPA, Dopamine, and Noradrenalin structures.
3. The figure on the right shows the structure of the molecular ion SAM^+ (S-adenosyl-methionine). Using this structure, determine the structure of Homocysteine, which is obtained in the last stage.



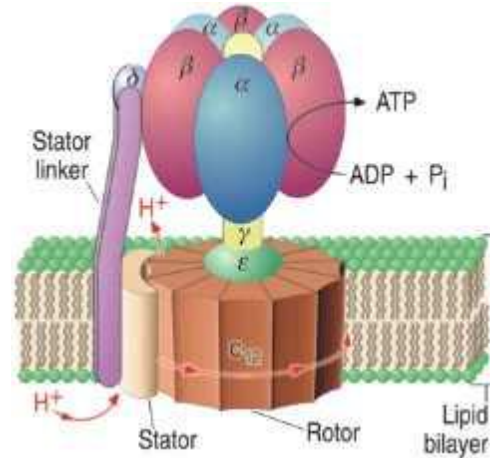
4. What stages of Epinephrine synthesis are catalyzed by oxidoreductase enzymes?
5. Pharmaceutical companies produce solutions of Epinephrine hydrochloride with a concentration of 1 mg / ml. How many Epinephrine molecules are there in a 1 ml ampoule?

Problem 18. Molecular motors.

Living cells use various molecular motors that convert chemical energy into mechanical energy. Below, we assume that the change in the Gibbs free energy of the reaction of $ATP + H_2O \rightarrow ADP + F_n$ is -50 kJ/mol at 298 K.



Bacteriophage



ATP synthase

Bacteriophages are viruses that bind to the cell wall of bacteria and push their DNA into the cytoplasm of bacteria (pictured on the left). Proteins located under the capsid act as engines and move DNA from the capsid cavity into the bacterial cytoplasm. The chemical energy of 1 molecule of ATP is used to move the DNA chain to one base pair.

1. The bacteriophage DNA chain has a length of 6.6 microns (the length of one DNA base pair is 0.34 nm), and the force required to move DNA into the bacterial cytoplasm was 50 pN. How many ATP molecules are used to completely move this chain of bacteriophage DNA into the bacterial cytoplasm? What is the efficiency (in%) of converting chemical energy to mechanical energy in this process?

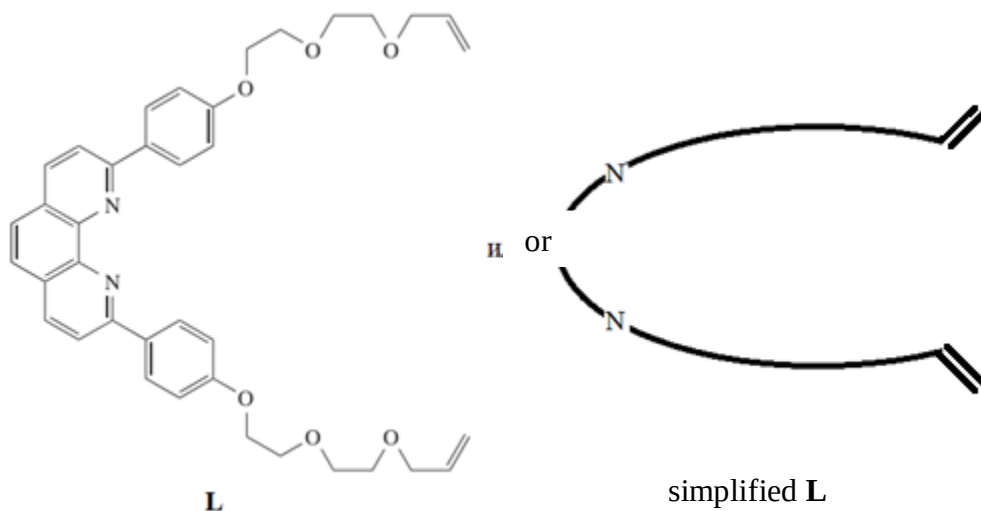
The picture on the right shows ATP synthase, which can synthesize or break down ATP depending on the state of the cell. But let's now talk about its synthesis.

2. ATP synthesis requires 25% more energy than the energy released in the ATP decomposition reaction. During one revolution of the motor protein ATP synthase, 3 ATP molecules are synthesized due to the electrochemical potential between the matrix and the intermembrane space of the mitochondria. In one revolution, 12 protons move from the intermembrane space to the matrix, rotating the protein's motor. Calculate the minimum electrochemical potential between the matrix and the mitochondrial intermembrane space (in mV) required for ATP synthesis.

3. The electrochemical potential between the matrix and the inter-membrane space of the mitochondria, without taking into account the difference in proton concentrations on both sides of the membrane, is 130 mV, which is less than the electrochemical potential calculated in question 2. To overcome this barrier, it is necessary to change the pH on both sides of the membrane. By how much (in mV) does the electrochemical potential differ in proton concentrations between the matrix and the mitochondrial intermembrane space, if the pH difference on both sides of the membrane is 1.0? This value is added with 130 mV and the total electrochemical potential is higher than that calculated in question 2. As a result, ATP synthase will work.

In 2016, Jean-Pierre Sauvage from the University of Strasbourg (France) became one of the winners of the Nobel Prize in Chemistry "for the design and synthesis of molecular machines" — individual molecules or molecular complexes that can perform certain movements when energy is supplied from outside. He proposed the method of "template synthesis". The essence of the method is as follows:

a) A complex between Cu^+ and **L**, with the composition $[\text{CuL}_2]^+$, is synthesized.



b) When the resulting $[\text{CuL}_2]^+$ complex is treated with a Grubbs catalyst, the **K₁** complex is obtained and gas is released (density 1.25 g / l at STP).

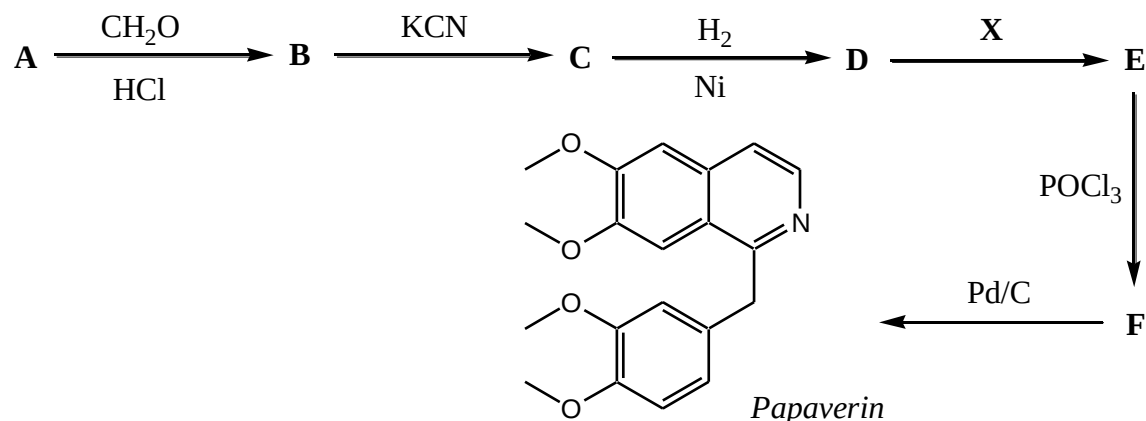
c) When the **K₁** complex is treated with an excess of CN^- ions, the **K₂** compound and the copper complex anion ($\omega_{\text{Cu}} = 55\%$) are formed.

4. Draw the structures of the complex $[\text{CuL}_2]^+$, **K₁**, compound **K₂**, and the complex copper anion. Use a simplified scheme of the **L** structure if necessary.

5. What class of compounds does **K₂** belong to?

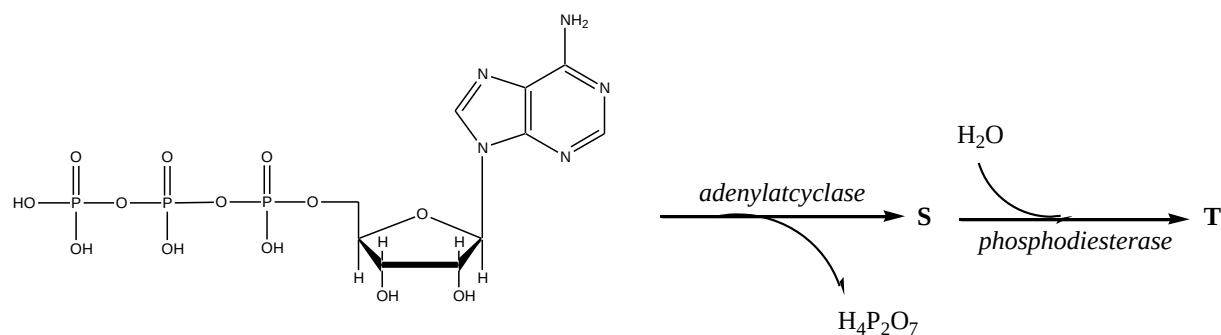
Task 19. Antispasmodic drugs.

Hypertension is a very common pathology. When blood pressure increases, patients need antihypertensive medications such as *Papaverine*. It belongs to a group of antispasmodic substances that relax smooth muscle cells in the walls of blood vessels. *Papaverine* is prepared by organic synthesis as follows:



- Determine compounds **A**, **B**, **C**, **D**, **E**, **F** and **X**, if there are three signals in the ^1H NMR spectrum of **A**, with an intensity ratio of 1:1:3. Note that organic compound **X** can be obtained by hydrolysis of compound **C**.
- To increase the solubility, *Papaverine* is used as a salt with hydrochloric acid. Write the structural formula of the Papaverine hydrochloride cation.
- Drotaverine* is an analog of *Papaverine* and has a gross formula with $\text{C}_{24}\text{H}_{31}\text{NO}_4$. Draw the *Drotaverine* **structure**. Note that it is an *E*-isomer and does not contain any methoxy groups.

The mechanism of action of antispasmodic drugs is based on the inhibition of the enzyme *phosphodiesterase*, which breaks down substance **S** into substance **T** in smooth muscle cells. And substance **S**, in turn, is obtained from ATP using the enzyme *adenylate cyclase*:



- Draw the structural formulas **S**, **T**. Note that in the diagram all acids are written in protonated form; **S** contains 4 cycles; in the cell, **T** is also obtained by direct hydrolysis of ATP.
- Inhibitors of the catalytic centers of enzymes often have a similar structure to the substrate of this enzyme. It is this structure that allows the inhibitor to "capture" the catalytic center of the enzyme and deactivate it. Use the example of the **S** and *Papaverine* structures to explain this similarity.

In the presence of **S** in the cell, the concentration of $\mathbf{M}^{2+}$ ions are maintained at the level of 1×10^{-7} M. And in order for a smooth muscle cell to contract, the concentration of this ion must reach up to 1×10^{-5} M. To achieve this concentration, 6.22 fg of $\mathbf{M}^{2+}$ ions ($1 \text{ fg} = 1 \times 10^{-15} \text{ g}$) should enter the cytoplasm of a smooth muscle cell in the shape of a cylinder (length – 200 micrometers, diameter – 10 micrometers).

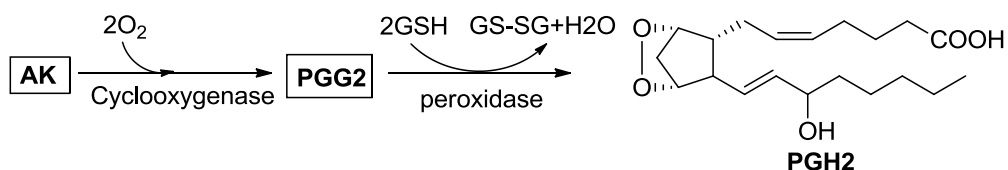
6. Determine the $\mathbf{M}^{2+}$ ion required for smooth muscle cell contraction.

Task 20. Prostaglandins.

Prostaglandins (**PG**) are *eicosanoids* that have high biological activity even at very low concentrations. They are involved in many processes. An imbalance in their synthesis leads to the development of many diseases. In the human body, many prostaglandins are formed from the polyunsaturated fatty acid **AK** (arachidonic acid (C_{20})).

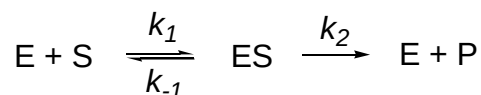
1. Give the structure of **AK**, the iodine number of which is 333.45. Note that the double bond closest to the carboxyl group is located between C_5 and C_6 , and the others are separated from each other by one methylene group, and yet, they all have a *Z*-configuration. *For information:* the iodine number corresponds to the number of grams of iodine that can be added to 100 g of a substance. For example, for monounsaturated oleic acid ($\text{C}_{17}\text{H}_{33}\text{COOH}$), the iodine number is 89.86.

The synthesis of all **PG** begins with the formation of prostaglandin H_2 (**PGH₂**) from **AK** in the following two stages:



2. Give the structure of **PGG₂**, how many new asymmetric carbon atoms appear during the oxidation of **AK** to **PGG₂**?

It was found that *the enzyme* oxidizing **AK** works only 2-4 minutes, and then completely loses its activity. This is because the product of this reaction is an enzyme *inhibitor*. This pattern is called "negative feedback". With its help, an excessive amount of the formed product inhibits the enzyme and thus maintains a constant concentration of **PG**. Below is a partial diagram of the above mentioned:



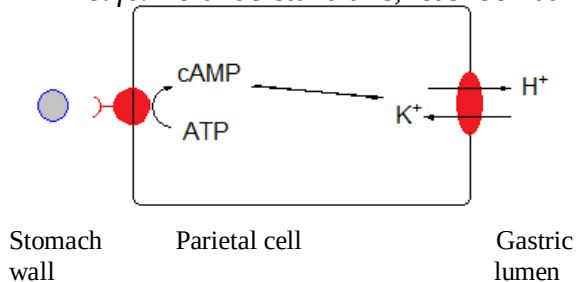
3. Does *the enzyme* bind to the reaction product (*inhibitor*) irreversibly?

4. Complete the diagram so that it fully demonstrates the "negative feedback" pattern.
5. Based on the scheme proposed by you, choose the most optimal option that can be used to re-activate the enzyme:
 - Increase the temperature
 - Increase the concentration of S
 - Reduce the concentration of P
 - Reduce the pH of the medium.

The above-mentioned regulatory mechanism is unique, which maintains a constant concentration of **PG**. But you can change these parameters by changing the activity of the *cyclooxygenase enzyme*. For example, *aspirin (acetylsalicylic acid)* irreversibly inhibits *cyclooxygenase*. In this case, the enzyme is modified by the serine residue and completely loses its enzymatic activity. In this case, an aromatic dibasic acid is formed from *aspirin*.

6. Write the equation for the reaction of irreversible inhibition of the enzyme, while denoting the enzyme as **E-Ser-OH**.

Aspirin suppresses the main signs of inflammation. But with stomach ulcers, this is *not safe*. To understand this, let's look at how *the parietal cells* of the stomach work:



Histamine (light gray bead) binds to the H₂-histamine receptor (red), resulting in the formation of cAMP from ATP. cAMP activates H⁺/K⁺-ATPase (red), resulting in H⁺/K⁺-ATPase pumping H⁺ into the lumen of the stomach and K⁺ back. **PG** and their analogues are inhibitors of H₂-histamine receptors.

7. Choose the reason why aspirin is contraindicated for stomach ulcers:
 - It will use up all the ATP
 - The concentration of **PG** increases and the inflammatory process begins
 - The concentration of histamine in the blood increases
 - The pH of the stomach contents decreases.