**Problem 1. Multicolored Mineral**

Natural mineral **X** is found in nature as crystals of yellow, green, blue, red and purple colors. Colorless crystals are rare.

**1.1**. Determine the formula of substance **X**, if it is known that the suspension obtained by processing powder **X** with sulfuric acid is capable of dissolving glass, and the mass fractions of the two elements that make up **X** differ by less than 5%.

**1.2.** In the natural mineral **X** chromium can substitute the cation in the lattice structure. Write down the electron configuration of the chromium atom that is in the same oxidation state as the metal in the mineral **X**.

**1.3.** What is the coordination polyhedra of the cation and anion of **X**?

**1.4**. Draw the crystal field splitting diagram of the chromium ion present in the crystal structure of X.

**1.5**. Calculate the CFSE and magnetic moment.

**1.6**. When treated with a hot diethylenetriaminepentaacetic acid (C14H23N3O10) solution, **X** dissolves. Draw the structure of the complex anion, knowing that the coordination number of the metal in it is the same as in **X**.

**1.7** The figure below shows the transmission spectra of one of the natural samples of **X**. Determine the color of the sample.
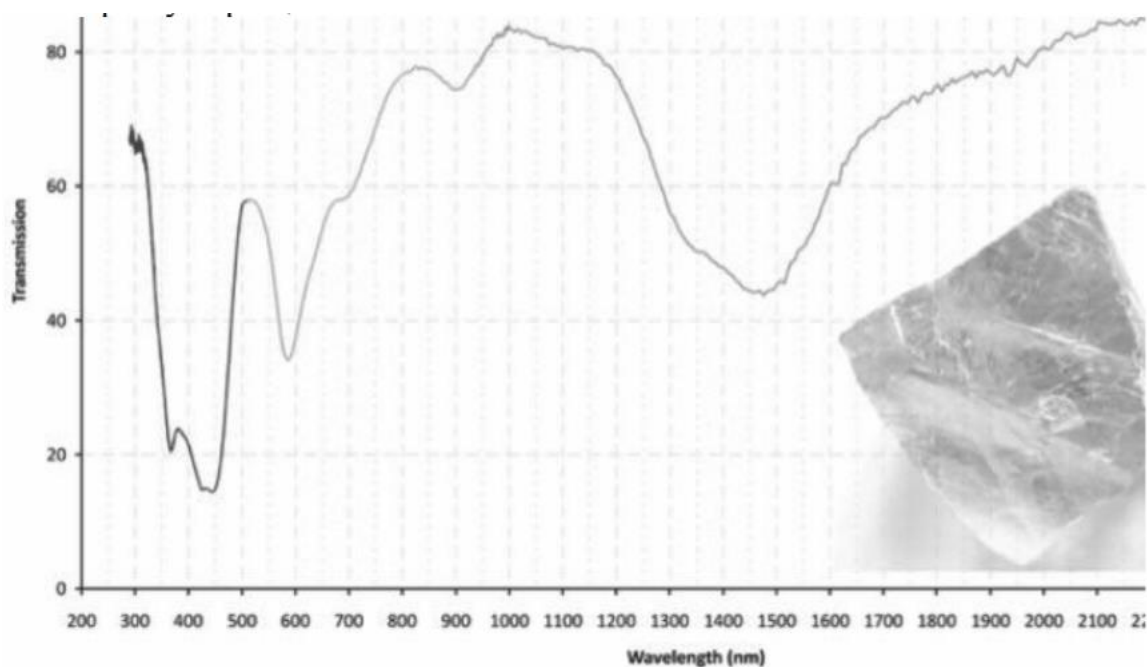
**1.8** The figure below shows the absorption spectrum of the colorless mineral **X** after its treatment with gamma rays. Determine the color of the mineral.
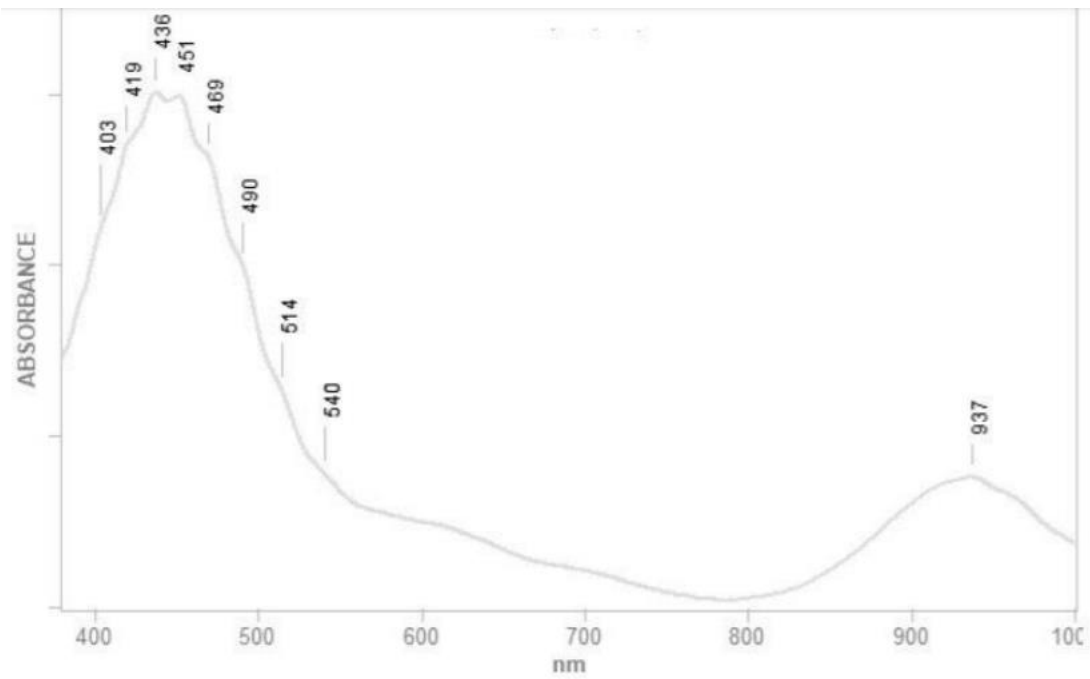


**1.9** What is the cause of the color that appeared after irradiation?

**Problem 2. Organic Synthesis**

Omitted.

**Problem 3. Determination of Ruthenium**

**A.** To 60 ml of an aqueous solution of ruthenium trichloride is added 3 ml of a 2% solution of 8-Ox (8-hydroxyquinoline), and then the pH is adjusted to a value of 4-6.5 with a buffer solution. The mixture obtained is heated for 30 min at 85 ° C to form a complex. After cooling to room temperature, the complex is extracted with chloroform. The extract obtained absorbs at a wavelength of 430 nm.

**3.1.** Give the structural formula of 8-hydroxyquinoline.

**3.2** To establish the composition of the Ru (III) - 8-Ox complex, a series of solutions with a total concentration of $C_{Ru} + C_{8-Ox} = 7.92 \cdot 10^{-6}$ M. Based on the data obtained from the table, determine the composition of the resulting complex and calculate the molar absorption coefficient ($\varepsilon$).

| $C_{Ru} \cdot 10^6$, моль/л | A ($\lambda = 430$ нм, $l = 10$ см) |
|:---:|:---:|
| 0.40 | 0.601 |
| 1.19 | 0.658 |
| 1.98 | 0.823 |
| 2.77 | 0.576 |
| 3.56 | 0.494 |
| 4.36 | 0.412 |
| 5.15 | 0.329 |
| 5.94 | 0.247 |
| 6.73 | 0.165 |

**3.3.** The ruthenium complex was extracted from 60 ml of an aqueous solution with chloroform with a total volume of 25 ml. Calculate the distribution coefficient and degree of extraction (%) of ruthenium, provided that in the aqueous phase its initial concentration is 90 µg / ml, and the concentration after extraction is 0.22 µg / ml. How many consecutive extractions with 1 ml portions can ruthenium be transferred from the aqueous phase to the chloroform layer in with such a degree of extraction?

**B**. Ru (IV) was determined by redox titration. Point equivalences were recorded potentiometrically relative to the calomel electrode. The titrant was generated electrochemically from a solution of 0.04 M CuSO4 in 0.25 M HCl.

**3.4.** Write the equation for the generation of titrant on the Pt electrode.

**3.5.** Is the Pt electrode the cathode or anode?

In one titration of 20.00 ml of a 1.720 mM [RuCl6] 2– solution, it was necessary to generate a titrant at a current of 9.685 mA for 5 min 43 s.

**3.6** Determine what the final oxidation state of ruthenium is. Confirm the answer by calculation.

**3.7** Calculate the titration step in the specified system (total ruthenium concentration −1.720 mM, total copper concentration — 0.04 M, concentration of unrelated ruthenium chloride — 0.25 M), defined as the difference between the potentials in the system 99% and 101% of the way to the equivalence point.

Note that the reduced form of ruthenium in this system is also a chloride complex - [RuCl6] n−. Neglect the hydrolysis and formation of copper(II) chloride complexes in calculations. Standard potentials of redox-pairs, stability constants of complexes and the solubility product CuCl is given below.

$$E^0(Cu^{2+}/Cu^+) = 0.16 \text{ B},$$

$$K_s(CuCl) = 1.2\cdot10^{-6},$$

$$\beta_1([CuCl]) = 7.4\cdot10^4,$$

$$\beta_2([CuCl_2]^-) = 3\cdot10^5,$$

$$\beta_3([CuCl_3]^{2-}) = 5\cdot10^6,$$

$$E^0(Ru^{4+}/Ru^{n+}) = 0.86 \text{ B},$$

$$lg\beta_6([RuCl_6]^{2-}) = 18.7,$$

$$lg\beta_6([RuCl_6]^{n-}) = 22.3.$$

## Problem 4. Fulvene

Fulvene (from lat. Fulvus - red) – is a hydrocarbon that is remarkable for the absorption of light in the visible region ($\lambda$max = 370 nm), as well as the presence of a noticeable dipole moment, which is uncharacteristic for small organic molecules. The noticeable dipole moment can be explained by the presence of two resonance structures of fulvene: non-polar and ionic.



неполярная          ионная
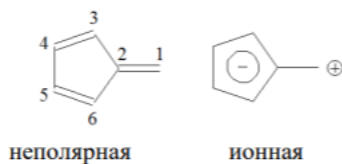
Left: Non-polar      Right: Ionic

**4.1** The table below shows the energy of the fulvene molecular orbitals and their coefficients in the linear combination of atomic orbitals (see atomic numbering above). Calculate the missing factors in the table.

| $\varepsilon$ | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ |
|---|---|---|---|---|---|---|
| $\alpha+2.11491\beta$ | 0.247276 | 0.522966 | 0.429374 | 0.385121 | 0.385121 | 0.429374 |
| $\alpha+\beta$ | 0.5 | 0.5 | 0 | -0.5 | -0.5 | 0 |
| $\alpha+0.618034\beta$ | 0 | 0 | -0.601501 | -0.371748 | 0.371748 | 0.601501 |
| $\alpha-0.254102\beta$ | **XXX** | **XXX** | -0.350542 | 0.279516 | 0.279516 | -0.350542 |
| $\alpha-1.61803\beta$ | 0 | 0 | 0.371748 | -0.601501 | 0.601501 | -0.371748 |
| $\alpha-1.86081\beta$ | 0.356568 | -0.663504 | **XXX** | -0.153468 | -0.153468 | **XXX** |

C1: _____          C2: _____

C3: _____          C6: _____

**4.2** Suppose that the wavefunction of fulvene can be represented as a linear combination of its two resonant forms: $\Psi = \Psi = c_{np}\Psi_{np} + c_{ion}\Psi_{ion}$. Calculate the magnitude of the coefficients with the Hückel method, based on the charges which are located on the methylene residue and on the five-membered ring.

$$|c_{np}| = \underline{\hspace{2cm}} \qquad\qquad |c_{ion}| = \underline{\hspace{2cm}}$$

**4.3** Calculate the enthalpy of the isomerization reaction from fulvene to benzene. Consider that:
**a)** when fulvene absorbs light with a wavelength of 370 nm the electron passes from the HOMO to the LUMO; **b)** the thermal effect of the isomerization reaction is due to only by changing the energy of the $\pi$-system; **c)** the values of $\alpha$ and $\beta$ are the same for benzene and fulvene.

$$\Delta_r H° = \underline{\hspace{3cm}}$$

Note: Numeric answers with an error of < 3% will be considered correct.

**Reference Information**
h = 2πħ = 6.626 · 10e−34 J ·s  c = 2.998 · 10e8 m / s

**Problem 5. Electrochemistry**

**5.1** At present, the quinhydrone electrode is widely used. In this electrode, quinone (Q) acts as the oxidized form, and hydroquinone (QH2) acts as the reduced form. Write down the equation of the reaction proceeding in the system consisting of quinhydrone and standard hydrogen electrodes.

**5.2**. For the reaction of hydroquinone oxidation with hydrogen peroxide, the standard Gibbs energy change is –220.65 kJ / mol at room temperature. Write down the equation of the corresponding reaction and calculate the standard value of the EMF arising in this circuit.

**5.3** Using the data given in the table, calculate the standard potential of the quinhydrone electrode.

**5.4** One of the advantages of the quinhydrone electrode is that its redox potential can be varied by introducing various substitutes into the benzene ring. For example, if nitro derivatives (QNO2 / QH2NO2) are used, the standard potential will be equal to 0.744 V; and if thio derivatives (QSMe / QH2SMe) are used, the potential is 0.605V. Explain why.

**5.5** What is the maximum work that can be extracted in a circuit that is based on the reaction between QNO2 and QH2SMe?

Quinone-hydroquinone pair is found in the respiratory systems. Currently, scientists are working on the creation of artificial analogues. In one of these analogues, a combination of a quinhydrone electrode and cobalt-copper oxide catalysts is used. In the catalytic part, hydroquinone is oxidized by oxygen in the air to quinone, then quinone is transferred to the second part of the fuel cell. There, the quinhydrone element acts as the cathode, and the hydrogen electrode serves as the anode.

**5.6** Write down the half-reactions occurring during the operation of this fuel cell, and an equation describing the cell.

In one experiment, the fuel cell was tested as follows: through the fuel cell at a temperature of 40 ° C and atmospheric pressure, an air stream was passed (21% oxygen and 78% nitrogen) at a rate of 60 ml / min, as well as a stream of hydrogen at a rate of 20 ml / min (temperature and pressure are the same).

**5.7**. Calculate the standard emf that occurred in the fuel cell during the experiment, the maximum power produced by the cell under these conditions, and the efficiency.

**Data:**

|  | $H_2O_2$ | $H_2O$ | $H_2$ | $O_2$ |
|---|---|---|---|---|
| $\Delta_f H°$, кДж/моль | −187.36 | −285.84 | 0 | 0 |
| $S°$, Дж/моль/К | 105.86 | 69.96 | 130.52 | 205.03 |

**Problem 6. Kinetics and catalysis**

An industrially important process for the production of ethylene oxide from C2H4 and oxygen is carried out at a temperature of 298 ° C on a silver catalyst:

2C2H4 + O2 -> 2C2H4O, with rate constant k_eff.
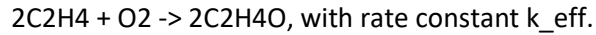
**6.1.** Write down the elemental balance equations for this reaction and express the partial pressure of the product through the initial and current partial pressure of oxygen.
C:
H:
O:
p(C2H4O):

A catalyst was prepared as spherical Ag particles of average diameter 40 nm. Each particle contains on average 192 active centers. Under the conditions of this problem, the order of the reaction is 1$^{st}$ order in ethylene and zero order in oxygen. All reactors have the same volume (80 ml) and constant catalyst loading (1.5 g Ag). First, the reaction was studied in a closed reactor. A mixture of argon (90 vol.%), ethylene and oxygen in a ratio of 1:1 was used at a total pressure of 2.0 MPa. After 10 minutes, the molar amount in the reactor was 0.3 mmol lower.

**6.2.** Calculate $k_{eff}$ with units.

**6.3.** Calculate the turnover frequency of the catalyst with units.

The reaction was studied in a perfect mixing flow reactor with two inputs: through one with a bulk velocity $U1$ the ethylene-argon mixture with a mass C2H4 content of 4.0%, and through the other - pure oxygen ($U2$). In stationary mode, the pressure in the streams and in the reactor was 2.0 MPa. The temperature of the streams is the same.

**6.4.** Calculate the volume flow ratio $U1 : U2$, at which ethylene and oxygen enter the reactor in stoichiometric amount.

**6.5.** Write down the expressions for the rate of change in the concentration of all compounds in the reaction in a flow-through mode and express the depth (??) of the reaction.

d[C2H4]/dt:
d[C2H4O]/dt:
d[O2]/dt:
[C2H4O]st/[C2H4]0:

**6.6** With a fixed oxygen flow of 0.14 ml / s and with varying ethylene flow, the maximum achievable ethylene conversion is 8.727%. Calculate from this data the ratio of the volume flow at the input U1/U2 at the optimal conversion.

**6.7** At elevated temperatures, a competing process is catalyzed with the formation of gas **X**. Draw the structural formula **X**, if it is known that the mass fraction carbon in it lies in the range from 27 to 30%.

**Problem 7. Polymer Chemistry**

The radical polymerization of methyl methacrylate is initiated by AIBN at 80 ° C.

**7.1**. Draw diagrams of chemical reactions, write down the corresponding kinetic equations and derive an expression for the polymerization rate (monomer consumption), and derive that the observed order of polymerization rate with respect to initiator is ½.

**7.2.** Determine the rate constant k_T of termination on the TEMPO radical, if the polymerization of 10 g of styrene (density 0.89 g / cm^3) was carried out in the presence of 4 * 10e-4 M AIBN and 1.3 * 10e–5 M TEMPO. The degree of polymerization of the obtained product is P_n = 26, the chain growth rate constant is k_p = 311 L / (mol · s).

Polymer product **P4** was synthesized as follows:
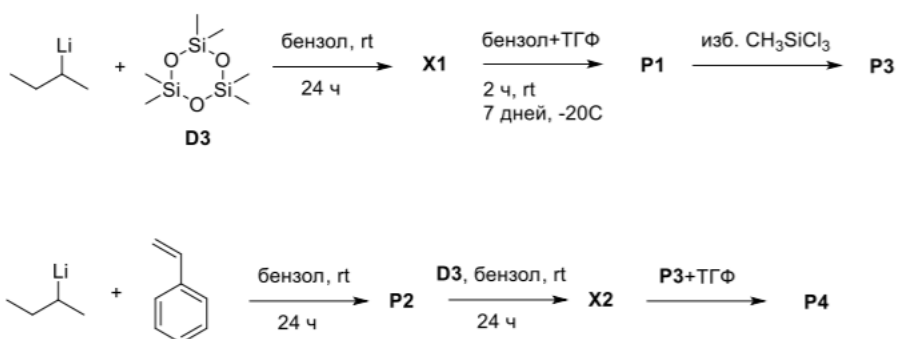


When answering the questions below, note that compound **D3** very slowly enters the described reactions in the environment of pure benzene and relatively quickly in a mixture of benzene with THF.

(бензол = benzene, ТГФ = THF, ч = hour, дней = day, избыток = изб. = excess)

**7.3.1**. Draw polymers **P1-P4.**

**7.3.2.** The chromatograms are shown below (dependence of the differential refractive index on the volume held). Match each chromatogram with one of products **P1 – P4** (if necessary, indicate whether these products were fractionated before recording the chromatogram). For chromatograms containing additional peaks in addition to the corresponding target products, explain the appearance of additional peaks (give the structures of the corresponding by-products).
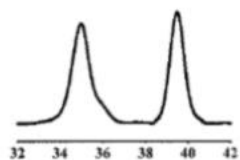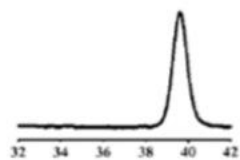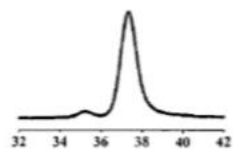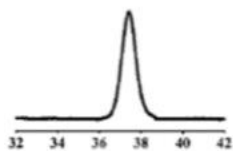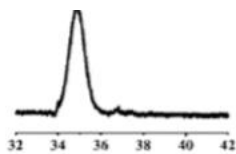


**7.3.3.** For product P4, list the signals in the 1H NMR spectrum. Label each signal with a Latin letter and indicate: a) the position of the corresponding proton in the structure; b) the type of splitting; and c) the relative integrated intensity (for signals for which it is possible)

**Problem 8. Substrate Inhibition**

In some cases, with increasing substrate concentration, the initial rate of the enzymatic reaction passes through a maximum and then decreases. Most often, this type of dependence can be quantitatively described on the assumption of the formation of a SES ternary complex that does not possess enzymatic activity (scheme 1):

$$E + S \underset{}{\overset{K_s}{\rightleftarrows}} ES \overset{k_{cat}}{\rightarrow} E + P \qquad\qquad (1)$$
$$\updownarrow K_s'$$
$$SES$$
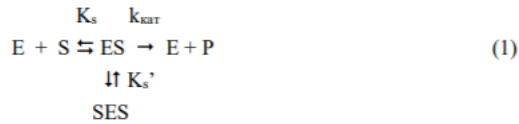
Assume the following:

a) $[S]\_0 \gg [E]\_0$
b) all equilibria in the system are established
c) initial conditions are considered, $[S] = [S]\_0$.

**8.1.** Derive the expression for the initial rate of the enzymatic reaction v_0.

**8.2.** Sketch a plot of v_0 versus [E]_0 and v_0 versus [S]_0.

**8.3.** Analyze the resulting expression for the initial velocity at high and low substrate concentrations. Write down the expressions for these conditions and the corresponding simplified expressions for v_0.

**8.4**. Does any part of the plot of the dependence of v_0 on [S]_0 coincide with that for the Michaelis-Menten two-stage scheme in the absence of substrate inhibition?

If yes, under what condition?

**8.5** Propose a method for determining k_cat, K_s and K_s' from experimental data.

Substrate inhibition at high concentrations will also be observed if the SES ternary complex retains activity, but less than the enzyme-substrate complex ES ($\beta < 1$).

**8.6**. Write down the kinetic scheme for the specified case.

**8.7.** Is it possible to distinguish between cases of complete and partial inactivity of SES graphically? If so, how?