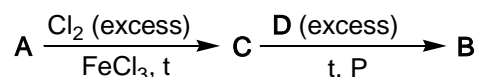
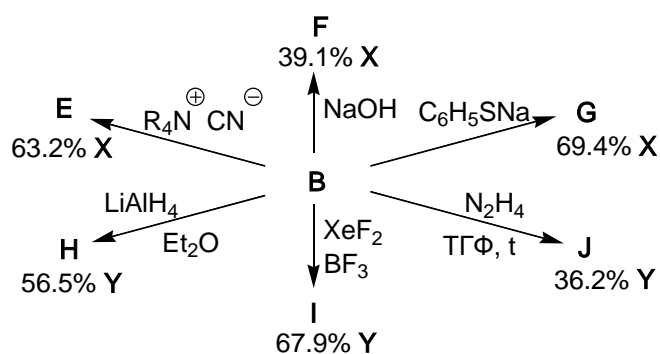


Problem 1

In 1960 the interesting effect, which was later utilized in preparation of new generation of liquid crystals, was discovered. Namely, equimolar mixture of two liquid binary compounds **A** (it contains 92.3% of element **X**, melting point 5.5°C) and **B** ($\omega_X = 38.7\%$ **X**, mp = 3.9°C) melts at much higher temperature (23.7°C) than pure compounds. Compound **B** can be synthesized from **A** according to scheme below, wherein reagent **D** is binary compound which contains 32.8% of element **Y**.



Compound **B** does not react with sodium at room temperature and with NaH even under heating. At the same time, **B** undergoes several transformations, some of them are given in the scheme.



- Decipher compounds **A** – **J** accounting for the following facts:
 - Compounds **A**, **B**, and **E** have the same symmetry.
 - C**, **E**, **I** are binary compounds.
 - Compound **I** has two types of **Y** atoms; in **J**, all atoms of **Y** are equivalent.
- In list of answers you can find a number of possible explanations of higher melting point of equimolar mixture of **A** and **B** in comparison with melting points of pure **A** and **B**. Point out the right explanation.

It is known that:

- in compound **C**, **X–X** bond length is 1.39 Å, **X–Cl** bond length is 1.75 Å
 - van der Waals radius of chlorine atom is 1.75 Å.
- Have compounds **A** and **C** the same symmetry? Confirm your answer by calculations. Transformation of **C** into **B** is stepwise process (**C** – **K1** – **K2** – **K3** – **K4** – **K5** – **B**).
 - Write down structural formula of compound **K2** accounting for fact that compound **K3** has two types of equivalent **X** atoms and one type of **Y** atoms.

Problem 2

One of the most important organic reactions is Friedel-Crafts alkylation of aromatic compounds, $\text{ArH} + \text{R} \xrightarrow{\text{AlCl}_3} \text{ArR} + \text{HX}$ (1). This reaction was discovered 1877 and found immediately the practical application despite the existence of some drawbacks.

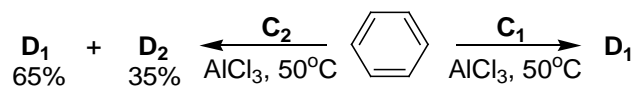
1. Write down products of reaction (1) between C_6H_6 and CH_3Cl for ArH:RX ratio of 4 : 1 (product **A**) and 1 : 4 (^1H NMR spectrum of the main product **B** contains two signals with the relative intensity of 6 : 1).

When mixture of C_6H_6 and CH_3Cl (1 : 2 molar ratio) was stirred in the presence of AlCl_3 under moderate heating for long enough time, the equilibrium mixture of dimethylbenzenes (xylenes) was formed.

2. Calculate a composition of this mixture at 50°C , using equation $\ln K = -\Delta G/RT$ and data given below. Point out which isomer is the most thermodynamically stable.

	<i>o</i> -xylene	<i>m</i> -xylene	<i>p</i> -xylene
$\Delta_f H$, kJ/mol	-24.4	-25.42	-24.34
S, J/mol·K	246.0	252.2	247.4

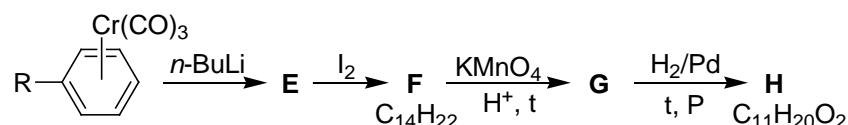
Alkylation of benzene with alkyl chloride **C**₁ (AlCl_3 , 50°C) affords product **D**₁; when isomeric alkyl chloride **C**₂ was used for alkylation, mixture of **D**₁ and isomeric product **D**₂ was obtained.



3. Write down structural formulae of compounds **C**₁, **C**₂, **D**₁, **D**₂ accounting for fact that $M(\text{D}) : M(\text{C}_6\text{H}_6) = 1.54$.

4. Based on previous discussion, point out drawbacks of Friedel-Crafts alkylation of arenes.

The progress in organometallic chemistry developed significantly the number of methods for arenes alkylation. Thus, alkylcyclohexanecarboxylic acid **H** was obtained according to the scheme below.



5. Write down structural formulae of compounds **E** – **H** accounting for ^1H NMR data of compound **F**. Namely, singlet (9H), two triplets (2H and 3H), and two multiplets (2H and 2H) are present in aliphatic region of this spectrum; singlet, two broadened doublets and double doublets are present in aromatic region of spectrum.

Problem 3

All arts consist in the investigation of the truth
Marcus Tullius Cicero (106 B.C. – 43 B.C.)

Parthenon – is the one of the most known monuments of the antiquity which is situated in the Athenian acropolis. This temple is dedicated to the goddess Athena who is the patroness of the city Athens, Greece. Actually, Parthenon is dilapidated and it has been doing repair works of its framework since 1975. The missing building blocks are produced from the same stone pits that in the antiquity's times and the same natural pigments are used to paint the sculptures and the edifice. There are all examples of natural pigments (minerals) in the museum of Parthenon. The table contains all necessary.

In this Problem you should determine the 6 most useful antiquity natural pigments.:

№	Pigment (Mineral)	Color	$\omega(M^*),\%$	Lost of the mass in % after calcination			
				without access of O ₂	and gaseous products formed	with access of O ₂	
I	μέλαν	Black	0	0	—	100	A
II	κύανος	Blue	55.311	30.764	A	30.764	A
III	χρυσόκολλα	Green	57.478	28.051	A	28.051	A
IV	αρρενικόν	Yellow	60.898	0	—	100 / 19.594**	B + D
V	σανδαράκη	Brown	70.025	0	—	100 / 7.543**	B + D
VI	κίναβαρι	Red	86.216	0	—	100 / 13.784**	B + C

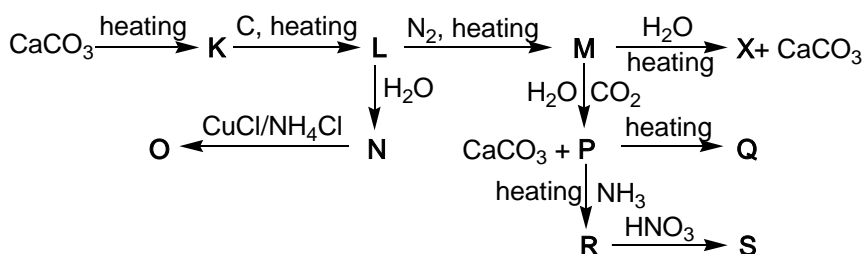
* M – metal or metalloid; ** This value is given after the condensation of compounds **D** and **C**.

It is known that the three of these six pigments are the binary compounds. One of the pigments is a simple compound. Two pairs of the pigments (II – III and IV – V) have the same qualitative composition. The gas **A** is formed when black pigment burn in air and also when blue or green pigments were thermally decomposed. The gas **B** is formed by the ignition of the three last pigments with access of O₂. In addition, except gas **B**, there is also formation of gas **D** (for pigments IV and V) or **C** (for pigment VI), which could be condensate by slight decreasing of temperature: the solid **D** and liquid **C** are formed. All pigments, except “μέλαν”, contain only one metal in their composition. Possible liberation of water as by-product is not pointed out.

1. Determine all pigments and unknown gases **A – D**.
2. Write the equations for all reaction discussed above.
3. Write one reaction for each of three cases, where gases **A** and **B** are formed simultaneously and: a) others products are not formed, b) water is also formed, c) water and another gas are also formed.

Problem 4

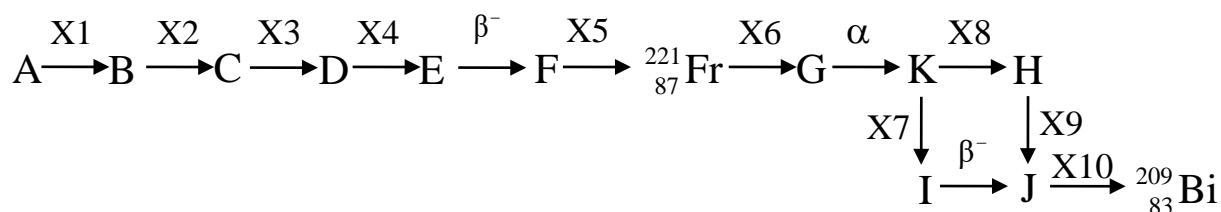
The scheme under consideration was realized successfully for atmospheric N_2 industrial binding at the beginning of the 20th century (Frank-Karo process). The formation of **M** salt (50% mass of calcium) is the key part of this scheme. Soon the Haber-Bosch process replaced the Frank-Karo one, but nevertheless nowadays the significant amounts of **L** and **M** are produced being the precursors for **N**, **O**, **P** and **Q** syntheses. **N** is a gas widely used in welding, **O** is its acyclic dimer being the important precursor for the chloroprene rubber production. **P** is a weak acid with $K_a = 5.4 \cdot 10^{-11}$, **Q** is a symmetric cyclic trimer of **P**. Several years ago **Q** was involved in the great scandal, being detected in milk products made in China. **R** is an extremely strong base, forming salts with acids, for example, the **S** salt with nitric acid. The interesting feature of **S** is that both cation and anion of **S** have the same geometry.



1. Determine the **K** – **S** substances.
2. Write down the reactions equations.
3. Draw the resonance structures and the resonance hybrid formulae for the cation and anion of **S**.

Problem 5

There are three natural radioactive series and one artificial. After alpha- and beta-radioactive transformations the series end with the formation of stable isotopes. The figure shows one of the series:



It is known that in this series $X_4 = X_1$ (X – type of decay). Radioactive decay proceeds as a first-order reaction: $dN / dt = -\lambda N$, where λ is the decay constant, N – number of radioactive nuclei at time t .

1. Determine the half-life time $T_{1/2}$ for **C**, knowing that of $7.24 \cdot 10^{12}$ atoms decays only one each second on the average. Determine element **C**, and then **D**, **E** and **F** используя the following data: a) in 500 years from 1 g of **C** $9.333 \cdot 10^{-6}$ moles of helium is released as a result of α -decay; b) the molar mass of **C** is by 2.533 times higher than the nuclear charge.

Only seven minerals of **I** are found naturally. Two of them are lorandite IAsS_x and vrbaitite $\text{I}_4\text{Hg}_3\text{Sb}_x\text{As}_8\text{S}_{20}$. The abundance of **I** in them is 60 and 28.6% (mass) respectively.

2. Determine the elements **I** and **J**, if the value of molar mass of **I** is by 2.580 times higher than the nuclear charge.

3. Radioactive sample weighting 3 g consists of isotopes **A1** (35% mass, $T_{1/2} = 2.1$ days) and **A2** (65% mass, $T_{1/2} = 4.4$ days). The mass number of **A1** is by 1 a.m.u. higher than that of **A**, and by 3 a.m.u. lower than for **A2**. Determine **A**, knowing that after 12 hours after preparation of the sample its activity was $4.61 \cdot 10^5$ Curie (1 Curie means $3.7 \cdot 10^{10}$ decays/s). Activity of the sample consisting of several isotopes is an additive quantity. The molar mass of **A** is by 2.548 times higher than the nuclear charge.

4. Determine nuclides **B**, **G**, **H**, **K**.

5. Write in the most detailed form an equation of nuclear reaction for alpha- and beta-decay, one example for each decay.

6. Calculate the binding energy (in MeV) per 1 nucleon for bismuth-209.

Precise mass of the particles (a.m.u.): atom – 208.980, proton – 1.0072747, neutron – 1.0086658, electron – $5.4857937 \cdot 10^{-4}$; $1 \text{ eV} = 1.602 \cdot 10^{-19} \text{ J}$, the speed of light in vacuum $c = 2.99792458 \cdot 10^8 \text{ m/s}$, $1 \text{ a.m.u.} = 1.66054 \cdot 10^{-27} \text{ kg}$.

Problem 6

Polymer macromolecules are not rigid. They reveal definite flexibility due to the rotation around single bonds in the main chain. The end-to-end distance for a polymeric molecule can adopt any value between zero and H , the macromolecule length in the fully stretched conformation (contour length). Accounting for all possible macromolecule conformations, the average end-to-end distance $\langle h \rangle$ can be calculated.

1. Draw the structure of the repeating unit of polypropylene (PP). Taking the C–C bond length as 1.5 \AA , calculate the length of the repeating unit l accounting for the valence angles. What is the length H of fully stretched PP molecule consisting of 1000 units?

Real macromolecules can be represented by various models. Thus, in the freely-jointed chain model, the repeating units are considered as rigid sticks that can be jointed at any angle. In this case $\langle h \rangle = L \sqrt{n}$ (l is the length of the repeating unit, n is the number of units in the macromolecule).

2. Based on the freely-jointed chain model, calculate the average end-to-end distance of the PP molecule consisting of 1000 repeating units.

Definite limitations are applied to the allowed angles in more realistic models, which makes jointing of the repeating units at arbitrary angles impossible. Nevertheless, a macromolecule can be represented as a set of freely-jointed *segments*, each of the latter being composed of a repeating units. Thus $\langle h \rangle = L \sqrt{N}$, L is the length of the segment, N is the number of the segments per macromolecule.

3. Within the model of the freely-jointed segments, express $\langle h \rangle$ as a function of the length of the repeating unit l and the number of the repeating units per segment a .

4. The experimental value of $\langle h \rangle$ for a PP molecule consisting of 1000 units was found as 17.3 nm. Calculate the segment length and the number of the repeating units in the segment.

Experimental values of a for six polymers (cellulose, poly(ethylene oxide), polystyrene, poly-(γ -benzyl- L -glutamate), poly(vinyl chloride), poly- p -benzamide) are given in the answer sheet.

5. Fill in the gaps (draw the missing repeating units of polymers) in the table in the answer sheet. Select the polymer with the most rigid chain. Note that poly(γ -benzyl- L -glutamate) exists in the α -helix form under experimental conditions.

Problem 7

Dark oxidation of a colorless chromogenic reagent **HD** by hydrogen peroxide practically does not occur. Under the conditions of UV photolysis, the peroxide forms hydroxyl radicals:



that rapidly interact with reagent **HD** added in advance:



The **D**[•] radicals instantly transform into the colored final product **P** (**D**[•] → **P**). Small aliquots are periodically taken from the reagent mixture and the concentration of **P** as function of time is measured. The initial concentrations of the reagents were: $c_{\text{HD}} = 1 \cdot 10^{-4}$ M, H_2O_2 3 M; reaction (2) rate constant k_2 was equal to $k_2 = 3 \cdot 10^7 \text{ M}^{-1}\text{sec}^{-1}$.

1. Calculate the average rate of formation of **P** ($d[\text{P}]/dt$, mol/L·sec), if it was constant during the 1st minute of reaction and the concentration of **P** at $t = 45$ sec was equal to $1.25 \cdot 10^{-5}$ M.

2. Given that the concentration of **OH**[•] radicals in the reaction is almost constant (and, accordingly, the rate of generation of radicals under UV light w_{in} is equal to the rate of their consumption by reaction 2), calculate the rate of generation of **OH**[•] radicals. Calculate the steady-state concentration of radicals (neglect the change in the concentration of reagent **HD**).

3. A similar system is used for the determination of trace iron. The determination is based on obtaining the hydroxyl radical from peroxide by the Fenton reaction:



with the result that the rate of product **P** formation increases. Let the system irradiated under the same conditions as above contain the former concentrations of H_2O_2 and **HD** plus a certain concentration of Fe^{2+} . Calculate this concentration (c_1), if $c_{\text{H}_2\text{O}_2} = 3$ M, the rate constant of reaction (3) $k_3 = 50 \text{ M}^{-1}\text{sec}^{-1}$, and the concentration of product **P** during the first 45 sec of reaction has reached $2.5 \cdot 10^{-5}$ M.

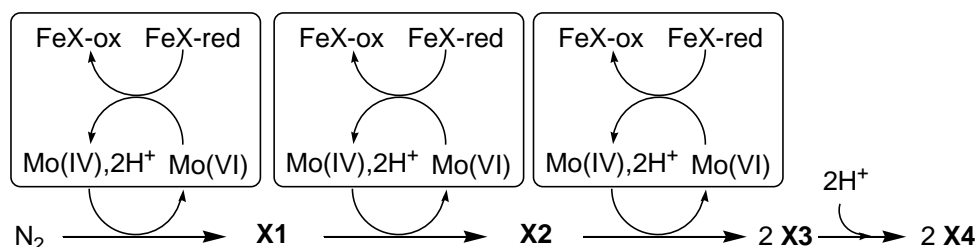
4. What will be the rate of product formation ($d[\text{P}]/dt$)₂, if the concentration of iron(II) c_2 in this solution will be equal to $7.5 \cdot 10^{-9}$ M?

Problem 8

Nitrogen is an important element in living nature. Fixation of atmospheric N_2 is a fundamental problem. Industrial processes are possible only under extreme conditions, thus being energy and resources consuming. In nature, nitrogen is fixed during thunderstorms or as a result of bacteria metabolism.

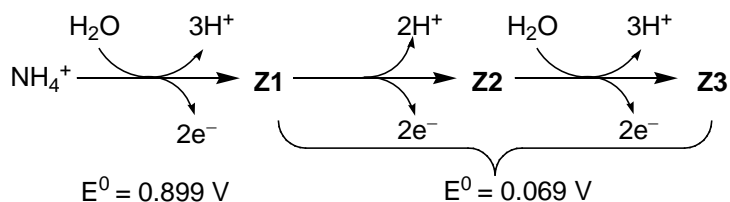
1. Write down reactions of a) industrial and b) natural N_2 fixation. Give conditions.
2. Soil bacteria bind $1.8 \cdot 10^{11}$ kg of N_2 per year (more than all the world industry!). Estimate the quantity (in moles) of nitrogen atoms fixed on 1 m^2 of soil per month. Take the Earth radius as 6400 km.

Nitrogen fixation occurs in nitrogenase enzymatic system (with Mo and Fe in the active site) under anaerobic conditions.



3. Determine the composition of **X1** – **X4**.
4. Ability to reduce gaseous (STP) hydrocarbon **Y1** to **Y2** is referred to as nitrogen-fixing potential of cells. Decipher **Y1** and **Y2** if mass fraction of carbon in **Y2** is by factor 1.077 lower than that in **Y1**.
5. Nitrogenase system is also capable of reduction of toxic (for man) anions according to the reaction equation: $X5 + 2e^- + 4H^+ \rightarrow X6 + X4$. In turn, **X6** is also enzymatically reduced affording solely **X4**. Decipher **X5** – **X6**.

Bacteria *Nitrosomonas* are capable of utilizing nitrogen compounds as an energy source:



6. Decipher **Z1** – **Z3** and calculate the free energy of $NH_4^+ \rightarrow Z3$ transformation (use $\Delta_r G = -F \sum n_i E_i^0$). Note that **Z2** is unstable.