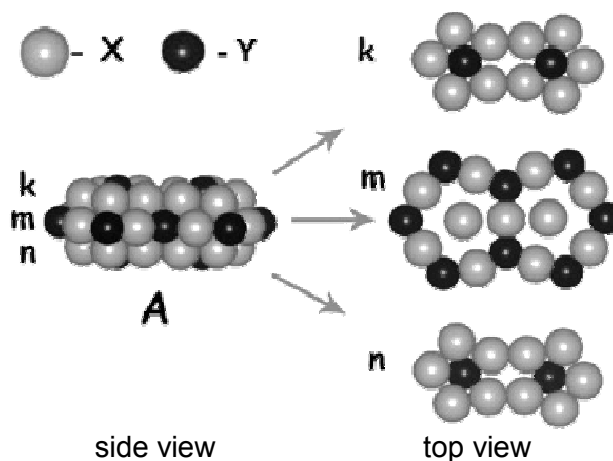


Problem 1

Any new stuff is elegantly clothed old one
Proverb

The complex metallic alloys – special type of compounds which are characterized by a large elementary cell which generally includes more than 100 atoms. Crystals of these compounds consist of atomic clusters which stabilize the structure. The atoms of the crystal which are not included in the cluster are labeled as “glue” atoms.

Compound $X_{13}Y_4$ has orthorhombic lattice ($\alpha = \beta = \gamma = 90^\circ$) with the cell parameters: $a = 8.16 \text{ \AA}$, $b = 12.34 \text{ \AA}$, $c = 14.45 \text{ \AA}$. Alloy density 4018 kg/m^3 . The crystals of this compound consist of 3-layer atomic clusters **A** (see figure, layers k, m, n) and “glue” atoms. One elementary cell contains 2 atomic clusters **A** and the number of “glue” atoms doesn’t exceed 30.



1. How many linear **Y–X–Y** bonds are there in a single cluster **A**?
2. Find the number of atoms in the elementary cell of $X_{13}Y_4$.
3. Decipher $X_{13}Y_4$, taking into account, that the mass of “glue” atoms comprises 12.27% of the total mass of the compound.

Compound $X_{13}Y_4$ is an efficient catalyst for hydrogenation of unsaturated hydrocarbons. The key process of the mentioned reaction is dissociation of hydrogen molecules on the metal surface. The dissociation activation energy on the compound surface at 300 K is 45% smaller than on the surface of pure metal **X**. The pre-exponential factor A is the same for both dissociations and besides that $k(X_{13}Y_4) / k(X) = 5 \cdot 10^7$.

4. Calculate the activation energies for hydrogen dissociation on $X_{13}Y_4$ and **X** surfaces.
5. Calculate the hydrogen dissociation rate constant for $X_{13}Y_4$ at 350 K, if $A = 10^5 \text{ mol/L}\cdot\text{s}$.

Physical constants: $R = 8.314 \text{ J/mol}\cdot\text{K}$, $N_A = 6.02 \cdot 10^{23} \text{ mol}^{-1}$.

Problem 2

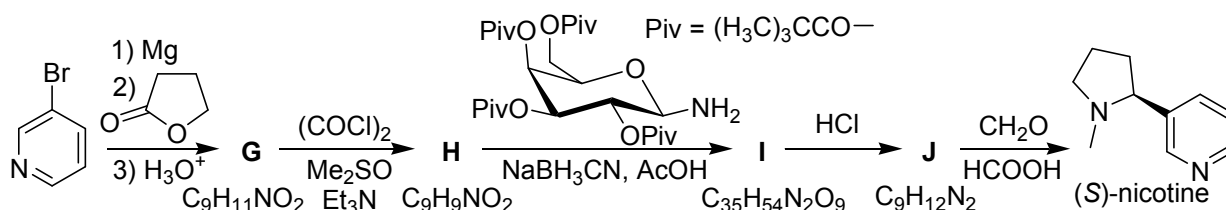
Nero Wolfe, a fictional character created by the mystery writer Rex Stout, was not only excellent armchair detective but also well-known amateur orchid grower. Some stories, devoted to Wolfe, includes description of the greenhouse disinfection using fumigation with cyanogas G, Nico Fume and ciphogene. Ciphogene is a fictional fumigant but two others were really used for this goal. Cyanogas G (compound **A**) is a poisonous liquid with b.p. 26.7°C . For safety, this was producing directly in a greenhouse from the “black cyanide” (compound **B** containing 30.4% of nitrogen). In the pure form, **B** is a white powder but commercial product contains some impurities providing black-gray coloration. In the presence of water (even in the wet air) **B** undergoes hydrolysis producing **A** and **C**.

1. Write formulae of compounds **A** – **C**.

At the present time other fumigants are usually applied. These are, in particular, phosphine (predominantly for treatment of grain elevators), chloropicrin, pyrethroids, which are toxic for insects but non-hazardous for human, as well as other agents. One of the methods for the phosphine preparation is the reaction of the aqueous solution or the suspension of **C** with white phosphorus (reaction 1). Chloropicrin (**D**, it contains 64.7% of chlorine by the weight) was for the first time synthesized by Stenhouse in 1848 by the reaction of picric acid with bleach powder. In this reaction (reaction 2) chloropicrin was a single organic product. Now **D** is synthesizing from one of two widely used solvents. Treatment of solvent **E** with acetyl nitrate ($\text{CH}_3\text{COONO}_2$) (reaction 3) and chlorination of solvent **F** in the alkaline medium (reaction 4) produce chloropicrin **D**.

2. Determine compounds **D** – **F**. Write equations for reactions 1 – 4.

Nico Fume was used as pesticide until now. However, since 1.1.2014 this is putted under restraint in the most countries. The active ingredient of Nico Fume is alkaloid (*S*)-nicotine isolated from leaves of tobacco (*Nicotiana tabacum*). There are many methods for synthesis of this alkaloid. One of them is given in the Scheme below.



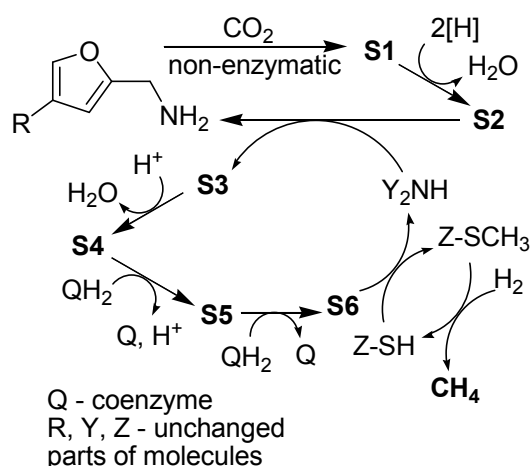
3. Decipher this scheme. Write down structural formulae of compounds **G** – **J**, accounting for the absolute configuration for the chiral centers.

Problem 3

Hydrocarbons are important raw material resources. The ways of their stock formation are still under dispute in academic community. Microorganisms (archaea *Methanococcus*) capable of methane synthesis from carbon dioxide and hydrogen have been recently found.

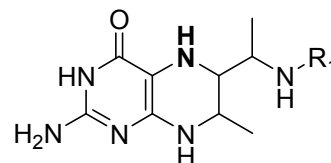
1. Write down the total equation of methane synthesis by archaea.

In reality, the synthesis is a multistep process, which occurs according to the scheme on the right.



2. Draw the structures of S1 and S2. In S3 – S6, indicate the oxidation state of the carbon atom originating from carbon dioxide.

3. The essential fragment of Y₂N–H structure is as follows:
Draw the structural formula of S4.



Methane is treated as a dangerous greenhouse gas. $6.00 \cdot 10^{14}$ g of methane annually replenish the atmosphere, 70% of the gas being of biogenic origin.

4. Suppose that methane forms a compact shell around the Earth at a definite height under the following conditions: pressure of 0.50 bar and temperature of -20°C . Calculate the annual increase in the shell thickness. Take the Earth radius as 6370 km.

The compound X makes the major contribution (estimated as 40 to 70%) to the formation of greenhouse effect on the Earth. X can be obtained in the reaction of two simple substances. X is completely absorbed by 0.1 M NaOH solution, whereas passing X over red-hot coal leads to the formation of a gas with relative density with respect to helium lower than 5.

5. Decipher X and write down equations of all the mentioned reactions.

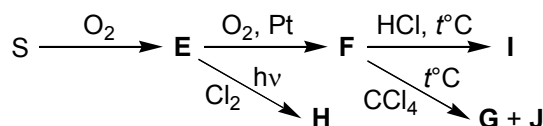
Problem 4

Young chemists studied the oxidation of potassium iodide with one and the same solution of permanganate but using different reaction conditions. Each of them weighed out 0.10 g of KI and started the experiments. First chemist spent 2.4 mL of KMnO_4 solution for the titration, while the second chemist spent 24 mL, and the third one spent 96 mL (!). It is also known that the third chemist titrated in the presence of an excess of barium nitrate.

1. Write down the reactions of titration.
2. Calculate the concentration of the permanganate solution used.
3. When iodide is titrated with permanganate to obtain iodine, it is difficult to observe the endpoint, because both iodine and the titrant are colored. For this reason, the titration is usually performed in an ice bath in the medium of 4 – 5 M HCl after an addition of a few milliliters of CCl_4 and shaking the reaction mixture. At first, the organic solvent layer is colored by iodine, and in the endpoint it becomes virtually colorless. Calculate the molar ratio of titrant and iodine for this case and write down the reaction equation, if 9.6 mL of 0.025 M permanganate solution was spent for the titration of 0.10 g of KI.
4. Let a 0.050 M solution of KMnO_4 contain 0.002 M Fe(III) and 0.003 M Cu(II). What kind of side reactions may occur during the titration of iodide to iodine with such a solution in an acidic medium (the endpoint is observed by an electrochemical method)? Will these side reactions interfere with the correct determination of the concentration of permanganate, and if the answer is yes, then will the concentration be overestimated or underestimated?

Problem 5

One may synthesize three colorless liquids **H**, **I** and **J** from sulfur S according to the next scheme. **E** and **G** are toxic gases, the density of **G** is 4.42 g/L under normal conditions, **F** is a solid substance with a low melting point. The hydrolysis of **H**, **I** and **J** by alkali solution action leads to the same mixture of water-soluble products, reacting with $\text{Ba}(\text{NO}_3)_2$ aqueous solution to precipitate **K** (mass m_1). After **K** decantation, the remaining solution may precipitate **L** (mass m_2) on acting of excess of AgNO_3 aqueous solution. Both **K** and **L** are white and insoluble in acids. For the case of **H** the m_1 / m_2 ratio equals to 0.814 while for both **I** and **J** it is twice as much. According to the IR-spectroscopy data, only spectrum of **I** in area $3500 - 3700 \text{ cm}^{-1}$ contains the valent vibrations with frequencies being the same as in the water molecule spectrum, but in **H** and **J** spectra such vibrations are absent.



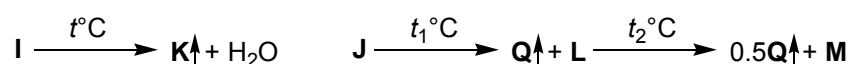
- Determine the E – L substances, taking into account that H, I, J have S atoms, but G hasn't.
- Write down the equations for the reactions of H – J synthesis and hydrolysis by the NaOH solution action.
- Draw the graphic formulae for G, H, I, J.

Problem 6

The data (mass %) about some Na and N or P containing neutral salts are given in the table below. The oxidation states of N and P lying in one line of the table are the same.

N-containing salts			P-containing salts		
Salt	% Na	% N	Salt	% Na	% P
A	46.9	9.5	E	42.1	18.9
B	27.1	16.5	F	22.5	30.4
C	33.3	20.3	G	36.5	24.6
D	43.4	26.4	H	26.1	35.2

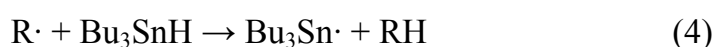
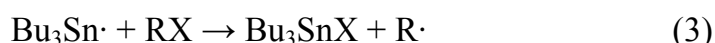
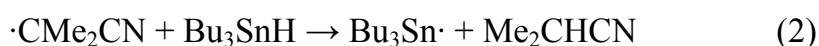
D and H are the salts of I and J acids respectively. Both of these acids are white solids, readily decomposed on heating. The thermolysis of I goes through one stage, while the thermal decomposition of J runs through two stages.



- Determine the chemical formulae of A – H and draw its graphic formulae.
Note: the graphic formula of polymer chain is to be drawn for F.
- Determine the I, J, K, L, M, Q formulae and write down the reaction equations of I and J thermolysis.
- Draw the graphic formula of a gas K and propose another substance forming the same decomposition products as in the case of I, draw the reaction equation.

Problem 7

Radical reactions are not very often using in the preparative organic chemistry. The main reason is the low selectivity of the most radical reactions. The synthetic potential of radical reactions is extended by use of special reagents and reaction conditions. For example, transformations of alkyl halides RX under the treatment with azobis(isobutyronitrile) – Bu_3SnH pair (system **I**) includes steps of initiation (1), $Bu_3Sn\cdot$ radical generation (2) and chain growth (3, 4):



1. Write down product of the reaction of 1-bromohexane with the system **I**.

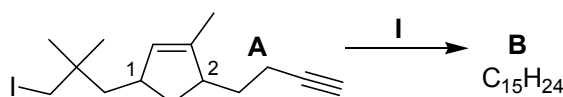
When 6-bromohex-1-ene was treated with system **I**, the cyclization of $R\cdot$ into two isomeric radicals $R1\cdot$ and $R2\cdot$ has priority of the step (4). The following reactions of radicals $R1\cdot$ and $R2\cdot$ by the step (4) lead to formation of products **P1** and **P2**, respectively.

2. Write down structural formulae of $R1\cdot$, $R2\cdot$, **P1** and **P2**.
3. Calculate the composition of the obtained mixture (in molar %), if, according to 1H NMR spectrum, the ration of methylene and methyl protons in this mixture is 2.8 : 1. Point out, kinetic or thermodynamic control determines this composition.

The reaction of **I** with non-branched acyclic bromodiene **X** generates radical $R\cdot$, which is transformed into 2-methylbicycloalkyl **Y** as a result of two consecutive intramolecular cyclizations.

4. Write down structural formulae of **X** and **Y** accounting for fact that size of rings in **Y** is the same as that for the major isomer in the mixture of **P1** and **P2**.

The treatment of iodide **A** with the system **I** induces tandem radical cyclization resulting in natural bioactive compound hirsutene (**B**) which belongs to the class of triquinanes (compounds containing three size-defined rings). In the scheme below atom C(1) in **A** has (*S*)-configuration, atom C(2) has (*R*)-configuration.



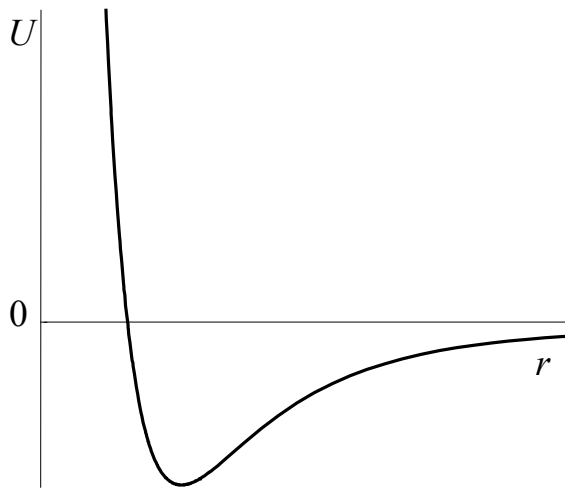
5. Write down structural formulae of **A** and **B** accounting for absolute configuration of the chiral centers.

Problem 8

Diatomic molecule with masses of atoms m_1 and m_2 can be considered as a *rigid rotator*, if rotation doesn't affect the equilibrium internuclear distance r_e . In quantum mechanics rotation energy of a molecule $E_{\text{rot}} = B_e J(J+1)$, where $J = 0, 1, 2, \dots$ – rotational quantum numbers, $B_e = \hbar^2/2I$ – rotational constant, $I = \mu r_e^2$ – moment of inertia, $\mu = m_1 m_2 / (m_1 + m_2)$ – the reduced mass of the molecule. In the ideal gas of diatomic molecules the occupancies of rotational levels are governed by Boltzmann distribution (N_J – number of molecules on the level with rotational number J , N – total number of molecules in the gas):

$$\frac{N_J}{N} \sim (2J+1) \exp\left[-\frac{B_e J(J+1)}{k_B T}\right]$$

1. Determine the value of J , corresponding to the rotation level most highly occupied by the N_2 molecules at 298 K? $I = 1.401 \cdot 10^{-46} \text{ kg} \cdot \text{m}^2$?



between them.

Lennard-Jones potential is used for description of the potential energy curves of diatomic molecules:

$$U(r) = 4\varepsilon \left[\left(\frac{r_0}{r} \right)^{12} - \left(\frac{r_0}{r} \right)^6 \right],$$

where r – distance between the nuclei, ε and r_0 – curve parameters. Zero energy level corresponds to the total energy of two atoms at infinite distance

2. a) On the axes of the graph $U(r)$ mark the points, corresponding to the parameters ε and r_0 . b) Find the equilibrium internuclear distance in the units of r_0 .

For gases of polar molecules the pure rotational spectra can be detected.

3. Calculate the frequencies (Hz) of the first two lines of the absorption spectrum BrF . $B_e = 7.093 \cdot 10^{-24} \text{ J}$. According to the selection rules only transitions $J \rightarrow J+1$ are possible at absorption.

If along with the rotation one takes into account the molecular vibration motion, its energy equals to the sum of $E_{\text{rot}} + E_{\text{vib}}$ (k – the force constant, $n = 0, 1, 2, \dots$ – the vibration quantum number):

$$E_{\text{vib}} = \hbar \omega \left(n + \frac{1}{2} \right) = \hbar \sqrt{\frac{k}{\mu}} \left(n + \frac{1}{2} \right)$$

4. For the molecule $^{127}\text{I}^{35}\text{Cl}$ $k = 239 \text{ N/m}$, $B_e = 2.26 \cdot 10^{-23} \text{ J}$. Find the wavelength at which light is absorbed by these molecules in the transition from the state with $J = 0$, $n = 0$ to the state with $J = 1$, $n = 1$?

In contrast to vibration frequency the force constant k does not change at isotopic substitution.

5. The line 1326 cm^{-1} is observed in the IR spectrum of $^{79}\text{Br}^{19}\text{F}$. Calculate the frequency (cm^{-1}) of the corresponding line in the IR spectrum of $^{81}\text{Br}^{19}\text{F}$.

Physical constants: Planck constant $h = 2\pi\hbar = 6.63 \cdot 10^{-34} \text{ J}\cdot\text{s}$, the light speed $c = 3 \cdot 10^8 \text{ m/s}$, Avogadro number $N_A = 6.02 \cdot 10^{23} \text{ mol}^{-1}$, 1 a.m.u. = $1.66 \cdot 10^{-27} \text{ kg}$, Boltzmann constant $k_B = 1.38 \cdot 10^{-23} \text{ J/K}$.