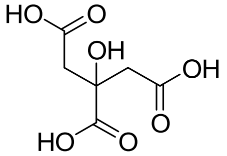
SECTION I. ANALYTICAL CHEMISTRY

Problem 1



Young chemistry fan Vasya weighed out 1.5 g of iron drawing pins and heated them in a 100 m*L* portion of citric acid (H_3Cit, see the scheme) solution. As soon as rust disappeared from the surface of the pins (but before the dissolution of iron started), he poured the liquid away and repeated heating with a fresh portion of citric acid solution. When the reaction finished, he filtered the solution (the weight of non-dissolved pins was 0.1 g) and evaporated it to dryness. Then Vasya placed the remaining dry salt (a neutral citrate monohydrate) into a weighed tube, sealed it with glass wool and ignited it in a ventilated room to prevent intoxication with the evolving gas. The solid product (its total weight was 1.0 g) was attracted by a magnet. When Vasya poured out the substance from the tube, he observed beautiful sparks appearing due to its spontaneous burning in air. Some soot was left on the tube walls after the experiment.

1. Write down the reactions of the dissolution of pins and rust **(**$Fe(OH)_3$), the simplest equation of citrate decomposition and the reaction of product combustion. Calculate the weight of the dissolved rust.

2. a) Calculate the minimal amount of sulfuric acid that should be diluted with water to yield 100 m*L* of solution that could completely dissolve 0.4 g of rust.

b) Estimate whether Vasya could completely dissolve such portion of rust using the same volume of lemon juice (67 g/*L* of citric acid). To do that, calculate the concentration of free Fe^{3+} in such a system.

3. Find the ratio of the dissolution rates in lemon juice and in 0.005 M sulfuric acid for a) rust and b) iron. In order to give the answer, you should calculate pH of the acid, write the reaction schemes and equations for their rates.

Solubility product of $Fe(OH)_3$: $K_s = [Fe^{3+}][OH^-]^3 = 4\cdot10^{-38}$. Acidity constants: $K_a(H_3Cit)$ $8.4\cdot10^{-4}$, $1.7\cdot10^{-5}$, $4\cdot10^{-7}$, $K_a(CH_3COOH)$ $1.74\cdot10^{-5}$. Stability constant of iron citrate complex: $\beta(FeCit) = [FeCit] / [Fe^{3+}][Cit^{3-}] = 10^{11.2}$. Molar fraction of citrate ion $\alpha = [Cit^{3-}] / c_{Cit}$ at different pH:

pH	1.0	1.4	1.8	2.2	2.6
$\alpha(Cit^{3-})$	$5.6\cdot10^{-12}$	$8.9\cdot10^{-11}$	$1.4\cdot10^{-9}$	$2.01\cdot10^{-8}$	$2.7\cdot10^{-7}$

pH	3.0	3.4	3.8	4.2
$\alpha(Cit^{3-})$	$3.08\cdot10^{-6}$	$2.83\cdot10^{-5}$	$2.09\cdot10^{-4}$	$1.27\cdot10^{-3}$

Problem 2

In order to determine the concentration of sulfur-containing anions in a sample collected from a sulfur spring, a 20 m*L* aliquot of the sample was treated with 0.2 m*L* of 6 M NaOH solution with subsequent addition of 0.2 m*L* of 1 M zinc acetate. The obtained precipitate was filtered and transferred into an Erlenmeyer flask. The filtrate **A** was kept for further tests.

1. Please provide the equation of the precipitation reaction.

After rinsing the precipitate with water and subsequently adding 1 m*L* of 6 M HCl and 10.00 m*L* of iodine solution (solution **I**) to it, the obtained solution was titrated with sodium thiosulfate (~0.025 M, titrant **II**) until the solution became straw-yellow coloured. At this point starch was added to the mixture and the titration continued until complete disappearance of blue colour. The volume of the titrant consumed was 15.77 m*L*.

2. Please provide equations of the two chemical reactions taking place during the test.

In order to standardize titrant **II**, its 10 m*L* aliquot was treated with an excess of KI, the obtained solution was acidified and titrated with a solution obtained by dissolving 2.675 g of anhydrous potassium iodate in 1 *L* of water (titrant **III**). The volume of titrant **III** consumed was 3.42 m*L*.

3. Provide the summary equation of the reactions occuring during the titration of thiosulfate with iodate.

Next, a 10 m*L* aliquot of iodine solution **I** was titrated with titrant **II** until the blue color of the starch indicator disappeared. The volume of titrant consumed was 19.75 m*L*.

4. Calculate the concentrations of iodate, thiosulfate and iodine (in mol/*L*); determine the amount of ZnS reacted as well as the concentration of sulfide ions in the sample (in mg/*L*).

5. Filtrate **A** was treated with 10 m*L* 1 M KI and starch. This solution was subsequently acidified and titrated with 0.1250 M potassium iodate standard solution until a stable blue colour of the solution was obtained. The volume of iodate titrant consumed in this process was 2.05 m*L*. Please provide the summary equation of the reaction taking place between sulfite and iodate ions, and calculate the concentration of sulfite ions in the sample in g/*L*.

6. The concentration of sulfite obtained earlier was positively biased due to the presence of thiosulfate ions in the sample. In order to determine the true concentration of sulfite ions in the sample, a newly obtained filtrate **A** was treated with an excess amount of formaldehyde. Please provide the equation of the reaction taking place during this treatment. This solution was titrated with 0.0104 M I_2. Determine the true concentration of sulfite ions in the sample (in g/*L*), given that 2.54 m*L* of iodine solution was consumed during titration.

Problem 3

A solution of $HAuCl_4$ ($c_{Au} = 4{\cdot}10^{-6}$ M) containing a stabilizer was heated in the presence H_2O_2, which yielded a colloidal solution of gold metal nanoparticles (AuNPs) of diameter $d = 10$ nm; the AuNPs concentration c_{AuNP} was $2.5{\cdot}10^{-8}$ M (in gold), while the rest of gold was left in the form of Au(III) (solution **1**).

1. Write down the reaction of formation of the AuNPs.

2. Nanometer-sized particles scatter light according to Rayleigh law: $I = knI_0V^2/\lambda^4$, where k is a constant, I and I_0 are the intensities of the scattered and incident light, respectively, n is the concentration of the nanoparticles, V is the volume of a nanoparticle, and λ is the wavelength. After the decomposition of hydrogen peroxide was completed, the light scattering of solution **1** started to gradually decrease. Write down the equation of a reaction that could explain such a decrease.

3. When some strong reducing agents are added to solution **1,** the growth of the already existing AuNPs resumes even at room temperature. A small volume of a solution of epicatechin gallate (EG), a strong reductant, was added to solution **1** to give a concentration of EG of $1{\cdot}10^{-7}$ M. What fold change in the intensity of Rayleigh scattering of solution **1** will be observed, if 1 mol of EG reduces 0.1 mol of gold ions?

4. What will be the minimum detectable concentration of EG, if the instrument can detect a $\geq$5% change in Rayleigh scattering?

5. Solution **1** was mixed with an equal volume of chlorinated tap water. What will happen to the AuNPs upon such mixing? Write down the equation of the reaction.

6. How will the intensity of Rayleigh scattering of solution **1** change upon mixing with a sample of such water? Draw a graph in the answer sheet.

7. A small volume of a positively charged synthetic polymer was added to solution **1**. The polymer adsorbs on the AuNPs causing their aggregation. Estimate the diameter D of such aggregates and the number α of AuNPs per an aggregate if the intensity of Rayleigh scattering of solution **1** increased by a factor of 10^2. Consider the aggregates as spheres consisting of the initial nanoparticles with packing density (fraction of the space filled) $\rho = 0.6$.

SECTION II. INORGANIC CHEMISTRY

Problem 1

The metal alkyl **MeR**$_n$ wasn't obtained so far and the attempts were made to obtain it by means of compounds containing **MeR**$_3$ group. In order to synthesize **MeR**$_3$**X** 9.75 g of metal (**Me**) were dissolved in aqua regia and 16.83 g (yield 65%) of red-brown crystals of acid **A** were obtained after recrystallization of HCl solution. After calcination of the crystals (300°C) 10.95 g of chloride metal (**Me**Cl$_n$) were received while the **Me** oxidation state was unchanged. The chloride reacted with Grignard reagent (**R**Mg**X**) in benzene and 10.14 g (yield 85%) of orange crystals of **MeR**$_3$**X** were formed. If the saturated solution of Ag_2O is added to the water solution of **MeR**$_3$**X** then light yellow substance **B** is formed. If thallium acetylacetonate ($TlC_5H_7O_2$) is added to the water solution of **MeR**$_3$**X** then light yellow substance **D** is formed. When equal mass portion of **MeR**$_3$**X**, **B** and **D** dissolve in 1 kg of benzene the freezing point depressions (Δt) relate as 1 : 1.428 : 2.165 correspondingly. The coordination number of **Me** in all compounds is equal to 6, the structural characteristics of **B** and **D** are shown in the table.

Compound	Bond distances, Å		Bond angles, degrees			
	Me–C	**Me**–O	C–**Me**–C	O–**Me**–O	Me–O–**Me**	C–**Me**–O
B	2.04	2.22	87	82	96	92; 176
D	2.05; 2.40	2.02	88; 178	125		93

It was expected that alkyl metal **MeR**$_n$ can be synthesized by the reaction of **MeR**$_3$**X** with Li**R** in hexane, but instead **MeR**$_n$ only complex **E** and Li**X** were formed in the reaction.

1. Determine **Me**, **Me**Cl$_n$, **A**, **R** and halogen **X** in **MeR**$_3$**X**.

2. Determine formula of **B**, **D** and **E**, taking into account that **B** and **MeR**$_3$**X** are isostructural and the molecule of **B** has twelve **Me**–C bonds.

3. Write the reaction equations.

4. Draw structural formula of **B**, **D** and anions in **A** and **E**.

5. Calculate the concentration of Ag^+ in the saturated solution of Ag_2O ($K_{sp} = [Ag^+][OH^-] = 2\cdot10^{-8}$) and indicate that it is sufficient for precipitation of Ag**X** ($K_{sp} = 2.3\cdot10^{-16}$).

6. Using the method of molecular orbitals explain the formation of the elongated bond **Me**–C (2.40 Å) in **D**.

Problem 2

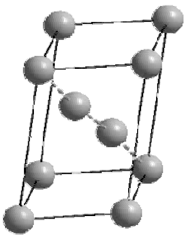
Phosphors, i.e. substances are capable of converting of absorbed energy into light emission, have a wide range of applications. Thus, the phosphor $\mathbf{A}_x\mathbf{B}_y\mathbf{C}_z Al_2O_4$, which is one of the best luminescent substances with strong and longtime emitting used in road markings, the dials appliances, firefighters equipment, navigation devices, and so on. The spectrum of its radiation gives rise to an emission band at 516 nm and caused by a change in the electronic configuration of the cation **B**.

1. To obtain 0.466 g of such phosphor the following reagents were taken: 0.295 g **A**CO_3, **C**$_mO_n$, **B**$_2O_3$ and Al_2O_3 oxides and carbon for partial reduction of **B**. Determine the molecular formula of the phosphor, if it is known that:

- 20.795 g **A**$_x$**B**$_y$**C**$_z$$Al_2O_4$ contains 0.1 mol of substance, $x + y = 0.895$;
- by dissolving the above sample of **A**CO_3 in nitric acid at 298 K and 1 atm 48.9 m*L* of gas released;
- the portion $1.73 \cdot 10^{-3}$ mol of **B**$_2O_3$, oxide contains $1.562 \cdot 10^{23}$ electrons;
- the nucleus of metal **C** contains 97 neutrons; $w(O) = 12.87\%$ in **C**$_mO_n$.

2. Simple substances **A**, **B** and **C** are dissolved in liquid ammonia forming a blue solution. Write the reactions equations. Determine the product formed by dissolving the **A**, **B** and **C** in ammonia, causes the solution color.

3. The figure shows an unit cell of **C**$_mO_n$, with oxygen atoms only. Calculate the number of atoms **C** in one unit cell.



4. Calculate the standard potential E^0 and determine which of the following Latimer diagrams corresponds to element **B**.

$$\begin{tikzcd}
X^{3+} \arrow[r, "E^0"] \arrow[rr, bend right, "-1.99\ V"'] & X^{2+} \arrow[r, "-2.81\ V"] & X
\end{tikzcd}
\qquad
\begin{tikzcd}
Y^{3+} \arrow[r, "E^0"] \arrow[rr, bend right, "-2.30\ V"'] & Y^{2+} \arrow[r, "-2.20\ V"] & Y
\end{tikzcd}$$

5. Write the change in electronic configuration of ion **B**, resulting in the luminescence of the phosphor and determine the phosphor colour.

6. Phosphors are synthesized at 1100 – 1300°C for 12 – 15 hours. To improve the sintering of the particles one used mineralizer, often it is boric acid. Using the table data, decode the compounds shown in the reaction scheme for the synthesis of the phosphor precursor **H** (**A**Al_2O_4).

H_3BO_3 → **E** + …
ACO_3 + **E** → **F** + …
ACO_3 + Al_2O_3 → **T** + **H** + **R** + CO_2↑
R + **F** → **H** + **E**
T + **E** → **H** + **F**

compound	ω, % mass. **A**	ω, % mass. O
F	50.58	36.95
R	28.48	36.41
T	63.66	23.26
H	42.59	31.14

Problem 3

Gaseous chlorine was first obtained by the Swedish chemist Carl Scheele in 1774 when interacting pyrolusite with hydrochloric acid. Currently, chlorine is produced on an industrial scale in large quantities.

1. Give the equation of the reaction, which allowed K. Scheele first obtain chlorine.

Chlorine is a very toxic gas. Several deep breaths of air, in which the chlorine content of 1000 ppm, is sufficient for death coming (ppm – one millionth fraction or parts per million).

The partial pressure of chlorine in the gaseous phase above the solution equilibrium is in direct ratio to the molar concentration of these particles in the solution. The value of the proportionality coefficient ($k(Cl_2)$, atm·dm^3/mol) depends on many factors: temperature, ionic strength, presence of other substances. In a first approximation for solutions with zero ionic strength its temperature dependence may be written as:

$$k(Cl_2) = 6.554 \cdot 10^5 \cdot \exp(-\frac{3163.7}{T}).$$

2. Calculate the mass concentration of molecular chlorine (in mg/dm^3) in saturated at 20.0°C solution, which occurs in equilibrium with air at atmospheric pressure of 750 mm Hg and with chlorine content equal to 1000 ppm.

The dynamic equilibrium between dissolved chlorine and water in solution is established. This equilibrium constant (K, mol^2/dm^6) and acid dissociation rate constant of the weak hypochlorous acid (pK_a) for solutions with low ionic strength in the temperature range 0 – 45°C depend on the temperature (T) as follows:

$$\lg K = -\frac{982798}{T^2} + \frac{5485.7}{T} - 10.7484; \quad pK_a = \frac{3000.0}{T} - 10.0686 + 0.0253T.$$

3. Calculate the molar concentration of hypochlorous acid and the pH in the solution of question 2.

4. For the purification of waste water the concentrated solutions obtained by dissolving chlorine in water at elevated pressure are used. Calculate solubility of chlorine (in g/dm^3) at 10.0°C and a partial pressure in the gaseous phase equal to 1.50 atm.

5. How will the solubility of chlorine change qualitatively in comparison with the solubility calculated in question 4, if it is used water with temperature 5°C? Briefly explain your answer.

6. Experimental solubility of chlorine in water is higher on about 0.6% compared with the value calculated in question 4. Briefly explain the cause of this phenomenon and write the corresponding reaction equation.

7. Since 1999 it is known the disinfection water technology using a binary gas **X**, with a density at STP more than 3 g/dm^3. One of methods of producing a gas **X** in an industrial scale is the action of chlorine gas on solid substance containing chlorine. Write the reaction equation for obtaining **X** by this method in industrial scale and write the reaction equation of obtaining of gaseous **X** in the laboratory. Draw the structural formula and specify the spatial structure of the molecule **X**.

8. Gas **X** is a reactive compound. Which products are formed by reacting **X** with an aqueous solution of NaOH? Write the equation of the corresponding reaction.

9. As a result of the impact of ozone on **X** substance **Y** is obtained. Write the equation of the corresponding reaction. Draw the structural formulae of particles present in liquid **Y**.

SECTION III. PHYSICAL CHEMISTRY

Problem 1

Substitution of an element in the molecule by another isotope changes the reaction rate, if the atom is involved in breaking or forming of chemical bonds at the rate-limiting stage of the reaction. This phenomenon is called *kinetic isotope effect* (KIE) and numerically it is characterized by the rate constants ratio k_H / k_D of the reaction involving hydrogen and deuterium substituted reagents. With the help of KIE the mechanisms of a large number of reactions were investigated.

1. Calculate the KIE for the reaction of bromination of acetone in acidic medium at 298 K. Assume that KIE is caused only by the difference in the activation energies of the reactions.

Reaction	$CH_3COCH_3 + Br_2$	$CD_3COCD_3 + Br_2$
E_A, kJ/mol	31.0	35.8

The rate of this reaction is described by the kinetic equation:

$$v = \frac{d[CD_3OCD_3]}{dt} = k[CD_3OCD_3]^n[Br_2]^m[H^+]^l,$$

where n, m, l – reaction orders for acetone, bromine and H^+, respectively.

	$[CD_3COCD_3]$, M	$[Br_2]$, M	$[H^+]$, M	v, $M\cdot s^{-1}$
1	0.3	0.05	0.05	$5.7\cdot10^{-5}$
2	0.3	0.1	0.05	$5.7\cdot10^{-5}$
3	0.3	0.05	0.1	$1.2\cdot10^{-4}$
4	0.4	0.2	0.2	$3.1\cdot10^{-4}$

2. a) Determine the n, m, и l from the given above experimental data.

b) What is the overall reaction order?

The mechanism of electrophilic aromatic substitution has the form:

$$C_6L_6 + E^{\oplus} \underset{k_2}{\overset{k_1}{\rightleftarrows}} C_6L_6E^{\oplus} \xrightarrow{k_3} C_6L_5E + L^{\oplus} \qquad (L = H \text{ or } D)$$

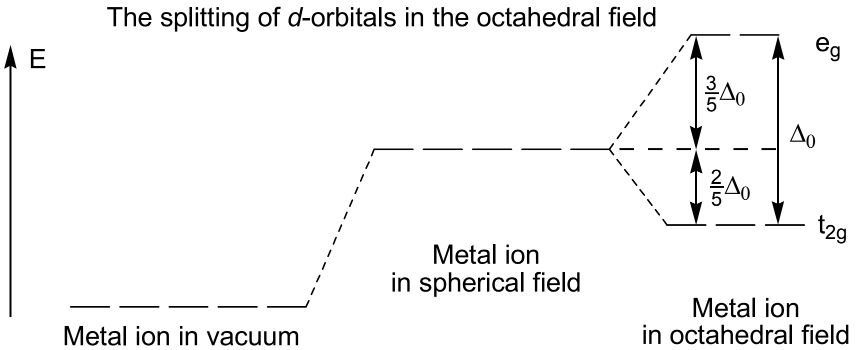
Electrophile	NO_2^+	$CH_3COCl/SbCl_5$
KIE	1	2.22

3. Based on the above data, indicate the limiting stage for both reactions.

Solution of $CuSO_4$ in normal water has blue color. The split energy (Δ_o) of *d*-level of Cu^{2+} ions in the octahedral ligand field for the complex $[Cu(D_2O)_6]^{2+}$ is equal to 14403 cm^{-1}. The Jahn – Teller effect is ignored. 1 $cm^{-1} = 1.986\cdot10^{-22}$ J.

Absorption region λ, nm		Substance color
Violet	400 – 424	Yellow
Green	490 – 575	Purple

Absorption region λ, nm		Substance color
Yellow	575 – 585	Blue
Red	647 – 710	Green



4. a) Write down the configuration of *d*-electrons of Cu^{2+} ion. b) Write down the configuration (in terms of t and e) of *d*-electrons Cu^{2+} ion in $[Cu(D_2O)_6]^{2+}$. c) Calculate the ligand field stabilization energy in cm^{-1}. d) Calculate the wavelength absorbed by the complex and specify the color of copper sulfate in heavy water D_2O. e) Is this complex paramagnetic or diamagnetic?

If the presence of oxygen isotopes is ignored, there are three isotopic species of water: H_2O, HDO and D_2O. In the mixture, the high rate isotope exchange takes place according to the reaction $H_2O + D_2O = 2HDO$ with the equilibrium constant $K_x = 4$.

5. Calculate the molar fraction of each species in natural water. Natural abundance (mol %) of isotopes H and D is equal to 99.985 and 0.015, respectively.

Many believe that prolonged boiling of drinking water is dangerous to health since the concentrations of heavy forms (HDO, D_2O) significantly increase due to higher volatility of ordinary water (H_2O).

6. Verify the validity of this statement by calculating for how many times the initial volume of water V_i exceeds the final volume V_f, remaining after evaporation, so that the concentration of HDO would increase by 15%. The liquid – vapor partition coefficient α at given temperature does not depend on the isotopic ratio D : H, and at the boiling point $\alpha = 1.013$. At the beginning of evaporation the mole fraction HDO was $3 \cdot 10^{-4}$.

Notes: 1) Coefficient α shows, for how many times the evaporation rate of pure ordinary water H_2O exceeds the rate for pure water HDO. 2) Neglect the presence D_2O in water. 3) Assume that H_2O – HDO solution is perfect and that the molar volumes of these substances are equal. *Physical constants*: gas constant R = 8.314 J/mol·K, Plank constant $h = 6.63 \cdot 10^{-34}$ J·s, Avogadro's number $N_A = 6.02 \cdot 10^{23}$ mol^{-1}, speed of light in vacuum $c = 3 \cdot 10^{8}$ m/s.

Problem 2

The rate of acidic hydrolysis $Co(en)_2Cl_2^+ + H_2O \rightarrow Co(en)_2(H_2O)Cl^{2+} + Cl^-$ is not depend on $[H^+]$, is described by the kinetic equation $w = kC_{Co(en)_2Cl_2^+}$ and has rate constants $k = 2.4\cdot10^{-4}$ (25°C) and $k = 8.1\cdot10^{-4}$ (35°C) for *cis*-complex, $k = 3.5\cdot10^{-5}$ (25°C) and $k = 1.5\cdot10^{-4}$ (35°C) for *trans*-complex. However, in the case of complexes with ligands, which are hard bases capable to form hydrogen bonds, the rate of hydrolysis depends on pH. Kinetic characteristics of the acid-basic hydrolysis $Co(en)_2F_2^+$ (table) were described by the mechanism:

$$Co(en)_2F_2^+ + H_2O \rightarrow Co(en)_2(H_2O)F^{2+} + F^- \qquad (k_3)$$

$$Co(en)_2F_2^+ + H^+ \rightleftarrows Co(en)_2F_2H^{2+} \qquad (K = 10.20)$$

$$Co(en)_2F_2H^{2+} + H_2O \rightarrow Co(en)_2(H_2O)F^{2+} + HF \qquad (k_4)$$

$[H^+]$, mol/*L*	10^{-4}	10^{-3}	10^{-2}	$5\cdot10^{-2}$	10^{-1}
$k_H\cdot10^3$, min^{-1}	6.173	7.716	21.74	63.42	91.84

1. Describe the hydrolysis of $Co(en)_2Cl_2^+$ by the two-stage mechanism (k_1; k_{-1}; k_2).

2. Using the method of stationary concentrations derivate the kinetic equation and indicate the condition of its agreement with the experimental one ($w = kC_{Co(en)_2Cl_2^+}$).

3. Derivate the expressions for α, calculate the mole fractions of $Co(en)_2F_2^+$ and $Co(en)_2F_2H^{2+}$ at pH = 2.

4. Display graphically the dependence $k_H = f(pH)$ and derivate the equation for k_H, which describe the dependence $k_H = f([H^+])$, using the expression for α.

5. Calculate the rate constants k_3 and k_4.

6. Indicate the process, which explain the sharp rise of k_H at pH < 2.

7. Write down the structural formula of the possible intermediates in the two-stage mechanism in the case of *trans*-$Co(en)_2Cl_2^+$.

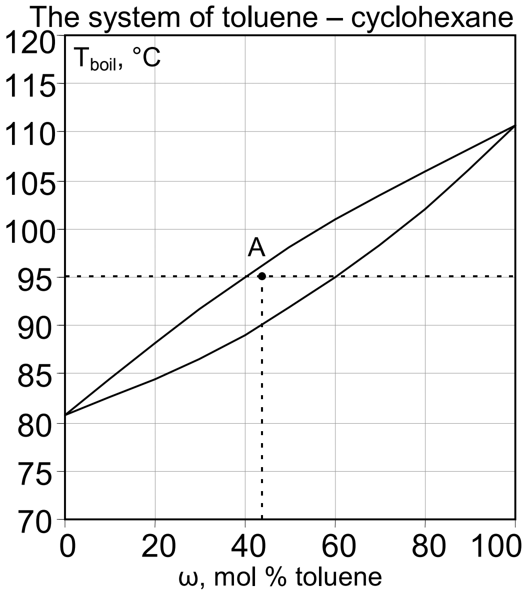
8. Calculate activation energy (E_A) for *cis*- and *trans*-$Co(en)_2Cl_2^+$ and enthalpy ($\Delta H^\#$) and entropy ($\Delta S^\#$) of formation of activated complex only for *cis*-complex ($k = Ae^{-E_A/RT} = 2.08\cdot10^{10}\,T\,e^{-\Delta G^\#/RT}$, $\Delta H^\# = E_A - RT$, T = 298 K).

Problem 3

A liquid mixture of substances 1 and 2 forms an ideal solution, so the Raul's law is valid $P_i = x_iP_i^0$, where P_i^0 – vapor pressure of pure component at a certain temperature. Let $P_1^0 / P_2^0 = r$, x and y – the molar fraction of the substance 2 in the liquid solution and its vapor, respectively, P – the total vapor pressure above the solution.

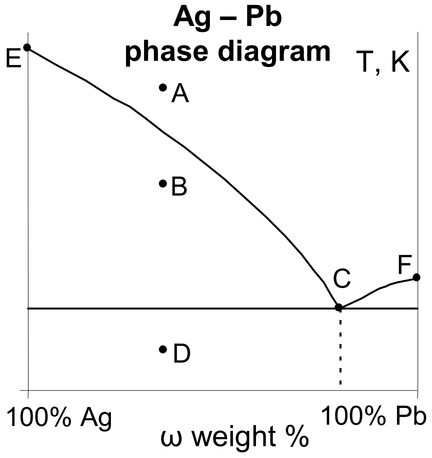
1. Based on the Raul's and Dalton's ($P_i = y_iP$), laws obtain the dependencies: a) P from x, b) y from x, c) P from y.

2. Using the lever rule, according to the diagram (see left figure) determine the composition (mol %) of both phases at the point A and the relative composition of phases of 1 mol of toluene – cyclohexane mixture at this point.



The Gibbs phase rule determines the number of thermodynamic degrees of freedom (f), i.e. the number of variables (pressure, temperature, concentration), which can be changed without changing the number of phases (F) in the system: $f = 2 + K - F$, where K – the number of components. The right figure shows a phase diagram T – x (P = const) of Ag – Pb with eutectic point.

3. Determine the nature of the phases and the number of degrees of freedom at points A – D (see the table in the answer sheet).



If in the binary system A – B the liquid phase can be considered as ideal solution, for the construction of the liquidus line (line E – C – F) you can use the *Schroeder equation*:

$$\frac{d\ln x_A}{dT} = \frac{\Delta H_A}{RT^2}, \qquad \frac{d\ln x_B}{dT} = \frac{\Delta H_B}{RT^2},$$

where T_A, T_B; ΔH_A, ΔH_B – temperature and melting enthalpy of the pure components.

4. Considering the melt (Ag – Pb) as ideal solution, determine the coordinates of the eutectic point (mole fraction of Pb and eutectic temperature T_E). The mole fraction of the silver is equal to 0.264, the melting point of silver T_m = 1235 K, enthalpy of fusion of silver $\Delta H_{\text{пл}}$ = 11.95 kJ/mol.

In the single-component system dependence of vapor pressure on temperature is determined by the Clausius – Clapeyron equation

$$\frac{d\ln P}{dT} = \frac{\Delta H_{vap}}{RT^2},$$

where ΔH_{vap} – heat of vaporization, which is assumed to be constant.

5. a) Find the temperature of the triple point T_{tr} of gallium from temperature dependence of the saturated vapor pressure of solid and liquid substances (atm):

$$\ln P_s = -32254 / T + 14.97, \ \ln P_{liq} = -31582 / T + 12.75.$$

b) Calculate the enthalpy of sublimation ΔH_{sub}, evaporation ΔH_{vap} and melting ΔH_m of the gallium (kJ/mol).

c) Calculate the standard entropy of vaporization ΔS^0_{vap} and entropy of melting ΔS_m (J/mol·K), $T_m = 303$ K, $T_{boil} = 2477$ K.

SECTION IV. LIFE SCIENCES AND POLYMERS

Problem 1

In 2014 the World was conquered by an “epidemics” of ice-cold water dousing. This philanthropic effort known as ALS Ice Bucket Challenge was aimed at fund raising to investigate the reasons behind amyotrophic lateral sclerosis (ALS), a serious neurodegenerative decease with yet unrevealed mechanisms of progress. In this task we will analyze the information about ALS known up-to-date.

A genetic defect of enzyme **E** is sometimes behind ancestral ALS cases. **E** catalyzes the reaction with the total equation:

$$2\mathbf{A1} + 2\mathbf{A2} \rightarrow H_2O_2 + O_2$$

Particle **A1** non-enzymatically reacts with molecule **A3** containing the same number of atoms as **A1**. As a result, **A4** (77.41% O by mass) is formed according to the following reaction equation:

$$\mathbf{A1} + \mathbf{A3} \rightarrow \mathbf{A4}$$

1. Determine molecular formulae of **A1** – **A4**.

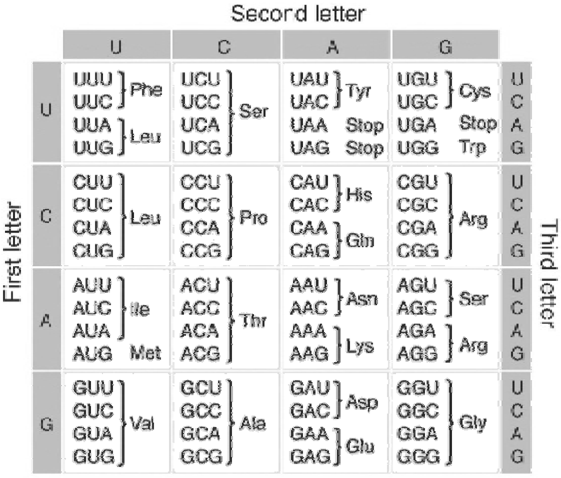
Particle **A5** found in nature is isomeric **A4**.

2. Draw structural formulae of **A4** and **A5**, and compare their toxicity to man.

E is encoded by the gene *SOD1*. ALS was found to be a result of single point mutations of *SOD1*, which appear as a change of the second nucleotide in the corresponding codons. As a result, an “improper” amino acid is incorporated into polypeptide chain (initial amino acid → mutant amino acid). Two major *SOD1* mutations can be written as Mut1 (**B1** → **B2**) and Mut2 (**B3** → **B1**).

3. Using the table of genetic code determine the amino acids **B1** – **B3** if it is known that these amino acids are encoded by the same number of codons, whereas the total number of purine bases in this codons exceeds that of pyrimidine ones.

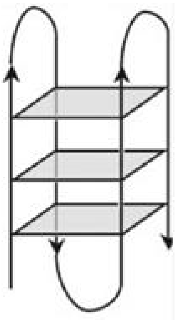
4. Indicate in the Answer Sheet whether the mutations Mut1 and Mut2 can be due to <u>single-step</u> chemical modifications of nitrogen bases in human DNA?



Second letter

First letter	U		C		A		G		Third letter
U	UUU	Phe	UCU	Ser	UAU	Tyr	UGU	Cys	U
	UUC		UCC		UAC		UGC		C
	UUA	Leu	UCA		UAA	Stop	UGA	Stop	A
	UUG		UCG		UAG	Stop	UGG	Trp	G
C	CUU	Leu	CCU	Pro	CAU	His	CGU	Arg	U
	CUC		CCC		CAC		CGC		C
	CUA		CCA		CAA	Gln	CGA		A
	CUG		CCG		CAG		CGG		G
A	AUU	Ile	ACU	Thr	AAU	Asn	AGU	Ser	U
	AUC		ACC		AAC		AGC		C
	AUA		ACA		AAA	Lys	AGA	Arg	A
	AUG	Met	ACG		AAG		AGG		G
G	GUU	Val	GCU	Ala	GAU	Asp	GGU	Gly	U
	GUC		GCC		GAC		GGC		C
	GUA		GCA		GAA	Glu	GGA		A
	GUG		GCG		GAG		GGG		G

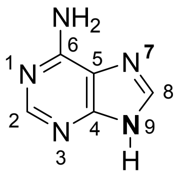
In March 2014 *Nature* published an article which reported that four-strain DNA fragments in non-coding region of gen *C9orf72* are responsible for sporadic cases of ALS (like that observed in the case of a well-known theoretical physicist Stephen Hawking). DNA quadruplexes are known to form in gene fragments containing repeated hexanucleotide sequences involving only two major (one purine and one pyrimidine) nitrogen bases. The molecular mass of the hexanuclotide with totally protonated phosphate groups is of 1913 Da.



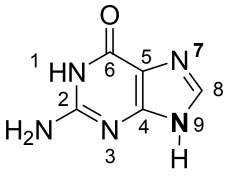
5. Draw the pair of major nitrogen bases linked by three hydrogen bonds (use dashed lines to show the hydrogen bonding).

6. Determine the nitrogen bases present in the hexanucleotide. Determine the number of each of these bases in the hexanucleotide.

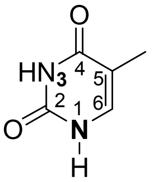
7. Draw the cross section of the DNA quadruplex (see the above figure) with 8 hydrogen bonds (use dashed lines to show these bonds). Note that in this case the hydrogen bonds formation involve also atoms which do not participate in hydrogen bonding in conventional DNA duplexes.



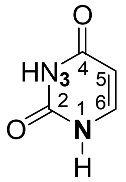
adenine



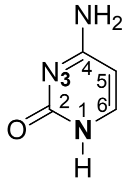
guanine



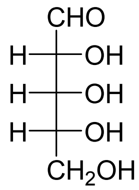
thymine



uracil



cytosine



D-ribose

Problem 2

Compound **X**, the major component of a promising blood substitute preparation, is obtained by the reaction between binary substances **B** and **C**. Substances **D** and **E** are formed in this reaction alongside with **X**. All the products (**X**, **D**, and **E**) are binary compounds and contain 39.20, 94.96, and 74.01% of element **Y** by mass, respectively. **D**, **E**, and **X** exist in three different aggregation states at 25°C and 1 atm.

1. Determine the element **Y** and formulae of **D** and **E**.

2. Relate **D**, **E**, and **X** with their aggregation states at 25°C and 1 atm.

The difference in the molecular masses of the heaviest and lightest isotopologs (molecules differing only in isotope content of atoms) of **X** equals 20 a.m.u. A doctor has a sample of an **X** isotopolog knowing only its molecular mass rounded to integer.

3. Determine the molecular formula of **X** if only isotopes met in nature are under consideration.

4. Determine the molecular masses of the isotopologs which the doctor can safely administer for therapy without getting additional information on the preparation.

X is free of multiple bonds. **X** is characterized by the existence of geometric isomers, the *trans*-isomer having a center of symmetry, and the *cis*-isomer having two-fold symmetry axis of rotation.

5. Draw the structural formula of **X**.

6. Indicate in the Answer Sheet the supplementary advantage of using **X** at extreme blood loss.

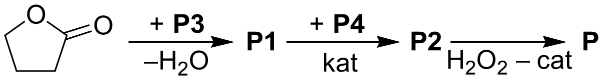
Physiological solution, the 0.9% by mass aqueous solution of sodium chloride, is the simplest blood substitute. This solution is isotonic (have identical osmotic pressure) to blood plasma.

7. Calculate the mass fraction of glucose in its aqueous solution isotonic to blood plasma.

Mannitol preparation, the 15% by mass aqueous solution of polyol mannitol ($C_6H_{14}O_6$), was previously introduced intravenously.

8. Indicate in the Answer Sheet the diseases when Mannitol administration is reasonable.

A salt-water solution of polymer **P** is another important blood substitute. Besides osmotic action, this preparation facilitates excretion of toxins from organism. **P** is obtained from butyrolactone according to the hereunder scheme (**P3** and **P4** are four-atomic gases at STP):



9. Decipher the structures of all unknown substances.

Problem 3

Modification of a carbon-chain polymer **A** with different reagents leads to the polymer **B** (54.53% C, 36.32% O, and 9.15% H). Thus, treatment of **A** with aqueous solution of alkali yields **B** and sodium acetate.

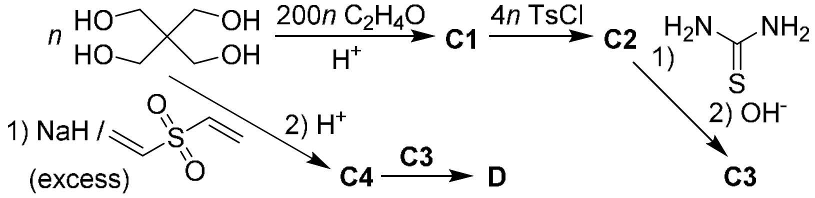
1. Determine the gross formula of the repeating unit of **B** and draw structures of the repeating units of **A** and **B**.

2. What products (besides **B**) are formed upon treatment of **A** with: a) aqueous solution of perchloric acid, b) excess of ethanol in an acidic medium, and c) excess of diethylamine?

A heterochain polymer **C** with the repeating unit isomeric to that of **B** is widely used in many technical and medicinal applications.

3. Draw the structure of **C**.

For many medicinal and biological applications, the water-soluble polymer **C** should be converted into an insoluble form (gel). For instance, this can be achieved by an exposure to ionizing radiation, the covalent linkages formed being hydrolytically stable. In order to prepare gels allowing controlled degradation under mild conditions, the polymer **C** is prepared starting from pentaerythritol and modified as shown in the hereunder scheme.



4. Draw the structures of **C1** – **C4** and that of the cross-linkage formed in the polymer **D**.

The polymer **B** can be cross-linked to yield a 3D network by simply treating it with sodium borate (a popular Slime toy is manufactured from this or similar gels).

5. Draw a fragment of **B** clearly showing the linkage formed after treatment with sodium borate.

Properties of polymers are strongly dependent on the structure of their chains. In particular, addition of asymmetric monomers can proceed in different ways. Let us consider this process using acrylamide CH_2=CHCONH_2 as an example and referring to the CH_2-group as the monomer “tail”, and to the CHCONH_2-group as its “head”.

6. a) Draw the macromolecules formed during radical polymerization of acrylamide with the active radical at the “head” and at the “tail” of the terminal unit.

b) Draw addition of the acrylamide unit to the macroradical at the “tail” of the terminal unit showing formation of the “tail” – “tail” and “tail” – “head” unit pairs.

Treatment of a sample of the polymer **B** with periodic acid resulted in a decrease of the average molecular mass down to 9000.

7. a) From the list given in the Answer Sheet, choose the most probable type of the units junction;

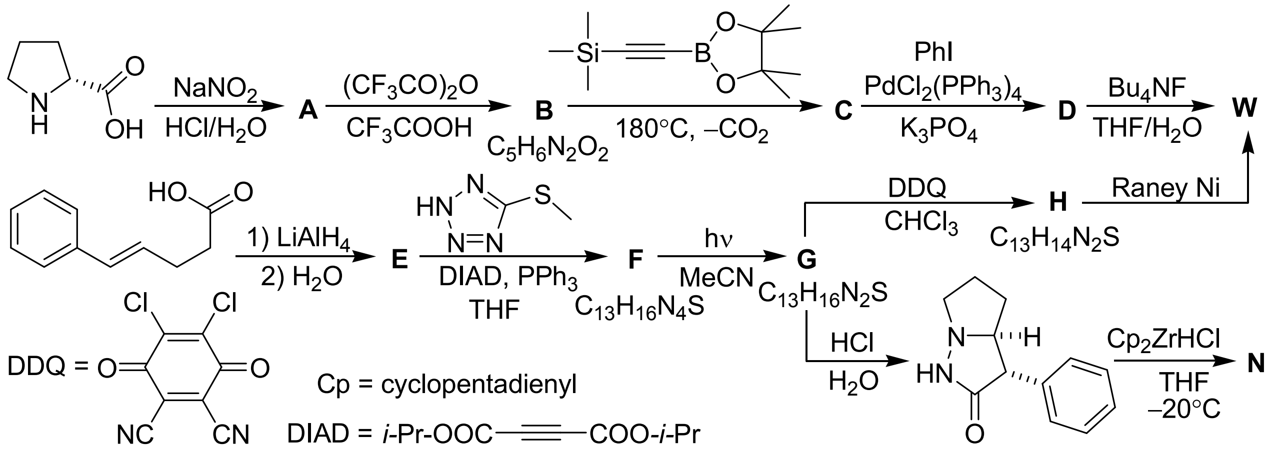
b) Draw the scheme of the reaction of **B** with periodic acid;

c) Determine the fraction of the “head” – “head” unit pairs in the starting polymer.

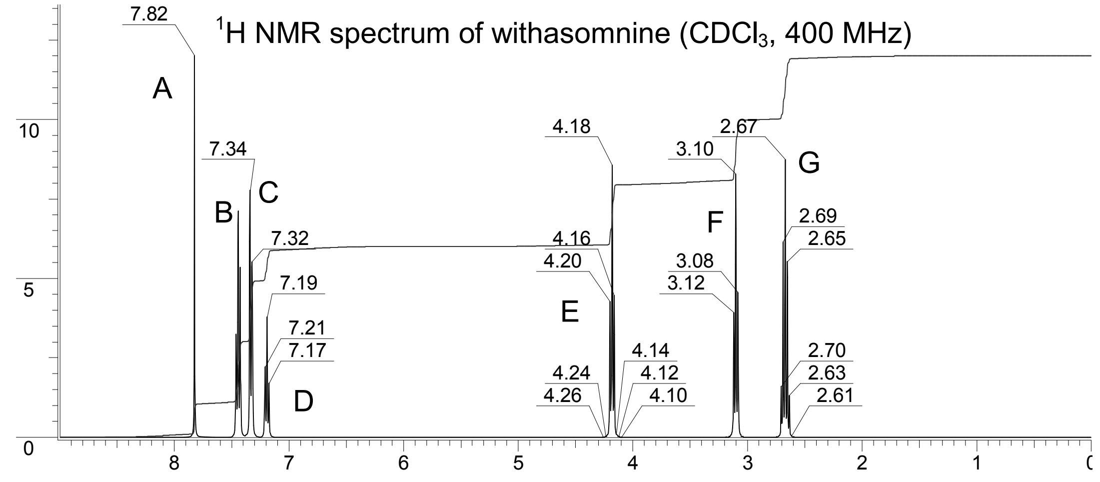
SECTION V. ORGANIC CHEMISTRY

Problem1

Organic compounds with N–N bond occur sparsely in Nature. In 1966 bioactive achiral compound **W** ($C_{12}H_{12}N_2$) was isolated from the roots of *Withania somnifera* (ashwagandha, Indian giseng); the important component in Ayurvedic medicine. This compound received name *withasomnine*. In 1994 from *Newbouldia laevis* a dihydro derivative of withasomnine was isolated. This compound **N** ($C_{12}H_{14}N_2$), which is referred to as *newbouldine*, exists in Nature as (*S*,*S*)-isomer. Methods for the syntheses of compounds **W** and (±)-**N** are given in the Scheme below. The key steps of syntheses are dipolar [3+2]-cycloadditions.



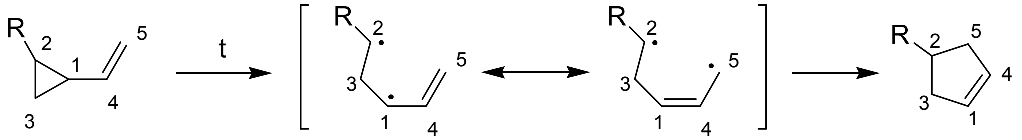
B is bicyclic mesoionic compound, i.e., heterocyclic compound with exocyclic atom(s) wherein charges are delocalized and a completely uncharged structure cannot be written. Both **W** and **N** have 10 signals in ^{13}C NMR spectra; ^1H NMR spectrum of **W** is given below.


^1H NMR spectrum of withasomnine ($CDCl_3$, 400 MHz)

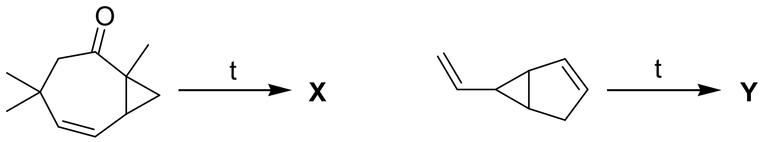
1. Decipher scheme. Write down structural formulae of compounds **A** – **H**, **N**, **W**.
2. Assign signals in ^1H spectrum of withasomnine (see answer sheets).
3. How many isomers of **F** can be formed in reaction of **E** with 5-(methylsulfanyl) tetrazole?

Problem 2

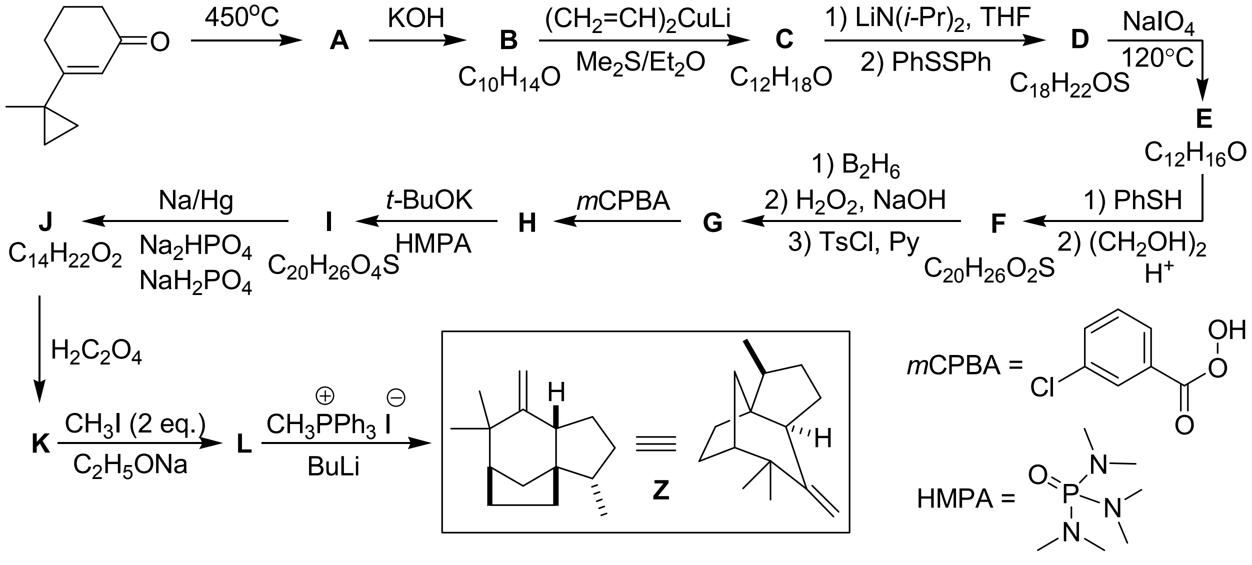
Vinylcyclopropane-to-cyclopentene rearrangement (VCR) as well as the analogous reactions of the corresponding heteroatom compounds are considered the important method for the synthesis of five-membered carbo- and heterocycles. These rearrangements can be performed under thermal, photochemical or catalytic activation. Thermal and photochemical reactions proceed via formation of the most stable biradical.



1. Write down structural formulae for products of two reactions given below accounting for facts that: a) both reactions are examples of VCR; b) molecule of **Y** has symmetry axis of the second order.



VCR was the first step in the total synthesis of terpene hydrocarbon (±)-zizaene (**Z**):



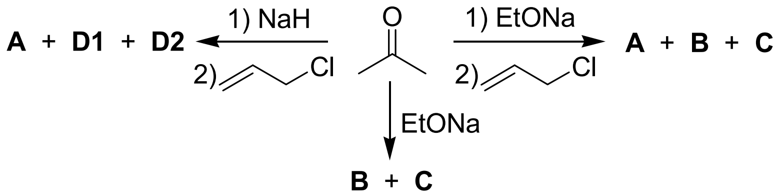
2. Write down extent of unsaturation in zizaene (**Z**)?

3. How many isomers can exist for zizaene?

4. Decipher scheme of this synthesis: write down structural formulae of compounds **A** – **L**.

Problem 3

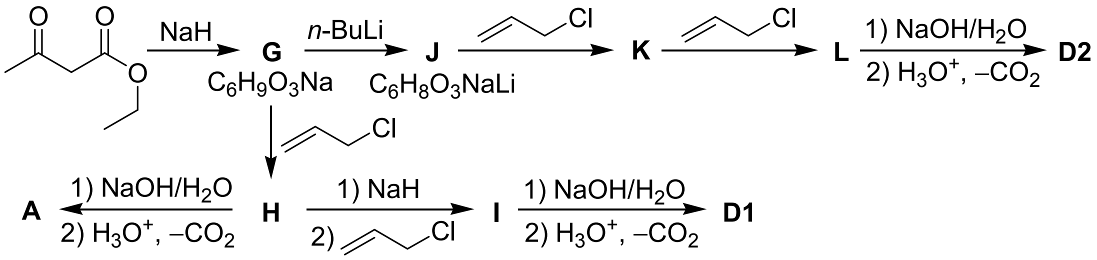
High C–H acidity of carbonyl compounds is widely using in organic synthesis for the preparation of new, more complex compounds. For example:



Compounds **D1** and **D2** are the major products when two-fold excess of allyl chloride is using. Ozonolysis of the product **A** followed by treatment of ozonide with zinc and acetic acid produces formaldehyde and compound **E** ($C_5H_8O_2$), the similar treatment of **C** affords acetone and **F** ($C_3H_4O_2$). Compound **C** is formed by dehydration of **B**. ^{1}H NMR spectra of **D2**, **E** and **F** contains, respectively, 5, 4 and 2 signals with the relative intensity of 2 : 2 : 1 : 1 : 1, 3 : 2 : 2 : 1 and 3 : 1.

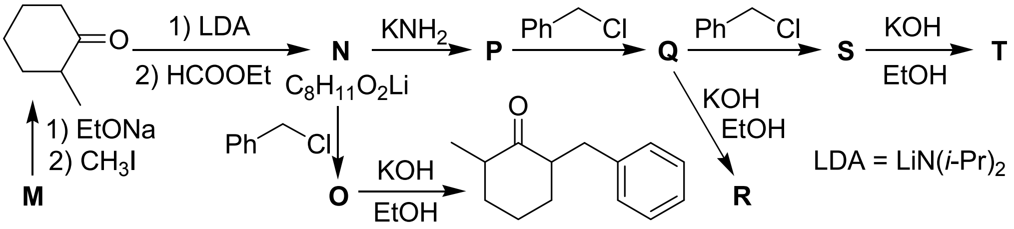
1. Write down structural formulae of **A**, **B**, **C**, **D1**, **D2**, **E** and **F**.

One of the best methods for the regioselective alkylation of ketones consists in an activation of the required α-carbon atom. For example:



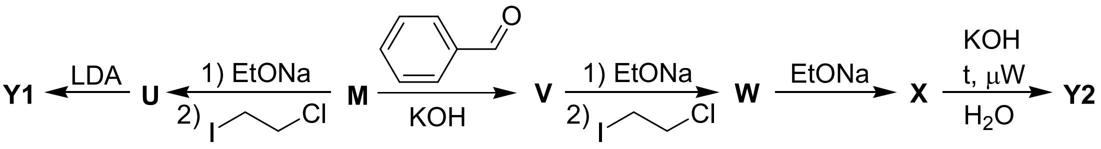
2. Write down structural formulae of compounds **G** – **L**.

Auxiliary functional groups can be used for the selective activation of one of the alternative α-carbon atoms:



3. Write down structural formulae of compounds **M** – **T**.

For the synthesis of cycloalkanones with geminal substitution, methods of blockage of one of the α-carbon methods is often used (μW is microwave irradiation):



4. Write down structural formulae of compounds **U** – **X**, **Y1** and **Y2**, if bicyclic compounds **Y1** and **Y2** are isomers, **Y2** having no carbonyl group.