# SECTION I. ANALYTICAL CHEMISTRY

Problem 1 (author L.I. Malinina)

1. Dissolution of iron pins: $Fe + 2H^+ = Fe^{2+} + H_2$ (1 point).

Dissolution of rust: $Fe(OH)_3 + 3H^+ = Fe^{3+} + 3H_2O$ (1 point).

Decomposition of iron(II) citrate: taking into account the appearing sparks, one may assume the formation of pyrophoric iron. As it follows from the text, the decomposition yields free carbon and CO. If all hydrogen transforms into water, the simplest version of the reaction equation looks as follows (2 points):

$$Fe_3[C_3H_5(O)(COO)_3]_2 \cdot H_2O = 3Fe + 9CO + 3C + 6H_2O$$
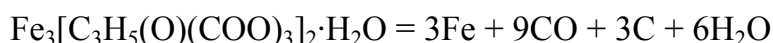
Combustion of pyrophoric iron: $Fe + O_2 \rightarrow Fe_2O_3 + Fe_3O_4$, or any reaction yielding iron oxides (1 point).

After the decomposition of iron(II) citrate the tube contains iron and soot (carbon) in a weight ratio of $56:12$. Consequently, 1 g of the substance in the tube contains $56/(56+12) = 0.82$ g of iron. So the weight of the dissolved rust is $1.5 - 0.82 - 0.1 = 0.58$ g (1 point, 6 points in total).

2. a) After the dissolution of a 0.4 g portion of rust, the total concentration of iron(III) in a 100 mL portion of solution is $0.4 / 107 / 0.1 = 0.037$ M. As there are no competing reactions (sulfate ion does not form stable complexes with iron), it is easy to find the minimal solution acidity after the dissolution using the solubility product $K_s = [Fe^{3+}][OH^-]^3$: $[H^+] = K_w([Fe^{3+}] / K_s)^{1/3} = 0.0097$ M, that is 0.49 mmol of sulfuric acid in a 100 mL solution. In addition, $0.037 \cdot 3 \cdot 0.1 \cdot 1000 / 2 = 5.6$ mmol of sulfuric acid has reacted with iron hydroxide, therefore, the total amount of sulfuric acid required for the dissolution is 6.1 mmol (2 points).
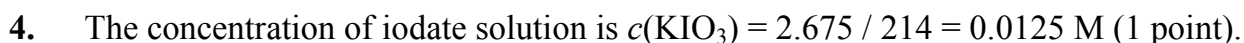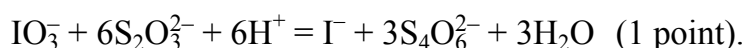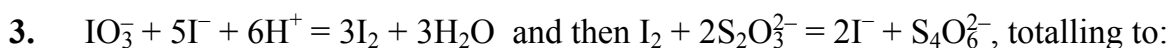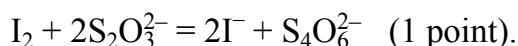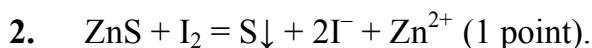
b) Citric acid concentration of 67 g/L ($M_w = 192$ g/mol) corresponds to its molar concentration of 0.349 M, and if all iron hydroxide is dissolved as $H_3Cit + Fe(OH)_3 = FeCit + 3H_2O$, then $0.349 - 0.037 = 0.312$ M of citric acid is left in the juice after the dissolution. The pH of such lemon juice estimated using H_3Cit dissociation by the first stage is about 1.8 ($[H^+] = (K_a c)^{1/2}$) (1 point for the pH value).

Concentration of free iron(III) decreases in the presence of citric acid due to complex formation. Equation $\beta = \frac{[FeCit]}{[Fe^{3+}][Cit^{3-}]}$ can be transformed using the molar fraction of citrate ion in solution: $\beta = \frac{[FeCit]}{[Fe^{3+}]c(H_3Cit)\alpha(Cit^{3-})}$. According to the table provided in the problem, at

pH 1.8 the molar fraction of citrate ion $\alpha(Cit^{3-})$ is $1.4 \cdot 10^{-9}$, i.e. if total citrate concentration is 0.349 M, free iron(III) concentration in solution is $[Fe^{3+}] = \dfrac{c(Fe)}{1 + \beta c(H_3Cit)\alpha(Cit^{3-})} = 4.7 \cdot 10^{-4}$ M (2 points). In this case the concentration product $[Fe^{3+}][OH^-]^3$ is $1.1 \cdot 10^{-40}$. This value is below the solubility product of $4 \cdot 10^{-38}$, so all the rust will be transferred into the solution (1 point, 6 points in total).

3. If only the first stage of acid dissociation is taken into account, pH of lemon juice is about 1.8 (see question 2), while pH of 0.005 M solution of sulfuric acid is 2. As the reaction equations in question 1 show, the rate of dissolution in acids is proportional to the third order of proton concentration ($v_1 = k_1[H^+]^3$) for iron hydroxide and second order of proton concentration ($v_2 = k_2[H^+]^2$) for iron (2 points). Consequently, according to the earlier estimated pH values of sulfuric acid and lemon juice, the rate ratio is $v(H_3Cit) / v(H_2SO_4) =$ $= 10^{-1.8 \cdot 3} / 10^{-2 \cdot 3} = 4$ for rust (i.e. rust dissolves in lemon juice 4 times faster than in sulfuric acid) and $10^{-1.8 \cdot 2} / 10^{-2 \cdot 2} = 2.5$ times for iron (0.5 points for each value, 3 points in total).

Problem 2 (author A.V. Bibin)

1. $S^{2-} + Zn^{2+} = ZnS\downarrow$ (1 point).

2. $ZnS + I_2 = S\downarrow + 2I^- + Zn^{2+}$ (1 point).

 $I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-}$ (1 point).

3. $IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O$ and then $I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-}$, totalling to:
$$IO_3^- + 6S_2O_3^{2-} + 6H^+ = I^- + 3S_4O_6^{2-} + 3H_2O \quad \text{(1 point)}.$$

4. The concentration of iodate solution is $c(KIO_3) = 2.675 / 214 = 0.0125$ M (1 point). The standardized concentration of sodium thiosulfate is

 $c(Na_2S_2O_3) = 0.0125$ M $\cdot$ 3.42 mL $\cdot$ 6 / 10.0 mL = 0.02565 M   (1 point).

Therefore, the concentration of iodine solution is $c(I_2) = 0.02565 \cdot 19.75 / (2 \cdot 10) = 0.02533$ M (1 point).

Now we have to calculate the amount of iodine (I_2) remaining in excess after the reaction with ZnS and titrated with thiosulphate: $n(\text{excess } I_2) = 0.02565 \cdot 15.77 / 2 = 0.2023$ mmol. The amount of zinc sulfide is equivalent to the amount of iodine consumed during the reaction with it: $n(S^{2-}) = n(ZnS) = n(\text{consumed } I_2) = 0.02533$ M $\cdot$ 10 mL − 0.2023 mmol = $= 0.0510$ mmol (2 points).

Therefore the concentration of sulfide ion in the sample is 0.051 mol · 32 g/mol · 1000 mL/L / 20 mL = 81.6 mg/L (1 point, 6 points in total).

5. The titration in acidified medium generates iodine:

$$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O,$$

which in turn reacts immediately with sulfite ions:

$$SO_3^{2-} + I_2 + H_2O = SO_4^{2-} + 2I^- + 2H^+$$
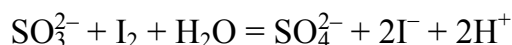
Therefore the summary reaction is (1 point): $3SO_3^{2-} + IO_3^- = 3SO_4^{2-} + I^-$

The amount of iodate is 2.05 mL · 0.1250 M = 0.2563 mmol; therefore the amount of sulfite ions in the sample was 0.2563 mmol · 3 = 0.7689 mmol, and its concentration is 0.7689 mmol · 80 g/mol / 20 mL = 3.08 g/L (1.5 points, 2.5 points in total).

6. Sulfite ions react with formaldehyde as per the following equation:

$$CH_2O + SO_3^{2-} + H_2O \rightarrow HO–CH_2–SO_3^- + OH^- \quad \text{(1 point)}.$$
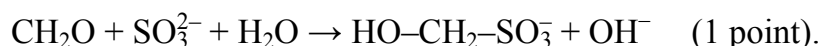
This allows iodometric determination of thiosulfate in the presence of sulfite ions. The amount of thiosulfate in 20 mL of sample therefore is equal to 0.0104 M · 2.54 mL · 2 = = 0.0528 mmol equiv. The amount of iodate consumed in the previous titration was 0.2563 mmol · 6 = 1.5378 mmol equiv. Therefore, the true amount of sulfite is equal to 1.5378 – 0.0528 = 1.4850 mmol equiv, or 0.7425 mmol / 20 mL = 0.0371 M. This is equivalent to 2.97 g/L (1.5 points, 2.5 points in total).

Problem 3 (author M.K. Beklemishev)

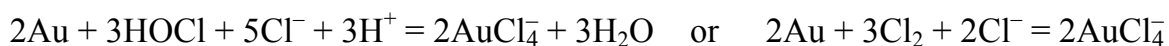**1.** $2AuCl_4^- + 3H_2O_2 \rightarrow 2Au\downarrow + 8Cl^- + 3O_2 + 6H^+$ (2 points)

2. A decrease in light scattering may imply a decrease in the average size of the particles, for instance, their partial dissolution as a result of comproportionation (2 points):

$$2Au + AuCl_4^- + 2Cl^- \rightarrow 3AuCl_2^-$$
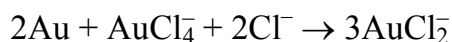
3. A portion of gold corresponding to 10% of the concentration of EG will be reduced, i.e., $1 \cdot 10^{-8}$ M. Thus, the concentration of AuNPs will be $3.5 \cdot 10^{-8}$ M (in gold), having increased by a factor of $3.5 \cdot 10^{-8}$ / $2.5 \cdot 10^{-8}$ = 1.4. The intensity of Rayleigh scattering is proportional to square volume, therefore, it will increase 1.4^2 = 1.96 times (2 points).

4. An increase in Rayleigh scattering by a factor of 1.05 corresponds to an increase in the volume of AuNPs by a factor of $\sqrt{1.05}$ = 1.025, i.e. the amount of the additionally reduced gold will be 0.025 · 0.74 · $2.5 \cdot 10^{-8}$ M = $4.6 \cdot 10^{-10}$ M Au(III), or (after division by 0.1) $4.6 \cdot 10^{-9}$ M EG (2 points).

5. Chlorine and hypochloric acid will oxidize the gold nanoparticles, for example (2 points for any of the two equations):

$$2Au + 3HOCl + 5Cl^- + 3H^+ = 2AuCl_4^- + 3H_2O \quad \text{or} \quad 2Au + 3Cl_2 + 2Cl^- = 2AuCl_4^-$$

6. The intemsity of light scattering will sharply fall twofold as a result of mixing with an equal volume of the sample (0.5 points) and then will be gradually falling as a result of oxidation of AuNPs by chlorine and reducing their size (1.5 points, 2 points in total).

7. Let the number of nanoparticles per a volume unit of solution **1** be n particles/mL and the particle volume in solution **1** be equal to V_1. The change in these values after the formation of the aggregates containing α nanoparticles each and the Rayleigh scattering intensity can be written as follows:

Solution	Particles per volume unit	Volume of the particle	Intensity of light scattering
Initial solution **1**	n	V_1 (nanoparticle)	$I_1 \sim nV^2$
After aggregation	n/α (aggregates)	$\alpha V_1/\rho$ (aggregate)	$I_2 \sim n/\alpha \cdot (\alpha V/\rho)^2 =$ $= n\alpha V^2/\rho^2$

Therefore, $I_2 : I_1 = \alpha/\rho^2$ (note that *aggregation* of nanoparticles increases the intensity of scattering proportionally to the *number* of the AuNPs in an aggregate, as opposed to the situation with *increasing the volume* of individual nanoparticles). As stated in the problem situation, the intensity of scattering I increased by a factor of 10^2, therefore, $\alpha = 10^2\rho^2 = 36$ (2 points).

The volume of an aggregate of volume D can be written as follows: $V_{agr} = \frac{4}{3}\pi(D/2)^3$; on the other hand, $V_{agr} = \alpha V_1/\rho = \alpha/\rho \cdot \frac{4}{3}\pi(d/2)^3$, where d is the diameter of a nanoparticle; hence, $D^3 = d^3\alpha/\rho$ and $D = d\sqrt[3]{\alpha/\rho} = 10\sqrt[3]{36/0.6} = 39$ nm (1 point, 3 points in total).

SECTION II. INORGANIC CHEMITSTRY
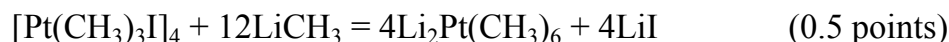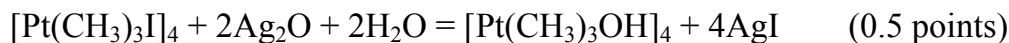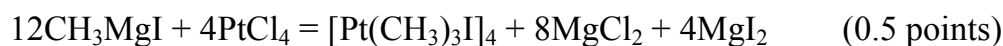
Problem 1 (authors G.M. Rozantsev, V.E. Shvartsman)

1. $Me \rightarrow MeCl_n$ with consideration of 65% yield of **A**, $\dfrac{9.75 \cdot 0.65}{A_{Me}} = \dfrac{10.95}{A_{Me} + 35.5n}$, obtain the equation $A_{Me} = 48.78n$. When $n = 4$, $A_{Me} = 195.1$ g/mol, then **Me** – Pt (2 points), chloride $MeCl_n$ – $PtCl_4$ (1 point).

If **A** – H_2PtCl_6 (c.n. of Pt equals six), then the mass must be equal to m $= \dfrac{9.75 \cdot 0.65 \cdot 410}{195} =$ $= 13.33$ g, but not 16.83 g (like in condition of the problem). This distinction indicates that the composition of **A** – $H_2PtCl_6 \cdot aZ$, where Z is H_2O, or NO, or HNO_3. Per 1 mol of Pt the molar mass of **A** is more than H_2PtCl_6 at $\Delta M = \dfrac{(16.83 - 13.33) \cdot 195}{9.75 \cdot 0.65} = 108$ g/mol, that corresponds $a = \dfrac{108}{18} = 6$ mol of H_2O (in the cases of NO and HNO_3, a is fractional). Acid **A** – $H_2PtCl_6 \cdot 6H_2O$ (1 point).

R – radical C_bH_{2b+1} $PtCl_4 \rightarrow Pt(C_bH_{2b+1})_3X$ taking into account of 85% yield of $Pt(C_bH_{2b+1})_3X$, $\dfrac{10.95 \cdot 0.85}{337} = \dfrac{10.14}{198 + 42b + M_X}$. Then $169 = 42b + M_X$ and $b = \dfrac{169 - M_X}{42}$. Only in case of **X** – I ($M_X = 127$ g/mol) the value of b is not fractional ($b = 1$). Therefore, **R** – CH_3 (1 point) and halogen **X** – I (1 point), and MeR_3X – $Pt(CH_3)_3I$ (the simplest formula) (6 points in total).

2. $\Delta t = \dfrac{m_{subst} \cdot K_к}{M_{subst} \cdot m_{solv}}$. If $m_{solv} = 1$ kg, and m_b – are equal for **B**, **D** and $[Pt(CH_3)_3I]_m$, so Δt relate as $2.165 : 1.428 : 1 = 1/M(\textbf{D}) : 1/M(\textbf{B}) : 1/M([Pt(CH_3)_3I]_m)$, and molar masses, as $M(\textbf{D}) : M(\textbf{B}) : M([Pt(CH_3)_3I]_m) = 1 : 1.516 : 2.165$. Since **B** and $[Pt(CH_3)_3I]$ are isostructural and during the formation of **B** AgI precipitates, so I^- is substituted by the anion Y^-, **B** – $Pt(CH_3)_3Y$ with $M_B = \dfrac{1.516 \cdot 367}{2.165} = 257$ g/mol Then $M_Y = 257 - (367 - 127) = 17$ g/mol and Y^- – OH^-, and **B** – $Pt(CH_3)_3OH$ (the simplest formula). Taking into account 12 bonds Pt–C **B** is tetramer $[Pt(CH_3)_3OH]_4$ (1 point); and $m = 4$, $[Pt(CH_3)_3I]_4$ (1 point). The simplest formula **D** – $Pt(CH_3)_3(C_5H_7O_2)$ with M $= 339$ g/mol, and molecular formula $[Pt(CH_3)_3(C_5H_7O_2)]_l$ M $= \dfrac{367 \cdot 4}{2.165} = 678$ g/mol. Then $l = \dfrac{678}{339} = 2$ and **D** – $[Pt(CH_3)_3(C_5H_7O_2)]_2$. As c.n. of Pt equals 6 and LiI is formed, so **E** – $Li_2Pt(CH_3)_6$ (1 point, 3 points in total).

3. (3 points in total) $3Pt + 18HCl + 4HNO_3 = 3H_2PtCl_6 + 4NO + 8H_2O$ (0.5 points)

$H_2PtCl_6 \cdot 6H_2O = 2HCl + 6H_2O + PtCl_4$ (0.5 points)

$$12CH_3MgI + 4PtCl_4 = [Pt(CH_3)_3I]_4 + 8MgCl_2 + 4MgI_2 \qquad \text{(0.5 points)}$$

$$[Pt(CH_3)_3I]_4 + 2Ag_2O + 2H_2O = [Pt(CH_3)_3OH]_4 + 4AgI \qquad \text{(0.5 points)}$$

$$[Pt(CH_3)_3I]_4 + 4Tl(C_5H_7O_2) = 2[Pt(CH_3)_3(C_5H_7O_2)]_2 + 4TlI \qquad \text{(0.5 points)}$$

$$[Pt(CH_3)_3I]_4 + 12LiCH_3 = 4Li_2Pt(CH_3)_6 + 4LiI \qquad \text{(0.5 points)}$$

4. (0.25 points for each structure, 1 point in total)
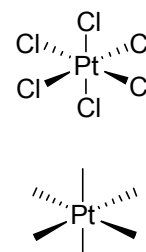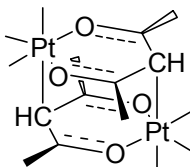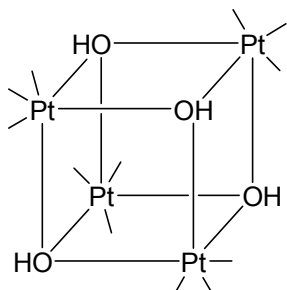
5. $\frac{1}{2}Ag_2O_{(s)} + \frac{1}{2}H_2O = Ag^+_{(sol)} + OH^-_{(sol)}$ $K_s = [Ag^+][OH^-] = S^2 = 2 \cdot 10^{-8}$; $S = [Ag^+] =$

$= 1.41 \cdot 10^{-4}$ mol/L (0.5 points). To precipitate AgI it is necessary

$[I^-] \geq \frac{K_s}{[Ag^+]} = \frac{2.3 \cdot 10^{-16}}{1.41 \cdot 10^{-4}} = 1.63 \cdot 10^{-12}$ mol/L, that is certainly achieved

(0.5 points, 1 point in total).

6. Since the carbon atom in CH of the anion $C_5H_7O_2^-$ is valence-saturated, the three-center bond H–C–Pt is formed (1 point).
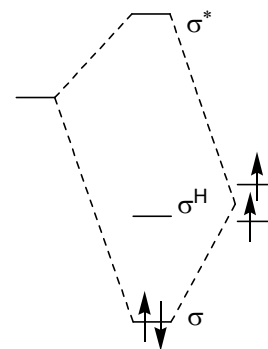
Problem 2 (author D.G. Gulevich-Syrlybaeva)

1. The reaction of the dissolution of ACO_3 in nitric acid: $ACO_3 + 2HNO_3\text{(conc.)} =$

$= A(NO_3)_2 + 2H_2O + CO_2\uparrow$ $v_{CO_2} = \frac{pV}{RT} = \frac{101325 \cdot 48.9 \cdot 10^{-6}}{8.314 \cdot 298} = 2 \cdot 10^{-3}$ mol of carbon dioxide.

According to the stoichiometry of the reaction: $v_{CO_2} = v_{ACO_3}$; $M(ACO_3) = 0.295 / 2 \cdot 10^{-3} =$

147.5 g/mol. $A_r(A) = 147.5 - 60 = 87.5$ g/mol, what corresponds to strontium.

The structural unit of the oxide B_2O_3 contains $1.562 \cdot 10^{23} / (1.73 \cdot 10^{-3} \cdot 6.02 \cdot 10^{23}) = 150$

electrons. The serial number of metal $B = (150 - 3 \cdot 8) / 2 = 63$. It corresponds to europium.

Then we can define the metal C:

m	n	$A_r(C)$	C
1	1	108.32	Ag
2	1	54.15	–
2	3	162.48	Dy
3	4	144.42	–

Silver isn't suitable for the number of neutrons, so C_mO_n is Dy_2O_3.

A – Sr, B – Eu, C – Dy, B_2O_3 – Eu_2O_3. To determine x, y and z form the system of equations:

$$\begin{cases} 87.6x + 152y + 162.5z + 118 = 20.795 / 0.1 = 207.95 \\ x + y = 0.895 \\ 2x + 2y + 3z + 6 - 8 = 0 \end{cases} \Rightarrow \begin{cases} x = 0.8923 \\ y = 0.0027 \\ z = 0.07 \end{cases}$$

The formula of the phosphor is $Sr_{0.8923}Eu_{0.0027}Dy_{0.07}Al_2O_4$ (0.75 points for **A**, 1.5 points for **B**, 0.5 points for each **C** and its oxide, 2 points for determination of phosphor formula, 5.25 in total).

2. $M + (6 + 2x)NH_{3(liq)} = [M(NH_3)_6]^{n+}{}_{(sol)} + ne^- \cdot xNH_{3(sol)}$; M = Sr, Eu, Dy.

The blue color of the solution occurs due to solvated electron: $e^- \cdot xNH_{3(sol)}$ (0.5 points for the reaction equation, 0.5 points for the solvated electron, 1 point in total).

3. Number of oxygen atoms in one unit cell: $8 \cdot \frac{1}{8} + 2 \cdot 1 = 3$ (0.5 points). $N(O) : N(Dy) = = 3 : 2$, from the formula Dy_2O_3. One unit cell has 2 atoms of dysprosium (0.5 points, 1 point in total).

4. Europium electronic configuration $[Xe]4f^7 5d^0 6s^2$. 50% occupancy of the $4f$ sublevel improves the stability of the oxidation state of europium +2, compared to other $4f$-elements. Latimer diagram with letter **X** corresponds to europium. $E^0(Eu^{3+}/Eu^{2+}) = -1.99 \cdot 3 + 2.81 \cdot 2 = = -0.35$ V. $E^0(Eu^{3+}/Eu^{2+}) > E^0(Eu^{2+}/Eu)$, that indicates high stability of the oxidation state +2. $E^0(Y^{3+}/Y^{2+}) = -2.30 \cdot 3 + 2.20 \cdot 2 = = -2.5$ V (0.75 points for each calculation of E^0, 0.5 points for corresponding diagram, 2 points in total).

5. The luminescence of the phosphor occurs due to the configuration change from $4f^6 5d^1$ to $4f^7$ of Eu^{2+} ions (1.5 points). The spectrum of its radiation give rise to an emission band at 516 nm, this corresponds to green color (0.5 points, 2 points in total).

6. Metal **A** can be determined according to the table data concerning to its content in the precursor of phosphor **H**: $A_A / (A_A + 26.98 \cdot 2 + 16 \cdot 4) = 0.4259$, $A_A = 87.5$ g/mol, which corresponds to the strontium. **H** – $SrAl_2O_4$. The reaction of the decomposition of boric acid, indicates that the compound **E** is boron oxide B_2O_3. Therefore, compound **F** formed in the reaction **E** with strontium carbonate must contain boron. Let the weight of **F** is equal to 100 g, then the formula of this compound $\frac{50.58}{87.5} : \frac{12.47}{10.8} : \frac{36.95}{16} = 0.578 : 1.155 : 2.309 = = 1 : 1.998 : 3.99 \approx 1 : 2 : 4$. **F** – SrB_2O_4. Similarly determine compounds **T** and **R**: $\frac{63.66}{87.5} : \frac{13.08}{26.98} : \frac{23.26}{16} = 0.728 : 0.485 : 1.454 = 1.5 : 1 : 3 = 3 : 2 : 6$, **T** – $Sr_3Al_2O_6$; $\frac{28.48}{87.5} : \frac{35.11}{26.98} : \frac{36.41}{16} = 0.325 : 1.301 : 2.276 = 1 : 4 : 7$, **R** – $SrAl_4O_7$ (0.75 points for each **H**, **F**, **R**, **T** and **E**, 3.75 points in total).

Problem 3 (author V.N. Khvalyuk)

1. When action of concentrated hydrochloric acid on mineral pyrolusite (basic substance MnO_2) by heating the following reaction takes place (0.5 points):

$$MnO_2 + 4HCl = MnCl_2 + Cl_2\uparrow + H_2O$$

2. The chlorine content of 1000 ppm (in case of gases it is volume or molar ratio) corresponds to its mole fraction $= \frac{1000}{1000000} = 10^{-3}$. The partial pressure of chlorine is $10^{-3} \cdot 750 / 760 = 9.87 \cdot 10^{-4}$ atm (0.5 points).

At 20.0°C $k_{20}(Cl_2) = 6.554 \cdot 10^5 \exp(-\frac{3163.7}{273.15 + 20.0}) = 13.476$ atm·dm³/mol (0.5 points).

At partial pressure of chlorine $9.87 \cdot 10^{-4}$ atm its molar concentration in the solution is equal to $\frac{9.87 \cdot 10^{-4}}{13.476} = 7.32 \cdot 10^{-5}$ mol/dm³. Mass concentration of Cl_2 in such solution is equal to $7.32 \cdot 10^{-5} \cdot 70.9 = 5.19 \cdot 10^{-3}$ g/dm³ $= 5.19$ mg/dm³ (1 point, 2 points in total).

3. The equilibrium takes place in solution: $\quad Cl_2 + H_2O \rightleftarrows H^+ + Cl^- + HOCl$

In the presence of any significant amounts of HCl dissociation of very weak HOCl (K_a order of $10^{-7} - 10^{-8}$) can be neglected.

$$K = \frac{[H^+][Cl^-][HOCl]}{[Cl_2]}$$

At 20.0°C $\lg K = -\frac{982798}{(273.15 + 20.0)^2} + \frac{5485.7}{273.15 + 20.0} - 10.7484 = -3.472$ and this equilibrium constant is $K = 10^{-3.472} = 3.373 \cdot 10^{-4}$ (1 point).

From the equilibrium equation it follows that $[H^+] = [Cl^-] = [HOCl]$. Substituting the above values in the expression for the constant, we have: $K = \frac{[HOCl][HOCl][HOCl]}{[Cl_2]} = 3.373 \cdot 10^{-4}$ Solving this equation, we obtain $[HOCl] = 2.91 \cdot 10^{-3}$ M (1 point). Since $[H^+] = [HOCl]$, the pH of the solution is $-\lg 2.91 \cdot 10^{-3} = 2.54$ (1 point, 3 points in total).

4. In solution the chlorine is present as Cl_2, Cl^- and HOCl. Since $[Cl^-] = [HOCl]$, the total solubility of chlorine is $[Cl_2] + [HOCl]$ (0.5 point).

At 10.0°C $k_{10}(Cl_2) = 6.554 \cdot 10^5 \exp(-\frac{3163.7}{273.15 + 10}) = 9.205$ atm·dm³/mol. When chlorine partial pressure is 1.50 atm molar concentration of Cl_2 in saturated solution is $1.50 / 9.205 = 0.163$ mol/dm³ (1 point).

At 10.0°C $\lg K = -\frac{982798}{(273.15 + 10.0)^2} + \frac{5485.7}{273.15 + 10.0} - 10.7484 = -3.633$ and this equilibrium constant is $K = 10^{-3.633} = 2.328 \cdot 10^{-4}$. HOCl concentration in the solution is equal to $(0.163 \cdot 2.328 \cdot 10^{-4})^{1/3} = 0.0336$ M (1 point).

Solubility of chlorine at $10.0°C$ is $0.163 + 0.0336 = 0.1966$ M, which is $0.1966 · 70.9 = 13.94$ g/dm^3 (0.5 points, 3 points in total).

5. Considering that the solubility of gases usually decreases with increasing temperature one can be expected that the solubility of chlorine at $5°C$ will also be higher than at $10°C$. However, at low temperatures chlorine forms clathrates of varying composition with water (including classic $8Cl_2·46H_2O$), which precipitate as solid. It is not possible to cook at lower temperatures concentrated chlorine solutions, even at its high partial pressure (1 point).

6. The solution contains chloride ions, which can form complex with the chlorine, and thereby the solubility of chlorine increases (1 point):

$$Cl_2 + Cl^- = Cl_3^-$$

7. The molar mass of the gas **X** $M(\mathbf{X}) > 3 · 22.4 = 67.2$ g/mol. This molar mass excludes ozone. Instead of chlorine oxide ClO_2 is applied for water disinfection. In 95% of industrial methods for preparing ClO_2 the starting reagent is sodium chlorite, $NaClO_3$. The method of production ClO_2 described in problem bases on processing of solid sodium chlorite by chlorine (diluted with nitrogen or air) (1 point):

$$2NaClO_2 + Cl_2 = 2NaCl + 2ClO_2$$
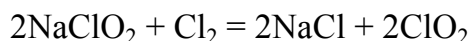
One of the reactions used in the laboratory scale for synthesis of ClO_2 – interaction of oxalic acid and potassium chlorate (1 point):

$$2KClO_3 + 2H_2C_2O_4 = K_2C_2O_4 + 2CO_2 + 2ClO_2 + 2H_2O$$
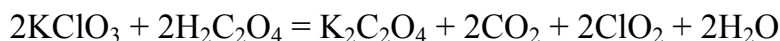
The structural formula of chlorine oxide (IV): . The molecule has an angular structure, the angle between bonds is slightly less than $120°$ because of the lone electron pairs of the central atom (0.5 points, 2.5 points in total).

8. $2ClO_2 + 2NaOH = NaClO_2 + NaClO_3 + H_2O$ (0.5 points)

9. $2ClO_2 + 2O_3 = Cl_2O_6 + 2O_2$ (0.5 points)

The particles present in the liquid Cl_2O_6 (0.25 points for each particle, 1.5 points in total):
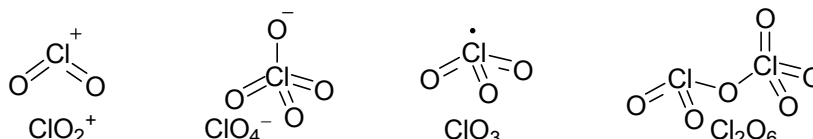
SECTION III. PHYSICAL CHEMISTRY

Problem 1 (author D.G. Gulevich-Syrlybaeva)

1. KIE is the ratio of the rate constants of reactions with substances containing different isotopes of hydrogen, so we have (0.5 points):

$$k_H / k_D = \exp \frac{E_A(D) - E_A(H)}{RT} = \exp \frac{35.8 - 31.0}{8.314 \cdot 0.298} = 6.94 \approx 7$$

2. a) The ratio of the rates in different experiments: $\frac{v_3}{v_2} = \frac{1.2 \cdot 10^{-4}}{5.7 \cdot 10^{-5}} = 2.1 = \frac{k \cdot 0.3^n \cdot 0.05^m \cdot 0.1^l}{k \cdot 0.3^n \cdot 0.05^m \cdot 0.05^l} =$

$= 2^l \Rightarrow l = \frac{\ln 2.1}{\ln 2} = \frac{0.742}{0.693} = 1.07 \approx 1$, therefore, the reaction has first order by H^+. $\frac{v_2}{v_1} = \frac{5.7 \cdot 10^{-5}}{5.7 \cdot 10^{-5}} =$

$= 1 = \frac{k \cdot 0.3^n \cdot 0.1^m \cdot 0.05}{k \cdot 0.3^n \cdot 0.05^m \cdot 0.05} = 2^m$, $m = 0$ – zero order by bromine, the reaction rate doesn't depend

on the concentration of Br_2. $\frac{v_4}{v_3} = \frac{3.1 \cdot 10^{-4}}{1.2 \cdot 10^{-4}} = 2.583 = \frac{k \cdot 0.4^n \cdot 0.2}{k \cdot 0.3^n \cdot 0.1} = 1.33^n \cdot 2$, $n = \frac{\ln 1.29}{\ln 1.33} = \frac{0.255}{0.285} =$

$= 0.89 \approx 1$, reaction order by CD_3COCD_3 equals to 1 (1.25 points for each reagent's order).

b) The overall reaction order is the sum of the reaction orders by reagents: $1 + 0 + 1 = 2$ (0.5 points, 4.25 points in total).

3. Substitution of an element with another isotope changes the reaction rate, only if the atom is involved into the rate-limiting step. In the case of nitration reaction $k_H / k_D = 1$, then reaction (1) is the limiting one. For acylation reactions KIE is different from 1, then the breaking of C–H or C–D bonds occurs at the rate-limiting stage. This is reaction (3) (0.25 points for each reaction, 0.5 points in total).

4. a) d^9 (0.25 points); b) $t_{2g}^6 e_g^3$ (1 point); c) $E_{stab} = (0.4x - 0.6y)\Delta_0 = \frac{3}{5}\Delta_0$, where x, y – the number of electrons on the upper and lower electronic d-levels, respectively. $E_{stab} = \frac{3}{5}\Delta_0 =$

$= 8641.8$ cm^{-1} (1.5 points); d) $\Delta = hc / \lambda$. The wavelength of the absorbed light $[Cu(D_2O)_6]^{2+}$

$\lambda = \frac{hc}{\Delta} = \frac{6.626 \cdot 10^{-34} \cdot 3 \cdot 10^8}{2.86 \cdot 10^{-19}} = 695$ nm, which corresponds to green color of the solution (0.75 points for wavelength, 0.25 points for color); e) If the particle has no unpaired electrons, their magnetic moments cancel each other and the total magnetic moment of the particle is zero – this particle is diamagnetic. At presence of the unpaired electrons paramagnetic properties are revealed. The electronic configuration of Cu^{2+} is $3d^9$, $[Cu(D_2O)_6]^{2+}$ is paramagnetic (0.25 points, 4 points in total).

5. Denoting by x, y, z the mole fractions of H_2O, D_2O, HDO, we get the system

$$x + y + z = 1 \qquad \frac{2y + z}{2x + z} = \frac{D}{H} = \beta = \frac{15}{99985} \qquad \frac{z^2}{xy} = K_x = 4$$

Eliminating x and y we find:

$$x = -\frac{z}{2} + \frac{1}{1+\beta}, \qquad y = -\frac{z}{2} + \frac{\beta}{1+\beta}, \qquad (1 - \frac{K_x}{4})z^2 + \frac{K_x}{4}z - \frac{\beta K_x}{(1+\beta)^2} = 0$$

Final solution (2.5 points for the system of equations, 0.5 points for each mole fraction):

$$x = \frac{1}{(1+\beta)^2} = 0.9997, \qquad y = \frac{\beta^2}{(1+\beta)^2} = 2.25 \cdot 10^{-8}, \qquad z = \frac{2\beta}{(1+\beta)^2} = 2.99955 \cdot 10^{-4}.$$

So, the amount of D_2O is negligible (4 points in total).

6. Let V_{Di} and V_{Df} – initial and final volumes of HDO. According to the problem

$$\frac{V_{Di}}{V_i} = r = 3 \cdot 10^{-4}, \qquad \frac{V_{Df}}{V_f} = kr = 1.15 \cdot 3 \cdot 10^{-4}.$$

Current relative amounts of evaporating isotopomers H_2O and HDO are connected by the relation

$$\frac{dV_H}{V_H} = \alpha \frac{dV_D}{V_D} \quad \Rightarrow \quad \frac{d(V - V_D)}{V - V_D} = \alpha \frac{dV_D}{V_D} \quad \Rightarrow \quad \ln(V - V_D) = \alpha \ln V_D + \text{const}$$

From the last equation for the initial and final values we get

$$\frac{V_i - V_{Di}}{V_f - V_{Df}} = \left(\frac{V_{Di}}{V_{Df}}\right)^\alpha$$

Excluding by (1) the volumes related to HDO, we find:

$$\frac{V_i}{V_f} = \left(\frac{1-r}{1-kr}\right)^{\frac{1}{\alpha-1}} k^{\frac{\alpha}{\alpha-1}} = \left(\frac{1-3\cdot10^{-4}}{1-1.15\cdot3\cdot10^{-4}}\right)^{\frac{1}{0.013}} \cdot 1.15^{\frac{1.013}{0.013}} = 53860$$

This result shows that prolonged boiling of water at home conditions can't bring any harm (0.5 points for the differential equation, 0.25 points for the equation after integration, 1 point for the calculating volumes, 1.75 points in total).

Problem 2 (authors E.N. Shved, G.M. Rozantsev)

1. (2 points in total) $\quad Co(en)_2Cl_2^+ \rightleftharpoons Co(en)_2Cl^{2+} + Cl^- \ (k_1; k_{-1})$ (1 point)

$$Co(en)_2Cl^{2+} + H_2O \rightarrow Co(en)_2(H_2O)Cl^{2+} \ (k_2) \qquad \text{(1 point)}$$

2. $w = kC_{Co(en)_2Cl_2^+}$; for $Co(en)_2Cl^{2+}$ stationary approximation $dC_{Co(en)_2Cl^{2+}}/d\tau = 0$ and

$k_1 C_{Co(en)_2Cl_2^+} = k_{-1} C_{Co(en)_2Cl^{2+}} C_{Cl^-} + k_2 C_{Co(en)_2Cl^{2+}}$. Then $C_{Co(en)_2Cl^{2+}} = \frac{k_1}{k_{-1}C_{Cl^-} + k_2} C_{Co(en)_2Cl_2^+}$ and

$w = \frac{k_1 k_2}{k_{-1}C_{Cl^-} + k_2} C_{Co(en)_2Cl_2^+}$ (2 points). If $k_2 \gg k_{-1}C_{Cl^-}$, then $w = k_1 C_{Co(en)_2Cl_2^+}$ coincides with the experimental (1 point, 3 points in total)

3. $K = \dfrac{[Co(en)_2F_2H^{2+}]}{[Co(en)_2F_2^+][H^+]}$; $C_{Co(en)_2F_2H^{2+}} = [Co(en)_2F_2^+] + [Co(en)_2F_2H^{2+}] = [Co(en)_2F_2^+](1 + K[H^+])$;

$[Co(en)_2F_2^+] = \dfrac{C_{Co(en)_2F_2^+}}{1 + K[H^+]}$ $\qquad \alpha_{Co(en)_2F_2^+} = \dfrac{1}{1 + K[H^+]}$ $\qquad$ (0.5 points)

$[Co(en)_2F_2H^{2+}] = \dfrac{K[H^+]C_{Co(en)_2F_2^+}}{1 + K[H^+]}$ $\qquad \alpha_{Co(en)_2F_2H^{2+}} = \dfrac{K[H^+]}{1 + K[H^+]}$ $\qquad$ (0.5 points)

$\alpha_{Co(en)_2F_2^+} = \dfrac{1}{1 + 10.20 \cdot 10^{-2}} = 0.9074 \; (90.74\%)$ $\qquad$ (0.5 points);

$\alpha_{Co(en)_2F_2H^{2+}} = 1 - 0.9074 = 0.0926 \; (9.26\%)$ $\qquad$ (0.5 points, 2 points in total).

4. $w = k_3[Co(en)_2F_2^+] + k_4[Co(en)_2F_2H^{2+}] =$

$\dfrac{k_3}{1 + K[H^+]}C_{Co(en)_2F_2H^{2+}} + \dfrac{k_4K[H^+]}{1 + K[H^+]}C_{Co(en)_2F_2H^{2+}} =$

$\dfrac{k_3 + k_4K[H^+]}{1 + K[H^+]}C_{Co(en)_2F_2H^{2+}}$ (1 point) $\quad k_H = \dfrac{k_3 + k_4K[H^+]}{1 + K[H^+]}$ and

$w = k_H C_{Co(en)_2F_2H^{2+}}$ (0.5 points)

(1 point for plot, 2.5 points in total)
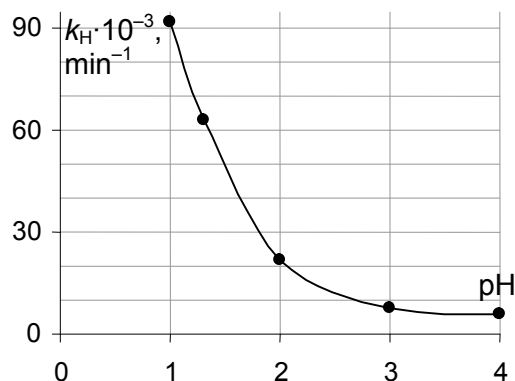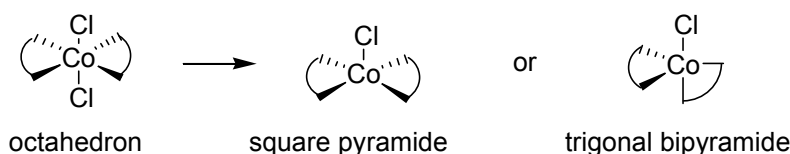
5. $k_H + k_H K[H^+] = k_3 + k_4K[H^+]$

$6.173 \cdot 10^{-3} + 6.173 \cdot 10^{-3} \cdot 10.20 \cdot 10^{-4} = k_3 + 10.20 \cdot 10^{-4}k_4$

$7.716 \cdot 10^{-3} + 7.716 \cdot 10^{-3} \cdot 10.20 \cdot 10^{-3} = k_3 + 10.20 \cdot 10^{-3}k_4$

$k_4 = 0.176$ (1 point); $\qquad k_3 = 6.00 \cdot 10^{-3}$ (1 point, 2 points in total).

6. The sharp rise of k_H at pH < 2 is caused by acidic catalysis.

7. (0.5 points for each intermediate structure, 1 point in total)

octahedron $\qquad$ square pyramide $\qquad$ or $\qquad$ trigonal bipyramide

8. From the Arrhenius equation $k_1 = Ae^{-E_A/RT_1}$ and $k_2 = Ae^{-E_A/RT_2}$ obtain $\dfrac{k_2}{k_1} = e^{\frac{-E_A}{R}(\frac{1}{T_2} - \frac{1}{T_1})}$

or $\ln\dfrac{k_2}{k_1} = \dfrac{E_A(T_2 - T_1)}{RT_1T_2}$ – Van't-Hoff equation. From it $E_A = \dfrac{RT_1T_2 \ln {k_2}/{k_1}}{T_2 - T_1}$.

For *trans*-isomer: $E_A = \dfrac{8.314 \cdot 308 \cdot 298 \cdot \ln\frac{1.5 \cdot 10^{-4}}{3.5 \cdot 10^{-5}}}{308 - 298} = 111052$ J/mol $\qquad$ (0.5 points)

For *cis*-isomer: $E_A = \dfrac{8.314 \cdot 308 \cdot 298 \cdot \ln\frac{8.1 \cdot 10^{-4}}{2.4 \cdot 10^{-4}}}{308 - 298} = 92822$ J/mol $\qquad$ (0.5 points)

$\Delta H^{\#} = 92822 - 8.314 \cdot 298 = 90344$ J/mol $\qquad$ (0.5 points)

$$\ln k = \ln(2.08 \cdot 10^{10} \cdot T) - \Delta G^{\#}/RT$$

$$\Delta G^{\#} = RT \ln\frac{2.08 \cdot 10^{10} \cdot T}{k} = 8.314 \cdot 298 \cdot \ln\frac{2.08 \cdot 10^{10} \cdot 298}{2.4 \cdot 10^{-4}} = 93628 \text{ J/mol} \qquad (0.5 \text{ балла})$$

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}; \ \Delta S^{\#} = \frac{\Delta H^{\#} - \Delta G^{\#}}{T} = \frac{90344 - 93628}{298} = -11.02 \text{ J/mol·K} \qquad (0.5 \text{ балла})$$

(2.5 points in total)

Problem 3 (author D.G. Gulevich-Syrlybaeva)

1. a) According to the Raul's law, partial pressure of the components in the vapor is $P_1 = (1 - x)P_1^0$, $P_2 = xP_2^0$, from which we obtain linear dependence (0.75 points):

$$P(x) = P_1 + P_2 = [(1 - r)x + r]P_2^0 \qquad (1)$$

b) According to Dalton's law $P_2 = yP$. Substituting this in the $P(x)$, we obtain (1 point):

$$y(x) = \frac{x}{r + (1 - r)x} \qquad (2)$$

c) Solving the equation (2) in terms of x, and substituting in (1), we find (1 point):

$$P(y) = \frac{P_1^0}{1 - (1 - r)y}$$

2. At 95°C in point A will be the liquid phase with molar fractions of 0.6 and the gas phase with molar fraction 0.4. To determine the composition of the liquid and the vapor, it is necessary to push through given point a node (in this case isotherm). The intersection of nodes with liquid line shows the composition of the liquid at this point: 60% toluene and 40% cyclohexane. The intersection of nodes with vapor line shows the composition of the gas phase: 40% toluene and 60% cyclohexane.

The system of toluene – cyclohexane
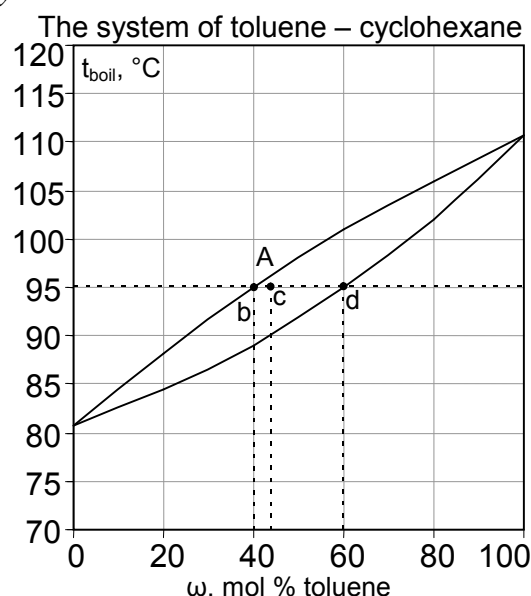
According to the lever rule $n_{liq} \cdot cd = n_g \cdot bc$, $n_{liq} / n_g = bc / cd$. bd = 0.6 − 0.4 = 0.2, bc = = 0.44 − 0.4 = 0.04, cd = 0.6 − 0.44 = 0.16. $(n_{liq} / 1 - n_g) = 0.04 / 0.16 = 0.25$. The relative content of the liquid phase is 33%, a pair of 67% respectively (composition of liquid and vapor 0.25 points, the relative amounts of the components 0.5 points, 1 point in total).

3. It necessary to consider that at $P = \text{const}$ phase rule takes the form $f = 1 + K - F$.

Point	Aggregate composition	F	f
A	melt Ag – Pb	1	2
B	melt Ag – Pb + solid Ag	2	1
C	melt Ag – Pb + solid Ag + solid Pb	3	0
D	solid Ag + solid Pb	2	1

(0.5 points for each composition, 0.25 points for each degree of freedom, 3 points in total)

4. Defining the integral form of the Schroeder equation, we obtain: $\ln x_A = \dfrac{\Delta H_A}{R}(\dfrac{1}{T_A} - \dfrac{1}{T})$

Then find the eutectic temperature from the resulting equation:

$T_E = \Delta H_{m.A} / (\Delta H_{m.A} / T_A - R\ln x_{Ag}) = 11950 / (11950 / 1235 - 8.314 \cdot \ln(0.264)) =$
$= 576$ K (0.3 points).

The mole fraction of $x_{Pb} = 1 - 0.264 = 0.736$ (0.2 points, 0.5 points in total)

5. a) In the triple point the vapor pressure of the liquid and solid gallium are the same: $P_{liq} = P_s$. Equating the expressions, we obtain the equation for the temperature of the triple point: $-32254 / T + 14.97 = -31582 / T + 12.75$, from where $T_{tr} = 672 / 2.22 = 302.7$ K $\approx$ 303 K (1.75 points).

b) If we take the derivative by temperature from the equation

$$\ln P = -A / T + B, \tag{3}$$

$d\ln P / dT = A / T^2$, then from comparison with the Clausius – Clapeyron it is seen that the parameter A in the empirical dependence is the enthalpy of the phase transition, divided by the gas constant. $\Delta H_{sub} = 32254 \cdot 8.314 = 268.2$ kJ/mol, $\Delta H_{vap} = 31582 \cdot 8.314 = 262.6$ kJ/mol. From the Hess law $\Delta H_m = \Delta H_{sub} - \Delta H_{vap} = 268.2 - 262.6 = 5.6$ kJ/mol (1 point for each ΔH_{sub} and ΔH_{vap}, 1.5 points for ΔH_m).

c) The saturated vapor pressure over liquid gallium can be treated as the equilibrium constant for the "reaction" Ga(l) = Ga(g). Using the basic formula of chemical thermodynamics $\ln K_P = -\Delta_r G^0 / RT$, we can write:

$$\ln P = -\frac{\Delta H_{vap}^0}{RT} + \frac{\Delta S_{vap,T}^0}{R} \tag{4}$$

Icon of standard state of enthalpy doesn't matter, because the enthalpy of evaporation depends on temperature, and hence pressure. For the entropy this icon and the icon of temperature are important. Comparing expressions (4) and (5), we conclude that the free term in (4) is the $\Delta S_{vap}^0 / R$; $T = T_{boil}$, because at this temperature the pressure $P = 1$ atm, i.e., the standard value. $\Delta S_{vap}^0 = 12.75 \cdot 8.314 = 106.0$ J/mol·K. The entropy of melting must be found at the melting temperature, so $\Delta H_m = \Delta H_m / T_m = 5600 / 303 = 18.48$ J/mol·K (1.25 points for each ΔS_{vap}^0 and ΔS_m, 7.75 points in total)

SECTION IV. LIFE SCIENCES AND POLYMERS

Problem 1 (authors Yu.S. Golovko, B.N. Garifullin)

1. The total number of atoms in two reagents equals 6 (4 oxygen and 2 hydrogen atoms). Two variants are possible with due account for coefficients before **A1** and **A2**: OH + O (1) or O_2 + H (2). Variant (1) corresponds to the reaction of short-living hydroxyl radical and atomic oxygen, this process being hardly possible in living matter. Variant (2) describes the reaction of charged particles (superoxide anion O_2^- and proton H^+). This reaction is catalyzed in organisms by a copper and zinc containing enzyme superoxide dismutase.

Molecule **A3** contains at least two atoms. Then, **A1** is superoxide anoin. Accordingly, particle **A4** composed of 4 atoms is a monoanion (to provide for balances on atoms and charges). If **A4** contains n oxygen atoms ($n = 0$ or 1) the molar mass M of **A3** is: $M(\textbf{A3}) = 20.67n + 9.34$. A reasonable answer is found only with $n = 1$: $M(\textbf{A3}) = 30.01$ g/mol, which corresponds to nitrogen(II) oxide NO. Then, the molecular formula of **A4** is NO_3^- (0.5 point for each of **A1** – **A4**, 2 points in total).

2. The reaction of superoxide anion with NO leads to peroxynitrite $^-$O–O–N=O (**A4**), which is isomeric to nitrate ion (**A5**).
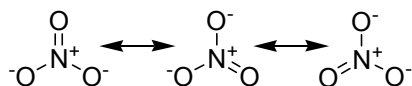
Salts of nitric acid are characterized by low toxicity for man, still can cause methemoglobinemia pathology in the case of babes. Peroxynitrite being a strong oxidizer is much more dangerous for mammals.

In general, accumulation of active forms of oxygen with pronounced oxidative ability (**A1** и **A4**) can lead to the death of spinal medulla and/or cerebrum motor neurons resulting in ALS (0.5 point for each of **A4**, **A5** and choice, 1.5 points in total).

3. Amino acid **B1** is present in both cases, which means that some of the codons **B1** – **B3** have the first and third letters identical and differ only in the second one. Only amino acids encoded by two and four codons are left under consideration. Phe–Tyr–Cys and Val–Ala–Gly meet the requirement of the same number of codons. Still, the codons encoding Phe–Tyr–Cys are characterized by a larger number of pyrimidine bases as compared to that of purine ones. Thus, the correct answer is Val–Ala–Gly. The given conditions are insufficient for unambiguously attributing **B1** – **B3** with particular amino

acids Val, Ala, and Gly (4 points for the correct combination of amino acids, 0.5 point for the note about impossibility of unambiguous attributing, 4.5 points in total).

4. Biochemical modification of a purine base into a pyrimidine one within nucleic acid (transversion) as well as single-step transformations C → T and T → C (transactions) are impossible with any reagent (1 point).

5. (1 point)

guanine ⋯ cytosine
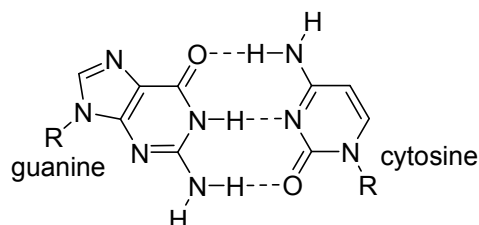
6. The molecular masses of totally protonated dTMP, dCMP, dAMP и dGMP are 323.2, 307.2, 331.2, and 347.2 a.m.u., respectively. The average molar mass of dNMP in the hexanucleotide is: $M_{av} = \dfrac{1913 + 5 \cdot 18}{6} = 333.8$ a.m.u. It is seen that hexanucleotide must contain dGMP. Two equations can be written to decipher the other (pyrimidine) nucleotide. Further solution is given for the correct variant (dCMP): $347.2n + 307.6(6 - n) = 1913 + 5 \cdot 18$, where n is the number of dGMP residues. Then, hexanucleotide is ($n = 4$) G_4C_2 (1 point for each choice (G and C), 0.5 point for the correct ratio of G and C, 2.5 points in total).

7. Since there 8 hydrogen bonds in the quadruplex cross-section, each nitrogen base is involved into 4 bonds (variants 1 and 2 on the hereunder figure). Asymmetric variant 3 is impossible, since one of the bases should be involved into 6 hydrogen bonds in this case.
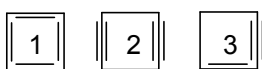
G_4 is in agreement with variant 1 (hydrogen bonds are formed between Watson-Crick side of one base and Hoogsteen side of the other base).
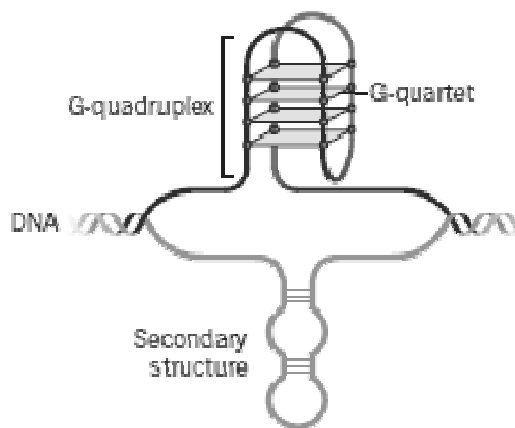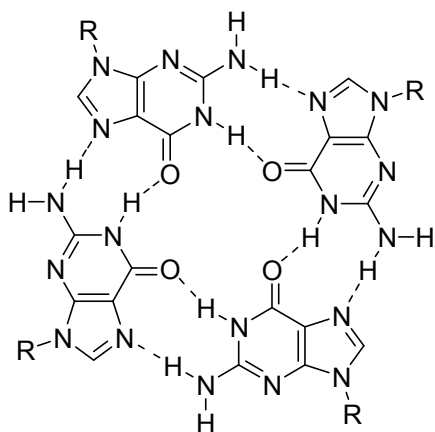
RNA polymerase initiating translation originally binds to the fragment of gene *C9orf72* capable of quadruplex formation. Any changes of the fragment secondary structure lead to disruption of matrix RNA and corresponding proteins formation (2.5 points).

Problem 2 (authors B.N. Garifullin, Yu.S. Golovko)

1. **E** is characterized by an anomalously high (by mass) content of element **Y** (94.96%). One can suppose that hydrogen is the second element in **E**. Denoting **Y** valency by n one gets: $M(\mathbf{Y}) = \dfrac{94.96 \cdot 1.008 \cdot n}{5.04} = 19.00n$. The only reasonable solution is found at $n = 1$. Then **Y** is F, and **E** is HF existing in gaseous form at 25°C and 1 atm. Let us determine the second element (**Z** with the oxidation state of m) in the compound **D**: $M(\mathbf{Z}) = \dfrac{60.80 \cdot 19.00 \cdot m}{39.20} = 29.47m$. Only cobalt Co ($m = 2$) is left under consideration if chemistry reasons are taken into account. Then **D** is CoF_2, an ionic compound with crystalline structure (1 point for the calculations, 0.5 point for each element and each substance, 3 points in total).

2. **E** is a gas, **D** is a solid, then **X** is a liquid (1 point in total; 0.5 point in the case of only one match).

3. Three fluorine-containing binary products are formed as a result of the reaction, one of these being cobalt(II) fluoride. These facts strongly suggest a well known fluorinating agent cobalt(III) fluoride CoF_3 as one of the initial binary substances. Then the fluorinated substance turns out to be a hydrocarbon, and **X** is perfluoro-hydrocarbon. $n(C) : n(F) = \dfrac{100 - \omega(F)}{A_r(C)} : \dfrac{\omega(F)}{A_r(F)} = 1 : 1.8 = 5 : 9$. $C_{10}F_{18}$ is the gross formula of **X** accounting for odevity of the number of fluorine atoms. Let us determine the molecular formula of **X**. Three nuclides (^{12}C, ^{13}C, and ^{14}C) are known for carbon. It is not needed to know the number of fluorine isotopes met in nature to conclude that it is only one (^{19}F) based on the problem conditions (the difference of 20 a.m.u. is theoretically possible only for C_1F_{18}). Thus, the difference in the **X** isotopologs masses is exclusively due to the distribution of carbon nuclides. Having in mind $A_r(^{14}C) - A_r(^{12}C)$, one gets for 10 carbon atoms the difference of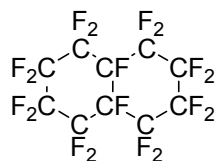 just $10 \cdot 2 = 20$ a.m.u. Thus, the gross formula of **X**, $C_{10}F_{18}$, coincides with the molecular one (1 point for the calculations, 1 point for the answer, 2 points in total).

4. Administration of drugs based on radioactive ^{14}C isotope creates a danger of radiation sickness. Only two isotopologs of **X** with the molecular masses of 462 a.m.u. (all carbons

^{12}C) and 463 a.m.u. (9 carbons ^{12}C and 1 carbon ^{13}C) are absolutely harmless. Isotopologs with higher molecular masses can theoretically contain ^{14}C (1 point).

5. Consideration of possible variants leads to the structure of perfluorodecalin (2 points)

$$
\begin{array}{c}
\text{F}_2 \quad \text{F}_2 \\
\text{C} \quad \text{C} \\
\text{F}_2\text{C} \diagup \quad \diagdown \text{CF} \diagup \quad \diagdown \text{CF}_2 \\
\text{F}_2\text{C} \diagdown \quad \diagup \text{CF} \diagdown \quad \diagup \text{CF}_2 \\
\text{C} \quad \text{C} \\
\text{F}_2 \quad \text{F}_2
\end{array}
$$

6. Perfluorodecalin is characterized by gas transport function (1 point).

7. Osmotic pressure is a colligative (dependant only on the number of particles) characteristics. Since physiological solution and glucose solution to be determined are isotonic to blood plasma, they are mutually isotonic. Sodium chloride is totally dissociated in a diluted aqueous solution. $\frac{0.9 \cdot 2}{58.5} = 0.031$ moles of particles are found per $100 - 0.9 = 99.1$ g of water in the isotonic salt solution. Then $\omega(\text{glucose}) = \frac{0.031 \cdot 180}{0.031 \cdot 180 + 99.1} = 0.053 \approx 5\%$. Pharmaceutical industry manufactures ampoules and vials containing 5% aqueous solution of glucose for intravenous administration at different pathologies (1.5 points).

8. Mannitol being a polyol does not dissociate in aqueous solution. Since it has the molar mass close to that of glucose, it is clear without calculations that the 15% mannitol solution is hypertonic (hyperosmotic) as compared to blood plasma. Such solutions can be used only in cases of excessive accumulation of a hypotonic liquid in tissues to provide for water evacuation into the blood-stream with osmolarity increased by introduction of the mannitol solution. Such cases are given in the first and second choices. It is worth mentioning that the protein present in the intraocular fluid in the concentration of 1% cannot produce any serious osmotic pressure because of its high molecular mass. Instead, it provides for slight oncotic pressure (0.5 point for each variant, 1 point in total).

9. There are only few four-atomic gases at STP. Since polymer **P** was obtained by radical polymerization, the vinyl system of monomer **P2** could have been formed as a result of acetylene (**P4**) addition. Condensation accompanied by water release suggests ammonium as **P3**. Then, the scheme of polyvinylpyrrolidone synthesis is (0.5 point for each substance, 2.5 points in total):
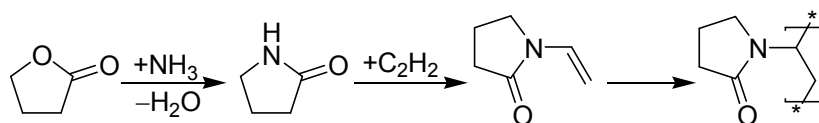
Problem 3 (author E.A. Karpushkin)

1. The ratio of elements in **B** is as follows: $n(\mathrm{C}) : n(\mathrm{H}) : n(\mathrm{O}) = \dfrac{54.53}{12.01} : \dfrac{9.15}{1.008} : \dfrac{36.32}{16.00} =$

$= 4.54 : 9.08 : 2.27 = 2 : 4 : 1$. It is evident from the formula of the repeating unit (C_2H_4O) that there are no multiple bonds in the polymer. As **B** is formed as a result of alkaline hydrolysis, it is an alcohol, polyvinyl alcohol being the simplest option. As **B** is formed from **A** alongside with sodium acetate, **A** is polyvinyl acetate (0.5 point for each structure, 1 point for the calculation, 2 points in total).
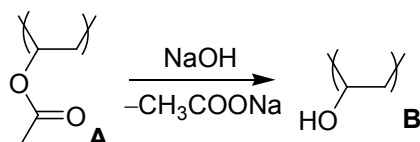
2. Various routes of polyvinyl acetate hydrolysis yielding polyvinyl alcohol are described. Acid hydrolysis (a) gives acetic acid, whereas the acetate fragment of **A** is released in the form of ethyl acetate in the presence of ethanol (b) and N,N-diethylacetamide is formed in the presence of diethylamine (c) (1 point for each product, 3 points in total).

3. The only heteroatom in the structure of **C** (oxygen) should be located in the polymer main chain. Polyethylene glycol $(CH_2CH_2O)_n$ is the most probable choice (1 point).
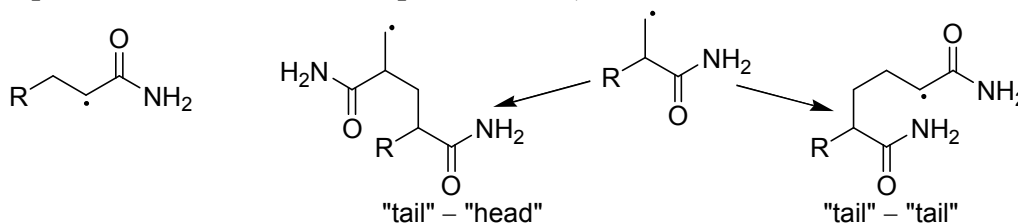
4. Two chains (of four) connected via the linkage are shown hereunder in the structure of **D**, whereas the other two chains are denoted as R (1 point for each of **C1**, **C2**, and **C4**; 0.5 point for each of **C3** and **D**; 4 points in total).
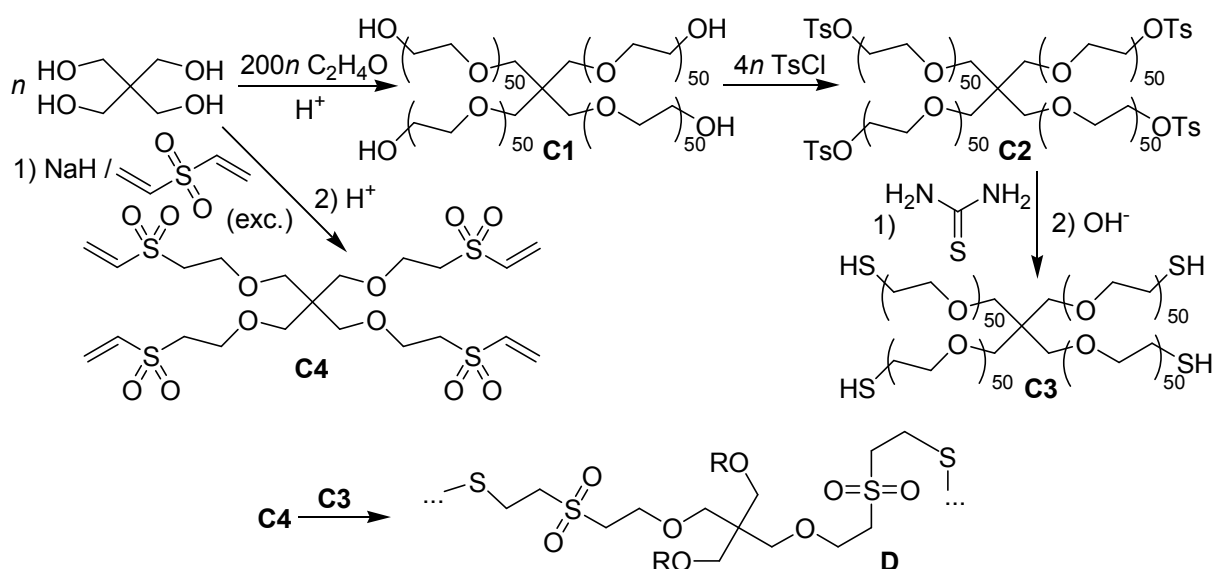

5. Chains of **B** linked upon treatment with sodium borate (1 point):
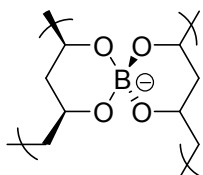
6. (0.25 point for each structure, 1 point in total)

"tail" – "head"   "tail" – "tail"

7. Polymerization of vinyl acetate mainly occurs via formation of the "head" – "tail" unit pairs: the secondary "tail" macroradical is more stable than the primary "head" one, whereas addition of the monomer "head" is advantageous due to the steric reasons. Nevertheless, polymerization is not completely regular, and other unit pairs are present in the polymer. The type of units junction is preserved upon hydrolysis of polyvinyl acetate giving polyvinyl alcohol. Hydrolysis of the "head" – tail" and "tail" – "tail" units yields the pairs of –CHOH– groups separated by one or two methylene groups, such fragments being inert towards periodic acid. Hydrolysis of the "head" – "head" units gives a pair of hydroxyl groups at adjacent carbon atoms of the main chain (α,β-diols). Such fragments are degraded by periodic acid:
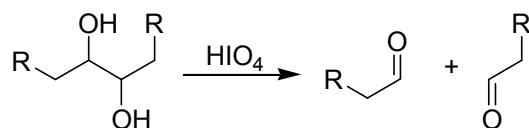

Let us estimate the amount of such unit pairs in the starting polymer. The degree of polymerization of the degradation products is of $9000 / 44 \approx 205$ (the chain is sufficiently long, which allows neglecting the masses of the terminal groups if these are different from hydrogen and hydroxyl group). Hence, the "head" – "head" unit pairs in the starting polymer are separated by about 205 junctions of other types, and the fraction of the "head" – "head" unit pairs is of 0.49% (1 point for each of ii. a – c, 3 points in total).

SECTION V. ORGANIC CHEMISTRY

Problem 1 (author D.M. Volochnyuk)

1. The problem contains some prompts. The most important one is the structure of the intermediate. This allows for solving problem even you do not know the bases of NMR spectroscopy. The molecular formula of the given intermediate is $C_{12}H_{14}N_2O$, it has two chiral centers; both have (*S*)-configuration. Therefore, the formation of **N** is accompanied by the loss of oxygen atom but stereocenters are intact. It is possible to conclude that this step is the reduction of C=O group to CH–OH followed by the water elimination producing an imine function. This intermediate itself is formed during the hydrolysis of **G** which has molecular formula of $C_{13}H_{16}N_2S$. It means that during this reaction oxygen atom replaces an CH_2S moiety. We know that 5-(methylsulfanyl)tetrazole participated in the formation of **G**. So, we can conclude that during the hydrolysis, $CH_3S–$ is substituted by –OH and a formal product (imino alcohol) undergoes the tautomerization into more stable amide.
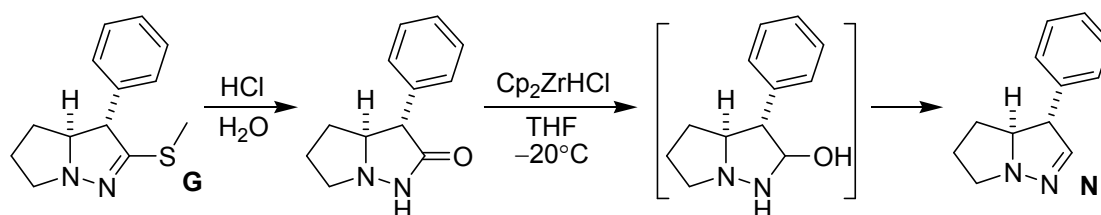

Accounting for molecular formulae of **H** and **W**, fact that **N** is dihydro derivative of **W** and that withasomnine is achiral, we can deduce structures of these compounds.
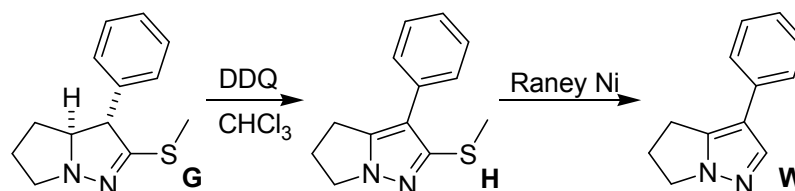

The problem contains the statement that the key steps in syntheses of both **W** and **N** are [3+2]-cycloadditions. For **N** formation, this cycloaddition can occur only on the step of the **F** transformation into **G**. Indeed, the formation of **E** is the reduction of acid into alcohol ($C_{11}H_{14}O$). During the next step an oxygen atom is substituted by $C_2H_2N_4S$ (or, more exactly, –OH group by $C_2H_3N_4S$ moiety). This is the condensation reaction between an alcohol and 5-(methylsulfanyl)tetrazole with the elimination of water and the production of (5-phenylpent-4-en-1-yl)-substituted tetrazole.
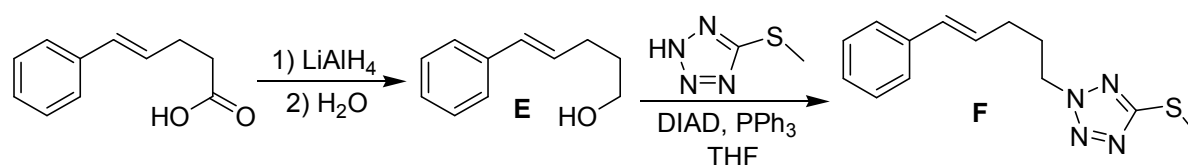
G is a bicyclic compound. The comparison of its structure and structure of **F** shows that during the irradiation, the tetrazole fragment lost N_2 molecule. The formed 1,3-zwitter-ion participated in the intramolecular [3+2]-cycloaddition affording a five-membered ring.
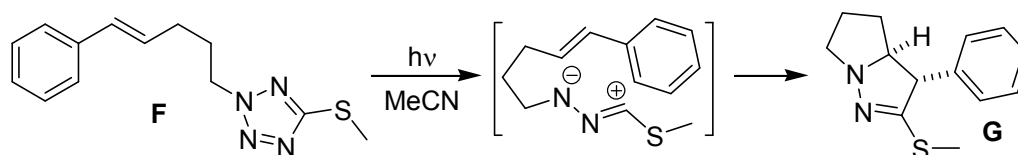

In the upper part of the scheme, the first step is the nitrosation of the glycine nitrogen atom furnishing compound **A** ($C_5H_8N_2O_3$). So, **B** is formed as a result of the **A** dehydration. In this case, it is possible only if the ketene is formed. However, such ketene is not bicyclic mesoionic compound. Therefore, the ketene moiety reacts with the nitroso group producing a new ring. Elimination of CO_2 proceeds during the next step. Evidently, this fragment is present in **B** in the latent form. The formed intermediate reacts with alkyne affording the product of [3+2]-cycloaddition which has a core of withasomnine. The transformation of **C** into **D** is the cross-coupling reaction. The product is transformed into **W** under treatment with Bu_4NF. This reagent can efficiently remove a silyl group but not a boronic ester moiety. These conclusions allow for writing structural formulae of **A** – **D**.
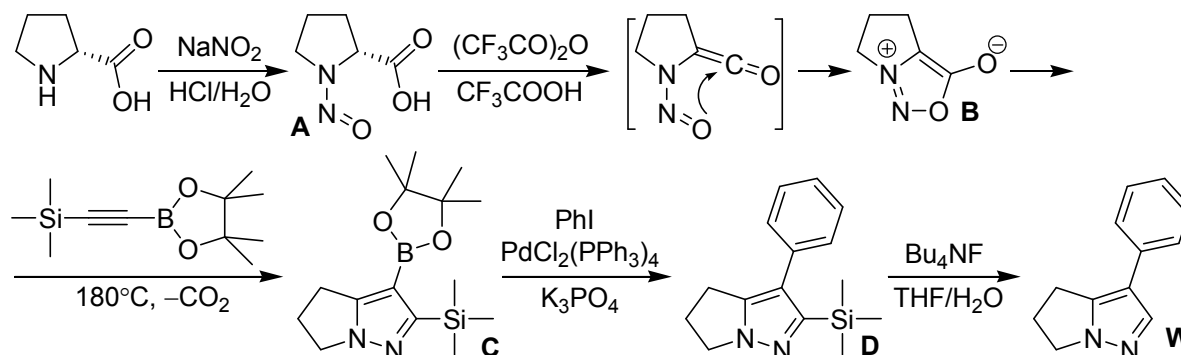

(2 points for structure of **B**, other structural formulae – 1 point for each, 11 points in total)

2. The upper-field signal (2.7 ppm) belongs to CH_2 group which is the most distal from the pyrazole ring. The signal of protons of CH_2 group connected to the nitrogen atom (4.2 ppm) is in lower field than the signal of CH_2 group connected to the carbon atom (3.10 ppm). In aromatic region, proton **A** only is appeared as singlet. So, it is the proton of the pyrazole ring. Intensity of the signal **D** demonstrates clearly that this corresponds to the proton in *para*-position of the benzene ring. The selection of signals for *ortho*- and *meta*-protons is the less clear. Pyrazole fragment is a weak donor. Therefore, the signal of *ortho*-, protons is located in the upper field than the signal of *meta*-protons.
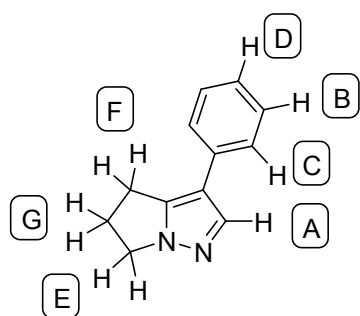
(1 point if aromatic protons are marked as **A** – **D** and aliphatic protons are marked as **E** – **G**, however there are mistakes in both groups; 2 points if there are wrong assignments for one group only; 3 points for right assignment of all signals).

3. Two isomers as two isomeric tetrazoles (1*H*- and 3*H*-) can exist (1 point).
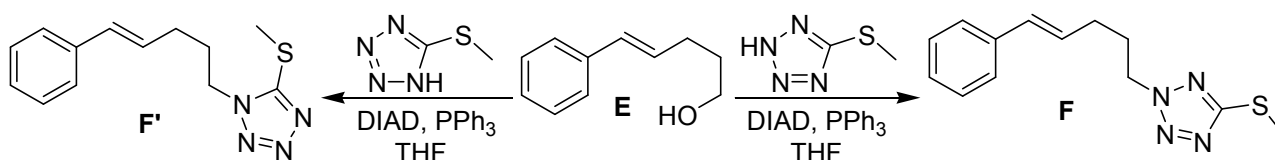

Problem 2 (author D.V. Kandaskalov)

**1.** Reaction mechanism is given in the problem. So, answer is quite clear.
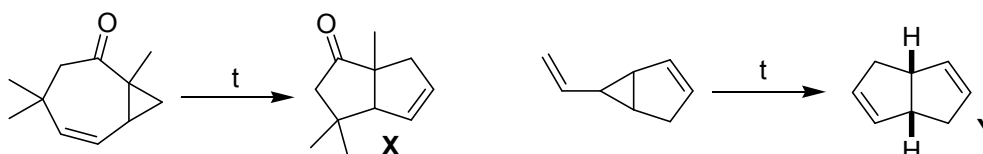
(2 structural formulae, 0.75 points for each, 1.5 points in total)

2. Zizaene is tricyclic compound. It has also one C=C bond. Therefore, extent of unsaturation is 4 (0.5 points).

3. Zizaene has 4 asymmetric carbon atoms. However, due to the cage structure of this hydrocarbon the configurations of 3 asymmetric carbon atoms (tertiary and two quaternary) are interlocked. As a result, instead of 16 stereoisomer only 4 isomers can exist (1 point).
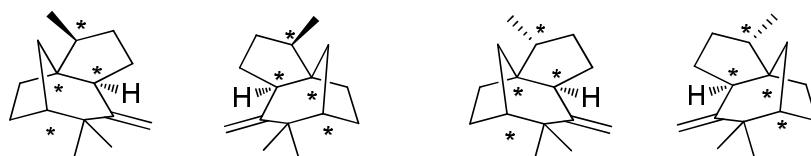

4. VCR is the first step of this synthesis. The resulting hexahydroindanone **A** ($C_{10}H_{14}O$) undergoes base-induced isomerization into more stable ketone **B** having conjugated system of multiple bonds. Compound **C** has 2 carbon and 4 hydrogen atoms more than **B**. This shows that vinyl group was added to **B**. Indanone fragment is present in compound **L** which is transformed into zizaene by Wittig reaction with phosphorus ylide. This allows for concluding that 1,4-addition via nucleophilic attack onto β-carbon atom occurs in this reaction. Due to steric demands, nucleophile attacks from the side opposite to side wherein methyl group is present. The structure of zizaene shows that two rings have *cis*-connection.
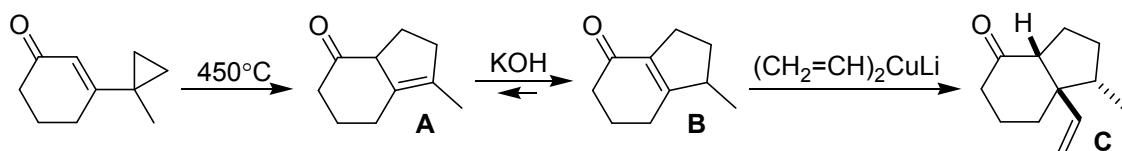
Molecular formulae demonstrate that during **C** to **D** transformation hydrogen atom is replaced by C_6H_5S fragment. The bulky base (LDA) deprotonates more accessible α-carbon atom (CH_2). Fragment C_6H_5S is connected with this atom. Oxidation of PhS-group followed by PhSOH elimination affords α,β-unsaturated ketone **E**:
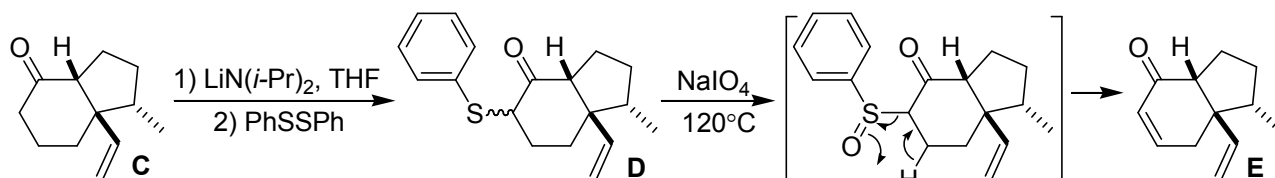
Molecular formula of **F** shows that $E \rightarrow F$ step includes Michael addition of thiol to conjugated C=C bond and then transformation of ketone into ketal. Hydroboration followed by oxidation of borane with H_2O_2 leads to product of anti-Markovnikov alkene hydration. This alcohol was then transformed into tosylate **G**.
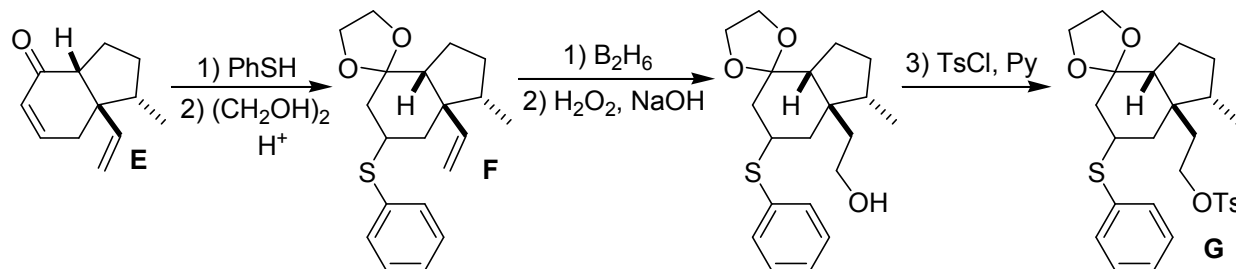

The comparison of molecular formulae of **I** and **J** shows that during this step $C_6H_5O_2S$ fragment was replaced by hydrogen atom. It is possible to conclude that oxidation of **G** with *meta*-chloroperbenzoic acid produces the corresponding sulfone which undergoes reductive elimination under treatment with sodium amalgam. Therefore, **I** formation is accompanied by TsOH elimination. Accounting for zizaene structure, we can conclude that this is the result of CH–SO₂Ph fragment deprotonation and nucleophilic substitution of tosylate by carbanion.
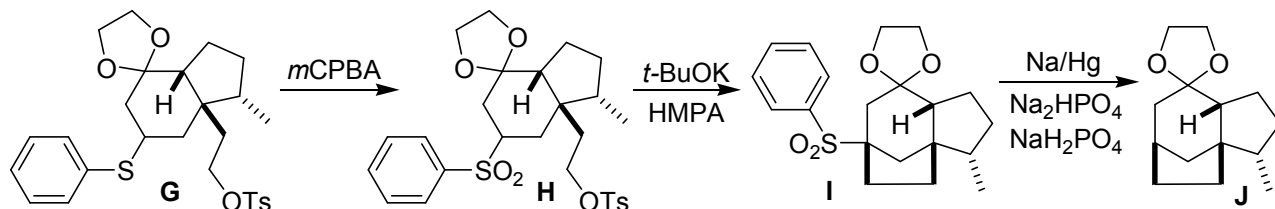

The final steps are quite clear as molecule of **J** resembles the target molecule of zizaene (12 structural formulae, 1 point for each; 12 points in total).
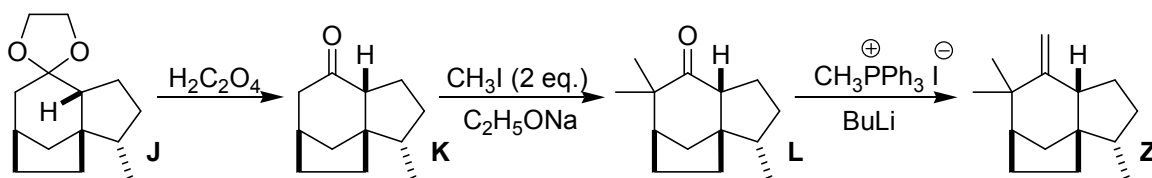
Problem 3 (author E.N. Shved)

1. Treatment of ketones with bases produces enolate ions reaction of which with RCl leads to alkylation of α-carbon atom (use of excess of RCl yields polyalkylation products). In the presence of base only ketones undergo aldol condensation. Therefore, **B** and **C** are products of condensation. Accounting for problem condition, we can write structures (7 structural formulae, 0.5 point for each, 3.5 points in total):
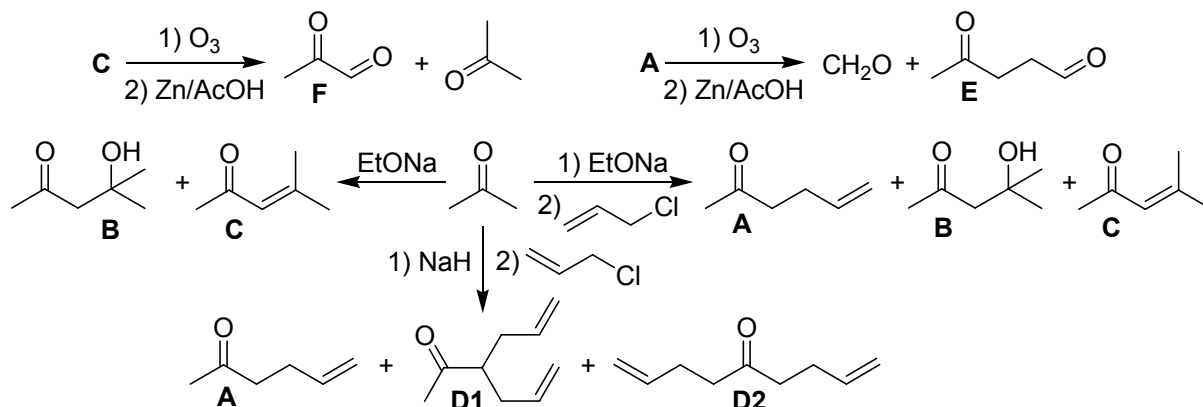
2. Accounting for the determined structures of **A**, **D1** and **D2** as well as activation of one of α-carbon atoms by ethoxycarbonyl group, we can deduce that the primary product is enolate **G**, the secondary product is dianion **J**. In this dianion C4 atom is much more basic than C2 atom. Therefore, C4 atom is alkylated furnishing **K**. Monoanion is alkylated at C2 atom (6 structural formulae, 0.5 point for each; 3 points in total):
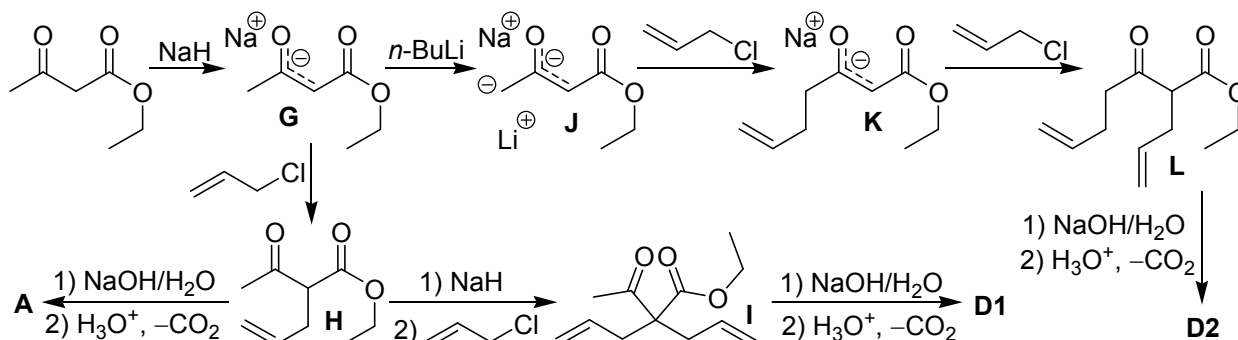
3. The treatment of **M** with sodium ethoxide and CH_3I produces 2-methylcyclohexanone. Therefore, **M** is cyclohexanone. Reaction of anion of methylcyclohexanone with ethyl formate is introduction of auxiliary group. Further scheme is similar to the previous one. The last step is the removal of auxiliary CHO group:
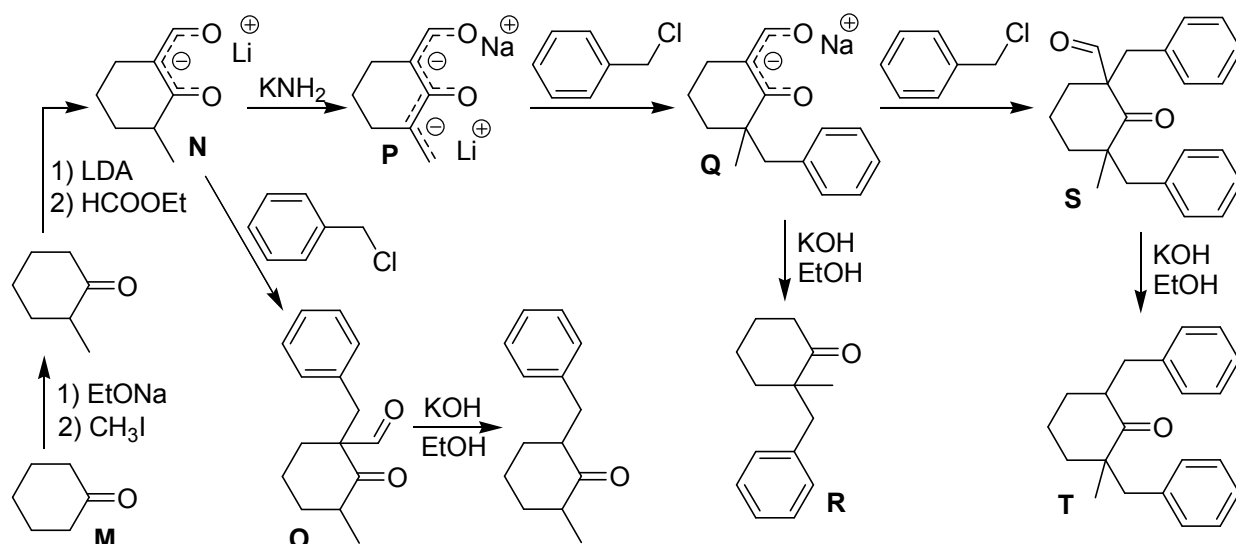
(8 structural formulae, 0.5 point for each; 4 points in total)

4. We know that **Y1** and **Y2** are bicyclic compounds. **Y1** is formed by alkylation of cyclohexanone **M** with 1-chloro-2-iodoethane followed by treatment with bulky base. In 1-chloro-2-iodoethane iodine is substituted much faster than chlorine. Reaction of cyclohexanone with PhCHO produces product of aldol condensation. As **Y2** is isomer of **Y1**, we can conclude that benzylidene fragment was removed at the last step. However, this reaction proceeds under vary hard conditions at which cyclopropyl ketone moiety is unstable. The prompt is statement that **Y2** contains no carbonyl group. Therefore, **Y2** has C=C and C–O bonds. During retro-aldol reaction cyclopropyl ketone fragment undergoes rearrangement into dihydrofuran moiety (structural formulae of **U** – **X** – 0.5 point for each; formula of **Y1** – 1 point, formula of **Y2** – 1.5 points, 4.5 points in total):