

## Problem 1

In Jules Verne's novel "The Mysterious Island", the chemical engineer Smith built a battery to power the telegraph:

«Smith decided to make the simplest battery, similar to the one invented by Becquerel in 1820. The engineer made several glass jars and filled them with nitric acid. Then he plugged each jar with a stopper, passing through it a glass tube, the lower end of which was plugged with a clay sleeve wrapped with a piece of rag. Through the upper end of this tube he poured a solution of potash. Smith then took two zinc plates and immersed one in nitric acid and the other in a solution of potash. An electric current immediately arose and went from the plate inserted in (1) to the plate inserted in (2). When these plates were connected with a metal wire, the plate in the tube became (3), and the plate in the jar became (4) the pole of the device. The result was a source of current, quite sufficient to set in motion an electric telegraph.»

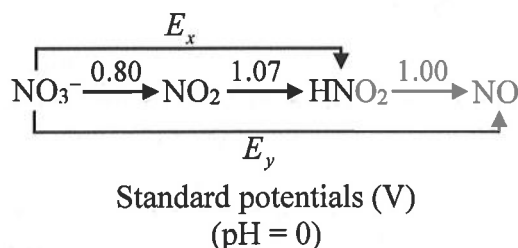
- Why is it not possible to use zinc electrodes (as in the book)?
  - What other material for electrodes can one try to find on the island, given that it does not contain noble metals?

Correcting the mistake of the author of the novel, we will further assume that the plates (electrodes) of the battery are made of an inert material.

- Fill in the four gaps (1) – (4) in the passage from the book with the words "positive", "negative", "tube", "jar".

In an acidic environment formed by nitric acid, there are particles indicated in the Latimer diagram (see figure).

- Find standard potentials  $E_x^\circ$  and  $E_y^\circ$ ;
  - Get the dependence of the potential on the pH of the solution for three cases at 25°C;
  - Specify the most thermodynamically favorable process at unit concentrations of other particles.



- Indicate the cathode and anode in the battery, their half-reactions and the overall reaction.
- Calculate the EMF of the battery in a fully charged state, assuming that the pH = 2 for the solution in the jar and pH = 11 for the tube.
- How many ( $N$ ) batteries must be connected in series in order for the telegraph to work, which needs a voltage of 4.5 V?
- Calculate the Gibbs energy and the equilibrium constant of the reaction in the battery.

Reference data:  $E^\circ(\text{K}^+/\text{K}) = -2.93$  V,  $E^\circ(\text{O}_2/\text{H}_2\text{O}) = 1.23$  V,  $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76$  V,  $F = 96485$  C/mol,  $R = 8.314$  J/mol·K.

## Problem 2

Surface-active species (surfactants) are adsorbed at an interface between phases, thus reducing its tension. The surface tension of aqueous  $n$ -pentanol solution under air can be described via the Szyszkowski equation  $\sigma = K - L \ln(1 + Mc)$ , with  $K = 72.8$  mN/m,  $L = 16.7$  mN/m,  $M = 66$  L/mol, and  $c$  being concentration of the alcohol in the solution.

- Determine the surface tension of pure water.
- Determine the lowest limit of  $n$ -pentanol detection in the aqueous solution by measuring the surface tension, if the latter can be measured with accuracy of  $\pm 2\%$ .

Adsorption ( $\Gamma$ , mol/m<sup>2</sup>) of a surfactant with the formation of its monolayer at the interface can be described via the Gibbs equation  $\Gamma = \frac{\Gamma_{\max} Mc}{1 + Mc} = \frac{L}{RT} \frac{Mc}{1 + Mc}$ , with  $\Gamma_{\max}$  being the highest possible adsorption (mol/m<sup>2</sup>),  $L$  and  $M$  being the Szyszkowski equation parameters.

- Calculate  $\Gamma_{\max}$  for  $n$ -pentanol adsorption at the water–air interface and determine the area  $s_0$  per a molecule in the saturated adsorbed monolayer.

If the area of the surface at which the adsorption occurs can hardly be measured, the adsorption can be expressed per mass of the sorbent (mol/g). In this case, the Gibbs equation is still correct, yet the

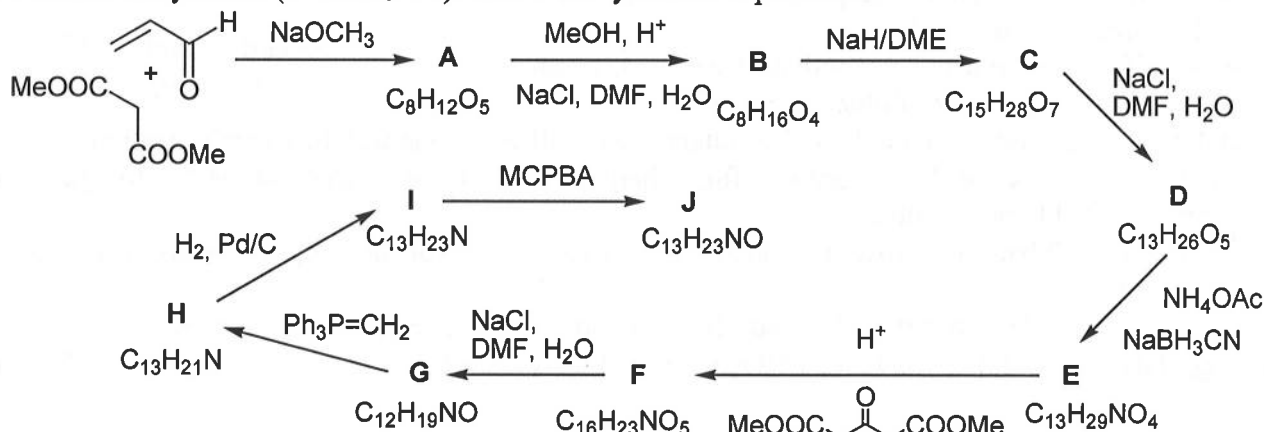
parameters  $M$ ,  $L$  are different from these for the water–air interface. To study  $n$ -pentanol adsorption at active carbon, 1g of the carbon sample was put in the alcohol solutions (25 mL each) with different concentration ( $c_0$ ). Upon the equilibration, the carbon was filtered off, and surface tension of the filtrate ( $\sigma$ ) was determined. The obtained data are in the table below:

$c_0$ , mol/L	$\sigma$ , mN/m
0.05	59.4
0.10	50.8
0.15	44.2
0.2	38.9

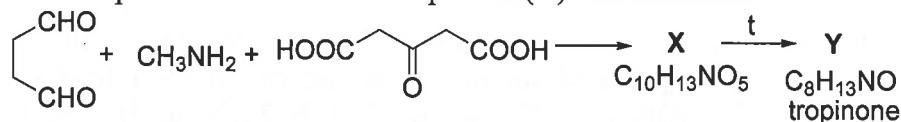
- Determine the alcohol concentration in the filtrate at its different starting concentrations and calculate the  $n$ -pentanol adsorption on carbon (mol/g) in each of the four experiment runs. Fill in the table in the Answer Sheet.
- Draw a plot of  $c/\Gamma$  as a function of  $c$  ( $c$  being the equilibrium alcohol concentration). Using the obtained data, determine the highest possible adsorption  $\Gamma_{\max}$  of the alcohol on the carbon (mol/g).
- Assuming that the area per molecule is the same in the adsorption layer at the water–air and water–carbon interfaces, calculate specific surface area of the carbon ( $\text{m}^2/\text{g}$ ).

### Problem 3

Ladybugs play an important ecological role in controlling the population of some harmful insects such as aphids. Ladybugs have few natural enemies due to their defense mechanism based on releasing a fluid that contains cokineline (**J**  $\text{C}_{13}\text{H}_{23}\text{NO}$ ). Below its synthesis is presented.



The key step in this synthesis is the Robinson-Scheppf reaction, which was first used as a method for obtaining the bicyclic compound **X** from which tropinone (**Y**) was obtained:



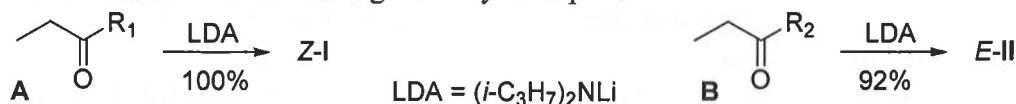
- Decipher the structures of **X** and **Y** considering that the Robinson-Scheppf reaction is a sort of a double Mannich reaction.
- Decode substances **A** – **J** if the IR spectrum of **A** contains a band at  $1720\text{ cm}^{-1}$ , and  $^1\text{H}$  NMR spectrum of **D** contains 5 signals in with integrated intensities 6:2:2:2:1.

### Problem 4

Aldol condensation is a universal method for the formation of a C–C bond. It is important to discuss the stereochemical regularities of this reaction.

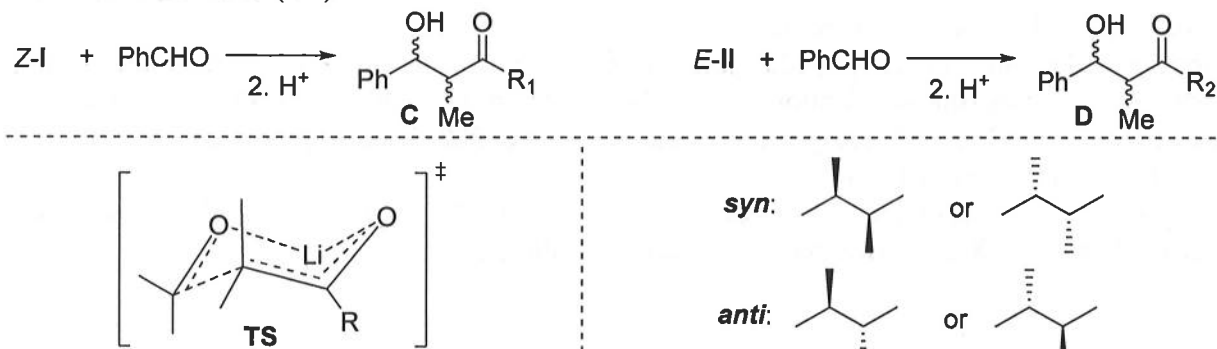
- Give the structures of achiral carbonyl compounds and products of their aldol condensation if this product contains: a) 0 chiral centers; b) 1 chiral center; c) 2 chiral centers.

To minimize side processes, pre-prepared enolates are often used, the stereochemistry of which depends significantly on the structure of the starting carbonyl compound.



2. Determine the structure of **A**, **B**, lithium enolates **Z-I** and **E-II** if the <sup>1</sup>H NMR spectrum of **A** contains quadruplet (2H), triplet (3H) and singlet (9H). The <sup>1</sup>H NMR spectrum of **B** contains singlet (2H), quadruplet (2H), singlet (3H), triplet (3H), singlet (6H). **B** is obtained regioselectively by the reaction:  $\text{C}_x\text{H}_y + \text{RCOCl}/\text{AlCl}_3 \rightarrow \text{B}$ . Determine the structures of  $\text{C}_x\text{H}_y$  and  $\text{RCOCl}$ .

Aldol condensation exhibits high stereoselectivity when pre-prepared enolates are used. The stereochemistry of the products is determined by the geometry of the enolate (**Z/E**). To predict the predominant diastereomer (*syn*-/*anti*-) of the condensation product, it was proposed to use the 6-membered transition state (**TS**):



3. Add substituents in **TS** for the reactions of **Z-I** and **E-II** with  $\text{PhCHO}$ . Based on structure of **TS**, determine the structure of predominantly formed diastereomer of **C** and **D**. Consider the geometry of the enolate (**Z/E**) and the fact that the bulky substituent occupies the equatorial position preferentially.

4. Indicate in the answer sheet how the geometry of the initial enolate is related to the stereochemistry of the final condensation product

5. Indicate the configurations of the chiral centers (*R/S*) in your product **C**.

Dubois found that the carbonyl compound **E** is converted to enolate **III** by treatment with  $\text{LiOH}$ . Subsequent reaction with *i*- $\text{PrCHO}$  followed by hydrolysis leads to the product **F** ( $w_{\text{O}} = 20.51\%$ ).

6. Based on paragraphs 2–4, depict the structures of **E**, **III** and **F**, taking into account stereochemistry. <sup>1</sup>H NMR spectrum of **F** contains 2 signals of the same intensity.

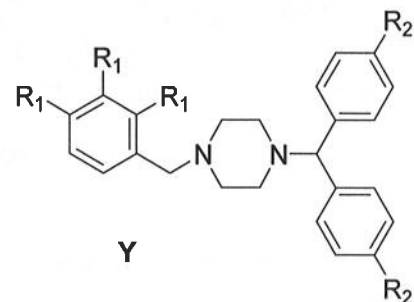
## Problem 5

During the recent Winter Olympics in Beijing, serious attention was drawn to the skater K. Valieva, who had been tested positive for Trimetazidine.

A version was suggested in media that the drug appeared in the organism due to administration of Lomerizine (**Y**,  $M = 468 \text{ g/mol}$ ), a pain killer approved by the World Anti-Doping Agency (WADA) and widely used for treatment of migraines. According to the WADA protocols, **X** is one of metabolites of **Y**, which complicates search for of intentional Trimetazidine administration.

1. Deduce all possible structures of **Y**, if all its unknown substituents (those but H) totally contain four elements ( $e_1, e_2, e_3, e_4$ ) in the molar ratio of 2:3:3:9. Show calculations.

Liquid chromatography–mass spectrometry (LC-MS) is the major method used for determination of **X** and **Y**. The drug actually used by an athlete can be distinguished by the presence of the compound **Z** in the urine. **Z** is formed from **Y** in a one-step process catalyzed by the same enzyme responsible for the one-step transformation of **Y** into **X**. The LC-MS spectra of both **X** and **Z** contain one peak of the protonated molecule ( $[\text{X}+\text{H}]^+$  in the case of **X** and  $[\text{Z}+\text{H}]^+$  in the case of **Z**), as well as the signals from



the major destruction products ( $X_1^+$  and  $Z_1^+$  ions, respectively). The difference in the  $m/z$  values in the case of both ions ( $[X+H]^+ - X_1^+$  and  $[Z+H]^+ - Z_1^+$ ) is the same and equals 86.

2. Determine the sum of the molecular masses of **X** and **Z** with an accuracy to integer. Note that this question is independent of the previous one.

An oxygen containing compound  $Z_2$  is the major metabolite of **Z**.  $Z_2$  is formed in one enzymatically catalyzed step and contains 4 types of H atoms.

3. Draw the structures of **Z** and  $Z_2$ .

Formation of more hydrophilic metabolites is the major strategy of clearance of **Y** in organisms. Three of its metabolites  $Y_1 - Y_3$  are structural isomers, whereas the fourth one ( $Y_4$ ) has the molecular mass by 30 g/mol higher than that of  $Y_1$ .

4. Draw only one of the possible structures of each of  $Y_1$  and  $Y_4$ , if  $Y_1 - Y_4$  contain one and only one group identical for all the compounds, the group contributing to higher hydrophilicity.  $Y_1$ - $Y_4$  are formed from **Y** in one step.

5. Draw the finally disclosed formula **X**.

Organisms use the same metabolic strategies for **X** and **Y**. When using LC-MS to check the fact of administration of **X**, one should monitor the signals from the protonated molecules of two metabolites ( $X_1$  and  $X_2$ ) with  $m/z$  of 253 and 333, respectively, and from the common major product of their destruction in the form of  $M^+$  ion with  $m/z$  of 167.

6. Propose one variant of the structures of each of  $X_1$  and  $X_2$ , if the hydrophilicity increases in the sequence of **X**,  $X_1$ , and  $X_2$ , whereas  $X_2$  is formed in man directly from  $X_1$ .

## Problem 6

Iodine is widely used in medicine as an antiseptic. Since this substance is slightly soluble in water (3450 ml of water is needed to dissolve 1.00 g of the substance), an alcoholic solution of iodine and a Lugol's solution are practically used.

1. Calculate the molar concentration (M) of iodine in a saturated aqueous solution (consider that the volume does not change when iodine is dissolved).

When iodine is extracted from the aqueous phase by an organic solvent, for example, carbon tetrachloride ( $CCl_4$ ), an equilibrium  $I_{2(aq)} \rightleftharpoons I_{2(org)}$  is established, which is described by the distribution constant

$$K_D = \frac{[I_2]_{org}}{[I_2]_{aq}}$$

A certain amount of  $CCl_4$  was added to the saturated iodine solution in water, and the extraction was performed. The mass fraction of iodine in the organic phase was 57.2 times greater than in the aqueous phase. Consider the densities of aqueous solutions equal to the density of water (1 g/ml) and organic solutions – the density of  $CCl_4$  (1.59 g/ml).

2. Calculate  $K_D$  for iodine distribution between the aqueous phase and  $CCl_4$ .

Lugol's solution is a solution of  $I_2$  in a 10% (by weight) aqueous solution KI. In such a solution, the iodine solubility is increased due to the formation of a complex ion  $I_3^-$  according to the equation:



3. Analyze the structure of  $I_3^-$  ion using the valence shell electron pair repulsion (VSEPR) theory – specify the type of the molecule ( $AX_nE_m$ , X – ligands, E – electron pairs bonded to the central atom A) and the I–I–I angle.

To find  $K_I$ , 100 ml of Lugol's solution was taken (take the density also equal to 1 g/ml) and extracted with tetrachloromethane with a volume of 50 ml. Titration of 10.00 ml of aliquots of organic and aqueous phases required 3.70 and 13.90 ml of sodium thiosulfate solution with a concentration of 0.2500 M, respectively.

4. Write equations for the reactions of thiosulfate ions with  $I_2$  and  $I_3^-$  that occur during titration.

5. Calculate the mass fraction of  $I_2$  in the analyzed Lugol's solution and the  $K_I$  constant. If you haven't got an answer to question 2, use the value  $K_D = 150$ .

## Problem 7

If you heat the tip of a steel needle to red heat in the flame of an alcohol lamp, and then quickly bring it into a flask with oxygen, then the needle burns with a bright flame, scattering sparks like a Bengal fire. This forms a solid black substance.

1. Give the equation for the reaction that occurs when a steel needle burns in oxygen.

Iron will not burn without heating and without oxygen, as you know. You can find a description of experiments on the preparation of "pyrophoric iron" in books on entertaining chemistry and in the Internet, "*pyrophoric iron*" burns out without heating on contact with air, almost like a steel needle. At the first stage of its preparation, a solution of potassium oxalate (or oxalic acid) should be added to an excess of an aqueous solution of ferrous sulfate. In this case, a yellow compound **A** precipitates (mass fraction of oxygen 53.36%).

2. Determine the formula of **A**.

At the second stage, the resulting precipitate should be filtered, dried, and then strongly heated in a test tube closed with a cotton swab. As a result, according to the authors, "*pyrophoric iron*" is obtained. If the test tube with the resulting black powder is cooled to room temperature, and then, after removing the cotton swab, the contents are slowly poured out, then upon contact with air, the resulting product "lights up", scattering bright sparks.

3. Give the equation of the chemical reaction of obtaining "*pyrophoric iron*" proposed by the authors of the publications.

An experimental study showed that if the thermal decomposition of **A** is carried out in a vacuum, then after its complete decomposition, a gas mixture is formed, the density of which at 280°C and 110.8 kPa is 0.6507 g/dm<sup>3</sup>.

4. Determine the formulas of the substances that are contained in the gas mixture formed after the complete decomposition of **A** in a vacuum, and calculate their mole fractions.

5. Give the equation for the reaction that occurs during the decomposition of **A** in vacuum.

6. Give the equation for the combustion of "*pyrophoric iron*".

7. Why does the resulting product "burn" when exposed to air?

7.1. the resulting product is a very strong reducing agent;

7.2. the product is formed in the form of very small particles (nanoparticles);

7.3. combustion of the product starts due to the presence of impurities in the air;

7.4. the enthalpy of reaction between the product and oxygen is positive;

7.5. along with the main product during decomposition, a catalyst is formed, which sharply accelerates the reaction of the main decomposition product with oxygen;

7.6. combustion starts due to gases formed during decomposition.

## Problem 8

Element **X** forms a wide variety of oxyacids in which it exhibits different oxidation states. Despite this, the structural principle underlying these compounds is not complicated – they always contain the element **X** in a tetrahedral (or slightly distorted tetrahedral) environment and contain a double bond with oxygen **X=O**.

A simple substance **X** reacts and dissolves in a concentrated solution of sodium hydroxide upon the heating. There are many products of this reaction, but the main ones are gas **G** and salt **B1**. Acidification of a solution of salt **B1** produces acid **A1**, which can be isolated individually by prolonged extraction with diethyl ether from aqueous solutions. The acid **A1** is white crystals with a melting point of 26.5°C.

If another allotropic modification of **X** is oxidized by sodium chlorite or hydrogen peroxide in an alkali, salt **B2** is formed. Acid dihydrate **A2** ( $\omega(\text{H}_2\text{O}) = 18.18\%$ ) is isolated from salt **B2** by ion exchange on a cation exchange column. The **A2** is further subjected to vacuum dehydration over  $\text{P}_2\text{O}_5$  to obtain an anhydrous acid. The **A2** acid molecules have such symmetry elements as the inversion center, the 2-fold rotation axis, and the mirror plane perpendicular to it.

The acid **A2** decomposes at 73°C, however, even with slight heating, two processes can proceed in parallel: isomerization (rearrangement) to acid **A3**, as well as disproportionation with the formation of a

mixture of equimolar amounts of two acids – **A4** and **A5**. The **A3** acid molecules no longer have a 2-fold rotation axis and a mirror plane, and according to NMR spectroscopy on **X** nuclei, there are two nonequivalent **X** atoms in the structure. The **A4** and **A5** acid molecules are very similar – both have a mirror plane, but **A5** contains a larger number oxygen atoms, which gives it another mirror plane (perpendicular to the first plane) and a 2-fold rotation axis that passes along the line of intersection of the planes.

The formal oxidation state of element **X** increases in the series of acids **A1** – **A4** – **A2** – **A5**.

1. Identify the unknown compounds and write down the equations of the mentioned chemical reactions.
2. Draw the structure of the molecules of acids **A1** – **A5**, taking into account the indicated symmetry elements.

There are other oxyacids of **X**, but many of them are difficult to isolate in pure form, and their salts are mainly known. Thus, the series of normal sodium salts **B6** – **B7** – **B8** contains the same number of sodium and **X** atoms. The number of oxygen atoms in this series increases by one, and the mass fraction of oxygen in **B6** and **B7** is 38.10% and 40.91%, respectively.

3. Determine the composition of salts **B6** – **B8**.
4. Suggest the structure of anions of acidic residues in **B6** – **B8**.