Problem 1

In the presence of hydrogen sulfide in air silver tarnishes, becoming covered with a film of silver sulfide. To clean a silver coin from plaque of sulfide, it was placed in a beaker with an aluminum foil at the bottom, and a pre-boiled solution of baking soda (20 g in 0.4 L) was added. As a result, the foil dissolves and the silver original shine is restored.

Supporting data: p$K_{a1}(H_2CO_3)$ = 6.36, p$K_{a2}(H_2CO_3)$ = 10.3; p$K_{a1}(H_2S)$ = 7, p$K_{a2}(H_2S)$ = 12.9; $\beta([Al(OH)_4]^-) = 7.7\cdot10^{33}$; $K_s(Al(OH)_3) = 1.9\cdot10^{-33}$; $K_s(Ag_2S) = 8\cdot10^{-51}$

1. Write down the balanced equations of the following reactions:

a) formation of silver sulfide on the surface of the silver coin in air,

b) boiling of baking soda,

c) between aluminum foil and silver sulfide in the solution of boiled soda.

2. Calculate the pH of the soda solution upon the completion of reaction 1b.

3. Calculate the minimum mass of aluminum foil required to clean a silver coin (thickness 2 mm, diameter 20 mm) if the sulfide layer is 42 nm thick (ρ = 7.317 g/cm³).

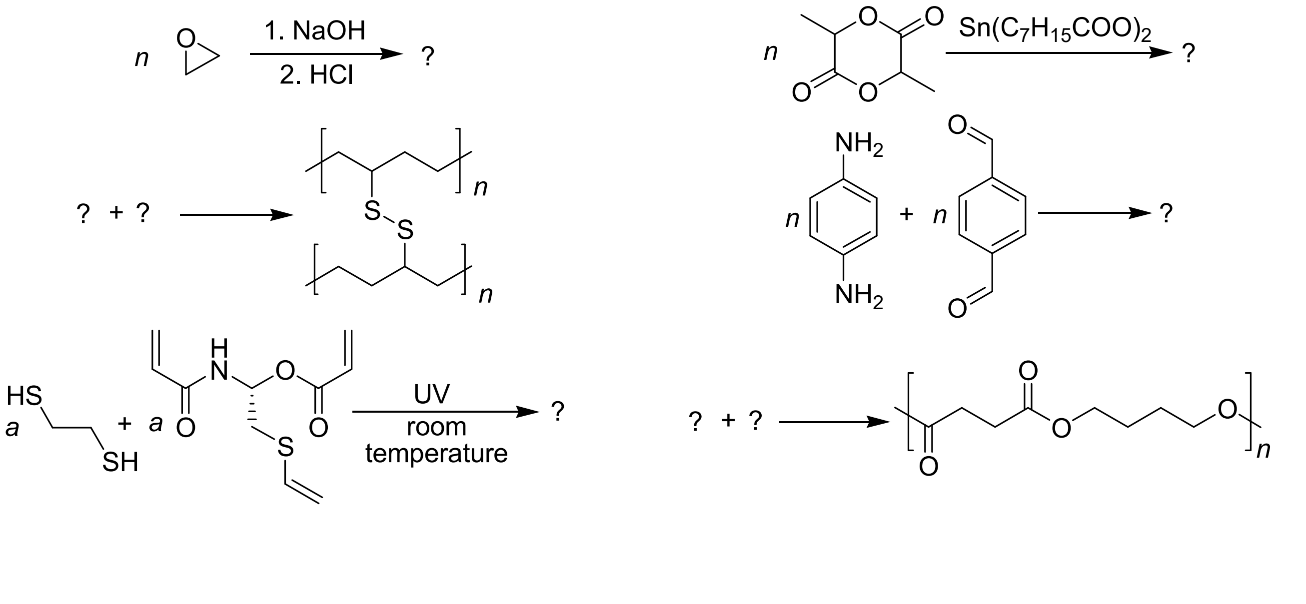
4. What proportion of aluminum that has reacted under the conditions described above is in the form of a hydroxocomplex $[Al(OH)_4]^-$?

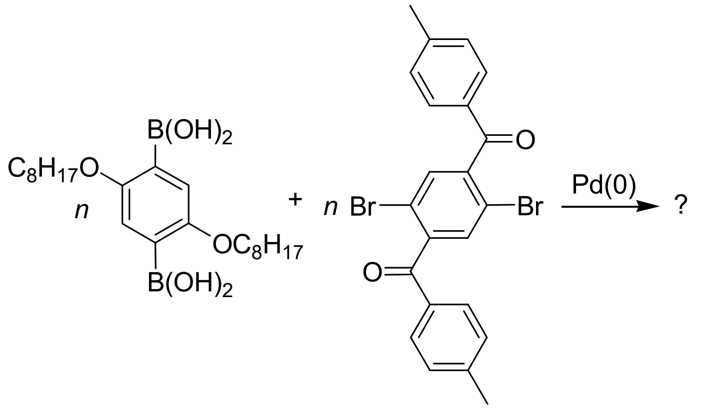
5. In this method aluminum and silver form a galvanic pair upon contact. Which of the metals is the cathode and which is the anode? Write down the corresponding half-reactions.

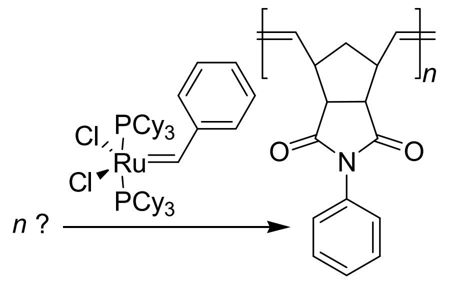
Problem 2

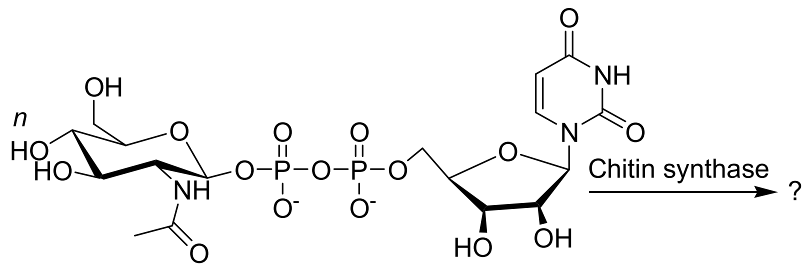
Natural and synthetic polymers are essential both in everyday life and in biomedical applications. The structural limit comes only from imagination of chemists, as many classical organic chemistry reactions can be transformed into polymerizations technologies.

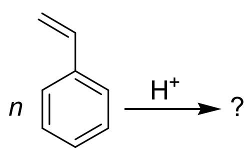
1. You will find 10 examples of polymerization reactions below. Certain parts (starting compound(s) or product(s)) are missing there. Complete the reactions.











Note: the linkage between units in chitin is analogous to that in cellulose.

Problem 3

Mineral **A** was used in ancient times for refining glass. For some time, it was considered a type of magnetite, although it is not attracted by a magnet. Subsequently, the Swedish chemist Scheele discovered a new metal **X** in this mineral, which can exhibit different oxidation states. As a consequence, solutions of compounds of this metal can have different colors. Compound $\mathbf{X_1}$, which is blue-colored, can be turned into $\mathbf{X_2}$, that has a green color and can be further converted into violet $\mathbf{X_3}$ and then into pink $\mathbf{X_4}$.

$$\mathbf{X_1}\ \text{(blue)} \underset{\mathbf{2}}{\overset{\mathbf{1}}{\rightleftarrows}} \mathbf{X_2}\ \text{(green)} \underset{\mathbf{4}}{\overset{\mathbf{3}}{\rightleftarrows}} \mathbf{X_3}\ \text{(violet)} \underset{\mathbf{6}}{\overset{\mathbf{5}}{\rightleftarrows}} \mathbf{X_4}\ \text{(pink)}$$

1. Identify metal **X**, if its percentage in **A** ω(X) = 63.22%. Give the historical name and the composition of mineral **A**.

2. Identify compounds $\mathbf{X_1}$ – $\mathbf{X_4}$. Mass fractions of oxygen in the $\mathbf{X_1}$ – $\mathbf{X_3}$ anions are equal.

3. Write equations for the reactions **1** – **6**.

4. When $\mathbf{X_4}$ interacts with ammonium hydrogen phosphate in ammonia aqueous solution, a white precipitate $\mathbf{X_5}$ is formed, which decomposes on heating to form $\mathbf{X_6}$. Draw the structure of the $\mathbf{X_6}$ anion, give the reaction equations and the composition of the resulting compounds taking into account that the mass fraction of ω(X) in $\mathbf{X_6}$ is 38.73%.

5. One example of obtaining element **X** in an unstable oxidation state is the reaction of $\mathbf{X}Cl_2$ with $LiAlH_4$ under pressure of CO to form **C**. Determine the composition of the resulting compound using Sidgwick's rule: in stable complex compounds the central metal atom surrounds itself with such a number of ligands that the number of electrons in the outer electron shell equals to 18. Give the reaction equation of **C** with Cl_2 and the composition of the resulting compound **D**.

Problem 4

In connection with the COVID-19 pandemic additional sanitary and epidemiological requirements were introduced. Thus it was impossible to get into public places without measuring body temperature, which was carried out using pyrometers and thermal imagers. These devices provide fast data acquisition, but their accuracy is much lower than contact thermometers, among which mercury is the most widely used. Upon contact with the object of measurement, the volume of mercury changes due to thermal extension according to the formula: $V = V_0(1 + \alpha\Delta T)$, where V_0, V are the initial and final volume of Hg, α is the temperature coefficient of volumetric expansion, ΔT is the difference between the initial and final temperatures.

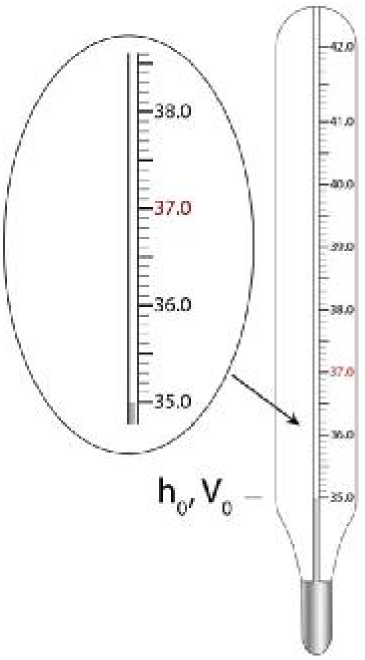


Fig. 1. Mercury thermometer before starting measurements

1. Determine if a person is sick if, when measuring his temperature 115 J of heat was transferred to mercury. Hg density $\rho = 13.55$ g/cm^3, heat capacity of liquid Hg $c = 27.88$ J/mol·K, $\alpha = 1.8\cdot10^{-4}$ K^{-1}. The scale division is 1 mm (Fig. 1), the initial temperature of mercury is 35.0°C. The signal of the onset of the disease is 37.0°C. The diameter of the column of mercury $d = 1$ mm.

The mercury thermometer has a number of disadvantages, including difficulty of using it in the regions with cold climate.

2. Based on the equilibrium condition $\Delta_{melt}G = 0$, determine the freezing point of Hg; $\Delta_{melt}H = 2.29$ kJ/mol, $\Delta_{melt}S = 0.034$ J/K. The thermometer contains 0.7 g Hg.

3. Using the relation $\delta Q = TdS$, determine the change in entropy of 0.7 g of mercury when the temperature rises from $T_i = -60$ to $T_f = +40$°C, c(Hg, s) = 28.28 J/mol·K. Note that the desired change is the sum of the entropy changes in the tree stages of heating. If you failed answering question 2, provide a formula for calculating ΔS with an unknown melting point.

Electrochemically produced mercury amalgams are used to lower the freezing point.

4. a) Write down the process equations; b) Determine the composition ω(wt %) of thallium amalgam Tl·nHg, obtained by electrolysis of thallium formate solution for 5 min with a current of 0.73 A using a mercury cathode weighing 5 g; c) Determine the density of gases evolved at the anode at 298 K and $p = 1$ atm.

The main disadvantage of mercury thermometers is high toxicity of Hg, which can lead to spilled mercury poisoning. To remove small drops of mercury that cannot be collected mechanically, a solution of potassium permanganate with hydrochloric acid or a dilute solution of iron(III) chloride are used.

5. Write down the equations for the reactions mentioned.

Physical constants: $R = 8.314$ J/mol·K, Faraday constant $F = 96\,485$ C/mol.

Problem 5

Acetic acid (K_a = $1.75 \cdot 10^{-5}$) is often used as a preservative, which contributes to the making of acidic medium and prevents the multiplication of botulism spores under anaerobic conditions, which can accidentally get into the canned food with soil particles. At pH < 4.6 botulism spores are not reproduced and the toxin is not produced. Vinegar (9% aqueous solution (density 1011.0 g/dm^3)), is most often used as a seasoning and for canning in domestic conditions as well as vinegar essence, which is a 70% aqueous solution (density 1068.5 g/dm^3) of acetic acid.

1. At 20°C, there are two glass cylinders 250 cm^3 by volume on the table, both contain 200 cm^3 of 70% and 86% aqueous solutions of acetic acid, respectively. How can one determine what solution is contained in each of the cylinders if it is not possible to carry out a chemical analysis, but there is reference data?

2. What volume of 9% vinegar should be taken to prepare 12.0 dm^3 of a marinade for preserving mushrooms with a pH = 3.5?

3. The young chemist made a mistake in his calculations and prepared a marinade with a pH 2.5. Calculate the mass of baking soda that should be added to 12.0 dm^3 of such a marinade in order to raise its pH to 3.5 (when calculating, assume that the volume of the solution and its density do not change with the addition of soda).

In everyday life, vinegar is also used in baking pastry from yeast-free dough. To make the confectionery "pomp", baking soda is used, which is "quenched" beforehand – a small amount of vinegar is added and only then the resulting mixture (baking powder) is added to the dough. The amount of vinegar should be strictly defined (about a teaspoon of baking soda – the same amount of vinegar), since an excess of baking soda in a confection greatly impairs its quality (gives a "metallic" taste) due to the formation of sodium carbonate when heated during baking.

4. Give the chemical reaction equations occurring during the baking process, in which, due to the non-gaseous product at normal conditions it becomes possible to subsequently increase the volume (pomp) of the dough based on flour, water, sugar and salt.

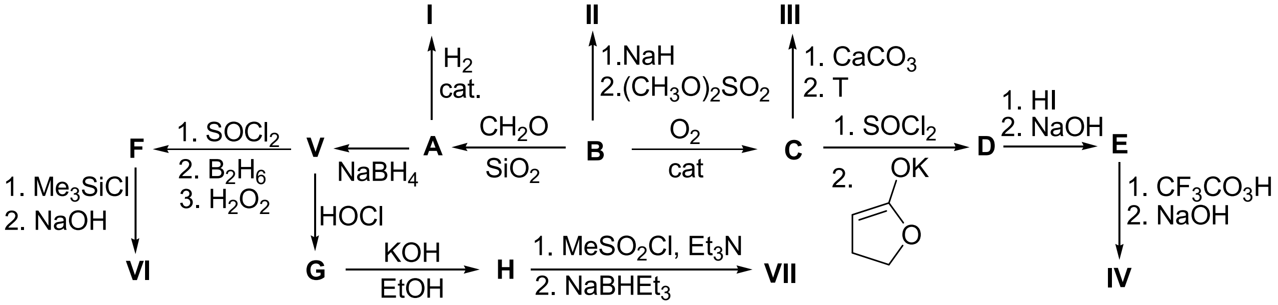
5. Calculate the maximum volume (at normal conditions) of carbon dioxide that can be released during baking of a dough with added baking powder, consisting of 1 teaspoon (5.0 g) baking soda and 1 teaspoon (5.0 cm^3) 9% vinegar.

Problem 6

The term "chemical structure" was first introduced by A.M. Butlerov on September 19, 1861 in a report "On the chemical structure of substances" of the Congress of German naturalists and doctors in Speyer. One of the experimental confirmations of this theory was the synthesis of isomeric butanols, which, with the same composition, had different physical and chemical properties. In this problem, it is proposed “to synthesize” all isomeric substances C_3H_6O and “measure” a number of their properties.

1. Draw the structures of all C_3H_6O isomers taking into account the stereochemistry.

2. Decode compounds **A** – **H**. Match the correspondence between the column compounds **I** – **VII** and Arabic numbers in the answer sheet.



3. For each compound **1** – **8** estimate the range of boiling point: < 25°C (***a***), 25 – 60°C (***b***), > 60°C (***c***). In the answer sheet, it is enough to indicate the range in the column T_{bp}.

4. Determine the number of signals in the ^{1}H NMR spectrum for each compound.

Problem 7

Anionic chain polymerization includes the stages of initiation (1 and 2), chain propagation (3), and chain termination (4). In the scheme, I, M, and P_i denote the molecules of initiator, monomer, and the polymer with degree of polymerization *i*, whereas I^- and P_i^- are the initiator and polymer species bearing a site active in polymerization (anion); the symbols above the arrows are the corresponding rate constants.

1) $I \xrightarrow{k_{i,1}} I^-$

2) $I^- + M \xrightarrow{k_{i,2}} P_1^-$

3) $P_n^- + M \xrightarrow{k_p} P_{n+1}^-$

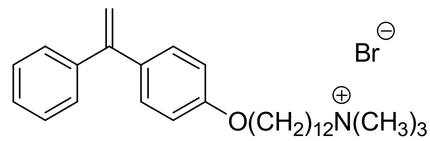
4) $P_n^- + P_m^- \xrightarrow{k_t} P_{n+m}$

If the rate constants of the given stages are related as $k_t << k_p = k_{i,2} << k_{i,1}$ and the monomer reactivity is independent of the nature of the anionic species it is added to, the polymerization affords almost monodisperse polymer (that consisting of the molecules of equal molecular mass).

1. Write down the expression for the monomer concentration as a function of time at the initial concentrations of monomer $[M]_0$ and initiator $[I]_0$, if the above assumptions are valid.

2. Sketch the average degree of polymerization *p* of the product in the described system as functions of the monomer conversion *q* and time *t*.

To obtain a nanocomposite material, compound **A** (0.52 g) was stirred with aqueous suspension of 1.00 g of sodium form of montmorillonite **MontONa** until equilibrium. **MontONa** is a layered silica-alumina clay with exchange capacity 0.92 meq/g (an equivalent corresponds to a mole of the acidic exchange sites in the sodium form). 1.20 g of the modified montmorillonite **MontOI** was isolated upon drying. A solution of *sec*-butyllithium in benzene was added to **MontOI**, the mixture was kept until equilibrium, and the excess of low-molecular compounds was washed out on a filter. The obtained initiator **MontOI*** was mixed with a solution of 25 g of styrene in benzene, the polymerization was carried out to the monomer conversion of 85% and then quenched by an excess of methanol; thus, **MontOP** (nanocomposite material containing inorganic nanoparticles and polymer **P**) was obtained.



A

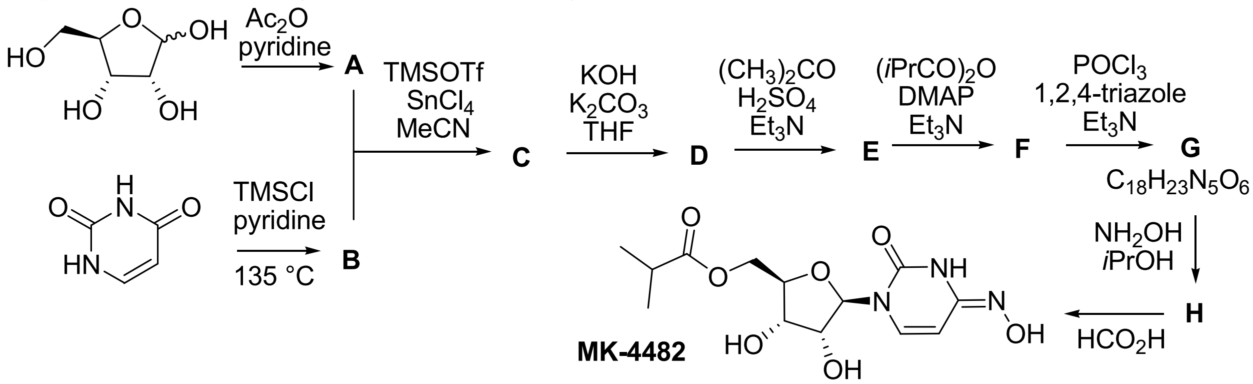
3. a) Write the equation of the reaction between **MontONa** and **A** and calculate the equilibrium constant of the reaction. b) Write the equation of the reaction between **MontOI** and *sec*-butyllithium. Give the unchanged part of montmorillonite as **MontO**.

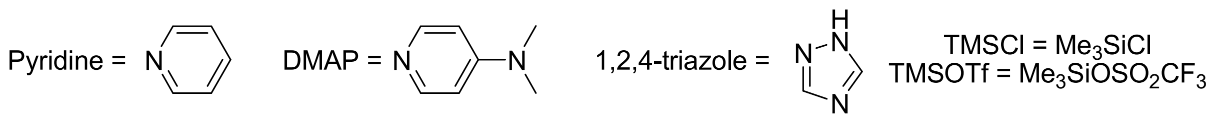
4. Determine the mass fraction of montmorillonite in the obtained composite and draw the structure of the prepared macromolecules **P** clearly showing the degree of polymerization and the terminal groups.

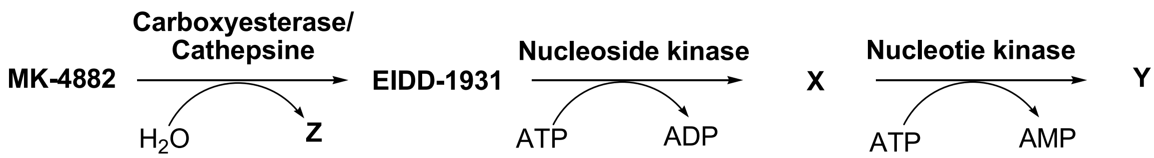
Problem 8

"If society has a technical need, that helps science forward more than ten universities"
Friedrich Engels

The lifetime of bringing novel drugs to the market on average takes around 20 years and over 1 billion dollars. However, emergency situations such as pandemic outbreaks of the SARS-CoV-2, significantly shorten the time for this process. **MK-4482** is a ribonucleoside currently in clinical trials for the treatment of COVID-19. It was originally explored as an anti-influenza therapeutic due to its' convenient oral dosage, however, it was readily redirected in the area of COVID-19 because of the similarity between these 2 viruses. The initial synthesis of **MK-4482** was based on classical approaches and total yield was < 10%. **MK-4482** is a pro-drug and therapeutically inactive. Its active form is **EIDD-1931**. **MK-4482** penetrates infected cells more efficiently than **EIDD-1931** and then requires subsequent activation by intracellular enzymes.







1. Decode the compounds **A** – **H** and the scheme of **MK-4482** activation.

EIDD-1931 exists in its tautomeric form, *which mimics 2 essential nucleosides in the synthesis of viral RNA*. This mimicry results in erroneous base pairing hindering viral replication.

2. Draw the two tautomeric form of **EIDD-1931** and draw the correct base pairing of the tautomers with either guanosine or adenosine.