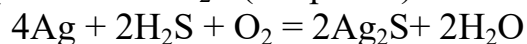


Problem 1 (author Nikitina V.N.)

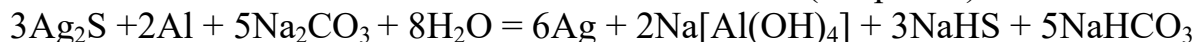
1. a) Silver sulfide is formed on the surface of a silver coin as a result of oxidation with atmospheric oxygen in the presence of H₂S (0.5 points):



b) During boiling, hydrocarbonate decomposes to give carbonate and carbon dioxide (0.5 points):



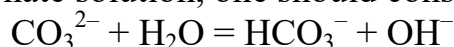
c) Aluminum reduces silver from sulfide in alkaline media (1.5 points):



2. The pH of solution is determined by sodium carbonate, since the amounts of hydrosulfide and hydrocarbonate formed in the reaction can be neglected (0.5 points).

$$C(\text{Na}_2\text{CO}_3) = \frac{1}{2} \cdot 20 \text{ g} / 84 \text{ g/mol} / 0.4 \text{ L} = 0.2976 \approx 0.3\text{M}$$

To calculate the pH of a carbonate solution, one should consider its hydrolysis:



The equilibrium constant of this reaction (0.5 points)

$$K_{\text{eq}} = \frac{[\text{HCO}_3^-][\text{OH}^-]}{[\text{CO}_3^{2-}]} = \frac{[\text{HCO}_3^-]K_w}{[\text{CO}_3^{2-}][\text{H}^+]} = K_w / K_{a2},$$

where $K_{a2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$. In our case $[\text{OH}^-] = [\text{HCO}_3^-]$, since these two particles are formed mainly by the reaction above, then $K_{\text{eq}} = \frac{[\text{OH}^-]^2}{[\text{CO}_3^{2-}]} \approx \frac{[\text{OH}^-]^2}{c_{\text{CO}_3^{2-}}} = K_w / K_{a2}$.

Therefore $[\text{OH}^-] = (c_{\text{CO}_3^{2-}} \cdot K_w / K_{a2})^{1/2} = 7.74 \cdot 10^{-3}$, pOH = 2.1, pH = 11.9 (1.5 points)

3. Let us calculate the minimum mass of aluminum foil for reaction 1c. To do this, it is necessary to calculate the volume of sulfide covering the coin (product of the coin area by the thickness of the coating). The surface area of the coin S is the sum of the areas of two circles of radius $r = 1 \text{ cm}$ and the side surface of thickness d and length $2\pi r$ (0.5 points):

$$S = 2\pi r^2 + 2\pi r d = 7.54 \text{ cm}^2$$

Let us calculate the mass of sulfide in the surface layer with a thickness of $l = 42 \text{ nm}$ (0.5 points):

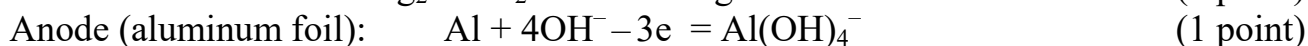
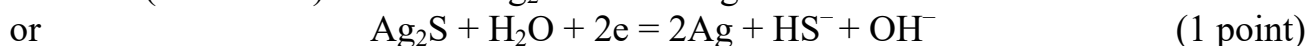
$$m(\text{Ag}_2\text{S}) = \rho S l = 7.32 \text{ g/cm}^3 \cdot 7.54 \text{ cm}^2 \cdot 42 \cdot 10^{-7} \text{ cm} = 0.232 \text{ mg}$$

Foil mass corresponding to this amount of silver sulfide (0.5 points):

$$m(\text{Al}) = 0.232 \text{ mg} / 247.8 \text{ g/mol} \cdot 2/3 \cdot 27 \text{ g/mol} = 0.0168 \text{ mg}$$

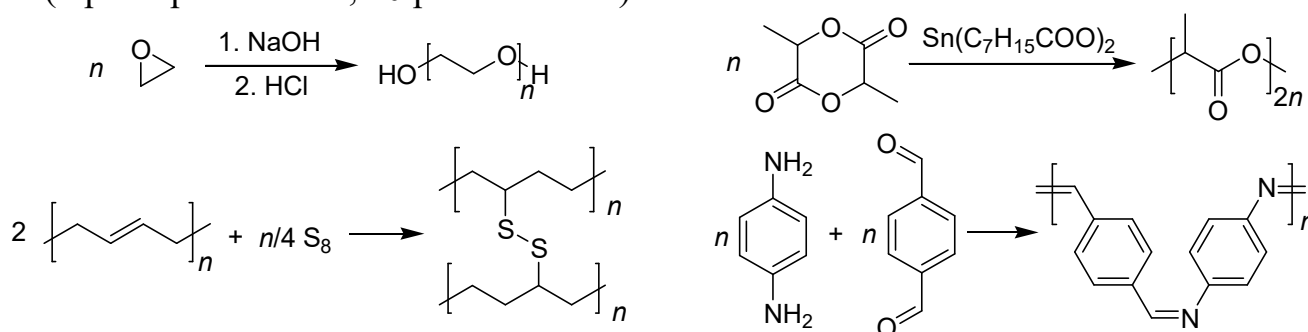
4. From the expression for the complex stability constant it follows that $[\text{Al}(\text{OH})_4^-] / [\text{Al}^{3+}] = \beta(\text{Al}(\text{OH})_4^-) \cdot [\text{OH}^-]^4 = 3 \cdot 10^{25}$. Thus, almost all aluminum is bound in the hydroxocomplex: $\alpha[\text{Al}(\text{OH})_4^-] = 100\%$ (1.5 points)

5. Aluminum and silver form a galvanic pair when in contact. In this case, the reduction reaction proceeds at the cathode, and oxidation at the anode. Therefore, the cathode is the silver coin, and the aluminum foil is the anode:

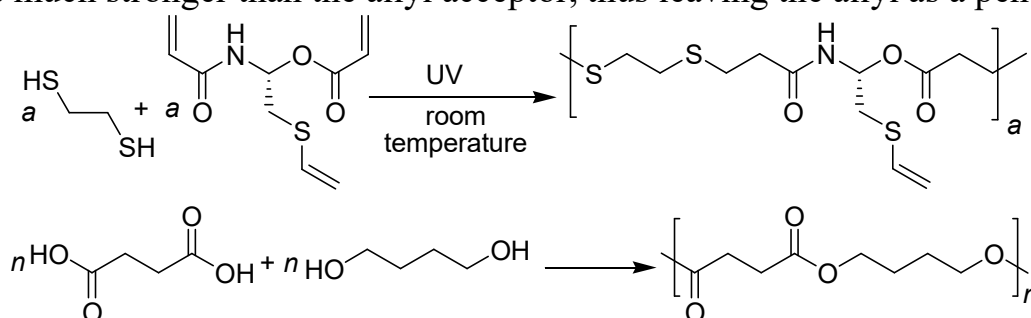


Problem 2 (authors Ilievski F., Karpushkin E.A.)

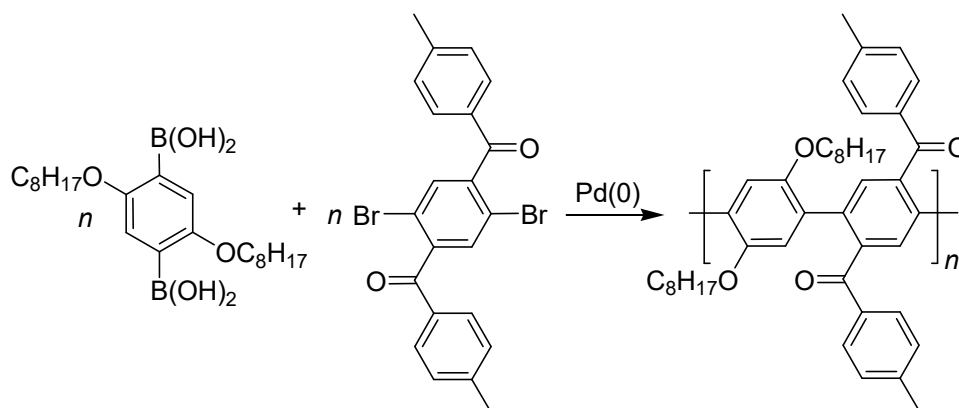
1. (1 point per reaction, 10 points in total)



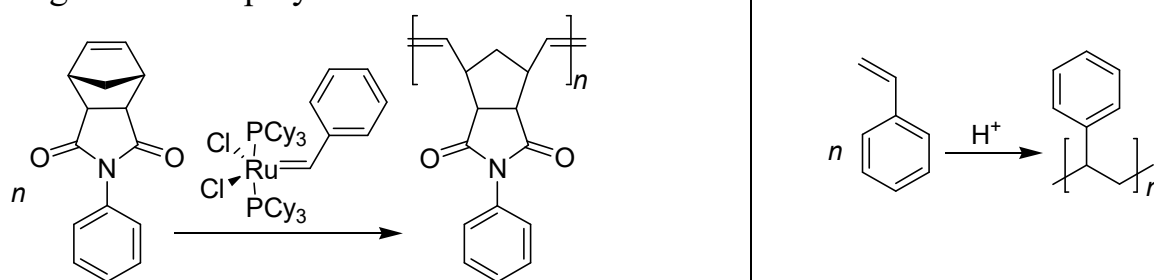
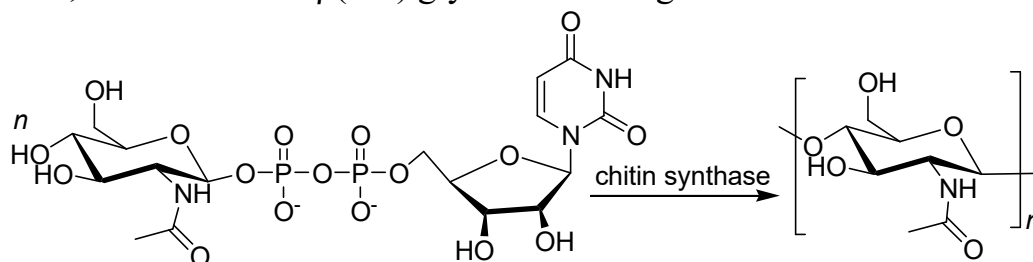
UV-initiated thia-Michael addition polymerization. Note that the acrylate Michael acceptor is much stronger than the allyl acceptor, thus leaving the allyl as a pendant group.



Suzuki polycondensation:



Ring-opening metathesis polymerization:

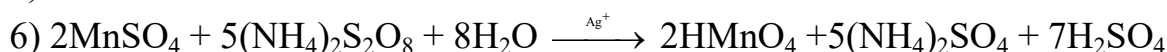
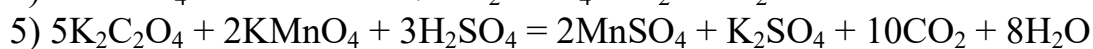
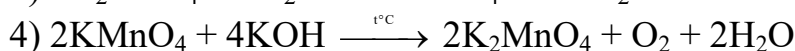
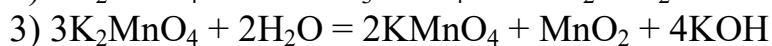
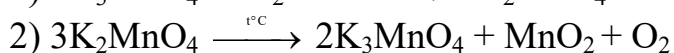
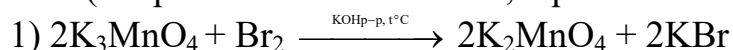
As in cellulose, chitin contains $\beta(1-4)$ glycosidic linkages:

Problem 3 (author Mezentsev-Cherkes I.V.)

1. По описанию и приведенной цветовой схеме можно предположить, что зашифрованы соединения марганца. Подтвердим это предположение расчетом. Для металлов широко известны кислородсодержащие минералы, поэтому запишем состав как X_nO_m . The formula must satisfy the equation $\omega(X) = M \cdot n / (M \cdot n + 16 \cdot m)$. Taking $n = 1$ and $m = 2$ we find that $M(X) = 55$ g/mol and the mineral is pyrolusite, MnO_2 (1 point for calculation, 0.25 points for the formula and the historical name).

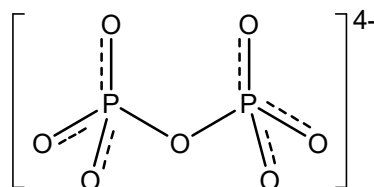
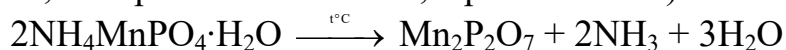
2. Taking into account the color and the fact that the mass fractions of oxygen are equal, it can be assumed that the charge of an anion and the oxidation state of a central atom are changed, which leads to MnO_4^{3-} , MnO_4^{2-} , MnO_4^- and Mn^{2+} for $X_1 - X_4$ respectively (0.25 point for each compound, cation may vary, 1 point in total).

3. (0.5 points for each reaction, 3 points in total)

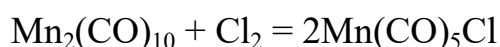


4. $MnSO_4 + (NH_4)_2HPO_4 + NH_3 \cdot H_2O = NH_4MnPO_4 \cdot H_2O \downarrow + (NH_4)_2SO_4$ (0.5 points for the reaction and 0.5 points for $NH_4MnPO_4 \cdot H_2O$)

If we assume that there is only one Mn atom in the X_6 compound, the molar mass will be 142, which after considering every possible combination with P and O will lead to a dead end. The presence of nitrogen is excluded due to the fact that on heating ammonium will volatilize as ammonia. Therefore, we can assume to be two manganese atoms in X_6 . Then the molar mass is 284, which corresponds to manganese pyrophosphate (0.75 points, 0.5 points for the reaction, 0.75 points for structure, 3 points in total).



5. Taking into account the Sidgwick's rule, we can come to the conclusion that in the compound $Mn(CO)_5$ there is one electron missing for the 18 electronic environment. Therefore, only in the case of the formation of dimers the Sidgwick rule is fulfilled; compound **C** corresponds to $Mn_2(CO)_{10}$ (0.5 points). In the reaction with chlorine one electron is provided to the coordination environment of manganese. Thus, the composition of the compound **D** corresponds to $Mn(CO)_5Cl$ (0.5 points, 0.5 points for the reaction, 1.5 points in total):

**Problem 4 (author Gulevich D.G.)**

1. In order to determine the temperature of a person by thermometer in figure, you need to find the change in the volume of mercury. Knowing the value of division and determining the height h from the volume of the cylinder ($\pi r^2 h$), we find the final

temperature. During measurements the amount of heat $Q = cm\Delta T$ was transferred to the mercury, where $m = \rho V_0$ – mercury mass. Change in the volume of mercury under heating $\Delta V = V - V_0 = V_0\alpha\Delta T$, from where

$$\Delta V = \frac{\alpha \cdot Q \cdot A_r(\text{Hg})}{\rho(\text{Hg}) \cdot c(\text{Hg,l})}$$

$$h = \frac{\alpha \cdot Q \cdot A_r(\text{Hg})}{\rho(\text{Hg}) \cdot c(\text{Hg,l}) \cdot \pi \cdot r^2} = \frac{1.8 \cdot 10^{-4} \text{ K}^{-1} \cdot 115 \text{ J} \cdot 200.6 \text{ g/mol}}{13.55 \text{ g/cm}^3 \cdot 27.88 \text{ J/mol} \cdot \text{K} \cdot 3.14 \cdot (0.5 \cdot 10^{-1})^2 \text{ cm}^2} = 1.4 \text{ cm}.$$

Since the scale of the thermometer is 1 mm, the mercury has risen by 14 divisions and the human temperature is 36.4°C, i.e. the person is healthy (2 points).

2. During the phase transition, the change in entropy is $\Delta_{\text{tr}}H/T_{\text{tr}}$, the freezing point of mercury (1 point)

$$T = \frac{m(\text{Hg}) \Delta_{\text{melt}}H}{A_r(\text{Hg}) \Delta_{\text{melt}}S} = \frac{0.7 \text{ g}}{200.6 \text{ g/mol}} \frac{2.29 \text{ kJ/mol}}{0.034 \text{ J/K}} = 235 \text{ K} = -38^\circ\text{C}$$

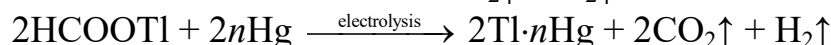
3. The change in entropy ΔS of mercury with an increase in temperature from -60 to $+40^\circ\text{C}$ consists of ΔS_1 when heating liquid mercury from -60°C to the melting point, $\Delta_{\text{melt}}S$ and ΔS_2 when heating liquid mercury from -38°C to 40°C (1 point for each calculation stage, 3 points in total).

$$\Delta S_1 = v \cdot c_s \ln \frac{T_{\text{melt}}}{T_i} = 3.5 \cdot 10^{-3} \cdot 28.28 \cdot \ln \frac{235}{213} = 9.72 \cdot 10^{-3} \text{ J/K},$$

$$\Delta S_3 = v \cdot c_l \ln \frac{T_f}{T_{\text{melt}}} = 3.5 \cdot 10^{-3} \cdot 27.88 \cdot \ln \frac{313}{235} = 2.80 \cdot 10^{-2} \text{ J/K}.$$

$$\Delta S = \Delta S_1 + \Delta_{\text{melt}}S + \Delta S_2 = 9.72 \cdot 10^{-3} = 3.40 \cdot 10^{-2} + 2.80 \cdot 10^{-2} = 7.17 \cdot 10^{-2} \text{ J/K}.$$

4. a) During electrolysis the following processes occur:



b) According to Faraday's law, we determine the mass of thallium released at the cathode:

$$m(\text{Tl}) = \frac{A_r(\text{Tl}) \cdot I \cdot t}{n_e \cdot F} = \frac{204.4 \cdot 0.73 \cdot 5 \cdot 60}{96485} = 0.464 \text{ g}, \text{ therefore}$$

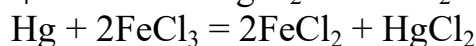
$$\omega(\text{Tl}) = \frac{m(\text{Tl})}{m(\text{Hg}) + m(\text{Tl})} = \frac{0.464}{5 + 0.464} \cdot 100\% = 8.5\%.$$

c) A mixture of hydrogen and carbon dioxide will be released on the anode. By the reaction stoichiometry $v(\text{CO}_2) = v(\text{Tl}) = 2v(\text{H}_2) = 2.26 \cdot 10^{-3} \text{ mol}$. Then the molar fractions of carbon dioxide and hydrogen in the gas mixture will be equal to 0.67 and 0.33 respectively. Average molar mass of the gas mixture $M_{\text{cp}} = 0.67 \cdot 44 + 0.33 \cdot 2 = 30.1 \text{ g/mol}$. Then by the Mendeleev – Clapeyron equation

$$\rho = \frac{\overline{M} \cdot p}{RT} = \frac{30.14 \cdot 10^{-3} \cdot 101325}{8.314 \cdot 298} = 1.23 \text{ kg/m}^3.$$

(0.5 points for the processes on the electrodes, 1 point for calculation of the mass of Tl, 0.25 points for determination of the amalgam composition, 0.5 points for calculation of the average molar mass of the gas mixture, 0.25 points for determination of density, 3 points in total).

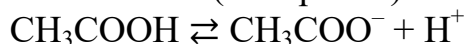
5. (0.5 points for each, 1 point in total)



Problem 5 (author Khvalyuk V.N.)

1. Unlike most other acids, the density of aqueous solutions of CH_3COOH changes non-monotonically with an increase in the mass fraction of the acid: it increases to 1.0700 g/cm^3 (78–80% acid), and then decreases. As a result, at 20°C 70 % and 86% aqueous solutions have the same density equal to 1.0685 g/cm^3 . Therefore, by measuring the density of a solution with a hydrometer, it is impossible to determine where which solution is. To solve the problem, small volumes of water should be added to each of the solutions, mixed and the density of the resulting solutions should be measured again. In the case of a 70% solution, dilution will lead to a decrease in the density of the solution, and in the case of an 86% solution, to an increase. The correct answer is e (1 point).

2. Electrolytic dissociation of acetic acid (0.25 points):



The constant of equilibrium (K_a acetic acid) (0.25 points):

$$K_a = \frac{c(\text{H}^+) \cdot c(\text{CH}_3\text{COO}^-)}{c(\text{CH}_3\text{COOH})} = 1.75 \cdot 10^{-5}$$

Let's designate the analytical concentration (all forms) of acetic acid in the marinade as c_0 . The concentration of H^+ ions in the marinade is $10^{-\text{pH}} = 10^{-3.50} \text{ mol/dm}^3$. According to the equation, the concentration of CH_3COO^- ions is also $10^{-3.50} \text{ mol/dm}^3$, i.e. $10^{-3.50} \text{ mol/dm}^3$ CH_3COOH underwent dissociation. Then the equilibrium concentration of the molecular form of the acid is equal to $c(\text{CH}_3\text{COOH}) = (c_0 - 10^{-3.50})$. Substitute these values into the expression for the equilibrium constant (0.5 points):

$$\frac{10^{-3.50} \cdot 10^{-3.50}}{c_0 - 10^{-3.50}} = 1.75 \cdot 10^{-5}$$

Solving this equation we get $c_0 = 6.03 \cdot 10^{-3} \text{ mol/dm}^3$. $M(\text{CH}_3\text{COOH}) = 60 \text{ g/mol}$ (0.5 points)

To prepare 12.0 dm^3 marinade one should take $6.03 \cdot 10^{-3} \cdot 12.0 = 72.36 \cdot 10^{-3} \text{ mol}$ or

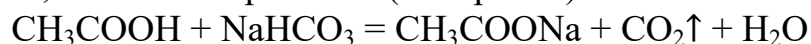
$72.36 \cdot 10^{-3} \cdot 60 = 4.34 \text{ g CH}_3\text{COOH}$. Required volume of 9% vinegar is equal to $\frac{4.34}{0.09 \cdot 1.070}$

$= 45.1 \text{ cm}^3$ (0.5 points, 2 points in total)

3. Before adding of baking soda $c(\text{H}^+) = 10^{-\text{pH}} = 10^{-2.50} \text{ mol/dm}^3$ (0.25 points):

$$\frac{10^{-2.50} \cdot 10^{-2.50}}{c_0 - 10^{-2.50}} = 1.75 \cdot 10^{-5}$$

Solving this equation we get $c_0 = 0.5746 \text{ mol/dm}^3$. In the initial marinade (before the addition of baking soda), the analytical acid concentration is 0.5746 mol/dm^3 . When baking soda is added, the reaction proceeds (0.25 points):



Suppose that to achieve the final result ($\text{pH} = 4.0$), $x \text{ mol}$ of solid NaHCO_3 should be added for each 1 dm^3 of the marinade. After adding soda, the concentration of CH_3COOH in the marinade will be $(0.5746 - x) \text{ mol/dm}^3$. Since the pH in the final marinade should be equal to 3.5, then $c(\text{H}^+)$ in it: $10^{-3.5} \text{ mol/dm}^3$. Consequently, $10^{-3.5} \text{ mol/dm}^3$ CH_3COOH should dissociate to form of $10^{-3.5} \text{ mol/dm}^3$ of each of the H^+ and CH_3COO^- ions. Then the equilibrium concentration of the molecular form CH_3COOH will be $(0.5746 - x - 10^{-3.5}) \text{ mol/dm}^3$. The CH_3COONa formed in the reaction completely dissociates with the formation of $x \text{ mol/dm}^3$ of CH_3COO^- ions. Then the equilibrium concentration of CH_3COO^- ions will be equal to $(10^{-3.5} + x) \text{ mol/dm}^3$. Substitute the

equilibrium concentrations of all particles in the expression for the dissociation constant

(0.5 points): $\frac{10^{-3.5} \cdot (x + 10^{-3.5})}{0.5746 - x - 10^{-3.5}} = 1.75 \cdot 10^{-5}$

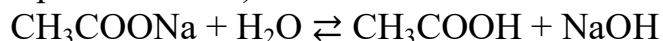
Solving this equation we get $x = 0.0298$ (1 point).

$M(\text{NaHCO}_3) = 84 \text{ g/mol}$. Therefore, one should add $0.0298 \cdot 12 = 0.3576 \text{ mol}$ or $0.3576 \cdot 84 = 30.0 \text{ g NaHCO}_3$ to 12.0 dm^3 of marinade (1 point, 3 points in total)

4. If in the process of "quenching" you mix soda and acetic acid in a molar ratio of 1 : 1, then they will completely react and, due to the small volume of the reaction mixture, this will lead to a very rapid release of all carbon dioxide into the atmosphere. There will be practically no effect of "raising" the dough from adding such a mixture to the dough. Therefore, this reaction can NOT be the interaction of components in the process of "quenching":



For the effect of "swelling" to be observed, it is necessary that the reaction of the formation of CO_2 occurs in the volume of the dough during the heating of the product in the oven at the initial stage of baking, but until the moment when a crust forms on the surface of the product, which will not allow the dough to increase in volume due to gas evolution. This cannot be a thermal decomposition reaction of baking soda (although this will lead to an increase in the volume of the dough due to the released CO_2), but in this case the reaction product is sodium carbonate, which impairs the taste of the final product, which is unacceptable. In addition, in this case, the role of acetic acid and the need for the stage of "quenching" the soda are not at all clear. The process that will allow the formation of a "lush" dough is the hydrolysis of sodium acetate, which is formed at the stage of "quenching" of soda (2.0 points in total).



As the temperature rises, the hydrolysis of CH_3COONa intensifies, and the resulting acetic acid reacts with the "unquenched" baking soda to form CO_2 , which raises the dough. The resulting sodium acetate undergoes hydrolysis again and is involved in the gas formation process many times, theoretically until it is completely consumed of NaHCO_3 .

5. In 5.00 g it consists $\frac{5.00}{84} = 0.0595 \text{ mol} = 59.5 \text{ mmol NaHCO}_3$ (0.5 points).

In 5.0 cm^3 of 9% vinegar it consists $\frac{0.09 \cdot 5.00 \cdot 1.07}{60} = 8.03 \cdot 10^{-3} \text{ mol} = 8.03 \text{ mmol}$

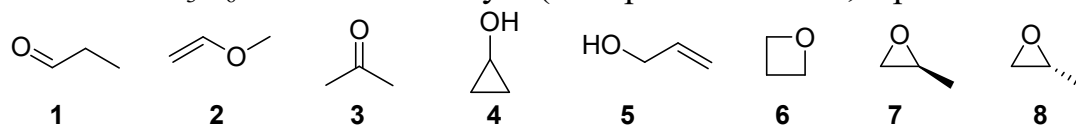
CH_3COOH (0.5 points).

The baking powder contains $(59.5 - 8.03) = 51.47 \text{ mmol}$ of unquenched NaHCO_3 (0.5 points).

As mentioned in paragraph 4, the sodium acetate formed at the quenching stage repeatedly participates in the process of gas formation, theoretically (if we exclude the volatilization of the acid outside the dough) until all the soda has reacted with the formation of CO_2 . Therefore, the maximum amount of CO_2 produced will be equal to $51.47 \cdot 10^{-3} \cdot 22.4 = 1.15 \text{ dm}^3$ (0.5 points, 2 points in total)

Problem 6 (authros Volochnyuk D.M., Avramenko N.N.)

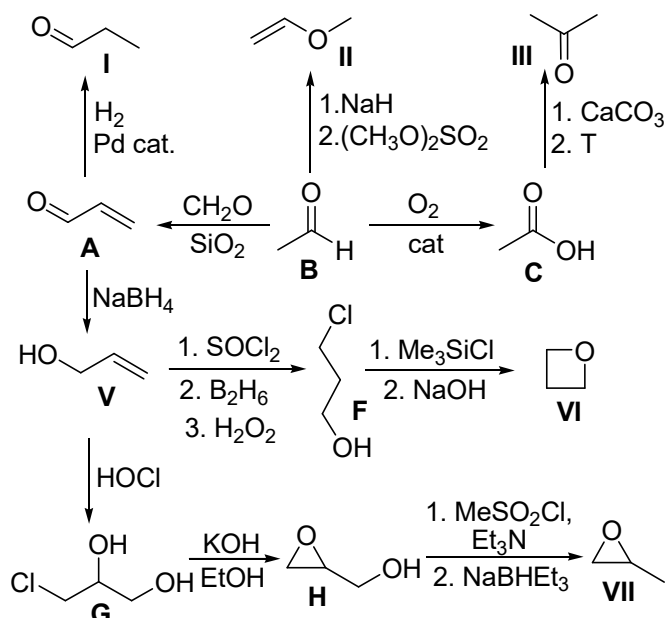
1,2. The solution to this problem would be best to start with a drawing of all the possible isomers of formula C_3H_6O . There are only 8 (0.25 points for each, 2 points in total).



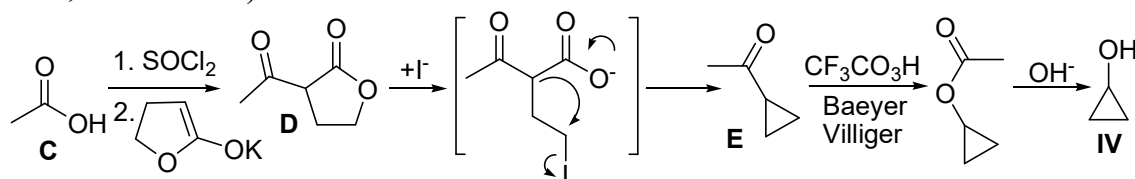
There are a large number of solutions of this problem, but their idea is common.

First of all, it is necessary to find the transformation that unambiguously leads to some isomer. For example, heating **C** (which can be acid because it reacts with thionyl chloride) with calcium carbonate is the classic method to obtain acetone. Due to this, he got his name acetone from lat. *acetum* – vinegar. Therefore, **C** is acetic acid, and **III** is acetone.

After that the part of the chain is deciphered based on basic knowledge of organic chemistry.

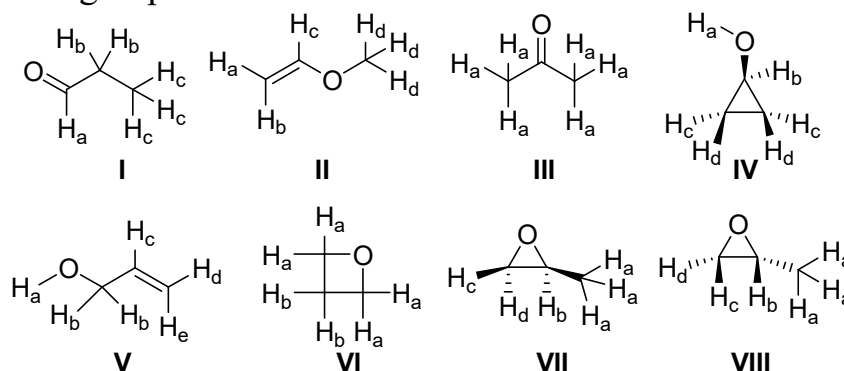


Decryption of the last part of the chain can cause some difficulties. However, this can be done using the elimination method. Of the isomeric compounds, cyclopropanol remained, respectively, this is **IV**. Further, in CF_3CO_3H , it is necessary to recognize the reagent for the Bayer-Villiger reaction. So, **E** is cyclopropyl methyl ketone. On the other hand, **D** is a cyclic enolate acylation product. Mechanically, its conversion to cyclopropyl methyl ketone is represented as ring opening – decarboxylation – ring closure (4 structures, 0.25 points, 2 points in total and 0.5 points for each structure and plus 0.1 point for each compliance, 4.8 in total).



3. Alcohols, due to hydrogen bonds, have the highest T_{bp} – category *c*. Non-cyclic ethers have the smallest T_{bp} – category *a*. the rest are *b* (see table).

4. The number of signals in the 1H NMR spectrum corresponds to the number of nonequivalent proton groups.



N	T _{bp}	¹ H NMR	N	T _{bp}	¹ H NMR
I	<i>b</i> (49°C)	3	V	<i>c</i> (97°C)	5
II	<i>a</i> (6°C)	4	VI	<i>b</i> (50°C)	2
III	<i>b</i> (56°C)	1	VII	<i>b</i> (35°C)	4
IV	<i>c</i> (101°C)	4	VII	<i>b</i> (35°C)	4

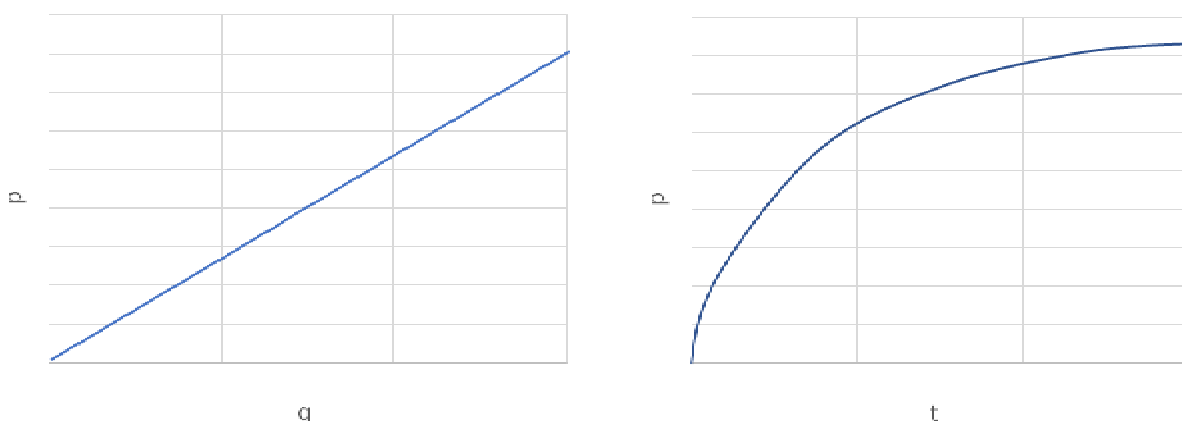
(i. 3 – 0.2 points for each cell in the table, 1.6 points in total; i. 4 – 0.2 points for each cell in the table, 1.6 points in total)

Problem 7 (author Karpushkin E.A.)

1. Monomer M is consumed in the reactions 2, 3, and 4. The monodisperse product is obtained under conditions of fast (instant) initiation followed by slow propagation of the chains. Termination does not compete with propagation (k_t is much less than other rate constants), hence reaction 4 can be neglected. Therefore, $\frac{d[M]}{dt} = -k_{i,2}[I^-][M] - k_p[P_n^-][M]$.

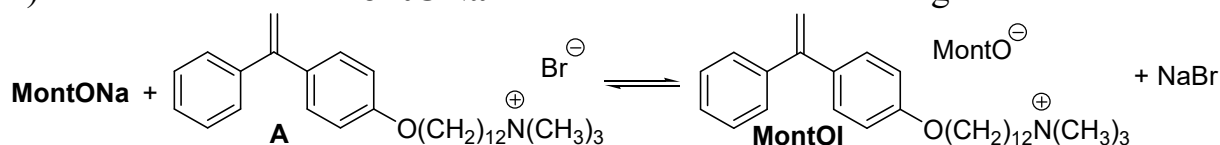
At each moment, total concentration of the anionic species (I^- and P_n^-) equals the starting concentration of the initiator, whereas rate constants of reactions 2 and 3 are equal. Thus, $\frac{d[M]}{dt} = -k_p[I]_0[M]$. This is the first-order kinetic equation with the solution as $[M] = [M]_0 e^{-k_p[I]_0 t}$ (the answer with $k_{i,2}$ instead of k_p also accepted) (2 points)

2. Since the growth of the macromolecules is uniform, the average degree of polymerization is proportional to the amount of the consumed monomer, which is proportional to the conversion. Hence, average degree of polymerization is a linear increasing function of the conversion starting from the origin. Since the polymerization rate is decreased with the monomer consumption (i. 1), the rate of the conversion growth is steadily decreased. The conversion equals $1 - \frac{[M]}{[M]_0} = 1 - e^{-k_p[I]_0 t}$, and the required plot is an increasing curve achieving its maximum value.



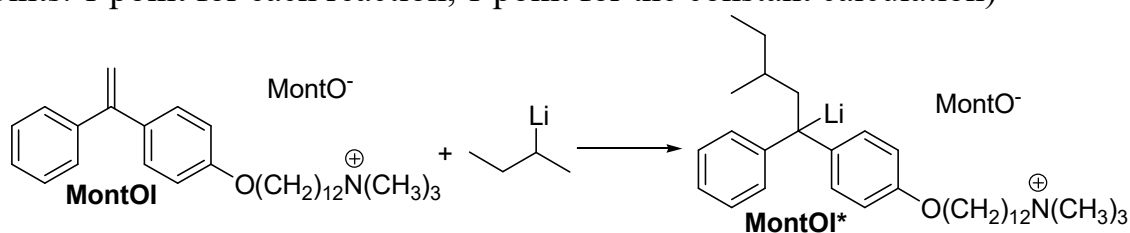
Any plot in agreement with the equation given as the answer in i. 2, if any, is considered correct (2 points, 1 point for each plot).

3. a) The interaction of **MontONa** with **A** is a reversible exchange:

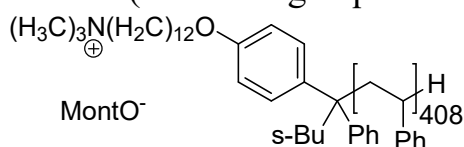


with the equilibrium constant of $K = \frac{[\text{MontOI}][\text{NaBr}]}{[\text{MontONa}][\text{A}]}$. The initial amount of **MontONa** is $1.00 \text{ g} \cdot 0.92 \text{ meq/g} = 0.92 \text{ meq}$ (an equivalent in this reaction corresponds to a mol of the acidic exchange sites in the sodium form), and the initial amount of **A** is $0.52 \text{ g} / 500.56 \text{ g/mol} = 1.04 \text{ mmol}$. With an account for the molar masses of the cation of **A** (420.66 g/mol) and sodium (22.99 g/mol), the exchange reaction involving 1 mmol of the acidic sites of montmorillonite leads to an increase in its mass by 0.40 g. Since the montmorillonite mass increased by 0.20 g, the reaction involved 0.50 mmol of each of **A** and acidic sites of **MontONa**, giving 0.50 mmol of **MontOI** and NaBr. Then $K = \frac{0.50 \cdot 0.50}{(0.92 - 0.50)(1.04 - 0.5)} = 1.1$.

b) (3 points: 1 point for each reaction, 1 point for the constant calculation)



4. $25 \text{ g} \cdot 0.85 / 104.15 \text{ g/mol} = 204 \text{ mmol}$ of styrene involved in the polymerization corresponds to 0.50 mmol of the initiator **MontOI***, hence the degree of polymerization equals 408, and the polymer structure (do not forget quenching with methanol) is:

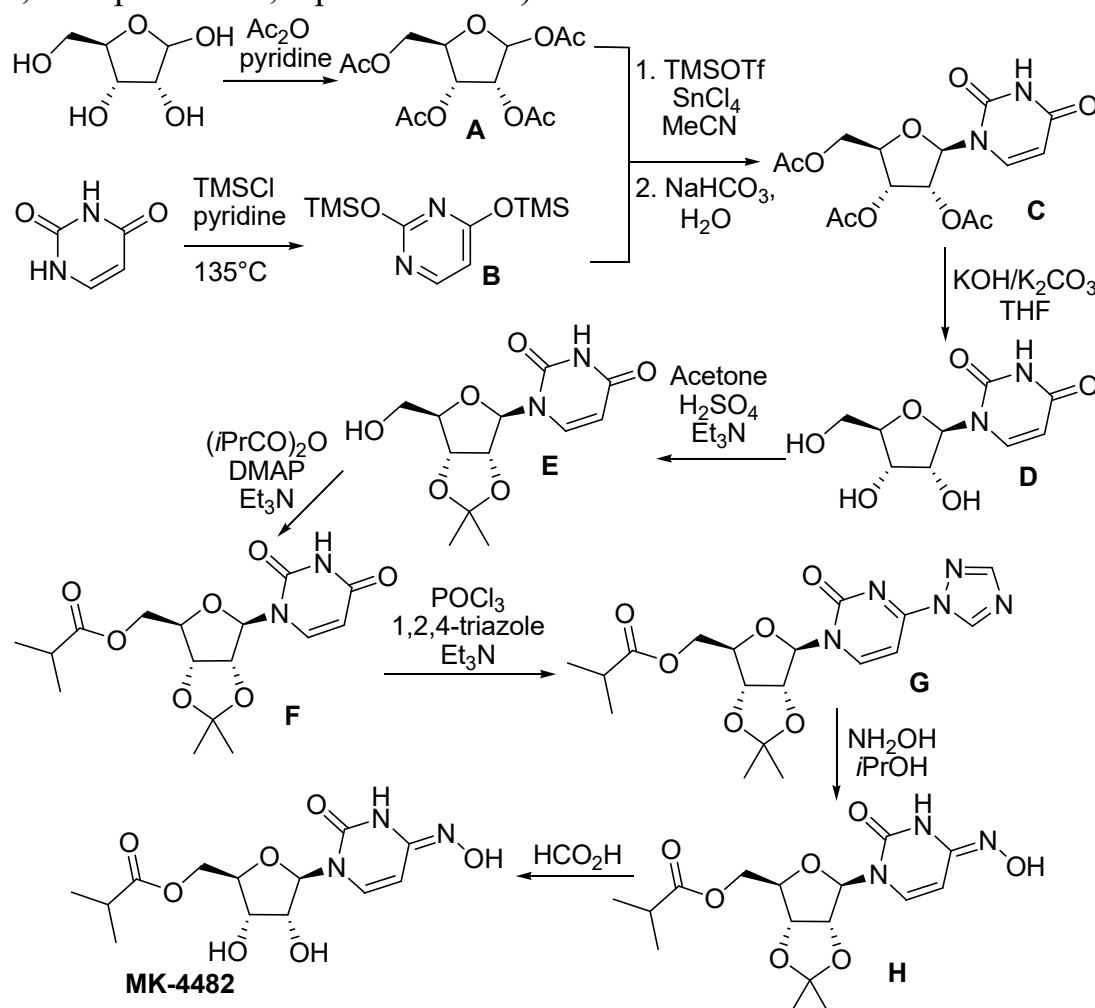


1 eq. of montmorillonite corresponded to 420.66 g (cation of **A**) + 57.12 g (*sec*-butyl group) + $408 \cdot 104.15 \text{ g}$ (styrene units) + 1.008 g (terminal hydrogen atom) = 42972 g of the polymer. Total exchange capacity of **MontONa** equals 0.92 meq/g but only 0.50 mmol/g of the acidic sites are modified with the initiator and thus active in polymerization (i. 3a), hence equivalent mass of **MontO** in polymerization (sodium ion excluded) = $1000 / 0.50 - 22.99 = 1977 \text{ g}$. Thus, mass fraction of **MontO** in the composite is $1977 / (1977 + 42972) = 4.4\%$ (3 points).

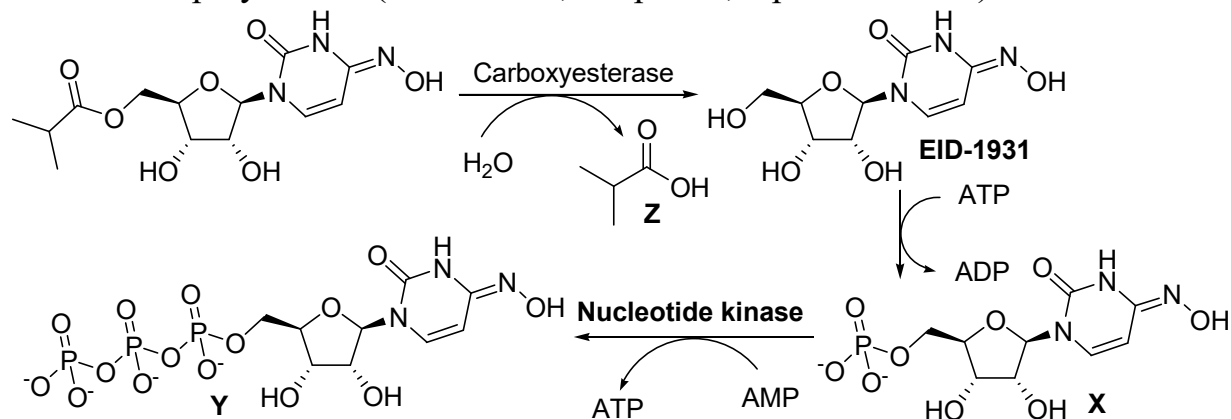
Problem 8 (author Ilievski F.)

1. The scheme is rather straightforward and can be approached from many directions. If we compare the structure of **MK-4482** and the starting molecule of ribose, we can see that the anomeric site at the **MK-4482** has the β -configuration. Based on the scheme, one can conclude that this stereoselective linkage occurs in the convergent step between **A** and **B**. Based on reaction conditions, the structure of **A** and **B** can be easily deduced as pentaacetylated ribose as well as bi-protected tautomer of the uracil. The reaction between **A** and **B** is the so called improved variation of the silyl-Hilbert-Johnson reaction, where the nucleoside structure is formed and the TMSO group is removed. Then the alkaline hydrolysis removed the acetyl protecting group from OH-functions leading to uridine **D**. Transformation of **D** to **F** results in installation of acetonide protection group (compound **E**) with subsequent esterification of the primary group with isobutyric anhydride.

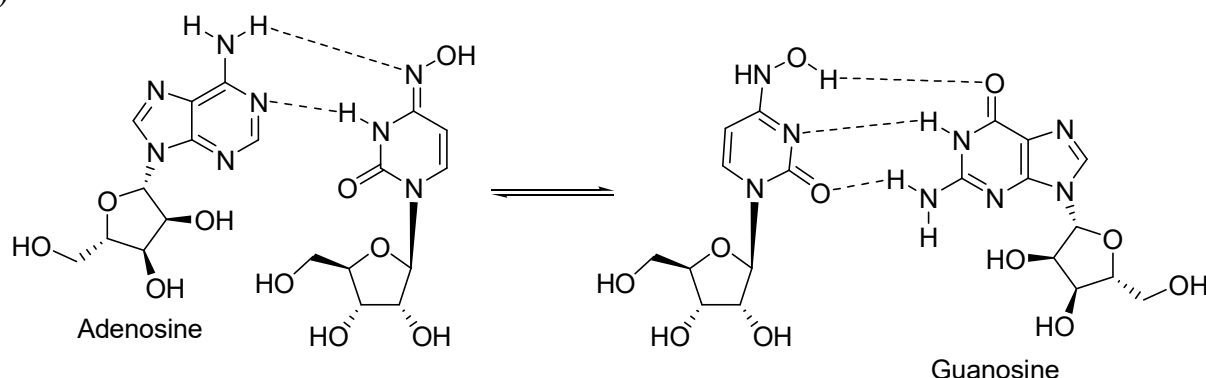
Afterwards introducing an triazole moiety at the enol tautomer of the uracil segment leads to compound **G**. Finally, a nucleophilic substitution with hydroxylamine gives compound **H**, which after acetamide deprotection in weakly acidic environment affords **MK-4482** (8 structures, 0.75 point each, 6 points in total).



The proposed reaction scheme is quite clear and can be inferred from the phosphorylation and the enzyme presence. Namely, the carboxypeptidase cleaves the isobutyryl fragment, giving **EIDD-1931** which makes this nucleoside a substrate for a phosphokinase, yielding the monophosphate. Monophosphates per se do not penetrate the cell due to their high negative charge. Moreover, the transformed nucleoside into nucleotide is rapidly diphosphorylated giving the active nucleotide triphosphate, which is a substrate to RNA-dependent RNA polymerase (4 structures, 0.5 points, 2 points in total).



2. The structure of the tautomers shows the hydrogen donor and acceptor moieties for formation of Watson-Crick pairs. Analogously to uridine, the tautomerism occurs at the hydroxamate segment which in the case of pairing with adenosine, the –OH group must be oriented trans. (0.5 points for each tautomer, 0.5 point for each base pairing, 2 points in total).



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