

39th



International Chemistry Olympiad

**8 theoretical problems
2 practical problems**

THE THIRTY-NINTH INTERNATIONAL CHEMISTRY OLYMPIAD 15–24 JULY 2007, MOSCOW, RUSSIAN FEDERATION

THEORETICAL PROBLEMS

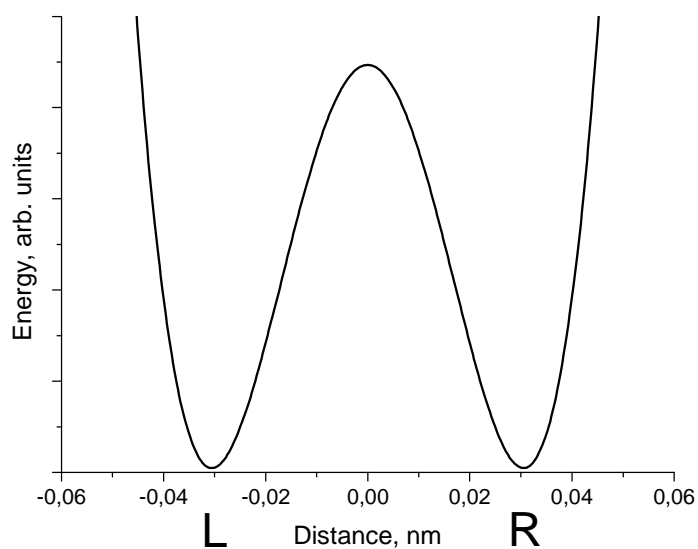
PROBLEM 1

Proton tunneling

Proton tunneling through energy barriers is an important effect, which can be observed in many complex species containing hydrogen bonds (DNA, proteins, etc.). Propanedial (malonaldehyde) is one of the simplest molecules for which intramolecular proton transfer can occur.

- 1.1 Draw the condensed formula of propanedial and the structures of two of its isomers, which can exist in equilibrium with propanedial.
- 1.2 In a water solution propanedial is a weak acid, its strength being comparable with that of acetic acid. Specify the acidic hydrogen atom. Explain its acidity (choose one version in the Answer Sheet).

On the plot below an energy profile of the intramolecular proton transfer is given (the dependence of energy on the distance of proton motion (in nm)). Energy curve has a symmetric double-well form.

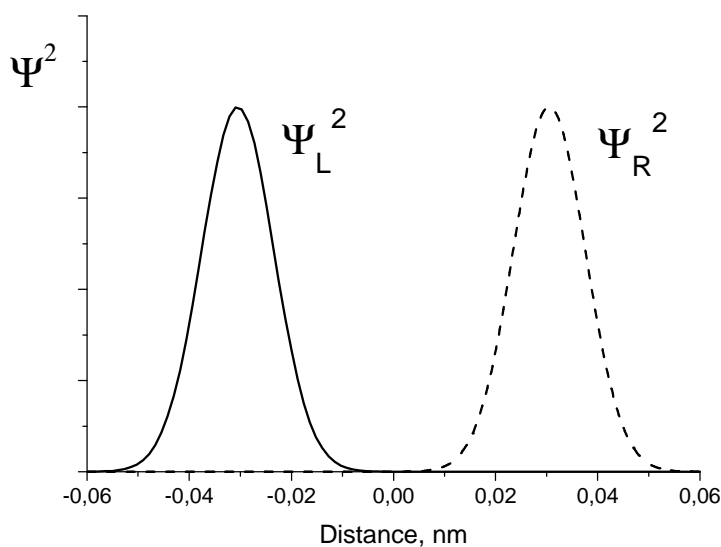


1.3 Draw the structures corresponding to two minima on this curve.

A proton is delocalized between two atoms and oscillates between two minima L and R with an angular frequency $\omega = 6.48 \times 10^{11} \text{ s}^{-1}$. Probability density for a proton depends on time as follows:

$$\Psi^2(x,t) = \frac{1}{2} \left[\Psi_L^2(x) + \Psi_R^2(x) + (\Psi_L^2(x) - \Psi_R^2(x)) \cos(\omega t) \right],$$

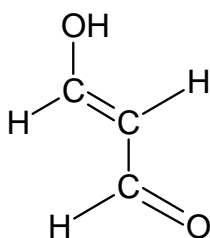
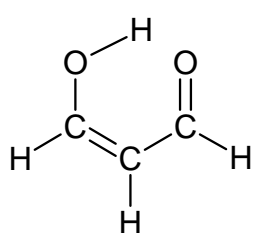
wavefunctions $\Psi_L(x)$ and $\Psi_R(x)$ describe a proton localized in the left and right wells, respectively:



- 1.4 Write down the expressions for the probability density at three moments: (a) $t = 0$, (b) $t = \pi/(2\omega)$, (c) $t = \pi/\omega$. Sketch the graphs of these three functions.
- 1.5 Without calculations, determine the probability of finding the proton in the left well at $t = \pi/(2\omega)$
- 1.6 How much time is required for a proton to move from one well to another? What is the proton mean speed during the transfer?
- 1.7 From the energy curve, estimate the uncertainty of the position of proton forming hydrogen bonds. Estimate the minimal uncertainty of the proton speed. Compare this value with that obtained in 1.6 and draw a conclusion about the proton tunneling (choose one of the versions in the Answer Sheet).

SOLUTION

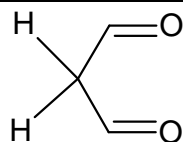
- 1.1 The structures of propanedial and two of its isomers:



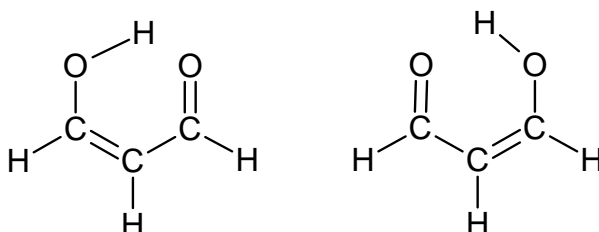
- 1.2 Acidic hydrogen atom is in CH_2 (in enol forms acidic hydrogen is in OH).
The stability of propanedial is caused by (one of the following answers had to be chosen):
- the stability of carbanion due to conjugation with two carbonyl groups,
 - weakness of $\text{C}-\text{H}$ bond in a carbonyl group,
 - hydrogen bonds between two propanedial molecules.

The first answer is correct.

- 1.3 The distance between two minima on the energy curve is 0.06 nm. In a purely aldehyde form



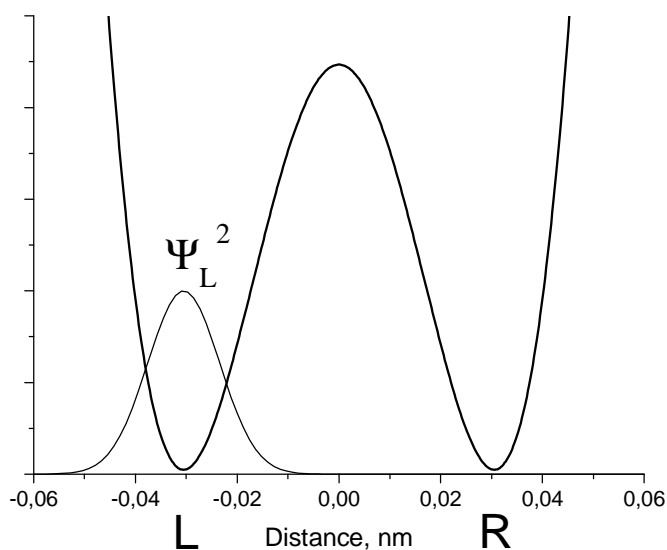
such distance between two possible positions of proton is impossible. Tunneling takes place only in enol Z-form:



1.4 Expressions and plots of probability density

$$(a) \quad \Psi^2(x,0) = \frac{1}{2} [\Psi_L^2(x) + \Psi_R^2(x) + \Psi_L^2(x) - \Psi_R^2(x)] = \Psi_L^2(x)$$

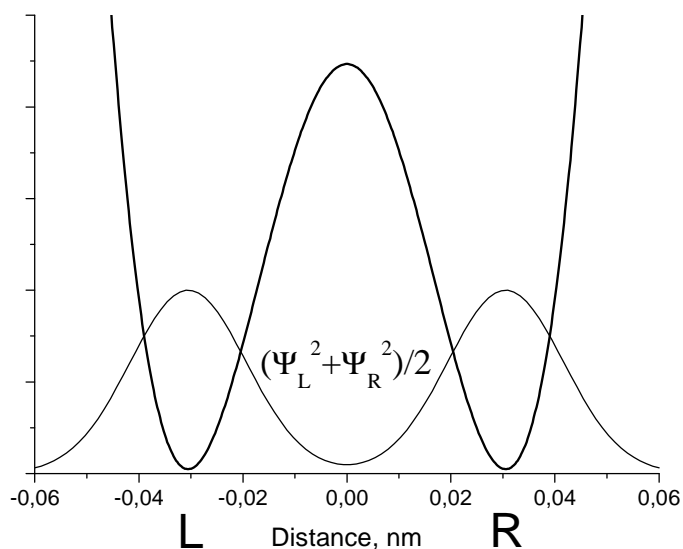
The probability density is concentrated in the left well:



(b) In the middle of the time interval

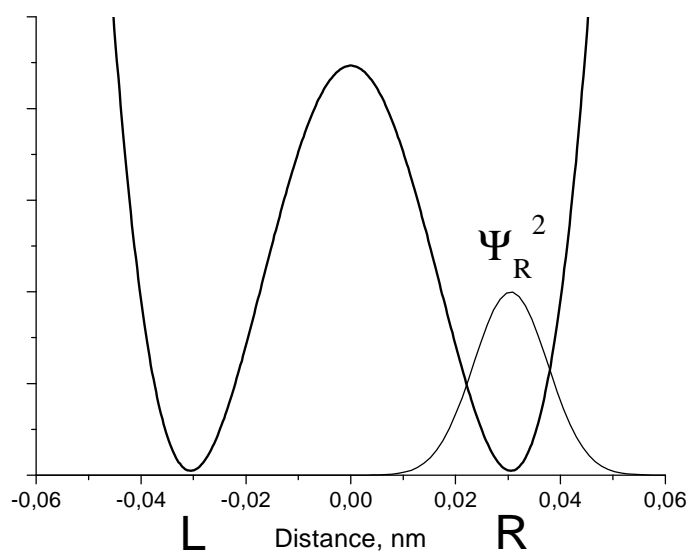
$$\Psi^2\left(x, \frac{\pi}{2\omega}\right) = \frac{1}{2} [\Psi_L^2(x) + \Psi_R^2(x)]$$

The probability density has a symmetric form, a proton is delocalized between two wells:



$$(c) \quad \Psi^2\left(x, \frac{\pi}{\omega}\right) = \frac{1}{2} [\Psi_L^2(x) + \Psi_R^2(x) - \Psi_L^2(x) + \Psi_R^2(x)] = \Psi_R^2(x)$$

The probability density is concentrated in the right well:



1.5 The probability of finding the proton in the left well is 1/2, because probability function is symmetric, and both wells are identical.

1.6 The time of transfer from one well to another is $t = \pi / \omega$.

$$t = \frac{3.14}{6.48 \times 10^{11}} = 4.85 \times 10^{-12} \text{ s.}$$

The proton velocity:

$$v = \frac{0.06 \times 10^{-9}}{4.85 \times 10^{-12}} = 12 \text{ m s}^{-1}.$$

- 1.7** The uncertainty of proton position is approximately equal to half of the distance between minima, that is 0.03 nm (0.06 nm will be also accepted).

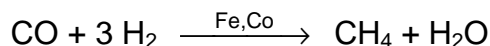
The minimal uncertainty of velocity can be obtained from the uncertainty relation:

$$\Delta v = \frac{h}{2 m \Delta x} = \frac{1.055 \times 10^{-34}}{2 \times \frac{0.001}{6.02 \times 10^{23}} \times 0.03 \times 10^{-9}} \approx 1000 \text{ m s}^{-1}.$$

Comparing this uncertainty with the velocity 12 m s^{-1} we see that the notion of proton velocity during transfer from one well to another is senseless. Therefore, proton tunneling is a purely quantum phenomenon and cannot be described in classical terms. The second conclusion is correct.

PROBLEM 2**Nanochemistry**

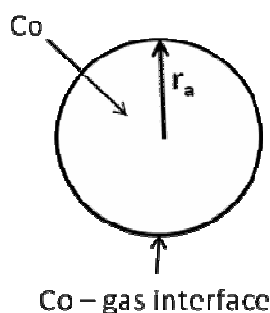
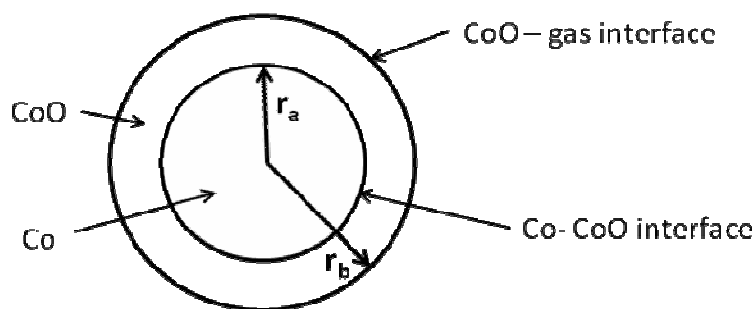
Metals of the iron subgroup are effective catalysts of hydrogenation of CO (Fischer-Tropsch reaction)



Catalyst (e.g. cobalt) is often used in the form of solid nanoparticles that have a spherical structure (fig.1). The reduction in size of the catalyst increases catalytic activity significantly. The unwanted side-reaction however involves the oxidation of the catalyst:



Solid cobalt oxide (bulk) is formed in the reaction vessel. This causes an irreversible loss of the catalyst's mass. Solid cobalt oxide can also be deposited on the surface of Co(s). In this case the new spherical layer is formed around the surface of the catalyst (see figure 2) and the catalytic activity drops.

**Fig. 1****Fig. 2**

Let us see how formation of nanoparticles affects the equilibrium of reaction (1).

$$G^{\circ}(r) = G^{\circ}(\text{bulk}) + \frac{2\sigma}{r} V$$

- 2.1** Calculate the standard Gibbs energy $\Delta_r G^{\circ}(1)$ and the equilibrium constant for the reaction (1) at $T = 500 \text{ K}$.
- 2.2** Calculate the equilibrium constant for reaction (1) when the cobalt catalyst is dispersed in the form of spherical particles (Fig. 1) of radius:

(a) 10^{-8} m ,

(b) 10^{-9} m .

The surface tension at the Co-gas interface is 0.16 J m^{-2} . CoO forms a bulk phase.

The mixture of gases involved in the Fischer-Tropsch (CO , CH_4 , H_2 , H_2O) reaction was put into a reaction vessel containing the cobalt catalyst. The total pressure is $p = 1$ bar, temperature is $T = 500$ K. The mole fraction of hydrogen (%) in the mixture is 0.15 %.

- 2.3** At what minimum mole fraction of water (%) in the gas mixture the unwanted spontaneous oxidation of the catalyst becomes possible so that solid bulk CoO may appear in the system? Assume that cobalt catalyst is in the form of
- a bulk phase
 - spherical nanoparticles with $r_a = 1$ nm (Fig. 1).
- 2.4** What would you suggest to protect Co nanoparticles from the spontaneous oxidation with the formation of bulk CoO at a constant ratio $p(\text{H}_2\text{O})/p(\text{H}_2)$ and a constant temperature:
- to increase r_a ;
 - to decrease r_a ;
 - change of r_a has no effect.

Assume now that solid cobalt oxide forms a spherical layer around a nanoparticle of cobalt. In this case the nanoparticle contains both a reactant (Co) and a product (CoO) (Fig. 2).

In the following problems denote surface tensions as $\sigma_{\text{CoO-gas}}$, $\sigma_{\text{CoO-Co}}$, radii as r_a , r_b , molar volumes as $V(\text{Co})$; $V(\text{CoO})$.

- 2.5** Write down the expression for the standard molar Gibbs function of CoO.
- 2.6** Write down the expression for the standard molar Gibbs function of Co.

Hint. If two spherical interfaces surround a nanoparticle, the excess pressure at its centre is given by the expression

$$P_{in} - P_{ex} = \Delta P = \Delta P_1 + \Delta P_2 = 2 \frac{\sigma_1}{r_1} + 2 \frac{\sigma_2}{r_2}$$

r_i , σ_i are radius and surface tension at the spherical interface i , respectively.

- 2.7** Express the standard Gibbs energy of the reaction (1) $\Delta_r G^0(1, r_a, r_b)$ in terms of $\sigma_{\text{CoO-gas}}$, $\sigma_{\text{CoO-Co}}$, r_a , r_b , $V(\text{Co})$; $V(\text{CoO})$ and $\Delta_r G^0(1)$.
- 2.8** When spontaneous oxidation of Co begins the radii of two layers in the nanoparticle (Fig. 2) are almost equal, $r_a = r_b = r_0$, and $\Delta_r G^0(1, r_a, r_b) = \Delta_r G^0(1, r_0)$. Assume that

$\sigma_{\text{CoO-gas}} = 2\sigma_{\text{CoO-Co}}$. Which plot in the Answer Sheet describes correctly the dependence of $\Delta_r G^0(1, r_0)$ on r_0 ?

- 2.9 What would you choose to protect Co nanoparticles from the spontaneous formation of the external layer of CoO at a constant ratio $p(\text{H}_2\text{O})/p(\text{H}_2)$ and a constant temperature:
- increase r_0
 - decrease r_0
 - change of r_0 has no effect.

Reference data:

Substance	ρ , g cm ⁻³	$\Delta_f G_{500}^0$, kJ mol ⁻¹
Co (s)	8.90	
CoO (s)	5.68	-198.4
H ₂ O (gas)		-219.1

SOLUTION

2.1 The Gibbs energy and the equilibrium constant of reaction (1)

$$\Delta_r G_{500}^0(1) = \Delta G_{f,500}^0(\text{CoO}, \text{s}) - \Delta G_{f,500}^0(\text{H}_2\text{O}, \text{g}) = -198.4 + 219.1 = 20.7 \text{ kJ mol}^{-1}$$

$$K = e^{-\frac{\Delta_r G_{500}^0(1)}{RT}} = e^{-\frac{20700}{8.314 \times 500}} = 6.88 \times 10^{-3}$$

2.2 The standard Gibbs energy of the reaction (1) with the spherical cobalt nanoparticles of radius r_a is

$$\begin{aligned} \Delta_r G_{500}^0(1, r_a) &= G_{\text{bulk},500}^0(\text{CoO}, \text{s}) + G_{500}^0(\text{H}_2, \text{g}) - G_{500}^0(\text{H}_2\text{O}, \text{g}) - G_{\text{sph}}^0(\text{Co}) = \\ &= G_{500}^0(\text{CoO}, \text{s}) + G_{500}^0(\text{H}_2, \text{g}) - G_{500}^0(\text{H}_2\text{O}, \text{gas}) - \left(G_{500}^0(\text{Co}, \text{s}) + \frac{2\sigma_{\text{Co-gas}} V(\text{Co})}{r_a} \right) = \\ &= \Delta_r G_{500}^0(1) - \frac{2\sigma_{\text{Co-gas}} V(\text{Co})}{r_a}; \end{aligned}$$

$$V(\text{Co}) = \frac{M_{\text{Co}}}{\rho(\text{Co})} = \frac{1 \times 10^{-6} \times 59.0}{8.90} = 6.6 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

for spherical particles with $r_a = 10^{-8}$, 10^{-9} m one gets, respectively

$$\frac{2\sigma_{\text{Co-gas}} V(\text{Co})}{r_a} = 210 \text{ and } 2100 \text{ J mol}^{-1}$$

$\Delta_r G_{500}^0(1, r_a)$ is equal to 20.5 (a), and 18.6 (b) kJ mol^{-1} , respectively.

The equilibrium constant is calculated from the equation

$$K(1, r_a) = \exp\left(-\frac{\Delta_r G_{500}^0(1, r_a)}{RT}\right)$$

$$K(1, r_a) = 7.22 \times 10^{-3}; \quad r_a = 10^{-8} \text{ m} \quad K(1, r_a) = 11.4 \times 10^{-3}; \quad r_a = 10^{-9} \text{ m}$$

2.3 The standard Gibbs energy for reaction (1) involving nanoparticles of cobalt is

$$\Delta_r G_{500}^0(1, r_a) = \Delta_r G_{500}^0(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\text{Co})$$

$\Delta_r G_{500}^0(1)$ is 20.7 kJ mol^{-1} . For spherical cobalt particles with $r_a = 1 \text{ nm}$ $\Delta_r G_{500}^0(1, r_a)$ is 18.6 kJ mol^{-1} .

Solid cobalt oxide can be formed spontaneously when Gibbs energy of reaction (1) is negative. The inequality for bulk cobalt is:

$$\Delta_r G(1) = \Delta_r G_{500}^0(1) + RT \ln\left(\frac{p(\text{H}_2)}{p(\text{H}_2\text{O})}\right) = \Delta_r G_{500}^0(1) - RT \ln\left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)}\right) \leq 0$$

and for spherical cobalt nanoparticles with $r_a = 1 \text{ nm}$:

$$\begin{aligned} \Delta_r G(1, r_a) &= \Delta_r G_{500}^0(1, r_a) + RT \ln\left(\frac{p(\text{H}_2)}{p(\text{H}_2\text{O})}\right) = \\ &= \Delta_r G_{500}^0(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\text{Co}) - RT \ln\left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)}\right) \leq 0 \end{aligned}$$

$\Delta_r G_{500}^0(1)$ is equal to 20.7 kJ mol^{-1} . For spherical cobalt particles with $r_a = 1 \text{ nm}$ equals to 18.6 kJ mol^{-1}

2.4 For the spontaneous oxidation

$$\Delta_r G(1, r_a) = \Delta_r G_{500}^0(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\text{Co}) - RT \ln \left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)} \right) \leq 0$$

and

$$\Delta_r G_{500}^0(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\text{Co}) \leq RT \ln \left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)} \right)$$

The left hand side of the last inequality becomes more positive with the increase of r_a . At certain point the inequality will be disturbed and the spontaneous oxidation will not take place. So, to protect cobalt nanoparticles from the spontaneous oxidation in this case one has to lengthen the radius r_a . The answer (a) is correct.

2.5 The equation for the standard molar Gibbs function of CoO (external layer) reads:

$$G_{\text{sph}}^0(\text{CoO}, r_b) = G_{\text{bulk}}(\text{CoO}) + \frac{2\sigma_{\text{CoO-gas}}}{r_b} V(\text{CoO}) = G^0(\text{CoO}, \text{s}) + \frac{2\sigma_{\text{CoO-gas}}}{r_b} V(\text{CoO})$$

2.6 The equation for the standard molar Gibbs function of Co (internal layer) reads:

$$\begin{aligned} G_{\text{sph}}^0(\text{Co}, r_a, r_b) &= G_{\text{bulk}}(\text{Co}) + V(\text{Co}) \left(\frac{2\sigma_{\text{CoO-gas}}}{r_b} + \frac{2\sigma_{\text{CoO-Co}}}{r_a} \right) = \\ &= G^0(\text{Co}, \text{s}) + V(\text{Co}) \left(\frac{2\sigma_{\text{CoO-gas}}}{r_b} + \frac{2\sigma_{\text{CoO-Co}}}{r_a} \right) \end{aligned}$$

The expression in brackets gives the additional pressure in the internal layer (see the Hint).

2.7 The standard Gibbs energy for reaction (1) with the double-layered nanoparticles is

$$\begin{aligned} \Delta_r G^0(1, r_a, r_b) &= G_{\text{sph}}^0(\text{CoO}, r_b) + G^0(\text{H}_2, \text{gas}) - G^0(\text{H}_2\text{O}, \text{gas}) - G_{\text{sph}}^0(\text{Co}, r_a, r_b) = \\ &= G^0(\text{CoO}, \text{s}) + G^0(\text{H}_2, \text{gas}) - G^0(\text{H}_2\text{O}, \text{gas}) - G^0(\text{Co}, \text{s}) + \\ &\quad + \frac{2\sigma_{\text{CoO-gas}}}{r_b} V(\text{CoO}) - 2V(\text{Co}) \left(\frac{\sigma_{\text{CoO-gas}}}{r_b} + \frac{\sigma_{\text{CoO-Co}}}{r_a} \right) = \\ &= \Delta_r G^0(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_b} (V(\text{CoO}) - V(\text{Co})) - \frac{2\sigma_{\text{CoO-Co}}}{r_a} V(\text{Co}) \end{aligned}$$

2.8 Under the assumptions made

$$\begin{aligned}\Delta_r G^0(1, r_a, r_b) &= \Delta_r G^0(1, r_0) = \\ &= \Delta_r G^0(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_b} (V(\text{CoO}) - V(\text{Co})) - \frac{2\sigma_{\text{CoO-Co}}}{r_a} V(\text{Co}) = \\ &= \Delta_r G^0(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_0} \left(V(\text{CoO}) - \frac{3}{2} V(\text{Co}) \right)\end{aligned}$$

The term in brackets in the right-hand side is positive

$$\left(V(\text{CoO}) - \frac{3}{2} V(\text{Co}) \right) = 6.56 \times 10^{-6} \text{ m}^3$$

$\Delta_r G^0(1, r_0)$ is directly proportional to $\left(\frac{1}{r_0} \right)$. The plot (a) is correct.

2.9 The spontaneous forward reaction (1) is possible, when $\Delta_r G(1, r_0) \leq 0$, and

$$\Delta_r G^0(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_0} \left(V(\text{CoO}) - \frac{3}{2} V(\text{Co}) \right) \leq RT \ln \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}}$$

The term in brackets in the left-hand side is positive. The left hand side of the inequality becomes more positive with the decrease of r_0 . At certain point the inequality will be violated and the spontaneous oxidation will not take place.

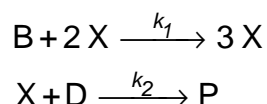
In order to protect nanoparticles from oxidation in this case one has to shorten the radius r_0 .

The answer (b) is correct.

PROBLEM 3**Unstable chemical reactions**

Many chemical reactions display unstable kinetic behavior. At different conditions (concentrations and temperature) such reactions can proceed in various modes: stable, oscillatory or chaotic. Most of these reactions include autocatalytic elementary steps.

Consider a simple reaction mechanism involving autocatalytic step:



(B and D are reagents, X is an intermediate and P is a product).

- 3.1** Write down the overall reaction equation for this two-step mechanism. Write the rate equation for X.
- 3.2** Deduce a rate equation using steady-state approximation. Find the orders:
- a partial reaction order with respect to B;
 - a partial reaction order with respect to D;
 - the overall order of a reaction.

Let the reaction occur in an open system where reagents B and D are being continuously added to the mixture so that their concentrations are maintained constant and equal: $[\text{B}] = [\text{D}] = \text{const}$.

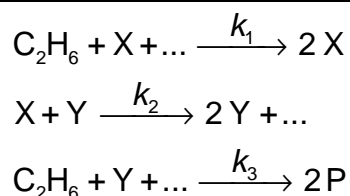
- 3.3** Without solving the kinetic equation draw the kinetic curve $[\text{X}](t)$ for the cases:

$$1) [\text{X}]_0 > \frac{k_2}{k_1}; \quad 2) [\text{X}]_0 < \frac{k_2}{k_1}.$$

- 3.4** Without solving the kinetic equation draw the kinetic curve $[\text{X}](t)$ for the case when the reaction proceeds in a closed vessel with the initial concentrations: $[\text{B}]_0 = [\text{D}]_0$,

$$[\text{X}]_0 > \frac{k_2}{k_1}.$$

Much more complex kinetic behavior is possible for the reactions with several intermediates. Consider a simplified reaction mechanism for cold burning of ethane in oxygen:



Under specific conditions this reaction displays oscillatory behavior:

Intermediates are peroxide $\text{C}_2\text{H}_6\text{O}_2$ and aldehyde $\text{C}_2\text{H}_4\text{O}$, P is a stable product.

3.5 Identify X, Y, and P. Fill the blanks in the reaction mechanism.

Behavior of unstable reactions is often controlled by temperature which affects the rate constants. In the above oxidation mechanism oscillations of concentrations are possible only if $k_1 \geq k_2$. Parameters of the Arrhenius equations were determined experimentally:

Step	A, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	E_A , kJ mol^{-1}
1	1.0×10^{11}	90
2	3.0×10^{12}	100

3.6 What is the highest temperature at which oscillatory regime is possible? Show your calculations.

SOLUTION

3.1 The overall reaction equation



The kinetic equation for X

$$\frac{d[\text{X}]}{dt} = k_1[\text{B}][\text{X}]^2 - k_2[\text{D}][\text{X}]$$

3.2 Under the steady-state conditions

$$\frac{d[\text{P}]}{dt} = k_2[\text{D}][\text{X}] = k_1[\text{B}][\text{X}]^2,$$

whence

$$[X] = \frac{k_2[D]}{k_1[B]}$$

$$\frac{d[P]}{dt} = \frac{k_2^2[D]^2}{k_1[B]}$$

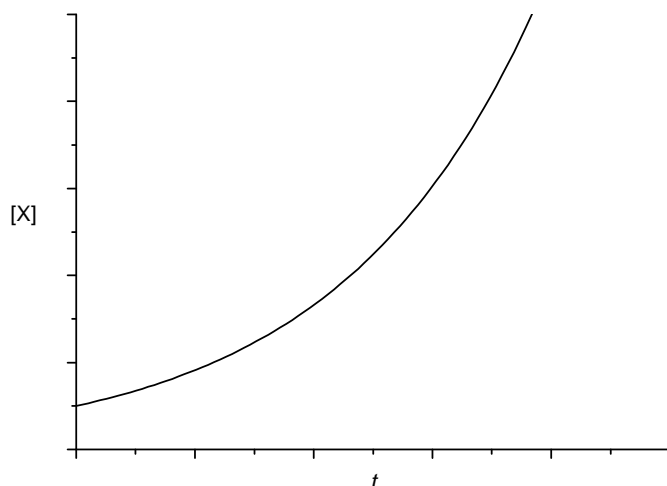
The reaction order is 2 with respect to D, and -1 with respect to B.

The overall order is 1.

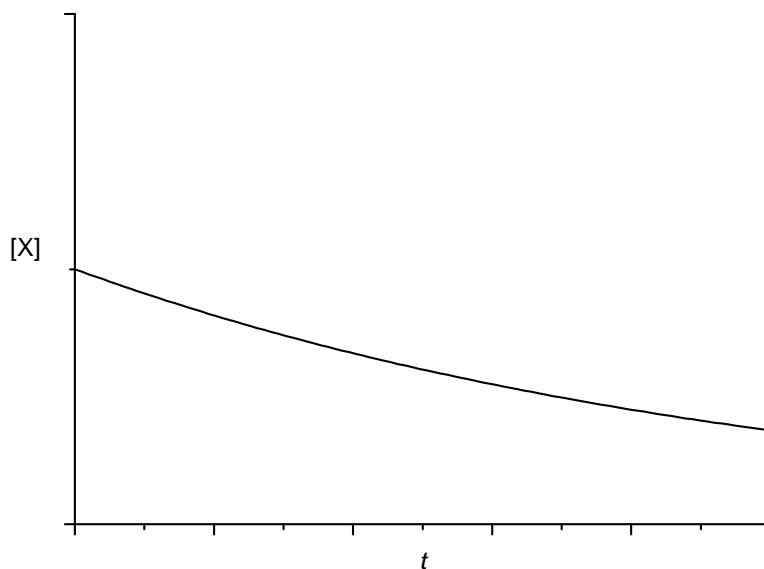
3.3 In an open system the initial reaction rate is:

$$\frac{d[X]}{dt} = [B][X](k_1[X] - k_2)$$

1) If $[X]_0 > k_2/k_1$, then $d[X]/dt > 0$ at any time, and the concentration of X monotonically increases:



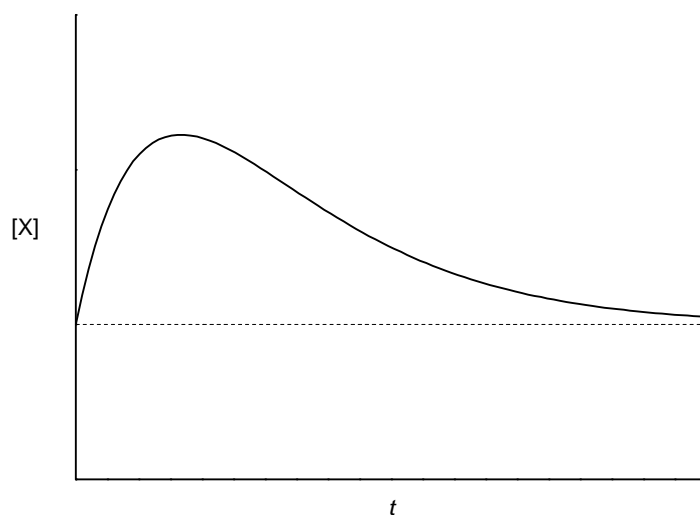
2) If $[X]_0 < \frac{k_2}{k_1}$, then $\frac{d[X]}{dt} < 0$ at any time, and the concentration of X monotonically decreases:



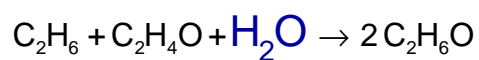
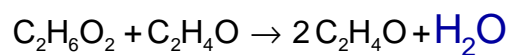
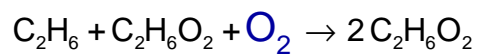
3.4 In a closed system the initial reaction rate is:

$$\left. \frac{d[X]}{dt} \right|_{t=0} = k_1[B]_0[X]_0^2 - k_2[D]_0[X]_0 = [B]_0[X]_0 (k_1[X]_0 - k_2) > 0$$

Hence, at the beginning of the reaction [X] increases but it cannot increase infinitely and finally goes to its initial value, because the second reaction is irreversible:



3.5 X – C₂H₆O₂, Y – C₂H₄O, P – C₂H₆O. Dots denote O₂ and H₂O.



3.6 At the highest possible temperature the rate constants are equal:

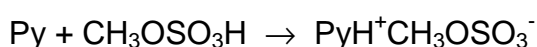
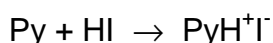
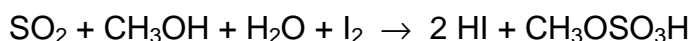
$$A_1 \exp\left(-\frac{E_{A,1}}{RT}\right) = A_2 \exp\left(-\frac{E_{A,2}}{RT}\right)$$

$$T = \frac{E_{A,2} - E_{A,1}}{R \ln \frac{A_2}{A_1}} = 354 \text{ K}$$

PROBLEM 4

Determination of water by Fischer titration

Determination of water by the classical Fischer method involves titration of a sample solution (or suspension) in methanol by a methanolic iodine solution, containing also an excess of SO₂ and pyridine (C₅H₅N, Py) – Fischer reagent. The following reactions occur during the titration:



Iodine content is usually expressed in mg of water reacting with 1 cm³ of the titrant solution (hereunder T, mg cm⁻³), which equals the mass of water (mg) reacting with 1.00 cm³ of the iodine solution. T is determined experimentally by titration of a sample with a known water content. The sample may be, for example, a hydrated compound or a standard solution of water in methanol. In the latter case it should be taken into account that methanol itself can contain certain amount of water.

In all calculations please use the atomic masses accurate to 2 decimal points.

4.1 Sometimes titration of water is performed in pyridine medium without methanol. How would the reaction of I₂ with SO₂ and H₂O occur in this case? Write down balanced reaction equation.

Calculate the T values of iodine solution in each of the following cases:

- 4.2** 12.20 cm³ of Fischer reagent solution were used for titration of 1.352 g of sodium tartrate dihydrate Na₂C₄H₄O₆ · 2 H₂O.
- 4.3** A known amount of water (21.537 g) was placed into a 1.000 dm³ volumetric flask which was filled by methanol up to the mark. For titration of 10.00 cm³ of the obtained solution, 22.70 cm³ of Fischer reagent solution were needed, whereas 2.20 cm³ of iodine were used for titration of 25.00 cm³ of methanol.
- 4.4** 5.624 g of water were diluted by methanol up to a total volume of 1.000 dm³ (solution **A**); 22.45 cm³ of this solution were used for titration of 15.00 cm³ of a Fischer reagent (solution **B**).

Then 25.00 cm³ of methanol (of the same batch as used for the preparation of solution **A**) and 10.00 cm³ of solution **B** were mixed, and the mixture was titrated by the solution **A**. 10.79 cm³ of the latter solution were spent.

4.5 An inexperienced analyst tried to determine water content in a sample of CaO using Fischer reagent. Write down the equation(s) of reaction(s) demonstrating possible sources of errors.

For the titration of 0.6387 g of a hydrated compound Fe₂(SO₄)₃ · x H₂O, 10.59 cm³ of iodine solution (T = 15.46 mg/cm³) were consumed.

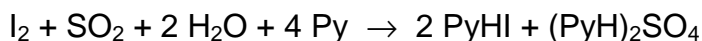
4.6 What other reaction(s), beside those given in the problem, can occur during the titration? Write down the equations of two such processes.

4.7 Write down an equation of the overall reaction of Fe₂(SO₄)₃ · x H₂O with the Fischer reagent.

4.8 Calculate the composition of the hydrate Fe₂(SO₄)₃ · x H₂O (x = integer).

SOLUTION

4.1 Equation:



4.2 T is equal to:

$$M(\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2 \text{H}_2\text{O}) = 230.05 \text{ g mol}^{-1} \quad 2 \times M(\text{H}_2\text{O}) = 36.04 \text{ g mol}^{-1}$$

$$m(\text{H}_2\text{O}) = \frac{1.3520 \times 36.04}{230.05} = 0.2118 \text{ g} = 211.8 \text{ mg}$$

$$T = \frac{211.8}{12.20} = 17.36 \text{ mg cm}^{-3}$$

$$T = 17.36 \text{ mg cm}^{-3}$$

4.3 T is equal to:

$$\text{Volume of iodine consumed for } 10 \text{ cm}^3 \text{ of pure CH}_3\text{OH} = \frac{2.20 \times 10.00}{25.00} = 0.88 \text{ cm}^3$$

$$T = \frac{21.537 \times 0.01 \times 10^3}{22.70 - 0.88} = 9.87 \text{ mg cm}^{-3}$$

More exactly

10.00 cm³ of the solution contains $\frac{(1000 - 21.5) \times 10.00}{1000} = 9.785$ cm³ of methanol.

Volume of iodine consumed for 9,785 cm³ of pure CH₃OH = $\frac{2.20 \times 9,785}{25.00} = 0.86$ cm³

$T = \frac{21.537 \times 0.01 \times 10^3}{22.70 - 0.86} = 9.86$ mg cm⁻³

T = 9.87 mg cm⁻³

4.4 T is equal to:

Approach 1

Let 1 cm³ of CH₃OH contains x mg H₂O, then 1 cm³ of **A** contains

[(1.000 - 0.006) x + 5.624] mg H₂O.

15.00 T = 22.45 (0.994 x + 5.624) - 1st titration,

10.00 T = 25.00 x + 10.79 (0.994 x + 5.624) - 2nd titration.

Hence, x = 1.13 mg cm⁻³, T = 10.09 mg cm⁻³ (10.10 without taking into account 0.994 factor)

Approach 2

Let y cm³ of **B** be consumed for the titration of water, contained in 1 cm³ of CH₃OH.

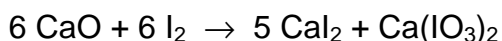
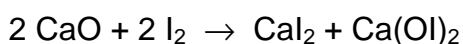
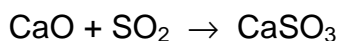
Then $T = \frac{22.45 \times 5.624}{15.00 - 22.45 \times 0.994 \times y}$ (1st titration) = $\frac{10.79 \times 5.624}{10.00 - 25.00 y - 10.79 y}$

(2nd titration).

Hence, y = 0.1116 and T = 10.10 mg cm⁻³

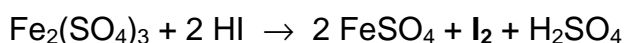
T = 10.09 mg cm⁻³ (10.10 without taking into account 0.994 factor)

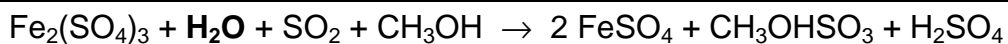
4.5 Equation(s):



(Instead of CaO, Ca(OH)₂ may be written.)

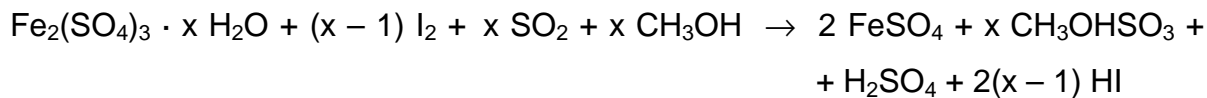
4.6 Equation(s):





(or in ionic form)

4.7 Equation:



4.8 The composition of the crystalhydrate is:

$$M(\text{Fe}_2(\text{SO}_4)_3 \cdot x \text{H}_2\text{O}) = 399.9 + 18.02 x$$

$$m(\text{H}_2\text{O}) = \frac{0.6387 \times 18.02 x}{(399.9 + 18.02 x)}$$

$$m(\text{H}_2\text{O}) = 10.59 \text{ cm}^3 \times 15.46 \text{ mg cm}^{-3} \times 0.001 \text{ g mg}^{-1} \times \frac{x}{x-1}$$

$$0.1637 \times (399.9 + 18.02 x) = 11.51 x - 11.51$$

$$x = 8.994 \approx 9$$

Formula: $\text{Fe}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$

PROBLEM 5

A mysterious mixture (organic hide-and-seek game)

An equimolar mixture **X** of three colourless organic liquids **A**, **B**, **C** was treated by water containing a drop of hydrochloric acid at heating to give (after separation from water) a 1 : 2 (molar ratio) mixture of acetic acid and ethanol without any other components. A catalytic amount (one-two drops) of concentrated sulfuric acid was added to the mixture after hydrolysis and after a long reflux (boiling with reflux condenser) a compound **D**, a volatile liquid with pleasant smell, was formed in 85% yield. Compound **D** is not identical with any of **A**, **B**, **C**.

5.1 Draw the structure of compound **D**?

5.2 Which class of organic compounds does **D** belong to? Choose the proper variant from those given in the Answer Sheet.

5.3 Even if the reflux is continued twice as long, the yield of **D** would not exceed 85%. Calculate the expected yield of **D** if 1 : 1 (molar ratio) mixture of ethanol and acetic acid is taken. Assume that: a) volumes do not change during the reactions; b) all concomitant factors, such as solvent effects, non-additivity of volumes, variation of temperature, etc. are negligible. If you cannot make a quantitative estimate, please indicate whether the yield will be: a) the same (85 %); b) higher than 85 %; c) lower than 85 %.

¹H NMR spectra of compounds **A**, **B**, **C** look very similar and each shows singlet, triplet and quartet with the ratio of integral intensities equal to 1 : 3 : 2.

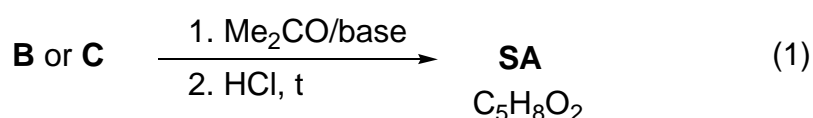
The same mixture **X** was subjected to alkaline hydrolysis. **A** remained unchanged, and was separated. After acidification and short boiling the remaining solution gave 2 : 3 (molar ratio) mixture of acetic acid and ethanol with evolution of gas.

The mixture **X** (3.92 g) was dissolved in diethyl ether and underwent hydrogenation in the presence of Pd on charcoal catalyst. 0.448 dm³ (standard conditions) of hydrogen were absorbed, but after the reaction **A** and **C** were isolated unchanged (3.22 g of mixture were recovered) while neither **B**, nor any other organic compounds, except diethyl ether, could be identified after hydrogenation.

5.4 Determine and draw the structures of **A**, **B**, and **C**.

5.5 Which intermediate compounds are formed during the acidic hydrolysis of **C** and the basic hydrolysis of **B**.

The reaction of either **B** or **C** with acetone (in the presence of a base) with subsequent acidification by dilute HCl at gentle heating gives the same product, senecioic acid (**SA**), a compound widely occurring in Nature. Alternatively, senecioic acid can be obtained from acetone by treating it with concentrated HCl and subsequent oxidation of the intermediate product by iodine in alkaline solution. The latter reaction gives, besides sodium salt of senecioic acid, a heavy yellow precipitate **E** (see the scheme 2).

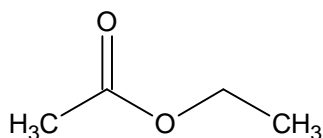


5.6 Determine the structure of senecioic acid and draw the reaction scheme leading to senecioic acid from acetone.

5.7 Give structure of **E**

SOLUTION

5.1 Structure of product **D**



Ethyl acetate, ethyl ethanoate

5.2 Which class of organic compounds does **D** belong to? Check the appropriate box.

ketones	ethers	acetals	esters	alcohols	aldehydes	glycols
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

5.3 The expected yield of **D**

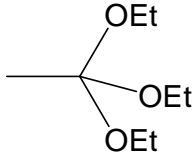
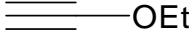
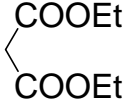
The reaction is an equilibrium without any further actions. Qualitative estimation:
The yield is lower than 85 %.

Assuming that the reaction is at equilibrium and that the equilibrium constant is supposed not to vary with temperature and composition of the reaction mixture, we can calculate:

$$K = \frac{[\text{AcOEt}][\text{H}_2\text{O}]}{[\text{AcOH}][\text{EtOH}]} = \frac{(0.85)^2}{0.15 \times 1.15} = 4.2$$

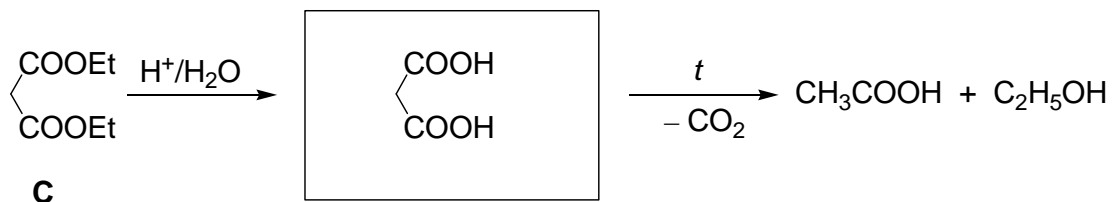
Using this constant calculation of yield in 1 : 1 mixture gives 67 %.

5.4 The structures of **A**, **B**, and **C**.

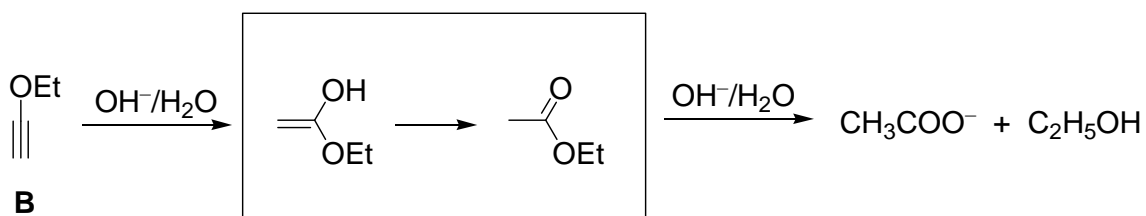
 <p>$\text{CH}_3\text{C}(\text{OEt})_3$</p> <p>triethyl orthoacetate, 1,1,1-triethoxyethane</p>	 <p>$\text{HC}\equiv\text{COEt}$</p> <p>ethoxyacetylene, ethynylethyl ether</p>	 <p>$\text{CH}_2(\text{COOEt})_2$</p> <p>diethyl malonate</p>
A	B	C

5.5 Draw in the boxes intermediate compounds formed during the acidic hydrolysis of **C**, and basic hydrolysis of **B**.

a) Malonic acid is formed as intermediate in the hydrolysis of diethyl malonate:

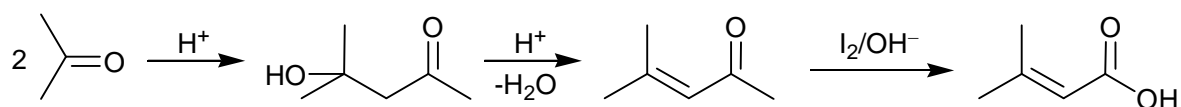


b) Hydrolysis of ethoxyacetylene starts from the addition of hydroxide to the triple bond to give unstable enolic form of ethylacetate, into which it immediately is transformed



5.6 The structure of senecioic acid:

From acetone alone the synthesis includes aldol condensation and dehydration with subsequent iodoform reaction:



5.7 The structure of **E**.

Iodoform, triiodomethane, CHI_3

PROBLEM 6**Silicates as the base of the Earth crust**

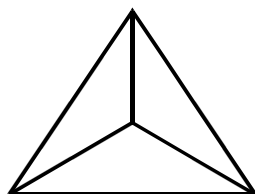
Silica and compounds derived from it, silicates, constitute ca. 90 % of the Earth crust substances. Silica gives rise to a beautiful material – glass. Nobody knows exactly how glass was discovered. There is a well-favored story related to Phoenician sailors who fused occasionally sea sand and soda ash. It is likely that they discovered the secret of “liquid glass” (LGL) – sodium metasilicate (Na_2SiO_3) soluble in water.

6.1 The solution of LGL was used earlier as office glue. Write down the net ionic equation accounting for the ability of LGL to set in air.

Hydrolysis of LGL in water allows obtaining a colloidal solution of silicic acid.

6.2 Complete the Table in the Answer Sheet. Write down the net ionic equations matching the processes enumerated in the Table. For each process check the “Yes” box if it leads to changes of pH. Otherwise check the “No” box.

The structure of species occurring in aqueous solutions of silicates is rather complex. However, it is possible to distinguish the main building block of all species – orthosilicate tetrahedron (SiO_4^{4-} , **1**):

**(1)**

For $[\text{Si}_3\text{O}_9]^{n-}$ ion found in aqueous solutions of silicates:

6.3 Determine the charge (n).

6.4 Determine the number of oxygen atoms bridging adjacent tetrahedra.

6.5 Depict its structure joining together several tetrahedra (**1**). Take into account that any adjacent tetrahedron shares one vertex.

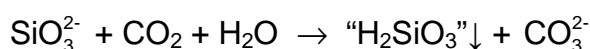
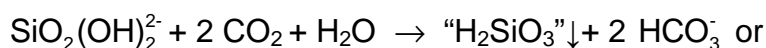
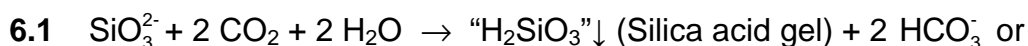
Charged monolayers with the composition $[\text{Si}_4\text{O}_{10}]^{m-}$ are found in kaolinite (clay).

6.6 Using the same strategy as in **6.3** - **6.5**, depict a fragment of the layered structure joining 16 tetrahedra (**1**). Note that 10 tetrahedra have shared vertices with 2 neighbours each, and the rest 6 have shared vertices with 3 neighbours each.

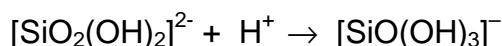
Being placed into the LGL solution, salts of transition metals give rise to fancy “trees” tinted relevant to the colour of the salt of the corresponding transition metal. Crystals of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ produce “trees” of blue colour, whereas those of $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ form green “trees”.

- 6.7** Determine the pH of 0.1 M aqueous solution of copper sulphate at 25 °C assuming that its hydrolysis occurs in small degree only. Use the value of the first acidity constant of $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ $K_a^1 = 1 \times 10^{-7}$.
- 6.8** Write down equation of a reaction between aqueous solutions of CuSO_4 and sodium metasilicate (LGL). Take into account the pH values of aqueous solutions of the salts.

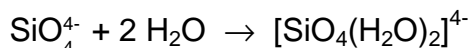
SOLUTION



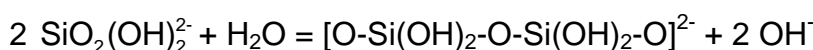
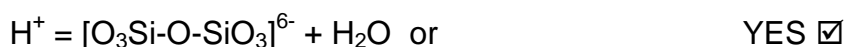
- 6.2** a) protonation of ortho-silicate ions leading to the formation of Si-OH groups:



- b) formation of hydrated $[\text{SiO}_4(\text{H}_2\text{O})_2]^{4-}$ anions NO



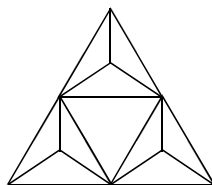
- c) polycondensation of ortho-silicate ions leading to the formation of Si-O-Si bonds



6.3 $n = 6$ (assuming oxidation numbers of silicon (+4) and oxygen (-2), or taking into account its structure and the charge of orthosilicate ion (-4))

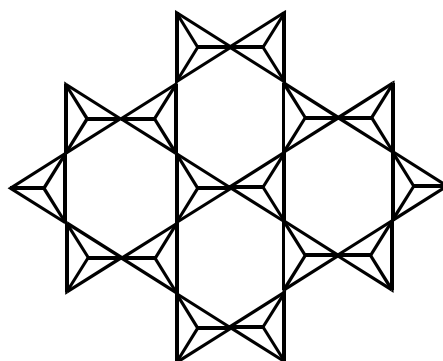
6.4 $\text{Si}_3\text{O}_9 \equiv 3 [\text{SiO}_4] - 3 \text{O}$, i.e. there are 3 oxygen atoms bridging adjacent tetrahedra

6.5



6.6 $m = 4$ (assuming oxidation numbers of silicon (IV) and oxygen (-II), or taking into account its structure and the charge of orthosilicate ion (-4))

$\text{Si}_4\text{O}_{10} \equiv 4[\text{SiO}_4] - 6 \text{O}$, i. e. the formula of the tetrahedron is now $\text{SiO}_{2.5}$, which is possible if 1 O atom belongs to this tetrahedron and the other three are shared between 2 tetrahedra (their contribution = 3/2). This is possible if the tetrahedra are set on a plane and joined together through all apexes of their bases.



6.7 $\text{Cu}(\text{H}_2\text{O})_4^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{OH})(\text{H}_2\text{O})_3^+ + \text{H}_3\text{O}^+$,
 $[\text{H}^+] \approx (c K_a)^{1/2} = 1 \times 10^{-4}$, $\text{pH} = -\log[\text{H}^+] = 4$
 $\text{pH} = 4$

6.8 $\text{CuSO}_4 + \text{Na}_2\text{SiO}_3 + 2 \text{H}_2\text{O} \rightarrow \text{Cu}(\text{OH})_2 \downarrow + \text{“H}_2\text{SiO}_3\text{”} \downarrow + \text{Na}_2\text{SO}_4$

or

$2 \text{CuSO}_4 + \text{Na}_2\text{SiO}_3 + 2 \text{H}_2\text{O} \rightarrow \text{Cu}_2(\text{OH})_2\text{SO}_4 \downarrow + \text{“H}_2\text{SiO}_3\text{”} \downarrow + \text{Na}_2\text{SO}_4$

This (or those) reaction(s) (apart from formation of copper silicate) can be deduced from the fact that the reaction describes mutual (self-amplifying) hydrolysis. It comes

from the previous parts of the task: pH of LGL is greater than 7 (see questions **6.2**), and pH of copper sulfate solution is less than 7 (see **6.7**).

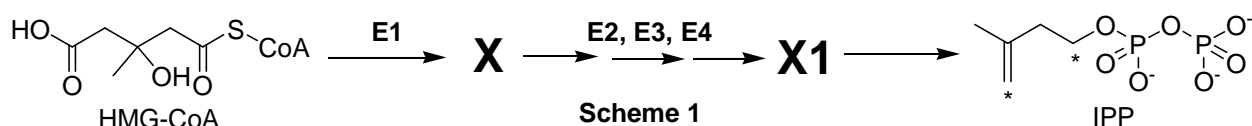
PROBLEM 7

Atherosclerosis and intermediates of cholesterol biosynthesis

Cholesterol is a lipid wide-spread in living nature. Disruption of its metabolism leads to atherosclerosis and related potentially fatal diseases.

Substances **X** and **Y** are two key intermediates of cholesterol biosynthesis in animals.

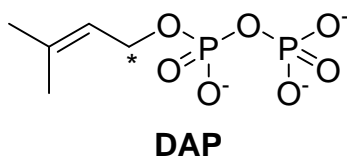
X is an optically active monocarboxylic acid composed of atoms of only three elements. It is formed in organisms from (S)-3-hydroxy-3-methylpentanedioyl-coenzyme A (HMG-CoA). This reaction is catalyzed by enzyme **E1** (which catalyses two types of reactions) and does not involve water as a substrate. **X** is further metabolized into **X1** through a three-stage process requiring enzymes **E2**, **E3**, **E4**, which catalyze reactions of one and the same (and only one) type. Finally, **X1** spontaneously (non-enzymatically) decomposes to give isopentenyl pyrophosphate (3-methylbut-3-enyl diphosphate, IPP) and inorganic products:



7.1 In the Answer Sheet, choose the reaction type(s) for **E1** and **E3**.

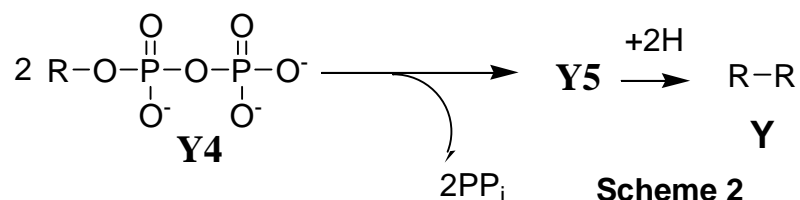
7.2 Draw the structure of **X** with stereochemical details and indicate absolute configuration (R or S) of the stereocenter.

Y is an unsaturated acyclic hydrocarbon. Its reductive ozonolysis leads to a mixture of only three organic substances **Y1**, **Y2** and **Y3** in a molar ratio of 2:4:1. **Y** is formed as a result of a number of successive coupling reactions of two isomeric substances: IPP and dimethyl allyl pyrophosphate (3-methylbut-2-enyl diphosphate, DAP) with subsequent reduction of a double bond in the final coupling product **Y5**. Carbon atoms IPP and DAP involved in the formation of C-C bonds during biosynthesis of **Y** are marked with asterisks.



7.3 Write down the overall reaction equation for reductive ozonolysis of DAP, if dimethyl sulfide is used as the reducing agent.

The product of the final coupling reaction (hydrocarbon **Y5**) is formed when two hydrocarbon residues (R) of intermediate **Y4** are combined:



At each coupling stage but that shown in Scheme 2, pyrophosphate is released in a molar ratio of 1 : 1 to the coupling product.

- 7.4** Determine molecular formula of **Y**, if it is known that **Y2** and **Y3** contain 5 and 4 carbon atoms, respectively.
- 7.5** Calculate the number of IPP and DAP molecules needed to give **Y5**, if it is known that all carbon atoms of isomeric pyrophosphates are incorporated into **Y**.
- 7.6** Draw the product of coupling reaction of one IPP molecule with one DAP molecule (C-C bond can be formed only by carbon atoms marked with asterisks), if it is known that subsequent reductive ozonolysis of the product of the coupling reaction gives **Y1**, **Y2** and one more product, the latter containing phosphorus.

The only double bond reduced in **Y5** during its metabolism into **Y** was formed in the reaction described in Scheme 2. All double bonds in **Y** and **Y4** exist in trans configuration.

7.7 Draw structures of **Y** and **Y4** with stereochemical details.

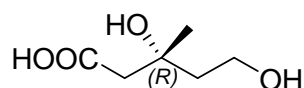
SOLUTION

7.1 **E2 - E4** catalyze one and the same (and only one) reaction type. The only reaction which can be carried out three times in a row is monophosphorylation (all the rest reaction types are not consistent with either initial or final products). This is also supported by presence of pyrophosphate residue in IPP and liberation of inorganic products (including inorganic phosphate) upon spontaneous decomposition of **X1**.

X is a monocarboxylic acid composed of atoms of three elements: carbon, hydrogen and oxygen. It can contain neither sulfur which is found in CoA nor phosphorus which is introduced into intermediates on the pathway from HMG-CoA towards IPP or present in CoA. Thus, **E1** catalyzes non-hydrolytic removal of CoA from HMG-CoA and is not involved in phosphorylation. Since water is not a substrate in this reaction, liberation of CoA must be conjugated with another reaction which affects the carboxylic group esterified in HMG-CoA. The only possible variant is its 4 electron reduction towards hydroxyl group. **E1** can not catalyze dehydration because of optical activity of **X** (removal of water leads to the loss of sole chiral center). Decarboxylation is excluded, since **X**, being an acid, must contain a carboxylic group. Oxidation of tertiary hydroxyl group in HMG-CoA according to β -oxidation mechanism is impossible. Further evidence comes from the fact that the carboxylic group initially involved in thioester bond formation is present as the residue of hydroxyl group in IPP. So:

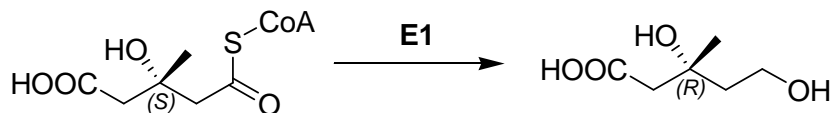


7.2 Based on the reaction types catalyzed by **E1** and configuration of HMG-CoA stereocenter, the structure of **X** is:

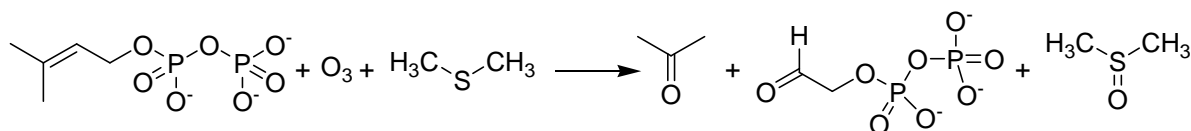


X, mevalonic acid

Note the absolute configuration of the chiral center is changed as a result of HMG-CoA metabolism into mevalonic acid due to alteration of substituents priority.



7.3 Reaction equation for reductive ozonolysis:



7.4 DAP molecule contains only one carbon atom which can be involved in the formation of C–C bond during **Y** biosynthesis. Irrespective of the way this molecule is incorporated in **Y**, ozonolysis of this fragment will lead to dimethyl ketone (acetone). (See DAP ozonolysis reaction in 7.2.1). Thus, acetone can be unambiguously attributed to **Y1**, since it contains 3 carbon atoms (**Y2** and **Y3** contain 5 and 4 carbon atoms, respectively). Taking into account the ratio between ozonolysis products, we have:

$$n_Y(\text{C}) = 2 \cdot n_{Y1}(\text{C}) + 4 \cdot n_{Y2}(\text{C}) + n_{Y3}(\text{C}) = 2 \cdot 3 + 4 \cdot 5 + 4 = 30$$

Y is an acyclic molecule, thus DAP residues can be found only at its ends. **Y** has only two ends, since IPP contains only two elongation sites (at least three such sites are needed to get a branched molecule). Since reductive ozonolysis of one **Y** molecule produces two acetone molecules, **Y** contains 30 carbon atoms.

To determine the number of hydrogen atoms double bonds in **Y** should be counted. Formation of each double bond reduces by 2 the number of hydrogen atoms in the coupling product as compared to the sum of atoms of starting substances. The ratio of **Y** to the sum of its ozonolysis products is 1:7 (2+4+1), which corresponds to 6 double bonds in **Y**. Then, by using the general formula for alkanes we have:

$$n(\text{H}) = 2 \cdot n_Y(\text{C}) + 2 - 2 \cdot n_{\text{C}=\text{C}} = 30 \cdot 2 + 2 - 6 \cdot 2 = 50$$

Y (squalene) formula – $\text{C}_{30}\text{H}_{50}$.

Number of carbon atoms: <u>30</u>	Work: $n_Y(\text{C}) = 2 \cdot n_{Y1}(\text{C}) + 4 \cdot n_{Y2}(\text{C}) + n_{Y3}(\text{C}) = 2 \cdot 3 + 4 \cdot 5 + 4 = 30$
Number of hydrogen atoms: <u>50</u>	Work: $n(\text{H}) = 2 \cdot n_Y(\text{C}) + 2 - 2 \cdot n_{\text{C}=\text{C}} = 30 \cdot 2 + 2 - 6 \cdot 2 = 50$

Gross formula of **Y** $\text{C}_{30}\text{H}_{50}$

7.5 IPP and DAP are structural isomers containing 5 carbon atoms each. Since all carbon atoms of these substances are found in **Y**, one can calculate the total quantity of IPP and DAP molecules needed to synthesize **Y**:

$$n(\text{IPP\&DAP}) = n_Y(\text{C})/5 = 30/5 = 6$$

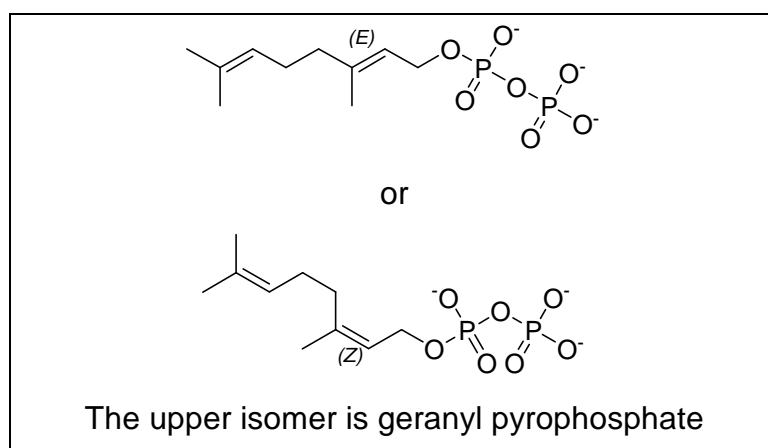
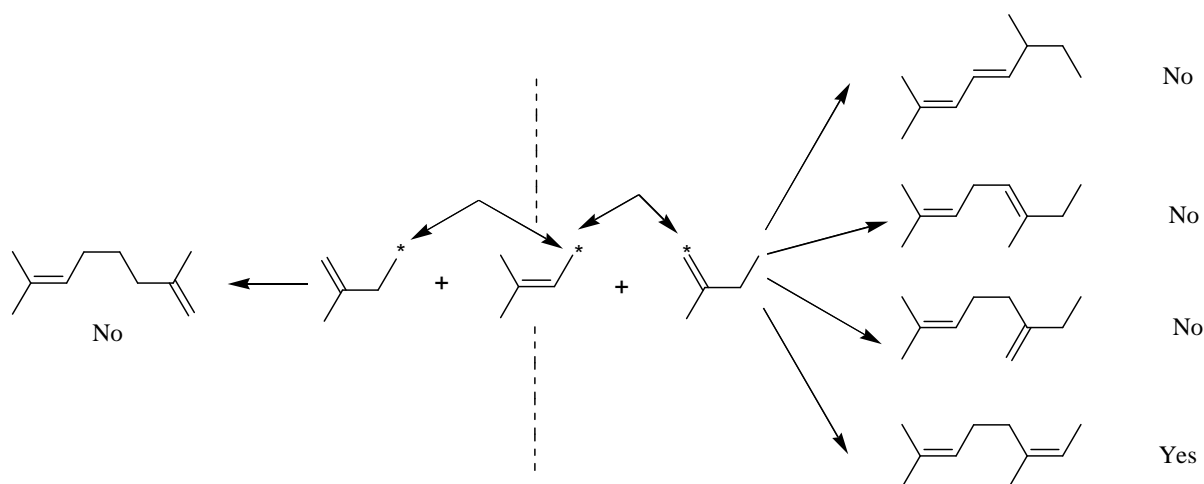
The number of DAP molecules was determined earlier and is equal to 2. Then, 4 molecules of IPP are needed.

$$n(\text{IPP\&DAP}) = n_{\text{Y}}(\text{C})/5 = 30/5 = 6$$

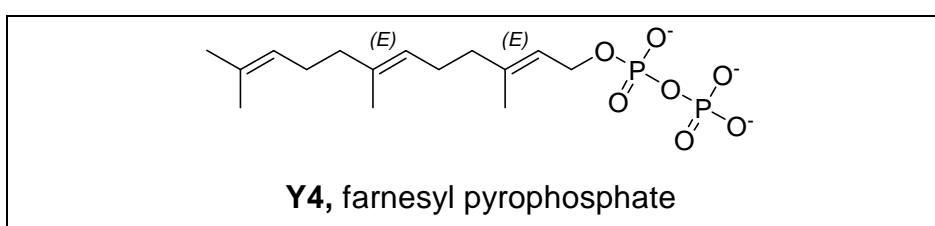
Number of DAP molecules: 2

Number of IPP molecules: 4

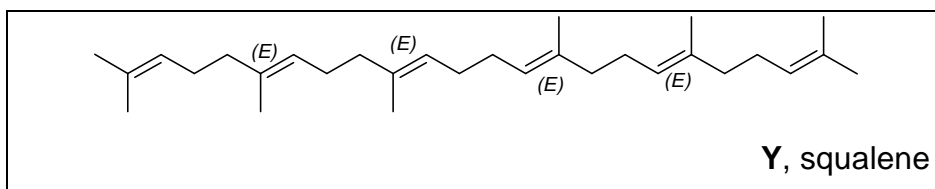
7.6 All possible combinations that do not alter hydrocarbon skeleton are given below (pyrophosphate fragments not shown). Two groups of products differing in carbon atoms involved in coupling reaction are separated by the dashed line. IPP fragments should be attached to DAP so that ozonolysis of the product leads to **Y2** containing 5 carbon atoms. Only one variant is possible if stereochemistry is not taken into consideration and two variants with stereochemical details



7.7 It is seen from the coupling reaction (Scheme 2) that **Y4** contains 15 carbon atoms or 1 DAP and 2 IPP fragments, the latter being attached to the former consecutively. It is important to note that **Y3** can not be found in two hydrocarbon residues originating for **Y4**, since **Y3** is formed as a result of ozonolysis in a molar ratio of 1 : 1 to **Y**. Thus, geranyl phosphate is the intermediate on the way to **Y** (all double bonds in trans configuration). Attachment of the next IPP fragment to geranyl phosphate leads to the product giving 1 molecule of **Y1** and 2 molecules of **Y2** upon its ozonolysis. Thus, **Y4** structure with stereochemical details:



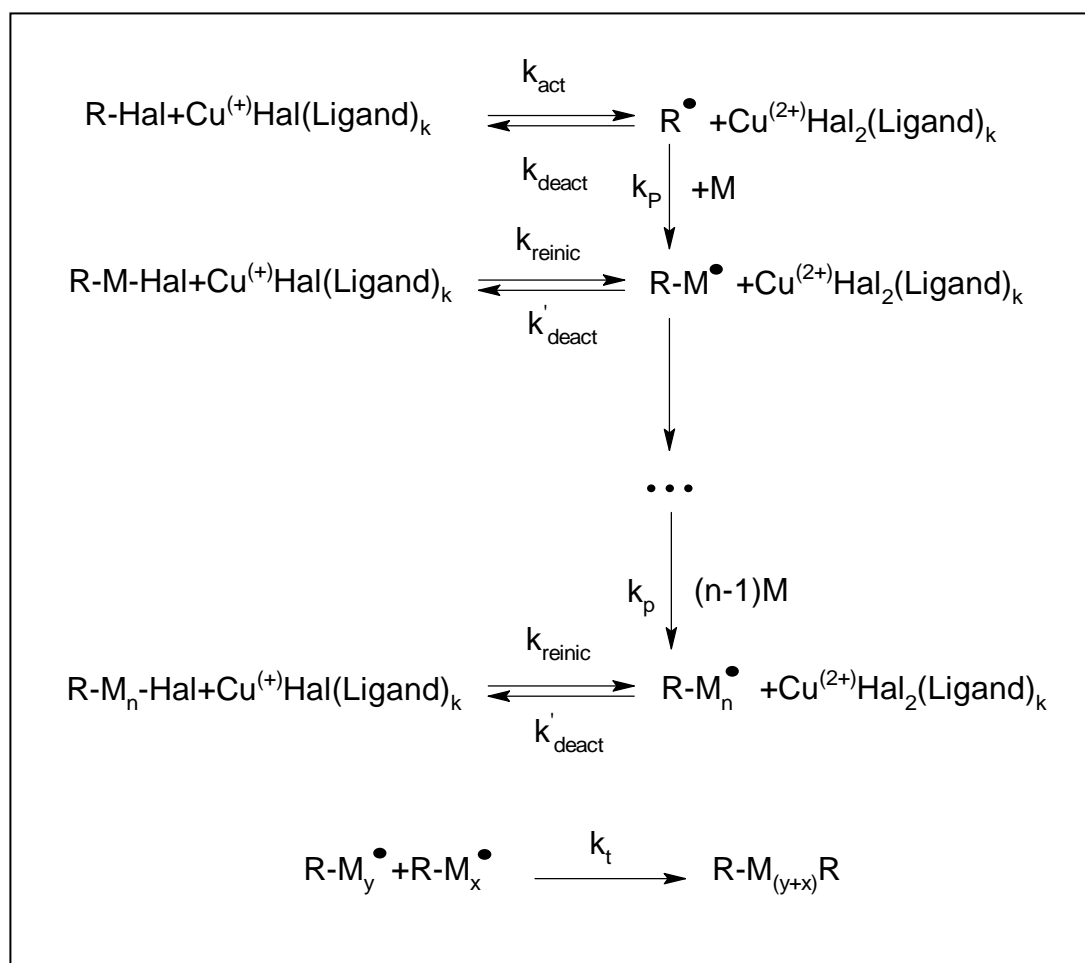
Combining two hydrocarbon fragments of **Y4** and taking into account that the double bond between them is being reduced we get the following structure of **Y**:



PROBLEM 8

ATRP allows new polymers

ATRP (Atom Transfer Radical Polymerization) is one of the most promising novel approaches towards polymer synthesis. This modification of radical polymerization is based on a redox reaction of organic halides with complexes of transition metals, Cu (I) in particular. The process can be described by the following scheme (M – monomer, Hal – halogen):



The reaction rate constants are:

k_{act} - all activation reactions, k_{deact} – all reversible deactivation reactions, k_p - chain propagation, and k_t - irreversible termination.

8.1 Write down expressions for the rates of ATRP elementary stages: activation (v_{act}), deactivation (v_{deact}), propagation (v_p) and termination (v_t). Write down generalized equation assuming just one reacting species R'X.

Consider that the total number of polymeric chains is equal to that of initiator molecules. Assume that at each moment throughout polymerization all chains are of the same length.

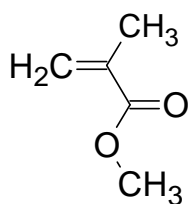
8.2 Compare the rate of deactivation to the rates of ATRP elementary stages.

Dependence of monomer concentration ($[M]$) on reaction time (t) for ATRP is:

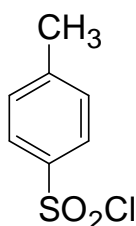
$$\ln\left(\frac{[M]}{[M]_0}\right) = -k_p [R\cdot] t,$$

$[M]_0$ - initial monomer concentration, k_p - rate constant of propagation, $[R\cdot]$ - concentration of active radicals.

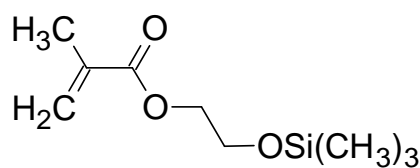
To prepare a polymer sample by using ATRP, catalytic amounts of CuCl, organic ligand (L) and 31.0 mmol of monomer (methylmethacrylate, or MMA) were mixed. The reaction was initiated by adding 0.12 mmol of tosyl chloride (TsCl). Polymerization was conducted for 1400 s. k_p is $1616 \text{ L mol}^{-1}\text{s}^{-1}$, and the steady state concentration of radicals is $1.76 \times 10^{-7} \text{ mol dm}^{-3}$.



MMA



TsCl



HEMA-TMS

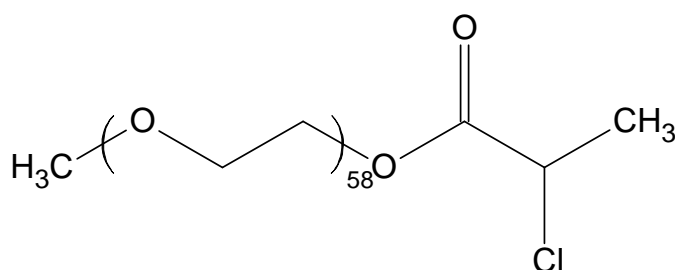
8.3 Calculate mass (m) of the polymer obtained.

In another experiment the time of MMA polymerization was changed, all the rest reaction conditions being the same. The mass of the obtained polymer was 0.73 g. Then 2-(trimethylsilyloxy)ethyl methacrylate, HEMA-TMS (23.7 mmol) was added to the mixture and polymerization was continued for another 1295 s. MMA and HEMA-TMS reactivities are the same under reaction conditions.

8.4 Calculate degree of polymerization (DP) of the obtained polymer.

8.5 Depict the structure of the obtained polymer (including end groups), showing MMA and HEMA-TMS units as A and B, respectively. If necessary, use the symbols in the copolymer structure representation: block (block), stat (statistical), alt (alternating), grad (gradient), graft (grafted). For example, (A₆₅-graft-C₁₀₀)-stat-B₃₄ means that chains of polymer C are grafted on units A in the statistical copolymer of A and B.

ATRP was applied to synthesize two block copolymers, P₁ and P₂. One block in both block-copolymers was the same and was synthesized from mono-(2-chloropropionyl)-polyethylene oxide used as a macroinitiator:



The other block in P₁ consisted of styrene (C), and in P₂ of p-chloromethylstyrene (D) units.

¹H NMR spectra of the macroinitiator, P₁ and P₂ are given below. Integral intensities of characteristic signals can be found in the table.

- 8.6** Assign ¹H NMR signals to substructures given in the Answer Sheet.
- 8.7** Determine molar fractions of units C and D and molecular weights of P₁ and P₂.
- 8.8** Write down all possible reactions of activation occurring during the synthesis of P₁ and P₂. You may use R symbol to depict any unchanged part of the macromolecule, but you should specify what substructure you use it for.
- 8.9** Draw the structure of P₁ and one of possible structures of P₂ representing poly(ethylene oxide) chain by a wavy line and showing units of co-monomers as C and D, respectively.

Thus:

$$V_{\text{deact}} \gg V_{\text{act}}$$

The portion of active radicals must be small, so the equilibrium is shifted towards dormant species.

$$V_{\text{deact}} \gg V_p$$

Propagation rate should be much slower than that of deactivation to make chains propagate with equal rate.

$$V_{\text{deact}} \gg V_t$$

Termination does not occur since the total number of polymer chains is equal to a certain constant number – number of initiator molecules.

$$V_{\text{deact}} \gg V_{\text{act}}$$

$$V_{\text{deact}} \gg V_p$$

$$V_{\text{deact}} \gg V_t$$

8.3 Calculation of mass (m) of the obtained polymer.

1st variant

$$[M] = [M]_0 \exp(-k_p [R\cdot] t) \text{ or } n(\text{MMA}) = n_0(\text{MMA}) \exp(-k_p [R\cdot] t)$$

Quantity of MMA monomer remaining after polymerization during 1400 s is

$$31.0 \times \exp(-1616 \times 1.76 \times 10^{-7} \times 1400) = 20.8 \text{ mmol.}$$

Quantity of monomer consumed during polymerization: $31 - 20.8 = 10.2 \text{ mmol}$

Mass of the obtained polymer is

$$m = \Delta n(\text{MMA}) \times M(\text{MMA}) = \frac{10.2}{1000} \times 100.1 = 1.03 \text{ g}$$

2nd variant

$$[M] = [M]_0 \exp(-k_p [R\cdot] t) \text{ or } n(\text{MMA}) = n_0(\text{MMA}) \exp(-k_p [R\cdot] t)$$

Quantity of MMA monomer consumed during 1400 seconds of polymerization is

$$\begin{aligned} \Delta n(\text{MMA}) &= n_0(\text{MMA}) (1 - \exp(-k_p \times [R\cdot] \times t)) = 31.0 \times (1 - 1616 \times 1.76 \times 10^{-7} \times 1400) = \\ &= 10.2 \text{ mmol} \end{aligned}$$

Mass of the obtained polymer is:

$$m = \Delta n(\text{MMA}) \times M(\text{MMA}) = (10.2 / 1000) \times 100.1 = 1.03 \text{ g}$$

3rd variant

$$\ln\left(\frac{[M]}{[M]_0}\right) = -k_p[R\cdot]t = -1616 \times 1.76 \times 10^{-7} \times 1400 = -0.398$$

$$\frac{[M]}{[M]_0} = e^{-0.398} = 0.672$$

$$\frac{[M]}{[M]_0} = \frac{n(\text{MMA})}{n_0(\text{MMA})}$$

$$n(\text{MMA}) = 0.672 \times n_0(\text{MMA}) = 20.8 \text{ mmol}$$

Quantity of monomer consumed during polymerization is $31 - 20.8 = 10.2$ mmol.

Mass of the obtained polymer is

$$m = \Delta n(\text{MMA}) \times M(\text{MMA}) = (10.2/1000) \times 100.1 = 1.03 \text{ g}$$

8.4 Calculation of degree of polymerization (DP) of the obtained polymer.

The number of growing chains is equal to the number of TsCl molecules (0.12 mmol)

At the first stage, 7.3 mmol of MMA was consumed (0.73 / 100.1).

The total quantity of monomers at the beginning of the 2nd stage is $23.7 + 23.7 = 47.4$ mmol.

Since the monomers have the same reactivity, they will be involved in polymerization with the same rate.

Quantity of monomers consumed during the second stage is

$$\Delta n = n_0(1 - \exp(-k_p[R\cdot]t)) = 47.4(1 - \exp(-1616 \times 1.76 \times 10^{-7} \times 1295)) = 14.6 \text{ mmol.}$$

Totally $7.3 + 14.6 = 21.9$ mmol of monomers was polymerized during two stages.

$$\text{DP} = 21.9 / 0.12 = 182.5$$

DP = 182 – 183 (all answers within this range are credited)

8.5 Structure of the obtained polymer.

The product of polymerization is a block copolymer because it was obtained by sequential polymerization on living chains.

The first block is built of MMA units solely. The DP is $7.3 / 0.12 = 60.8 \approx 61$ monomer units.

The second block is obtained by copolymerization of two competing monomers with the same reactivity. So, it is a statistical copolymer. Fractions of A and B in the 2nd block are equal because their concentrations in the reaction mixture at the beginning

of the 2nd stage were equal. The DP of the 2nd block is $183 - 61 = 122$ monomer units (121 is also correct if the total DP in **8.2.2** is 182).

Ts-A₆₁-block-(A-stat-B)₆₁-Cl or Ts-A₆₁-block-(A₆₁-stat-B₆₁)-Cl

8.6 Assignment of NMR signals to substructures given in the Answer Sheet.

	a, b, g
	c
	d
	e
	f

8.7 Determination of molar fractions of units C and D and molecular weights of P₁ and P₂.

Intensity of multiplets b and g is 40.2, so intensity per 1 proton is $40.2 / 4 / 58 = 0.173$ for both copolymer spectra

Intensity of multiplet c is 13.0, which is equivalent to $13.0 / 0.173 = 75$ protons. Taking into account that each styrene ring has 5 aromatic protons, DP of styrene block is $75 / 5 = 15$.

Molar fraction of styrene units in P₁ is $15 / (15 + 58) = 20.5 \%$

Intensity of multiplet d is 10.4, which is equivalent to $10.4 / 0.173 = 60$ protons. Since each monomer unit of p-chloromethylstyrene has 4 protons, DP of PCS is $60 / 4 = 15$.

Molar fraction of D is $15 / (15 + 58) = 20.5\%$

$$M(P_1) = 15.03 + 58 \times 44.05 + 72.06 + 15 \times 104.15 + 35.45 = \mathbf{4240}$$

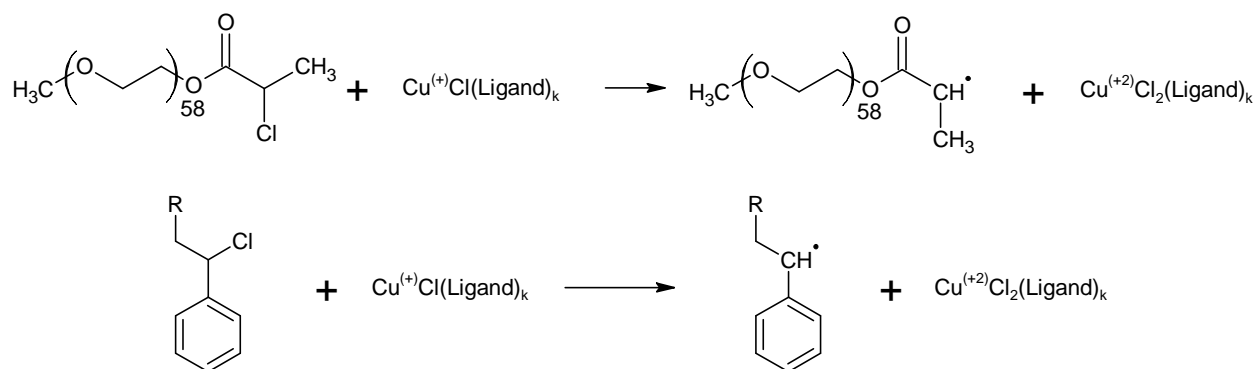
$$M(P_2) = 15.03 + 58 \times 44.05 + 72.06 + 15 \times 152.62 + 35.45 = \mathbf{4967}$$

$$M(P_1) = 4240 \quad ; \quad M(P_2) = 4967$$

$$n(C) = 20.5\% \quad ; \quad n(D) = 20.5\%$$

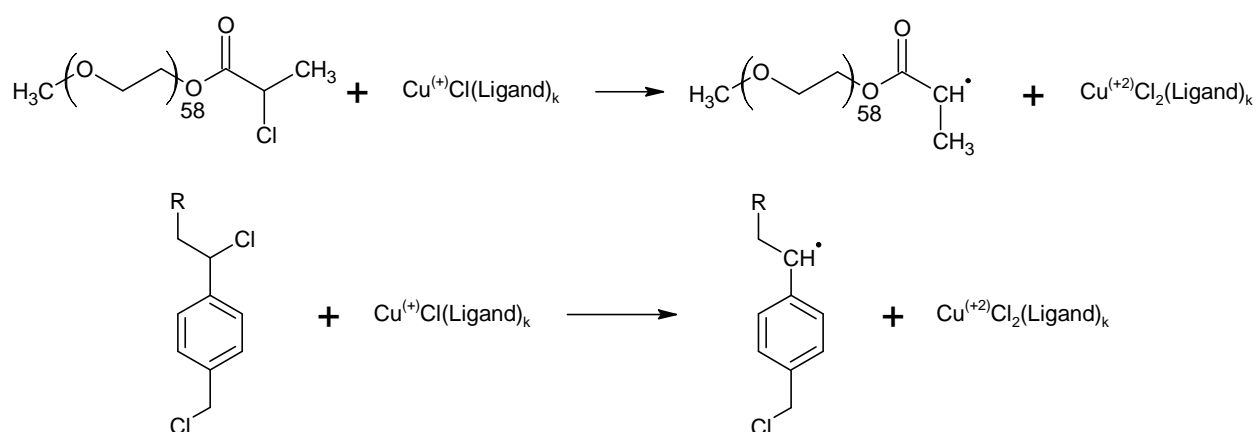
8.8 All possible reactions of activation occurring during the synthesis of P₁ and P₂.

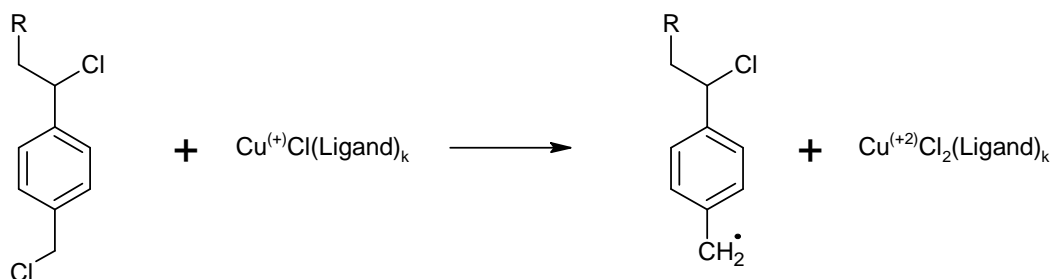
P₁:



Here R is used for the macroinitiator fragment with one or several styrene units attached.

P₂:





Here R is used for the macroinitiator fragment with one or several p-chloromethylstyrene units attached.

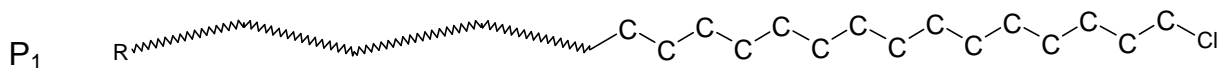
8.9 The structure of P₁ and one of possible structures of P₂

P₁ is a block copolymer of PEO and PS. The PS block contains 15 units.

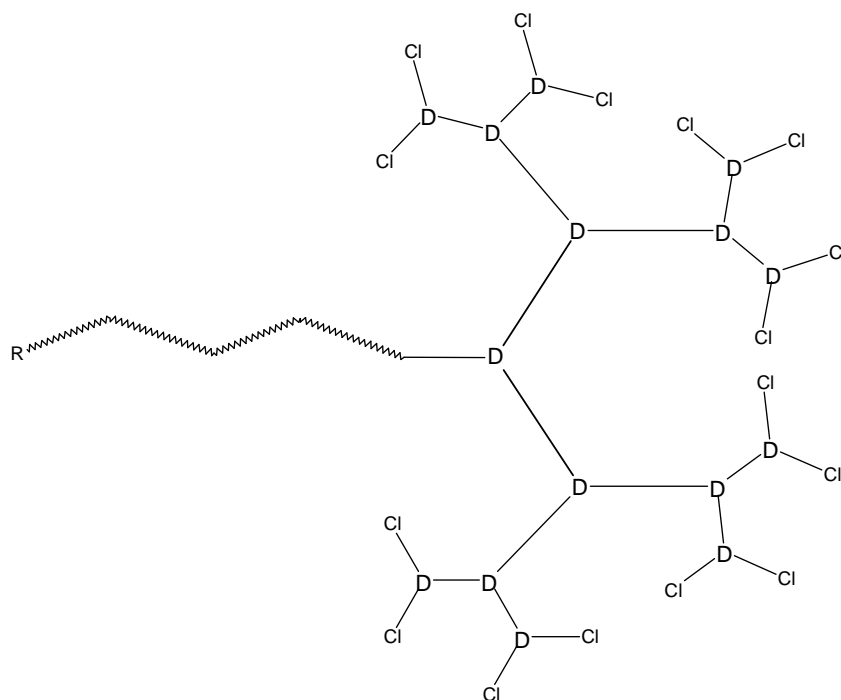
P₂ is a block copolymer composed of PEO block and branched styrene block.

The integral intensity of multiplet f is 2.75, so $2.75/0.173=15.9$, that is about 16 protons or 8 chloromethyl groups.

d) If there is no branching in molecule P₂, it would contain 15 chloromethyl groups. Each branching reduces the number of such groups by 1. Thus P₂ has $15 - 8 = 7$ branchings. Every structure with 7 branchings is correct if each monomer unit is linked with not more than 3 other monomer units



P₂

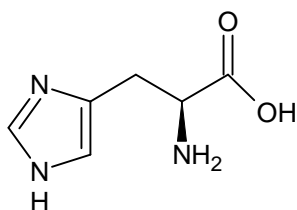


PRACTICAL PROBLEMS

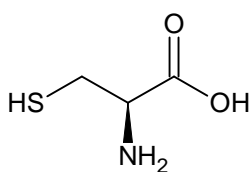
PROBLEM 1 (Practical)

Ion-exchange chromatography of amino acids

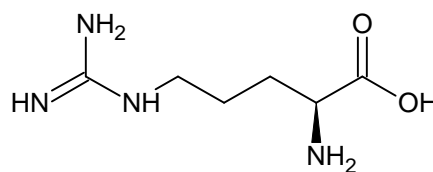
Ion-exchange chromatography is an important analytical and preparative method, which allows fractioning of charged substances. Interaction of ionic groups of the substances with counterions attached to the resin is behind the method. In this task you will have to carry out separation of a given mixture of three amino acids followed by quantitative assay of individual amino acids eluted from the column by using specific chromogenic reactions. Since queues of students are possible at spectrophotometers, we strongly suggest you starting the exam with Problem 1.



His



Cys



Arg

Three amino acids (see the structures above) are present in the mixture. These are histidine, cysteine, and arginine. Cross-linked sulfonated polystyrene is used as a cation-exchange resin (see the picture of the system below). At the beginning of the experiment the column is equilibrated with Eluent 1 (*pH* 4.9).

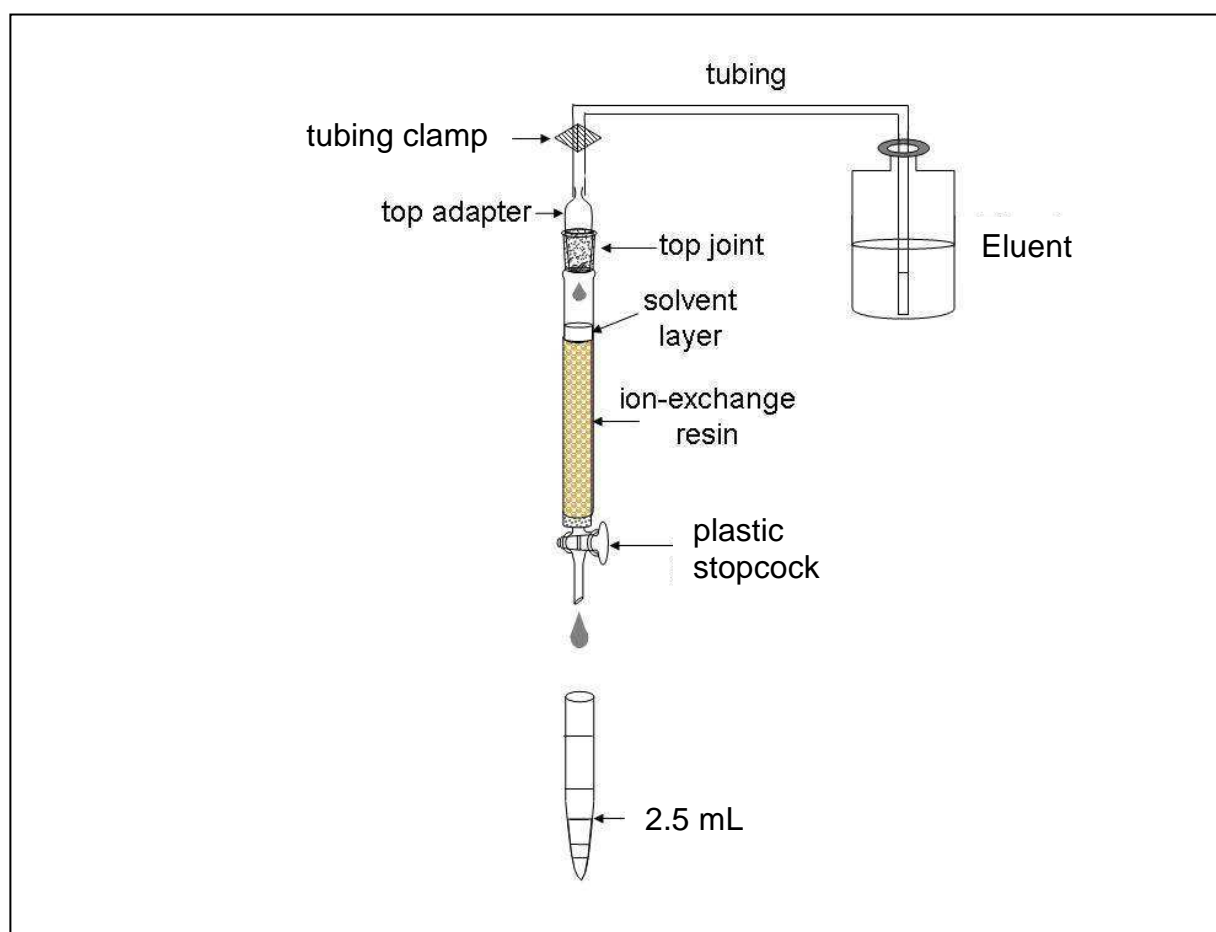
Procedure

Chromatography. Step 1

Apply the given solution of a mixture of amino acids to the column. First, open the stopcock to allow the solvent in the column draining into the Erlenmeyer flask labelled "Waste" so that the solvent is level with the top of packing material, still preventing the resin surface from drying off. Close the stopcock and carefully add the analyzed solution to the top of the column by using a syringe. Open the stopcock and let the sample soak inside the gel (drain the solvent into the "Waste" flask). Close the stopcock and add about 1 cm³ of Eluent 1 (corresponds to ~ 1 cm of liquid in the column) by carefully releasing the

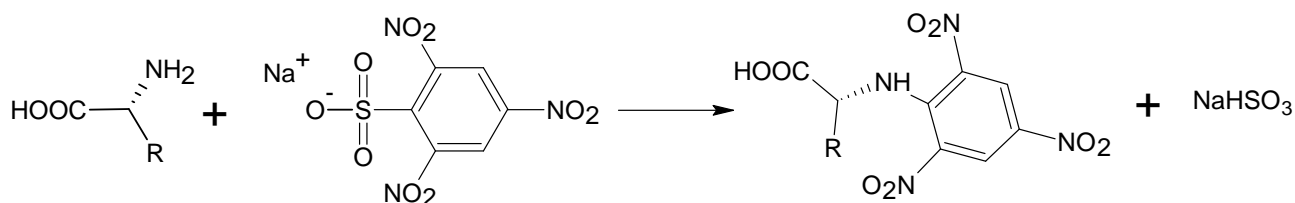
tubing clamp. Attach the top joint tightly, fixing the column with one hand and the adaptor with the other (be sure that the joint is fitted closely to the column). Replace the "Waste" flask at the stand with the test tubes in the rack. Release the tubing clamp and open the stopcock to let the eluent flow down through the column. Proceed with elution. (Always pen the stopcock to start elution and close the stopcock to stop it).

Collect the fractions in the test tubes up to the volume of 2.5 cm³ (as shown in the Picture). If needed, label them with marker. After collecting each 4 to 8 fractions stop elution and carry out qualitative analysis of the collected samples.



Qualitative analysis of samples

Qualitative assay of amino acids is based on the reaction of their α -amino groups with sodium 2,4,6-trinitrobenzene sulfonate (TNBS):



The assay is carried out in the wells of a polystyrene plate, each well corresponding to a definite test tube. Before starting the assay, mix 1 cm³ of TNBS solution with 10 cm³ of carbonate buffer solution and place 0.1 cm³ of the resulting mixture into half of the plate wells (from A1 to H5). Then add 0.1 cm³ of the analyzed fraction into a well. Start with A1 well and continue with B1, C1, etc (move top to bottom and left to right). If an amino acid is present in the analyzed fraction, intense yellow coloration will develop in the corresponding well within 3 min. Use the coloration in the first well as the reference. To reliably estimate the coloration, place the plate on the white sheet of paper.

Note: all aliquots of 0.1 cm³ should be added by using the pipettor. We expect you to use one tip for all fractions of a single peak.

1.1 a Draw the profile of coloration intensity (qualitatively) on the plate sketch in the Answer Sheet. Use the following symbols: (-) – no coloration, 1 – weak coloration, 2 – moderate coloration and 3 – intense coloration. Keep drawing the profile during the whole chromatography process.

Continue collecting fractions and analyzing them until you get at least two wells with coloration as in A1 well, which will indicate that the first amino acid has left the column completely (end of the first peak).

Chromatography. Step 2

As soon as you are finished with collecting the first peak, change to Eluent 2. To do so, close the stopcock, fix the tubing clamp (Important!), disconnect the tubing leading to the bottle with Eluent 1 and connect the tubing leading to the bottle with Eluent 2. Attach the top joint tightly.

1.1 b Indicate when the eluents have been changed by drawing lines between the corresponding wells on the plate sketch.

Continue elution, collecting fractions and carrying out qualitative analysis of samples as described above.

Chromatography. Step 3

As soon as you are finished with collecting the second peak, change to Eluent 3 as described in Step 2. Continue chromatography until the third amino acid leaves the column completely.

Stop chromatography by closing the stopcock and fixing the clamp.

Based on the results of qualitative analysis, choose the fractions which contain the amino acids.

1.1 Write down in the Answer Sheet the labels of wells corresponding to the chosen fractions.

1.2 Combine the fractions from each peak and measure the volumes of combined fractions using a measuring cylinder. Report the volumes of combined fractions excluding amounts used for the qualitative analysis. Write down the obtained results in the Answer Sheet.

Pour combined fractions in the amber glass vials labelled "Peak 1", "Peak 2", "Peak 3". Prepare samples for quantitative spectrophotometric analysis as described below.

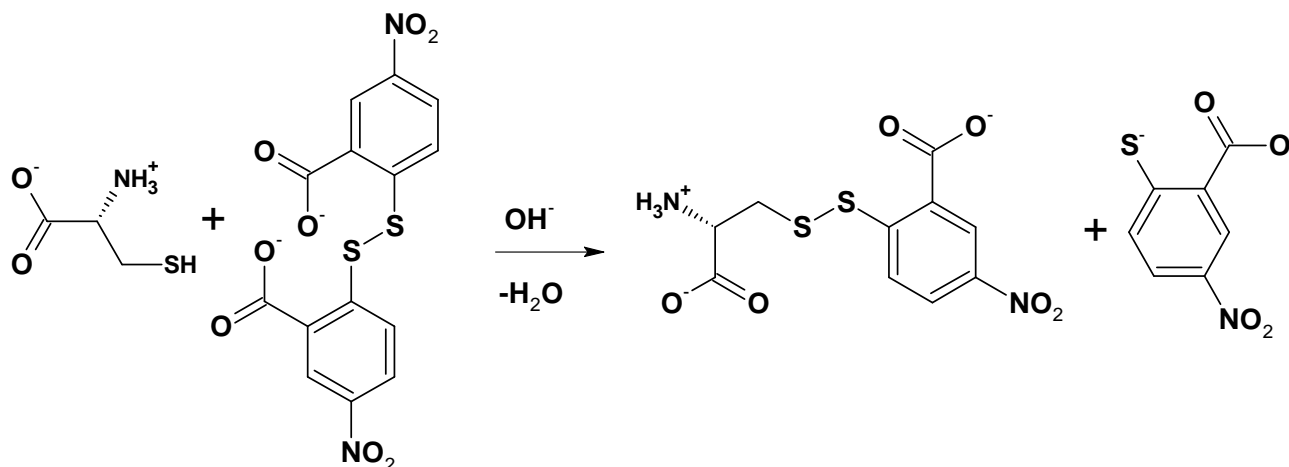
When finished with Practical exam, close the vials and leave them on the table. The combined fractions will be subsequently analyzed by lab staff.

Spectrophotometric analysis

For each probe, you should submit two cells to the operator. Prepare the probes as follows.

Important! When storing, always put cell in the cell holder! All cells have 2 ribbed and 2 working vertical surfaces. While operating with cells, do not touch working surfaces, otherwise you may get incorrect values of absorbance.

Assay 1 (peak 1). Cysteine concentration is determined by the Ellmann reaction:



Test tube A₁ (Reference).

Place 0.1 cm³ of Eluent 1 from plastic microtube into a test tube and add 2.9 cm³ of Ellmann reagent (DTNB).

Test tube B₁ (Sample).

Place 0.1 cm³ of the analyzed solution into a test tube and add 2.9 cm³ of Ellmann reagent (DTNB).

Mix the contents of the test tubes thoroughly and transfer each mixture to the corresponding cells labelled A₁ (for reference) and B₁ (for sample).

Assay 2 (peak 2). Determination of histidine concentration is based on the ability of imidazole moiety to react with diazonium compounds (Pauli reaction).

Test tube A₂ (Reference).

Place 2.8 cm³ of Tris-HCl buffer solution into a test tube, add 0.1 cm³ of Eluent 2 from plastic microtube and 0.1 cm³ of Pauli reagent.

Test tube B₂ (Sample).

Place 2.8 cm³ of Tris-HCl buffer solution into a test tube, add 0.1 cm³ of the analyzed solution and 0.1 cm³ of Pauli reagent.

Mix the contents of the test tubes thoroughly and transfer each mixture to the corresponding cells labelled A₂ (for reference) and B₂ (for sample).

Assay 3 (peak 3).

Determination of arginine concentration is based on the ability of guanidinium moiety to react with some phenols under alkaline and oxidative conditions (Sakaguchi reaction).

Test tube A₃ (Reference).

Place 0.1 cm³ of Eluent 3 into a test tube and add 1.5 cm³ of 10 % NaOH solution, 1 cm³ of 8-hydroxyquinoline solution and 0.5 cm³ of sodium hypobromite solution.

Test tube B₃ (Sample).

Place 0.1 cm³ of the analyzed solution into a test tube and add 1.5 cm³ of 10 % NaOH solution, 1 cm³ 8-hydroxyquinoline solution and 0.5 cm³ of sodium hypobromite solution.

Shake the test tubes vigorously for 2 min (**Important!**) and observe formation of orange colour. Add 0.2 cm³ of 8 M urea solution to each test tube, mix the contents and transfer about 3 cm³ of each mixture to the corresponding cells labelled A₃ (for reference) and B₃ (for sample).

All mixtures should be analyzed by spectrophotometry not earlier than 10 min and not later than 2 h after preparation. Submit the set of 6 cells to the spectrophotometer operator. In case of a queue at the spectrophotometer, ask the operator to put your student code on the list at the signboard. You will be invited by the operator in due time. Meanwhile, you can answer the theoretical question and start fulfilling Problem No 2.

In case your sample(s) have not been subjected to studies within the proper time interval (which is quite improbable), prepare the sample(s) afresh.

Get the print-offs with the spectra of your samples and check it. Sign the print-offs and get the operator's signature.

1.3 Determine absorbance at the corresponding wavelengths and calculate the content (in mg) of each amino acid in the mixture you were given. The optical length is 1.0 cm. Complete the Answer Sheets taking into account that one mole of each amino acid gives one mole of the corresponding product.

Reference data:

The values of extinction coefficients: Product of Ellmann reaction: 13600 M ⁻¹ cm ⁻¹ at 410 nm Product of Pauli reaction: 6400 M ⁻¹ cm ⁻¹ at 470 nm Product of Sakaguchi reaction: 7700 M ⁻¹ cm ⁻¹ at 500 nm	Molar masses of the amino acids. Cysteine: 121 g mol ⁻¹ Histidine: 155 g mol ⁻¹ Arginine: 174 g mol ⁻¹
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1.4 Draw three resonance structures of the species responsible for mixture coloration as a result of Ellmann reaction.

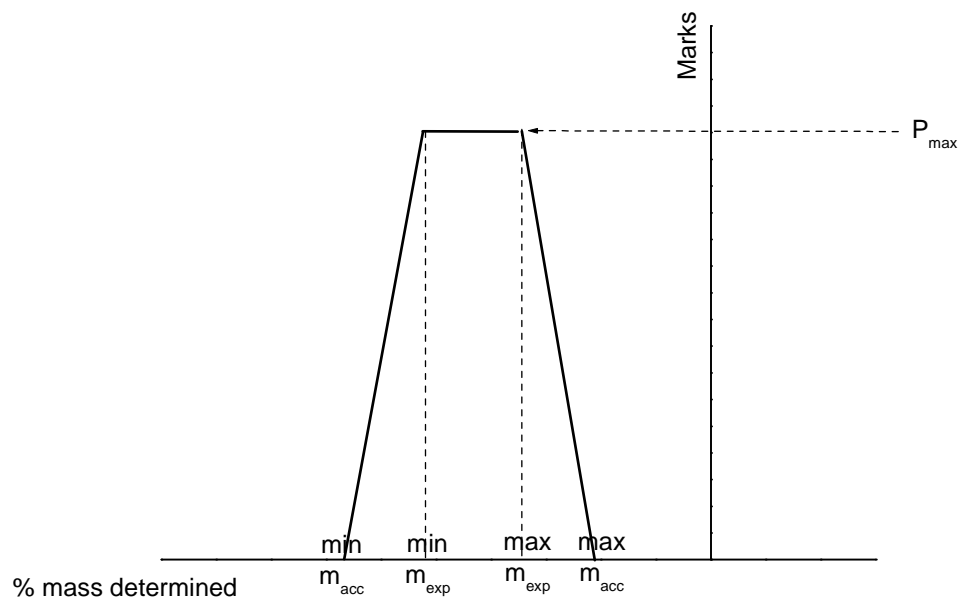
SOLUTION

1.2 – 1.3

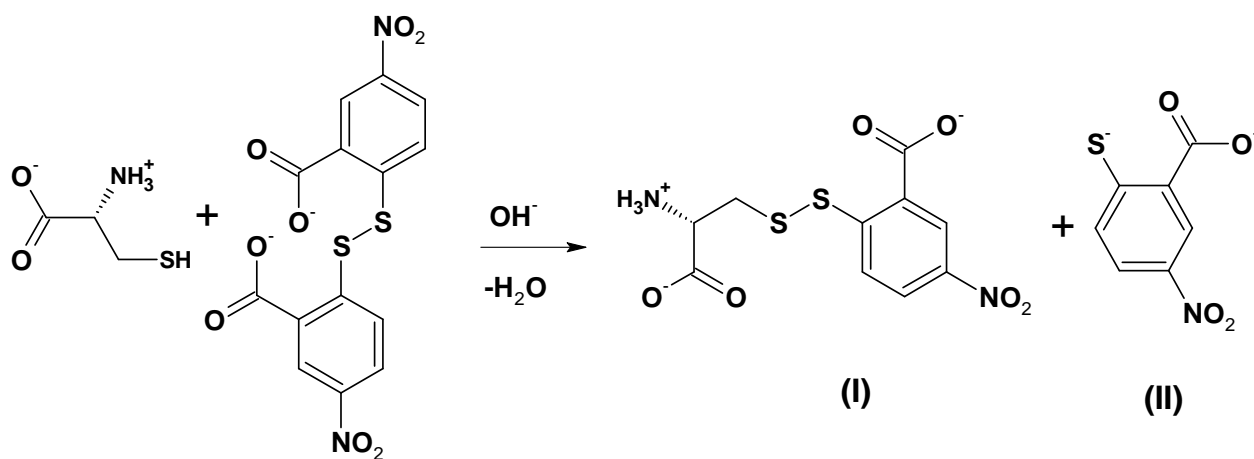
$$\text{Content of an amino acid} = \frac{A_{\lambda} n V M}{\epsilon l},$$

A_{λ} is the absorbance of the sample calculated from the spectra, l is the optical length (1.0 cm), n is the dilution factor determined as a ratio of the aliquot of analyzing solution (0.1 cm³) and the final volume of the sample in the cells, V is the volume of the combined fraction from the corresponding peak, and M is the molar mass of the amino acid.

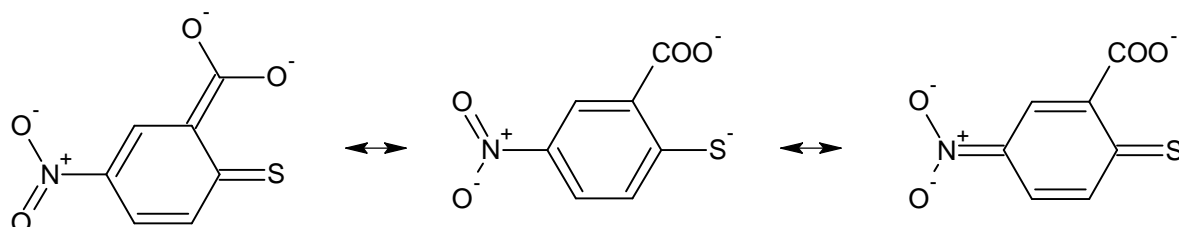
Content of each amino acid is determined by using the following plot (values recalculated from volumes reported by students and absorbance values recorded by spectrophotometer).



1.4 As it is given in the task text, mixed disulfide and 2-thio-5-nitrobenzoic acid are formed in the reaction.



Under slightly alkaline conditions, thiol group of (II) dissociates, and thiophenolate-anion is formed. Resonance structures can be realized for this compound:



The electronic structure of asymmetrical disulfide (I) does not differ considerably from that of the original Ellmann reagent. Therefore, it can be concluded that the compound responsible for coloration is thiophenolate-anion (a form containing C=S bond).

PROBLEM 2 (Practical)

Determination of Carbonate and Hydrogen Phosphate in an Abrasive Sample

Na_2CO_3 , CaCO_3 and Na_2HPO_4 are the main constituents of abrasive powders. In this task you will have to determine carbonate and hydrogen phosphate ions in an abrasive sample by two acid-base titrations.

First, the exactly known amount of hydrochloric acid (taken in an excess) is added to the sample. As a result, hydrogen phosphates are transformed into H_3PO_4 , whereas carbonates into CO_2 which is further removed by boiling. Calcium ions initially present in the sample pass into the solution. Because of possible interference in subsequent analysis, they are precipitated as CaC_2O_4 and filtered off prior to the titration.

Next, the phosphoric acid formed is subjected to two titrations with pre-standardized NaOH solution and two different indicators: Bromocresol Green (BCG) and Thymolphthalein (TP). First, H_3PO_4 (and excess of HCl) is titrated to H_2PO_4^- ion, the endpoint lying in slightly acidic medium (pH of ~ 4.5). It corresponds to the colour change of BCG from yellow to blue. The second titration proceeds till HPO_4^{2-} is formed. The endpoint of the second titration corresponds to the color change of TP from colourless to blue (moderately alkaline medium, pH of ~ 10).

The content of CO_3^{2-} ions in the sample is calculated by finding the difference between:

- the amount of the titrant equivalent to the initial amount of HCl (taken for the sample dissolution) and
- the amount of the titrant corresponding to the second endpoint (TP).

The content of HPO_4^{2-} is calculated by finding the difference between the amounts of the titrant consumed to achieve two endpoints (TP and BCG).

Procedure

Step 1. Dissolution of the sample and removal of CO_2

To the sample of the abrasive powder in a beaker covered with watch glass add 10.00 cm^3 (exactly, with a pipette! Carefully, not removing the glass and avoiding losses because of splashing!) of ca. 1 mol dm^{-3} HCl (see the exact concentration of the acid on the label). After the most intensive stage of gas evolution is completed, heat

carefully the solution in the beaker (covered with watch glass) on a heating plate until the gas evolution stops. Then bring the solution to boiling and boil it carefully for 2 – 3 min.

Step 2. Precipitation of calcium

Remove the beaker from the plate; wash the steam condensate from the watch glass down to the beaker with distilled water. Add 1 – 2 cm³ of 15 % K₂C₂O₄ solution with measuring cylinder. Put the beaker aside until the most part of the precipitate is formed (usually takes 10 to 20 min). Spend this time for standardization of the titrant solution of NaOH (see the procedure hereunder).

Step 3. Standardization of NaOH solution

Place with a pipette 10.00 cm³ of HCl solution into a 100 cm³ volumetric flask, make up to the mark with distilled water and mix. Fill the burette with NaOH solution. Transfer with a pipette 10.00 cm³ of the diluted HCl solution from the volumetric flask to an Erlenmeyer flask. Add 1 – 2 drops of Thymolphthalein solution and titrate with NaOH solution until blue coloration stable on swirling for 5 – 10 s appears.

Here and after. Repeat the titrations as necessary. It is desirable that the highest and the lowest titrant volume values differ not more than by 0.10 cm³. Report all the final volume values with 0.01 cm³ accuracy.

2.1 a Complete the table in the Answer Sheet.

2.1 b Calculate the concentration of NaOH solution (in mol dm⁻³).

Step 4. Filtering off calcium oxalate

After the most part of CaC₂O₄ precipitates filter the precipitate off collecting the filtrate into a 100 cm³ volumetric flask. Slight turbidity in the filtrate is admissible, since small amounts of calcium oxalate do not interfere in the titration. Wash the filter with distilled water; make up the solution in the flask to the mark with distilled water and mix. Put the used filter into the waste basket.

Step 5. Sample titration against Bromocresol Green

Transfer with a pipette a 10.00 cm³ aliquot of the sample solution coming from the

step 4 from the volumetric flask to an Erlenmeyer one, and add 3 drops of BCG solution. Prepare in another Erlenmeyer flask a reference solution by adding 3 drops of 15 % NaH_2PO_4 solution and 3 drops of BCG solution to 15 – 20 cm^3 of distilled water. Titrate the sample solution with NaOH solution until the colour coincides with that of the reference solution.

2.2 Complete the table in the Answer Sheet.

Step 6. Sample titration against thymolphthalein

Transfer with a pipette a 10.00 cm^3 aliquot of the sample solution coming from the step 4 from the volumetric flask to an Erlenmeyer one. Add 2 drops of TP solution and titrate with NaOH solution until blue coloration stable on mixing for 5 – 10 s appears.

2.3 Complete the table in the Answer Sheet.

Step 7. Calculations

2.4 Calculate the mass of CO_3^{2-} in the sample.

2.5 Calculate the mass of HPO_4^{2-} in the sample.

Step 8. Additional questions to the problem

Answer the additional questions in the Answer Sheets.

2.6a Indicate one reaction (write down the equation) for a process interfering in the sample analysis you have carried out in the presence of Ca^{2+} .

2.6b A list of mistakes possible at different steps is given in the table in the answer sheet.

Indicate which of the mistakes can lead to errors in CO_3^{2-} and/or HPO_4^{2-} content determination. Use the following symbols: “0” if no error is expected, “+” or “–” if the result is higher (positive error) or lower (negative error) than the true one.

SOLUTION

2.1 a, 2.2, 2.3

The values of the final volumes $V_{1,f}$, $V_{2,f}$, and $V_{3,f}$, (as reported in the Answer Sheet) were graded according to a scheme approved by the International Jury.

The values of $\Delta V_{\text{expected}}$ and $\Delta V_{\text{acceptable}}$ (in cm^3) are listed in the table below.

	$\Delta V, \text{cm}^3$	
	expected	acceptable
$V_{1,f}$	0.10	0.25
$V_{2,f}$	0.15	0.40
$V_{3,f}$	0.15	0.40

2.1 b Calculation of NaOH concentration

$$c(\text{NaOH}) = \frac{c(\text{HCl}) \times V(\text{HCl}) \times V(\text{aliquot})}{V(\text{flask}) \times V(\text{NaOH})} = \frac{1.214 \text{ mol dm}^{-3} \times 10.00 \text{ cm}^3 \times 10.00 \text{ cm}^3}{100.0 \text{ cm}^3 \times V_{1,f} \text{ cm}^3}$$

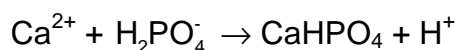
2.4 Calculation of the mass of CO_3^{2-}

$$\begin{aligned} m(\text{CO}_3^{2-}) &= M(\text{CO}_3^{2-}) \times 1/2 \times \frac{c(\text{NaOH}) \times (V_{1,f} - V_{3,f}) \times V(\text{flask})}{V(\text{aliquot})} = \\ &= 60.01 \text{ g mol}^{-1} \times 1/2 \times \frac{c(\text{NaOH}) \text{ mol dm}^{-3} \times (V_{1,f} - V_{3,f}) \text{ cm}^3 \times 100.0 \text{ cm}^3}{10.00 \text{ cm}^3} \times 0.001 \text{ dm}^3/\text{cm}^3 = \end{aligned}$$

2.5 Calculation of the mass of HPO_4^{2-}

$$\begin{aligned} m(\text{HPO}_4^{2-}) &= M(\text{HPO}_4^{2-}) \times \frac{c(\text{NaOH}) \times (V_{3,f} - V_{2,f}) \times V(\text{flask})}{V(\text{aliquot})} = \\ &= 95.98 \text{ g mol}^{-1} \times \frac{c(\text{NaOH}) \text{ mol dm}^{-3} \times (V_{3,f} - V_{2,f}) \text{ cm}^3 \times 100.0 \text{ cm}^3}{10.00 \text{ cm}^3} \times 0.001 \text{ dm}^3/\text{cm}^3 = \end{aligned}$$

2.6 a



or

