CHEMISTRY: ART, SCIENCE, FUN

THEORETICAL EXAMINATION

PROBLEMS

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MOSCOW, RUSSIA

24848 characters in Problems and Answer Sheets

Official English version

General Directions

- Write your name and code number on each page of the answer sheet.
- You have 5 hours to fulfil the task. Failure to stop after the STOP command may result in zero points for the task.
- Write answers and calculations within the designated box.
- Use only the pen and the calculator provided.
- There are **18** pages of Problems (incl. Cover Sheet and Periodic Table) and **22** pages of Answer Sheet.
- An English-language version is available.
- You may go to the restroom with permission.
- After finishing the examination, place all sheets including Problems and Answer Sheet in the envelope and seal.
- Remain seated until instructed to leave the room.

Constants and useful formulas

Gas constant	$R = 8.314\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
Avogadro constant	$N_A = 6.022\cdot10^{23}\ \text{mol}^{-1}$
Planck constants	$h = 6.626\cdot10^{-34}\ \text{J}\cdot\text{s}$
	$\hbar = 1.055\cdot10^{-34}\ \text{J}\cdot\text{s}$
Speed of light	$c = 3.00\cdot10^{8}\ \text{m}\cdot\text{s}^{-1}$

Uncertainty relation	$\Delta x \cdot \Delta p \geq \frac{\hbar}{2}$
Gibbs energy of a condensed phase at pressure p	$G = pV + \text{const}$
Excess pressure caused by surface tension	$\Delta P_{\text{in}} = 2\sigma / r$
Relation between equilibrium constant and Gibbs energy	$RT \ln K = -\Delta_r G^\circ$
Gibbs energy at constant temperature	$\Delta G = \Delta H - T\Delta S$
Isotherm of a chemical reaction	$\Delta G = \Delta G^\circ + RT\cdot\ln Q$ with $Q = \frac{\text{product of } c(\text{products})}{\text{product of } c(\text{reactants})}$
Arrhenius equation	$k = A\exp\left(-\frac{E_A}{RT}\right)$
Osmotic pressure of a solution	$p = cRT$
Beer- Lambert law	$A = \log\frac{P_0}{P} = \varepsilon lc$

$V(\text{cylinder}) = \pi r^2 h$
$S(\text{sphere}) = 4\pi r^2$
$V(\text{sphere}) = \frac{4}{3}\pi r^3$

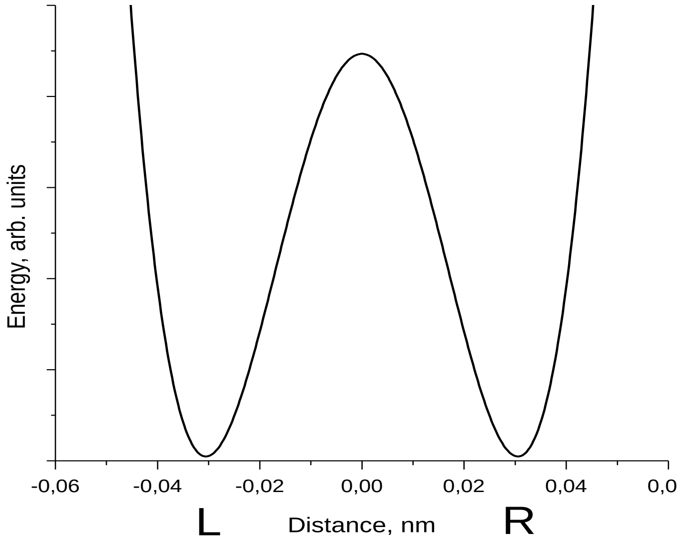
Problem 1. Proton tunneling

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.

1.1.1 *Draw the condensed formula of propanedial and the structures of two of its isomers, which can exist in equilibrium with propanedial.*

1.1.2 *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.

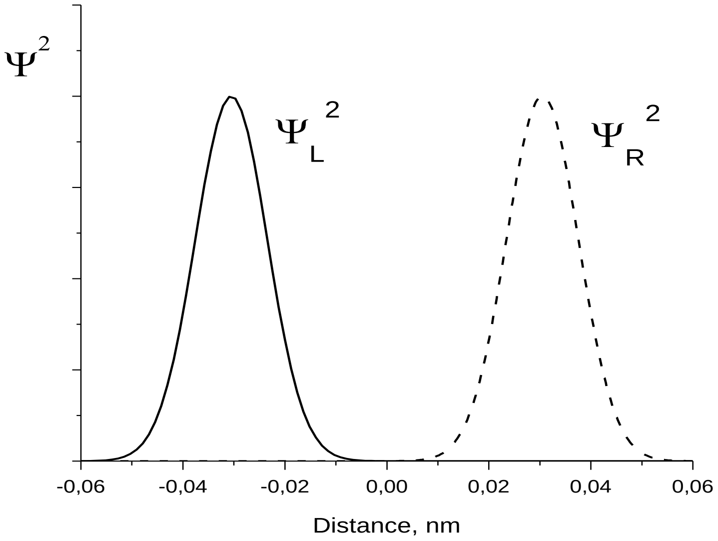


1.2.1 *Draw the structures corresponding to two minima on this curve.*

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

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

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



1.3.1 *Write down the expressions for the probability density at three moments: (a) t = 0, (b) t = π/(2ω), (c) t = π/ω. Sketch the graphs of these three functions.*

1.3.2 *Without calculations, determine the probability of finding the proton in the left well at t = π/(2ω)*

1.3.3 *How much time is required for a proton to move from one well to another? What is the proton mean speed during the transfer?*

1.3.4 *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* ***1.3.3*** *and draw a conclusion about the proton tunneling (choose one of the versions in the Answer Sheet).*

Problem 2. Nanochemistry

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

$$CO + 3H_2 \xrightarrow{Fe,\ Co} CH_4 + H_2O$$

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:

$$Co(s) + H_2O\ (gas) \rightleftharpoons CoO(s) + H_2\ (gas) \qquad (1)$$

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.

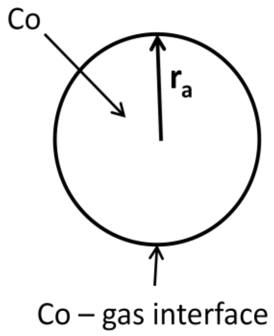


Fig. 1

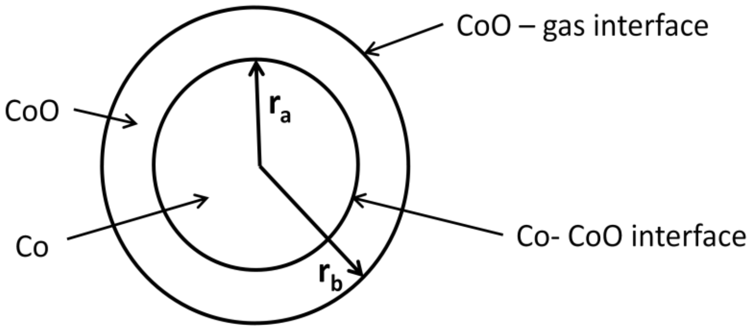


Fig. 2

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

$$G^0(r) = G^0(\text{bulk}) + \frac{2\sigma}{r}V$$

2.1.1 *Calculate the standard Gibbs energy* $\Delta_r G^0(1)$ *and the equilibrium constant for the reaction (1) at T = 500 K.*

2.1.2 *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 reaction (CO, CH_4, H_2, H_2O) 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%.

2.2.1 *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) a bulk phase
(b) spherical nanoparticles with r_a = 1 nm (Fig. 1).

2.2.2 *What would you suggest to protect Co nanoparticles from the spontaneous oxidation with the formation of bulk CoO at a constant ratio* $p(\mathrm{H_2O})/p(\mathrm{H_2})$ *and a constant temperature:*

(a) to increase r_a;
(b) to decrease r_a;
(c) 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(Co); V(CoO).

2.3.1 *Write down the expression for the standard molar Gibbs function of CoO.*

2.3.2 *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

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

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

2.3.3 *Express the standard Gibbs energy of the reaction (1)* $\Delta_\mathrm{r}G^0(1, r_\mathrm{a}, r_\mathrm{b})$ *in terms of $\sigma_{CoO\text{-}gas}$, $\sigma_{CoO\text{-}Co}$, r_a, r_b, V(Co); V(CoO) and* $\Delta_\mathrm{r}G^0(1)$.

2.3.4 *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* $\Delta_\mathrm{r}G^0(1, r_\mathrm{a}, r_\mathrm{b}) = \Delta_\mathrm{r}G^0(1, r_0)$. *Assume that* $\sigma_{\text{CoO-gas}} = 2\sigma_{\text{CoO-Co}}$ *. Which plot in the Answer Sheet describes correctly the dependence of* $\Delta_\mathrm{r}G^0(1, r_0)$ *on* r_0 *?*

2.3.5 *What would you choose to protect Co nanoparticles from the spontaneous formation of the external layer of CoO at a constant ratio* $p(\mathrm{H_2O})/p(\mathrm{H_2})$ *and a constant temperature:*

a) increase r_0
b) decrease r_0
c) change of r_0 has no effect.

Reference data:

Substance	ρ, g/cm^3	$\Delta_\mathrm{f}G^\circ_{500}$, kJ/mol
Co (s)	8.90	
CoO (s)	5.68	–198.4
H_2O (gas)		–219.1

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:

$$\mathrm{B} + 2\mathrm{X} \xrightarrow{k_1} 3\mathrm{X}$$

$$\mathrm{X} + \mathrm{D} \xrightarrow{k_2} \mathrm{P}$$

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

3.1.1 *Write down the overall reaction equation for this two-step mechanism. Write the rate equation for X.*

3.1.2 *Deduce a rate equation using steady-state approximation. Find the orders:*
(i) a partial reaction order with respect to B;
(ii) a partial reaction order with respect to D;
(iii) 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: [B] = [D] = const.

3.2.1 *Without solving the kinetic equation draw the kinetic curve [X](t) for the cases: 1)* $[X]_0 > k_2/k_1$*; 2)* $[X]_0 < k_2/k_1$*.*

3.2.2 *Without solving the kinetic equation draw the kinetic curve [X](t) for the case when the reaction proceeds in a closed vessel with the initial concentrations:* $[B]_0 = [D]_0$, $[X]_0 > k_2/k_1$*.*

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:

$$\mathrm{C_2H_6} + \mathrm{X} + \ldots \xrightarrow{k_1} 2\mathrm{X}$$

$$\mathrm{X} + \mathrm{Y} \xrightarrow{k_2} 2\mathrm{Y} + \ldots$$

$$\mathrm{C_2H_6} + \mathrm{Y} + \ldots \xrightarrow{k_3} 2\mathrm{P}$$

Under specific conditions this reaction displays oscillatory behavior.

Intermediates are peroxide $C_2H_6O_2$ and aldehyde C_2H_4O, P is a stable product.

3.3.1 *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, $\mathrm{cm^3 \cdot mol^{-1} \cdot s^{-1}}$	E_A, $\mathrm{kJ \cdot mol^{-1}}$
1	$1.0 \cdot 10^{11}$	90
2	$3.0 \cdot 10^{12}$	100

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

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 SO_2 and pyridine (C_5H_5N, Py) – Fischer reagent. The following reactions occur during the titration:

$SO_2 + CH_3OH + H_2O + I_2 = 2HI + CH_3OSO_3H$
$Py + HI = PyH^+I^-$
$Py + CH_3OSO_3H = PyH^+CH_3OSO_3^-$

Iodine content is usually expressed in mg of water reacting with 1 mL of the titrant solution (hereunder *T*, mg/mL), which equals the mass of water (mg) reacting with 1.00 mL 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 I_2 with SO_2 and H_2O occur in this case? Write down balanced reaction equation.*

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

4.2.1. 12.20 mL of Fischer reagent solution were used for titration of 1.352 g of sodium tartrate dihydrate $Na_2C_4H_4O_6{\cdot}2H_2O$.

4.2.2. A known amount of water (21.537 g) was placed into a 1.000 L volumetric flask which was filled by methanol up to the mark. For titration of 10.00 mL of the obtained solution, 22.70 mL of Fischer reagent solution were needed, whereas 2.20 mL of Fisher regent solution were used for titration of 25.00 mL of methanol.

4.2.3. 5.624 g of water were diluted by methanol up to a total volume of 1.000 L (solution **A**); 22.45 mL of this solution were used for titration of 15.00 mL of a Fischer reagent (solution **B**).
Then 25.00 mL of methanol (of the same batch as used for the preparation of solution **A**) and 10.00 mL of solution **B** were mixed, and the mixture was titrated by the solution **A**. 10.79 mL of the latter solution were spent.

4.3. *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 $Fe_2(SO_4)_3{\cdot}xH_2O$, 10.59 mL of iodine solution (*T* = 15.46 mg/mL) were consumed.

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

4.4.2. *Write down an equation of the overall reaction of $Fe_2(SO_4)_3{\cdot}xH_2O$ with the Fischer reagent.*

4.4.3. *Calculate the composition of the hydrate $Fe_2(SO_4)_3{\cdot}xH_2O$ (x = integer).*

Problem 5. A mysterious mixture (organic hide-and-seek game)

An equimolar mixture **X** of three colorless organic liquids **A**, **B**, **C** was treated by water with 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. To the mixture after hydrolysis a catalytic amount (one-two drops) of concentrated sulfuric acid was added, and after 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 to any of **A**, **B**, **C**.

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

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

5.1.3 *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%.*

^{1}H 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.

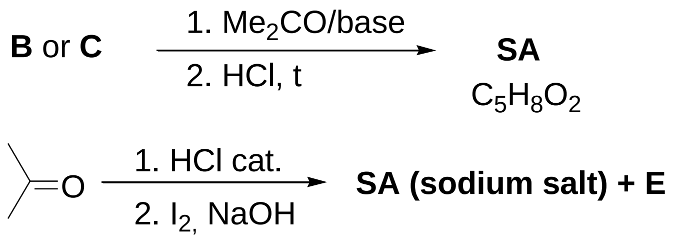
The same mixture **X** was subjected to alkaline hydrolysis. **A** remained unchanged, and was separated. The remaining solution after acidification and short boiling gave 2:3 (molar ratio) mixture of acetic acid and ethanol with evolution of gas.

The mixture **X** (3.92 g) was dissolved in diethyl ether and underwent hydrogenation in the presence of Pd on charcoal catalyst. 0.448 L (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.

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

5.2.2 *Which intermediate compounds are formed during the acidic hydrolysis of **C**, and 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).



(1)

(2)

5.3.1 *Determine the structure of senecioic acid and draw the reaction scheme leading to SA sodium salt from acetone.*
5.3.2 *Give structure of* ***E****.*

Problem 6. Silicates as the base of the Earth crust

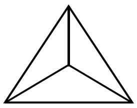
Silica and compounds derived from it, silicates, constitute ca. 90 % of the Earth crust substances. Silica gives rise to a beautiful material – glass. Nobody knows exactly how glass was discovered. There is a well-favored story related to Phoenician sailors who fused occasionally sea sand and soda ash.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

6.1.1 *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.

6.1.2. *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 $[Si_3O_9]^{n-}$ ion found in aqueous solution of silicates:

6.2.1 *Determine the charge (n).*

6.2.2 *Determine the number of oxygen atoms bridging adjacent tetrahedra.*

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

Charged monolayers with the composition $[Si_4O_{10}]^{m-}$ are found in kaolinite (clay).

6.2.4 *Using the same strategy as in **6.2.1-6.2.3**, depict a fragment of the layered structure joining 16 tetrahedra **(1)**. Note that 10 tetrahedra have shared vertices with 2 neighbors each, and the rest 6 have shared vertices with 3 neighbors each.*

Being placed into the LGL solution, salts of transition metals give rise to fancy "trees" tinted relevant to the color of the salt of the corresponding transition metal. Crystals of $CuSO_4 \cdot 5H_2O$ produce "trees" of blue color, whereas those of $NiSO_4 \cdot 7H_2O$ form green "trees".

6.3.1 *Determine the pH of 0.1 M aqueous solution of copper sulfate at 25°C, assuming that its hydrolysis occurs in small degree only. Use the value of the first acidity constant of* $[Cu(H_2O)_4]^{2+}$ $K_a^I = 1 \cdot 10^{-7}$ *M.*

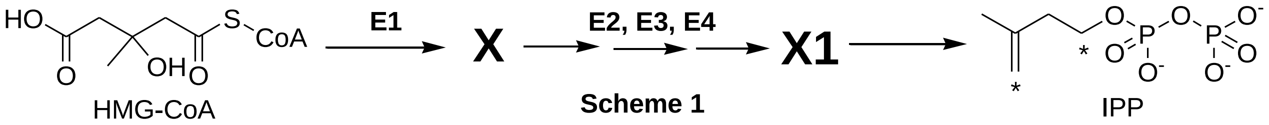
6.3.2 *Write down equation of a reaction between aqueous solutions of* $CuSO_4$ *and sodium metasilicate (LGL). Take into account the pH values of aqueous solutions of the salts.*

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.

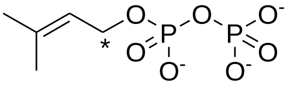
X is an optically active monocarbonic acid composed of atoms of only three elements. It is formed in organisms from (*S*)-3-hydroxy-3-methylpentanedioyl-coenzyme A (HMG-CoA). This reaction is catalyzed by enzyme **E1** (which catalyses two types of reactions) and does not involve water as a substrate. **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:



Scheme 1

7.1.1 *In the Answer Sheet, choose the reaction type(s) for* ***E1*** *and* ***E3****.*
7.1.2 *Draw the structure of* ***X*** *with stereochemical details and indicate absolute configuration (R or S) of the stereocenter.*

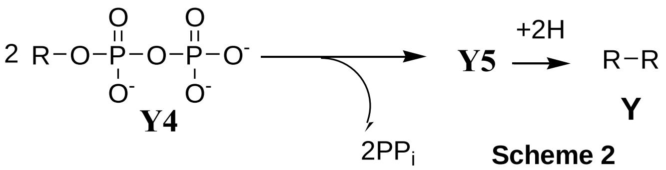
Y is an unsaturated acyclic hydrocarbon. Its reductive ozonolysis leads to a mixture of only three organic substances **Y1**, **Y2** and **Y3** in a molar ratio of 2:4:1. **Y** is formed as a result of a number of successive coupling reactions of two isomeric substances: IPP and dimethyl allyl pyrophosphate (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.



DAP

7.2.1 *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:



Scheme 2

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

7.2.2 *Determine molecular formula of* ***Y****, if it is known that* ***Y2*** *and* ***Y3*** *contain 5 and 4 carbon atoms, respectively.*
7.2.3 *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****.*

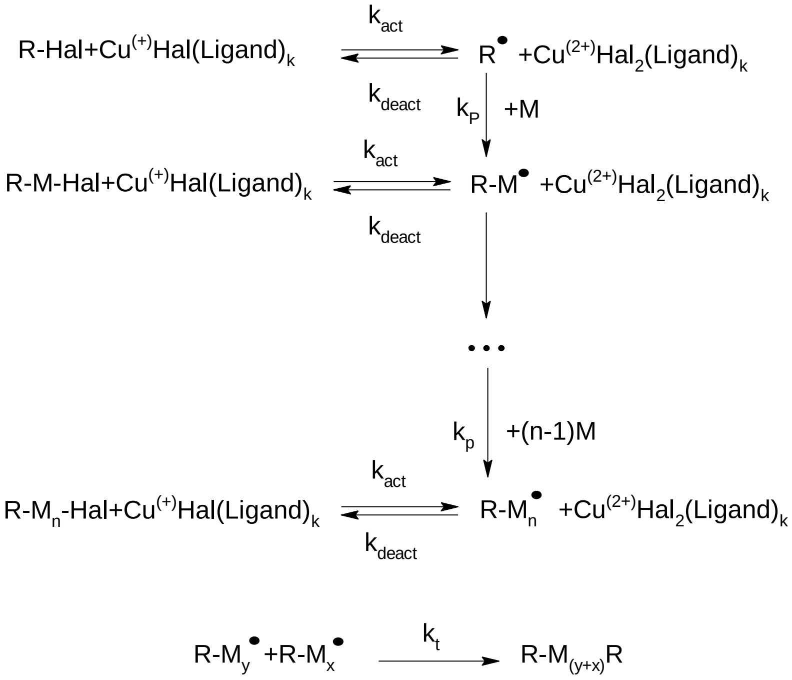
7.2.4 *Draw the product of coupling reaction of one IPP molecule with one DAP molecule (C-C bond can be formed only by carbon atoms marked with asterisks), if it is known that subsequent reductive ozonolysis of the product of the coupling reaction gives **Y1**, **Y2** and one more product, the latter 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.

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

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.

8.1.1 *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, where R' means any of R- or R-M_n- and X means Hal.*

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.

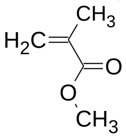
8.1.2 *Compare the rate of deactivation to the rates of ATRP elementary stages.*

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

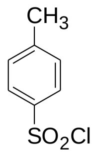
$$\ln\left(\frac{[M]}{[M]_0}\right) = -k_p \cdot [R^{\cdot}] \cdot t,$$

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

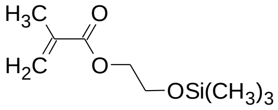
To prepare a polymer sample by using ATRP, catalytic amounts of CuCl, organic ligand (L) and 31.0 mmol of monomer (methylmethacrylate, or MMA) were mixed. The reaction was initiated by adding 0.12 mmol of tosyl chloride (TsCl). Polymerization was conducted for 1400 s. k_p is 1616 $L \cdot mol^{-1}s^{-1}$,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



MMA



TsCl



HEMA-TMS

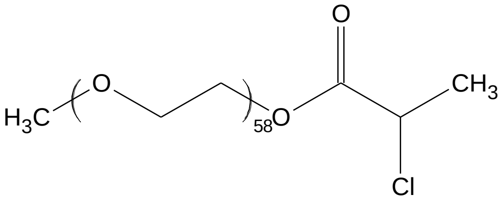
8.2.1 *Calculate mass (m) of the polymer obtained.*

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.

8.2.2 *Calculate degree of polymerization (DP) of the obtained polymer.*

8.2.3 *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, (A_{65}-graft-C_{100})-stat-B_{34} means that chains of polymer C are grafted on units A in the statistic 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.

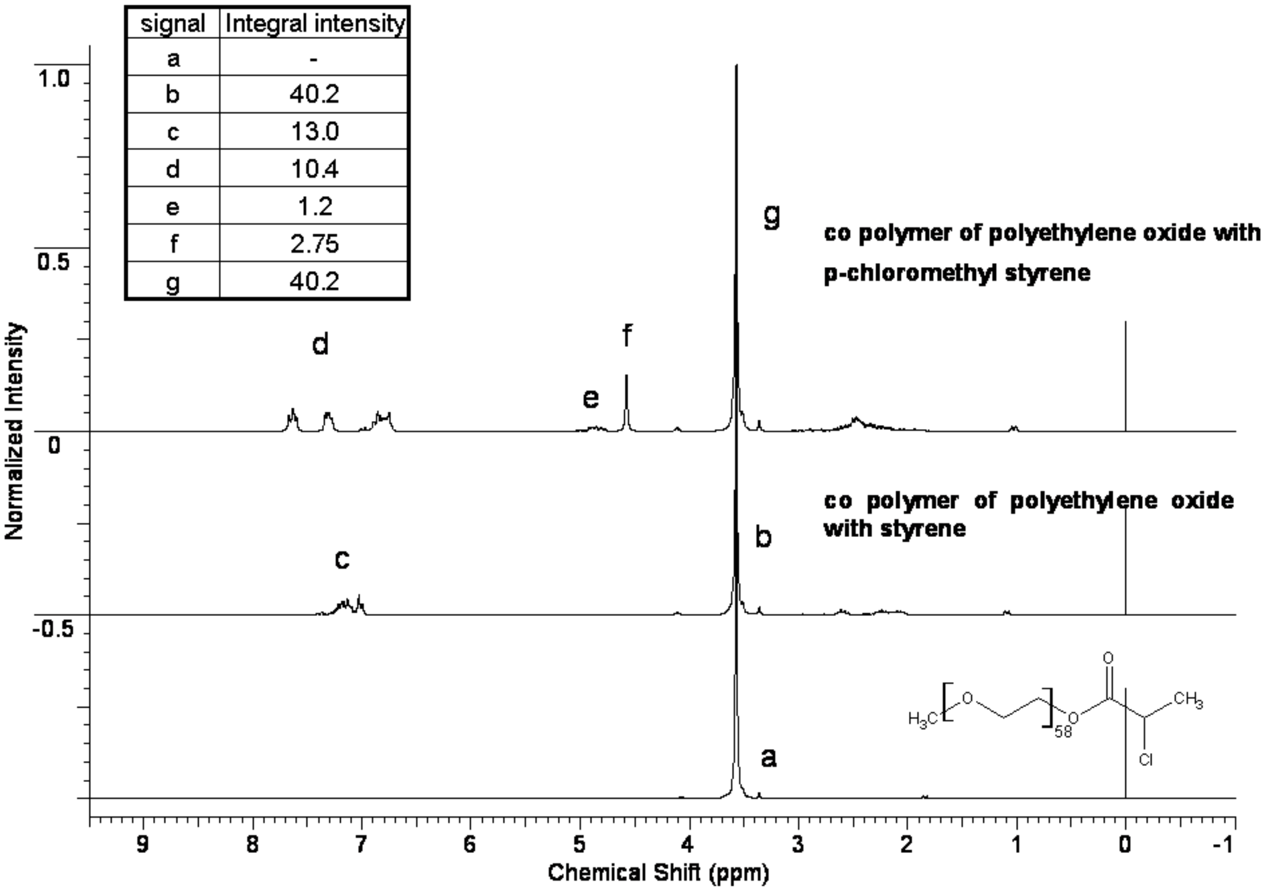
^{1}H NMR spectra of the macroinitiator, P1 and P2 are given below. Integral intensities of characteristic signals can be found in the table.

8.3.1 *Assign ^{1}H NMR signals to substructures given in the Answer Sheet.*

8.3.2 *Determine molar fractions of units C and D and molecular weights of P1 and P2.*

8.3.3 *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.*

8.3.4 *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.*



signal	Integral intensity
a	-
b	40.2
c	13.0
d	10.4
e	1.2
f	2.75
g	40.2

Periodic Table of Elements

with atomic masses

1 **H** 1.01																	2 **He** 4.00
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.88	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.61	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** 98.91	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.76	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.29
55 **Cs** 132.91	56 **Ba** 137.3	57-71	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.84	75 **Re** 186.21	76 **Os** 190.23	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.19	83 **Bi** 208.98	84 **Po** 208.98	85 **At** 209.99	86 **Rn** 222.02
87 **Fr** 223	88 **Ra** 226	89-103	104 **Rf** 261	105 **Db** 262	106 **Sg** 263	107 **Bh** 264	108 **Hs** 265	109 **Mt** 268									

57 **La** 138.91	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** 144.92	62 **Sm** 150.36	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04	71 **Lu** 174.97
89 **Ac** 227	90 **Th** 232	91 **Pa** 231	92 **U** 238	93 **Np** 237	94 **Pu** 244	95 **Am** 243	96 **Cm** 247	97 **Bk** 247	98 **Cf** 251	99 **Es** 252	100 **Fm** 257	101 **Md** 258	102 **No** 259	103 **Lr** 262

Official English version

CHEMISTRY: ART, SCIENCE, FUN

THEORETICAL EXAMINATION

SOLUTION and GRADING SCHEME

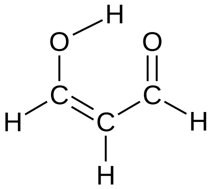
JULY 20, 2007
MOSCOW, RUSSIA

Official English version

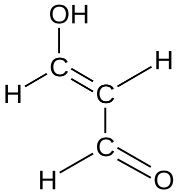
Problem 1. Proton tunneling

1.1.1 *The structures of propanedial and two of its isomers*

O=CH–CH$_2$–CH=O 1 mark



1 mark



1 mark

3 marks maximum

1.1.2

Acidic hydrogen atom is in CH$_2$ (in enol forms acidic hydrogen is in OH).

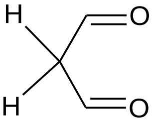
1 mark

Acidity of CH$_2$ group is caused by the stability of carbanion due to conjugation with two carbonyl groups. The first answer is correct.

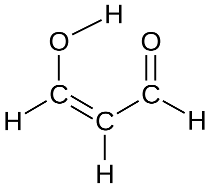
2 marks

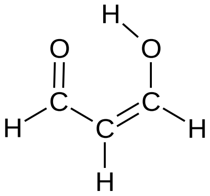
3 marks maximum

1.2.1 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:





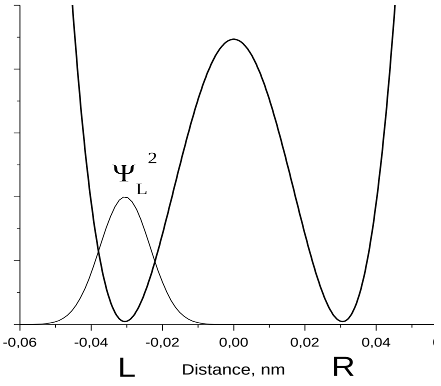
1 mark for each structure

2 marks maximum

1.3.1 *Expressions and plots of probability density*

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

The probability density is concentrated in the left well:

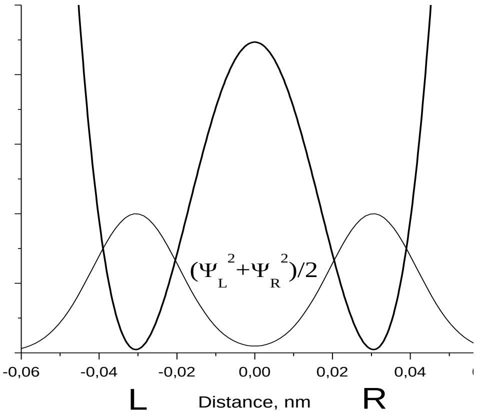


0.5 marks

(b) In the middle of the time interval

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

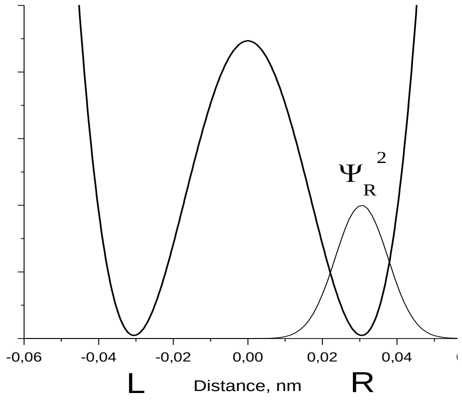
The probability density has a symmetric form, a proton is delocalized between two wells:



0.5 marks

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

The probability density is concentrated in the right well:



0.5 marks

4.5 marks maximum

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

2 marks

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

$$t = \frac{3.14}{6.48 \cdot 10^{11}} = 4.85 \cdot 10^{-12} \text{ s.}$$ 2 marks

The proton velocity:

$$V = \frac{0.06 \cdot 10^{-9}}{4.85 \cdot 10^{-12}} = 12 \text{ m/s.}$$ 2 marks

4 marks maximum

1.3.4

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).

1 mark

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

$$\Delta V = \frac{\hbar}{2m\Delta x} = \frac{1.055 \cdot 10^{-34}}{2 \cdot \frac{0.001}{6.02 \cdot 10^{23}} \cdot 0.03 \cdot 10^{-9}} \approx 1000 \text{ m/s.}$$ 3 marks

Comparing this uncertainty with the velocity 12 m/s 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*.

2 marks

6 marks maximum

Problem 2. Nanochemistry

2.1.1

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

$$\Delta_r G^0_{500}(1) = \Delta G^0_{f,500}(\mathrm{CoO,s}) - \Delta G^0_{f,500}(\mathrm{H_2O,g}) = -198.4 + 219.1 = 20.7\ \mathrm{kJ/mol}$$ 0.5 marks

$$K = e^{-\frac{\Delta_r G^0_{500}(1)}{RT}} = e^{-\frac{20700}{8.314\cdot 500}} = 6.88\cdot 10^{-3}$$ 0.5 marks

1 mark maximum

2.1.2

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

$$\Delta_r G^\circ_{500}(1, r_a) = G^0_{bulk,500}(\mathrm{CoO,s}) + G^0_{500}(\mathrm{H_2,g}) - G^0_{500}(\mathrm{H_2O,g}) - G^0_{sph}(\mathrm{Co}) =$$

$$= G^0_{500}(\mathrm{CoO,s}) + G^0_{500}(\mathrm{H_2,g}) - G^0_{500}(\mathrm{H_2O,gas}) - \left(G^0_{500}(\mathrm{Co,s}) + \frac{2\sigma_{\text{Co-gas}} V(\mathrm{Co})}{r_a} \right) =$$

$$= \Delta_r G^\circ_{500}(1) - \frac{2\sigma_{\text{Co-gas}} V(\mathrm{Co})}{r_a};$$

$$V(\mathrm{Co}) = \frac{M_{\mathrm{Co}}}{\rho(\mathrm{Co})} = \frac{10^{-6}\cdot 59.0}{8.90} = 6.6\cdot 10^{-6}\ \frac{\mathrm{m}^3}{\mathrm{mol}};$$

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

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

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

The equilibrium constant is calculated from the equation

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

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

2 marks maximum

2.2.1

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

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

$\Delta_r G^\circ_{500}(1)$ is 20.7 kJ/mol. For spherical cobalt particles with r_a = 1 nm $\Delta_r G^\circ_{500}(1, r_a)$ is 18.6 kJ/mol. Solid cobalt oxide can be formed spontaneously when Gibbs energy of reaction (1) is negative. The inequality for bulk cobalt is:

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

and for spherical cobalt nanoparticles with r_a = 1 nm:

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

$\Delta_r G^\circ_{500}(1)$ is 20.7 kJ/mol. For spherical cobalt particles with r_a = 1 nm $\Delta_r G^\circ_{500}(1, r_a)$ is 18.6 kJ/mol.

The minimum ratios $\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)}$ are 145.6 (a) and 87.7 (b), respectively.

The hydrogen pressure is

$$1\text{bar}\cdot 0.0015 = 1.5\cdot 10^{-3}\text{ bar}$$

The minimum pressures of water are
$1.5\cdot 10^{-3}\cdot 145.6 = 0.218$ bar (a) and $1.5\cdot 10^{-3}\cdot 87.7 = 0.132$ bar (b), for the bulk cobalt and for nanoparticles, respectively.

$H_2O\%$(bulk Co) = 21.8% $H_2O\%$(nanoparticles with $r_a = 1*10^{-9}$ m) = 13.2%.
We assume that bulk cobalt oxide is formed.

4 marks maximum

2.2.2

For the spontaneous oxidation

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

and

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

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 marks maximum

2.3.1

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

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

1 mark

2.3.2

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

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

$$= G^\circ(\text{Co,s}) + V\left(\text{Co}\right)\left(\frac{2\sigma_{\text{CoO-gas}}}{r_b} + \frac{2\sigma_{\text{CoO-Co}}}{r_a}\right)$$

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

5 marks maximum

2.3.3

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

$$\Delta_r G^0(1,r_a,r_b) = G^0_{sph}(\text{CoO},r_b) + G^\circ(\text{H}_2,gas) - G^\circ(\text{H}_2\text{O,gas}) - G^0_{sph}(Co,r_a,r_b) =$$

$$= G^\circ(\text{CoO,s}) + G^\circ(\text{H}_2,gas) - G^\circ(\text{H}_2\text{O,gas}) - G^\circ(\text{Co,s}) +$$

$$+\frac{2\sigma_{\text{CoO-gas}}}{r_b}V(\text{CoO}) - 2V(\text{Co})\left(\frac{\sigma_{\text{CoO-gas}}}{r_b} + \frac{\sigma_{\text{CoO-Co}}}{r_a}\right) =$$

$$= \Delta_r G^\circ(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_b}\left(V(\text{CoO}) - V(\text{Co})\right) - \frac{2\sigma_{\text{CoO-Co}}}{r_a}V(\text{Co})$$

2 marks maximum

2.3.4.

Under the assumptions made

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

$$= \Delta_r G^\circ(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_0}\left(V(\text{CoO}) - \frac{3}{2}V(\text{Co})\right)$$

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

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

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

3 marks maximum

2.3.5.

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

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

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.

2 marks maximum

Problem 3. Unstable reaction

3.1.1 The overall reaction equation

$$\mathrm{B} + \mathrm{D} \rightarrow \mathrm{P}$$ 1 mark

The kinetic equation for X

$$\frac{d[\mathrm{X}]}{dt} = k_1[\mathrm{B}][\mathrm{X}]^2 - k_2[\mathrm{D}][\mathrm{X}]$$ 1 mark

<u>2 marks maximum</u>

3.1.2 Under the steady-state conditions

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

whence

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

$$\frac{d[\mathrm{P}]}{dt} = \frac{k_2{}^2[\mathrm{D}]^2}{k_1[\mathrm{B}]}$$ 3 marks

The reaction order is 2 with respect to D, –1 with respect to B; the overall order is 1

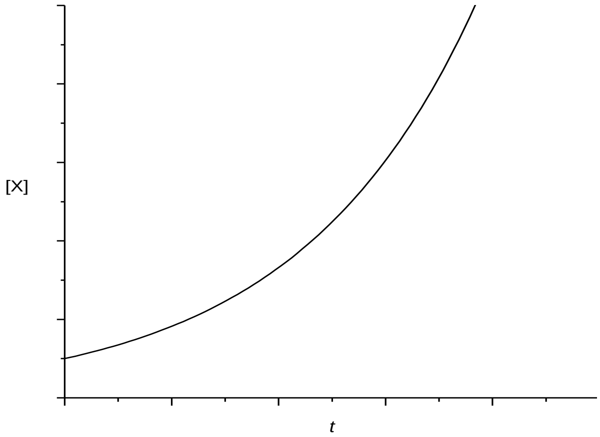
0.5 marks for each correct order

<u>4.5 marks maximum</u>

3.2.1 In an open system the initial reaction rate is:

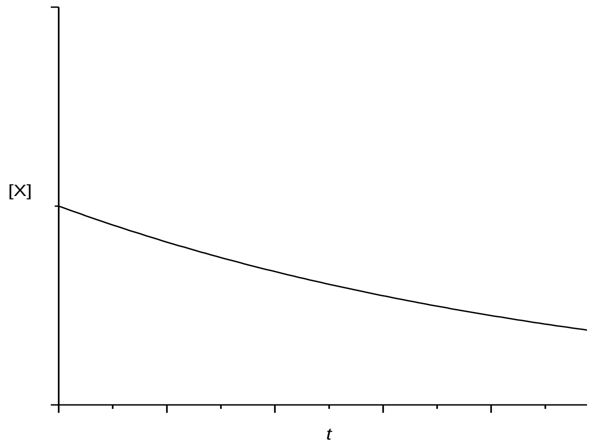
$$\frac{d[\mathrm{X}]}{dt} = [\mathrm{B}][\mathrm{X}]\left(k_1[\mathrm{X}] - k_2\right)$$

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



2 marks

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



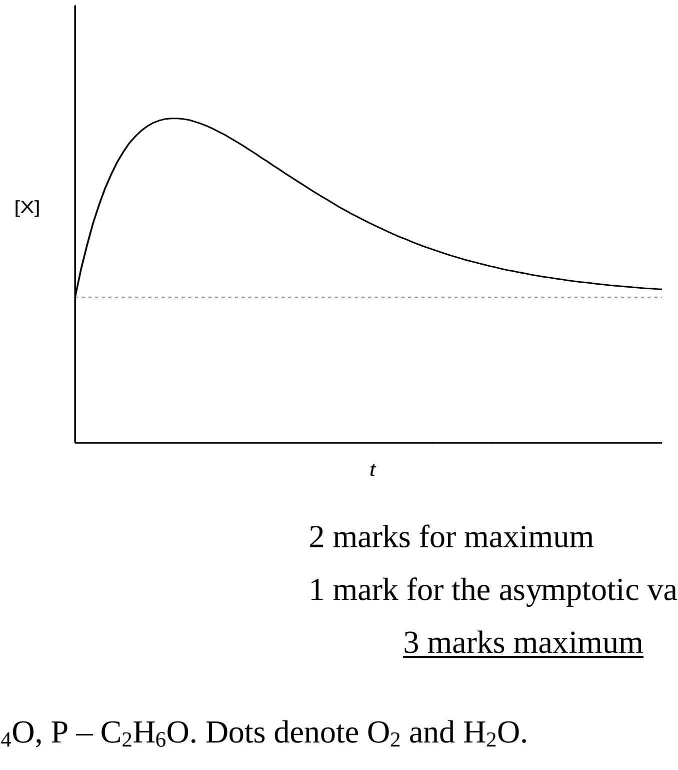
2 marks

4 marks maximum

3.2.2 In a closed system the initial reaction rate is:

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

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:



2 marks for maximum

1 mark for the asymptotic value

3 marks maximum

3.3.1 X – $C_2H_6O_2$, Y – C_2H_4O, P – C_2H_6O. Dots denote O_2 and H_2O.

$$C_2H_6 + C_2H_6O_2 + O_2 \rightarrow 2C_2H_6O_2$$
$$C_2H_6O_2 + C_2H_4O \rightarrow 2C_2H_4O + H_2O$$
$$C_2H_6 + C_2H_4O + H_2O \rightarrow 2C_2H_6O$$

0.5 marks for each unknown substance (X, Y, P, three blanks)

3 marks maximum

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

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

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

1 mark for the calculation
2 marks for the correct answer
3 marks maximum

Problem 4. Determination of water by Fischer titration

4.1. *Equation:*

$I_2 + SO_2 + 2\ H_2O + 4\ Py = 2\ PyHI + (PyH)_2SO_4$ 1 mark

(0.75 marks for not accounting for the formation of Py salts)

4.2.1. *T is equal to:*

$M(Na_2C_4H_4O_6 \cdot 2H_2O) = 230.05$ $2M(H_2O) = 36.04$

$m(H_2O) = 1.3520 \cdot 36.04 / 230.05 = 0.2118$ g = 211.8 mg

1 mark for the formula

$T = 211.8 / 12.20 = 17.36$ mg/mL

$T = 17.36$ *mg/mL*

0.25 marks for the correct result (within 2 digits)

<u>1.25 marks maximum</u>

4.2.2. *T is equal to:*

Your work:

Volume of iodine spent for 10 mL of pure $CH_3OH = 2.20 \cdot 10.00 / 25.00 = 0.88$ mL

0.5 marks for the correct formula of pure methanol titration)

$T = 21.537 \bullet 0.01 \bullet 10^3 / (22.70 – 0.88) = 9.87$ mg/mL

More exactly

10.00 mL of the solution contains $(1000-21.5) \times 10.00 / 1000 = 9.785$ mL of methanol

Volume of iodine spent for 9,785 mL of pure $CH_3OH = 2.20 \cdot 9,785 / 25.00 = 0.86$ mL

$T = 21.537 \bullet 0.01 \bullet 10^3 / (22.70 – 0.86) = 9.86$ mg/mL

1 mark for the formula of water titration, only 0.5 marks without subtracting 0.88

$T = 9.87$ *mg/mL* 0.25 marks for the correct result

<u>1.75 marks maximum</u>

4.2.3. *T is equal to:*

Your work:

Approach 1.

Let 1 mL of CH_3OH contain x mg H_2O, then 1 mL of **A** contains $((1.000 - 0.006)\cdot x + 5.624)$ mg H_2O.

$$\begin{cases} 15.00\cdot T = 22.45\cdot(0.994\cdot x + 5.624) & \text{– 1st titration,} \\ 10.00\cdot T = 25.00\cdot x + 10.79\cdot(0.994\cdot x + 5.624) & \text{– 2nd titration.} \end{cases}$$

Hence, $x = 1.13$ mg/mL, $T = 10.09$ *mg/mL* (10.10 without taking into account 0.994 factor)

Approach 2.

Let y mL of **B** be spent for the titration of water, contained in 1 mL of CH_3OH.

Then $T = \dfrac{22.45\cdot 5.624}{15.00 - 22.45\cdot 0.994\cdot y}$ (1st titration) $= \dfrac{10.79\cdot 5.624}{10.00 - 25.00y - 10.79y}$ (2nd titration).

Hence, $y = 0.1116$ and $T = 10.10$ mg/mL

$T = 10.09$ *mg/mL* (10.10 without taking into account 0.994 factor)

2 marks for the correct formulas (with or without taking into account 0.994 factor) and 0.25 marks for the correct result (10.10 or 10.09)

2.25 marks maximum

4.3. *Equation(s):*

$CaO + SO_2 = CaSO_3$
$2CaO + 2I_2 = CaI_2 + Ca(OI)_2$
$6CaO + 6I_2 = 5CaI_2 + Ca(IO_3)_2$

(Instead of CaO, $Ca(OH)_2$ may be written.)

1 mark for ANY correct equation

1 mark maximum

4.4.1 *Equation(s):*

$Fe_2(SO_4)_3 + 2HI = 2FeSO_4 + \mathbf{I_2} + H_2SO_4$ 1 mark

$Fe_2(SO_4)_3 + \mathbf{H_2O} + SO_2 + CH_3OH = 2FeSO_4 + CH_3OHSO_3 + H_2SO_4$ 1 mark

(or in ionic form)

2 marks maximum

4.4.2. *Equation:*

$Fe_2(SO_4)_3{\cdot}xH_2O$ + **$(x - 1)$**I_2 **+** xSO_2 + xCH_3OH = $2FeSO_4$ + xCH_3OHSO_3 + H_2SO_4 + $2(x - 1)HI$ 1 mark

4.4.3. *The composition of the crystallohydrate is:*

Your work:

$M(Fe_2(SO_4)_3{\cdot}xH_2O) = 399.9 + 18.02x$

m_{H2O} (g) = $\frac{0.6387 \cdot 18.02x}{(399.9 + 18.02x)}$; 1 mark

m_{H2O} (g) = $10.59(mL)\times 15.46(mg/mL)\times 0.001(g/mg)\times \frac{x}{x-1}$

1 mark

→

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

$x = 8.994$

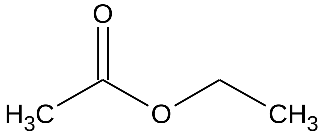
Formula: $Fe_2(SO_4)_3{\cdot}9\ H_2O$ $x = 9$

0.25 marks (for correct answer)

2.25 marks maximum

Problem 5. A mysterious mixture (organic hide-and-seek game)

5.1.1 *Structure of product* ***D***



Ethyl acetate, ethyl ethanoate

Any structural formula or any shorter versions ($CH_3COOC_2H_5$) including the adopted shortcuts for organic radicals (Me, Et, Ac), or systematic IUPAC name – 5 marks

5.1.2 *Which class of organic compounds does* ***D*** *belong to? Check the appropriate box.*
Note! *Only one checkmark is allowed. Several checkmarks will lead to 0 mark for this question.*

ketones	ethers	acetals	esters	alcohols	aldehydes	glycols
☐	☐	☐	☑	☐	☐	☐

The only correct answer is ester – 5 marks

5.1.3 *The expected yield of* ***D***

Your work:
Statement that the reaction is an equilibrium without any further actions – 1 mark
Answer to quantitative question: lower than 85% - 2 marks

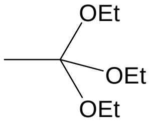
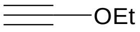
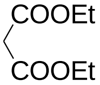
Qualitative estimation of yield can be done assuming that the reaction is at equilibrium, and that the equilibrium constant is supposed to not vary with temperature and composition of the reaction mixtures.

$$K = \frac{[\mathrm{AcOEt}][\mathrm{H_2O}]}{[\mathrm{AcOH}][\mathrm{EtOH}]} = \frac{(0.85)^2}{0.15\cdot 1.15} = 4.2$$

Calculation of yield using this constant in 1:1 mixture gives 67%

yield = 67%
maximum – 10 marks, if the yield is computed within 67±1% error limits

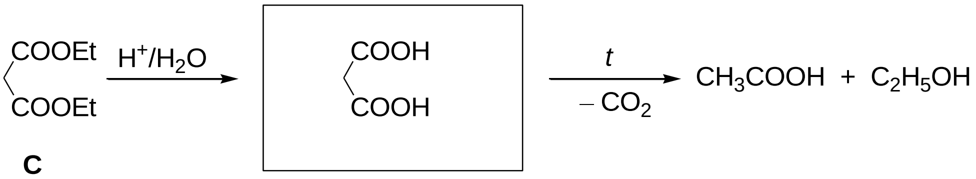
5.2.1 *The structures of* ***A***, ***B***, *and* ***C***.

 $CH_3C(OEt)_3$ triethyl orthoacetate, 1,1,1-triethoxyethane	 HC≡COEt ethoxyacetylene, ethynylethyl ether	 $CH_2(COOEt)_2$ diethyl malonate
A	***B***	***C***

Each structure represented by structural formula or unambiguous linear notation – 10 marks
Systematic name given in place of structure – 5 marks

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

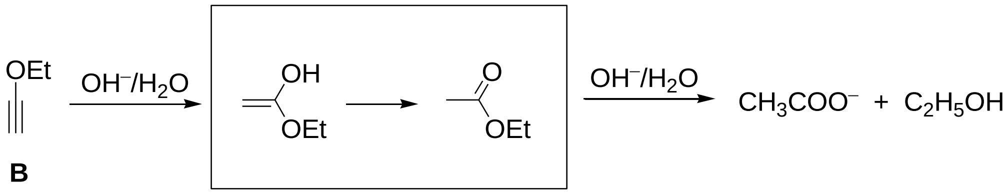
a) Malonic acid is formed as intermediate in the hydrolysis of diethyl malonate – 5 marks



C

Also accepted will be monoethyl malonate – 2 marks
maximum 5 marks

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

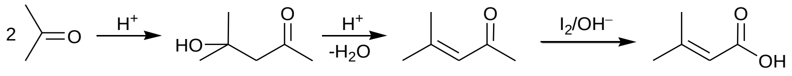


B

Indication of any of keto- or enol forms of ethylacetate – 5 marks
Hydrolysis of strong ether bond to give hydroxyacetylene, or any forms coming along this path (ketene, diketene) is impossible and is not allowed – 0 marks
Maximum for a) and b) together – 10 marks

5.3.1 *The structure of senecioic acid*

From acetone alone the synthesis includes aldol condensation, dehydration, with subsequent iodoform reaction
3 marks



Senecioic acid structure alone – 4 marks, with scheme - maximum 10 marks

5.3.2 *The structure of* ***E****.*

Iodoform, triiodomethane, CHI_3 – 5 marks

Problem 6. Silicates as the base of the Earth crust

6.1.1

$SiO_3^{2-} + 2CO_2 + 2H_2O = \text{“}H_2SiO_3\text{”}\downarrow$ (Silica acid gel) $+2HCO_3^-$ or
$SiO_2(OH)_2^{2-}+2CO_2+H_2O=\text{“}H_2SiO_3\text{”}\downarrow+2HCO_3^-$ or
$SiO_3^{2-} + CO_2 + H_2O = \text{“}H_2SiO_3\text{”}\downarrow + CO_3^{2-}$

3 marks maximum
2 marks if silicic acid is written in any form
1 mark if the reaction contains carbonate (or bicarbonate) ions with silicic acid missing

6.1.2

a) protonation of ortho-silicate ions leading to the formation of Si-OH groups
$SiO_4^{4-} + H_2O = [SiO_3(OH)]^{3-} + OH^-$ or
$SiO_4^{4-} + H^+ = [SiO_3(OH)]^{3-}$ or
$[SiO_2(OH)_2]^{2-}+ H^+= [SiO(OH)_3]^-$ Yes ☒ No ☐

b) formation of hydrated $[SiO_4(H_2O)_2]^{4-}$ anions
$SiO_4^{4-} + 2H_2O = [SiO_4(H_2O)_2]^{4-}$
Yes ☐ No ☒

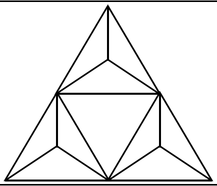
c) polycondensation of ortho-silicate ions leading to the formation of Si-O-Si bonds
$2\ SiO_4^{4-} + H_2O = [O_3Si\text{-}O\text{-}SiO_3]^{6-} +2\ OH^-$ or
$2\ SiO_4^{4-} + 2H^+ = [O_3Si\text{-}O\text{-}SiO_3]^{6-} + H_2O$ or
$2SiO_2(OH)_2^{2-} + H_2O = [O\text{-}Si(OH)_2\text{-}O\text{-}Si(OH)_2\text{-}O]^{2-} + 2\ OH^-$ Yes ☒ No ☐

9 marks maximum
2 marks for each correct reaction
1 mark for each correct choice of check-boxes

6.2.1 n= 6 (assuming oxidation numbers of silicon (+4) and oxygen (-2), or taking into account its structure and the charge of orthosilicate ion (-4))
2 marks maximum
1 mark penalty for miscalculation

6.2.2 $Si_3O_9 \equiv 3\ [SiO_4] - 3\ O$, i.e. there are 3 oxygen atoms bridging adjacent tetrahedra
2 points maximum
1 point penalty for miscalculation

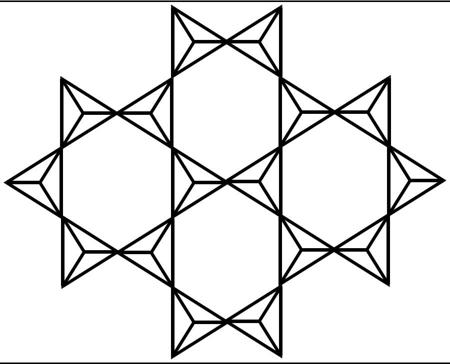
6.2.3



3 marks maximum

6.2.4

Calculations:
m=4 (assuming oxidation numbers of silicon (+4) and oxygen (-2), or taking into account its structure and the charge of orthosilicate ion (-4))
$Si_4O_{10} \equiv 4[SiO_4] - 6O$, i.e. the formula of the tetrahedron is now $SiO_{2.5}$, 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.



10 marks maximum

2 marks for charge determination

3 marks for determination of the number of oxygen bridges

5 marks for the correct structure

1 mark penalty if 6 to 15 tetrahedra shown, the connection being correct

3 marks penalty if less than 6 tetrahedra shown (i.e. it is not clear that polyhedra form layer)

4 marks penalty for connection via apexes, but in 3D network

4 marks penalty for connection via apexes, but in 1D chain

0 mark of 5 for any other structure

6.3.1

pH = 4

$$Cu(H_2O)_4^{2+} + H_2O = Cu(OH)(H_2O)_3^{+} + H_3O^{+},$$
$$[H^{+}] \approx (c\ K_a^{I})^{1/2} = 1\cdot10^{-4}\ M,\ pH = -\log[H^{+}] = 4$$

5 marks maximum

1 mark penalty for miscalculation

2 marks penalty for wrong expression of $[H^+]$ via K_a^I

2 marks penalty if there are some errors in definition of pH (e.g. using ln instead of lg)

3 marks penalty if the hydrolysis reaction is wrong

6.3.2

$CuSO_4 + Na_2SiO_3 + 2H_2O = Cu(OH)_2\downarrow + \text{“}H_2SiO_3\text{”}\downarrow + Na_2SO_4$

or $2CuSO_4 + Na_2SiO_3 + 2H_2O = (CuOH)_2SO_4\downarrow + \text{“}H_2SiO_3\text{”}\downarrow + Na_2SO_4$

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 **6.3.1**).

3 marks maximum

2 marks if reaction coefficients are wrong

1 mark if only one of two principal precipitates shown ($Cu(OH)_2\downarrow$ or “H_2SiO_3”↓)

Problem 7. Atherosclerosis and intermediates of cholesterol biosynthesis

7.1.1 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**.

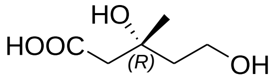
X is a monocarboxylic acid composed of atoms of three elements: carbon, hydrogen and oxygen. It can contain neither sulfur which is found in CoA nor phosphorus which is introduced into intermediates on the pathway from HMG-CoA towards IPP or present in CoA. Thus, **E1** catalyzes non-hydrolytic removal 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:

E1 *4, 5*

E3 *6*

12 marks maximum
E1: 9 marks if 2 variants are given and both are correct.
4 marks if only one variant is given and it is correct
4 marks if two correct and one incorrect variants are given
0 mark if one correct and any number of incorrect variants are given
0 mark if more than three variants are given.
E3: 3 marks if only correct variant is given. Otherwise 0 mark

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

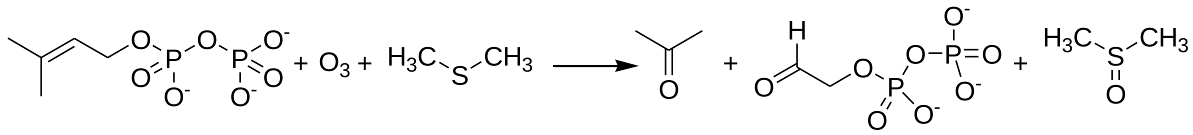


X, mevalonic acid

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.

12 marks maximum
8 marks for correct structural formula
4 marks for correct stereochemistry (only in case both the structure is correct and R-isomer is indicated; otherwise 0 mark).
No penalty for incorrect stereochemistry or absence of stereochemical information

7.2.1 Reaction equation for reductive ozonolysis



5 marks maximum

4.5 marks for correct products (1.5 marks each), incorrect structures not penalized

0.5 mark for correct equation coefficients

7.2.2 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:

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

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:

$$n(H)= 2*n_Y(C)+2–2*n_{c=c}=30*2 + 2 - 6*2 = 50$$

Y (squalene) formula – $C_{30}H_{50}$.

Number of carbon atoms 30	Work: $n_Y(C)= 2*n_{Y1}(C)+4*n_{Y2}(C)+ n_{Y3}(C)= 2*3 + 4*5 + 4 = 30$
Number of hydrogen atoms 50	Work: $n(H)= 2*n_Y(C)+2–2*n_{c=c}=30*2 + 2 - 6*2 = 50$
Gross formula of **Y** $C_{30}H_{50}$	

12 marks maximum

8 marks for correct justification of molecular formula

4 marks for correct molecular formula

7.2.3 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**:

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

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

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

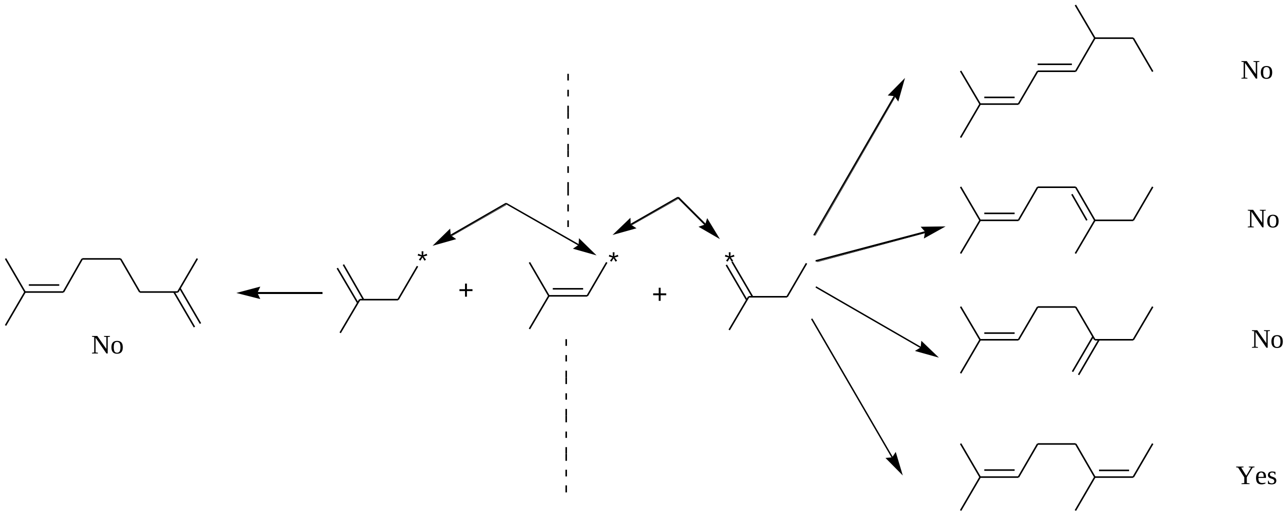
Number of DAP molecules 2 Number of IPP molecules 4

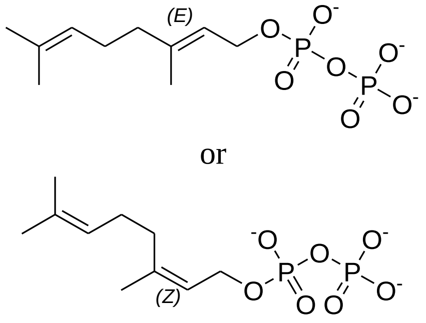
7 marks maximum

3.5 marks for calculation of the total number of DAP and IPP molecules

3.5 marks for correct individual numbers of DAP and IPP molecules

7.2.4 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





The upper isomer is geranyl pyrophosphate

8.5 marks maximum

8.5 marks for correct structure

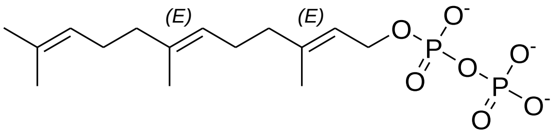
No penalty for stereochemistry, any correct structure is accepted

2.5 marks if ozonolysis of the product leads to acetone, but does not lead to the compound with 5 carbon atoms

2.5 marks if ozonolysis of the product leads to the compound with 5 carbon atoms, but does not lead to acetone

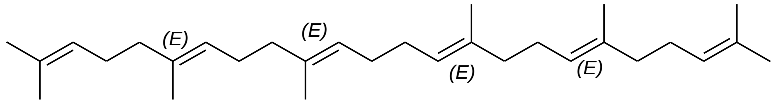
0 mark for any other variant

7.2.5 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:



Y4, farnesyl pyrophosphate

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**:



Y, squalene

16 marks maximum

9 marks for farnesyl pyrophosphate (6.5 marks for correct structural formula and 2.5 marks for correct stereochemistry)

7 marks for squalene (5 marks for correct structural formula and 2 marks for correct stereochemistry)

2.5 marks penalty for unreduced double bond in squalene

Problem 8. ATRP allows new polymers

8.1.1 *Expressions for the rates of ATRP elementary stages: activation (v_{act}), deactivation (v_{deact}), propagation (v_p) and termination (v_t)*

$v_{act} = k_{act}\cdot[\text{R-Hal}]\cdot[\text{CuHal(Ligand)}_k]$	2 marks
$v_{deact} = k_{deact}\cdot[\text{R}^{\cdot}]\cdot[\text{CuHal}_2\text{(Ligand)}_k]$	2 marks
$v_p = k_p\cdot[\text{R}^{\cdot}]\cdot[\text{M}]$	2 marks
$v_t = 2k_t\cdot[\text{R}^{\cdot}]^2$	2 marks (no penalty for missing 2)
	8 marks maximum

8.1.2 *Comparison of rates of ATRP elementary stages*

Since all the chains grow with equal rate, the process proceeds as living polymerization. Living radical polymerization is possible only if concentration of active radicals is low to prevent chain transfer and termination. So:

$$v_{deact} >> v_{act}$$

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

$$v_{deact} >> v_p$$

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

$$v_{deact} >> v_t$$

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

$v_{deact} >> v_{act}$	3 marks
$v_{deact} >> v_p$	3 marks
$v_{deact} >> v_t$	3 marks
	9 marks maximum

8.2.1 *Calculation of mass (m) of the obtained polymer.*

1st variant

$[M] = [M]_0 \exp(-k_P[R\cdot]t)$ or $n(MMA) = n_0(MMA)\exp(-k_P[R\cdot]t)$ 1 mark

Quantity of MMA monomer remaining after polymerization during 1400 s is

$31.0\cdot\exp(-1616\cdot 1.76\cdot 10^{-7}\cdot 1400) = 20.8$ mmol. 2 marks

Quantity of monomer consumed during polymerization: 31-20.8=10.2 mmol 1 mark

Mass of the obtained polymer is $m = \Delta n(MMA)\cdot M(MMA) = (10.2/1000)\cdot 100.1 = 1.03$ g 1 mark

2nd variant

$[M] = [M]_0 \exp(-k_P[R\cdot]t)$ or $n(MMA) = n_0(MMA)\exp(-k_P[R\cdot]t)$ 1 mark

Quantity of MMA monomer consumed during 1400 seconds of polymerization is

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

3 marks

Mass of the obtained polymer is $m = \Delta n(MMA)\cdot M(MMA) = (10.2/1000)\cdot 100.1 = 1.03$ g 1 mark

3rd variant

$\ln\left(\dfrac{[M]}{[M]_0}\right) = -k_P[R\cdot]t = -1616\cdot 1.76\cdot 10^{-7}\cdot 1400 = -0.398$ 1 mark

$\dfrac{[M]}{[M]_0} = e^{-0.398} = 0.672$ 1 mark

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

$n(MMA) = 0.672\cdot n_0(MMA) = 20.8$ mmol 1 mark

Quantity of monomer consumed during polymerization is 31-20.8=10.2 mmol 1 mark

Mass of the obtained polymer is $m = \Delta n(MMA)\cdot M(MMA) = (10.2/1000)\cdot 100.1 = 1.03\,\mathrm{g}$ 1 mark

m = 1.03 g 5 marks maximum

8.2.2 *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) 2 marks

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. 2 marks

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

$\Delta n = n_0(1-\exp(-k_P[R\cdot]t)) = 47.4(1-\exp(-1616\cdot 1.76\cdot 10^{-7}\cdot 1295)) = 14.6$ mmol. 4 marks

Totally 7.3+14.6 = 21.9 mmol of monomers was polymerized during two stages. 2 marks

DP = 21.9/0.12 = 182.5 1 mark

DP = *182-183 (all answers within this range are credited)* 11 marks maximum

8.2.3 *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 ≈ 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-A_{61}-block-(A-stat-B)$_{61}$-Cl or Ts-A_{61}-block-(A_{61}-stat-B_{61})-Cl

14 marks maximum

4 marks for block copolymer with blocks A and co-AB

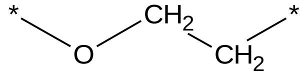
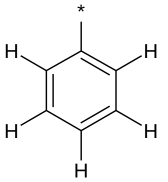
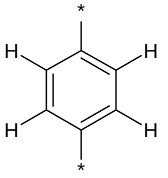
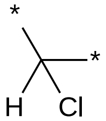
4 marks for an indication of the statistic character of the 2nd block

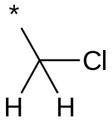
1 mark for equal fractions of A and B in the 2nd block

2 marks for correct DPs of each block

1 mark for indication of terminal groups

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

	a, b, g 3x1.5 marks
	c 2 marks
	d 2 marks
	e 4 marks

	f 4 marks

16.5 marks maximum

8.3.2 *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 2 marks

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.** 2 marks

Molar fraction of styrene units in P1 is 15/(15+58) = **20.5%** 1 mark

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. 2 marks

Molar fraction of D is 15/(15+58) = **20.5%** 1 mark

M(P1) = 15.03+58x44.05+72.06+15x104.15+35.45 = **4240** 2 marks

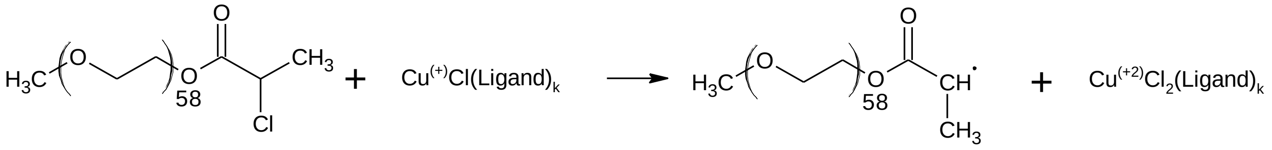
M(P2) = 15.03+58 x44.05+72.06+15x152.62+35.45 = **4967** 2 marks

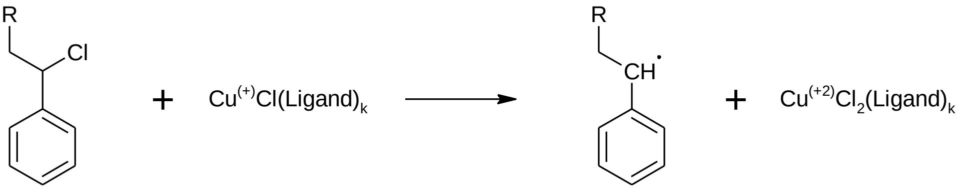
M(P1) = 4240
M(P2) = 4967
n(C) = 20.5%
n(D) = 20.5%
12 marks maximum

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

10 marks maximum

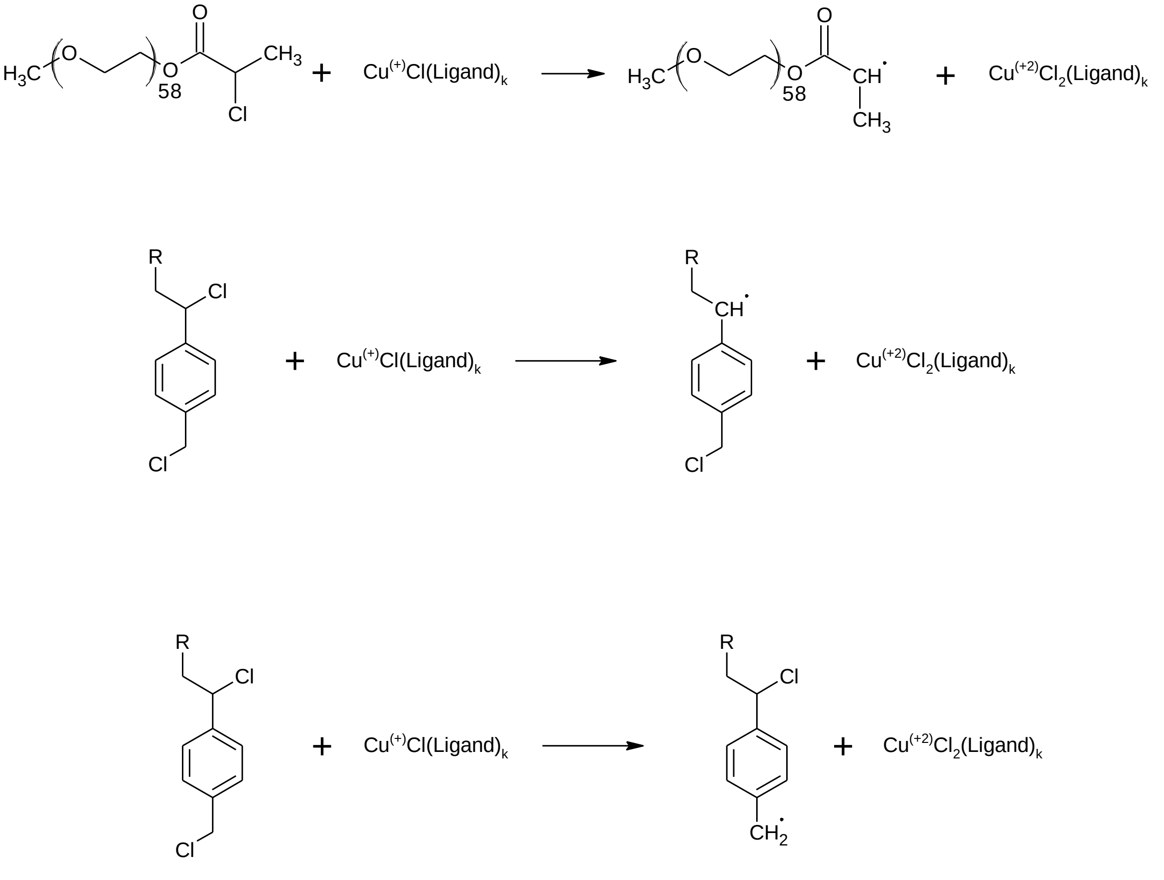
P1: (1.5+2) marks





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

P2: (1.5+2+3) marks



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

8.3.4 *The structure of P1 and one of possible structures of P2*

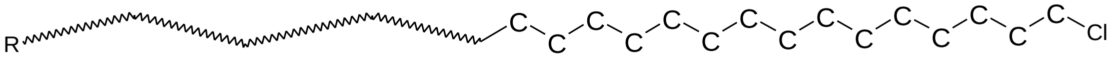
P1 is a block copolymer of PEO and PS. The PS block contains 15 units.

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

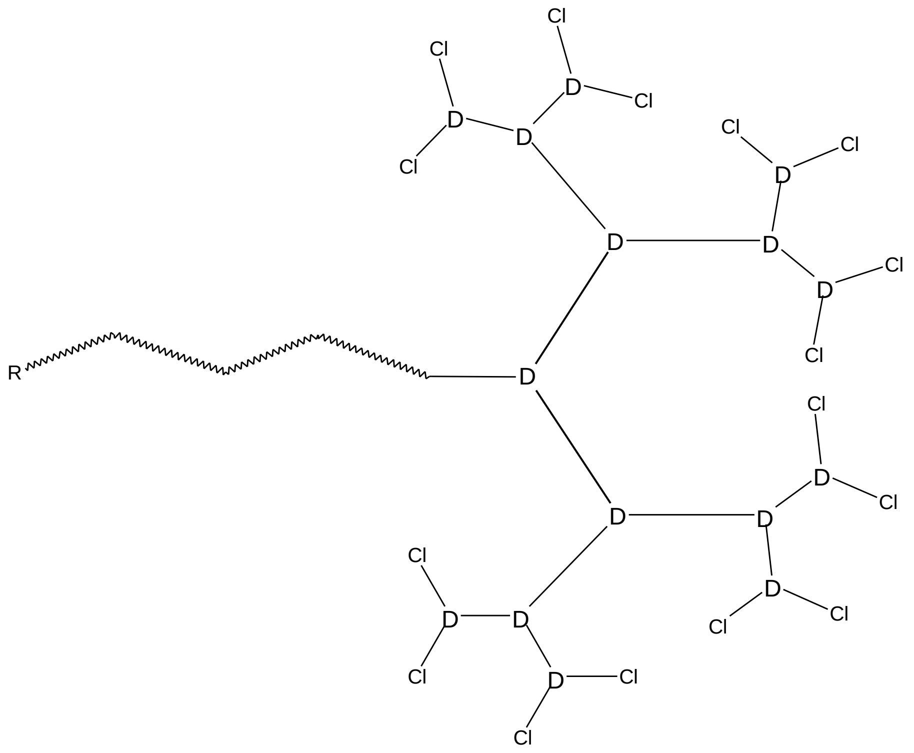
The integral intensity of multiplet f is 2.75, so 2.75/0.173=15.9, that is about 16 protons or 8 chloromethyl groups.

d) If there is no branching in molecule P2, it would contain 15 choromethyl 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

P1



P2



13.5 marks maximum
2 marks for P1
7.5 marks for completely correct structure of P2
4 marks for structure of P2 with nonzero but incorrect number of branchings

4 marks penalty if there is a unit linked with more than 3 other monomer units

CHEMISTRY: ART, SCIENCE, FUN

PRACTICAL EXAMINATION

PROBLEMS

JULY 18, 2007
MOSCOW, RUSSIA

21408 characters in Problems and Answer Sheets

General Directions

- **safety rules** follow them as in the Preparatory problems described, no eating or drinking is allowed in the lab.
- **violating safety rules** you get one warning, offend again: you are out.
- **problem booklet** 12 pages (incl. cover sheet and Periodic table of elements) with 2 problems. Start with problem 1.
- **time** 5 hours; 30 minutes warning before the end.
- **answer sheets: 5** pages (incl. cover sheet).
- **your name and student code** write it on **every** answer sheet.
- **answers** only in the appropriate places of the answer sheets, nothing else will be marked. Relevant calculations have to be shown.
- **use only the pen and calculator provided.**
- **results** the number of significant figures in numerical answers must conform to the rules of evaluation of experimental error. Mistakes will result in penalty points even if your experimental technique is flawless.
- **burette** read it as accurately as possible.
- **more chemicals** needed? Ask your lab assistant. No penalty for this.
- **Extra sample to be analyzed or broken column** a penalty of 10 marks.
- **questions** concerning safety, apparatus, chemicals, organization, toilet break: **ask your lab assistant.**
- **chemical waste** put it only in the designated containers.
- **official English-language version available** on request **for clarification only.** Ask your lab assistant.
- **after the stop signal** put your answer sheets and spectra in the envelope (don’t seal), deliver them to your lab assistant. Keep the problem booklet together with the pen and calculator.
- **You must stop your work immediately after the stop signal has been given. A delay of 5 minutes will result in zero points for the current task.**
- **During the Practical examination some of your glassware and plastics may have to be used more than once. Clean it carefully.**

List of Chemicals

Reagent	Quantity	Placed in	Labeled
Task 1			
Eluent 1	100 mL	Amber glass bottle*	Eluent 1
Eluent 1	1 mL	Plastic microtube	Eluent 1
Eluent 2	50 mL	Amber glass bottle*	Eluent 2
Eluent 2	1 mL	Plastic microtube	Eluent 2
Eluent 3	50 mL	Amber glass bottle*	Eluent 3
Eluent 3	1 mL	Plastic microtube	Eluent 3
0.5 M Carbonate buffer solution, pH 9.5	10 mL	Glass vial	$NaHCO_3$
0.5 M Tris-HCl buffer solution, pH 8.5	10 mL	Glass vial	Tris-HCl
Mixture of amino acids to be analyzed**	1.2 mL	Plastic microtube	A number between 301 and 600
Ellmann reagent: 0.2 M Phosphate buffer solution containing 10 mM EDTA and 3 mM 5,5’-Dithiobis(2-nitrobenzoic acid), pH 7.0	10 mL	Glass vial	DTNB
Pauli’s reagent: solution of sodium 4-diazonium-benzenesulfonate in 0.1 M aqueous HCl	1 ml	Plastic microtube	Pauli
Sodium hydroxide, 10% aqueous solution	10 mL	Glass vial	NaOH 10%
8-Hydroxyquinoline, 5.2 mM solution in ethanol/n-butanol (9:1) mixture	5 ml	Glass vial	8-HQ
Sodium hypobromite, 0.24 M solution in 10% aqueous NaOH	1.2 ml	Plastic microtube	NaBrO
2,4,6–Trinitrobenzenesulfonic acid, 3.4 mM aqueous solution	1 mL	Plastic microtube	TNBS
8 M Aqueous urea solution	1 mL	Plastic microtube	Urea
Task 2			
HCl, standard solution, ~1 M (see exact value on the label)	40 mL	Amber glass vial	HCl <and exact concentration>
NaOH (to be standardized)	200 mL	Amber glass vial	NaOH
Powdery sample to be analyzed**	0.5 – 1 g	150 mL beaker covered with watch glass	<number of workplace>
H_2O distilled	400 mL	Plastic wash bottle	H_2O
H_2O distilled (shared between 2 students)	30 mL	Glass drop bottle	H_2O
H_2O distilled (for common use)	5 L	Bottle with tubing and clamp on top of the bench	H_2O
NaH_2PO_4, 15% solution (shared between 2 students)	20 mL	Glass drop bottle	NaH_2PO_4 15%
Bromocresol Green, 0.5% solution in 20% ethanol (shared among 3-4 students in a raw)	30 mL	Glass drop bottle	Bromcresol green
Thymolphthalein, 0.5% solution in ethanol (shared among 3-4 students in a raw)	30 mL	Glass drop bottle	Thymolphtalein
$K_2C_2O_4$, 15% solution (shared between 2 students)	50 mL	Amber glass vial	$K_2C_2O_4$ 15%

*Fixed on the top shelf (do not try to remove), with connected tubing and clamp

**10 marks penalty for an extra portion of the sample

Components of Eluents 1 to 3

Eluent 1: 0.1 M aqueous sodium citrate, 50 mM sodium chloride, 40 mM thiodiglycol, 1 mM caprylic acid, 0.1% Brij-35; pH 4.9.

Eluent 2: 0.2 M aqueous sodium phosphate, 0.1% Brij-35; pH 7.0.

Eluent 3: 0.2 M aqueous sodium hydroxide.

Apparatus and Suppliers

Item	**Quantity**
Test tube rack	1
Laboratory stand	1
Chromatography column with ion-exchange resin	1
Laboratory stand with white covering	1
Double clamp for burette	1
Ring for funnel	1
25 mL Burette	1
100 mL flask labeled “Waste”	1
100 mL Volumetric flask	2
100 mL Erlenmeyer flask	2
Syringe with needle	1
Graduated test tubes for collecting fractions and preparing mixtures	50
96-well plate	1
Pipettor (micropipette) with fixed volume of 0.1 mL	1
Disposable tips (in blue plastic cup)	20
Spectrophotometric cuvettes labeled “A1”, “B1”, “A2”, “B2”, “A3”, “B3” in cuvette holder	6
10 mL Graduated plastic pipettes	3
10 mL Glass pipette	1
Pipette filler	1
3-Way Bulb	1
Glass rod	1
Filter funnel	1
Small funnel	1
60 mL Amber glass vials for combined fractions (peaks)	3
10 mL Measuring cylinder labeled “$K_2C_2O_4$ 15%” (shared between 2 students)	1
10 mL Measuring cylinder (shared between 2 students)	1
50 mL Measuring cylinder	1
100 mL Measuring cylinder labeled “H_2O” (shared among 3-4 students in a row)	1
Plastic plate with filters*** (shared among 3-4 students in a row)	3 filters per student
Heating plate (for common use in a fume hood)	6 plates per hood
Rubber protection tips (for common use a fume hood)	6 pairs per hood
Spectrophotometer (shared by a group of students; see the number of the spectrophotometer to be used at your bench “SP____”)	
Marker	1
Ruler	1
White sheet of paper	1

***If needed, ask your lab assistant for extra filters.

Safety regulations, S-phrases, R-phrases

Disodium hydrogen phosphate	R:36/37/38 S:26-36
Ethylenediaminetetraacetic acid, disodium salt	R:36/37/38 S:26-36/37/39
Tris-HCl	R:36/37/38 S:26-36
Arginine	R:36 S:26
Cysteine	R:22
Histidine	S:22-24/25
Hydrochloric acid	R:34-37 S:26-36-45
Sodium 4-diazoniumbenzenesulfonate	R:1-37/37 S:26-36
Sodium hydroxide	R:34-35 S:26-36-37/39-45
8-Hydroxyquinoline	R:22-36/37/38 S:26-36/37
Ethanol	R:11 S:7-16
Butanol-1	R:10-22-37/38-41-67 S:7/9-13-26-37/39-46
Sodium hypobromite	R31-34 S:26-36-45
5,5’-Dithiobis(2-nitrobenzoic acid)	R:36/37/38 S:26-36
2,4,6-Trinitrobenzene sulfonic acid	R: 1-22-36/38-43 S: 26-36/37
Sodium chloride	R:36 S:26
Thiodiglycol	R:36 S:26
Caprylic acid	R:34 S:26-27-45-36/37/39
Brij-35	R:36/37/38 S:26-36
Sodium dihydrogen phosphate	S:22-24/25
Sodium carbonate	R:36 S:22-26
Calcium carbonate	R:41-37/38 S:26-39
Bromocresol Green	S:22-24/25
Thymolphthalein	S:22-24/25
Potassium oxalate	R:34 S:26-27-36/37/39

Risk Phrases

Indication of Particular Risks

R1: **Explosive when dry**
10: **Flammable**
22: **Harmful if swallowed**
31: **Contact with acids liberates toxic gas**
34: **Causes burns**
35: **Causes severe burns**
36: **Irritating to the eyes**
37: **Irritating to the respiratory system**
41: Risk of serious damage to eyes
43: **May cause sensitization by skin contact**
67: Vapors may cause drowsiness and dizziness

Combination of Particular Risks

R24/25: **Toxic in contact with skin and if swallowed**
36/37/38: **Irritating to eyes, respiratory system and skin**
36/38: **Irritating to eyes and skin**
37/38: **Irritating to respiratory system and skin**

Safety Phrases

Indication of Safety Precautions

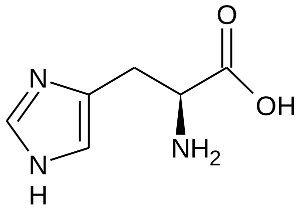
S13: Keep away from food, drink and animal feeding stuffs
22: **Do not breathe dust**
26: **In case of contact with eyes, rinse immediately with plenty of water and seek medical advice**
27: **Take off immediately all contaminated clothing**
36: **Wear suitable protective clothing**
39: **Wear eye/face protection**
45: **In case of accident or if you feel unwell, seek medical advice immediately (show label where possible)**
46: **If swallowed, seek medical advice immediately and show this container or label**

Combination of Safety Precautions

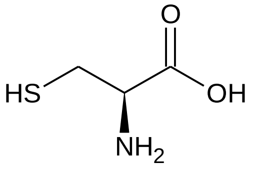
7/9: Keep container tightly closed and in a well-ventilated place
24/25: **Avoid contact with skin and eyes**
36/37/39: Wear suitable protective clothing, gloves and eye/face protection
37/39: Wear suitable gloves and eye/face protection

Problem 1. Ion-exchange chromatography of amino acids

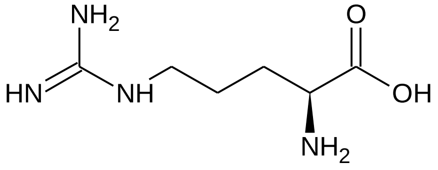
Ion-exchange chromatography is an important analytical and preparative method, which allows fractioning of charged substances. Interaction of ionic groups of the substances with counterions attached to the resin is behind the method. In this task you will have to carry out separation of a given mixture 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

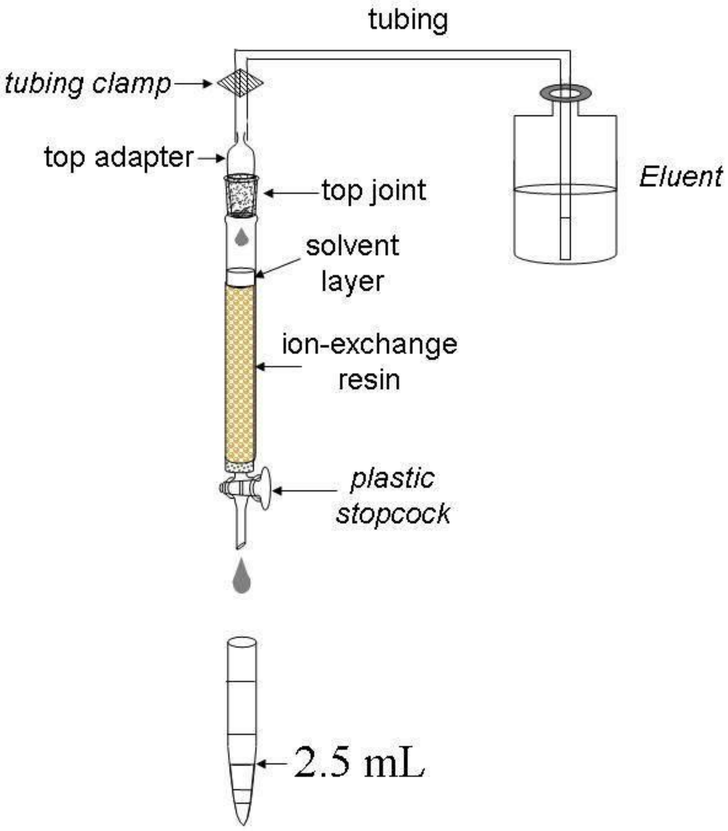
Three amino acids (see the structures above) are present in the mixture. These are histidine, cysteine, and arginine. Cross-linked sulfonated polystyrene is used as a cation-exchange resin (see the picture of the system below). At the beginning of the experiment the column is equilibrated with Eluent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

Procedure

Chromatography. Step 1

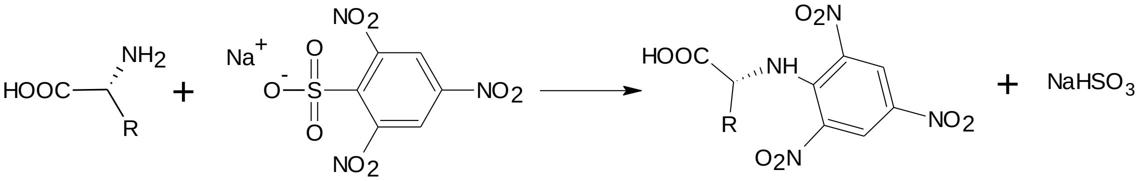
Apply the given solution of a mixture of amino acids to the column. First, open the stopcock to allow the solvent in the column draining into the Erlenmeyer flask labeled “Waste” so that the solvent is level with the top of packing material, still preventing the resin surface from drying off. Close the 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 mL 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 open 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 mL (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 mL of TNBS solution with 10 mL of carbonate buffer solution and place 0.1 mL of the resulting mixture into half of the plate wells (from A1 to H5). Then add 0.1 mL 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 mL should be added by using the pipettor. We expect you to use one tip for all fractions of a single peak.

1.1a *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.

1.1b *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.

1.1c *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.*

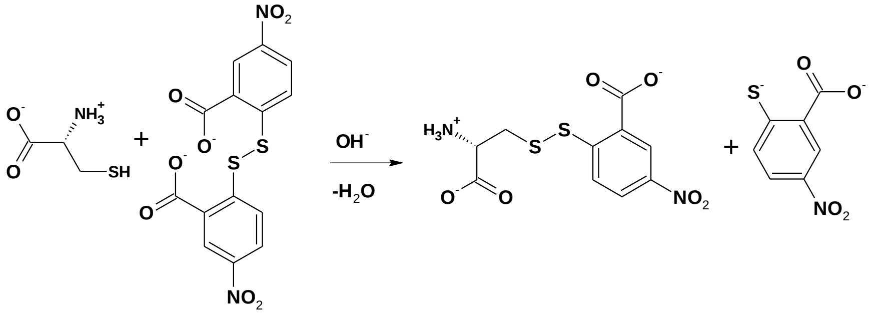
Pour combined fractions in the amber glass vials labeled “Peak 1”, “Peak 2”, “Peak 3”. Prepare samples for quantitative spectrophotometric analysis as described below.

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 cuvettes to the operator. Prepare the probes as follows.
Important! When storing, always put cuvettes in the cuvette holder! All cuvettes have 2 ribbed and 2 working vertical surfaces. While operating with cuvettes, 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 mL of Eluent 1 from plastic microtube into a test tube and add 2.9 mL of Ellmann reagent (DTNB).
Test tube B1 (Sample). Place 0.1 mL of the analyzed solution into a test tube and add 2.9 mL of Ellmann reagent (DTNB).
Mix the contents of the test tubes thoroughly and transfer each mixture to the corresponding cuvettes labeled 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 mL of Tris-HCl buffer solution into a test tube, add 0.1 mL of Eluent 2 from plastic microtube and 0.1 mL of Pauli reagent.
Test tube B2 (Sample). Place 2.8 mL of Tris-HCl buffer solution into a test tube, add 0.1 mL of the analyzed solution and 0.1 mL of Pauli reagent.

Mix the contents of the test tubes thoroughly and transfer each mixture to the corresponding cuvettes labeled 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 mL of Eluent 3 into a test tube and add 1.5 mL of 10% NaOH solution, 1 mL of 8-hydroxyquinoline solution and 0.5 mL of sodium hypobromite solution.
Test tube B3 (Sample). Place 0.1 mL of the analyzed solution into a test tube and add 1.5 mL of 10% NaOH solution, 1 mL 8-hydroxyquinoline solution and 0.5 mL of sodium hypobromite solution.

Shake the test tubes vigorously for 2 min (**Important!**) and observe formation of orange color. Add 0.2 mL of 8 M urea solution to each test tube, mix the contents and transfer about 3 mL of each mixture to the corresponding cuvettes labeled 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 cuvettes 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:	Molar masses of the amino acids.
Product of Ellmann reaction: 13600 $M^{-1}cm^{-1}$ at 410 nm	Cysteine 121 g/mol
Product of Pauli reaction: 6400 $M^{-1}cm^{-1}$ at 470 nm	Histidine 155 g/mol
Product of Sakaguchi reaction: 7700 $M^{-1}cm^{-1}$ at 500 nm	Arginine 174 g/mol

1.4. *Draw three resonance structures of the species responsible for mixture coloration as a result of Ellmann reaction.*

Problem 2. 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 color 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 colorless 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:

a) the amount of the titrant equivalent to the initial amount of HCl (taken for the sample dissolution) and
b) 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 mL (**exactly, with a pipette! *Carefully*, not removing the glass and avoiding losses because of splashing!**) of ca. 1 mol/L 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 mL of 15% $K_2C_2O_4$ 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 mL of HCl solution into a 100 mL volumetric flask, make up to the mark with distilled water and mix. Fill the burette with NaOH solution. Transfer with a pipette 10.00 mL 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 mL. Report all the final volume values with 0.01 mL accuracy.

2.1a *Complete the table in the Answer Sheet.*
2.1b *Calculate the concentration of NaOH solution (in mol/L).*

Step 4. Filtering off calcium oxalate
After the most part of CaC_2O_4 precipitates filter the precipitate off collecting the filtrate into a 100 mL 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 mL 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 mL of distilled water. Titrate the sample solution with NaOH solution until the color 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 mL 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.

Periodic Table of Elements

with atomic masses

1 **H** 1.01																	**2** **He** 4.00
3 **Li** 6.94	**4** **Be** 9.01											**5** **B** 10.81	**6** **C** 12.01	**7** **N** 14.01	**8** **O** 16.00	**9** **F** 19.00	**10** **Ne** 20.18
11 **Na** 22.99	**12** **Mg** 24.31											**13** **Al** 26.98	**14** **Si** 28.09	**15** **P** 30.97	**16** **S** 32.07	**17** **Cl** 35.45	**18** **Ar** 39.95
19 **K** 39.10	**20** **Ca** 40.08	**21** **Sc** 44.96	**22** **Ti** 47.88	**23** **V** 50.94	**24** **Cr** 52.00	**25** **Mn** 54.94	**26** **Fe** 55.85	**27** **Co** 58.93	**28** **Ni** 58.69	**29** **Cu** 63.55	**30** **Zn** 65.39	**31** **Ga** 69.72	**32** **Ge** 72.61	**33** **As** 74.92	**34** **Se** 78.96	**35** **Br** 79.90	**36** **Kr** 83.80
37 **Rb** 85.47	**38** **Sr** 87.62	**39** **Y** 88.91	**40** **Zr** 91.22	**41** **Nb** 92.91	**42** **Mo** 95.94	**43** **Tc** 98.91	**44** **Ru** 101.07	**45** **Rh** 102.91	**46** **Pd** 106.42	**47** **Ag** 107.87	**48** **Cd** 112.41	**49** **In** 114.82	**50** **Sn** 118.71	**51** **Sb** 121.76	**52** **Te** 127.60	**53** **I** 126.90	**54** **Xe** 131.29
55 **Cs** 132.91	**56** **Ba** 137.3	**57-71**	**72** **Hf** 178.49	**73** **Ta** 180.95	**74** **W** 183.84	**75** **Re** 186.21	**76** **Os** 190.23	**77** **Ir** 192.22	**78** **Pt** 195.08	**79** **Au** 196.97	**80** **Hg** 200.59	**81** **Tl** 204.38	**82** **Pb** 207.19	**83** **Bi** 208.98	**84** **Po** 208.98	**85** **At** 209.99	**86** **Rn** 222.02
87 **Fr** 223	**88** **Ra** 226	**89-103**	**104** **Rf** 261	**105** **Db** 262	**106** **Sg** 263	**107** **Bh** 264	**108** **Hs** 265	**109** **Mt** 268									
			57 **La** 138.91	**58** **Ce** 140.12	**59** **Pr** 140.91	**60** **Nd** 144.24	**61** **Pm** 144.92	**62** **Sm** 150.36	**63** **Eu** 151.96	**64** **Gd** 157.25	**65** **Tb** 158.93	**66** **Dy** 162.50	**67** **Ho** 164.93	**68** **Er** 167.26	**69** **Tm** 168.93	**70** **Yb** 173.04	**71** **Lu** 174.97
			89 **Ac** 227	**90** **Th** 232	**91** **Pa** 231	**92** **U** 238	**93** **Np** 237	**94** **Pu** 244	**95** **Am** 243	**96** **Cm** 247	**97** **Bk** 247	**98** **Cf** 251	**99** **Es** 252	**100** **Fm** 257	**101** **Md** 258	**102** **No** 259	**103** **Lr** 262

CHEMISTRY: ART, SCIENCE, FUN

Official English version

PRACTICAL EXAMINATION

SOLUTION and
GRADING SCHEME

JULY 18, 2007
MOSCOW, RUSSIA

Official English version

Problem 1. Ion-exchange chromatography of amino acids.

1.1a 3 marks for each peak if at least two blank wells between peaks
9 marks maximum.

1.1b Not graded.

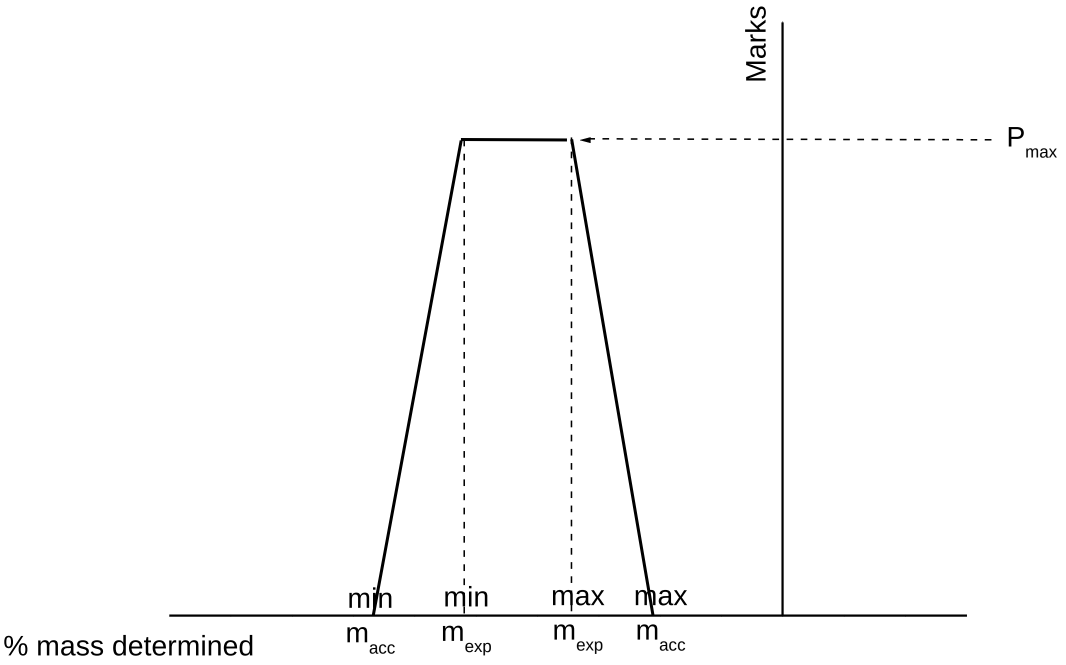
1.1.c 1 point for each proper choice. Combined mixtures should include all fractions identified as "2" and "3" and should be free of fractions without amino acids. Fractions identified as "1" may be or may be not included.
3 marks maximum.

1.2-1.3

Content of an amino acid = $\dfrac{A_\lambda \cdot n \cdot V \cdot M_W}{\varepsilon \cdot l}$,

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 mL) and the final volume of the sample in the cuvette, V is the volume of the combined fraction from the corresponding peak, and M_W is the molar mass of the amino acid.
3 marks for correct formula,
3 marks for correct determination of optical densities (1 mark for each assay)
1 mark penalty for miscalculation.

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)



Scoring:

m < min m_{acc} OR m > max m_{acc} 0 marks

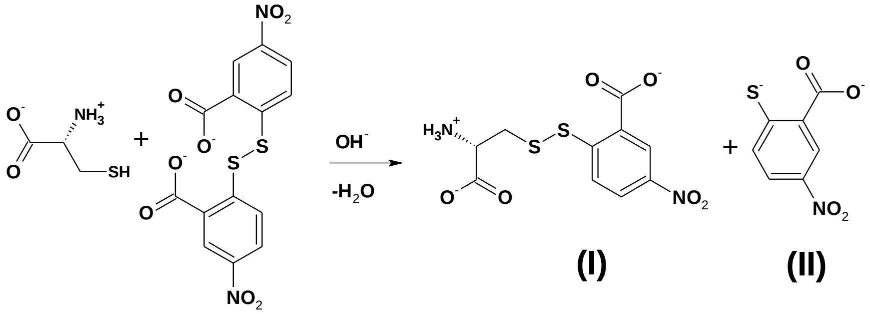
min m_{acc} < m < min m_{exp} $$P_{\max}\frac{(m-\min\ m_{acc})}{(\min\ m_{\exp}-\min\ m_{acc})}$$ marks

min m_{exp} < m < max m_{acc} P_{max} marks

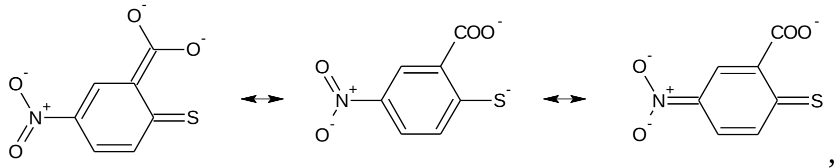
Amino acid	Min m_{acc}/m_{exact} ·100%	Min m_{exp}/m_{exact} ·100%	Max m_{exp}/m_{exact} ·100%	Max m_{acc}/m_{exact} ·100%	P_{max}
Cys	70%	85%	110%	115%	22
His	60%	85%	110%	115%	22
Arg	25%	45%	65%	85%	22

72 marks maximum

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).

2 marks for three correct ionized structures, one of which contains C=S bond

1 mark for three other structures, all without C=S bond

1 mark for less than three structures, one of which contains C=S bond.

2 marks maximum.

Problem 2. Determination of carbonate and hydrogen phosphate in an abrasive sample.

2.1a, 2.2, 2.3 The values of the final volumes $V_{1,\mathrm{f}}$, $V_{2,\mathrm{f}}$, and $V_{3,\mathrm{f}}$, (as reported in the Answer Sheet) are graded according to the following scheme:

$\Delta V = |V_{\mathrm{reported}} - V_{\mathrm{true}}|$,

V_{reported} is either $V_{1,\mathrm{f}}$, $V_{2,\mathrm{f}}$, and $V_{3,\mathrm{f}}$, V_{true} is the corresponding master value (will be given with the copies of students' works).

Value of ΔV	Marks
$\Delta V \le \Delta V_{\mathrm{expected}}$	25
$\Delta V \ge \Delta V_{\mathrm{acceptable}}$	0
$\Delta V_{\mathrm{expected}} \le \Delta V \le \Delta V_{\mathrm{acceptable}}$	$25 \times \left(\dfrac{\Delta V_{acceptable} - \Delta V}{\Delta V_{acceptable} - \Delta V_{\exp ected}} \right)$

The values of $\Delta V_{\mathrm{expected}}$ and $\Delta V_{\mathrm{acceptable}}$ (in mL) are listed in the table below.

	ΔV, mL	
	expected	acceptable
$V_{1,\mathrm{f}}$	**0.10**	**0.25**
$V_{2,\mathrm{f}}$	**0.15**	**0.40**
$V_{3,\mathrm{f}}$	**0.15**	**0.40**

<u>25 marks maximum for each titration</u>

2.1b *Calculation of NaOH concentration*

Your work

c(NaOH) = $\dfrac{c(HCl) \times V(HCl) \times V(aliquot)}{V(flask) \times V(NaOH)} = \dfrac{1.214\ (mol/L) \times 10.00 (mL) \times 10.00 (mL)}{100.0 (mL) \times V_{1,f}\ (mL)} =$

=

c(NaOH) = __________ mol/L

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

Your work

$m(CO_3^{2-})$ (g) =

$M(CO_3^{2-}) \times 1/2 \times \dfrac{c(NaOH) \times (V_{1,f} - V_{3,f}) \times V(flask)}{V(aliquot)} =$

$=60.01\ (g/mol) \times 1/2 \times \dfrac{c(NaOH)\ (mol/L) \times (V_{1,f} - V_{3,f})\ (mL) \times 100.0\ (mL)}{10.00\ (mL)} \times 0.001\ (L/mL) =$

=

$m(CO_3^{2-})$ = __________ g

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

Your work $m(\mathrm{HPO_4^{2-}})\ (g) =$ $= \mathrm{M(HPO_4^{2-})} \times \dfrac{c(NaOH) \times (V_{3,f} - V_{2,f}) \times V(flask)}{V(aliquot)} =$ $= 95.98\ (g/mol) \times \dfrac{c(NaOH)\ (mol/L) \times (V_{3,f} - V_{2,f})\ (mL) \times 100.0\ (mL)}{10.00\ (mL)} \times 0.001\ (L/mL) =$ $=$ $m(\mathrm{HPO_4^{2-}})$ = __________ g

2.1b, 2.4, 2.5

Correctness of calculations is graded by:

1) comparing the numerical result (including the number of significant figures) reported by a student with that obtained **from the student's data** using correct method of calculation;

2) checking out the a student's way of calculation.

<u>5 marks maximum for completely correct calculation of each value</u>

Penalty for errors in calculations or data presentation.

	Error type	Penalty marks (for calculation of each value)
1	Incorrect method of calculation	-5
2	Mistakes in dilution factor	-1
3	Confusion between units of measurement	-1
4	Mistake in stoichiometric (equivalency) relationships	-1
5	More or less than 4 significant figures in *c*(NaOH)	-0.5*
6	More than 4 or less than 3 significant figures in $m(\mathrm{CO_3^{2-}})$ and $m(\mathrm{HPO_4^{2-}})$	-0.5*
7	Rounding errors affecting the 1st or 2nd significant figures in the final result	-0.5**
8	Miscalculations and slips	-0.2 per error

*Only the number of significant figures in the final answer is taken into account.

Not applied if the error originates from insufficient number of significant figures in previously calculated *c*(NaOH). **No double penalty!

2.6a

$\mathrm{Ca^{2+} + H_2PO_4^- \rightarrow CaHPO_4 + H^+}$ or $\mathrm{3Ca^{2+} + 2HPO_4^{2-} \rightarrow Ca_3(PO_4)_2 + 2H^+}$

In course of these processes free protons evolve influencing the results of titration.

1 mark if the Answer Sheet contains at least one correct reaction equation. Incorrect equations are not penalized.

2.6b

Mistake	Error	
	CO_3^{2-} content	HPO_4^{2-} content
Below pH 4.5 (first endpoint, V_2) H_2CO_3 is not titrated Between pH 4.5 and 10 (second endpoint, V_3) H_2CO_3 is titrated **Thus, increase of V_3 ; V_1 and V_2 unchanged**	-	+
No influence, $C_2O_4^{2-}$ is too weak base	0	0
Increase of V_1 and proportional decrease of *c*(NaOH) [as *c*(NaOH)V_1 is equivalent to the initial amount of standard HCl and so remains constant]**; V_2 and V_3 unchanged**	-	-
Losses of sample leads to proportional **decrease of V_2 and V_3 and therefore V_3-V_2; V_1 unchanged**	+	-
Increase of V_2, V_1 and V_3 unchanged	0	-
Increase of V_3, V_1 and V_2 unchanged	-	+