Mock IChO

Theoretical Exam

Instructions

• This theoretical exam contains **16 pages** (including this one and the periodic table on the next page).

• You may begin writing as soon as the Start command is given.

• You have **2 hours** to complete the exam.

• All results and answers must be clearly written in pen in their respective designated areas on the exam papers. Answers written outside the answer boxes will not be graded.

• Write your student code clearly in the area on the top left on all pages (including this one, and the periodic table on the next page).

• If you need more space for scratch work, use the back side of the exam sheets. Remember that nothing outside the designated areas will be graded.

• Use only the pen and calculator provided.

• You must stop your work immediately when the Stop command is announced. Failure to stop writing by ½ minute or longer will lead to nullification of your theoretical exam.

• After the Stop command has been given, place your exam booklet back in your exam envelope and wait at your seat. The exam supervisor will come to collect the envelope.

• If you forgot formulae or relevant physical constants, then you are screwed since I was too lazy to copy those into this document.

• The sources and answers to these questions can be found online.

Periodic Table of the Elements

Problem 1 (2007/pp5/abridged)   16% of the total

	1.1	1.2	1.3	1.4	1.5	Total
Points Possible	4	4	4	6	2	20
Score						

Nanochemistry has sparked much excitement in the recent years and a large amount of research has been dedicated to understanding of nanomaterials. Single-walled carbon nanotubes (SWNTs) are a universally known example of such materials. SWNT can be thought of as a sheet of graphite rolled into a seamless cylinder (d ≈ 1.5 nm). These cylindrical carbon "molecules" might provide components for molecular electronic devices of the future. The properties of nanometer-scale materials are size- and shape-dependent.

Saturated vapor pressure of a small spherical particle (crystalline or liquid) is higher than that of the bulk phase of the same material. At equilibrium the molar Gibbs functions of the condensed phase and vapor are equal.

The substance inside a small spherical sample is under excess pressure, caused by surface tension:

$$\Delta P = \frac{2\sigma}{r}$$

r – the radius of the spherical sample, σ – the surface tension at the "condensed phase-vapor" interface.

The increase of the internal pressure results in a change in the molar Gibbs energy of the substance inside the spherical sample. This molar Gibbs energy of the spherical phase is larger than that of the bulk phase. The difference in the Gibbs energy of the spherical sample and the bulk phase is equal to $V\Delta P$.

V is the molar volume of the liquid or solid substance.

1.1 The saturated vapor pressure of water at T = 298 K is 3.15×10–2 bar. Calculate the saturated vapor pressure of the spherical droplets of water with the radius of: i) 1 μm and ii) 1 nm. The surface tension at the liquid-vapor interface of water is 0.072 J/m2.

1.2 Assuming that the substance retains properties of a bulk while the difference between its saturated vapor pressure and the saturated pressure of the bulk is less than 1%, what is the minimum radius of the spherical sample that can still be considered as a bulk phase? How many molecules of water are there in such a droplet?

1.3 Few droplets of mercury were put inside a SWNT maintained at 400 K. What is the minimum vapor pressure of mercury inside the tube? The saturated vapor pressure of bulk mercury is 1.38×10^{-3} bar, the density of mercury $\rho(Hg) = 13.5$ g/cm3 , the surface tension at the liquid-vapor interface of mercury is 0.484 J/m2 at the given temperature.

1.4 The boiling point of benzene at the standard atmospheric pressure is $T_b = 353.3$ K. Estimate the boiling point (T^*) of the finely dispersed liquid benzene at the standard atmospheric pressure if the sample consists of droplets with the radius r = 50 nm. The surface tension of benzene near the boiling point is 0.021 J/m2 and its density is 0.814 g/cm3, and Hvap = 30720 J/mol is the molar enthalpy of vaporization of benzene.

1.5 In general, properties of the bulk and nano-sized material composed by one and the same substance A are different. Which of the following thermodynamic constants will decrease when passing from the bulk to the nano-scaled material?

	Solubility of A in any solvent
	The boiling temperature at atmospheric pressure
	The saturated vapor pressure over solid substance A
	The equilibrium constant of a chemical reaction, where A is a reagent
	The equilibrium constant of a chemical reaction, where A is a product

Problem 2 (2007/pp9)   15% of the total

	2.1	2.2	2.3	2.4	2.5	Total
Points Possible	6	3	2	1	6	18
Score						

Pyrolysis is an important industrial process for conversion of coal to liquid fuels and chemical feedstocks. The structure of coal can be viewed as a three-dimensional network of polycyclic aromatic building blocks joined together by short aliphatic bridges. In model pyrolysis studies, α,ω-diphenylalkanes are sometimes used as model compounds for coal.

Thermal decomposition of 1,3-diphenylpropane gives toluene and styrene as the major products and ethylbenzene and other hydrocarbons as byproducts. The following mechanism of decomposition has been proposed (the first step is the slowest):

$$PhCH_2CH_2CH_2Ph \xrightarrow{k_1} PhCH_2\cdot + PhCH_2CH_2\cdot \quad (1)$$
$$\underset{S}{} \qquad\qquad \underset{1}{} \qquad \underset{2}{}$$

$$PhCH_2CH_2\cdot + PhCH_2CH_2CH_2Ph \xrightarrow{k_2} PhCH_2CH_3 + Ph\overset{\bullet}{C}HCH_2CH_2Ph \quad (2)$$
$$\underset{3}{}$$

$$PhCH_2\cdot + PhCH_2CH_2CH_2Ph \xrightarrow{k_3} PhCH_3 + Ph\overset{\bullet}{C}HCH_2CH_2Ph \quad (3)$$
$$\underset{P_1}{}$$

$$Ph\overset{\bullet}{C}HCH_2CH_2Ph \xrightarrow{k_4} PhCH{=}CH_2 + PhCH_2\cdot \quad (4)$$
$$\underset{P_2}{}$$
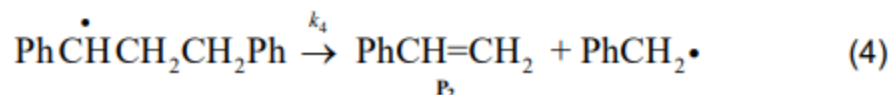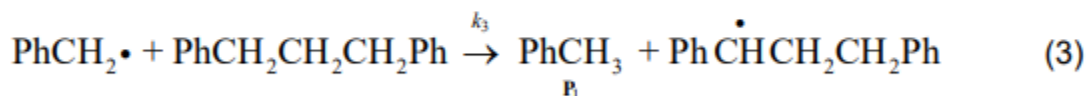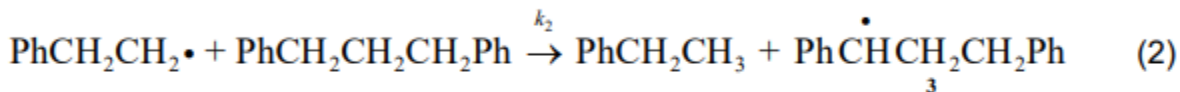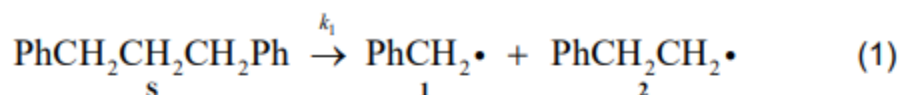
2.1 Applying the steady-state approximation for the radical 2, derive the rate equation for the side reaction of ethylbenzene formation.

2.2 What is the ratio between the steady-state concentrations of the radicals 1 and 3?

2.3 Additionally, two free radicals can recombine. The rate constant of recombination kR is supposed to be the same for all radicals. Why could we neglect these reactions in the steady-state equations in questions 1 and 2?

2.4 One of the radicals is present in the reaction mixture at much higher concentration than others. This radical is (CHOOSE ONE OPTION):

	Ph(C*)HCH2CH2Ph, because it is the most stable one
	Ph(C*)H2 radical, because the rate constant of β-scission reaction (4) is higher than the rate constant of chain propagation reaction (3).
	PhCH2(C*)H2 radical, because it accumulates in the system.

2.5 Obtain the rate equation for toluene formation. Determine the reaction order. Express the effective activation energy via the activation energies of elementary steps.

Problem 3 (2007/pp13)   12% of the total

	3.1	3.2	3.3	Total
Points Possible	5	5	5	15
Score				

Compounds of sulfur in its lower oxidation states are present in many industrial wastes (metallurgy, production of paper, chemical) and are dangerous ecotoxicants. The prevalent forms of sulfur in lower oxidation states in solutions are sulfide, sulfite, and thiosulfate ions. Their content can be determined by redox titration under different conditions.
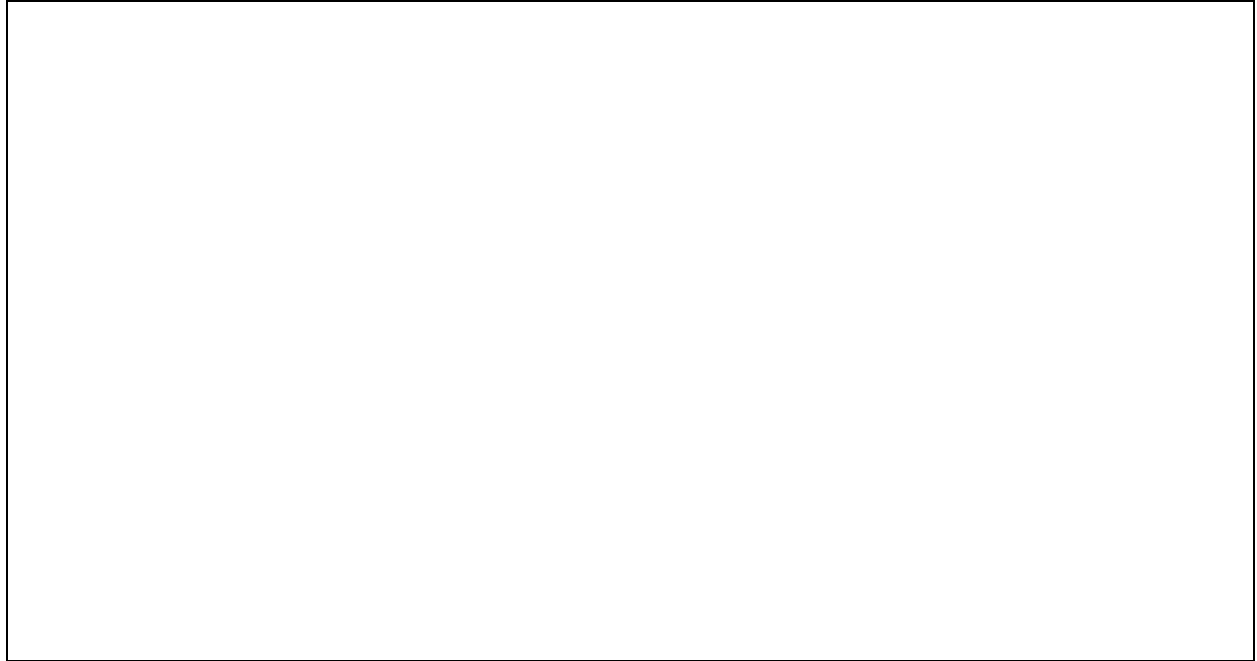
For each procedure, answer the following questions:

   a) **Write down the net ionic equations of the reactions taking place during the analysis.**
   b) **Which ion, sulfide, sulfite, or thiosulfate, can be determined from this method?**
   c) **Calculate the concentration of this ion in the initial solution.**
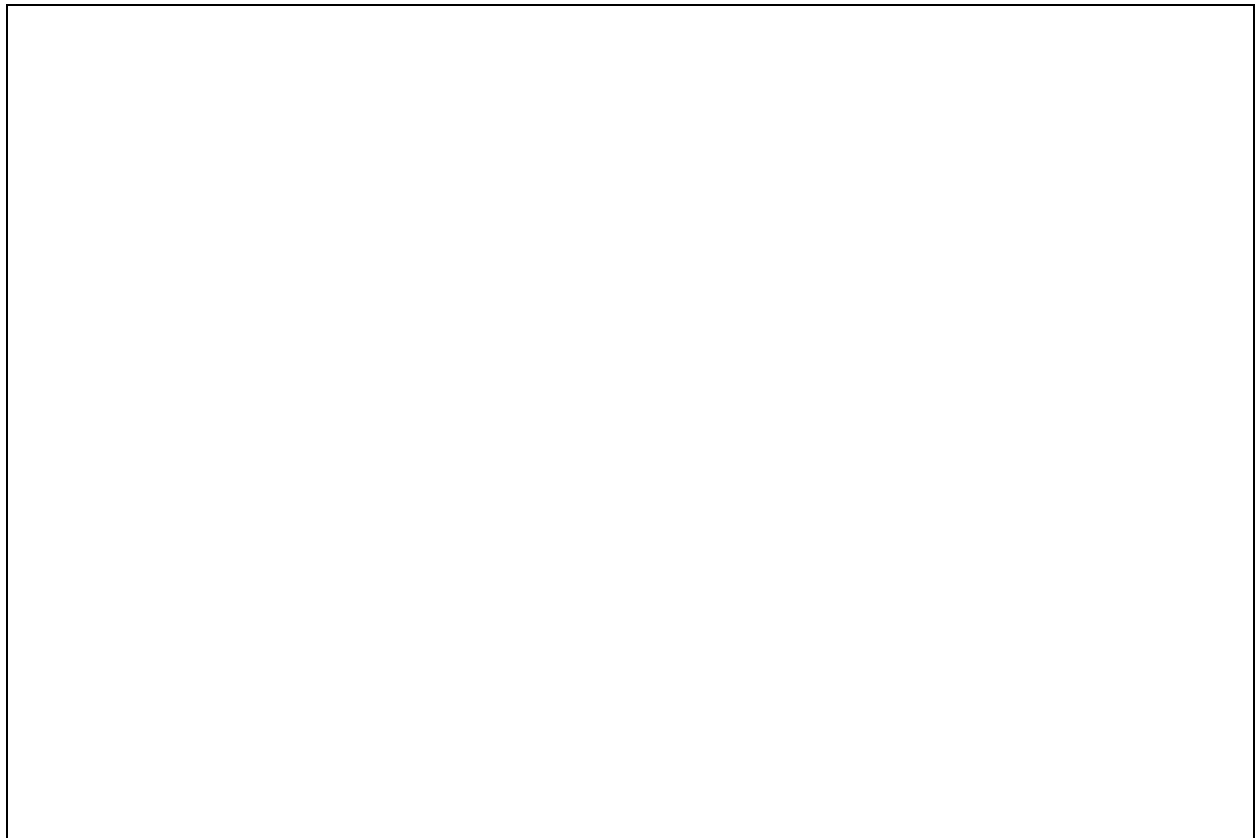
3.1 PROCEDURE 1: To a 20.00 mL sample containing sulfide, sulfite, and thiosulfate an excess of ZnCO3 suspended in water was added. Upon completion of the reaction the solution was filtered into a 50.00 mL volumetric flask and diluted to the mark. To 20.00 mL of the filtrate an excess of aqueous formaldehyde was added. The mixture was acidified with acetic acid and titrated with 5.20 mL of 0.01000 M standard solution of iodine.

3.2 PROCEDURE 2: A 20.00 mL sample of the 0.01000 M iodine solution was acidified with acetic acid and then combined with 15.00 mL of the filtrate from Procedure 1. The mixture was titrated with 6.43 mL of the 0.01000 M sodium thiosulfate standard solution.

3.3 PROCEDURE 3: A 10.00 mL sample of 0.05000 M iodine solution was acidified with acetic acid and then 10.00 mL of the original sample containing sulfide, sulfite, and thiosulfate were added. The mixture was titrated with 4.12 mL of 0.05000 M sodium thiosulfate standard solution.

Problem 4 (1988/2/abridged)   14% of the total

	4.1	4.2	4.3	Total
Points Possible	12	2	3	17
Score				

Upon heating of a mixture of **A** and fluorine (molar ratio 1 : 9, pressure approximately 1 MPa) to 900 °C three compounds (**B**, **C** and **D**) are formed. All three products are crystalline solids at ambient temperature with melting points below 150 °C. The fluorine content of **C** is found to be 36.7 % and that of **D** 46.5 % (by weight). When **B** is treated with anhydrous HOSO2F at -75 °C a compound **E** is formed:

B + HOSO2F → **E** + HF

E is a solid which is stable for weeks at 0 °C, but decomposes in days at room temperature. The electron density distribution of **E** obtained through X-ray diffraction studies is shown on two intersecting, mutually perpendicular planes.

The numbers indicated on the maps relate to the electron density in the neighbourhood of the atoms of **E** as a function of the spatial coordinates. The maxima found in these maps coincide with the locations of the atoms and the values are approximately proportional to the number of electrons in the atom in question. (The figure is too blurry to use in this problem, hence consider the following information: There are maxima at electron densities 52, 52, 52, 58, 58, 104, and 350 respectively at coordinates:

(-100,0,125), (100, -125, 0), (-100,0,-125), (100,100,0), (100,0,460), (0,0,0), (0,0,300). (coordinates in pm)

4.1 Identify the compounds **A-E**. Draw the geometric structure of compound **E**.

A		Structure of E:
B		
C		
D		
E		

4.2 When 450.0 mg of **C** was treated with an excess of mercury, 53.25 ml of **A** was liberated at a pressure of 101.0 kPa and a temperature of 25 °C. Calculate the relative atomic mass of **A**.

4.3 The original mixture was hydrolysed in water. **B** reacts to **A** while liberating oxygen and producing aqueous hydrogen fluoride. Hydrolysis of **C** leads to **A** and oxygen (in molar ratio of 4 : 3) and yields an aqueous solution of **A**O3 and hydrogen fluoride. **D** hydrolyses to an aqueous solution of **A**O3 and hydrogen fluoride. Write the equations for these three reactions.

You may use the space below for scratch work.

Problem 5 (Russia 2009/11/4)   14% of the total

	5.1	5.2	5.3	Total
Points Possible	4	5	2	11
Score				

In 1912, Ludwig Claisen discovered that heating O-allylphenols leads to them to 2-allylphenols. This rearrangement named after him was the first example of a [3,3]-sigmatropic rearrangement.

It was used, for example, to synthesize the antimicrobial agent lanceolatin B:
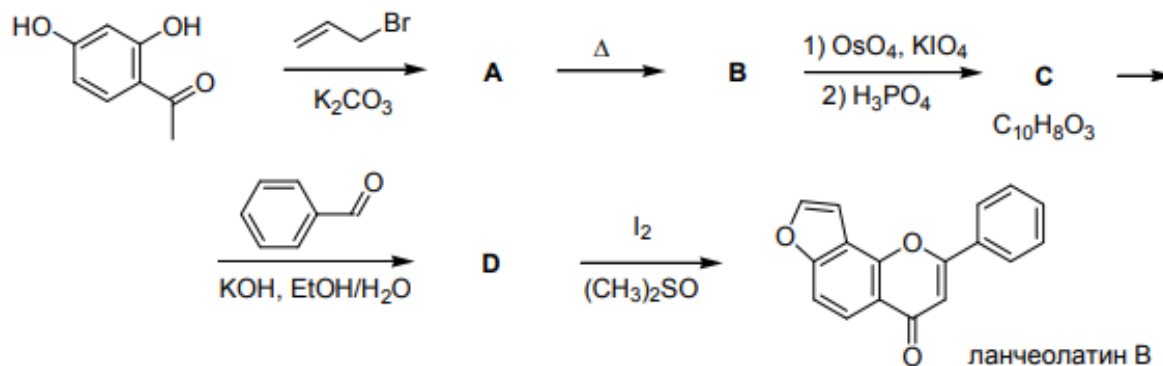
5.1 Draw the structures of compounds **A-D**.

A	B	C	D

Later, Claisen rearrangements were developed, in which a fragment of an allyl vinyl ether is generated in situ. Thus, the allyl esters of carboxylic acids enter into a rearrangement with sequential treatment with lithium diisopropylamide and trimethylchlorosilane, followed by heating:
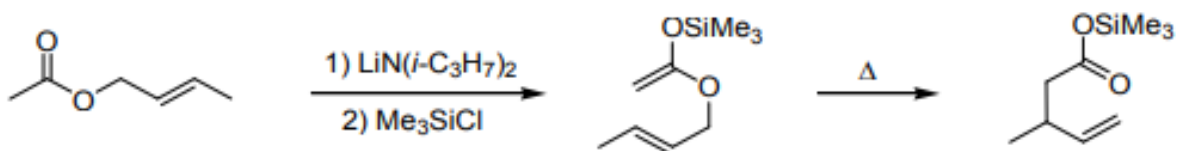
This rearrangement has recently been used in the synthesis of racemic muscon. The last stages of this synthesis are shown in the diagram: (Note: The transformation from I to muscon is done with pyridine)

мускон
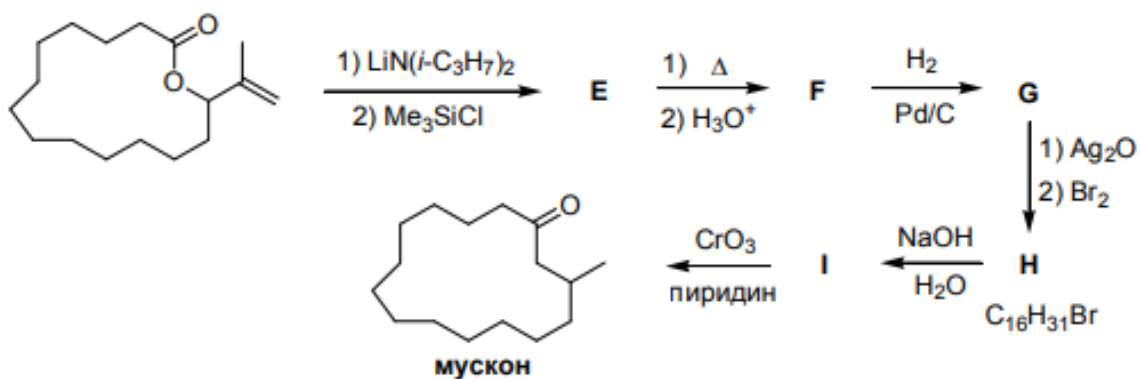
5.2 Draw the structures of compounds **E-I**.

E	F	G
H	**I**	**J (from 5.3)**

Another type of Claisen rearrangement occurs when allyl alcohols are treated with orthoesters in the presence of acid catalysts. For example, consider the interaction of triethyl orthoacetate and 3-hydroxy-2,6-dimethylhepta-1,6-diene:

$$+ \quad CH_3C(OC_2H_5)_3 \quad \xrightarrow{H^+} \quad J$$
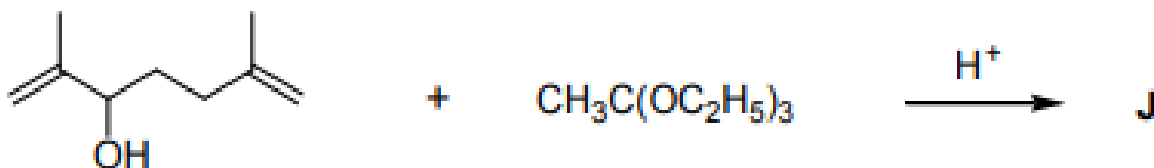
5.3 Draw the structure of compound **J** (Use the space above from 5.2).

Problem 6 (Austria/2013/4/abridged)   16% of the total

	6.1	6.2	6.3	6.4	6.5	6.6	Total
Points Possible	3	4	5	2	1	3	18
Score							

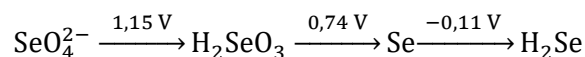Selenium is a rare trace element, which nevertheless plays an important role in our body. Usually it is ingested as selenate SeO_4^{2-} or selenite SeO_3^{2-}, and then converted to H_2Se in the organism.

The following Latimer-diagram with standard potentials is given:

$$SeO_4^{2-} \xrightarrow{\ 1,15\ V\ } H_2SeO_3 \xrightarrow{\ 0,74\ V\ } Se \xrightarrow{\ -0,11\ V\ } H_2Se$$

6.1 Calculate the standard potential for the conversion of selenate to H_2Se, the respective biochemical standard potential at pH=7, as well as the free standard enthalpy, also at pH=7.

In the next step, H_2Se using ATP reacts to the selenium compound X, which is necessary for the formation of selenium containing enzymes. X consists of four different elements, six atoms, has a charge of 2-, and a selenium fraction of 49.68 % (w/w).

6.2 Determine the constitutional formula of this anion.

One of the most important functions in the human body selenium has in the amino acid selenocysteine. There, a selenium atom replaces the sulphur atom of the amino acid cysteine. In some enzymes it is indispensable as active centre. There were investigations to find out why in special enzymes selenium cannot be replaced by the chemically similar sulphur. An important difference could be the different pK_a-values: in selenocysteine the Se-H-group shows a pK_a-value of 5.2, in cysteine the pK_a-value of the S-H-group amounts to 8.5.

6.3 Calculate the degree of dissociation of both groups at pH=7.

The amino acid selenocysteine, occurring in nature, has the following formula:
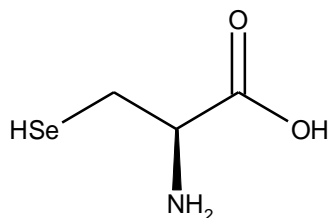
6.4.   Tick the correct answer(s):

	This is R-selenocysteine
	This is S-selenocysteine
	This is D-selenocysteine
	This is L-selenocysteine

Glutathione-peroxidase (GPx) is an important enzyme, which also contains the amino acid selenocysteine. The function of this enzyme is its antioxidative effect. GPx reacts with peroxides generated in the organism destroying them. The GPx-selenium acid (GPx-SeOH) which is formed in this reaction, continues to react with glutathione (G-SH), and the initial form of GPx is re-established.

As a model compound for this reaction, hydrogen peroxide is used, which is a representative for all peroxides.

You are given the biochemical standard potentials of the following reactions:

$H_2O_2 + 2\ H^+ + 2\ e^- \rightleftharpoons 2\ H_2O$ $E°' = +1.349\ V$

$G\text{-}S\text{-}S\text{-}G + 2H^+ + 2\ e^- \rightleftharpoons 2\ G\text{-}SH$ $E°' = -0.240\ V$

$NADP^+ + 2\ H^+ + 2\ e^- \rightleftharpoons NADP{\cdot}H + H^+$ $E°' = -0.315\ V$

$R\text{-}Se\text{-}Se\text{-}R + 2\ H^+ + 2\ e^- \rightleftharpoons 2\ R\text{-}Se\text{-}H$ $E°' = -0.488\ V$
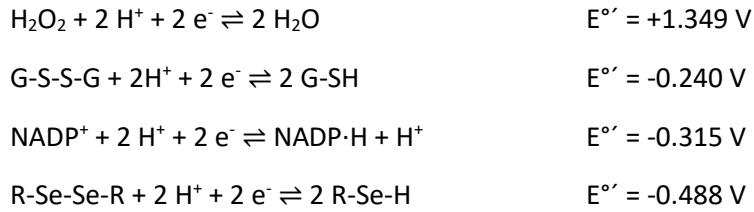
The reaction follows the given scheme:
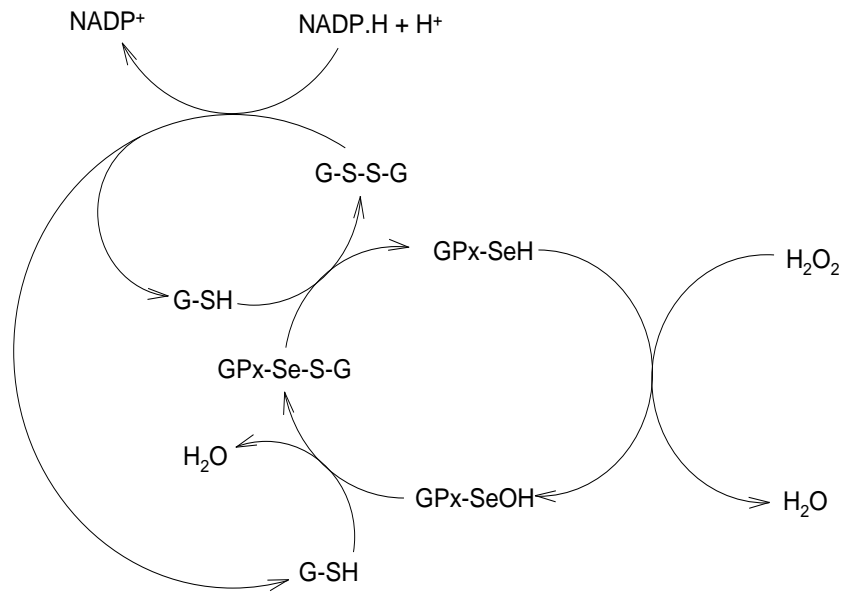
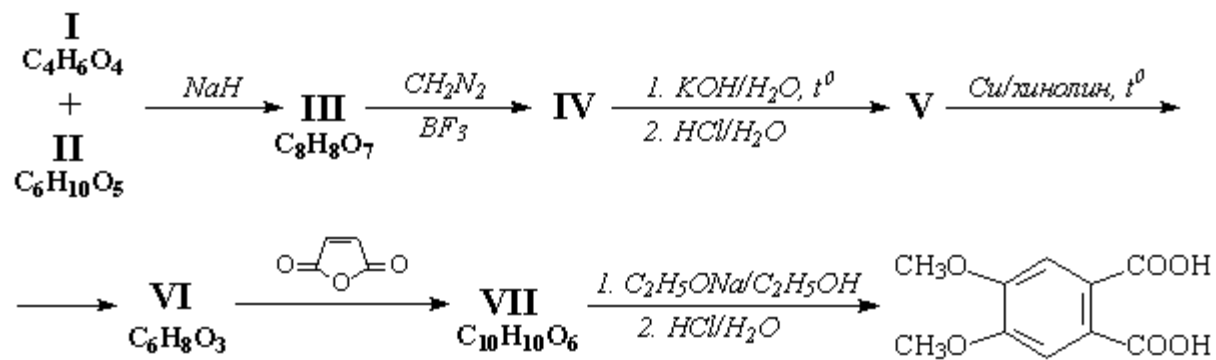**6.5** Write the overall reaction of hydrogen peroxide.

6.6. Calculate $\Delta E°'$, $\Delta G°'$ as well as K' for this reaction.

Problem 7 (Russia/2004/3)   13% of the total

	7.1	Total
Points Possible	9	9
Score		

Consider the following scheme (V->VI is copper/quinoline):

$$\textbf{I} \quad C_4H_6O_4$$
$$+$$
$$\textbf{II} \quad C_6H_{10}O_5$$

$$\xrightarrow{NaH} \textbf{III} \quad C_8H_8O_7 \xrightarrow[BF_3]{CH_2N_2} \textbf{IV} \xrightarrow[\substack{1.\ KOH/H_2O,\ t^0 \\ 2.\ HCl/H_2O}]{} \textbf{V} \xrightarrow{Cu/хинолин,\ t^0}$$

$$\longrightarrow \textbf{VI} \quad C_6H_8O_3 \xrightarrow{\substack{O=\text{(maleic anhydride)}=O}} \textbf{VII} \quad C_{10}H_{10}O_6 \xrightarrow[\substack{1.\ C_2H_5ONa/C_2H_5OH \\ 2.\ HCl/H_2O}]{}$$

[structure: CH$_3$O- and CH$_3$O- substituted benzene ring bearing two –COOH groups]

7.1 Draw the structures of compounds **I – VII**.

I (2pt)	II (2pt)	III
IV	**V**	**VI**
VII	Draw something nice here ☺	