XVIII Baltic Chemistry Olympiad

Theoretical Problems

Code: ....

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16-18 April 2010

Tartu, Estonia

Instructions

- Write your code on the first page.
- You have 5 hours to work on the problems. Begin only when the START command is given.
- All results must be written in the appropriate boxes. Anything written elsewhere will not be graded. Use the reverse of the sheets if you need scratch paper.
- Write relevant calculations in the appropriate boxes when necessary. If you provide only correct end results for complicated problems, you receive no score.
- You must stop your work immediately when the STOP command is given. A delay in doing this by 5 minutes may lead to cancellation of your exam.
- Do not leave your seat until permitted by the supervisors.
- This examination has 23 pages.
- The official English version of this examination is available on request only for clarification.

Constants and Formulae

Avogadro constant:	N_A = 6.022·10^{23} mol^{-1}	Ideal gas equation:	$pV = nRT$
Gas constant:	R = 8.314 J K^{-1} mol^{-1}	Gibbs energy:	$G = H - TS$
Faraday constant:	F = 96485 C mol^{-1}	$\Delta_r G^o = -RT\ln K = -nFE^o_{cell}$	
Planck constant:	h = 6.626·10^{-34} J s	Nernst equation:	$E = E^o + \frac{RT}{zF}\ln\frac{P_{ox}}{P_{red}}$
Speed of light:	c = 3.000·10^{8} m s^{-1}	Logarithm	$\ln x = 2.303\log x$
Zero of the Celsius scale:	273.15 K	Lambert-Beer law:	$A = \log\frac{I_0}{I} = \varepsilon cl$

In equilibrium constant calculations all concentrations are referenced to a standard concentration of 1 mol/dm^3. Consider all gases ideal throughout the exam.

Periodic table with relative atomic masses

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.008																	2 He 4.003
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 24.30											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	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 65.38	31 Ga 69.72	32 Ge 72.64	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 95.96	43 Tc -	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 137.33	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 207.2	83 Bi 208.98	84 Po -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -							

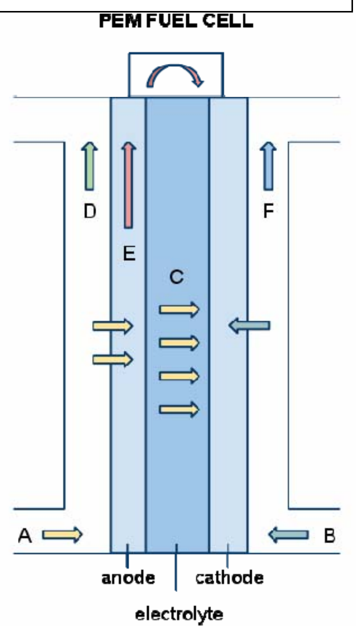
57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm -	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97
89 Ac -	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -

1. Ethanol as sourse of energy 10 p

Since ancient times ethanol has been used for lamp oil and cooking, along with plant and animal oils. Nowadays vast majority of ethanol is used as fuel and is produced in large scale by fermentation, in which certain species of yeast metabolize sugar producing ethanol. It can be said that sunlight is used to run the engine of a vehicles, as a simple sugar is created in the plant by photosynthesis, and during ethanol combustion carbon dioxide and water are produced with a release of energy.

a) Write chemical equations for sugar synthesis, ethanol production and combustion.

Early in 1860 Nikolaus August Otto used ethyl alcohol as a fuel in internal combustion engine. Today ethanol may be used as a fuel to power both direct-ethanol fuel cells (DEFC) and combustion engines. One of the first DEFC, which schematic diagram is given, was introduced in the ShellEco-Marathon in 2007.



b) Identify chemical species **A**–**F** on figure.

c) From thermodynamic data calculate DEFC maximal energy conversion efficiency ratio: $\eta = \Delta_r G^0 / \Delta_r H^0$ (25 °C).[1]

compound	O_2	H_2	CO_2	H_2O	C_2H_5OH	$C_6H_{12}O_6$
ΔH^0, kJ mol^{-1}	0	0	−394	−286	−278	−1273
S^0, J mol^{-1} K^{-1}	205	131	214	70	161	212

[1] Give all the ansvers with two signifant numbers.

d) For comparison calculate efficiency of combustion engine running on Otto cycle using equation for maximal efficiency: $\eta = 1 - 1/r^{(\gamma-1)}$, where $\gamma = C_p/C_V \approx 1.4$, r is compression ratio which equals 9 and 12.5 for ethanol and gasoline, respectively. Assume, that only half of the efficiency is achieved in practice.

There are several unsolved issues concerning DEFC, thus, in closer perspective it is more promising to convert ethanol into hydrogen in order to use the latter in typical hydrogen fuel cell.

e) Using given data calculate the maximal energy conversion efficiency ratio ($\eta = \Delta_r G^0/\Delta_r H^0$) of the hydrogen fuel cell.

To be realistic, it should be considered that in order to move a vehicle the electric energy must be converted into mechanical. Let's assume that conversion efficiency of subsystems are: 90% for invertor, 90% for motor, and 90% for gas compressor. Overall conversion efficiency ratio may be compared to energy conversion efficiency ratio of combustion engine in which chemical energy is directly converted to mechanical.

f) Estimate overall efficiency of hydrogen vehicle.

g) Name one-two main advantages of **i)** ethanol over gasoline fuel in internal combustion engine; **ii)** fuel cell over internal combustion engine.

2. Synthesis and Aquation of Fluoropentaaquachromium(III) ion[2] 10 p

5.0 cm^3 2.0 M chromium(III) perchlorate and 5.0 cm^3 2.0 M potassium fluoride were brougt together; the solution was boiled under reflux for 3 hours and cooled to 0 °C, and the precipitate **X** was removed. The density of all solutions is 1.1 g/cm^3.

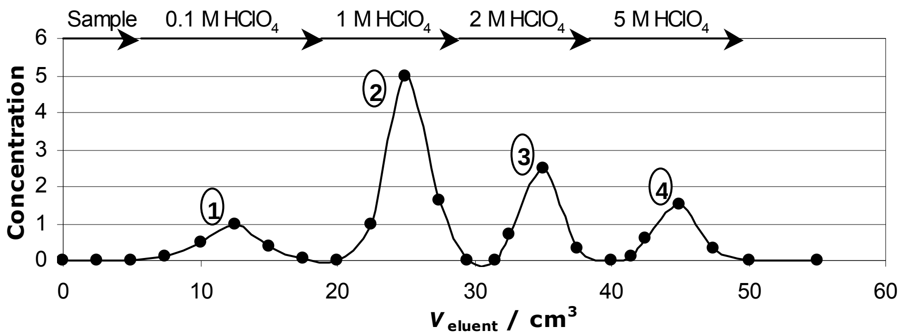
a) In the water solution the chromium(III) perchlorate is presented as aquachromium cation with co-ordination number equal to six. Write the formula of aquachromium cation and the precipitate **X**.

b) During the reflux the water in the inner sphere of the complex is replaced by anion. Write the equation of reaction.

c) The solubility product of the salt **X** is K_{sp} = 2.9·10^{-3} at 0 °C, but it is possible to dissolve 10.9 g of the salt in 5<u>0</u> g water at 100 °C (ρ = 1.1 g/cm^3). Calculate how many grams of salt **X** did precipitate during the cooling process.

[2] The problem is based on T.W. Swaddle, E.L. King *Inorg. Chem.* 4 (1965) 532.

d) The reaction mixture contained various complexes of chromium. Cation-exchange (contains R-SO_3H groups) separation allowed isolation of hexaaquachromium(III) ions, fluoropentaaqua-chromium(III) ions, difluorotetraaquachromium(III) ions and hydrolytic dimers of chromium. During the eluation process the sample was first taken into the column and afterwards the ions were eluated out using $HClO_4$ with varing concentration. Identify to which species the peaks correspond on the chromatogram.



Which compound would come out of the column during the process of taking the sample into the column?

The contents of chromium and fluoride in purified fluoropentaaquachromium(III) ions was established. 10.0 cm^3 of the sample was first decomposed using the alkaline solution of hydrogen peroxide. The fluoride ion is liberated and the oxydation state of chromium changes from III to VI. After that the sample was divided into two equal parts. First part was acidified using conc. HCl and then 3 g KI was added. After standing 5 min the solution was titrated using 18.5 cm^3 0.0975 M $Na_2S_2O_3$. The endpoint was determined using starch solution. The second part was analysed using the fluoride ion selective electrode which was calibrated using solutions with known concentration of F^-. The equation of calibration curve was $E = 183\ \text{mV} - 56\ \text{mV} \cdot \log\left[F^-\right]$. The reading of the voltmeter was 252.6 mV and the final volume of the solution was 1$\underline{0}$ cm^3 after adjusting the pH of the solution to six.

e) Write all the equations of chemial reactions in the analysis process and calculate the ration of *n*(F)/*n*(Cr) in the sample.

The pseudo first order rate coefficient of aquation of fluoropentaaquachromium(III) ion

$[Cr(H_2O)_5F]^{2+} + H^+ + H_2O = [Cr(H_2O)_6]^{3+} + HF$ (**I**)

is

$$k = \frac{2.303\left(\left[CrF^{2+}\right]_0 - \left[CrF^{2+}\right]_\infty\right)}{t\left(\left[CrF^{2+}\right]_0 + \left[CrF^{2+}\right]_\infty\right)} \log \frac{\left[CrF^{2+}\right]_0^2 - \left[CrF^{2+}\right]\left[CrF^{2+}\right]_\infty}{\left[CrF^{2+}\right]_0\left(\left[CrF^{2+}\right] - \left[CrF^{2+}\right]_\infty\right)}$$

where $\left[CrF^{2+}\right]_0 = 5.28 \cdot 10^{-3}$ M is the starting concentration and $\left[CrF^{2+}\right]_\infty$ equilibrium concentration of the complex ion.

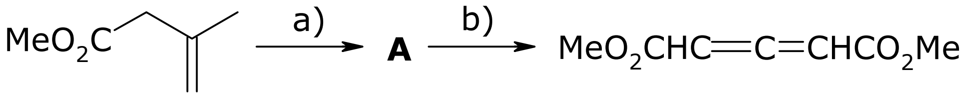
f) Calculate the time *t* (h) needed to aquate 7$\underline{0}$% of the complex ion at 77.2 °C if the concentration of hydrogen ions is 0.414 M, the rate constant is $4.40 \cdot 10^{-6}$ s^{-1} and equilibrium constant of the reaction is 0.048. The water is in excess and not included in the equilibrium constant.

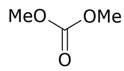
The hydrofluoric acid is weak acid.

g) Calculate pK_a(HF) at 25ºC if the equilibrium constant of the
$[Cr(H_2O)_6]^{3+} + F^- = [Cr(H_2O)_5F]^{2+} + H_2O$ (**II**)
reaction is K = $2.1 \cdot 10^4$ (25 °C) and for the reaction (**I**) the reaction enthalpy is –5.41 kJ/mol.

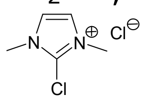
3. Asymmetry without asymmetric center 10 p

Allenes are not only versatile starting materials in organic synthesis but also present an interesting case of molecular chirality. Since it is quite difficult to synthesize allenes in stereoselective manner, they are first obtained as racemic mixture and then resolved into individual enantiomers. One of the ways of synthesizing allenes in depicted below.



a) $^{i-}Pr_2NLi$, THF; then addition of 

;

b) 

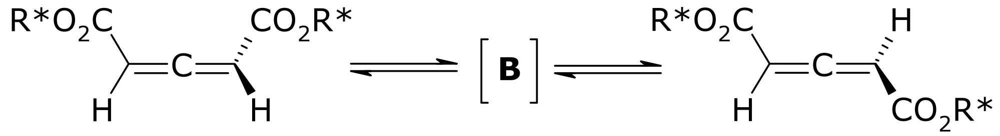
, Et_3N, CH_2Cl_2, room temperature

a) Identify symmetric structure **A**. Keep in mind that this reaction is not very efficient and **A** is only one of few possible products in this reaction.

A

b) Provide the mechanism for conversion of **A** into an allene.

One of the methods to produce allenes in pure enantiomeric form is dynamic resolution of racemic mixtures. The method takes advantage of quick epimerization and the low solubility of one of the stereoisomers. Epimerization means interconversion of one enantiomer into another proceeding through a common intermediate **B** (see scheme below). Since all of the compounds are in the equilibrium, the position of the equilibrium is shifted in the direction of the less soluble stereoisomer, which is then collected as a precipitate.



diastereomer 1 diastereomer 2

Reaction conditions: room temperature, Et_3N (0.05 Eq), pentane; R* is (-)-menthyl

c) Provide the structure of **B**.

B

In order to establish the absolute configuration of the allene **X** obtained by dynamic resolution, one can follow a method developed by Agosta in 1964. To better understand the essence of the method let us consider all transformations performed on BOTH enantiomers.

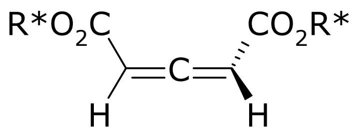
The allene ester is first hydrolyzed to dicarboxylic acid and then in Diels-Alder reaction with cyclopentadiene is transformed into a mixure of separable products.

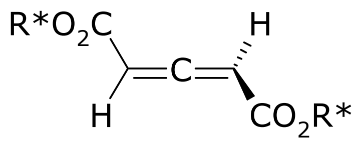
$$R^{*}O_2CHC{=}C{=}CHCO_2R^{*} \xrightarrow{a)} HO_2CHC{=}C{=}CHCO_2H \xrightarrow{b)} \mathbf{C_{1\text{-}4}}$$

Single enantiomer

a) NaOH; b) cyclopentadiene

d) Provide structures for ALL possible adducts with cyclopentadiene that could be formed from EACH allene enatiomer (**C**$_{1-4}$ from one allene enantiomer, and **C**$_{5-8}$ from the other). You are allowed to use molecular models provided by organizers.





C$_{1-4}$ **C**$_{5-8}$

C$_{1\text{-}4}$ **C**$_{5\text{-}8}$

Each of the individual compounds $C_{1\text{-}8}$ is then subjected to 2 test reactions: a) iodolactonization and b) cyclic anhydride formation.

$$\mathbf{D} \xleftarrow{\text{a)}} \mathbf{C} \xrightarrow{\text{b)}} \mathbf{E}$$

a) I_2, $NaHCO_3$; b) acetic anhydride

e) In your list of adducts, identify which structures **C**$_{1\text{-}8}$ are capable of giving desired products in BOTH test reactions. Draw equation for ONE iodolactonization reaction (**D**) and ONE cyclic anhydride formation (**E**).

The compound(s) **C** that gives positive result in both test reactions is (are) then degraded according to the following scheme. The product of the reaction **F** ($C_7H_{10}O$) is optically active compound.

$$\mathbf{C} \xrightarrow{\text{a)-d)}} \mathbf{F} \quad C_7H_{10}O$$

a) Pd/C, H_2; b) CH_2N_2; c) O_3; d) HCl, reflux

In summary, the explicit assignment of the absolute configuration by method of Agosta is based on the fact that one enantiomer of **F** can only be produced from (R)-allene, while the opposite enantiomer of **F** stems only from the (S)-allene.

f) In aforementioned case of dynamic resolution of allenes the degradation yields exclusively (1S,4R)-**F** stereoisomer. Draw the structure of **F**.

F

g) Based on the structure of compound (1S,4R)-F and identification method by Agosta suggest the structure of allene **X**, which was obtained by dynamic resolution.

X

4. Environmental hazards **10 p**

Around World War II Jinzu River in Toyama prefecture Japan was contaminated with element $\mathbf{X_1}$ compounds and nowadays Japan still is one of top three producers of this element. Element $\mathbf{X_1}$ accumulates in rice and can cause Itai-Itai disease in humans; it also replaces calcium in bones. This element is produced from compound **A** which is its only mineral of practical importance. Compound **A** is also a direct band gap semiconductor and has many applications for example in light detectors and as thermally stable pigments.

Binary compound **A** contains also nonmetallic element $\mathbf{Y_1}$ and this compound forms minerals greenockite (first discovered in Scotland and named after the land owner Lord Greenock) and hawleyite. The first mineral has hexagonal structure while second mineral has cubic structure. Mass fraction of $\mathbf{X_1}$ in compound **A** is 77.6%.

Element $\mathbf{X_1}$ can be obtained from **A** by roasting it in air. Obtained oxide is treated with sulfur trioxide to form $\mathbf{X_1}$ sulfate which is dissolved in water and electrolyzed.

a) Determine element $\mathbf{X_1}$, show your calculations!

b) Write equations for all mentioned reactions taking place in element production!

c) Calculate mass of metal $\mathbf{X_1}$ which can be obtained by electrolysis of 0.15 M metal sulfate solution with 0.5 A current and one hour long.

d) Write electron formula for element $\mathbf{X_1}$ ions in sulfate solution, knowing that there are no f electrons in this ion.

e) Table with lattice parameters for greenockite and hawleyite is shown bellow. Calculate Z value (number of "molecules" in unit cell) for hawleyite as well as density for greenockite.

Cell parameters of minerals are given below:

Parameter	Greenockite	Hawleyite
System	hexagonal	cubic
Parameters	*a* = *b* = 3.82 Å *c* = 6.26 Å γ = 120° (angle between *a* and *b*)	*a* = 5.818 Å
Z	2	?
Density	?	4.87 g·cm^{-3}

Practically important is also compound **B** which is used for production of solar energy panels and which contains nonmetallic element $\mathbf{Y_2}$. Mass fraction of element $\mathbf{X_1}$ in compound **B** is less than 50% and it is known that element $\mathbf{Y_2}$ is in same group as element $\mathbf{Y_1}$ but electronegativity for element $\mathbf{Y_2}$ is smaller than for $\mathbf{Y_1}$.

f) Determine element $\mathbf{Y_2}$, show your calculations!

Usually element $\mathbf{X_1}$ is found together with element $\mathbf{X_2}$ which is placed in same group in periodic table. Binary compound of element $\mathbf{X_2}$ with $\mathbf{Y_1}$ crystallizes in cubic face centered crystals (FCC) with parameter a = 5.406 Å. Density of this compound is 4.09 g/cm^3.

g) Determine element $\mathbf{X_2}$, show your calculations!

h) Order all possible binary compounds from elements $\mathbf{X_1}$, $\mathbf{X_2}$, $\mathbf{Y_1}$ and $\mathbf{Y_2}$ in order of increasing covalent bond content and decreasing ionic bond content!

Elements $\mathbf{X_1}$ and $\mathbf{X_2}$ can be separated also due to different solubilities of their hydroxides. Hydroxides and carbonates are the forms of $\mathbf{X_1}$ compounds which are now found in Jinzu River bed ($\mathbf{X_1}$ concentration aprox. 2 ppm).

i) Which element ($\mathbf{X_1}$ or $\mathbf{X_2}$) hydroxide has better solubility in alkaline solutions? Explain it with atomic structure of elements.

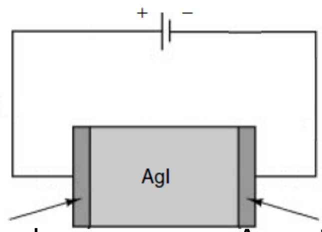
It is possible to answer next question without answering previous ones!

j) Calculate solubility (express in mol/L) of both compounds in water pH = 10.0! Take into account complex ion formation! All necessary data are given in table In the table logarithms of the overall formation constants are given.

	I	**II**
pK_{sp} of hydroxide	14.14	16.5
pK_1	4.17	4.40
$pK_{1,2}$	8.33	11.30
$pK_{1,2,3}$	9.02	14.14
$pK_{1,2,3,4}$	8.62	17.66

5. Half solid half melted 10 p

In 1914, Tubandt and Lorenz showed that solid silver iodide above 147 °C transforms into α-AgI modification that is good electrical conductor. Temperature of 147 °C may be considered as melting point for silver ion sublattice. The remaining iodide ion sublattice is stable until 557 °C. It was determined that iodide ions form body centered cubic (BCC) sublattice with lattice constant (lattice parameter) $5.04 \cdot 10^{-10}$ m.



In picture the principal scheme of Tuband's electrochemical cell is shown.

In this cell silver electrodes 0.1000 g each were placed in contact with both sides of solid AgI pellet Then electric current of 35.2 mA was flowed for 15.5 min. After that silver electrodes where taken off the pellet and were placed into two labelled 100.0 cm^3 volumetric flasks (label "**Solution A**" for anode and "**Solution B**" for cathode). Excess of diluted HNO_3(aq) was added into both flasks. After dissolution of metallic electrodes both volumetric flasks were filled with distilled water till calibration mark. **Solution A** and **Solution B** were used for titration of 10.00 cm^3 samples of 0.0113 $mol \cdot dm^{-3}$ NaCl solution that contains small amount of K_2CrO_4. Endpoint for these titrations were appearance of brick-red precipitate.

a) Write half-reactions that represent what was happening at the anode and at the cathode during the electric current flow.

At the anode:

At the cathode:

b) Write balanced chemical equation that is proceeding during action of diluted nitric acid HNO_3(aq) onto electrodes.

Balanced equation:

c) Write formula of the brick-red compound that precipitates at the titration endpoint.

Formula of brick-red compound:

d) Calculate the ratio V(Solution **A**)/V(Solution **B**) (ratio of volumes of respectively solutions that were used up for the titration of samples of NaCl solution).

ratio V(Solution A)/V(Solution B) = __________

e) Determine radius of iodide ion in BCC sublattice.

Radius of I^- = __________

f) Calculate density of solid AgI conductor.

Density of the AgI conductor = __________

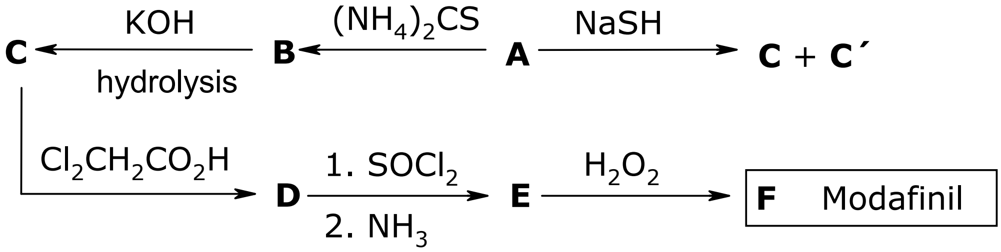
g) AgI is light sensitive compound suitable for photography. After development of black-white photo the image should be "fixed" by dissolving away all remaining silver iodide (or other silver salts). Sodium thiosulfate $Na_2S_2O_3$ is suitable fixing agent. Under reaction with silver iodide it produces compound that contains 26.9% of silver by mass. Write chemical equation that shows what is happening during the "fixing" black-white photo.

Equation:

6. Modafinil – work without sleep ? 10 p

Modafinil was originally created to treat narcolepsy (a condition when a person falls asleep at inappropriate times), but it spread widely among students and businessmen. Although a productive day after a sleepless night sounds unbelievable, it is not the only effect of modafinil; it also acts as an antidepressant and improves memory in some cases. Modafinil has a considerably smaller list of side effects than caffeine but due to its unknown long-term effects it remains a prescription drug. Yet this doesn't scare most of its users off, who buy it from the internet shops or illegal dealers.

An industrial synthesis scheme of Modafinil is presented below. In the ^{1}H NMR spectrum of compound **A** there is one singlet (6.0 ppm) and ten times more intensive multiplet (7.3 ppm). In its mass spectrum two peaks of equal intensity for the molecular ion are observed at 246 and 248 m/z. After treating compound **A** with sodium hydrosulfide a side product **C**′ was detected, therefore to avoid its formation one additional step was introduced in the synthesis.



a) Draw the structural formulas of all letter-named compounds.

b) Present the mechanism for the reaction **D** → **E**.

Modafinil is actually a mixture of two enantiomers, where only the R isomer shows the indicated biological activity.

c) Draw the structural formula of the active enantiomer of Modafinil.