

**UNIVERSITY OF TARTU
THE GIFTED AND TALENTED DEVELOPMENT
CENTRE**

**54th
ESTONIAN NATIONAL
CHEMISTRY OLYMPIAD**

Edited by

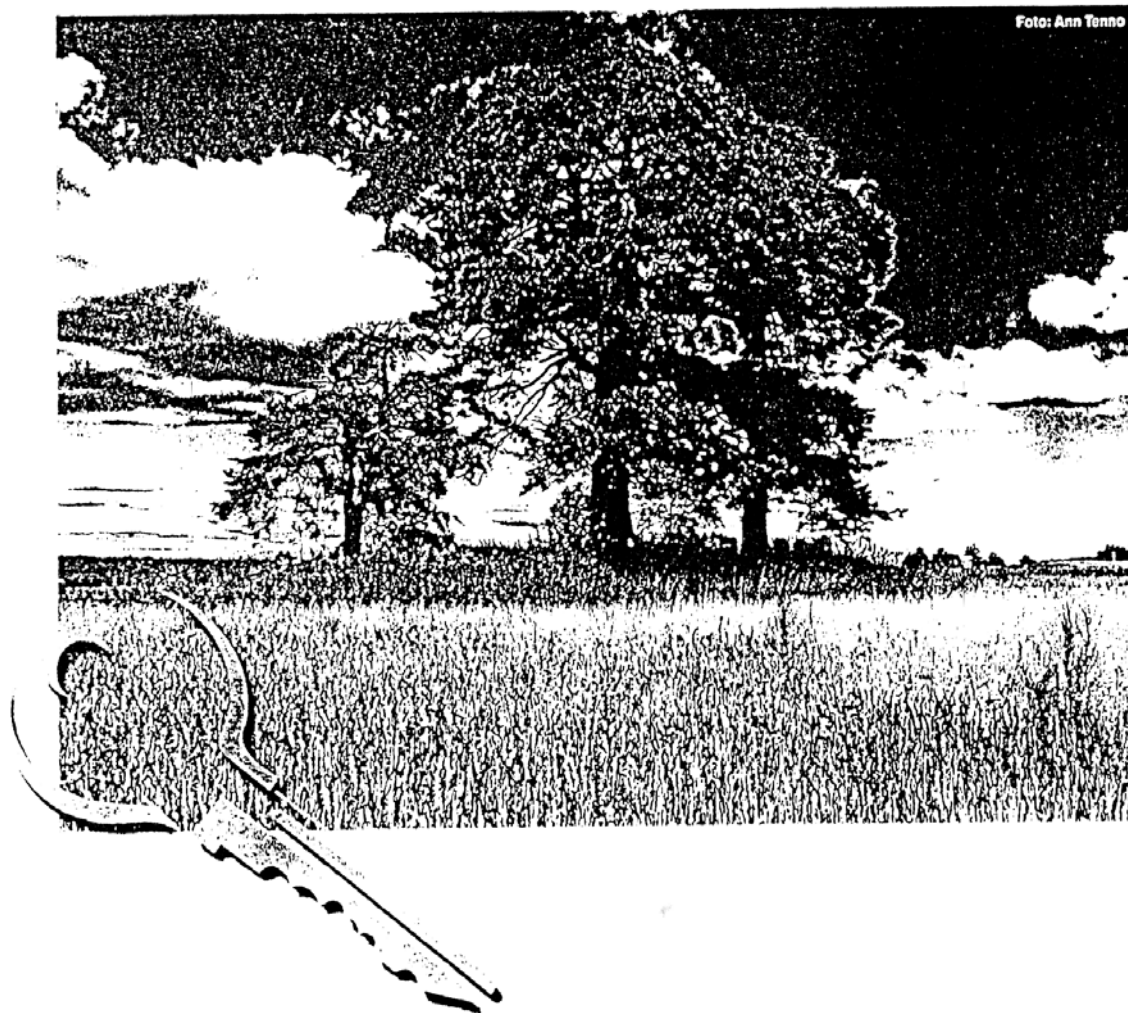
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TARTU 2007

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National Theoretical Examination: 10th Grade

Problems

Diversity of Coloured Compounds

1. Metal **X** forms three oxides: **A**, **B** and **C**. Compound **B** is green and it is used in oil colour production. The oxidation state of **X** in both hydroxide **D** and oxide **B** is the same. Compound **E** is obtained upon dissolving **D** in hydrochloric acid. When **D** is dissolved in potassium hydroxide a emerald-green compound **F** is formed. A yellow compound **G** is afforded on reaction of **F** with bromine under basic conditions, or on melting of **B** with KClO_3 and KOH . In both reactions, in addition to compound **G**, a corresponding potassium halide is formed. On acidification the solution of **G** turns orange and a compound **H** is formed. When concentrated sulphuric acid is added to a concentrated solution of **H**, dark-red needle-like crystals of **C** start to precipitate.

The solutions of salts that have the same oxidation state of **X** as in **B**, are usually bluish violet and turn green on heating. This is explained by formation of isomeric hydrates. A complex $\text{XCl}_3 \cdot 6\text{H}_2\text{O}$ was isolated in three forms. Namely, as bluish violet (**I**), dark green (**K**), and light green (**L**) crystals. On mixing a freshly prepared solution of **I** with silver nitrate all chlorine is precipitated, while 2/3 and 1/3 chlorine is precipitated from **K** and **L** solutions, respectively.

- a) Identify the element **X** and compounds **A-H**.
b) Write balanced equations for the following transformations: i) $\text{D} + \text{HCl} \rightarrow$, ii) $\text{D} + \text{KOH} \rightarrow$, iii) $\text{F} + \text{Br}_2 + \text{KOH} \rightarrow$, iv) $\text{B} + \text{KOH} + \text{KClO}_3 \rightarrow$, v) $\text{G} \rightarrow \text{H}$, vi) $\text{H} + \text{conc. H}_2\text{SO}_4 \rightarrow$.
c) Identify compound **I**, **K** and **L** based on the fact **I**, **K** and **L** have the same quantitative and qualitative composition, but react with silver nitrate differently. The coordination number of **X** is six in all three cases.

Dilution of Ethanol

2. The composition of ethanol solutions is expressed in volume-volume percentage (% v/v). The densities of water, absolute ethanol, and 40.0% v/v ethanol aqueous solution at 20 °C are 0.99820, 0.78924 and 0.94805 g/cm³, respectively.
- a) Calculate in what volume (in liters) of 96.2% v/v ethanol solution (0.80608 g/cm³) there is exactly 4000 dm³ of ethanol.
b) Calculate how many liters of water will be required to prepare 15000 dm³ 40.0% v/v of ethanol solution from i) absolute ethanol, ii) 96.2% v/v ethanol. iii) Calculate the difference in liters and in percent of water that is required for the preparation of 40.0% v/v ethanol solution from 96.2% v/v ethanol solution and absolute ethanol.

Purity Grade of Compounds

3. In chemical experiments, the purity of the starting material and the composition of impurities/additives are of great importance. For his experiments, Thomas needed KBr with at least 95.0% purity. In order to determine the purity of an available inorganic compound, he weighed out 0.8230 g of KBr and dissolved it in water. Then to the resulting solution, 31.20 cm³ of 0.2180 M AgNO₃ aqueous solution was added. For the back-titration of an excess of AgNO₃ 19.30 cm³ of 0.04480 M NH₄SCN solution was required.
- Write balanced ionic equations for aforementioned reactions.
 - Calculate **i)** the amount of excess AgNO₃, **ii)** mass of KBr in the resulting solution, **iii)** purity of KBr in the sample (in per cent), assuming that there are no traces of other halides in the technical grade KBr.
 - Can Thomas use the provided stock of KBr for his experiment(s)?

Chemistry of Lanthanides

4. Monazite [(Ln,Th)PO₄] is one of the raw mineral sources of lanthanides (Ln). In mineral the salts consist of oxygen-containing anions, and the ore contain one additional actinide(IV) salt. The ore is first crushed to a fine powder. Then, by using physical methods, the metal content is raised up to 60.0% as a mixture of lanthanide and thorium salts (La 20.0 %, Ce 43.0%, Pr 4.5%, Nd 16.0%, Th 9.0% and other lanthanides and yttrium). The concentrated ore is then treated with sulphuric acid (**reaction 1**), followed by NaOH for several hours at 150 °C until a precipitate is formed (**reaction 2**). Thereafter it is treated with HCl at 70 °C (pH 3-4) (**reaction 3**). As a result, the precipitate partially dissolves. The remaining precipitate is filtered off and heated. An oxide containing 12.12% oxygen is formed (**reaction 4**). The filtrate contains lanthanide(III) chlorides and on its treatment with a Na₂CO₃, lanthanide carbonates precipitated out of the solution (**reaction 5**).
- Write balanced equations for **reactions 1-5** for Ln and Th if no change in oxidation states occurs.
 - Monazite contains all lanthanides but one. Name the lanthanide that is not found in the ore.
 - How many kilograms of sodium hydroxide are needed to treat 1.00 kg of concentrated monazite ore?
 - How many liters of HCl solution (37.0%, 1.18 g/cm³) are needed in order to dissolve the precipitate formed from 1.00 kg of concentrated monazite ore after treatment with sodium hydroxide?
- The neodymium obtained from monazite is employed in Nd lasers and Nd-Fe-B alloy used in permanent magnets.
- Calculate the mass of Nd₂(CO₃)₃·3H₂O in grams that can be obtained from 1.00 kg of monazite.
 - Calculate the volume of metallic Nd in cm³ that can be obtained from 1.00 kg of monazite provide that d_{Nd} = 7.01 g/cm³.

Liquefied Gas

5. A small camping gas cylinder contains 450 g of liquefied gas, which consists of butane (60% w/w), propane (20% w/w), and isobutane (10% w/w). The combustion enthalpy, ΔH_c° , is -2877.6 kJ/mol for butane.

a) Write balanced equations for full combustion of **i)** butane and **ii)** propane.

b) Calculate combustion enthalpies of **i)** isobutane and **ii)** propane from enthalpies of formation.

c) Calculate the volume of gas (in liters) contained in the cylinder at standard conditions (1 atm, 25° C).

d) Calculate the heat quantity released upon full combustion of the liquefied gas from cylinder.

compound	ΔH_f° / kJ/mol
H ₂ O (l)	-285.8
C ₃ H ₈ (g)	-103.8
C ₄ H ₁₀ (g)	-134.2
CO ₂ (g)	-393.5

The Origin of the Atmosphere

6. At time when life originated on Earth, the composition of the atmosphere differed from it is now: gas **A**, methane, ammonia, and other gases were largely present while the simple compound **B** was almost absent. Because of chemical processes in organisms, the amount of **A** began to decrease while the amount of **B** began to rise. Today **B** is largely present in the Earth's atmosphere due to photosynthesis ($n\mathbf{A} + n\text{H}_2\text{O} \rightarrow n\mathbf{B} + (\text{CH}_2\text{O})_n$). Initially, **B** began to accumulate in the atmosphere when Fe^{2+} present in seawater was oxidized to Fe^{3+} . The gaseous layer that protects Earth from UV radiation is made of **C**, an allotrope of **B**. All these changes have helped to promote biodiversity on Earth.

Under certain conditions, a compound **D** may be formed in both the atmosphere and living organisms. The radicals, eventually leading to aging, were emitted on degradation of **D**. **D** contains hydrogen and oxygen only and exhibits reducing as well as oxidizing properties.

a) Write formulae for **A-D**, name the compounds

b) Write balanced equations for the following transformations: **i)** $n\mathbf{A} + n\text{H}_2\text{O} \rightarrow n\mathbf{B} + (\text{CH}_2\text{O})_n$, **ii)** $\mathbf{D} \rightarrow \mathbf{B}$, **iii)** $\text{Fe}(\text{OH})_2 + \mathbf{B} + \text{H}_2\text{O} \rightarrow$ and **iv)** $\mathbf{B} \leftrightarrow \mathbf{C}$.

c) Based on the redox properties of **D**, write electron-half- and overall equations, identify oxidizer and reducer: **i)** $\mathbf{D} + \text{KI} + \text{H}_2\text{SO}_4 \rightarrow$ and **ii)** $\mathbf{D} + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \rightarrow$.

Solutions

1. a) **X** – Cr, chromium
A – CrO, chromium(II) oxide
B – Cr₂O₃, chromium(III) oxide
C – CrO₃, chromium(VI) oxide
D – Cr(OH)₃, chromium(III) hydroxide
E – CrCl₃, chromium(III) chloride
F – K₃[Cr(OH)₆], potassium hexahydroxochromate(III)
G – K₂CrO₄, potassium chromate
H – K₂Cr₂O₇, potassium dichromate
- b) i) Cr(OH)₃ + 3HCl = CrCl₃ + 3H₂O
 ii) Cr(OH)₃ + 3KOH = K₃[Cr(OH)₆]
 iii) 2K₃[Cr(OH)₆] + 3Br₂ + 4KOH = 2K₂CrO₄ + 6KBr + 8H₂O
 iv) Cr₂O₃ + 4KOH + KClO₃ = 2K₂CrO₄ + KCl + 2H₂O
 v) 2K₂CrO₄ + H₂SO₄ = K₂Cr₂O₇ + K₂SO₄ + H₂O
 vi) K₂Cr₂O₇ + conc. H₂SO₄ = 2CrO₃↓ + K₂SO₄ + H₂O
- c) **I** – [Cr(H₂O)₆]Cl₃
K – [Cr(H₂O)₅Cl]Cl₂·H₂O
L – [Cr(H₂O)₄Cl₂]Cl·2H₂O

2. a) **V(96.2% v/v ethanol solution)** = $\frac{4000 \text{ dm}^3}{0.962} = 4158 \text{ dm}^3 \approx \mathbf{4160 \text{ dm}^3}$

b) i) $m(\text{ethanol}) = 15000 \text{ dm}^3 \cdot \frac{1000 \text{ cm}^3}{1 \text{ dm}^3} \cdot 0.4 \cdot \frac{0.78924 \text{ g}}{1 \text{ cm}^3} = 4.735 \cdot 10^6 \text{ g}$

$$m(40\% \text{ v/v ethanol solution}) = 15000 \text{ dm}^3 \cdot \frac{1000 \text{ cm}^3}{1 \text{ dm}^3} \cdot \frac{0.94805 \text{ g}}{1 \text{ cm}^3} = 1.422 \cdot 10^7 \text{ g}$$

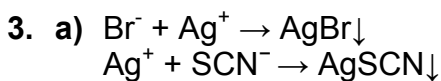
$$\mathbf{V(H_2O)} = (14.22 - 4.735) \cdot 10^6 \text{ g} \cdot \frac{1 \text{ cm}^3}{0.99820 \text{ g}} \cdot \frac{1 \text{ dm}^3}{1000 \text{ cm}^3} = 9502 \text{ dm}^3 \approx \mathbf{9500 \text{ dm}^3}$$

ii) $m(96.2\% \text{ v/v ethanol solution}) = \frac{15000 \text{ dm}^3 \cdot 0.4 \cdot 1000 \text{ cm}^3}{0.962} \cdot \frac{0.80608 \text{ g}}{1 \text{ cm}^3} = 5.028 \cdot 10^6 \text{ g}$

$$\mathbf{V(H_2O)} = (14,22 - 5,028) \cdot 10^6 \text{ g} \cdot \frac{1 \text{ cm}^3}{0.99820 \text{ g}} \cdot \frac{1 \text{ dm}^3}{1000 \text{ cm}^3} = 9210 \text{ dm}^3 \approx \mathbf{9200 \text{ dm}^3}$$

c) $\Delta \mathbf{V(H_2O)} = (9502 - 9210) \text{ dm}^3 = 293 \text{ dm}^3 \approx \mathbf{300 \text{ dm}^3}$

$$\% = \frac{293 \text{ dm}^3}{9210 \text{ dm}^3} \cdot 100 = 3.17 \approx \mathbf{3}$$



b) i) $n(\text{AgNO}_3 \text{ excess}) = n(\text{NH}_4\text{SCN}) = 19.30 \text{ cm}^3 \cdot \frac{1 \text{ dm}^3}{1000 \text{ cm}^3} \cdot \frac{0.04480 \text{ mol}}{1 \text{ dm}^3} =$
 $= 8.646 \cdot 10^{-4} \text{ mol}$

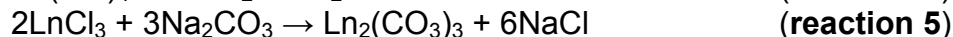
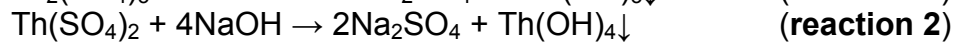
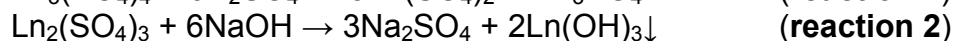
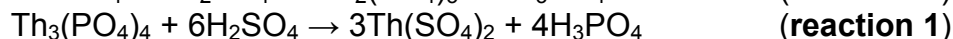
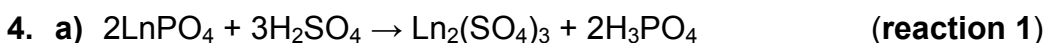
ii) $n(\text{AgNO}_3 \text{ overall}) = 31.20 \text{ cm}^3 \cdot \frac{1 \text{ dm}^3}{1000 \text{ cm}^3} \cdot \frac{0.2180 \text{ mol}}{1 \text{ dm}^3} =$
 $= 6.8016 \cdot 10^{-3} \text{ mol}$

$n(\text{KBr}) = n(\text{AgBr}) = (6.8016 - 0.8646) \cdot 10^{-3} \text{ mol} = 5.937 \cdot 10^{-3} \text{ mol}$

$m(\text{KBr}) = 5.937 \cdot 10^{-3} \text{ mol} \cdot 119.01 \text{ g/mol} = \mathbf{0,7066 \text{ g}}$

iii) $\%(\text{KBr}) = \frac{0.7066 \text{ g}}{0.8230 \text{ g}} \cdot 100 = \mathbf{85.85}$

c) No, he can not



b) **Promethium.** Pm is an radioactive element and decomposes in Nature.

c) $M(\text{Ln, Th}) = \frac{0.6 \cdot (31 + 4 \cdot 16)}{0.4} \text{ g/mol} = 142.46 \text{ g/mol}$

$M(\text{Ln}) = \left(\frac{142.46 \text{ g}}{1 \text{ mol}} - \frac{3}{4} \cdot 0.09 \cdot \frac{232.04 \text{ g}}{1 \text{ mol}} \right) \cdot \frac{1}{0.91} \text{ g/mol} = 139.33 \text{ g/mol}$

$n(\text{NaOH}) = \frac{3}{1} \cdot 1000 \text{ g} \cdot 0.6 \cdot 0.91 \cdot \frac{1 \text{ mol}}{139.33 \text{ g}} + \frac{4}{1} \cdot 1000 \text{ g} \cdot 0.6 \cdot 0.09 \cdot \frac{1 \text{ mol}}{232.04 \text{ g}}$

=

$= 11.76 \text{ mol} + 0.9309 \text{ mol} = 12.68 \text{ mol}$

$m(\text{NaOH}) = 12.68 \text{ mol} \cdot 40.0 \text{ g/mol} = 507.5 \text{ g} \approx \mathbf{508 \text{ g}}$

d) $n(\text{HCl}) = n(\text{Ln}) = 11.76 \text{ mol}$

$V(\text{HCl}) = 11.76 \text{ mol} \cdot \frac{36.5 \text{ g}}{1 \text{ mol}} \cdot \frac{1}{0.37} \cdot \frac{1 \text{ cm}^3}{1.18 \text{ g}} \cdot \frac{1 \text{ dm}^3}{1000 \text{ cm}^3} = \mathbf{0.983 \text{ dm}^3}$

e) $m(\text{Nd}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}) = 1000 \text{ g} \cdot 0.600 \cdot 0.160 \cdot \frac{1 \text{ mol}}{144.2 \text{ g}} \cdot \frac{1}{2} \cdot \frac{522.6 \text{ g}}{1 \text{ mol}} = \mathbf{174}$

g

f) $V(\text{Nd}) = 1000 \text{ g} \cdot 0.600 \cdot 0.160 \cdot \frac{1 \text{ cm}^3}{7.01 \text{ g}} = \mathbf{13.7 \text{ cm}^3}$

5. a) i) $C_4H_{10} + 6,5O_2 = 4CO_2 + 5H_2O$
 ii) $C_3H_8 + 5O_2 = 3CO_2 + 4H_2O$
 b) i) $\Delta H_c^\circ(\text{isobutane}) = [5 \cdot (-285.8) + 4 \cdot (-393.5) - (-134.2)] \text{ kJ/mol} =$
 $= -2868.8 \text{ kJ/mol}$
 ii) $\Delta H_c^\circ(\text{propane}) = [4 \cdot (-285.8) + 3 \cdot (-393.5) - (-103.8)] \text{ kJ/mol} =$
 $= -2219.9 \text{ kJ/mol}$

c) $n(\text{butane}) = 450 \text{ g} \cdot 0.6 \cdot \frac{1 \text{ mol}}{58 \text{ g}} = 4.655 \text{ mol}$

$n(\text{isobutane}) = 450 \text{ g} \cdot 0.1 \cdot \frac{1 \text{ mol}}{58 \text{ g}} = 0.776 \text{ mol}$

$n(\text{propane}) = 450 \text{ g} \cdot 0.3 \cdot \frac{1 \text{ mol}}{44 \text{ g}} = 3.07 \text{ mol}$

$n(\text{gas}) = (4.655 + 0.776 + 3.07) \text{ mol} = 8.50 \text{ mol}$

$V = \frac{nRT}{p} = 8.501 \text{ mol} \cdot 0.082 \frac{\text{atm} \cdot \text{dm}^3}{\text{mol} \cdot \text{K}} \cdot 298 \text{ K} \cdot \frac{1}{1 \text{ atm}} = 207.7 \text{ dm}^3 \approx$

$\approx 210 \text{ dm}^3$

- d) Released heat quantity:

$q = - \left(4.655 \text{ mol} \cdot \frac{-2877.6 \text{ kJ}}{1 \text{ mol}} + 0.776 \text{ mol} \cdot \frac{-2868.8 \text{ kJ}}{1 \text{ mol}} + 3,07 \cdot \frac{-2219.9 \text{ kJ}}{1 \text{ mol}} \right) \cdot$
 $\cdot \frac{1 \text{ MJ}}{1000 \text{ kJ}} = 22.437 \text{ KJ} = 22 \text{ MJ}$

6. a) A – CO_2 , carbon dioxide

B – O_2 , oxygen

C – O_3 , ozone

D – H_2O_2 , hydrogen peroxide

- b) i) $nCO_2 + nH_2O = nO_2 + (CH_2O)_n$

ii) $2H_2O_2 = O_2 \uparrow + 2H_2O$

iii) $4Fe(OH)_2 + O_2 + 2H_2O = 4Fe(OH)_3$

iv) $3O_2 = 2O_3$

- c) i) $H_2O_2 + 2KI + H_2SO_4 = I_2 + K_2SO_4 + 2H_2O$

$2O^{-1} + 2e^{-} = 2O^{-II}$ Oxidizer

$2I^{-} - 2e^{-} = I_2$ Reducer

ii) $3H_2O_2 + K_2Cr_2O_7 + 4H_2SO_4 = 3O_2 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$

$2Cr^{VI} + 6e^{-} = 2Cr^{III}$ Oxidizer

$2O^{-1} - 2e^{-} = O_2^0$ |·3 Reducer

National Theoretical Examination: 11th Grade

Problems

A Record from Iron Mountain Mine

1. Extremely acidic mine waters (pH = -3.6) have been reported encountered in Iron Mountain Mine, near Redding CA. High acidity is probably contributed by oxidation of pyrite since the mine waters are rich in iron sulphates. Due to high concentrations, iron cations and sulphate anions make up the hydrated minerals (see Table) which do not contain over one Fe²⁺ ion.

mineral	Fe, %
melanterite	20.09
szomolnokite	32.86
copiapite	22.34
romerite	20.84
kornelite	21.23
rhomboglass	17.39

- Determine formulae of melanterite, szomolnokite, romerite, and kornelite, if they may contain SO₄²⁻ and Fe³⁺ or Fe²⁺, while both types of iron ions are present in romerite.
- Determine formulae of copiapite and rhombic glass provided that copiapite contains Fe²⁺, Fe³⁺, SO₄²⁻, OH⁻ and 20 water molecules while rhombic glass contains H₃O⁺, Fe³⁺ and SO₄²⁻.
- Write balanced equations for **i)** the oxidation of pyrite (%(Fe) = 46.5) by Fe³⁺ and **ii)** the oxidation of Fe²⁺ just formed in **i)** by oxygen.
- Write balanced reaction for formation of minerals, in which pH **i)** decreases, **ii)** increases.

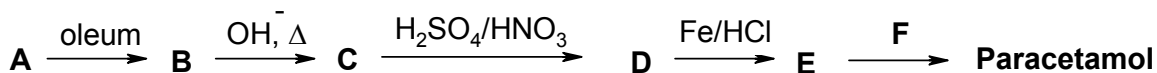
Iron concentrations (g/dm³) of two collected samples are shown in Table.

code	pH	c(Fe) _{overall}	c(Fe ²⁺)
90WA109	-0.7	86.2	79.7
90WA110A	-2.5	124	34.5

- What minerals may correspond to samples 90WA109 and 90WA110A?

Synthesis of Paracetamol

2. Paracetamol is a non-steroidal anti-inflammatory drug with the systematic name *N*-(4-hydroxyphenyl)acetamide. The synthetic route to paracetamol is shown below:



Compound **B** contains 45.6% carbon, 3.8% hydrogen, 30.3% oxygen, and 20.3% sulphur by mass. Compound **C** is a weak acid and the products of its combustion are only carbon dioxide and water.

- Write structural formulas for **A–E** and name these compounds.

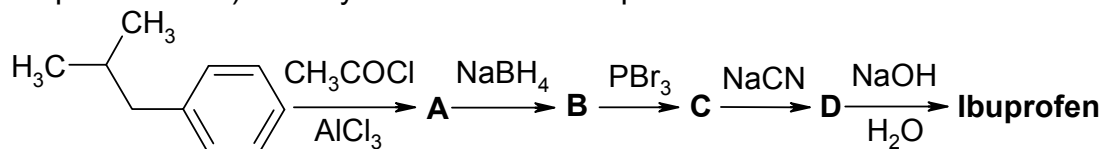
- b) Draw the mechanisms for transformations **A** → **B** and **B** → **C**, name the reaction types.
- c) What by-product is formed in reaction **C** → **D**?
- d) i) Which acetylating agent **F** can be used? ii) Why reagent **F** is taken in 10% excess?

Daniell-Jacobi Galvanic Cell

3. The Daniell-Jacobi galvanic cell (electrochemical cell) consists of copper and zinc rods, which are placed into copper(II) and zinc sulphate solutions, respectively. The solutions are connected *via* salt bridge. The concentration and volume of the solutions are 0.100 M and 1.00 dm³, respectively. Standard electrode potentials of copper and zinc are 0.340 V and -0.763 V.
- a) Write ionic equations for (i) anodic and (ii) cathodic processes that take place in the galvanic element.
- b) Schematically draw the galvanic cell with positive electrode on your right.
- c) Calculate electromotor force (zero-current potential) of galvanic cell in the beginning of the working cycle (T = 298 K).
- d) Calculate the maximum electric charge that can be obtained from galvanic cell.
- e) John Frederic Daniell (1790–1845) was the first professor of chemistry and meteorology at King's College, London. In which Baltic university did Moritz Hermann (Boris Semyonovich) von Jacobi work during 1835–1837?

Synthesis of Ibuprofen

4. Ibuprofen is yet another non-steroidal anti-inflammatory drug (*cf* problem 2 for paracetamol). The synthetic route to Ibuprofen is shown below:



Ibuprofen contains 75.68% carbon, 8.81% hydrogen, and 15.51% oxygen by mass.

- i) Determine the molecular formula of Ibuprofen. ii) Name the starting material.
- a) Write planar structural formulas for **A–D**.
- b) Write spatial structural formulas for (*R*)- and (*S*)-isomers of Ibuprofen.

Blood Phosphate Buffer

5. Buffer solutions are able to retain constant pH when small amount of acid/base is added. One of the buffer systems that regulate the pH of blood (= 7.4) is a phosphate buffer, which consists of H_2PO_4^- and HPO_4^{2-} . If an acid or a base is added, these ions interchange. The pH of a phosphate buffer solution can be calculated from Henderson–Hasselbach equation:

$$\text{pH} = \text{pK} - \log \left(\frac{[\text{H}_2\text{PO}_4^-]}{[\text{HPO}_4^{2-}]} \right), \text{ where } \text{pK} = 6.86.$$

The ability of maintaining a constant pH is defined by the buffer capacity β . It is equal to the amount of H^+ (β_{H^+}) or OH^- (β_{OH^-}) added to one liter of solution which changes pH by one unit.

- Calculate **i)** the relative amount (in per cent) of H_2PO_4^- and HPO_4^{2-} and **ii)** the concentration (mmol/L) of H_2PO_4^- and HPO_4^{2-} in blood provided that overall phosphate concentration is 1.2 mmol/L.
- Calculate buffer capacities of the blood phosphate buffer β_{H^+} and β_{OH^-} .
- What does blood buffer better: lactic acid (pK = 3.9) or carbonate ions (pK = 10.2)?

The Story of Blue Vitriol

6. In 1597, Andreas Libavius, a German doctor, was experimenting with blue vitriol trying to find a remedy to cure gashes and cancer. On addition of ammonia solution to a solution of blue vitriol, a light-blue precipitate (%Cu) = 49.4) was formed (**reaction 1**). Libavius added some more ammonia and the solution turned intensively blue (**reaction 2**). At that time, neither he nor his contemporaries could think of an explanation.

Today we know that Libavius was the first to obtain a complex compound. When diluted sulphuric acid is added to the last solution, light blue precipitate reappears (**reaction 3**). It instantly disappears but the solution turns again light blue like in the beginning of the experiment.

- Determine formula and name of **i)** light blue precipitate, **ii)** a complex that colours the solution intensive blue.
- Write balanced equations for **reactions 1-3**.
The structure of blue vitriol is well understood today., Copper coordination number is six in it and one of the five water molecules is "free", i.e. it is not coordinated to copper and the number of hydrogen bonds is maximal.
- Draw the environment (primary coordination sphere) of copper in blue vitriol, which is formed from water molecules and sulfate ions.
- Draw Lewis structure of sulphate ion.
- How many hydrogen bonds are there per one copper atom in blue vitriol?
- Which atoms does the "free" water molecule interact with?

Solutions

1. a) Suppose that the empiric formula is $(\text{FeSO}_4)_x[\text{Fe}_2(\text{SO}_4)_3]_y \cdot z\text{H}_2\text{O}$, then
 $M_r(\text{mineral}) = 152 \cdot x + 400 \cdot y + 18 \cdot z$

$$M_r(\text{melanterite}) = \frac{55.85}{0.2009} = 278 \quad \text{FeSO}_4 \cdot 7\text{H}_2\text{O} \quad (x = 1, y = 0, z = 7)$$

$$M_r(\text{szomolnokite}) = \frac{55.85}{0.3286} = 170 \quad \text{FeSO}_4 \cdot \text{H}_2\text{O} \quad (x = 1, y = 0, z = 1)$$

$$M_r(\text{romerite}) = \frac{55.85(x + 2y)}{0.2084} = 268(x + 2y)$$

If $x = y = 1$, then $M_r(\text{romerite}) = 804$ and $z = 14$ **$\text{FeFe}_2(\text{SO}_4)_4 \cdot 14\text{H}_2\text{O}$**

$$M_r(\text{kornelite}) = \frac{55.85(x + 2y)}{0.2123} = 263(x + 2y)$$

If $x = 0$ and $y = 1$, then $M_r(\text{kornelite}) = 526$ and $z = 7$ **$\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$**

- b) $M_r(\text{copiapite}) = 152 \cdot x + 400 \cdot y + 18 \cdot y - w \cdot (96.07 - 2 \cdot 17.02)$

$$M_r(\text{copiapite}) = \frac{55.85(x + 2y)}{0.2234} = 250(x + 2y) \quad \text{FeFe}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$$

$(x = w = 1, y = 2, z = 20)$

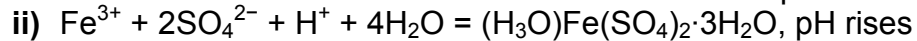
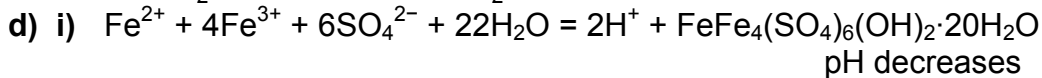
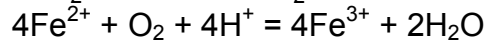
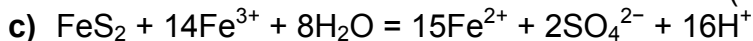
Suppose that the empiric formula is $\text{Fe}_k(\text{H}_3\text{O})_l(\text{SO}_4)_m \cdot n\text{H}_2\text{O}$, then

$$M_r(\text{rhombohedral glass}) = 55.85 \cdot k + 19.03 \cdot l + 96.07 \cdot m + 18 \cdot n$$

(due to the charge balance: $3 \cdot k + l = 2 \cdot m$)

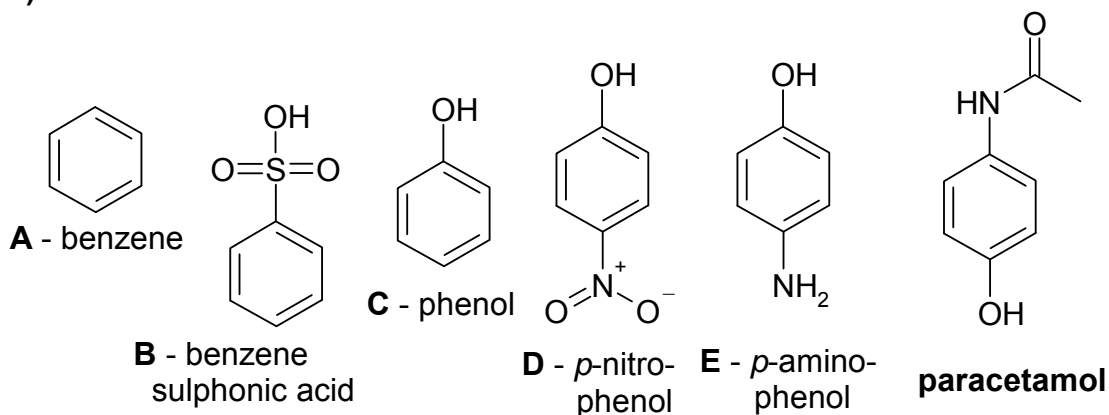
$$M_r(\text{rhombohedral glass}) = \frac{55.85 \cdot k}{0.1739} = 321k \quad (\text{H}_3\text{O})\text{Fe}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$$

$(k = l = 1, m = 2, n = 3)$

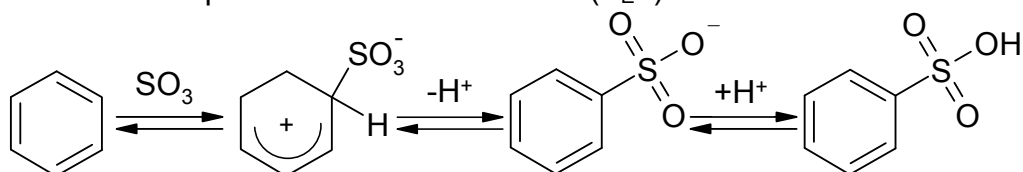


- e) 90WA109 – melanterite or szomolnokite
 90WA110A – romerite

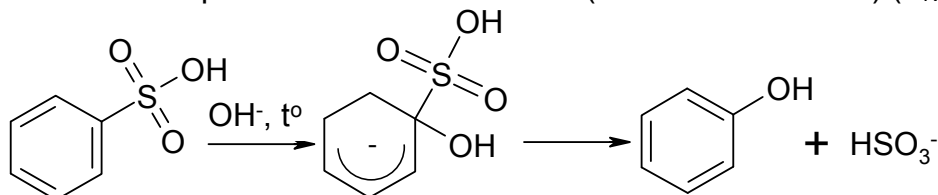
2. a)



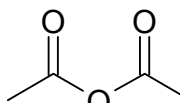
b) A → B electrophilic aromatic substitution (S_E2)

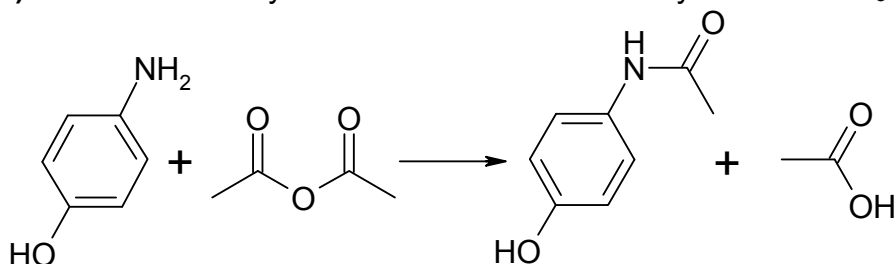


B → C nucleophilic aromatic substitution (addition-elimination) (S_NAr)



c) *o*-nitrophenol

d) i) F = acetic anhydride  or acetyl chloride CH_3COCl



ii) Since the reaction is bimolecular, it would have taken a considerably longer time for reaction to complete if the starting materials were both taken in equivalent amounts.

3. a) i) $Zn = Zn^{2+} + 2e^-$ ii) $Cu^{2+} + 2e^- = Cu$

b) (-) Zn | ZnSO₄ || CuSO₄ | Cu (+)

$$c) \text{ EMF} = E(\text{Cu}^{2+}/\text{Cu}) - E(\text{Zn}^{2+}/\text{Zn}) = E^0(\text{Cu}^{2+}/\text{Cu}) - E^0(\text{Zn}^{2+}/\text{Zn}) - \frac{RT}{zF} \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$\text{EMF} = 0.340 \text{ V} - (-0.763 \text{ V}) - \frac{RT}{2F} \ln 1 = \mathbf{1.103 \text{ V}}$$

d) Galvanic element works until all Cu^{2+} is reduced

$$q = \frac{2}{1} \cdot 1 \text{ dm}^3 \cdot 0.1 \frac{\text{mol}}{\text{dm}^3} \cdot 96485 \frac{\text{A} \cdot \text{s}}{\text{mol}} = \mathbf{19\,300 \text{ C}}$$

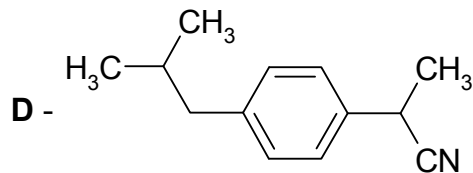
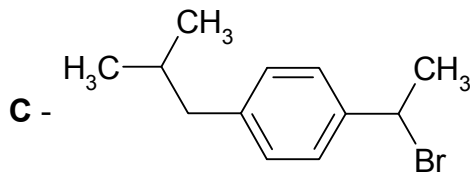
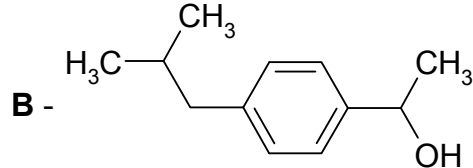
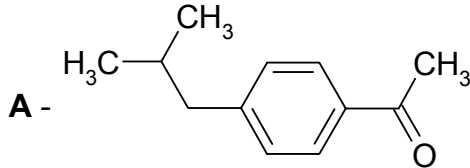
e) University of Tartu

$$4. \text{ a) i) } \text{C} : \text{H} : \text{O} \Leftrightarrow \frac{75.68}{12.0} : \frac{8.81}{1.01} : \frac{15.51}{16.0} \Leftrightarrow 6.31 : 8.72 : 0.97 \Leftrightarrow 13:18:2$$

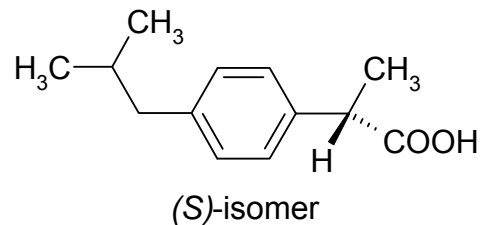
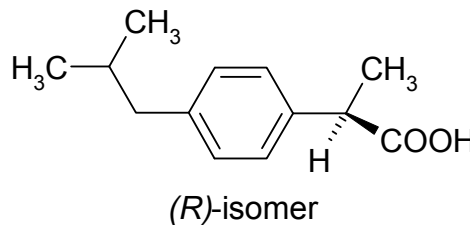
The molecular formula of Ibuprofen is $\mathbf{C_{13}H_{18}O_2}$

ii) 1-isobutylbenzene

b)



c)



$$5. \text{ a) i) } 7,4 = 6,86 - \log \frac{[\text{H}_2\text{PO}_4^-]}{[\text{HPO}_4^{2-}]} \quad \frac{[\text{H}_2\text{PO}_4^-]}{[\text{HPO}_4^{2-}]} = 0,288$$

$$\%(\text{H}_2\text{PO}_4^-) = \frac{0,288}{1+0,288} \cdot 100 = 22,4 \approx \mathbf{22}$$

$$\%(\text{HPO}_4^{2-}) = \frac{1}{1+0,288} \cdot 100 = 77,6 \approx \mathbf{78}$$

$$\text{ii) } [\text{H}_2\text{PO}_4^-] = 0,224 \cdot 1,2 \text{ mmol/L} = 0,269 \text{ mmol/L} \approx \mathbf{0,27 \text{ mmol/L}}$$

$$[\text{HPO}_4^{2-}] = 0,776 \cdot 1,2 \text{ mmol/L} = 0,931 \text{ mmol/L} \approx \mathbf{0,93 \text{ mmol/L}}$$

$$\text{b) } 6,4 = 6,86 - \log \frac{[\text{H}_2\text{PO}_4^-] + \beta_{\text{H}^+}}{[\text{HPO}_4^{2-}] - \beta_{\text{H}^+}} \quad \frac{0,269 + \beta_{\text{H}^+}}{0,931 - \beta_{\text{H}^+}} = 2,88$$

$$\beta_{H^+} = 0.65 \text{ mmol/l}$$

$$8.4 = 6.86 - \log \frac{[H_2PO_4^-] - \beta_{OH^-}}{[HPO_4^{2-}] + \beta_{OH^-}}$$

$$\frac{0,269 - \beta_{OH^-}}{0,931 + \beta_{OH^-}} = 0.0288$$

$$\beta_{OH^-} = 0.24 \text{ mmol/l}$$

c) **Lactic acid** because the buffer capacity for phosphate buffer is greater for acid ($\beta_{H^+} > \beta_{OH^-}$).

6. a) i) $Cu_2SO_4(OH)_2$ – copper(II) sulphate hydroxide

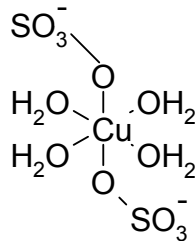
$[Cu(NH_3)_4]SO_4$ – copper(II) tetraammine sulphate

b) $2CuSO_4 + 2NH_3 + 2H_2O = Cu_2SO_4(OH)_2 \downarrow + (NH_4)_2SO_4$ (reaction 1)

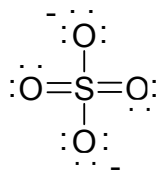
$Cu_2SO_4(OH)_2 + (NH_4)_2SO_4 + 6NH_3 = 2[Cu(NH_3)_4]SO_4 + 2H_2O$ (reaction 2)

$[Cu(NH_3)_4]SO_4 + 2H_2SO_4 = CuSO_4 + 2(NH_4)_2SO_4$ (reaction 3)

c)

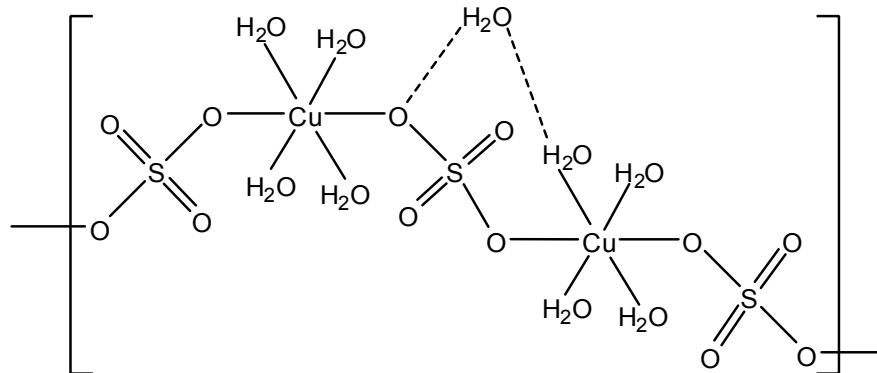


d)



e) There are ten hydrogen atoms overall, therefore there are **ten** hydrogen bonds

f) Four water molecules that are coordinated to copper atom can give eight hydrogen bonds. Two of them coordinate interact with the “free” water molecule and the remaining six interact with sulphate ion. Every sulphate ion can give eight hydrogen bonds.



National Theoretical Examination: 12th Grade

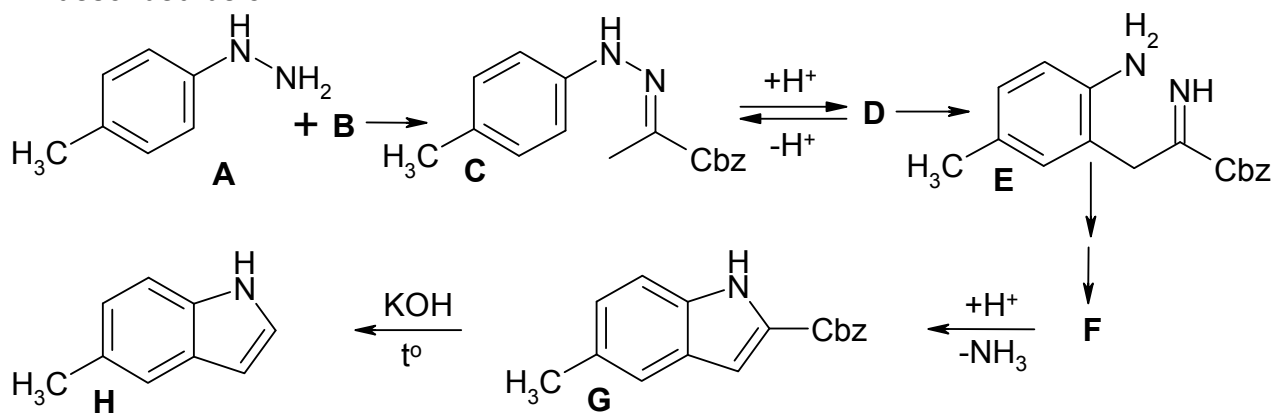
Problems

Bioenergetics

1. In mammalian cell, the energy required to support life processes is gathered from adenosine triphosphate (ATP) hydrolysis, which can collectively be presented by the following reaction $\text{ATP} = \text{ADP} + \text{P}_i$, where ADP is adenosine diphosphate and P_i is phosphate. The overall amount of ATP in human is only several tens of grams and can be additionally synthesized to meet the cell's immediate demand for ATP. The ATP synthesis takes place thanks to the energy that is obtained on oxidation of energy-rich compound NADH (nicotinamide adenine dinucleotide) by inhaled oxygen. The corresponding reaction consists of two half-reactions: $\text{NAD}^+ + \text{H}^+ + 2\text{e}^- = \text{NADH}$, with $E_1^0 = -0.32 \text{ V}$ and $\frac{1}{2}\text{O}_2 + 2\text{e}^- + 2\text{H}^+ = \text{H}_2\text{O}$, with $E_2^0 = 0.82 \text{ V}$.
- a) Calculate (i) the quotient ($Q = [\text{products}]/[\text{reagents}]$) for ATP hydrolysis under physiological conditions (37°C) if $[\text{ATP}] = 3.4 \text{ mM}$, $[\text{ADP}] = 1.3 \text{ mM}$ and $[\text{P}_i] = 4.8 \text{ mM}$ and (ii) the change in Gibbs free energy (ΔG) under the same conditions, given that $\Delta G^\circ = -30.5 \text{ kJ/mol}$. $\Delta G = -RT \ln K + RT \ln Q$
- b) Write (i) balanced equation for NADH oxidation and calculate (ii) the standard potential and (iii) the change in standard free energy.
- c) How many ATP molecules can be synthesized at the price of Gibbs free energy harvested from oxidation of one NADH molecule? The efficiency coefficient for this process is 63%.

Fischer's Indole Synthesis

2. Indoles are aromatic heterocycles that extensively used for preparation of a variety of biological active compounds. One of the most known methods employed indole construction is known as the Fischer indole synthesis after Nobel laureate Emil Fischer (1852-1919). The modern indole synthesis is described below:



In step **D**→**E**, [3,3]-sigmatropic rearrangement takes place and as a result of it N-N bond is cleaved and one C-C bond is formed. Compound **F** contains amino moiety. In step **E**→**F**, as consequence of C-N bond formation a five-membered cycle is formed. Cbz (benzyloxycarbonyl; -C(O)OCH₂Ph) is a protecting group.

a) Write planar structural formulas for **B**, **D**, **F**.

Protective groups are widely exploited in organic synthesis to protect and/or activate moieties. In general, they have to be easily deblocked giving volatile and less reactive compounds. In this particular case, electron withdrawing Cbz enhances positive charge on adjacent carbon and therefore promotes cyclization **E** → **F**.

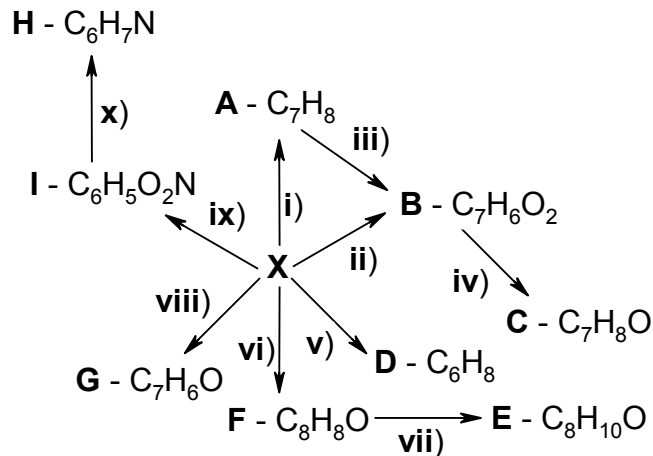
b) Which compounds are formed in Cbz deprotection **G** → **H**?

Sensitive Display

3. The Japanese scientists developed a new type of touch-sensitive display, which is the most precise and transparent to date. In order to uncover the structure of the display rivals bombarded it with argon ions and detected the displaced species with mass spectrometer. The ion bunch gradually deepened the hole and it was possible to ascertain the composition of different layers. The display had five unknown layers that were placed on LCD display. The first (**I**; external) layer was made of material **A** that contained seven elements with atomic masses 28, 27, 11, 40, 137, 88, and 16, which were present in the following mass ratio 280:79:31:36:45:42:486. The purpose of the second layer (**II**) was to glue the first and the third layer together and was of no interest to the researches. Ions with mass-to-charge ratio 108 were obtained from the third layer (**III**) and could conduct electricity (as detected by electron microscopy). The bulk of this layer was composed of organic polymer **B**, which monomer unit had molecular weight of 192. The structural analysis data showed the presence of *para*-substituted benzene derivative, two symmetrical ester bonds and ethylene group. The fourth layer (**IV**) was only 5 μm thick and was composed mostly of compound **B**. It was covered with a semi-conducting material **D**, which included elements with the following atomic masses 115, 119 and 16. Based on signals obtained, it was deduced that the molar ratio of the two elements with the biggest atomic masses was 9 to 1. The bottom fifth layer (**V**) was made of **B**. The rivals are still unsure how the layers serve to improve the properties of the new display.
- Name material **A** and determine both qualitative and quantitative composition of the mixture of oxides.
 - What compound is responsible for the conducting areas in the third layer and why they use precisely this compound?
 - Write structural formula of a monomer unit of polymer **B**.
 - Determine qualitative and quantitative composition of material **D** (oxidation states of components in **D** are maximum)?

Derivatives of Benzene

4. **X** is an unsaturated cyclic compound that can be afforded by trimerization of ethyne. **X** is extensively used in organic chemistry and is a starting material for a great number of compounds. This is depicted on the following scheme of transformations. Further reagent(s)/reaction conditions may be used: KMnO_4 , OH^- , t° ; H_2 (+ catalyst); $\text{CH}_3\text{COBr}/\text{FeBr}_3$; $\text{HNO}_3/\text{H}_2\text{SO}_4$; Na/NH_3 ; LiAlH_4 ; CO , HCl , AlCl_3 ; $\text{CH}_3\text{Cl}/\text{AlCl}_3$; first NaOH , CO_2 (under pressure), then H^+ ; Sn , HCl ; $\text{CH}_3\text{ONa}/\text{CH}_3\text{OH}$. One of the conditions will remain unused.

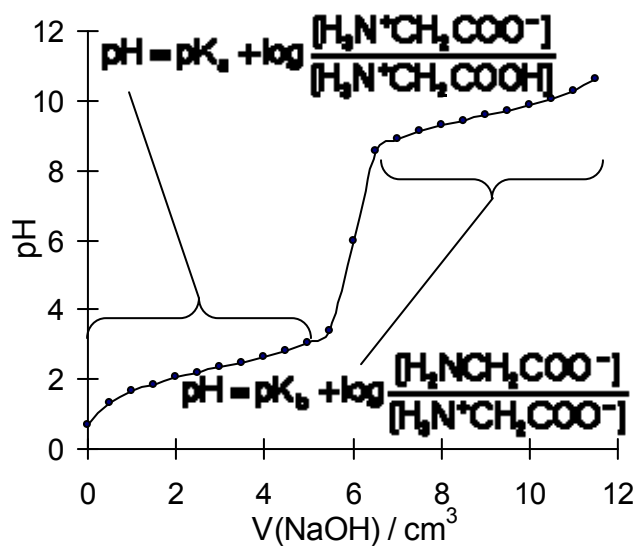


- State the name of the class of compounds to which all the unknown belong to?
- Write planar structural formulas for **A-I** and **X** and name these compounds.
- Allocate the appropriate reagents for the corresponding transformations i)-x).

Acid-Base Properties of Glycine

5. To describe the acid-base properties of amino acid glycine (in form $\text{H}_3\text{N}^+\text{CH}_2\text{COOH}$) a titration curve was obtained by titration of glycine with NaOH solution. Carboxyl and amino groups define acid-base properties. Undissociated amino group is RNH_3^+ , while dissociated one is RNH_2 . Both groups have good buffering properties at a certain pH range, and therefore in these circumstances Henderson-Hasselbach equation may be applied for pH calculation.

- Write ionic equations for glycine two step reaction with NaOH .
- In which form is glycine present i) in the beginning of the titration curve ($\text{pH} < \text{pK}_a$), ii) in end of the titration curve ($\text{pH} > \text{pK}_b$)?



- c) At an isoelectric point (when $\text{pH} = (\text{pK}_a + \text{pK}_b)/2$), the net charge of glycine is zero and the amino acid is present in solution as zwitterion. Write the glycine molecule in its zwitterionic form (NB! Identify the charges if any).
- d) Calculate the percentage of glycine found as $\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-$, when i) $\text{pH} = \text{pI}$, ii) $\text{pH} = 2.817$ ($\text{pK}_a = 2.34$), iii) $\text{pH} = 10.057$ ($\text{pK}_b = 9.58$).

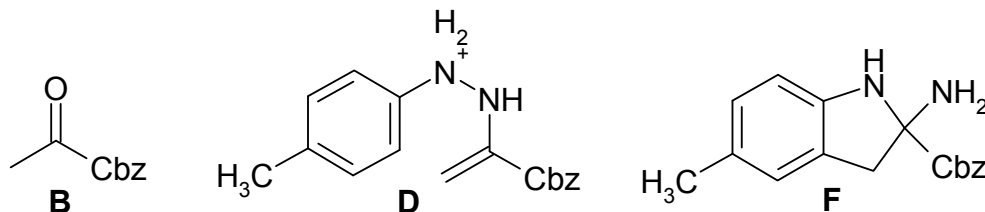
Aerobic and Anaerobic Respiration of Bacteria

6. In anaerobic respiration, microorganisms use a strong acid **B** anion **A** as an electron acceptor instead of oxygen. In both **A** and **B**, the element **X** is in its highest oxidation state. As a part of this type of respiration a systematic reduction of **A** occur. First, the oxidation state of **X** decreases by 2 units that afford an anion **C** of a weak acid **D**. Then **C** can be transferred back into environment. Other bacteria reduce **C** to an acrid colourless gas **F**, which forms a cation **E** in aqueous solution. Another type of bacteria gradually reduces **C** to a colourless gas **G**, which may be transformed to a sweet gas **I**, and finally to a simple compound **K** (widely used as an inert gas). At the same time, the element **X** is used as an energy source in aerobic respiration. One type of bacteria oxidize **F** to **C**, others oxidize **C** to give **A** that goes into soil. **B** decomposes minerals and induces corrosion of constructions. Until recent it was thought that **X** is involved in nutrition solely in aerobic organisms. However, *Brocadia anammoxidans* use **F** as a source of energy and **C** for respiration. As a result of the last process **K** is formed.
- a) Write formulas for **A**, **B**, **C**, **D**, **E**, **F**, **G**, **I**, **K**, and **X**; name them.
- b) Write equations for the following reactions (add water if needed): i) $\text{A} + \text{e}^- + \text{H}^+ \rightarrow \text{C}$, ii) $\text{C} + \text{e}^- + \text{H}^+ \rightarrow \text{F}$, iii) $\text{C} + \text{e}^- + \text{H}^+ \rightarrow \text{G}$, iv) $\text{G} + \text{e}^- + \text{H}^+ \rightarrow \text{I}$, v) $\text{I} + \text{e}^- + \text{H}^+ \rightarrow \text{K}$, vi) $\text{E} + \text{C} \rightarrow \text{K}$, vii) $\text{F} + \text{O}_2 \rightarrow \text{C} + \text{H}^+$ and viii) $\text{C} + \text{O}_2 \rightarrow \text{A}$.
- c) Identify the electron donor and acceptor in the *Brocadia anammoxidans* digestion process.

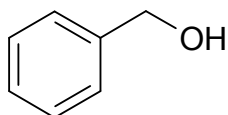
Solutions

1. a) i) $Q = \frac{[\text{ADP}] \cdot [\text{P}_i]}{[\text{ATP}]} = \frac{4.8 \cdot 10^{-3} \cdot 1.3 \cdot 10^{-3}}{3.4 \cdot 10^{-3}} = 1.8 \cdot 10^{-3}$
- ii) $\Delta G = \Delta G^0 + RT \ln Q =$
 $-30.5 \frac{\text{kJ}}{\text{mol}} + 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \cdot \frac{1 \text{kJ}}{10^3 \text{J}} \cdot 310 \text{ K} \ln 1.8 \cdot 10^{-3} =$
 $= -30.5 \text{ kJ/mol} - 16.2 \text{ kJ/mol} = \mathbf{-46.8 \text{ kJ/mol}}$
- b) i) $\text{NADH} + \frac{1}{2}\text{O}_2 + \text{H}^+ = \text{NAD}^+ + \text{H}_2\text{O}$
- ii) $E^0 = E_2^0 + (-E_1^0) = 0.82 \text{ V} + 0.32 \text{ V} = \mathbf{1.14 \text{ V}}$
- iii) $\Delta G^0 = -zFE^0 = 2 \cdot 96485 \frac{\text{J}}{\text{C} \cdot \text{V}} \cdot \frac{1 \text{kJ}}{10^3 \text{J}} \cdot 1.14 \text{ V} = \mathbf{220 \text{ kJ/mol}}$
- c) $N = \frac{-220 \text{ kJ/mol} \cdot 0.63}{-46.8 \text{ kJ/mol}} = \mathbf{3}$

2. a)



- b) CO_2 – carbon dioxide, (K_2CO_3 – potassium carbonate in KOH solution)
and



benzylic alcohol

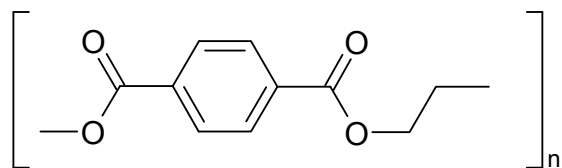
3. a) The first layer consists of borosilicate glass with the following composition: **SiO₂ (60 %)**, **Al₂O₃ (15 %)**, **B₂O₃ (10 %)**, **CaO (5.0 %)**, **BaO (5.0 %)**, **SrO (5.0 %)**.

Composition of oxide:

$$\%(\text{SiO}_2) = \frac{(28 + 2 \cdot 16) \cdot 280 / 28}{280 + 79 + 31 + 36 + 45 + 42 + 486} \cdot 100 = \frac{600}{999} \cdot 100 = \mathbf{60}$$

$$\%(\text{CaO}) = \frac{(40 + 16) \cdot 36 / 40}{280 + 79 + 31 + 36 + 45 + 42 + 486} \cdot 100 = \frac{50.4}{999} \cdot 100 = \mathbf{5.0 \text{ etc.}}$$

- b) **Silver** is used since it is the best known electric conductor and the cord from silver might be as small to be transparent.
- c) Polyethylene terephthalate



d) Material **D** is made from In_2O_3 and SnO_2 and acts as a semi-conductor. Contact with a conductive object (e.g. finger) results in a capacitance change and serves as a signal.

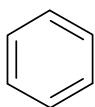
Let us suppose that there is 1 mol of SnO_2 (151 g/mol). Therefore there is 9/2 mol of In_2O_3 (278 g/mol).

$$\%(\text{In}_2\text{O}_3) = \frac{278 \cdot 9/2}{278 \cdot 9/2 + 151} \cdot 100 = 89.2\% = \underline{89\%}$$

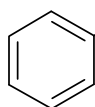
$$\%(\text{SnO}_2) = \frac{151}{151 + 278 \cdot 9/2} \cdot 100 = 10.8\% = \underline{11\%}$$

4. a) Arenes

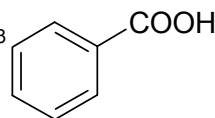
b)



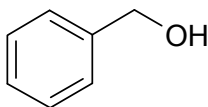
X
benzene



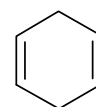
A
toluene



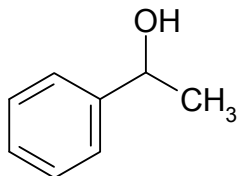
B
benzoic acid



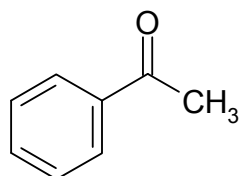
C
phenylmethanol
benzyl alcohol



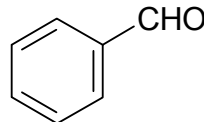
D
1,4-cyclohexadiene



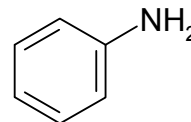
E
1-phenylethanol



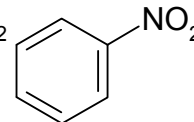
F
1-phenylethanone
acetophenone



G
benzaldehyde



H
aniline



I
nitrobenzene

c) i) $\text{CH}_3\text{Cl}/\text{AlCl}_3$

ii) first NaOH , CO_2 (under pressure), then H^+

iii) KMnO_4 , OH^- , t°

iv) LiAlH_4

v) Na/NH_3

vi) $\text{CH}_3\text{COBr}/\text{FeBr}_3$

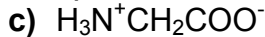
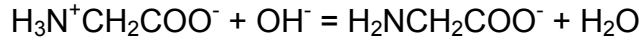
vii) H_2 (+ catalyst)

viii) CO , HCl , AlCl_3

ix) HNO_3 , H_2SO_4

x) Sn , HCl

5. a) $\text{H}_3\text{N}^+\text{CH}_2\text{COOH} + \text{OH}^- = \text{H}_3\text{N}^+\text{CH}_2\text{COO}^- + \text{H}_2\text{O}$



ii) $2.817 = 2.34 + \log \frac{[\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-]}{[\text{H}_3\text{N}^+\text{CH}_2\text{COOH}]}$ $\frac{[\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-]}{[\text{H}_3\text{N}^+\text{CH}_2\text{COOH}]} = 3$

$$[\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-] = 3[\text{H}_3\text{N}^+\text{CH}_2\text{COOH}]$$

$$c(\text{glycine}) = [\text{H}_3\text{N}^+\text{CH}_2\text{COOH}] + [\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-] = 4[\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-]$$

$$\%(\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-) = \frac{[\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-]}{c(\text{glycine})} \cdot 100 =$$

$$= \frac{3[\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-]}{4[\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-]} \cdot 100 = \frac{3}{4} \cdot 100 = 75$$

iii) $10.057 = 9.58 + \log \frac{[\text{H}_2\text{NCH}_2\text{COO}^-]}{[\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-]}$ $\frac{[\text{H}_2\text{NCH}_2\text{COO}^-]}{[\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-]} = 3$

$$[\text{H}_2\text{NCH}_2\text{COO}^-] = 3[\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-]$$

$$c(\text{glycine}) = [\text{H}_2\text{NCH}_2\text{COO}^-] + [\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-] = 4[\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-]$$

$$\%(\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-) = \frac{[\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-]}{c(\text{glycine})} \cdot 100 = \frac{1}{4} \cdot 100 = 25$$

6. a) **A** – NO_3^- , nitrate ion

B – HNO_3 , nitric acid

C – NO_2^- , nitrite ion

D – HNO_2 , nitrous acid

E – NH_4^+ , ammonium cation

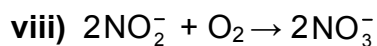
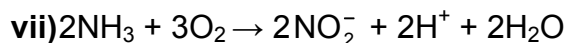
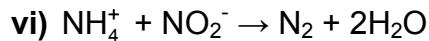
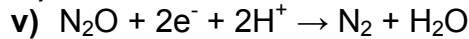
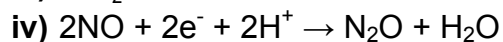
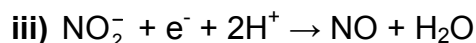
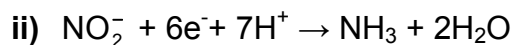
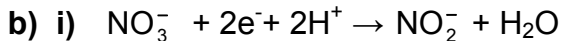
F – NH_3 , ammonia

G – NO , nitric oxide, nitrogen monoxide

I – N_2O , nitrous oxide, dinitrogen monoxide

K – N_2 , nitrogen

X – N , atomic nitrogen



c) In *Brocadia anammoxidans*, nitrite (**C**) is the electron acceptor, while ammonia (**F**) is the electron donor.

National Practical Examination: 10th Grade

Iodometric back-titration of sodium thiosulphate

$\text{Na}_2\text{S}_2\text{O}_3$ is used as a titrant for the redox (oxidation-reduction) titration. The solution is prepared from the solid $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ is not very stable on its own and may lose some of hydrate water. In addition, the $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ may contain impurities. Therefore, it is always necessary to conduct the determination of the precise concentration of $\text{Na}_2\text{S}_2\text{O}_3$, for which the following method is used.

The concentration of $\text{Na}_2\text{S}_2\text{O}_3$ is determined using $\text{K}_2\text{Cr}_2\text{O}_7$ solution of known concentration (carcinogenic!). A 0.005000 M $\text{K}_2\text{Cr}_2\text{O}_7$ solution is prepared in a 100.0 mL measuring flask using distilled water. Calculate the required amount of $\text{K}_2\text{Cr}_2\text{O}_7$ to prepare the solution and prepare the solution.

Rinse burette with $\text{Na}_2\text{S}_2\text{O}_3$ solution and fill it up to the necessary level. Transfer 10.00 mL of prepared $\text{K}_2\text{Cr}_2\text{O}_7$ solution into a 300 mL Erlenmeyer flask and add 7–10 mL of 6 M HCl (corroding and irritating!) followed by 7–10 mL of 10% KI solution. Cover the flask with glass and leave it for 5–10 minutes in the dark. Then, rinse the glass with water (add it into the titration flask) and add distilled water (ca. 100 mL). The solution is titrated until strawish yellow color appears. Add 1–2 mL of starch solution. The solution turns dark blue. Titrate the solution until it turns light green.

Calculate the required amount of $\text{K}_2\text{Cr}_2\text{O}_7$ to prepare the solution.

Write two balanced reaction equations.

Calculate the precise molar concentration of $\text{Na}_2\text{S}_2\text{O}_3$ solution.

National Practical Examination: 11th and 12th Grade

Synthesis of Glucose Pentaacetate

Peracetylated carbohydrates serve as starting material for the synthesis of a number of carbohydrates. In recent years, a greater attention was drawn to the application of undissolved catalysts and solventless reaction conditions. In experiment described below, you will synthesize glucose pentaacetate under solventless conditions with the use of undissolved catalyst.

Attach a round-bottom flask with a three-pronged clamp to a ring stand, drop a spin bar into the flask, and add 744 mg (4 mmol) of D-glucose. Transfer acetic anhydride (2.00 mL, d 1.082, originally kept in a test tube with a red cap) into the flask and turn on stir motor. Add 50% H₂SO₄/SiO₂ (30 mg). As a result, the reaction mixture will warm up. Attach condenser and leave the mixture to stir for 15 minutes.

Then add 20 mL of dichloromethane, followed by 25 mL of the saturated NaHCO₃ solution, stir the mixture for several minutes. Pour the solution (with the stirring bar) into a 50 mL plastic syringe-extractor supplied with a valve, which has to be fixed onto a ring stand with a clamp. Rinse the reaction flask with approximately 2-3 mL of dichloromethane and add it into the syringe. Wait until the layers separate and collect the organic fraction into a 100 mL Erlenmeyer flask designated with **P** for product. Collect the remaining liquid into another flask designated with **W** for waste. Transfer the contents of the **P** flask again into the syringe, add 25 mL of brine (saturated NaCl solution) and let it stir for several minutes. Wait until the layers separate, then collect the lower layer into the **P** flask and add some anhydrous MgSO₄. Shake up contents of flask and leave to stand approximately for 10 minutes. (The remaining liquid in the syringe should be transferred into the **W** flask with waste.) Filter the mixture into a weighed out round-bottom flask. Wash MgSO₄ on the filter with 2-3 mL of dichloromethane. Take approximately 0.5 mL of your solution with a pipette and place it into an eppendorf (this is the sample for thin-layer chromatography (TLC)).

Give the flask to the supervisor who will evaporate the solvent under reduced pressure on a rotary vaporizer. Perform TLC analysis with the remaining part of the solution. Use capillary to apply a drop of the solution onto a silica gel plate and eluate the plate in EtOAc/hexane 3:1. To visualize the plate, dip it into a developer solution (5% H₂SO₄ in ethanol), dry it on a filter paper and blow-dry it. Calculate R_f of the product. After receiving the flask with your product, weigh it out and calculate the yield.

Estonian team on International Chemistry Olympiads

Gold medal

Vladislav Ivaništšev 2003

Silver medal

Ain Uustare 1996
Valerija Sizemskaja 1997
Tavo Romann 2001
Pavel Starkov 2002
Vladislav Ivaništšev 2002
Kaur Adamson 2003
Kaur Adamson 2004
Andres Laan 2006

Bronze medal

Jaak Suurpere 1994
Jaak Suurpere 1995
Ain Uustare 1995
Artur Jõgi 1996
Aleksi Lulla 1996
Olga Tšubrik 1996
Olga Tšubrik 1997
Anton Samussenko 1997
Valerija Sizemskaja 1998
Erkki Tempel 1999
Kirill Vassilkov 2000
Tavo Romann 2000
Pavel Starkov 2001
Jevgenia Tamjar 2003
Anneli Kruve 2003
Olga Knjazeva 2004
Jasper Adamson 2004
Viktoria Prostakova 2004
Andres Laan 2005
Olga Jasnovidova 2005
Konstantin Ossipov 2005
Irina Tarassova 2006
Eliko Töldsepp 2006

Honorable mention

Ain Uustare	1994
Mati Mõttus	1994
Kaido Viht	1997
Aleksei Bredihhin	2000
Jevgenia Kozevnikova	2000
Mikk Eelmets	2001
Siim Karus	2002
Jevgenia Tamjar	2002

Participants

Ave Sarapuu	1994
Artur Jõgi	1995
Aleksei Lulla	1995
Ivo Antsi	1998
Ruslan Svetlitski	1998
Jan Klaasen	1998
Tavo Romann	1999
Jevgenia Kozevnikova	1999
Oksana Travnikova	1999
Indrek Koppel	2001
Mikk Müraus	2005
Elo Sõnajalg	2006

Participated three times

Ain Uustare	1994; 1995; 1996
Tavo Romann	1999; 2000; 2001

Participated twice

Jaak Suurpere	1994; 1995
Artur Jõgi	1995; 1996
Aleksei Lulla	1995; 1996
Olga Tšubrik	1996; 1997
Valeria Sizemskaja	1997; 1998
Jevgenia Kozevnikova	1999; 2000
Pavel Starkov	2001; 2002
Vladislav Ivaništšev	2002; 2003
Jevgenia Tamjar	2002; 2003
Kaur Adamson	2003; 2004
Andres Laan	2005; 2006

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