

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

**57<sup>th</sup> ESTONIAN NATIONAL  
CHEMISTRY OLYMPIAD**

Edited by

UNO MÄEORG

JAAK NERUT

VLADISLAV IVANIŠTŠEV

STANISLAV TOMINGAS

Translated by

DINA PRANT

VLADISLAV IVANIŠTŠEV

**TARTU 2010**

## CONTENTS

Theoretical Examination .....	3
9 <sup>th</sup> grade .....	3
Problems .....	3
Solutions .....	8
10 <sup>th</sup> grade .....	13
Problems .....	13
Solutions .....	18
11 <sup>th</sup> grade .....	23
Problems .....	23
Solutions .....	28
12 <sup>th</sup> grade .....	33
Problems .....	33
Solutions .....	38
Practical Examination .....	43
9th and 10th grade .....	43
Determination of iron(II) content .....	43
11th and 12th grade .....	44
Synthesis of 1,4-di-tert-butyl-2,5-dimethoxybenzene .....	44
Estonian team on International Chemistry Olympiads .....	45

## ***Theoretical Examination***

### **9<sup>th</sup> grade**

#### **Problems**

- 1. a)** Which of the listed phenomena are chemical? i) fusion of ice on the roads sprinkled with salt; ii) color change of leaves on the trees in autumn; iii) dissolution of limescale treated with vinegar; iv) rainbow appearance; v) corrosion of iron; vi) color change of copper coin into green; vii) aurora; viii) lightning stroke.
- b)** Write the formulas of sodium sulphite, calcium sulphide and ferric sulphate.
- c)** Determine the oxidation level of sulphur in all the substances given in point **b**).
- d)** How many H atoms are there in 380 grammes of 6.0% aqueous solution of  $(\text{NH}_4)_2\text{HPO}_4$  (in the whole aqueous solution!)?
- e)** Calculate mass concentration of Cu in compound  $\text{Bi}_2\text{Sr}_2\text{Ca}(\text{Cu}_{1-x}\text{Ni}_x)_2\text{O}_8$ , where  $x = 0,022$ .
- 2. a)** Fill in the table. You should pick a name of disperse system from the following list: aerosol, foam, suspension (sol-gel), solid foam, aerosol, emulsion. Choose examples out of the following: flower pollen in the air, milk, fog, lemonade foam, styrofoam, toothpaste.

disperse environment	state of disperse phase	name of disperse system	example
Gas	liquid		
	solid		
Liquid	gas		
	liquid		
	solid		
Solid	gas		

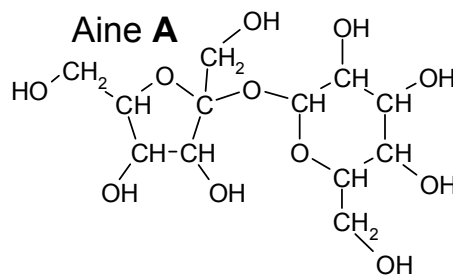
- b) What is the concentration of ball-like drops of oil (drop/cm<sup>3</sup>) in 150 cm<sup>3</sup> water emulsion, in which 50 cm<sup>3</sup> of oil is dispersed? An overall surface of all drops amounts to 3485 cm<sup>2</sup>. Assume that all drops are of the same size.

$$(S_{\text{sphere}} = 4r^2, V_{\text{sphere}} = 4/3r^3)$$

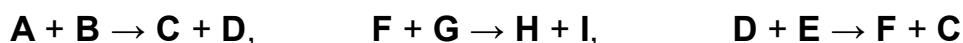
3. During the crisis Santa Claus brought Mari only two candles of different sizes. First of all Mari weighed the candles: the mass of small one was 116 g and mass of the bigger one 458 g. After observation Mari has found that it takes 18 hours to burn down the smaller candle. When the candle combustion products are bubbled through the lime slurry, white precipitate **X** is formed. From textbook Mari learned that candle paraffin consists of several hydrocarbons – its total formula might be put down as C<sub>25</sub>H<sub>52</sub>. Density of candle paraffin is 0.85 g/cm<sup>3</sup>. In a shop Mari found that the price of the small candle is 8 EEK, and of the big one – 30 EEK. The wrappings of both said that the candle contained 3.0% (by mass) of incombustible additives.
- a) Calculate the mass and volume of candle paraffin in small and big candles (without additives).
- b) Assume that paraffin of bigger candle is burnt with the same combustion rate as of the smaller one. Calculate in how many hours the big

- candle will be burnt down. Calculate the correlation of price and time for each candle and, according to this data, determine which buy is more profitable: of the small or big candle.
- c)** Write the equation of the total combustion of candle paraffin and equation of reaction that takes place when the combustion products are run through the lime slurry. How many grams of chalk can be obtained from the combustion products of the whole small candle if the white residue **X** that contains in chalk takes 98% (by mass)?
- d)** Write the equation for the reaction of total combustion of methane. How many  $\text{dm}^3$  of methane should be burnt (STP) in order to produce as much  $\text{CO}_2$  as it is obtained during the combustion of the whole small candle?
- 4.** 100 grams of aqueous solution contains 1.0%  $\text{CaCl}_2$  and 2.0%  $\text{AlCl}_3$ . With the help of ion exchanger it is necessary to purify water of salt impurities. In order to do this, solution is passed through cation exchanger resin which contains 1.0 ekv./kg of protons ( $\text{R-H}$ ) and anion exchanger resin which contains 1.2 ekv./kg of hydroxyl groups ( $\text{R-OH}$ ). 1 ekv. binding 1 mole of singly charged ions, 1/2 mole of doubly charged ions, or 1/3 mole of triple-charged ions.
- a)** Write the equations for the reactions that took place on cation exchanger and anion exchanger.
- b)** Calculate how many grams of both ion exchanger resins should be taken to remove dissolved salts? Assume that a total ion exchange takes place.
- Cation and anion exchangers are regenerated by adding hydrochloric acid and sodium hydroxide, respectively.
- c)** Write the equations of reactions that take place in ion exchangers.

5. A student burnt a widespread sweet substance **A**. Having made a certain assumption, he wrote a summarized equation like this  $\mathbf{A + B \rightarrow C + D}$ . Gaseous substance **D** was passed through a solution of substance **E**. A reaction between **D** and **E** took place: as a result substance **C** and salt **F** formed. Thereafter a greenish solution of salt **G** was added into tube. A reaction  $\mathbf{F + G \rightarrow H + I}$  took place. Substances **H** and **I** – are salts, salt **H** is insoluble in water and salt **I** – is a widely used seasoning.



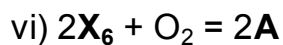
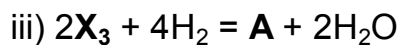
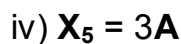
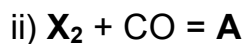
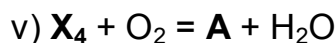
- a) Write formulas for substances **A–I** and names of substances **E–I**.
- b) Write the equations of the following reactions:



When salt **G** was added to solution, a green-brown residue was formed.

- c) Can we conclude that the salt **H** has green-brown colour? Explain your answer!
- d) How is it possible to determine experimentally the colour of insoluble salt if this salt is missing in a laboratory, but there are all other salts given in the solubility table? Provide an example.
- e) Describe a way for experimental obtaining of the solution that contains sodium and lead ions, and also giving  $\text{CaCO}_3$  precipitate. All soluble in water calcium and lead salts, sodium, baking soda ( $\text{NaHCO}_3$ ), hydrochloric acid, phenolphthalein, and water can be used. Write the equations for the reactions to be carried out!

6. Below are given six different schemes for obtaining substance **A** (coefficients are given):



In a reaction where substance **A** interacts with NaOH a salt is formed.

a) Write a brutto-formula for substance **A**. Which class of compounds does substance **A** belong to? Write a structural formula of substance **A** and its name.

Five out of substances  $\text{X}_1\text{--X}_6$  have complex structure, they belong to the following classes: oxides, alcohols, aldehydes (contain C=O group; suffix name: -al), and carbohydrates.

b) Write brutto-formulas for substances  $\text{X}_1\text{--X}_6$ , structural formulas (except for carbohydrate), the classes they belong to and their names.

c) Write the equation of reaction between substance **A** and sodium hydroxide.

## Solutions

1. a) Chemical are: ii), iii), v), vi)



d)  $m\left(\left(\text{NH}_4\right)_2\text{HPO}_4\right) = 380 \cdot 0,06 = 22,8 \text{ g}$

$$n\left(\left(\text{NH}_4\right)_2\text{HPO}_4\right) = 22,8 \text{ g} \cdot \frac{1 \text{ mol}}{132 \text{ g}} = 0,173 \text{ mol}$$

$$m(\text{H}_2\text{O}) = 380 - 22,8 = 357,2 \text{ g}, \quad n(\text{H}_2\text{O}) = 357,2 \text{ g} \cdot \frac{1 \text{ mol}}{18 \text{ g}} = 19,8 \text{ mol}$$

$$n(\text{H}) = (4 \cdot 2 + 1) \cdot 0,173 \text{ mol} + 2 \cdot 19,8 \text{ mol} = 41,2 \text{ mol}$$

$$N(\text{H}) = 41,2 \text{ mol} \cdot \frac{6,02 \cdot 10^{23}}{1 \text{ mol}} = 2,5 \cdot 10^{25}$$

e)  $M\left(\text{Bi}_2\text{Sr}_2\text{Ca}\left(\text{Cu}_{1-x}\text{Ni}_x\right)_2\text{O}_8\right) = \{2 \cdot 209 + 2 \cdot 87,6 + 1 \cdot 40,1 +$

$$+ 2 \cdot [(1 - 0,022) \cdot 63,5 + 0,022 \cdot 58,7] + 8 \cdot 16\} \text{ g/mol} = 888,1 \text{ g/mol}$$

$$\%(\text{Cu}) = \frac{2 \cdot (1 - 0,022) \cdot 63,5 \text{ g/mol}}{888,1 \text{ g/mol}} \cdot 100 = 14,0$$

2. a)

disperse environment	state of disperse phase	name of disperse system	example
Gas	liquid	aerosol	fog
	solid	aerosol	flower pollen in the air
Liquid	gas	foam	lemonade foam
	liquid	emulsion	milk
	solid	suspension (sol-gel)	toothpaste
Solid	gas	solid foam	styrofoam



b)

$$\begin{cases} S_{\text{oil}} = N_{\text{oil drop}} S_{\text{oil drop}} = N_{\text{oil drop}} \cdot 4\pi r^2 = 3485 \text{ cm}^2 & \text{(I)} \\ V_{\text{oil}} = N_{\text{oil drop}} V_{\text{oil drop}} = N_{\text{oil drop}} \cdot \frac{4}{3}\pi r^3 = 50 \text{ cm}^3 & \text{(II)} \end{cases}$$

$$N_{\text{oil drop}} \frac{4}{3}\pi r^3 / N_{\text{oil drop}} 4\pi r^2 = 50 \text{ cm}^3 / 3485 \text{ cm}^2 \quad \text{(II/I)}$$

$$r/3 = 0,0143 \text{ cm} \quad r = 3 \cdot 0,0143 \text{ cm} = 0,0430 \text{ cm}$$

$$N_{\text{oil drop}} = \frac{S_{\text{oil}}}{4\pi r^2} = \frac{3485 \text{ cm}^2}{4\pi(0,0430 \text{ cm})^2} = 150\,000$$

$$c = \frac{150\,000 \text{ drops}}{150 \text{ cm}^3} = \underline{1000 \text{ drop/cm}^3}$$

3. a)  $m(\text{paraffin, small}) = 116 \text{ g} \cdot (1 - 0,03) = \mathbf{113 \text{ g}}$

$$m(\text{paraffin, big}) = 458 \text{ g} \cdot (1 - 0,03) = \mathbf{444 \text{ g}}$$

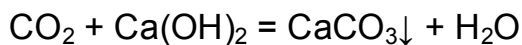
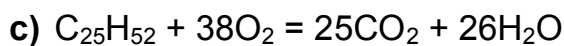
$$V(\text{paraffin, small}) = 113 \text{ g} \cdot \frac{1 \text{ cm}^3}{0,85 \text{ g}} = 132 \text{ cm}^3 \approx \mathbf{130 \text{ cm}^3}$$

$$V(\text{paraffin, big}) = 444 \text{ g} \cdot \frac{1 \text{ cm}^3}{0,85 \text{ g}} = 523 \text{ cm}^3 \approx \mathbf{520 \text{ cm}^3}$$

b)  $t(\text{big candle}) = \frac{18 \text{ h}}{113 \text{ g}} \cdot 444 \text{ g} = 70,7 \text{ h} \approx \mathbf{71 \text{ h}}$

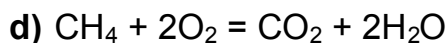
$$\text{Hind}(\text{small candle}) = \frac{8 \text{ EEK}}{18 \text{ h}} = 0,44 \text{ EEK/h} \approx \mathbf{0,4 \text{ EEK/h}}$$

$$\text{Hind}(\text{big candle}) = \frac{30 \text{ EEK}}{70,7 \text{ h}} = 0,42 \text{ EEK/h} \approx \mathbf{0,4 \text{ EEK/h}}$$

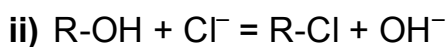
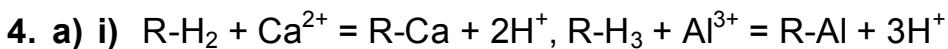


$$n(\text{paraffin, big}) = 113 \text{ g} \cdot \frac{1 \text{ mol}}{352 \text{ g}} = 0,321 \text{ mol}$$

$$m(\text{chalk}) = \frac{1}{1} \cdot \frac{25}{1} \cdot 0,321 \text{ mol} \cdot \frac{100 \text{ g}}{1 \text{ mol}} \cdot \frac{1}{0,98} = 819 \text{ g} \approx \mathbf{820 \text{ g}}$$



$$V(\text{CH}_4) = \frac{1}{1} \cdot \frac{25}{1} \cdot 0,321 \text{ mol} \cdot \frac{22,4 \text{ dm}^3}{1 \text{ mol}} = \mathbf{180 \text{ dm}^3}$$



b)  $n(\text{CaCl}_2) = 100 \text{ g} \cdot 0,01 \cdot \frac{1 \text{ mol}}{111 \text{ g}} = 0,00901 \text{ mol}$

$$n(\text{AlCl}_3) = 100 \text{ g} \cdot 0,02 \cdot \frac{1 \text{ mol}}{133 \text{ g}} = 0,0150 \text{ mol}$$

$$n(\text{Ca}^{2+}) = \frac{2}{1} \cdot 0,00901 \text{ mol} = 0,0180 \text{ ekv}$$

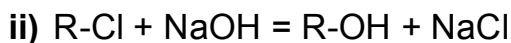
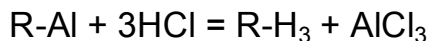
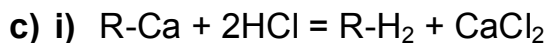
$$n(\text{Al}^{3+}) = \frac{3}{1} \cdot 0,0150 \text{ mol} = 0,0450 \text{ ekv}$$

$$n_{\text{cations}} = 0,0180 \text{ ekv} + 0,0450 \text{ ekv} = 0,0630 \text{ ekv}$$

$$n(\text{Cl}^-) = 2 \cdot 0,00901 \text{ ekv} + 3 \cdot 0,0150 \text{ ekv} = 0,0630 \text{ ekv}$$

$$m_{\text{cationite}} = 0,063 \text{ ekv} \cdot \frac{1 \text{ kg}}{1 \text{ ekv}} \cdot \frac{1000 \text{ g}}{1 \text{ kg}} = \mathbf{63 \text{ g}}$$

$$m_{\text{anionite}} = 0,063 \text{ ekv} \cdot \frac{1 \text{ kg}}{1 \text{ ekv}} \cdot \frac{1000 \text{ g}}{1,2 \text{ kg}} = 52,5 \text{ g} = \mathbf{53 \text{ g}}$$



5. a) **A** –  $C_{12}H_{22}O_{11}$

**B** –  $O_2$

**C** –  $H_2O$

**D** –  $CO_2$

**E** –  $NaOH$

**F** –  $Na_2CO_3$

**G** –  $FeCl_2$

**H** –  $FeCO_3$

**I** –  $NaCl$

b)  $C_{12}H_{22}O_{11} + 12O_2 = 11H_2O + 12CO_2$

$CO_2 + 2NaOH = Na_2CO_3 + H_2O$

$Na_2CO_3 + FeCl_2 = FeCO_3\downarrow + 2NaCl$

c) Can not be concluded.

e)  $2Na + 2H_2O = 2NaOH + H_2\uparrow$ .

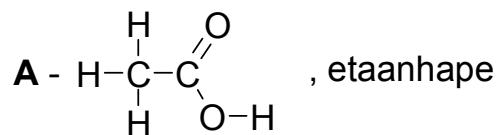
$NaHCO_3 + HCl = CO_2\uparrow + NaCl + H_2O$

$CO_2 + 2NaOH = Na_2CO_3 + H_2O$

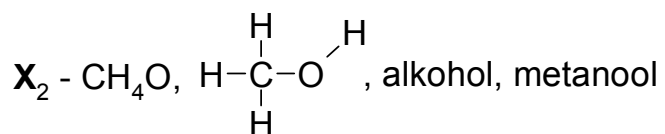
$Na_2CO_3 + Ca(NO_3)_2 = 2NaNO_3 + CaCO_3\downarrow$ .

Then add  $Pb(NO_3)_2$ .

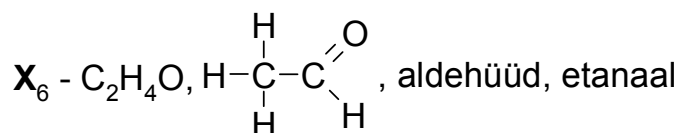
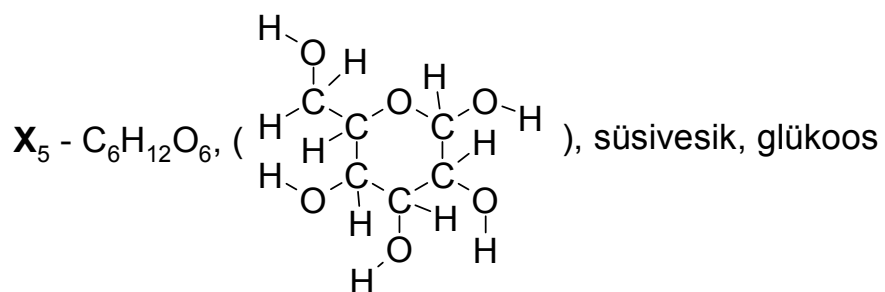
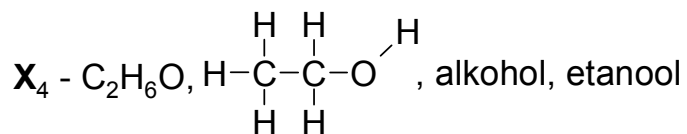
6. a) A - C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>



b) X<sub>1</sub> - O<sub>2</sub>, O=O, (lihtaine,) hapnik



X<sub>3</sub> - CO<sub>2</sub>, O=C=O, oksiid, süsinikdioksiid



c) CH<sub>3</sub>COOH + NaOH = CH<sub>3</sub>COONa + H<sub>2</sub>O

## 10<sup>th</sup> grade

### Problems

1.
  - a) Natural bromine is made of two isotopes:  $^{79}\text{Br}$  (78.918 a.u.) and  $^{81}\text{Br}$  (80.916 a.u.). Calculate composition by percentage of natural bromine if an average atomic mass equals 79.904 a.u. Provide an answer accurate within 3 significant digits.
  - b) In which volume ratio should 0.01 M and 0.1 M solutions be mixed so that a 0.02 M solution is obtained? Assume that densities of all solutions are equal.
  - c) How many grams of 10.0%  $\text{Na}_2\text{CO}_3$  solution and solid  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  should be mixed to prepare 350 g of 15.0%  $\text{Na}_2\text{CO}_3$  solution?
  - d) Explain what is more soluble in water: barium sulphite (solubility constant is  $5.0 \cdot 10^{-10}$ ) or barium carbonate ( $2.6 \cdot 10^{-9}$ )?
2. Andres thought that brutto-formula of orthosilicic acid  $\text{H}_4\text{SiO}_4$  may be referred to as hydroxide  $\text{Si}(\text{OH})_4$  and that formula of silane gas ( $\text{SiH}_4$ ) is similar to the one of acid ( $\text{H}_4\text{Si}$ ). So he tried to carry out a neutralization reaction between two of these substances, letting silane pass above the crystals of orthosilicic acid (1). By the end of reaction he noticed that crystals have signs of blown bubbles, which he explained by water vapor formation. In order to prove his conclusions about the solid product of reaction he passed heated to high temperature fluorine gas above it (2). Produced gases were passed through the aqueous solution of  $\text{H}_2\text{F}_2$  (3), on the surface of which took place a combustion reaction (4 – reaction of remaining  $\text{F}_2$  with water). In spectroscopic analysis of obtained aqueous solution, there were found marks of  $\text{H}_2\text{SiF}_6$ .
  - a) Write the equations for reactions (1-4) in a way how Andres understood processes.

In fact, there is a complex mixture of substances generated in the first reaction. All formed substances belong to the same class of compounds: the simplest contains 46.7% of silicium, the other – more complex ones 36.0% and 32.2% of Si.

- b) Prove with your calculations the formulas of compounds that were really formed and write the general formula of the representatives of this class.
  - c) Prove the formation of such substances i) in nature and ii) in given reaction (in fact, in the first reaction hydrogen is generated).
  - d) Explain what was wrongly interpreted by Andres on the second (2) stage.
3. Substances **A** and **B** are water soluble salts. **A** strong acid has anion similar to salt **A**. From anion of salt **A** and cation of salt **B** salt **D**, containing in sea water and used as the most widespread seasoning, is obtained. Cation of substance **A** hydrolyzes in water in one step, forming ion **E** with molar mass of 82.4 g/mol. Anion of substance **B** hydrolyzes in water in one step forming ion **F**, and insignificantly in two steps forming weak acid **G**, which is also contained in carbonated lemonade.

- a) Write formulas and names of **A–G**.

In 1 dm<sup>3</sup> of water were dissolved 0.2 moles of substance **A** and 0.3 moles of substance **B**.

- b) Write the equation of reaction that took place and the formulas of ions, found in obtained solution.
- c) Estimate pH of the medium of obtained solution. Give your comments.
- d) Provide an example of another salt which hydrolyzes completely and write the equation for the reaction of complete hydrolysis of the given salt.

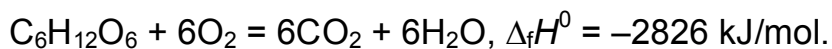
4. One of the several allotropes of element **A** is a semiconductor. Generally, in compounds, element **A** is trivalent. Colourless gas **B** consists of element **A** and nonmetal **X**, used in cleaning means; molecular formula of **B** can be written as **AX<sub>3</sub>**. If gas **B** is heated in hydrogen atmosphere, elementary compound **A** is formed. **A** is also formed by thermal decomposition of iodide **AI<sub>3</sub>** and in reaction of oxide **A<sub>2</sub>O<sub>3</sub>** with magnesium. The second product in three given reactions of **A** formation are strong acid **C**, elementary substance **D**, and oxide **E**, respectively.

When oxide **A<sub>2</sub>O<sub>3</sub>** reacts with coal and chlorine at high temperature, gas **B** is formed. **A** by-product of this reaction is a colourless poisonous gas **F**. Throughout further processing of gas **B** with water, by hydrolysis a strong acid **C** and weak acid **G** are formed. During the heating of one mole of weak acid **G**, one mole of water is produced and one mole of acid **H** is formed. During further heating of acid **H**, water is released and oxide **A<sub>2</sub>O<sub>3</sub>** is obtained again. If oxide **A<sub>2</sub>O<sub>3</sub>** is treated with nitrogen in presence of coal at 1800°C, a hexagonal polymeric compound **I** is produced and a by-product is again gas **F**. Compound **I** is used for the manufacture of temperature-resistant ceramic products and contains equal amounts of two elements.

- a) Write the formulas for substances **A–K**.
- b) Write the equations of all described reactions.
5. Combustion of organic compounds is an exothermic reaction. Energy produced in these processes is used for the performing of both biochemical and manufacturing processes. Thus, it is very important to be able to calculate this energy.
- a) On the basis of given enthalpies of formation, calculate the energy generated into our environment during the combustion of 1,00 mole of methane.  $\Delta_f H^0(\text{CH}_4) = -74.82 \text{ kJ/mol}$ ,  $\Delta_f H^0(\text{CO}_2) = -393.5 \text{ kJ/mol}$ ,

$$\Delta_f H^0(\text{H}_2\text{O}) = -285.8 \text{ kJ/mol}$$

- b)** Average daily power of adult equals 110 W (1 W = 1 J/s). Calculate how many grams of glucose is needed for human's normal vital activity assuming that the whole energy comes from the following reaction:



- c)** In foam fire extinguishers  $\text{CO}_2$  and water are obtained in the reaction of  $\text{NaHCO}_3$  and  $\text{H}_2\text{SO}_4$ . Calculate the volume of gas mixture generated while the fire is being extinguished, if a fire extinguisher is filled with  $\text{NaHCO}_3$  and  $\text{H}_2\text{SO}_4$  mixture of 2.0 kg with molar ratio is 1:1. Temperature of gas mixture coming from fire extinguisher is  $177^\circ\text{C}$ ; pressure equals 1235 Torr.

$$R = 0.082 \text{ atm}\cdot\text{dm}^3/(\text{K}\cdot\text{mol}), 760 \text{ Torr} = 1 \text{ atm}, pV = nRT).$$

- 6.** In a coal mine a sample of  $100 \text{ cm}^3$  of gas was taken from a rock fracture.  $10 \text{ cm}^3$  of sample were sent to spectrometric analysis that showed that sample consists of  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{H}_2$ , and  $\text{N}_2$ . In order to determine the percentage composition of gas mixture, the following experiments were carried out:

- i)**  $90 \text{ cm}^3$  of gas were passed through KOH solution.
- ii)** Remaining  $82 \text{ cm}^3$  were passed through the solution of benzene-1,2,3-triol ( $\text{C}_6\text{H}_6\text{O}_3$ , solution has a basic medium), which reacts only with oxygen.
- iii)** Remaining  $76 \text{ cm}^3$  were passed through the saturated with ammonia solution of copper (I) ammine-chloride ( $\%(\text{Cu}) = 47.7$ ) which binds all neutral oxides.
- iv)** From the remained  $64 \text{ cm}^3$  of gas mixture  $18 \text{ cm}^3$  were mixed with  $62 \text{ cm}^3$  of air. After the complete combustion and condensation of water, the volume of gas mixture reduced by  $9.0 \text{ cm}^3$ . During the mixture



combustion  $3.0 \text{ cm}^3$  of  $\text{CO}_2$  were generated.

All gas volumes are given at normal conditions.

- a)** Write the equations for reactions at stages **i)** and **iv)**.
- b)** Draw the structural formula of benzene-1,2,3-triol, knowing the fact that molecule contains hexatomic carbon ring.
- c)** Determine the structure of copper complex, formed in point **iii)** ( $\%(\text{Cu}) = 35.7$ ).
- d)** Calculate the composition (in percents by volume) of initial mixture of gases. Can one breathe with this mixture?

## Solutions

1. a)  $78,918 \cdot \%(^{79}\text{Br})/100 + (1 - \%(^{79}\text{Br})/100) \cdot 80,916 = 79,904$

$$0.01998\%(^{79}\text{Br}) = 1.012$$

$$\%(^{79}\text{Br}) = 50,7$$

$$\%(^{81}\text{Br}) = 100 - 50,65 = 49,3$$

b)  $c = \frac{n}{V} \Rightarrow n = c \cdot V$

$$n_1 = 0,01 \cdot V_1 \quad n_1 = 0,01 \cdot V_1$$

$$n_1 + n_2 = 0,02 \cdot (V_1 + V_2) \quad V_1 + V_2 = (0,01 \cdot V_1 + 0,1 \cdot V_2) \cdot 50$$

$$\frac{V_1}{V_2} = 8$$

c)  $m(\text{total Na}_2\text{CO}_3) = 350 \text{ g} \cdot 0,15 = 52,5 \text{ g}$

$$m(10\% \text{ solution}) = \frac{m_1(\text{Na}_2\text{CO}_3)}{0,1}$$

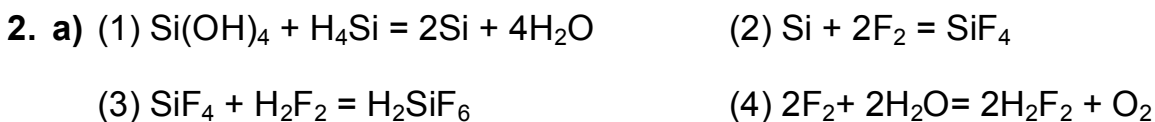
$$m(\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}) = 286 \cdot \frac{m_2(\text{Na}_2\text{CO}_3)}{106}$$

$$\begin{cases} m_1(\text{Na}_2\text{CO}_3) + m_2(\text{Na}_2\text{CO}_3) = 52,5 \text{ g} \\ \frac{m_1(\text{Na}_2\text{CO}_3)}{0,1} + 286 \cdot \frac{m_2(\text{Na}_2\text{CO}_3)}{106} = 350 \text{ g} \end{cases} \Rightarrow m_1 = 28,5 \text{ g ja } m_2 = 24,0 \text{ g}$$

$$m(10\% \text{ solution}) = \frac{28,5 \text{ g}}{0,1} = 285 \text{ g}$$

$$m(\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}) = 286 \cdot \frac{24,0 \text{ g}}{106} = 64,8 \text{ g}$$

d)  $\text{BaCO}_3$

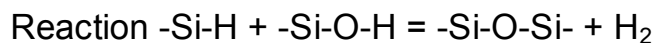
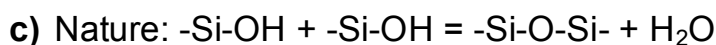


**b)  $m\text{SiO}_2 \cdot n\text{H}_2\text{O}$**

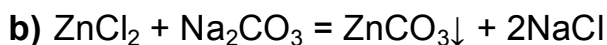
$$M_r = \frac{28,1}{0,467} = 60 \quad \text{SiO}_2$$

$$M_r = \frac{28,1}{0,36} = 78 \quad \text{SiO}_2 \cdot \text{H}_2\text{O}$$

$$M_r = \frac{2 \cdot 28,1}{0,322} = 174 \quad 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$$



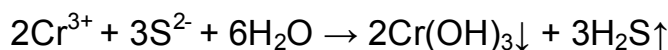
d) Andres thought that forms only  $\text{SiF}_4$ . However, in reaction of  $m\text{SiO}_2 \cdot n\text{H}_2\text{O}$  with fluorine  $\text{O}_2$ ,  $\text{H}_2\text{F}_2$ , and also  $\text{SiF}_4$  are obtained.

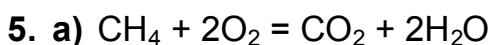
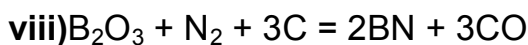
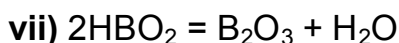
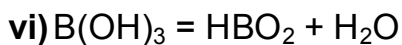
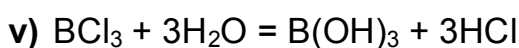
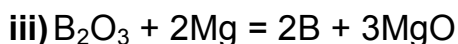
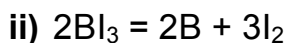
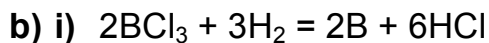
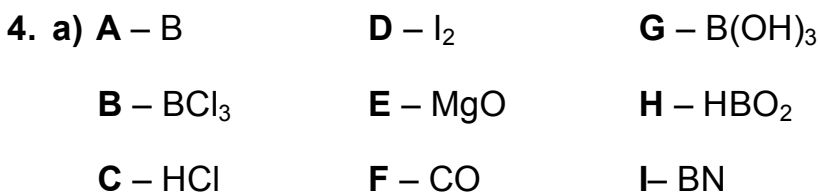


$\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{OH}^-$  (also small amount of  $\text{H}^+$ ).

c) Basic (pH > 7)

d) For example  $\text{Cr}_2\text{S}_3$





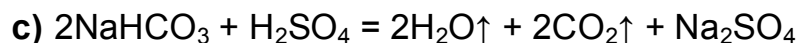
$$\Delta_c H^0(\text{CH}_4) = \Delta_f H^0(\text{CO}_2) + 2\Delta_f H^0(\text{H}_2\text{O}) - \Delta_f H^0(\text{CH}_4) - 2\Delta_f H^0(\text{O}_2)$$

$$\Delta_c H^0(\text{CH}_4) = [-393,5 + 2 \cdot (-285,8) - (-74,82) - 0] \text{ kJ/mol} = -890,3 \text{ kJ/mol}$$

$$Q = -1 \text{ mol} \cdot \frac{-890,3 \text{ kJ}}{1 \text{ mol}} = \underline{890 \text{ kJ}}$$

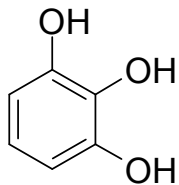
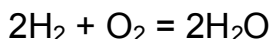
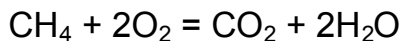
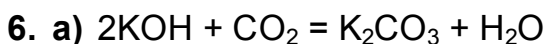
$$\text{b) } E = \frac{110 \text{ J}}{1 \text{ s}} \cdot 24 \text{ h} \cdot \frac{3600 \text{ s}}{1} = 9504 \text{ kJ}$$

$$m(\text{C}_6\text{H}_{12}\text{O}_6) = 9504 \text{ kJ} \cdot \frac{1 \text{ mol}}{2826 \text{ kJ}} \cdot \frac{180 \text{ g}}{1 \text{ mol}} = \underline{605 \text{ g}}$$



$$n(\text{NaHCO}_3) = n(\text{H}_2\text{SO}_4) = 2,0 \text{ kg} \cdot \frac{1000 \text{ g}}{1 \text{ kg}} \cdot \frac{1 \text{ mol}}{(84 + 98) \text{ g}} = 11 \text{ mol}$$

$$V = \frac{nRT}{p} = (11+11) \text{ mol} \cdot 0,082 \frac{\text{atm} \cdot \text{dm}^3}{\text{K} \cdot \text{mol}} \cdot (177 + 273) \text{ K} \cdot \frac{1}{1235 \text{ torr}} \cdot \frac{760 \text{ torr}}{1 \text{ atm}} = \underline{500 \text{ dm}^3}$$



b)

c) Reagent  $[\text{Cu}(\text{NH}_3)_x]\text{Cl}$ .

$$M_r(\text{reagent}) = \frac{63,55}{0,478} = 132,9 = 63,55 + x \cdot 17,03 + 35,45$$

$$x = 2 \quad [\text{Cu}(\text{NH}_3)_2]\text{Cl}$$

Product  $[\text{Cu}(\text{NH}_3)_x(\text{CO})_y]\text{Cl}$ .

$$M_r(\text{product}) = \frac{63,55}{0,357} = 178,0 = 63,55 + x \cdot 17,03 + y \cdot 28,01 + 35,45$$

$$x = 3 \text{ and } y = 1. \quad [\text{Cu}(\text{NH}_3)_3\text{CO}]\text{Cl}$$

d) Volumes of  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{CO}$  gases:

$$V(\text{CO}_2) = (90 - 82)\text{cm}^3 = 8 \text{ cm}^3 \quad \%_{\text{vol}}(\text{CO}_2) = \frac{8 \text{ cm}^3}{90 \text{ cm}^3} \cdot 100 = 8,8 \approx \mathbf{9}$$

$$V(\text{O}_2) = (82 - 76)\text{cm}^3 = 6 \text{ cm}^3 \quad \%_{\text{vol}}(\text{O}_2) = \frac{6 \text{ cm}^3}{90 \text{ cm}^3} \cdot 100 = 6,6 \approx \mathbf{7}$$

$$V(\text{CO}) = (76 - 64)\text{cm}^3 = 12 \text{ cm}^3 \quad \%_{\text{vol}}(\text{CO}) = \frac{12 \text{ cm}^3}{90 \text{ cm}^3} \cdot 100 = 13,3 \approx \mathbf{13}$$

Volume of  $\text{CH}_4$ ,  $\text{H}_2$  gases

$$V(\text{CH}_4) = V(\text{CO}_2) = 3 \text{ cm}^3 \quad V(\text{H}_2\text{O}) = 0 \quad V(\text{N}_2) = \text{const}$$

$$\Delta V = V_{\text{löpp}} - V_{\text{alg}} = V(\text{CO}_2) + V(\text{H}_2\text{O}) - V(\text{CH}_4) - V(\text{O}_2) - V(\text{H}_2)$$

$$V(\text{O}_2) = 2V(\text{CO}_2) + 0,5V(\text{H}_2)$$

$$\Delta V = -2V(\text{CO}_2) - 0,5V(\text{H}_2) - V(\text{H}_2) = -2V(\text{CO}_2) - 1,5V(\text{H}_2)$$

$$V(\text{H}_2) = [-\Delta V - 2V(\text{CO}_2)] : 1,5 = [ -(-9) - 2 \cdot 3 ] \text{ cm}^3 : 1,5 = 2 \text{ cm}^3$$

$$V(\text{CH}_4, \text{ sample}) = 3 \text{ cm}^3 \cdot \frac{64 \text{ cm}^3}{18 \text{ cm}^3} = 10,7 \text{ cm}^3$$

$$\%_{\text{vol}}(\text{CH}_4) = \frac{10,7 \text{ cm}^3}{90 \text{ cm}^3} \cdot 100 = 11,9 \approx \mathbf{12}$$

$$V(\text{H}_2, \text{ provov}) = 2 \text{ cm}^3 \cdot \frac{64 \text{ cm}^3}{18 \text{ cm}^3} = 7,11 \text{ cm}^3$$

$$\%_{\text{vol}}(\text{H}_2) = \frac{7,11 \text{ cm}^3}{90 \text{ cm}^3} \cdot 100 = \mathbf{7,9}$$

$$V(\text{N}_2) = (90 - 8 - 6 - 12 - 10,7 - 7,11) \text{ cm}^3 = 46,2 \text{ cm}^3$$

$$\%_{\text{vol}}(\text{N}_2) = \frac{46,2 \text{ cm}^3}{90 \text{ cm}^3} \cdot 100 = 51,3 \approx \mathbf{51}$$

It is imposible to breathe with this mixture of gases.

# 11<sup>th</sup> grade

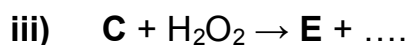
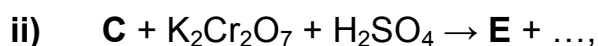
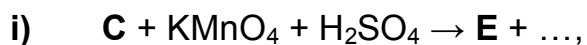
## Problems

1. In order to improve his financial state F. Meister – a student – decided to take part in an intellectual show “Who Wants to Become a Millionaire?”. Since the game took place on International Chemists’ Day, all the questions were about chemistry. First six questions were very simple but the other nine turned out to be a bit more complicated:
  - a) Which of the listed compounds are used as indicator in iodometric titration: A) EDTA, B) ascorbic acid, C) phenolphthalein, D) starch?
  - b) Which of the listed derivatives of carboxylic acid generally reacts with nucleophils: A) acid, B) chloride, C) ester, D) amide?
  - c) Which formula does a linear hydrocarbon have: A)  $C_nH_{2n-2}$ , B)  $C_nH_{2n}$ , C)  $C_nH_n$ , D)  $C_nH_{2n+2}$ ?
  - d) Which halogen has the isotope ratio of 3:1: A) Br, B) F, C) Cl, D) I?
  - e) Catalyst changes in the course of reaction: A) equilibrium, B) rate of the direct reaction only, C) rate of both direct and reverse reactions, D) Gibbs energy.
  - f) Which of the listed salts when heated does not produce ammonia: A) ammonium chloride, B) ammonium sulphate, C) ammonium nitrate, D) ammonium carbonate?
  - g) Which alkali metal is the most widespread in nature: A) Li, B) Na, C) K, D) Rb?
  - h) If we put equal amounts of moles of NaOH and HCl into pure water, pH of solution will be: A) acidic, B) basic, C) neutral, D) pH will be changing in time.
  - i) Thiosulphuric acid is: A)  $H_2S$ , B)  $H_2S_2O_3$ , C)  $H_2SO_5$ , D)  $H_2SO_4$ ?

2. Substance **A** is a gas, which density equals 0.97 relative to the density of the air. When substance **A** reacts with hydrogen, substance **B** with low reactivity is formed. Substance **A** reacts with water; as a result, a widely used solvent **C** is produced. In the presence of acid from two molecules of **C**, one molecule of volatile compound **D** is formed. Under the influence of the oxidants from compound **C**, substance **E**, which is used as a preservative, is generated. In acidic medium **C** and **E** react with one another, resulting in the formation of substance **F**.

a) Write structural formulas and names of substances **A–F**.

b) Write the equations of reactions:



3. 12-atomic cyclic compound **A** (6 atoms form a cycle) consists of elements **X**, **Y**, and **Z** as well as contains chemical bonds of three different types. All atoms of elements **X** and **Z** have equal number of chemical bonds in substance **A**. There are several ways to synthesize **A**. 1) Dimer **B** ( $M_r = 27.67$ ), consists of eight atoms of element **X** and **Y**. In the reaction of **B** with a known gas **C** (consists of atoms of **Y** and one atom of element **Z**,  $\%(\text{Y}) = 17.8$ ) substance **A** and elementary substance **D** are formed. 2) Throughout the reaction of three-element substance **E** and binary substance **F** (both **E** and **F** contain element **V**) substance **G** and diatomic gas **H** are generated. Substance **E** might be obtained in the reaction of gas **H** with gas **C**. Molecular mass of substance **G** containing four elements is by 103.34 atomic units more than the molecular mass of substance **A**. Six-membered ring of compound **G** is identical with ring of compound **A**. **G** only differs from substance **A** by the substitution of certain atoms in it. When **G** reacts with salt **I**, which



contains elements **W**, **X** and **Y** in molar ratio of 1:1:4, compounds **A** and **B** are formed and binary salt **J** is obtained. In the periodic table element **W** is placed in the same group with one of the elements containing in compound **G**, and in the same period with another element containing in compound **G**.

- a) Determine: i) formula of compound **B**; ii) formula of gas **C** as well as elements **X**, **Y** and **Z**. Show your calculations.
  - b) Draw structural formula for substance **A**.
  - c) Determine the formula of compound **G** and element **V**. Show your calculations.
  - d) Write the formulas of compounds **D**, **E**, **F**, **H**, **I** and **J**. Determine element **W**.
  - e) Write the equations for reactions: i)  $\mathbf{B} + \mathbf{C} \rightarrow \mathbf{A} + \mathbf{D}$ , ii)  $\mathbf{E} + \mathbf{F} \rightarrow \mathbf{G} + \mathbf{H}$ , iii)  $\mathbf{H} + \mathbf{C} \rightarrow \mathbf{E}$ , iv)  $\mathbf{G} + \mathbf{I} \rightarrow \mathbf{A} + \mathbf{B} + \mathbf{J}$ .
4. Infrared spectroscopy methods are very useful for distinguishing the functional groups of organic substances. In infrared spectroscopy wave number (and energy) of A–B bond stretching is expressed by formula:

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

where  $c$  – speed of light,  $k$  – force coefficient of of bond and  $\mu$  – is a reduced mass of atoms, forming the bond:

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

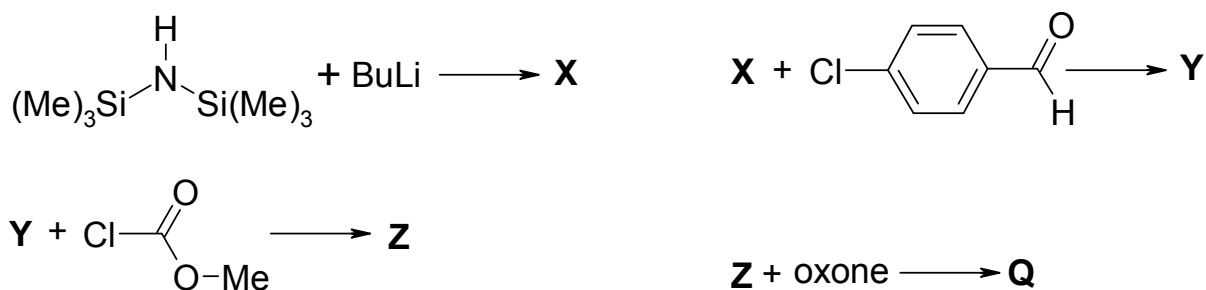
In a table are given values of wave numbers ( $\text{cm}^{-1}$ ) characterizing the vibration of given bonds (N–H, C–O, C=O, C–Cl, and O–H) in molecules which represent eight classes of organic compounds: ethers, primary alcohols, secondary amines, carboxylic acids, ketones, esters,

primary amides, acyl chlorides. All molecules contain only one or two unbranched carbon chain(s) consisting of three atoms.

I	II	III	IV	V	VI	VII	VIII
3292	1792	1716	1662	1119	1715	3650	1739
	917	3568	3366			1063	1188

- a) Draw structural formulas of molecules and write their systematic names.
  - b) Write the bonds N–H, C–O, C=O, C–Cl in ascending order of the wave number values. To estimate these values calculate the reduced mass of atoms, forming the bond. Assume that the force coefficient of a single/double bond is approximately the same for different bonds and the force coefficient of a double bond is greater than the force coefficient of a single bond.
  - c) According to wave number values determine which substance do they correspond to, considering that the greatest value of wave number corresponds to the stretching of O–H bond. Characteristic wave number of bond vibration might slightly change depending on the substance.
5. Cubane ( $C_8H_8$ ) with the density of  $1.29 \text{ g/cm}^3$  is the most dense hydrocarbon. When a volume unit of cubane is burnt, the amount of generated energy is 1.58 times more than from burning a volume unit of aromatic compound sterole ( $C_8H_8$ ) ( $0.909 \text{ g/cm}^3$ ), 1.80 times more than from burning of a volume unit of octane ( $0.703 \text{ g/cm}^3$ ), and 6.06 times more energy than when a volume unit of liquid hydrogen ( $0.070 \text{ g/cm}^3$ ) is burnt.
- a) Calculate how much energy ( $\text{kJ/dm}^3$ ) is generated when  $H_2$  is burnt. The formation enthalpies of  $CO_2$  and  $C_8H_{18}$  are  $-393,9 \text{ kJ/mol}$  and  $-250,0 \text{ kJ/mol}$  respectively.

- b) Calculate the combustion and formation enthalpies for cubane and sterole (kJ/mol).
- c) Explain why formation enthalpies of cubane and sterole are different.
6. Compound **Q** ( $C_9H_8O_3NCl$ ) is an example of quite atypical substance in which nitrogen that usually has nucleophilic properties is an electrophile since electronegative groups located near it, gradually reduce electron density. Substance **Q** reacts, for instance, with amino acid amides: as a result of this reaction a bioactive compounds of hydrazine are obtained. Substance **Q** is synthesized according to the following scheme:



What we know about the synthesis is that in the reaction  $\mathbf{X} \rightarrow \mathbf{Y}$  oxidation level of aldehydic carbon remains the same. Trimethylsilylic groups leave the original substance in two stages. To carry out reactions  $\mathbf{X} \rightarrow \mathbf{Y}$  and  $\mathbf{Y} \rightarrow \mathbf{Z}$  one needs a catalyst  $\text{TiCl}_4$ . Product **Q** contains two rings, one of which is significantly strained. Nitrogen takes the role of electrophile in compound **Q**. Oxone is an oxidizing agent.

- a) Write structural formulas for substances **X–Z** and **Q**.
- b) Write possible mechanism of reaction  $\mathbf{Y} \rightarrow \mathbf{Z}$  and provide explanations.
- c) Mark chiral center(s) in compound **Q**. Would it (they) be different in case potassium methylated reacted with compound **Q** by nitrogen atom?

## Solutions

1. a) D)

b) B)

c) D)

d) C)


e) C)

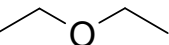
f) C)


g) B)

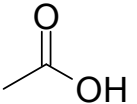
h) C)

i) B)

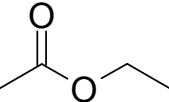
2. a) A -  , eteen  $\rho = \frac{28}{29} = 0,97$

D -  , dietüüleeter

B -  , etaan

E -  , etaanhape

C -  , etanool

F -  , etüületanaat

b) i)  $5\text{C}_2\text{H}_5\text{OH} + 4\text{KMnO}_4 + 6\text{H}_2\text{SO}_4 =$



ii)  $3\text{C}_2\text{H}_5\text{OH} + 2\text{K}_2\text{Cr}_2\text{O}_7 + 8\text{H}_2\text{SO}_4 =$



iii)  $\text{C}_2\text{H}_5\text{OH} + 2\text{H}_2\text{O}_2 = \text{CH}_3\text{COOH} + 3\text{H}_2\text{O}$

3. a) i) As  $27,67 : 8 = 3,46$  is a small number, compound should contain hydrogen atoms, thus  $M_r(\mathbf{B}) = N(\text{H}) \cdot A_r(\text{H}) + N(\mathbf{E}) \cdot A_r(\mathbf{E}) = 27,67$

If monomer formula is  $\mathbf{E}\text{H}_3$ , then:

$$6 \cdot 1,008 + 2 \cdot A_r(\mathbf{E}) = 27,67$$

$$A_r(\mathbf{E}) = 10,81, \mathbf{B} - \text{B}_2\text{H}_6.$$

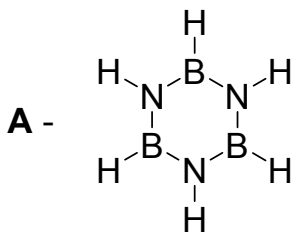
$$\text{ii) } \%(\text{H}) = \frac{N(\text{H}) \cdot A_r(\text{H})}{N(\text{H}) \cdot A_r(\text{H}) + A_r(\mathbf{Z})} = 0,178 \quad A_r(\mathbf{Z}) = 4,65N(\text{H})$$

If  $N(\text{H}) = 3$ , then  $A_r(\mathbf{Z}) = 14,0$ .  $\mathbf{C} - \text{NH}_3$

$\mathbf{X} - \text{B}$

$\mathbf{Y} - \text{H}$

$\mathbf{Z} - \text{N}$



b)

$$\text{c) } \Delta M_r = NA_r(\mathbf{V}) - NA_r(\text{H}) = 103,34 \quad A_r(\mathbf{V}) = \frac{103,34}{N} + 1,008$$

If  $N = 3$ , then  $A_r(\mathbf{V}) = 35,45$ ,  $\mathbf{V} - \text{Cl}$ ,  $\mathbf{G} - \text{B}_3\text{H}_3\text{N}_3\text{Cl}_3$

d)  $\mathbf{D} - \text{H}_2$

$\mathbf{E} - \text{NH}_4\text{Cl}$

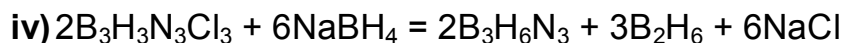
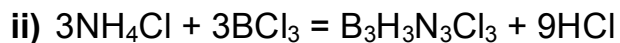
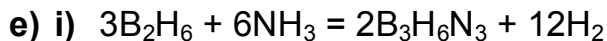
$\mathbf{H} - \text{HCl}$

$\mathbf{J} - \text{NaCl}$

$\mathbf{F} - \text{BCl}_3$

$\mathbf{I} - \text{NaBH}_4$

$\mathbf{W} - \text{Na}$ .



4. b) C-Cl < C-O < C=O < N-H

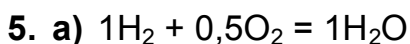
$$\text{N-H} \quad \mu = \frac{14 \text{ g/mol} \cdot 1 \text{ g/mol}}{14 \text{ g/mol} + 1 \text{ g/mol}} = 0,93 \text{ g/mol}$$

$$\text{C-O, C=O} \quad \mu = 6,9 \text{ g/mol}$$

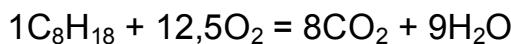
$$\text{C-Cl} \quad \mu = 9 \text{ g/mol}$$

a) and c)

Nr.	class	formula	bond	$\nu$ , $\text{cm}^{-1}$
V	ethers		C-O	1119
VII	primary alcohols		C-O O-H	1063 3650
I	secondary amines		N-H	3292
III	carboxylic acids		C-O C=O O-H	- 1716 3568
VI	ketones		C=O	1715
VIII	esters		C-O C=O	1188 1739
IV	primary amides		C=O N-H	1662 3366
II	acyl chlorides		C-Cl C=O	917 1792



$$\Delta_c H(\text{H}_2) = \Delta_f H(\text{H}_2\text{O}) = \frac{X \text{ kJ}}{1 \text{ dm}^3} \cdot \frac{1 \text{ cm}^3}{0,07 \text{ g}} \cdot \frac{1 \text{ dm}^3}{1000 \text{ cm}^3} \cdot \frac{2,016 \text{ g}}{1 \text{ mol}} = 0,0288X \text{ kJ/mol}$$



$$\Delta_c H(\text{C}_8\text{H}_{18}) = \frac{6,06}{1,80} \cdot \frac{X \text{ kJ}}{1 \text{ dm}^3} \cdot \frac{1 \text{ cm}^3}{0,703 \text{ g}} \cdot \frac{1 \text{ dm}^3}{1000 \text{ cm}^3} \cdot \frac{114,2 \text{ g}}{1 \text{ mol}} = 0,5469X \text{ kJ/mol}$$

$$\Delta_c H(\text{C}_8\text{H}_{18}) = 8\Delta_f H(\text{CO}_2) + 9\Delta_f H(\text{H}_2\text{O}) - [\Delta_f H(\text{C}_8\text{H}_{18}) + 12,5\Delta_f H(\text{O}_2)]$$

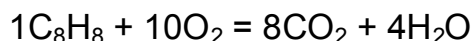
$$8 \cdot \frac{-393,9 \text{ kJ}}{1 \text{ mol}} + 9 \cdot \frac{0,0288X \text{ kJ}}{1 \text{ mol}} - \frac{-250 \text{ kJ}}{1 \text{ mol}} - 12,5 \cdot 0 = \frac{0,5469X \text{ kJ}}{1 \text{ mol}}$$

$$0,2877X = -2901,2 \quad X = -10084$$

b)  $\Delta_f H(\text{H}_2\text{O}) = 0,0288 \cdot (-10084 \text{ kJ/mol}) = -290,4 \text{ kJ/mol}$

$$\begin{aligned} \Delta_c H(\text{cubane}) &= \frac{6,06}{1} \cdot \frac{-10084 \text{ kJ}}{1 \text{ dm}^3} \cdot \frac{1 \text{ cm}^3}{1,29 \text{ g}} \cdot \frac{1 \text{ dm}^3}{1000 \text{ cm}^3} \cdot \frac{104,15 \text{ g}}{1 \text{ mol}} = \\ &= -4933 \text{ kJ/mol} = \mathbf{-4900 \text{ kJ/mol}} \end{aligned}$$

$$= -4431 \text{ kJ/mol} = \mathbf{-4400 \text{ kJ/mol}}$$

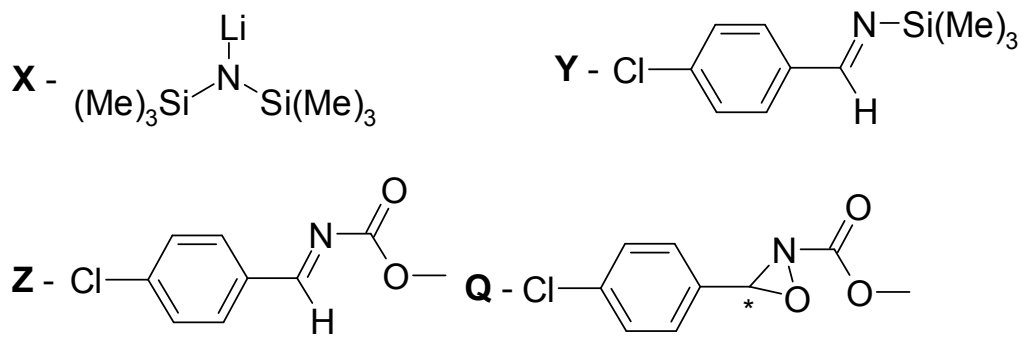


$$\begin{aligned} \Delta_f H(\text{cubane}) &= [8 \cdot (-393,9) + 4 \cdot (-290,4) - (-4933)] \text{ kJ/mol} = \\ &= \underline{620} \text{ kJ/mol} = \mathbf{600 \text{ kJ/mol}} \end{aligned}$$

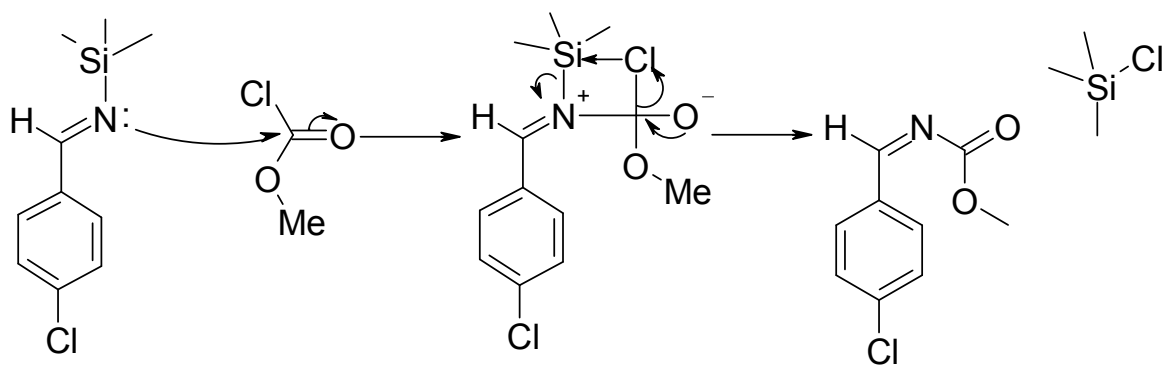
$$\begin{aligned} \Delta_f H(\text{styrene}) &= [8 \cdot (-393,9) + 4 \cdot (-290,4) - (-4431)] \text{ kJ/mol} = \\ &= \underline{118} \text{ kJ/mol} = \mathbf{100 \text{ kJ/mol}} \end{aligned}$$

c) Due to significant strain in cubane structure, and, on the other hand, aromaticity of styrene ring.

6. a) and c)



b)



c) No.



## 12<sup>th</sup> grade

### Problems

1. Years ago quicksilver and some of its compounds were used to treat numerous diseases and illnesses. For instance, substance **A** (i), produced as a result of quicksilver dissolution in *aqua regis*, is known as very good antiseptics. Substance **A**, when heated with quicksilver, gives salt **B** (ii) which earlier was used as a sedative. Both salts are also formed in the reaction of metal **X** with gas **C**, which consists of diatomic molecules. Gold and silver amalgams were used as tooth stopping. However, with the course of time it was discovered that quicksilver and its vapor cause severe poisoning. When quicksilver compounds get into organism, central nervous system as well as liver, kidneys and digestive apparatus suffer greatly. In organism  $\text{Hg}^{2+}$  ions form strong covalent bonds with sulphide groups of proteins (iii) causing the denaturation of latter ones.

One of the methods to discover quicksilver poisoning is to apply the reaction of  $\text{Hg}^{2+}$  ions with copper iodide (I) (iv). As a result, red-orange complex salt **D** is precipitated, in which coordination number of quicksilver metal equals four. In a wrongly prepared sample, copper iodide (I) in presence of nitric acid, might react with oxygen (v), which will distort the results of analysis. Indication of side reaction is the release of iodine that gives solution brownish color.

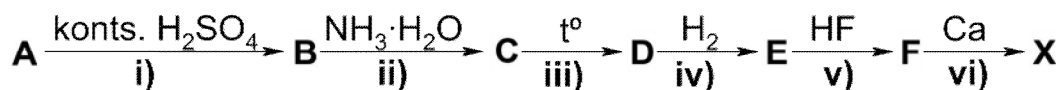
In order to clean the surface contaminated with quicksilver it is not enough to simply gather the metal, surface should be chemically demercurated. Acidified solution  $\text{KMnO}_4$  (vi) might be used for this purpose — released elementary substance **C** reacts further with Hg (vii) metal. One might also put sulphur (viii) onto contaminated surface.

- a) Write formulas and names for substances **A—D**.

- b) Write the following equations: i)  $\text{Hg} + \text{aqua regis} \rightarrow \dots + \text{NO} + \dots$ , ii)  $\text{Hg} + \text{A} \rightarrow$ , iii)  $\text{protein-SH} + \text{Hg}^{2+} \rightarrow$ , iv)  $\text{Hg}^{2+} + \text{CuI} \rightarrow \dots$ , v)  $\text{HNO}_3 + \text{CuI} + \text{O}_2 \rightarrow$ , vi)  $\text{KMnO}_4 + \text{HCl} \rightarrow$ , vii)  $\text{Hg} + \text{C} \rightarrow$ , viii)  $\text{Hg} + \text{S} \rightarrow$ .

- c) Which of two demercuration methods is more effective? Why?

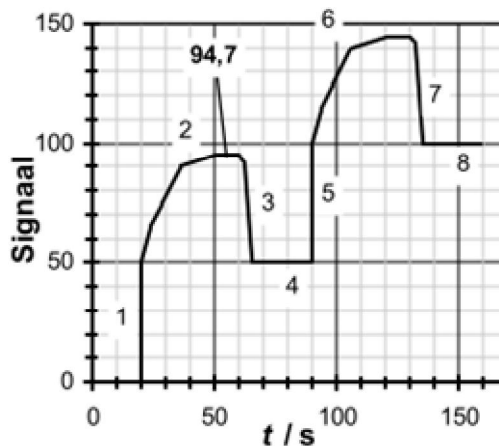
2. **X** is one of the most important raw substances of nuclear power engineering and is synthesized according to the following scheme:



Raw substance **A** is a mixed oxide ( $\%(\text{O}) = 15.2$ ) with a formula  $a\text{E} \cdot b\text{D}$ , where  $a$  and  $b$  are even numbers. Oxidation number of element **X** in oxide **D** is 1.5 times bigger than in binary substances **E** and **F**. Element **X** is included in binary cation of salt **B** ( $\%(\text{S}) = 8.74$ ) and anion of salt **C**. i, iv, and vi are redox reactions.

- a) By calculations, determine the formulas of substances **A** and **X**. Write formulas and names for the substances **A—F**, **X**.
- b) Write equations for reactions i)—vi).

3. Layer by layer formation of thin oxide films at the surface were studied using mass-sensitive sensor. Sensor shows a signal if the surface mass increase. The growth is proportional to the magnitude of the signal. Figure shows signal change during the formation of two layers of compound

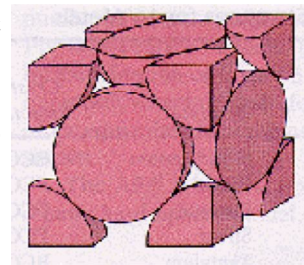


$\text{XO}_2$ . As a raw substance is used  $\text{XCl}_4$  vapor. At the first step molecules bind to the surface under investigation. Then the surface is saturated with chloride. Oxide is formed, when  $\text{H}_2\text{O}$  is introduced to the system. Inbetween layer formation system is cleaned of residual substances.  $\text{XCl}_4$  binds only to the clean surface or to a  $\text{XO}_2$  layer.

In order to transform sensor signal into mass units ( $\text{ng}/\text{cm}^2$ ) the value should be multiplied by constant  $K$ . Using the data provided in form of the figure, answer the following questions:

- a) Explain which subprocesses occurs during oxide layers formation, which is described by points 1–8 in the figure. How many layers would form in 600 s?
- b) Assuming that the number of moles of compound binded to the surface, which contain  $\text{X}$ , does not change during one cycle, by calculations determine element  $\text{X}$  and write equation for the reaction  $\text{XO}_2$  formation.
- c) Layers growth rate is  $1.9 \text{ nm}/\text{min}$  and density of one layer is  $5.7 \text{ g}/\text{cm}^3$ . Calculate the value of constant  $K$  (units  $\text{ng}/\text{cm}^2$ ).

4. Silver metal is represented as a face-centered cubic lattice. Its unit cell length is  $408.6 \text{ pm}$  ( $1 \text{ pm} = 10^{-12} \text{ m}$ ), Avogadro number is  $6.022 \cdot 10^{23} \text{ mol}^{-1}$ .



- a) Calculate radius of silver atom.
- b) Calculate density of silver (in  $\text{g}/\text{cm}^3$ ).
- c) Without calculating radius of atoms, compare atomic radius of copper, silver and gold, using symbols  $<$ ,  $>$  or  $\approx$ . Copper ( $8.95 \text{ g}/\text{cm}^3$ ), silver and gold ( $19.3 \text{ g}/\text{cm}^3$ ) have the same type of lattice.

5. Nitrogen dioxide is easily dimerized as a result of reaction  $2\text{NO}_2 = \text{N}_2\text{O}_4$ . This reaction serves as a good example of Le Chatelier principle in action. Since  $\text{NO}_2$  is a brown-colored gas,  $\text{N}_2\text{O}_4$  is colorless. As the ratio of gases in the mix depends on temperature, it is possible to draw conclusions about the displacement of equilibrium by observing color change.

The dependence of equilibrium constant on temperature is described by the equation van't Hoff, which may be written as follows:

$$\log\left(\frac{K_2}{K_1}\right) = -\frac{0,434\Delta_r H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

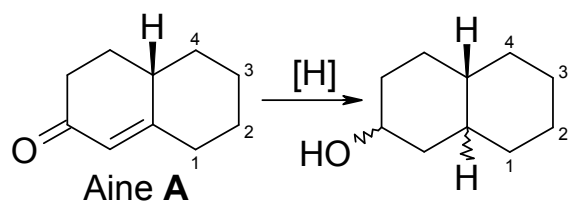
where  $R = 8,314 \text{ kJ}/(\text{mol}\cdot\text{K})$ .

- a) Calculate the standard reaction enthalpy. Formation enthalpies of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  at  $25^\circ\text{C}$  are  $33.18$  and  $9.16 \text{ kJ/mol}$ , respectively.
- b) Draw a graph which represents the dependence of  $\log K$  on the inverse value of temperature ( $T$ :  $25\dots 125^\circ\text{C}$ ) if at  $25^\circ\text{C}$  equilibrium constant equals  $6.75$ . Calculate the slope of this dependence both using van't Hoff equation and your graph.

To demonstrate the Le Chatelier principle in action, tubes closed at room temperature with equilibrium mixture of  $\text{NO}_2\text{--N}_2\text{O}_4$  were immersed in different liquids: hot water, mix of water and ice, liquid nitrogen.

- c) Describe the change of color and state of aggregation, which take place in tubes, immersed in three different liquids.
- d) At which tube condition equilibrium is settled in the fastest way? Explain.

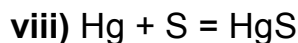
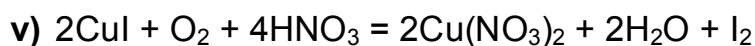
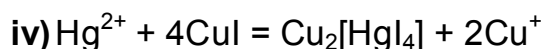
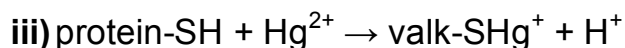
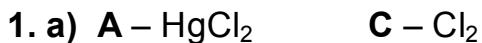
6. Substance **A** is a hexahydronaphthalenedione. Your task is to determine the position of the first ketonic group in the molecule of **A**, which might be in positions from 1 to 4. It is known that if we reduce ketonic groups C=O to hydroxyl groups C–O–H and double bonds to single, we will obtain 8 different stereoisomers, 4 of which are in meso-form, i.e. are optically non-active.



~~~~~ - rühm võib olla nii ühel kui ka teisel pool tasandit

- Determine the position of ketonic group in substance **A**.
- Draw projection formulas of possible products that are formed throughout the reduction of substance **A**. Which of the drawn molecules are the pairs of enantiomers?

## Solutions



d) Reaction with KMnO<sub>4</sub> is faster.



$$\%(\mathbf{X}) = \frac{(a + 3b) \cdot 16}{(a + 2b) \cdot A_r(\mathbf{X}) + (a + 3b) \cdot 16} = 0,152 \quad \text{or}$$

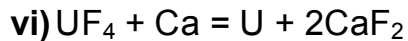
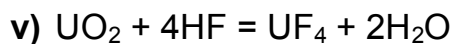
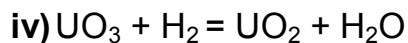
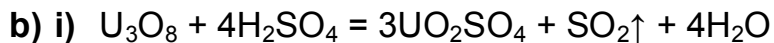
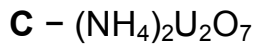
$$\%(\mathbf{X}) = \frac{(2a + 3b) \cdot 16}{(a + b) \cdot A_r(\mathbf{X}) + (2a + 3b) \cdot 16} = 0,152$$

$$A_r(\mathbf{X}) = 89,26 \frac{a + 3b}{a + 2b} \quad \text{or} \quad A_r(\mathbf{X}) = 89,26 \frac{2a + 3b}{a + b}$$

| a | b | A <sub>r</sub> ( <b>X</b> )        |                                    | a | b | A <sub>r</sub> ( <b>X</b> )        |                                    |
|---|---|------------------------------------|------------------------------------|---|---|------------------------------------|------------------------------------|
|   |   | aXO·bX <sub>2</sub> O <sub>3</sub> | aXO <sub>2</sub> ·bXO <sub>3</sub> |   |   | aXO·bX <sub>2</sub> O <sub>3</sub> | aXO <sub>2</sub> ·bXO <sub>3</sub> |
| 1 | 1 | 119 – Sn                           | 223 – Fr                           |   |   |                                    |                                    |
| 1 | 2 | 125                                | <b>238 – U</b>                     | 2 | 1 | 112 – Cd                           | 208                                |
| 1 | 3 | 128 – Te                           | 245                                | 3 | 1 | 107                                | 201 – Hg                           |
| 2 | 3 | 140 – Ce                           | 232 – Th                           | 3 | 2 | 115 – In                           | 214                                |



$$\%(\text{S}) = \frac{32}{366} \cdot 100 = 8,74$$



**3. a)** 1, 5 –  $\text{XCl}_4$  fast binding with the surface

2, 6 – saturation of the surface with  $\text{XCl}_4$

3, 7 – addition of water vapor

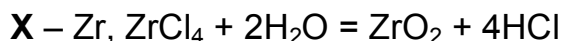
4, 8 – residual substances removal

$$N_{\text{number of layers}} = \frac{600 \text{ s} - 20 \text{ s}}{70 \text{ s}} = 8,3 = \mathbf{8}$$

**b)**

$$\begin{cases} m_1 = n \cdot M(\text{XCl}_4) = n [A_r(\text{X}) + 4 \cdot A_r(\text{Cl})] \text{ g/mol} \\ \qquad \qquad \qquad = n [A_r(\text{X}) + 141,8] \text{ g/mol} = 94,7 \cdot K \\ m_2 = n \cdot M(\text{XO}_2) = n [A_r(\text{X}) + 32] \text{ g/mol} = 50 \cdot K \end{cases}$$

$$\frac{A_r(\mathbf{X}) + 141,8}{A_r(\mathbf{X}) + 32} = \frac{94,7}{50} = 1,894 \quad A_r(\mathbf{X}) = \frac{1,894 \cdot 32 - 141,8}{1 - 1,894} = 91$$



$$\text{c) } h_{\text{width of the layer}} = 70 \text{ s} \cdot \frac{1,9 \text{ nm}}{1 \text{ min}} \cdot \frac{1 \text{ min}}{60 \text{ s}} = 2,22 \text{ nm}$$

$$\text{Density} = h_{\text{width of the layer}} \cdot \rho = 2,22 \text{ nm} \cdot \frac{1 \text{ cm}}{10^7 \text{ nm}} \cdot \frac{5,7 \text{ g}}{1 \text{ cm}^3} = 1,27 \cdot 10^{-6} \text{ g/cm}^2$$

$$K = \frac{1,27 \cdot 10^{-6} \text{ g/cm}^2}{50} \cdot \frac{10^9 \text{ ng}}{1 \text{ g}} = \mathbf{25 \text{ ng/cm}^2}$$

$$4. \quad \text{a) } r = \frac{\sqrt{2}a}{4} = \frac{\sqrt{2} \cdot 408,6 \text{ pm}}{4} = \mathbf{144 \text{ pm}}$$

$$\text{b) } \rho = \frac{m}{V} = \frac{nM}{a^3} = \frac{NM}{N_A a^3}$$

$$\rho = \frac{4 \cdot 107,9 \text{ g/mol}}{6,022 \cdot 10^{23} \text{ 1/mol} \cdot (408,6 \text{ pm} \cdot 1 \text{ cm}/10^{10} \text{ pm})^3} = \mathbf{10,5 \text{ g/cm}^3}$$

$$\text{c) } r \propto \sqrt[3]{A_r/\rho}$$

$$r_{\text{Cu}} < r_{\text{Ag}} \approx r_{\text{Au}} \quad (63,5/8,95 = 7,1 < 108/10,5 = 10,3 \approx 197/19,3 = 10,2)$$

$$5. \quad \text{a) } \Delta_r H^0 = \Delta_f H(\text{N}_2\text{O}_4) - \Delta_f H(\text{NO}_2) = (9,16 - 2 \cdot 33,18) \text{ kJ/mol} =$$

$$= \mathbf{-57,20 \text{ kJ/mol}}$$

$$\text{b) } \log K_2 = \log K_1 - 0,434 \Delta_r H/R(1/T_2 - 1/T_1)$$

$$\log K_{125^\circ\text{C}} = \log(6,75) - \frac{0,434 \cdot (-57200 \text{ J/mol})}{8,314 \text{ J/(mol} \cdot \text{K)}} \left( \frac{1}{(125 + 273) \text{ K}} - \frac{1}{(25 + 273) \text{ K}} \right)$$

$$\log K_{125^\circ\text{C}} = 0,83 - 2,52 = -1,69$$

| $T / ^\circ\text{C}$ | $1/T \cdot 10^3, 1/\text{K}$ | $\log K$ |
|----------------------|------------------------------|----------|
| 25                   | 3,36                         | 0,83     |
| 125                  | 2,51                         | -1,69    |



$$\text{Slope} = -0,434\Delta_r H/R = 2990 \text{ K}$$

$$\text{Slope} = \frac{1000 \text{ K}}{0,338} = \underline{3000 \text{ K}}$$

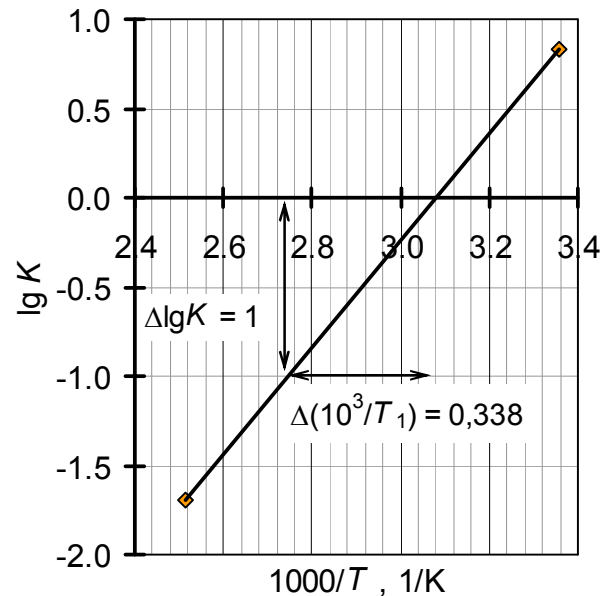
c) Hot water – mainly brown  $\text{NO}_2$

mix of water and ice – mainly colorless  $\text{N}_2\text{O}_4$ . (depending on  $\text{N}_2\text{O}_4$  pressure some of  $\text{N}_2\text{O}_4$  may form liquid drops)

liquid nitrogen – crystals of  $\text{N}_2\text{O}_4$ .

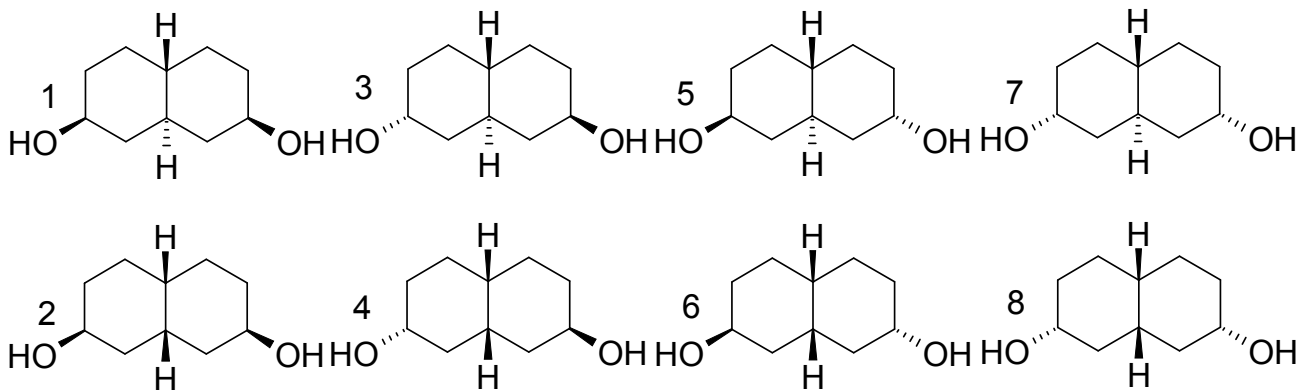
( $T_S(\text{N}_2\text{O}_4) = -11^\circ\text{C}$ )

d) In a hot water tube, as reaction rate is usually higher at higher temperatures.



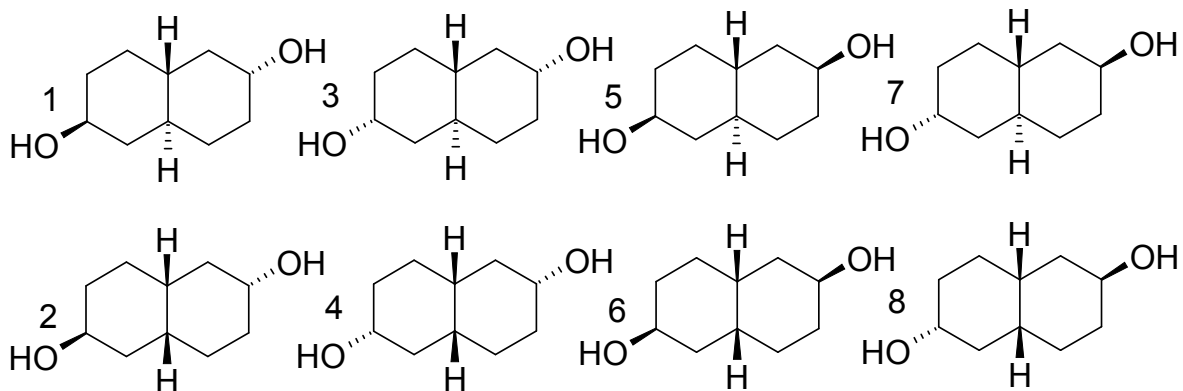
6. a)  $x = 2$ , A – 1,3,4,4a,5,6-hexahydronaphthalene-2,7-dion

b)  $x = 2$



1, 2, 7, 8 are meso-forms. 3 and 5, 4 and 6 are enantiomers.

$x = 3$



2 and 8 are identical. 1 and 7 are meso-forms.

$x = 1$  or  $4$  all structures are individual.

## ***Practical Examination***

### **9th and 10th grade**

#### **Determination of iron(II) content**

Permanganatometry unites titrimetric methods of analysis, which are based on oxidative properties of  $\text{KMnO}_4$ . Iron (II) reacts with  $\text{KMnO}_4$  (redox reaction takes place) and may be determined by direct method.

The iron solution (II) provided for analysis is given in a numbered flask. Transfer solution quantitatively from the flask to a volumetric flask ( $100\text{ cm}^3$ ). Fill the volumetric flask with distilled water up to the mark. Pipette  $10\text{ cm}^3$  of prepared solution to a conical flask ( $100\text{ cm}^3$ ), add 7– $10\text{ cm}^3$  of sulphuric and phosphoric acid mixture (mixture is prepared by blending of equal volumes of diluted 1:4  $\text{H}_2\text{SO}_4$  and concentrated  $\text{H}_3\text{PO}_4$ ). Titrate prepared solution with a standard  $\text{KMnO}_4$  solution until pale pink steady colour appears. You should titrate until you obtain three matching results.

#### **Hints**

1. In order not to mix up flasks, mark them.
2. After you fill up a burette, don't forget to take the funnel away.
3. Think through very carefully which flask is needed to be washed with distilled water, and which ones you should rinse with the next coming solution.

## 11th and 12th grade

### Synthesis of 1,4-di-*tert*-butyl-2,5-dimethoxybenzene

A stirred mixture of 1,4-dimethoxybenzene (360 mg) in glacial acetic acid (1.5 mL) contained in an Erlenmeyer flask of 50 mL is heated gently (water bath) until dissolved. *tert*-Butyl alcohol (0.6 mL) is then added using a pipette and the mixture is cooled in a crushed ice bath, while stirring is continued, and treated dropwise with concentrated sulfuric acid (~1.3–1.5 cm<sup>3</sup>). The addition is achieved using a Pasteur pipette and it must be ensured that each drop is mixed thoroughly with the reaction mixture before the next drop is added. The mixture is then removed from the ice bath, allowed to attain room temperature, and then stirred for a further 25 minutes. The mixture is again cooled in an ice-bath (0°C) whereon water (3 drops) is added VERY CAREFULLY with slow stirring. Crystallization of the product begins and is accelerated by the slow, careful addition of ice water (7.5 mL). After ca. 10 minutes the crystalline material is collected by filtration using a Hirsch funnel. The crystals are washed twice with water and allowed to dry. The product is recrystallized by dissolving in hot methanol (10 mL) and cooling in an ice bath and again collected using a Hirsch funnel. The material is allowed to dry on the air. The purity of the product (P) is determined by thin-layer chromatography using hexane and ethyl acetate mixture (7:1) as the eluent. The starting material (L) is run on the same TLC plate as a reference. Determine the R<sub>f</sub> -value of the product, of the starting material and of any contaminant in the product if present.

## ***Estonian team on International Chemistry Olympiads***

### **Gold medal**

Vladislav Ivaništšev 2003

Taavi Pungas 2009

### **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; 2007; 2008

Andi Kipper 2007

Taavi Pungas 2008

Gleb Široki 2009

### **Bronze medal**

Jaak Suurpere 1994; 1995

Ain Uustare 1995

Artur Jõgi 1996

Aleksei Lulla 1996

Olga Tšubrik 1996; 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 |
| Elika Tõldsepp      | 2006 |
| Taavi Pungas        | 2007 |
| Ivan Ogibalov       | 2007 |
| Jörgen Mersik       | 2008 |
| Svetlana Tšupova    | 2008 |
| Kadi-Liis Saar      | 2009 |

### **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 |
| Maksim Mišin         | 2009 |

### **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 four times**

Andres Laan                    2005; 2006; 2007; 2008

### **Participated three times**

Ain Uustare                    1994; 1995; 1996

Tavo Romann                   1999; 2000; 2001

Taavi Pungas                   2007; 2008; 2009

### **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