

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

**55TH
ESTONIAN NATIONAL
CHEMISTRY OLYMPIAD**

Edited by

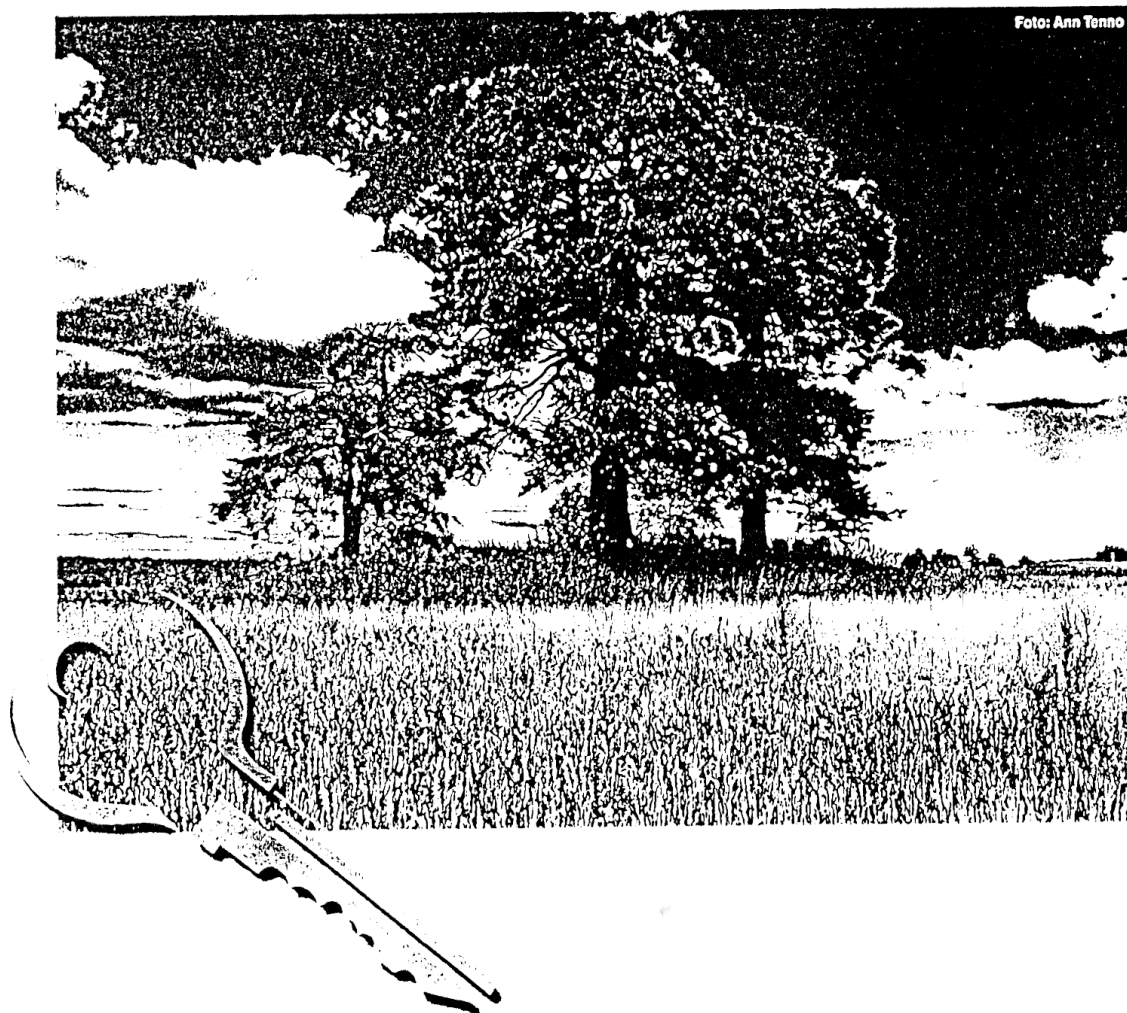
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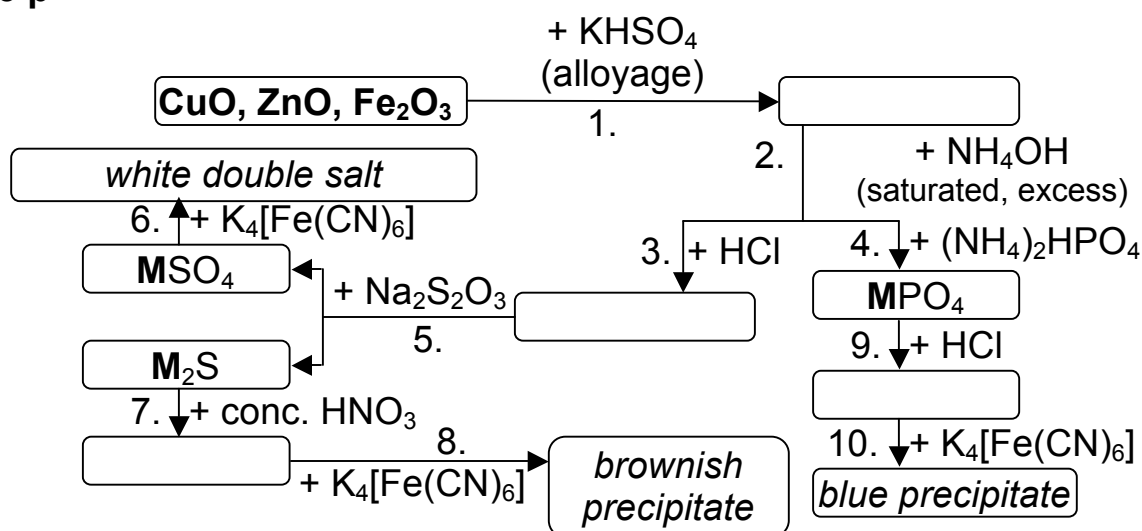
10th-12th Grade

National Theoretical Examination: 12th Grade

1. In 1961 Marcus found a guide to qualitative chemical analysis and prepared the task in identification of the composition of the mixture of oxides for course mates. The scheme of the analysis is shown below. At the present time atomic emission spectroscopy is used for the analysis of the same mixture.

Write the balanced equations for the reactions 1-10 taking place during the analysis of the mixture consisting of CuO , ZnO and Fe_2O_3 . Write the equation for the reaction 2, if NH_4OH is present **i)** not in excess and **ii)** in excess.

15 p

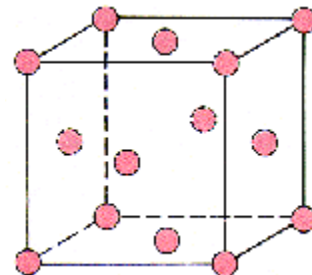


2. In 1886 C. Winkler, a German chemist, was experimenting with mineral argyrodite. He found argyrodite contains silver ($\overset{+1}{\text{Ag}}$), sulfur ($\overset{-2}{\text{S}}$) and the substance that could not be identified at once. After the weeks of experimenting it became clear that this new substance is new element **X** which properties were identical with the element which existence and the properties had been predicted by Mendeleev 15 years ago.

1,00 g of argyrodite was burned in air until SO_2 stopped emitting, a solid residue was dissolved in nitric acid. For determination of Ag^+ ions, 100,0 cm^3 0,100 M potassium cyanate solution was added which excess was titrated back with 9,69 cm^3 0,100 M Fe^{3+} containing solution. SO_2 was passed through $\text{Ba}(\text{OH})_2$ solution, 1,156 g of a precipitate was formed. The insoluble in nitric acid part of **A** was found to be an amphoteric oxide, which is soluble in both concentrated HCl and in NaOH solutions (colourless substances were formed).

- a) Calculate the masses and amounts of the following substances (in moles)
 i) silver and ii) sulfur. (4,5)
 b) Write the symbol of element **X** and determine the formula of argyrodite. (5,5)
 c) Write the equations of the reactions i) **A** + conc. HCl →, ii) **A** + NaOH(aq) →. (2) **12 p**

3. Human blood is colored red because hemoglobin, transporter of oxygen, contains iron in oxidized form. Octopus blood has another color because it contains oxidized form of another element. The unit cell of the crystal system for another element is given on the picture. Crystal system consists of identical tiny boxes, called unit cells. An atom can belong to several unit cells at once, for instance, 1/8 of the atoms centered at the apexes and 1/2 of the atoms positioned at the face centers belong to the given unit cell. The density of the element is 8920 kg/m^3 and the length of the unit cell edge is $a = 3,62 \cdot 10^{-8} \text{ cm}$.



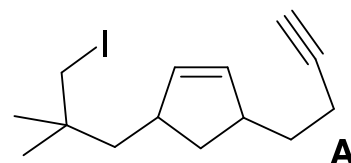
- a) How many atoms does the unit cell contain? (1)
 b) Calculate the volume of the unit cell and the volume occupied by the atoms in the unit cell. ($V_{\text{sphere}} = 4/3\pi r^3$) (5)
 c) Using calculations, determine the element is present in octopus blood. What color is octopus blood? (3) **9 p**
4. The annual consumption of electricity in Estonia is approximately 10000 GWh. Ecofriendly solar and wind energies depend on season, in addition, the energy should be somehow conserved in order to apply ecofriendly energies. For the purpose of retaining the annual energy reserve in Estonia:
- a) How many meters it is necessary to lift Lake Peipsi? (25 km^3)? (3)
 b) How many degrees it is necessary to heat Lake Peipsi? (2)
 c) How many kg of H_2 should be reserved to convert the energy into electricity using fuel cell? (2)
 d) How many kg of the mixture of deuterium and tritium (1:1) is needed, if the energy is obtained from it by transformation into helium? (3) **10 p**

Assume that power efficiency is 100% in all the cases.

Constants: $g = 9,8 \text{ [m} \cdot \text{s}^{-2} = \text{N} \cdot \text{kg}^{-1} = \text{J} \cdot \text{m}^{-1} \cdot \text{kg}^{-1} = \text{W} \cdot \text{s} \cdot \text{m}^{-1} \cdot \text{kg}^{-1}]$,

heat capacity of water is $4181 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ and enthalpy of formation of water is $286,6 \text{ kJ} \cdot \text{mol}^{-1}$, speed of light is $3,00 \cdot 10^8 \text{ m} \cdot \text{s}^{-1}$, $A_r(^4\text{He}) = 4,0026$, $A_r(^2\text{H}) = 2,0141$, $A_r(^3\text{H}) = 3,0160$, $A_r(^1\text{n}) = 1,0087$, G - giga (10^9).

5. Radical reactions are extensively used in organic chemistry. The synthesis of hirsutene that was separated from mycelium of fungus specie *Coriolus*



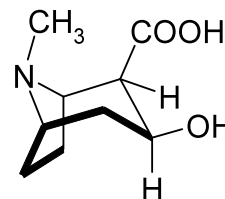
consors is discussed in this problem. Hirsutene is hydrocarbon that consists of three five-membered cycles and contains one double bond. It is obtained from compound **A** using the radical reaction. The initiator of the reaction is AIBN (2,2'-azobis-isobutyronitrile, $M_r = 164,2$), which is decomposed at 60 °C with formation of radical **B**.

a) Draw the structure of hirsutene. (2)

b) Draw the structures of AIBN and radical **B**. Write the balanced equation of the AIBN decomposition reaction. (3) 5 p

6. Doctors do not always have opportunity to use general anesthesia, in this cases surgeries are realized using local anesthesia. The history of local anesthetics opened with alkaloid cocaine which was separated from South American plant *Erythroxylon coca*. Cocaine had been used in medicine since the 19th century, but at the beginning of the 20th century it was banned as a strong drug.

When cocaine is hydrolyzed, ecgonine (on the picture) and two substances with relatively simple structures are formed: saturated alcohol **A** and aromatic monoprotic carboxylic acid



B. When a certain quantity of alcohol **A** is oxidized, according to the conditions it is possible to obtain 75.0 g of aldehyde or 115.0 g of acid. 20.0 g of 30.0% NaOH solution are needed for neutralization of 18.3 g of acid **B**.

a) Using calculations, determine the formulas of alcohol **A** and acid **B**, draw the structure of cocaine. (5)

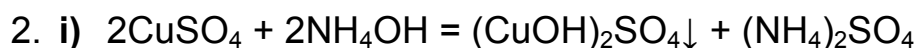
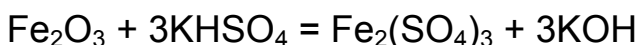
Using the structure of cocaine as the basis, chemists tried to prepare synthetical analogs of local anesthetics that were not drugs. One of the first these analogs using up to date was procaine. It can be obtained by the reaction of p-aminobenzoic acid with amino alcohol $R_2NCH_2CH_2OH$ in which $\%(\text{N})=12\%$, and R is saturated hydrocarbon radical.

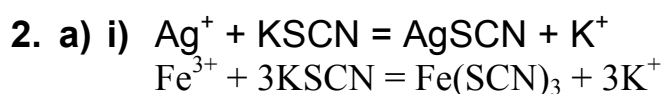
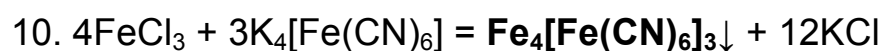
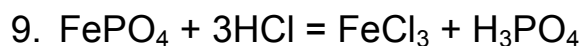
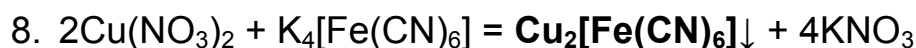
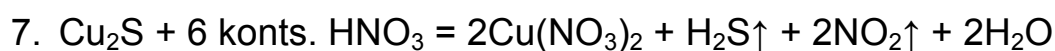
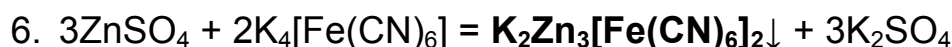
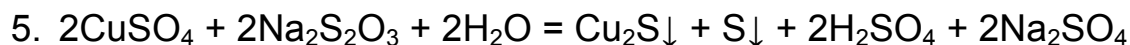
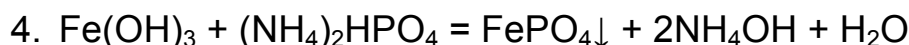
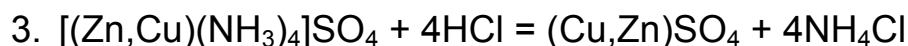
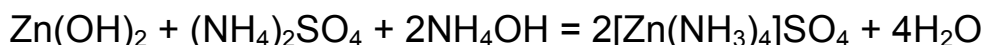
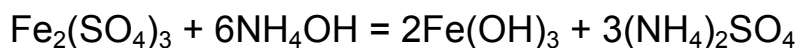
b) Using calculations, determine the formula of amino alcohol $R_2NCH_2CH_2OH$ and draw the structure of procaine. (3)

Anesthesiophore is the active group of a molecule that confers the anesthetic effect.

c) Using the similarity of the structures of cocaine and procaine, suggest the general structure of the anesthesiophore for cocaine and majority of its analogs. (1) 9 p

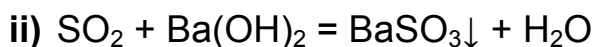
Solutions





$$\mathbf{n(\text{Ag}) = \left(\frac{1}{1} \cdot 100 \text{ cm}^3 \cdot \frac{0,01 \text{ mol}}{1 \text{ dm}^3} - \frac{3}{1} \cdot 9,69 \text{ cm}^3 \cdot \frac{0,01 \text{ mol}}{1 \text{ dm}^3}\right) \frac{1 \text{ dm}^3}{1000 \text{ cm}^3} = 0,00709 \text{ mol}}$$

$$\mathbf{m(\text{Ag}) = 0,007093 \text{ mol} \cdot \frac{107,9 \text{ g}}{1 \text{ mol}} = 0,765 \text{ g}}$$



$$\mathbf{n(\text{S}) = \frac{1}{1} \cdot 1,156 \text{ g} \cdot \frac{1 \text{ mol}}{217,4 \text{ g}} = 0,00532 \text{ mol}}$$

$$\mathbf{m(\text{S}) = 0,005317 \text{ mol} \cdot \frac{32,06 \text{ g}}{1 \text{ mol}} = 0,171 \text{ g}}$$

b) We have to find amount of Ag_2S in argyrodite and amount of remaining sulfur:

$$\mathbf{n(\text{Ag}_2\text{S}) = \frac{n(\text{Ag})}{2} = \frac{0,007093 \text{ mol}}{2} = 0,003547 \text{ mol}}$$

$$\mathbf{n(\text{S,rem}) = 0,005317 \text{ mol} - 0,003547 \text{ mol} = 0,00177 \text{ mol}}$$

The oxidation state of element X is positive.

$$\mathbf{m(\text{X}) = 1 \text{ g} - 0,7653 \text{ g} - 0,1705 \text{ g} = 0,06420 \text{ g}}$$

Atomic mass of element X in compound XiSj is:

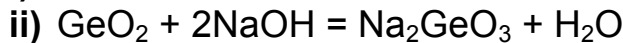
$$A(X) = \frac{m(X) \cdot 10,06420 \text{ g}}{i/j \times n(S, \text{rem}) \cdot 10,001770 \text{ mol}} = \dots$$

Potential compounds are $\mathbf{X_2S}$, \mathbf{XS} , $\mathbf{X_2S_3}$, $\mathbf{XS_2}$ etc. and j/i ratio is 0,5, 1, 1,5, 2 etc. Possible atomic masses of \mathbf{X} are (os = I), 36,3 (II), 54,4 (III), 72,5 (IV), 90,6 (V) etc. Tetravalent Ge can be correct only, GeS_2 .

$$n(\text{GeS}_2) = \frac{0,001770 \text{ mol}}{2} = 0,0008850 \text{ mol}$$

$$\text{Ag}_2\text{S} : \text{GeS}_2 = 0,003547 : 0,0008850 = 4 : 1$$

The formula of argyrodite is Ag_8GeS_6 .



The properties of germanium (Latin *Germania* for Germany) were similar to the element ekasilicon that Mendeleev predicted to exist. The discovery was an important confirmation of the idea of element periodicity.

3. a) $N = 6 \cdot \frac{1}{2} + 8 \cdot \frac{1}{8} = 3 + 1 = 4$

b) $V_{\text{unit cell}} = (3,62 \times 10^{-8} \text{ cm})^3 = 4,70 \times 10^{-23} \text{ cm}^3$

We have to find connection between the length of the unit cell a and the atomic radius r :

$$(r + 2r + r) = \sqrt{a^2 + a^2} = \sqrt{2a^2} = \sqrt{2}a \Rightarrow r = \frac{\sqrt{2}a}{4}$$

$$V_{\text{atom}} = 4 \cdot \frac{4}{3} \pi r^3 = 4 \cdot \frac{4}{3} \pi \left(\frac{\sqrt{2}a}{4} \right)^3 = \frac{\sqrt{2}}{6} \pi \cdot 4,70 \cdot 10^{-23} \text{ cm}^3 = 3,48 \cdot 10^{-23} \text{ cm}^3$$

$$\%_{\text{occupied}} = \frac{V_{\text{atom}}}{V_{\text{unit cell}}} \cdot 100 = \frac{3,48 \cdot 10^{-23}}{4,70 \cdot 10^{-23}} \cdot 100 = 74,0\%$$

c) $m_{\text{unit cell}} = \frac{m_{\text{unit cell}}}{n_{\text{unit cell}}} \cdot N_A = \frac{M}{n_{\text{unit cell}}} \cdot N_A$

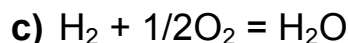
$$M = 4,7 \cdot 10^{-23} \text{ cm}^3 \cdot \frac{8,92 \text{ g}}{\text{cm}^3} \cdot \frac{1}{4} \cdot \frac{6,02 \cdot 10^{23}}{1 \text{ mol}} = 63,1 \text{ g/mol}$$

Element is **copper**. Octopus blood is colored **blue**.

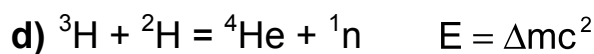
4. $E(\text{Germania}) = 10000 \times 610 \frac{10^9 \text{ W}}{1 \text{ GWh}} = 610 \times 10^9 \text{ W}$

a) $h = 3,6 \cdot 10^{16} \text{ J} \cdot \frac{1 \text{ m kg}}{9,8 \text{ J}} \cdot \frac{1}{25 \text{ km}^3} \cdot \frac{\text{km}^3}{10^9 \text{ m}^3} \cdot \frac{1 \text{ m}^3}{10^3 \text{ kg}} = 147 \text{ m} = 150 \text{ m}$

$$\text{b) } \Delta T = 3,6 \cdot 10^{16} \text{ J} \cdot \frac{1 \text{ kg K}}{4181 \text{ J}} \cdot \frac{1}{25 \text{ km}^3} \cdot \frac{\text{km}^3}{10^9 \text{ m}^3} \cdot \frac{1 \text{ m}^3}{10^3 \text{ kg}} = \mathbf{0,34 \text{ K}}$$



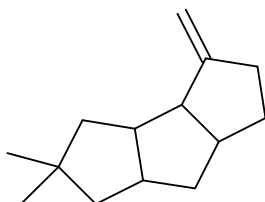
$$m(\text{H}_2) = 3,6 \cdot 10^{16} \text{ J} \cdot \frac{1 \text{ mol}}{286,6 \text{ kJ}} \cdot \frac{1 \text{ kJ}}{10^3 \text{ J}} \cdot \frac{2 \text{ g}}{1 \text{ mol}} \cdot \frac{1 \text{ kg}}{10^3 \text{ g}} = \mathbf{2,5 \cdot 10^8 \text{ kg}}$$



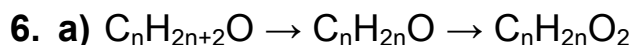
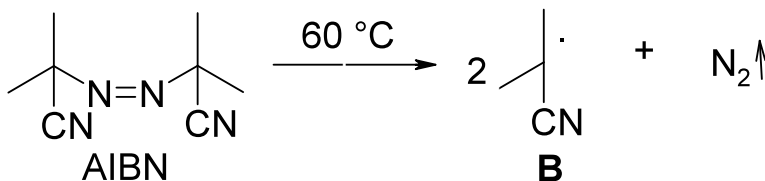
$$\Delta m = 3,6 \cdot 10^{16} \text{ J} \cdot \frac{1 \text{ s}^2}{(3 \cdot 10^8 \text{ m})^2} = 0,4 \text{ kg}$$

$$m({}^3\text{H} + {}^2\text{H}) = 0,4 \text{ kg} \cdot \frac{2,0141 + 3,0160}{2,0141 + 3,0160 - 4,0026 - 1,0087} = 107 \text{ kg} = \mathbf{110 \text{ kg}}$$

5. a)

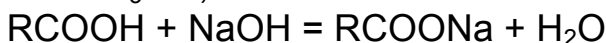


b)



$$n(\text{C}_n\text{H}_{2n}\text{O}) = n(\text{C}_n\text{H}_{2n}\text{O}_2) \quad \frac{75}{14n + 16} = \frac{115}{14n + 32} \Rightarrow n = 1$$

A – CH_3OH , methanol



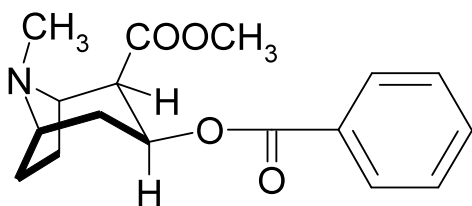
$$n(\text{RCOOH}) = \frac{1}{1} \cdot 20 \text{ g} \cdot 0,3 \cdot \frac{1 \text{ mol}}{40 \text{ g}} = 0,15 \text{ mol}$$

$$M(\text{RCOOH}) = \frac{18,3 \text{ g}}{0,15 \text{ mol}} = 122 \text{ g/mol}$$

$$M(\text{R}) = (122 - 45) \text{ g/mol} = 77 \text{ g/mol} \quad \text{R is benzene ring (C}_6\text{H}_5\text{-)}$$

B – $\text{C}_6\text{H}_5\text{COOH}$, benzoic acid

Cocaine can be considered as the product of double esterification of ecgonine: methanol reacts with carboxyl group and benzoic acid reacts with hydroxyl group.

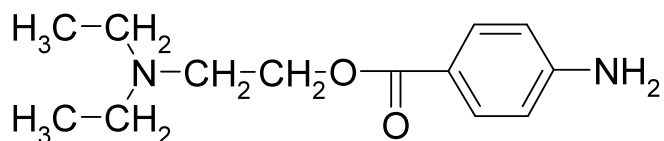


b) $R_2NCH_2CH_2OH$ $\% (N) = \frac{14}{2M(R) + 59} = 0,12 \Rightarrow M(R) = 29$

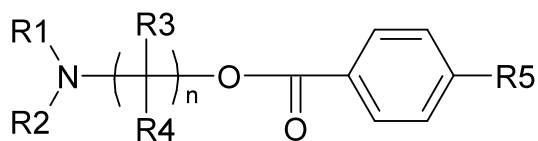
R is ethyl group (C_2H_5)

$(C_2H_5)_2NCH_2CH_2OH$

Reaction of amino alcohol with p-aminobenzoic acid gives procaine as the product



c) The comparison of the structures of cocaine and procaine shows that the probable structure of the anesthesiophore is



National Theoretical Examination: 11th Grade

1. A beaker with 12,00 g of CuSO_4 was set aside on vacation. One week later precisely $\frac{1}{3}$ of the salt transformed into pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$). 90,00 cm^3 of water were casually sloshed into the beaker during cleanup after vacation. After that all the charge was transferred into a flask filled with 300,0 cm^3 0,0400 M NaOH solution. A formed precipitate was separated and heated until a red substance was formed and its mass remained stable.
- Calculate the mass of the salt in the beaker one week later. (2)
 - Calculate the percentage of CuSO_4 in the formed solution. (1)
 - Write all the reactions taking place and name the compounds that contain copper. Calculate the mass of the substance after heating. (7)
- 10 p**

2. Hydrocarbon contains 87,27% carbon by mass, the relative density in gas phase with respect to hydrogen is less than 75. The structure consists of secondary and tertiary carbon atoms only and at least two six-membered cycles.
- Using calculations, determine the empirical formula and draw the structure of hydrocarbon. (5,5)
 - How many monochloro derivatives are formed during nonselective chlorination in sunlight? (1,5)
- 7 p**

3. A. Einstein made a riddle and he claimed that only 2% of the world's population could solve it. The following problem is a chemical analog of the riddle. There is a run of 5 pots with food colorings on a shelf and it is necessary to determine what substance is present in colored marchpane. The facts of the puzzle are given below.

Indigo carmine is colored blue. Curcumine is found in *curcuma* (spice). Riboflavin contains four OH-groups. The substance colored red stands on the left of the substance colored orange. The substance colored red is *E*-isomer. *Lemonade* contains the substance which is classified as salt. The substance in the flask right in the center contains two intramolecular hydrogen bonds. The wine-colored substance is **carotenoid**. Lycopine is first on the left. The substance related to **vitamins**

stands next to the substance is present in *melon*. The substance present in *almond* stands next to the substance related to **carotenoids**. The substance that is **polyphenol** contains carbonyl group. Lycopine stands next to the

pot nr.	1	2	3	4	5
color					
name					
structure, group					
class					
<i>food coloring</i>					

substance colored yellow. Carmoisine is

azo compound. The substance related to **vitamins** stands next to the substance that contains ten methyl groups. Fill the gaps in the table.
10 p

4. Phosphoric acid is a triprotic acid for which $K_1 = 7,6 \cdot 10^{-3}$, $K_2 = 6,2 \cdot 10^{-8}$, $K_3 = 4,4 \cdot 10^{-13}$.
- Draw a sketch of the titration curve of phosphoric acid titrated with NaOH solution (a plot of pH vs $V(\text{NaOH})$, without calculations) (2)
- A certain amount of 0,10 M NaOH solution was added to 50 cm³ 0,010 M H₃PO₄ solution in order to equalize amounts of NaH₂PO₄ и Na₂HPO₄.
- Calculate the pH of the initial solutions (NaOH и H₃PO₄). (4)
 - In the formed solution what are a weak acid and its corresponding salt? (1)
 - Calculate the pH of the formed solution and the volume of added NaOH solution, mark it on the graph. (2,5)
 - Calculate the change of the pH of the formed solution if 5,0 mg of solid NaOH is added. (3,5) **13 p**
5. Acid **A** consists of 3 elements. A metal wire was inserted into the flask with 75,0 g of 16,4% acid **A** aqueous solution. As a result, 0,672 dm³ (n.c.) of hydrogen was produced and a salt solution was formed. When an excess of AgNO₃ was added to the solution, 25,81 g of a white precipitate formed. The precipitate contained 75,26% silver by mass. No change of the mass of the wire was detected during the analysis.
- Determine the composition of the white precipitate and calculate the formula of acid **A**. (6)
 - What metal is the wire made from? (3)
 - Write the equations of all the reactions taking place. (2) **11 p**
6. Analyzed copolymer consists of monomer units of 1398 ethene molecules (CH₂CH₂), 466 α-methylstyrene molecules (C₆H₅C(CH₃)CH₂) and 699 propene molecules (CH₃CHCH₂).
- Assume that monomer units are positioned in the order of increasing molecular masses in the elementary unit of an ideal polymer. i) Estimate the molar mass of the polymer and ii) write the formula of the elementary unit of the polymer (symbols: monomer units of E – ethene, S – α-methylstyrene and P – propene), iii) find the number of the elementary units in the polymer molecule. (3,5)
- Actually, a polymer consists of chains of varying lengths which are characterized by average molar mass. Average molar mass M_{av} can be found by measuring of osmotic pressure Π of a diluted solution of polymer. Osmotic pressure Π (Pa) is directly proportional to the concentration of the solution (c ,

g/m^3): $\bar{M} = \frac{RTc}{\Pi}$, where R is gas constant and T is the temperature. The results of the measurement (25 °C) are shown in the table.

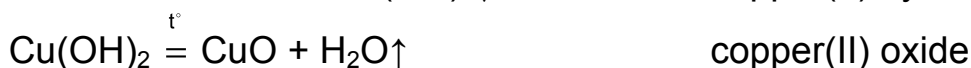
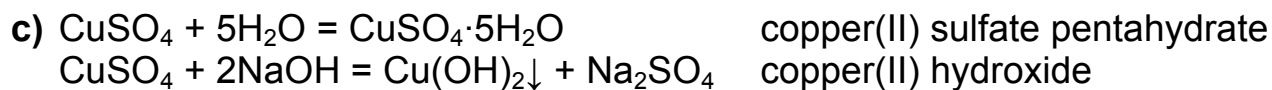
b) Sketch a plot of Π/RT vs. c, find the slope (give the units) and M_{av} . Is average polymer molecule longer in comparison with ideal molecule? (4)

c) How many carbon atoms are in average polymer chain if the structure of the elementary unit is the same as in ideal polymer? (1,5) **9 p**

Solutions

1. a) $m(\text{CuSO}_4) = 12 \text{ g} + \frac{1}{3} \cdot 12 \text{ g} \cdot \frac{1 \text{ mol}}{159,5 \text{ g}} \cdot \frac{5}{1} \cdot \frac{18 \text{ g}}{1 \text{ mol}} = \mathbf{14,26 \text{ g}}$

b) $\%(\text{CuSO}_4) = \frac{12 \text{ g}}{14,26 \text{ g} + 90 \text{ cm}^3 \cdot 1 \text{ g/cm}^3} \cdot 100 = \mathbf{11,51}$



$n(\text{CuSO}_4) = 12 \text{ g} \cdot \frac{1 \text{ mol}}{159,5 \text{ g}} = 0,07524 \text{ mol}$

$n(\text{CuSO}_4, \text{NaOH from}) = \frac{11 \text{ dm}^3 \cdot 0,04 \text{ mol}}{2} = 0,22 \text{ mol}$
 $\frac{0,006 \text{ mol}}{1000 \text{ cm}^3 \text{ dm}^3}$

CuSO_4 is in excess.

$m(\text{CuO}) = \frac{1}{1} \cdot \frac{1}{1} \cdot 0,006 \text{ mol} \cdot \frac{79,5 \text{ g}}{1 \text{ mol}} = \mathbf{0,477 \text{ g}}$

2. a) $M(\text{C}_x\text{H}_y) = \frac{x \cdot 12,01}{0,8727} = 13,76x$

$y = 13,76x - 12,01x = 1,75x$

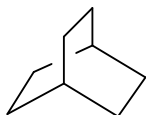
$x : y = x : 1,75x = 1 : 1,75 = 4 : 7$

The simplest empirical formula is C_4H_7 .

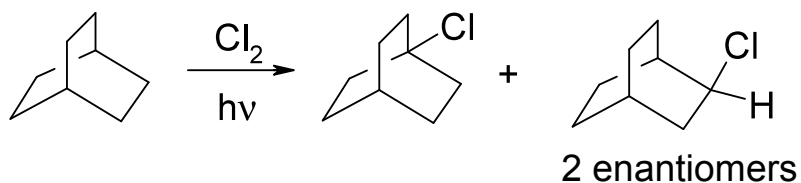
$\rho_{\text{H}_2} = 75 < \frac{M(\text{C}_x\text{H}_y)}{2}$

Π (Pa)	55,68	111,4	167,0
c (mg/cm ³)	2	4	6

Taking into account that $\rho_{\text{H}} = 75 < \frac{M(\text{C}_x\text{H}_y)}{2}$ and the structure consists of at least two six-membered cycles, the formula of hydrocarbon is C_8H_{14} .



b) Two different monochloro derivatives are formed. One of them can appear in the form of two enantiomers.

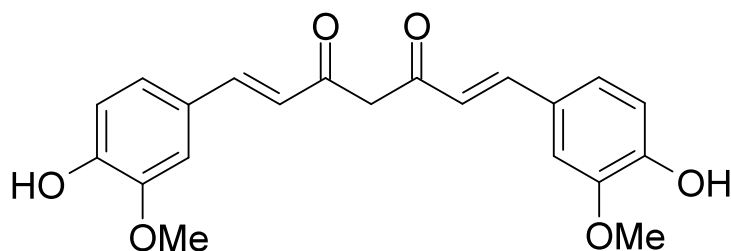


3. Table

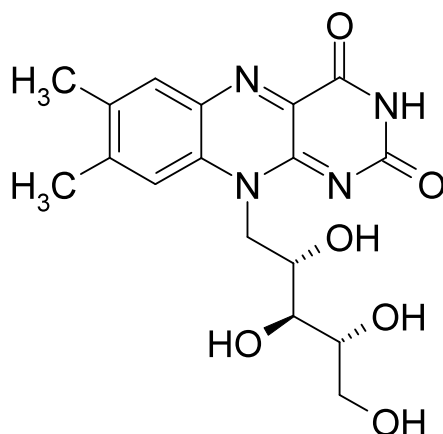
	1	2	3	4	5
Color	Dark-red	Yellow	Blue	Red	Yellowish-orange
Name	Lycopine	Riboflavin	Indigo carmine	Carmoisine	Curcumine
Structure, group	-CH ₃ (10 u)	-OH (4 u)	N-H·····O=C	E-isomer	C=O
Class	Carotenoid	Vitamine	Salt	Azo compound	Polyphenol
<i>Food coloring</i>	Melon	Almond	Limonade	Marchpane	Curcuma

Carmoisin is present in marchpane

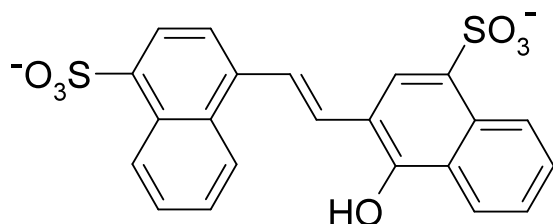
E100 Curcumine



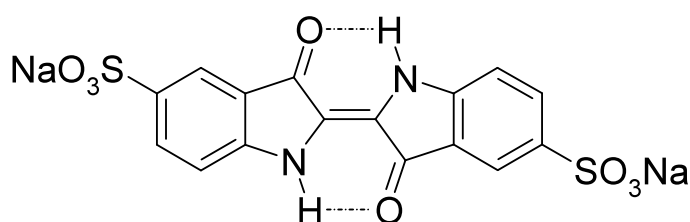
E101 Riboflavin



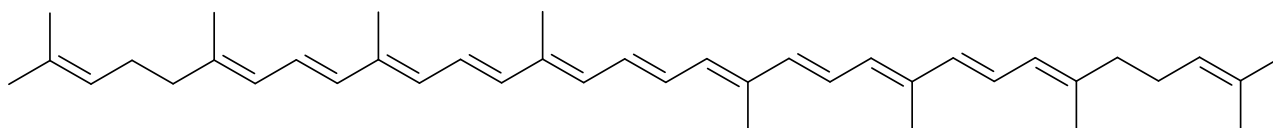
E122 Carmoisine



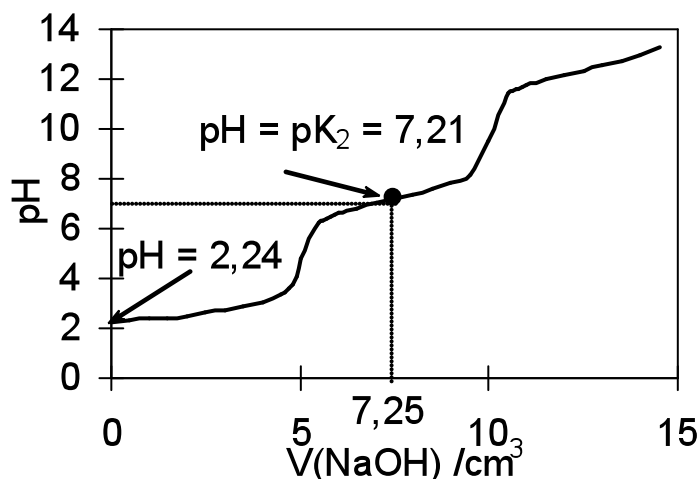
E132 Indigo carmine



E160d Lycopine



4. a) Titration curve of phosphoric acid. Titration curve has three steps because phosphoric acid is a triprotic acid.



- b) NaOH solution $\text{pH} = 14 - \text{pOH} = 14 + \log [\text{OH}^-] = 14 + \log 0,1 = 13$

H_3PO_4 solution



Mass balance: $c_{\text{acid}} = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-]$

Charge balance: $[\text{H}^+] = [\text{H}_2\text{PO}_4^-]$

From the first expression: $[\text{H}_3\text{PO}_4] = c_{\text{acid}} - [\text{H}_2\text{PO}_4^-] = c_{\text{acid}} - [\text{H}^+]$

$$K_1 = \frac{[\text{H}^+]^2}{c_{\text{acid}} - [\text{H}^+]} \quad [\text{H}^+] = K_1 \sqrt{\frac{c_{\text{acid}}}{K_1 + 1}}$$

$$[\text{H}^+] = -0,0076/2 + \sqrt{0,0076^2 / 4 + 0,0076 \cdot 0,01} = 0,0243$$

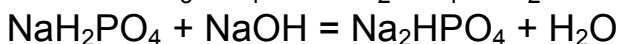
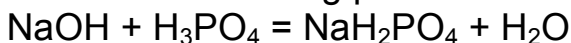
$$\text{pH} = -\log 0,0243 = 2,24$$

- c) In the formed buffer solution NaH_2PO_4 can be considered as a weak acid and Na_2HPO_4 as its corresponding salt.

$$\text{d) } \text{pH} = \text{pK}_2 + \log \frac{[\text{salt}]}{[\text{weak acid}]}$$

$$[\text{NaH}_2\text{PO}_4] = [\text{Na}_2\text{HPO}_4] \Rightarrow \text{pH} = \text{pK}_2 = -\log(7,6 \cdot 10^{-3}) = 7,21$$

The reactions taking place in the solution:



$$V(\text{NaOH}) = \left(\frac{1}{1} + \frac{1}{2}\right) \cdot 50 \text{ cm}^3 \cdot 0,01 \text{ M} \cdot \frac{1}{0,1 \text{ M}} = 7,5 \text{ cm}^3$$

$$\text{e) } n(\text{NaHPO}_4) = n(\text{NaHPO}_4)_{\text{initial}} = 50 \text{ cm}^3 \cdot 0,01 \frac{\text{mmol}}{\text{dm}^3} = 0,5 \text{ mmol}$$

$$= 2,5 \cdot 10^{-4} \text{ mol} = 0,25 \text{ mmol}$$

$$n(\text{NaOH})_{\text{added}} = 0,005 \text{ L} \cdot 0,25 \frac{\text{mol}}{\text{L}} = 0,00125 \text{ mol} = 1,25 \text{ mmol}$$

$$\text{pH} = 7,21 + \log \frac{(0,25 + 0,125) \text{ mmol}}{(0,25 - 0,125) \text{ mmol}} = 7,69$$

$$\Delta \text{pH} = 7,69 - 7,21 = 0,48$$

$$5. \text{ a) } \text{Ag}_n\text{X} \quad \%(\text{Ag}) = \frac{n \cdot A_r(\text{Ag})}{n \cdot A_r(\text{Ag}) + A_r(\text{X})} = 0,7526 \Rightarrow A_r(\text{X}) = 35,46n$$

The correct answer is $n = 1$ and $\text{X} = \text{Cl}$. The white precipitate is **AgCl**.

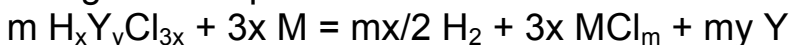
Acid **A** consists of H, Cl and unknown element **Y**.

$$N(\text{Cl}) = N(\text{AgCl}) = 25,81 \text{ g} \cdot \frac{1 \text{ mol}}{143,3 \text{ g}} = 0,18 \text{ mol}$$

$$N(\text{H}) = 2N(\text{H}_2) = 2 \cdot 0,672 \text{ dm}^3 \cdot \frac{1 \text{ mol}}{22,4 \text{ dm}^3} = 0,06 \text{ mol}$$

Because $N(\text{H}) : N(\text{Cl}) = 1 : 3$, **A** – $\text{H}_x\text{Y}_y\text{Cl}_{3x}$

The general equation of the reaction:



$$M(\text{A}) = 75 \text{ g} \cdot 0,164 \cdot \frac{x}{0,06 \text{ mol}} = 205x \text{ g/mol}$$

$$\text{If } x = 1, A_r(\text{Y}) = \frac{205 - 1,008 - 3 \cdot 35,45}{y} = \frac{97,642}{y}$$

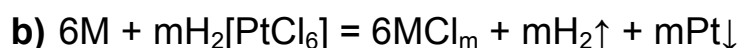
If $y = 1$, **Y** – Tc, If $y = 2$, **Y** – Ti, ...

Both the answers are not correct with respect to the statements of the problem.

$$\text{If } x = 2, A_r(\text{Y}) = \frac{2 \cdot 97,642}{y} = \frac{195,284}{y}$$

If $y = 1$, **Y** – Pt, If $y = 2$, **Y** – Tc, If $y = 3$, **Y** = Tc, ...

A – $\text{H}_2[\text{PtCl}_6]$ (Other answers are not correct with respect to the statements of the problem)

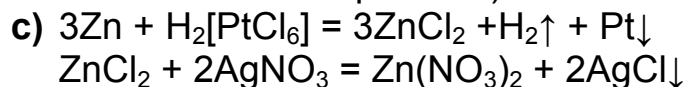


Because no change of the mass of the wire was detected

$$m(M) = m(\text{Pt}) = \frac{1}{2} \cdot 0,06 \text{ mol} \cdot \frac{195,08 \text{ g}}{1 \text{ mol}} = 5,8524 \text{ g}$$

$$M(M) = 5,8524 \text{ g} \cdot \frac{1}{6/m \cdot 0,03 \text{ mol}} = 32,51 \text{ g/mol}$$

If $m = 2$, $M = \text{Zn}$ (Other values are not correct with respect to the statements of the problem)



6. a) i) $M_{\text{ideal}} = \frac{28 \text{ g} + 118 \text{ g} + 42 \text{ g}}{1 \text{ mol} + 1 \text{ mol} + 1 \text{ mol}} = \frac{188 \text{ g}}{3 \text{ mol}} = 62,7 \text{ g/mol}$

ii) $E : P : S = 1398 : 699 : 466 = 6 : 3 : 2$
6E-3P-2S

iii) $M_{\text{unit}} = \frac{28 \text{ g} + 118 \text{ g} + 42 \text{ g}}{1 \text{ mol} + 1 \text{ mol} + 1 \text{ mol}} = \frac{188 \text{ g}}{3 \text{ mol}} = 62,7 \text{ g/mol}$

Number of the elementary units = $\frac{123500 \text{ g/mol}}{62,7 \text{ g/mol}} = 1969$

b) $\frac{\Pi}{RT} = \frac{55,68 \text{ N}}{\text{m}^2} \cdot \frac{1 \text{ mol} \cdot 1 \text{ K}}{8,314 \text{ N} \cdot \text{m}} \cdot \frac{1}{(273,15 + 25) \text{ K}} = 0,0225 \frac{\text{mol}}{\text{m}^3}$

Π (Pa)	55,68	111,4	167,0
c (mg/cm ³)	2	4	6
Π/RT	0,0225	0,0449	0,0674

Slope = $\frac{0,0449 - 0,0225}{4 - 2} = 0,0112 \frac{\text{mol}}{\text{m}^3}$

$\times \times \times = \frac{1 \text{ cm}^3 \text{ m}}{(4-2) \text{ mg} \cdot 10^6 \text{ cm}^3} = \frac{10^3 \text{ mg}}{2 \cdot 10^6 \text{ cm}^3} = 5 \cdot 10^{-4} \text{ mol/g}$

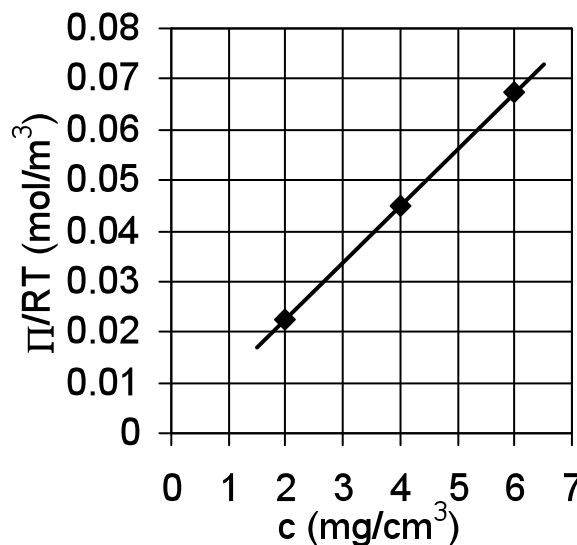
$M_{\text{av}} = \frac{89300 \text{ g/mol}}{1,12 \cdot 10^4 \text{ mol}} = 7,97 \text{ g/mol}$

Average polymer chain is **shorter** than in ideal molecule.

c) The number of carbon atoms in the repeating unit is $(6 + 2 + 3) \cdot 2 = 22$.

Number of units = $\frac{89300 \text{ g/mol}}{530 \text{ g/mol}} = 168$

$N(\text{C}) = 168 \cdot 22 = 3710$



National Theoretical Examination: 10th Grade

1. a) Write the electronic configuration of molybdenum. (1)
 b) What type are chemical bonds in the following substances: i) HClO_4 , ii) NaClO_4 , iii) Cs? (1,5)
 c) Write the structural formula of $\text{H}_2\text{S}_2\text{O}_3$ and find the oxidation states of all the atoms. (1,5)
 d) Calculate the i) molarity, ii) molality of 6,00 % HCl solution ($1,028 \text{ g/cm}^3$). (3)
 e) How many gas molecules are in the volume of 1 cm^3 at 1 Torr, 20°C ? $1 \text{ atm} = 760 \text{ Torr}$. (3) **10 p**

 2. Molecular motor (proton turbine) is moving power for some bacteria. It is powered by the flow of escaping H^+ ions. Proton turbine gives 20 kJ of energy per one mol of protons to a bacteria cell in physiological conditions.
 a) A bacterial colony of 10^9 units lives in a human digestive tract. Calculate the energy produced by the moving colony during one minute if each bacteria releases 10^7 protons during this time. (1,5)
 b) Calculate the change of the pH if all emitted protons are equally dispersed in the volume of human body (70 dm^3) (assume that the initial pH = 7 and buffer systems do not function). (3)
 c) If a human could transform the energy of proton turbine into work, how many minutes would a usual 100 W bulb work using 1 dm^3 of concentrated sulphuric acid (17,5 M) as a fuel? ($1 \text{ J} = 1 \text{ W} \cdot 1 \text{ s}$) (2,5) **7 p**

 3. Methanol (octane rating 113) is used in high performance automobile engines. A student tried to understand why methanol is used instead of petrol. For this purpose he calculated the enthalpies of combustion per gram for both the compounds. Assume that petrol consists of isooctane (octane rating 100) only.
 a) Write the structure and the systematic name of isooctane. (1)
 b) Write the chemical equations for the total burning of methanol and isooctane and calculate the standard enthalpies of combustion per mol and gram. (6)
 c) The student compared the enthalpies of combustions, but he did not understand why methanol is used. Explain why methanol is used as a fuel. Prompt: octane rating, chemical equations. (2) **9 p**
- | Substance | $\Delta_f H^\circ$
(kJ/mol) |
|--------------------------------------|--------------------------------|
| $\text{H}_2\text{O} (\text{l})$ | -285.8 |
| $\text{CO}_2 (\text{g})$ | -393.5 |
| $\text{CH}_3\text{OH} (\text{l})$ | -238.4 |
| $\text{C}_8\text{H}_{18} (\text{l})$ | -259.3 |
-
4. There are seven pure metals in a numbered flasks: Fe, Hg, Na, Al, Ca, Au and Sn. Metals in the flasks 1 and 3 do not produce hydrogen if treated with diluted

HCl solution. It is dangerous to let metal **1** contact with metal **3** because an alloy is easily formed. Metals **4** and **6** react vigorously with water. Metals **2** (with heating), **4**, **5** and **6** react with alkali aqueous solution. Metal **7** has a smaller density and a higher melting point than metal **3**. Metal **2** has a smaller density than metal **7** and it has a lower melting point than metal **3**. Metals **2**, **4** and **5** are liquids at 1000 °C; there are equal number of solids and gases at this temperature.

- a) Identify the metals in each flask. Arrange the metals in the order of increasing i) density and ii) melting point. (5,5)
- b) Write the equations of the reactions of the metals with i) diluted hydrochloric acid and ii) alkali aqueous solution. Write the names of the formed complexes. (6)
- c) Give the general name of metal **1** alloys with other metals. (0,5) **12 p**

5. A number of people have to eat a food with a low sodium content because of high blood pressure. LoSalt company sells the salt that contains approximately 66,6 % KCl and 33,4 % NaCl. A student was interested to determine the composition of the mixture. For this purpose he weighed 1,00 g of the heated salt, transferred it into a 100,0 cm³ flask and added distilled water to the mark. For the titration of 10,00 cm³ of this solution 29,60 cm³ of 0,05000 M AgNO₃ solution was required. Potassium chromate indicator was used.

- a) Write the equations of the reactions of i) chloride ion and AgNO₃ and ii) silver ion and potassium chromate. What happens if the solution is overtitrated? (3)
- b) Calculate the KCl content (in per cent) in the salt. (5,5)
- c) How many per cent is the difference between actual and labeled KCl content? (0,5) **9 p**

6. A powder of light-red pigment **C** can be prepared combining salts **A** and **B** aqueous solutions. Salt **B** is used in the glass and soap manufacture and it can be obtained by heating of soda. Salt **A** is a hygroscopic binary compound (%(**X**) = 54,6) which can be obtained by the reaction of iron triad metal **Y** and gaseous halogen **X**₂. Pigment **C** can be also synthesized by heating of salt **A**, **D** or **E** solution (all salts contain the same metal) and compound **F**. Salt **D** contains one of the anions present in aqua regia. Salt **E** anion originates from acetic acid. Compound **F** was the first organic substance prepared from inorganic materials. In industry **F** is obtained by the reaction of NH₃ and CO₂.

- a) i) Using calculations, determine metal **Y**. ii) Write the formulas for **A-F**, **X**₂, **Y** and name the compounds. (6)
- b) Write the following chemical equations: i) decomposition of soda, ii) **X**₂ + **Y** → **A**, ii) **A** + **B** → **C**, iii) 2NH₃ + CO₂ → **F** + (2)

Violet pigment **K** whose cation contains %(**N**) = 19,20, %(**Z**) = 75,28 and %(**H**) = 5,52 is used in cosmetics. Pigment is obtained by the reaction of acid

M, acid salt **N** (%N) = 12,18%) and brownish-black oxide **O** (%Z) = 63,19 %). Salt **N** contains salt **M** anion. Acid **M** is added in small portions into cold drinks. Metal os is III and phosphorus os reaches maximum in pigment **K**.

c) i) Using calculations, determine metal **Z** and the formula of pigment **K** if anion consists of O and P. ii) Write the formulas and names for **M-O**, **Z**.

(5) **13 p**

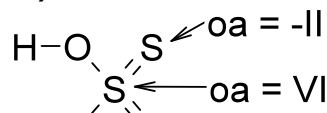
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1. a) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^5 5s^1$

b) i) all bonds (H-O, Cl=O, Cl-O) are polar covalent

ii) polar covalent bond: Cl=O and Cl-O, ionic bond: $\text{Na}^+ \text{ClO}_4^-$

iii) metallic bond



c) $\text{H}-\text{O} \quad \text{O}$ os(H) = I os(O) = -II

d) i) $c = m \cdot 0,06 \cdot \frac{1 \text{ mol}}{36,5 \text{ g}} \cdot \frac{1}{m} \cdot \frac{1,028 \text{ g}}{1 \text{ cm}^3} \cdot \frac{1000 \text{ cm}^3}{1 \text{ dm}^3} = 1,69 \frac{\text{mol}}{\text{dm}^3} = \mathbf{1,69 \text{ M}}$

ii) $c_m = m \cdot 0,06 \cdot \frac{1 \text{ mol}}{36,5 \text{ g}} \cdot \frac{1}{m} \cdot \frac{1}{1 - 0,06} \cdot \frac{1000 \text{ g}}{1 \text{ kg}} = 1,75 \frac{\text{mol}}{\text{kg}} = \mathbf{1,75 \text{ m}}$

m – mass of the solution

e) $R = \frac{pV}{nT} = 760 \text{ Torr} \cdot 22,4 \text{ dm}^3 \cdot \frac{1000 \text{ cm}^3}{1 \text{ dm}^3} \cdot \frac{1}{1 \text{ mol}} \cdot \frac{1}{273 \text{ K}} = 62360 \frac{\text{Torr} \cdot \text{cm}^3}{\text{mol} \cdot \text{K}}$

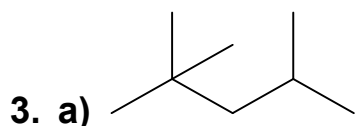
$$N = \frac{pV}{RT} \cdot N_A = 1 \text{ Torr} \cdot 1 \text{ cm}^3 \cdot \frac{1 \text{ mol} \cdot \text{K}}{62360 \text{ Torr cm}^3} \cdot \frac{1}{293 \text{ K}} \cdot 6,02 \cdot 10^{23} \frac{1}{\text{mol}} = 3 \cdot 10^{16}$$

2. a) $Q = 100 \frac{\text{J}}{\text{min}} \cdot \frac{1 \text{ mol}}{6,02 \times 10^{23} \text{ bacteria}} \cdot \frac{1020000 \text{ J}}{1 \text{ min}} \cdot \frac{1}{1 \text{ mol}} = \mathbf{1,68 \cdot 10^{-7} \text{ M}}$ +4

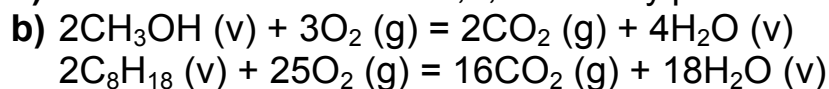
b) $c(\text{H}) = 10^{+9,7} \frac{\text{bacteria}}{\text{dm}^3} \cdot \frac{1 \text{ mol}}{6,02 \times 10^{23} \text{ bacteria}} \cdot \frac{1}{70 \text{ dm}^3} = \mathbf{1,002 \cdot 10^{-7} \text{ M}}$

$$\Delta \text{pH} = -\log(1,002 \cdot 10^{-7}) - 7 = \mathbf{-10^{-3}}$$

c) $t = \frac{2}{1} \cdot 1 \text{ dm}^3 \cdot \frac{17,5 \text{ mol}}{1 \text{ dm}^3} \cdot \frac{20000 \text{ J}}{1 \text{ mol}} \cdot \frac{1 \text{ s}}{100 \text{ J}} \cdot \frac{1 \text{ min}}{60 \text{ s}} = \mathbf{120 \text{ min}}$



2,2,4-trimethylpentane



$$\Delta H_{\text{combustion}}^\circ (\text{CH}_3\text{OH}) = \frac{1}{2} \times [2 \times (-393,5) + 4 \times (-285,8) - 2 \times (-238,4)]$$

$$= -726,7 \text{ kJ/mol}$$

$$\Delta H_{\text{combustion}}^\circ (\text{C}_8\text{H}_{18}) = \frac{1}{2} \times [16 \times (-393,5) + 18 \times (-285,8) - 2 \times (-259,3)]$$

$$= -5460,9 \text{ kJ/mol}$$

$$\Delta H_{\text{combustion}} (\text{CH}_3\text{OH}) = \frac{-726,7 \text{ kJ/mol}}{1 \text{ mol } 32,04 \text{ g}} = -22,68 \text{ kJ/g}$$

$$\Delta H_{\text{combustion}} (\text{C}_8\text{H}_{18}) = \frac{-5460,9 \text{ kJ/mol}}{1 \text{ mol } 114,2 \text{ g}} = -47,82 \text{ kJ/g}$$

c) On the one hand, the enthalpy of combustion of isooctane per mass is twice the enthalpy of combustion of methanol, hence, isooctane should be used as a fuel because it is more thrifty. On the other hand, methanol is used because

- octane rating of methanol is higher and it does not detonate so easily. Therefore in high performance engines the combustion of methanol goes more smoothly and the efficiency of engine is greater.
- less oxygen is needed to oxidize methanol in comparison with isooctane. Hence, more methanol than isooctane is consumed during one combustion cycle at constant volume and more energy is obtained during one cycle if methanol is used.

4. Reaction with hydrochloric acid: **1** and **3** are Au and Hg. It is confirmed by the

formation of the amalgam. Hg has the lowest melting point. Because metal **2** has a lower melting point than metal **3**, **3 must be Au** and **1 is Hg**. From the given metals Na and Ca react vigorously with water (**4** and **6**). With alkali aqueous solution react Na and Ca (**4** and **6**, reaction with water) and Al and Sn (**2** and **5**) because they are amphoteric metals. Heating is needed for

	$\rho / \text{g/cm}^3$	mp/ °C	bp/ °C
Hg	13,5	-39	357
Na	0,97	98	883
Sn	7,3	232	2602
Al	2,7	660	2519
Ca	1,5	842	1484
Au	19,3	1064	2856
Fe	7,9	1538	2861

Sn - metal 2, and **5 is Al**. Sn, Ca and Al are liquids at 1000 °C (because both Na and Ca are not liquids, but Na has a lower melting point, hence one of them - Na – is gas: the boiling point of Na is 883 °C), therefore **metal 4 is Ca** and **6 is Na**. Hg is gas at 1000 °C too, Au and Fe are solids. **Metal 7** reacts with HCl solution, but does not react with alkali, hence **Fe – metal 7**. Fe has a

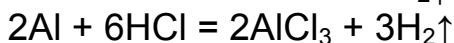
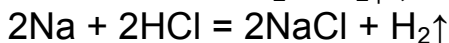
lower density than Au ($7,9 < 19,3 \text{ g/cm}^3$), but it has a higher melting point ($1538 > 1064 \text{ }^\circ\text{C}$). Sn has a lower density than Fe ($7,3 < 7,9 \text{ g/cm}^3$) and a lower melting point than Au ($232 < 1064 \text{ }^\circ\text{C}$).

a) 1 – Hg 2 – Sn 3 – Au 4 – Ca 5 – Al 6 – Na 7 – Fe

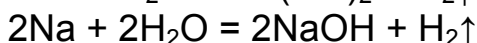
i) $\text{Na} < \text{Ca} < \text{Al} < \text{Sn} < \text{Fe} < \text{Hg} < \text{Au}$

ii) $\text{Hg} < \text{Na} < \text{Sn} < \text{Al} < \text{Ca} < \text{Au} < \text{Fe}$

b) i) $\text{M} + 2\text{HCl} = \text{MCl}_2 + \text{H}_2\uparrow$, kus $\text{M} = \text{Sn}, \text{Ca}, \text{Fe}$



ii) $\text{Sn} + 2\text{NaOH} + 2\text{H}_2\text{O} = \text{Na}_2[\text{Sn}(\text{OH})_4] + \text{H}_2\uparrow$
sodium tetrahydroxystannate(II)



$2\text{Al} + 6\text{NaOH} + 6\text{H}_2\text{O} = 2\text{Na}_3[\text{Al}(\text{OH})_6] + 3\text{H}_2\uparrow$
sodium hexahydroxyaluminate

$2\text{Al} + 2\text{NaOH} + 6\text{H}_2\text{O} = 2\text{Na}[\text{Al}(\text{OH})_4] + 3\text{H}_2\uparrow$
sodium tetrahydroxyaluminate

c) amalgams

5. a) i) $\text{Cl}^- + \text{AgNO}_3 = \text{AgCl}\downarrow + \text{NO}_3^-$

ii) $2\text{Ag}^+ + \text{K}_2\text{CrO}_4 = \text{Ag}_2\text{CrO}_4 + 2\text{K}^+$

After the equivalence point silver ions react with chromate ions and red silver chromate is formed.

$$\text{b) } n(\text{Cl}^-) = \frac{1}{1} \cdot \frac{100 \text{ cm}^3}{10 \text{ cm}^3} \cdot 29,60 \text{ cm}^3 \cdot \frac{1 \text{ dm}^3}{1000 \text{ cm}^3} \cdot \frac{0,05 \text{ mol}}{1 \text{ dm}^3} = 0,0148 \text{ mol}$$

$$\frac{m(\text{KCl})}{74,56} + \frac{1 - m(\text{KCl})}{58,44} = 0,0148 \quad m(\text{KCl}) = 0,625 \text{ g}$$

$$\%(\text{KCl}) = \frac{0,625 \text{ g}}{1 \text{ g}} \cdot 100 = 62,5$$

c) Difference ~~(66,662,5)%~~ **4,1%**

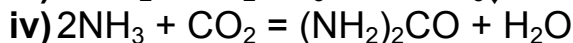
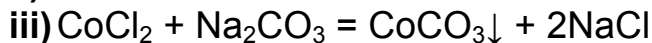
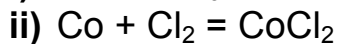
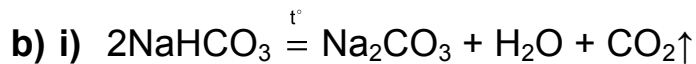
6. a) i) The general formula of salt **A** is YX_n . $M_r(\text{Y}) = \frac{n \cdot M_r(\text{X})}{0,546} \cdot (1 - 0,546)$

Because halogen is gaseous, the salt is fluoride or chloride. Calculations shows that no one of the iron triad fluorides is correct with respect to the statements of the problem. CoCl_2 is correct.

$$M_r(\text{Y}) = \frac{2 \cdot 35,5}{0,546} \cdot (1 - 0,546) = 59$$

Y – Co

- ii) **A** – CoCl_2 , cobalt(II) chloride
B – Na_2CO_3 , sodium carbonate
C – CoCO_3 , cobalt(II) carbonate
D – $\text{Co}(\text{NO}_3)_2$, cobalt(II) nitrate
E – $\text{Co}(\text{CH}_3\text{COO})_2$, cobalt(II) acetate
F – $(\text{NH}_2)_2\text{CO}$, carbamide or urea
X₂ – Cl_2 , chlorine
Y – Co, cobalt



c) i) The general formula of oxide **O** is Z_2O_n

$$\%(\text{Z}) = \frac{2 \cdot M_r(\text{Z})}{2 \cdot M_r(\text{Z}) + n \cdot 16} = 0,6319 \quad M_r(\text{Z}) = 13,73n$$

The correct answer is $n = 4$. Mn_2O_4 or MnO_2 **Z** – Mn

The composition of cation **K**:

$$N(\text{Mn}) = \frac{75,28}{54,94} = 1,37$$

$$N(\text{N}) = \frac{19,2}{14} = 1,37 \quad N(\text{H}) = \frac{5,52}{1,01} = 5,47$$

$$N(\text{Mn}) : N(\text{N}) : N(\text{H}) = 1 : 1 : 4$$

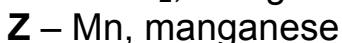
Cationic part of the pigment is $[\text{Mn}^{\text{III}}(\text{NH}_4^{\text{-III}})]^{4+}$

Taking into account that **K** anion contains also phosphorus and oxygen we have to choose the subscripts according to the oxidation states.



ii) **M** – H_3PO_4 , phosphoric acid

N – $\text{NH}_4\text{H}_2\text{PO}_4$, monoammonium phosphate $\%(\text{N}) = \frac{14}{115} = 12,18$



National Practical Examinations

9th and 10th Grade – Determination of nitrite content by permanganometric titration

Introduction

Potassium permanganate (KMnO_4) is a strong oxidizing agent in acidic media, which is used for different redox titrations. The major advantage of utilizing KMnO_4 as the titrant is that no indicator is needed due to its deep purple color. KMnO_4 is not a primary standard, therefore, the concentration of KMnO_4 is determined by titration with primary standard solution (for example, oxalic acid – $\text{H}_2\text{C}_2\text{O}_4$)

Determination of nitrite ions by permanganometric back titration

Theory

Nitrite ions (NO_2^-) are oxidized by KMnO_4 to nitrate ions (NO_3^-). NO_2^- determination by direct titration with KMnO_4 is not accurate. For this reason the analysis is realized using the following procedure. Firstly, NO_2^- ions present in the solution are oxidized by an excess volume of KMnO_4 . Then oxalic acid solution is added in excess. Excess volume of oxalic acid is determined by titration with KMnO_4 solution.

Procedure

For the analysis of the sample pipette $25,00 \text{ cm}^3$ potassium permanganate solution into a 300 cm^3 Erlenmeyer flask and add approximately 15 cm^3 1:4 diluted sulphuric acid (use centrifugal glass for measurement $10 + 5 \text{ cm}^3$).

Pipette $10,00 \text{ cm}^3$ of the sample solution to the mixture. Cover the flask and leave it to stand for 10-15 minutes for total nitrite ions oxidation.

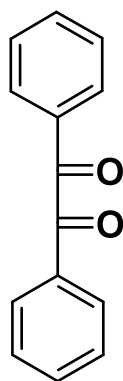
Add $25,00 \text{ cm}^3$ 0,02500 M oxalic acid solution to the flask. Shake the solution (avoid outflowing of the solution from the flask) and titrate an excess of oxalic acid with potassium permanganate solution until the solution is pink in color. The reaction is slow and pink color must be stable for some minutes in endpoint. Titrate until three constant results are obtained.

For determination of the precise concentration of KMnO_4 solution pipette $10,00 \text{ cm}^3$ oxalic acid solution (precise concentration is written on the vessel) into a 100 cm^3 beaker, add $7-10 \text{ cm}^3$ 1:4 diluted sulphuric acid and heat the solution. Do not allow the solution to boil because it can cause partial decomposition of oxalic acid. Titrate the heated solution with potassium permanganate solution until the solution is slightly pink in color. The solution must be hot during the titration because it helps to form a catalyst (MnSO_4). Despite heating the reaction can proceed slowly at first, but it is accelerated when some amount of oxalic acid is reacted.

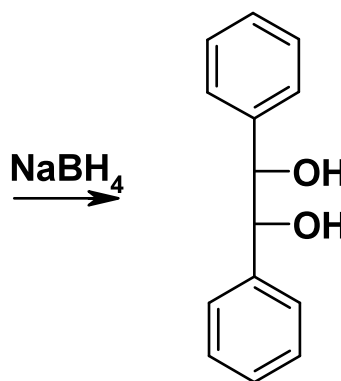
Titrate until three constant results are obtained.

11th and 12th Grade – Synthesis of Hydrobenzoin

Sodium borohydride was discovered in the 1943 by H. I. Schlesinger and H. C. Brown. Now it is one of cheapest and most employed reducing agents in organic synthesis. In this problem you will examine easy and convenient method of reduction by sodium borohydride.



Benzil



Hydrobenzoin

Procedure

Dissolve **0,5 g** of benzil in **5 cm³** 95% ethanol in a 50 ml Erlenmeyer flask. Then add **0,2 g** of sodium borohydride (in excess) at stirring.

The reaction mixture warms up moderately and yellow color disappears after 2-3 minutes. Attach a condenser and leave the mixture to stir for 10 minutes. Then add **5 cm³** of distilled water and heat the mixture until boiling is achieved. Add distilled water (ca 10 cm³) to the mixture until saturation is achieved (turbidity appears) and cool the flask with a cold water bath.

Sparkling thin crystals of hydrobenzoin are formed. Collect the product via vacuum filtration, wash the precipitate with small aliquots of cold water and dry the product in air. If hydrobenzoin is precipitated when solid NaCl added to the filtrate (until saturation is achieved), filter the product and weigh it separately.

TLC experiments

Determine the purity of the product by thin-layer chromatography on a silica gel plate, using **hexane and ethyl acetate mixture (3:1) as the eluting solvent**. Apply the spots of the product and starting material solutions separately on the plate. Calculate R_f values of the product, starting material and some impurity (if it is visible on the plate).



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