Tartu University

48th CHEMISTRY OLYMPIAD Final National Competition

2001

ESTONIA

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Problems

Form IX.

- **1.** A young chemist decided to measure the volume of a drop of water. He found out, that 110 drops were formed when $3,00 \text{ cm}^3$ of water were drained off from a buret. According to the chemistry handbook the approximate length of one molecule of water is 1,50 Å (angström) and $1 \text{ Å} = 10^{-10} \text{ m}$. Density of water is $1,00 \text{ g/cm}^3$; the Avogadro's constant is equal to $6.02 \cdot 10^{23} \text{ molecules/mole}$.
- a) For one drop of water calculate: i) volume, ii) weight, iii) number of moles, iv) number of water molecules contained in it.
- b) Use the data describing one drop of water [from item a)] to calculate molarity of water.
- **c)** Calculate the length of the chain formed by molecules of water contained in one drop. (For comparison: distance from Earth up to the Sun is equal to 150 millions kilometers.)
- **2.** The black gunpowder is a mixture made of the Indian saltpeter (KNO $_3$ 75%), sulfur (10%) and carbon (15%). Explosion of the gunpowder (alone) produces the following products: potassium sulfide (K_2S), carbon dioxide and nitrogen. Pure carbon can be obtained by the heat treatment of natural gas (CH $_4$). Wood charcoal contains 20 % of impurities except carbon (ash and moisture).
- **a)** 45 g of gunpowder were prepared using the wood charcoal (20% of impurities). Calculate **i)** weight of carbon and **ii)** percentage of carbon contained in a black powder.
- **b)** Write the equation for the reaction of the explosion of the gunpowder.
- c) For 100 grammes of gunpowder prepared of carbon black calculate whether i) all the carbon and ii) all the sulfur turned into corresponding reaction products at explosion (ie it was sufficient amount of the oxygen and potassium).

- 3. The compounds of the chemical element **Q** are widely distributed in nature, however it seldom occurs as an element. Element **Q** does not have any allotropic modifications. In the reaction with oxygen it gives products **A** and **B** with different quantitative composition. Compound **A** is neutral without any noticeable oxidative or reductive properties. In the reactions of compound **A** with binary compounds both bases and acids can be obtained. The occurring reactions are not redox reactions. Compound **B** possesses both oxidative and reductive properties. In the reaction with a strong oxidizer (for example KMnO₄ in acidic medium) compound **B** behaves as a reducer, being oxidized to element **Y**. At heating in presence of MnO₂ compound **B** disproportionates (ie the element is an oxidizing agent and the reducer at the same time) to give element **Y** and compound **A**. Reduction of compound **A** using active metals produces element **Q** as an elemental substance **X** and compound **D**, which can react with acids and acidic oxides with the formation of substance **A**. The compound **B** can oxidize a potassium iodide producing simple diatomic elemeny **Z** and hydroxide **C**.
- a) i) Identify an element Q and ii) write formulae and names for the each substances A, B,C, D, X, Y and Z.
- b) Write the equations for the following reactions of: i) formation of A, ii) A \rightarrow base, iii) A \rightarrow acid, iv) D + acid \rightarrow , v) D + acidic oxide \rightarrow .
- c) Write the equations for the following redox reactions and specify oxidation numbers of the elements: i) B $\xrightarrow{MnO_2}$ Y + A, ii) A \rightarrow X, iii) B \rightarrow Z + C.
- **4.** The name chlorophyll has no relation to a chemical element chlorine, it is derived from greek words *chloros* (greenish) ja *phyllon* (leaf). For the complete combustion of one mole of chlorophyll (892 g/mol) additional 71 moles of oxygen are required. Burning produces 2420 g of gas **A** (which makes the lemonade hiss); 648 g of substance **B** (which is the major component of lemonade); 44,8 dm³ of gas **C** (which is the major component of atmosphere) and 40,3 g of diatomic oxide **D**.
- a) Write formulas and names for each substance (A, B, C and D).
- **b)** Determine the quantity of every chemical element contained in one mole of chlorophyll.
- c) Use the calculated quantities, given molar mass and the value of the spent amount of oxygen, to find the brutto formula of chlorophyll's molecule.

Note: Atomic masses should be taken with accuracy of 0,1.

- **5.** A chemical element **X** is obtained from its oxide. This oxide has polymorphic modifications **A** and **B** (possessing identical qualitative and quantitative composition, but different crystal structure). The properties of the modifications **A** and **B** are very different. Modification **B** can be obtained by the reaction of chemical elements at high temperature; it is resistant and passive in relation to acids and bases. Compound **C**, which is a chloride of the element **X**, is used to obtain a substance **D** by precipitation; at cautious heating of **D** the polymorphic modification **A** is formed. Both the compound **D** and modification **A** can react with bases and acids. Substance **E** contains 12,9 % of an element **X** and its molecule also contains three atoms of a chemical element contained in a molecule of sodium chloride and 6 atoms of the most active nonmetal.
- a) Caclulate the molar mass of an element X using data that describes compound E and identify an element X.
- b) What method can be used to obtain the element X?
- c) i) Name the polymorphic modification **B. ii)** What application it has?
- d) Write the equations for the reactions of: i) formation of B, ii) formation of the compound C by the replacement reaction, iii) $C \to D$, iv) $D \to A$.
- e) Write the formulas of the substances A, C, D and E. Give the names for the substances A,C and D.
- **6.** The solubility (L) of the compound is determined as a maximum weight of solid or liquid substance, that can be dissolved in 100 g (precisely) of solvent at given temperature. $L(KNO_3, 10 \, ^{\circ}C) = 20.9$.
- 50.0 g KNO $_3$ were added to 200.0 g of 15.0% solution of KNO $_3$. The temperature of a solution was changed to 10 $^{\circ}$ C.
- a) Calculate the percentage of KNO₃ in the solution, obtained after stirring.
- **b)** Determine the mass of the obtained solution.

Form X

1. To a 380 g of 18,5% solution of K_2SO_4 (174 g/mole) an equivalent amount (necessary for reaction) of solid $Ba(NO_3)_2$ was added. Suspension was mixed, heated up and after that

filtered at 60 $^{\circ}$ C. A filtrate was cooled down to 10 $^{\circ}$ C and left to crystallize at this temperature. The solubility of KNO₃ (101 g/mole) in 100 g of water at 10 $^{\circ}$ C is equal to 20,9 g and its solubility at 100 $^{\circ}$ C – 246 g. Assume, that all processes proceeded quantitatively.

- a) i) Write the equation of the reaction. ii) Why was the filtration carried out at 60 °C?
- b) i) What substance and ii) how many grammes of it was obtained after filtration?
- c) How many grammes of the substance were in a solution i) before crystallization and ii) after crystallyzation.
- d) i) How many grammes of substance crystallized out and ii) what was the mass of the solution before crystallization
- 2. Three identical test tubes contain the same volume (á 1,00 sm³) of different liquids: A (1,00 g/cm³; 0,0556 mole), B (0,0240 mole) and C (0,0672 mole). Liquids A and B are colourless, liquid C is silvery. Liquids A and C do not react together and liquid A remains on a surface of liquid C. Liquids B and C do not mix and do not react together too, liquid B remains on a surface of liquid C. Liquids A and B violently react to give a 80,5% solution of a substance D. At simultaneous mixing of all three liquids a violent reaction takes place and at the end of the reaction the volume of liquid A is equal to its initial volume, the volume of liquid C makes 64,3% of its initial volume. The molar amounts of salt E and gas F formed during the reaction are equal and their sum is equal to initial molar amount of liquid B. Salt E is insoluble. Liquid B and gas F have an identical qualitative composition, however the degree of oxidation of one element of gas F is lesser for two units. For the calculations assume, that all the reactions proceed quantitatively and without any losses.
- a) Write formulas and names of the substances A, B, C, D, E and F.
- b) i) Write the equation for the reaction $A + B \rightarrow ii$) Calculate the percentage of the substance D in the formed solution.
- c) i) Determine the amount of the reacted substance C. ii) Write the equations for the reactions in which substance C participated.
- **d)** Use calculations to show, that the amount of substance **A** during reaction remains unchanged.
- e) Substantiate: i) why at mixing substances A, B and C together a reaction takes place.ii) why, although two products are possible, the salt E is formed.

- **3.** A new yellow pale mineral was discovered in 1960 in Poland. This mineral consists only of ions. One of these ions in a mineral exists in the same form as in a water solution. It is a binary tetratomic +1-charged cation. Each element of this mineral possess only one oxidation number, that is characteristic for a given element. The elemental analysis of a mineral gave the following data: 34,85 % Fe, 13,34 % S, 1,89 % H and 49,92 % O.
- a) Find the empirical formula of a mineral.
- **b)** What is the oxidation number of an iron?
- c) Write the ionic formula of a mineral that is in consensus with shown data.
- d) What is the name for that binary tetratomic +1-charged cation?
- **4.** Chemical element **X** acts as a very strong oxidizing agent. Most of the reactions, in which participates, proceed with explosion or with the formation of a flame. At contact with many metals and nonmetals the reaction takes place already at ambient temperature. Even steam and glass wool (combustible component is SiO_2) burn in an atmosphere of this element and in both cases the simple substance **Y** is formed. Burning of a glass wool produces also a complex compound **A**, at a burning of a water vapours complex compound **B** is formed. These complex compounds **A** and **B** can be obtained also at the addition reactions of the corresponding simple substances. $3A + 4H_2O \rightarrow$ orthosilicic acid + 2C. The substance **C** is a diprotic acid and it can be decomposed to give complex compounds **A** and **B**. Apatite $[Ca_5 (PO_4)_3X]$ contains 3,77 % of an element **X**.
- a) Determine an element X using calculations.
- **b)** Write the equations of the reactions: **i)** $X + H_2O$, **ii)** $X + SiO_2$,
 - iii) X + simple substance \rightarrow A, iv) X + simple substance \rightarrow B, v) 3A \rightarrow C, vi) C \rightarrow A + B.
- c) Write the formulas and names for elements X and Y and for substances A, B and C.
- **5.** Total volume of the three colourless gases at standard conditions is equal to 1000 cm³. After the ignition with a spark a mix of two colourless gaseous products is formed, its volume at the same conditions decreased by 100 cm³ in compare with a total volume of an initial mixture. Depending on a ratio of the volumes of gases in the initial mixture the average molar mass of a final mixture is equal to 40,4 g/mol or 41,4 g/mol. The barbotation of the gaseous products of the reaction through an excess of water solution of NaOH yields to the increase of a mass of the solution by 1,375 grammes (one product is formed).

- **a)** Substantiate, why only three gases are in agreement with the provided data. Identify these gases.
- **b)** For a gaseous mixture write the equations of the reactions of **i)** burning and **ii)** absorption.
- c) Calculate the volume of each gas: i) in the initial mixture and ii) in the final mixture.
- **d)** Determine the molar masses of each final mixture of gases and specify to what initial mixture it will match.
- **6.** At a reaction of solid **A** with a hydrochloric acid the gas **B** is released. Gas **B** possesses off-flavour and burns in air producing gas **C** with a characteristic sharp smell. The gases **B** and **C** quite well dissolve in water and draining of the obtained water solutions together leads to the precipitation of substance **D**. Reaction between gases **B** and **C** is exothermic, so upon the end of the reaction the formed products are in a liquid and gaseous phase. At cooling (depending on the conditions) the solid compounds **E** or **F** can be formed. At heating the substances **D**, **E** and **F** react with hydrogen, oxygen, carbon and with all metals (except for gold and platinum). The substances **D**, **E** and **F** react with a powder of metal **G** to form substance **A**. The oxidation number of the metal **G** can be equal to II or III. 2,00 g of a powder of metal **G** react with the diluted hydrochloric acid in an inert atmosphere to produce 803 cm³ of hydrogen.
- a) Identify substances D, E and F and give their names and formulas.
- b) i) Write the equation of a reaction $G + HCI \rightarrow$, ii) Calculate molar mass of metal G. iii) Identify substance A.
- c) Write the equations for the reactions and give the names for all the substances: i) $A \to B$, ii) $B \to C$, iii) $B + C \xrightarrow{\text{in water solution}}$, iv) $B + C \xrightarrow{\text{in a gaseous phase}}$, v) $D + H_2 \to$, vi) $D + O_2 \to$, vii) $D + \text{carbon} \to$.

Form XI

1. A plate of the metal **X** was brought for analysis to a laboratory. A lab assistant has cut two pieces of the same weight from a plate and placed one of them into a solution of a lead salt, the second one – into the solution of copper salt. After the certain time the weight of the first piece has increased by 19,0% and the weight of the second piece has decreased by 9,8%.

Assume, that the rates of the reactions are identical and also the oxidation numbers of all metals in compounds are equal to II. The metal **X** can reduce the hydrogen ions from the diluted sulfuric acid and its sulfate is well soluble in water.

- a) Write the ionic equations: i) X + lead salt, ii) X + copper salt (leave X unidentified).
- **b)** Use the values of the changes of weight of the plates to make appropriate equations and identify metal **X**.
- c) Find the molar mass of metal **X**, if the electrolysis is done during 1 hour at current 1,000 A led to the increase of weight of the cathode by 2,097 g. F=96485 A·s/mol.
- **d)** Write the equations of the reactions described in item **c)** and write what electrodes are necessary for this experiment (you can choose among graphite and metal electrodes, it is also possible to use sulfuric acid)
- **2.** Full (quantitative) oxidation of the optically active compound **A**, containing phenyl group, with a potassium permanganate in acidic medium produced a compound **B**, which molar mass is equal to the molar mass of the compound **A**. The interaction between compounds **A** and **B** leads to formation of the liquid **C** with the brutto formula $C_{15}H_{14}O_2$. Under treatment with NaOH the liquid **C** can be hydrolyzed producing compounds **A** and **D**.
- a) i) To what class of organic compounds does the compound C belong? ii) Use brutto formulas to write the equation of the reaction of hydrolysis with sodium hydroxide.
- **b)** Write and substantiate the structural formulas of the compounds **A** and **B**.
- c) Using structural formulas write i) the scheme of the reaction $A \to B$ and ii) equation for the reaction $A + B \to C$.
- **d)** Determine the oxidation numbers of carbon atoms, that do not participate in the formation of cycles in compounds **A** and **B**; write the equation of the redox reaction **A** + KMnO₄ \rightarrow .
- **3.** Complete combustion of 949 mg of organic substance produced 1,15 dm 3 of a carbon dioxide and water, which volume is 1000 times smaller (4 $^{\circ}$ C).
- **a)** Find the empirical formula of this substance.
- **b)** Draw the structural formulas for the possible isomers, that correspond to the obtained empirical formula, and give their regular names.
- **c)** Draw *R* and *S* configurations for the one of the possible stereoisomers.

- **4.** At the electrolysis of water solution of compound **A** (sodium ethanate) the substances **B**, **C**, **D** and **E** are formed. At reaction of substance **D** with water solution of substance **C** both normal salt **F** and acid salt **G** can be formed. At dehydrogenation of compound **B** the substance **H** is formed. At reaction of substance **H** with bromine the compound **I** is formed. Heating of the compound **I** in a KOH/HOCH₂CH₂OH medium produces compound **J**, which can be utilized as an initial substance for the obtaining of benzene. At the irradiation of benzene with UV three valent isomers of benzene (**K**, **L** and **M**) are obtained (number of C-C bonds changes, while the number of C-H bonds remains constant). The structure of the molecule **K** has two cycles, **L** three and **M** five cycles.
- a) For substances B, C, D, E, F, G, H, I and J write their formulas and names.
- b) Write the equations of the reactions i) $B \to H$, ii) $H \to I$, iii) $I \to J$, iv) $D \to F$, v) $D \to G$.
- c) Write the structural formulas for the possible isomers of benzene (K, L and M)
- **5.** The pH value of a human's blood is in an interval of 7,35-7,45. The constancy of such narrow interval of pH vaues is provided by the interactions of different buffer systems. The most important buffer system is a carbonate buffer, which is prepared by a salt (HCO_3^-) and acid (H_2CO_3) in molar ratio 20:1 (precisely). The exhaled CO_2 is released out from a metacarbonic acid, which participates in equilibrium in a blood.
- a) For the I and II dissociation stages of metacarbonic acid write i) the equation of the dissociation and ii) the expressions for the ionization constants K_1 ja K_2 .
- **b)** For buffer system HCO_3^- - H_2CO_3 calculate **i)** pH value and **ii)** [H⁺], if pK₁ = 6,10 (assume that II stage of ionization does not contribute to the equilibrium).
- **c)** With the help of the formula for the calculation of pH prove, whether the respiration must be accelerated or retarded in order to achieve the initial value of pH, if the pH of a blood has decreased.
- **6.** The metals **X** and **Y** can possess two identical oxidation numbers in compounds. The compound of metal **X**, in which it has lower oxidation number, is strong reducer. The compound of metal **Y** with higher oxidation number is a strong oxidizing agent. The element **X** reacts with sulfur to give yellow compound **A.** The reaction of the ions of an element **Y** with iodide iones in water solution produces yellow precipitate **B.** These substances are stable. At a reaction of metal **X** with the very diluted nitric acid the main products are NO and the ion of metal **X**, which is a well known reducing agent in organic chemistry. Metal **Y** and its oxide with

higher oxidation number is used in construction of a source of electricity, that reversibly works in an acidic medium. The compound of metal **Y** with lower oxidation number is formed at discharge of this electrical supply. Metal **X** is generally used for protection of iron against staining. The treatment of metal **X** with the chlorine yields to formation of a volatile compound **C**. This method can be used for the regeneration of metal **X**. At a very low temperature the metal **X** can turn into a powder, that is an allotropic modification of this element. The metal **X** forms meta acid **D**. The metal **Y** forms oxide **E**, which can be viewed as a salt of an ortho acid of metal **Y**. Molecule of this salt contains only seven atoms. The metal **Y** in oxide **E** has both oxidation numbers.

- a) Identify metals X and Y and write their names.
- b) Write the equations for the reactions: i) $X + S \rightarrow A$, ii) salt of $Y + KI \rightarrow B$, iii) $X + HNO_3$ (diluted) \rightarrow salt of X.
- a) Write the scheme of an electric supply made on the basis of an element Y (electrodes, electrolyte, poles).
- **b)** For the discharge of the source of electricity described in item **c)** write **i)** equation of the cathodic reaction, **ii)** equation of the anodic reaction, **iii)** equation of the total reaction.
- c) Write i) formula of the compound **D** and ii) formula of the compound **E** and specify the oxidation numbers of metals **X** and **Y**.

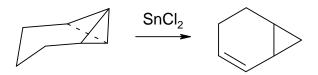
Form XII

- 1. During the World War II Denmark was occupied. The fascists wanted to confiscate the Nobel medal of Niels Bohr, the winner of the Nobel Prize. This medal was made of an alloy of gold (23 carats) and silver (1 carat). According to a history, Niels Bohr put his medal into a flask with *aqua regia*. Germans looked for a medal everywhere but all these efforts were unsuccesful, whereas a flask with the medal stood on the bookshelf and everybody saw it. After the War Niels Bohr regenerated the precious metal with the help of electrolysis and pleased the Swedish monetary court yard to use the obtained metal to make a new medal.
- a) Describe, what was happened to a medal in *aqua regia* and write the equation of the appropriate reaction.

- **b)** What active reagent is formed in *aqua regia* that played the main role in dissolving of precious metal?
- c) Write the equations for the reactions, that occured at the regeneration of the metali) on the cathode and ii) on the anode.
- **d)** Calculate the initial weight of the Nobel medal, if the efficiency of the electrolysis, which was done during 4 hours at a current 20 A, was 90 % (by current). All given numbers must be considered as exact. The answer should be given within 5 significant digits.

Note: In a case of alloys of precious metals 1 carat means 1/24 from weight of an alloy.

- **2.** Triene A (brutto formula $C_{10}H_{12}$) reacts with ozone to give ozonide **B**, that consists of 5 cycles. At hydrolysis of one molecule of ozonide **B** in reducing medium the only products of a reaction are two symmetric molecules **C**, each of which contains 3 carbonyl groups. Oxidation of a substance **C** with hot concentrated nitric acid produces the first member of homologous series of dicarboxylic acids, **D**, and the second member, **E**, (symmetric). The dicarboxylic acid **D** is crystallized with two molecules of crystal water to give the substance **F**. The substance **F** is decomposed at heating to give oxides. An exact sample of substance **F** is used for standartization of a KMnO₄ solution.
- a) Write the planar structural formulas of i) substance A and ii) substance B.
- b) Write equations for reactions (use plane structural formulas): i) ${\bf B} \to {\bf C}$ and ii) ${\bf C} \to {\bf D} + {\bf E}$
- c) Write equations of the reactions: i) $\mathbf{F} \xrightarrow{\circ_{\mathsf{t}}}$ and ii) $\mathbf{D} + \mathsf{KMnO}_4 + \mathsf{H}_2\mathsf{SO}_4 \rightarrow$.
- **d)** Calculate the amount of substance **F**, if it is known that after its thermal decomposition the volume of the formed gases at 100 °C is equal to 1,53 dm³.
- **e)** Calculate the molar concentration of a solution of KMnO₄, if it is known that the amount of the compound **F**, calculated in item **d)** was dissolved to prepare 100 cm³ of a solution and 13,2 cm³ of KMnO₄ were spent for titration of 10 cm³ of the obtained solution.
- **3.** At isomerization reactions the qualitative and quantitative composition of a molecule remains unchanged. The compounds of the transition metals are usually used as catalysts in these reactions. The initial compound for the following reactions of isomerization is the compound **A** tricyclo $[4,1,0,0^{2,7}]$ heptane. The following isomerization proceeds with a help of the catalyst SnCl₂:



The isomer **B** is formed from a compound **A** with the help of the catalyst $AgBF_4$ and the isomer **C** is formed from a compound **A** with the help of the catalyst $[Rh(CO)_2CI]_2$. Molecules of isomers **B** and **C** contain only one cycle. At hydrogenation of substance **B** with the Pt-catalyst the saturated hydrocarbon **D** is formed. The compound **D** can also be obtained at hydrogenation of toluene under elevated pressure. In molecules of the compounds **B** and **D** the location of the carbon atoms in a skeleton is the same. At oxidation of the compound **B** (under the treatment with $KMnO_4/H^+$) the CO_2 is released and then substance **E** is formed, which is a ketodicarboxylic acid. At further heating in the same medium one molecule of CO_2 is released from compound **E** and the intermediate compound **F** is formed, which is very quickly oxidized to 1,5-pentadicarboxylic acid (compound **G**).

The compound **C** can be obtained from cycloheptene according to the following scheme:

NBS is N-bromosuccinimide, which is used for so-called allylic bromination. At allylic bromination the bromoderivative is obtained, in which the double bond of an alkene is conserved.

- a) Write the equation of the reaction using structural formulas: toluene \rightarrow compound **D** and give the nomenclature names for the compounds.
- b) To draw structural formulas of 7 possible isomers, which carbon skeleton and composition match the skeleton and composition of the compound B and at hydrogenation of which the compound D is formed.
- c) Write schemes of the reactions using structural formulas: i) $B \to E$, ii) $E \to F$, iii) $F \to G$
- d) Draw the structural formulas of i) the compound H and ii) the compound C.
- **4.** The binary compound **A** contains 20,24 % of metal **X**. The electrolysis of one mole of a melt **A** produces 1 mole of metal **X** and 1,5 moles of element **B**, which density by CO_2 is equal to 1,611. The substance **A** reacts with hydride **C** to give compounds **D** and **E**. At electrolysis of a melt of compound **E** the molar amount of metal **Y** is two times larger then

the molar amount of an element **B**. The compound **D** consists of six atoms and does not contain an element **B**. Molar mass of the compound **D** makes 28,5 % from molar mass of the compound **A**. The compounds **A** and **D** are very often used in organic synthesis. At ambient temperature the compound **D** can react with different amounts of *tret*-butanol, yielding respectively compounds **F**, **G** and **H**. At heating of the compound **H** with *tret*-butanol the compound **I** is formed. At formation of the specified compounds the different amounts of hydrogen are released out. The compounds **F**, **G**, **H** and **I** react with water solution of NaOH to give *tret*-butanol, base **J**, hexahydroxy complex compound and in case of compounds **F**, **G** and **H** the hydrogen is also released. In case of compound **I** no hydrogen is released. At the reaction of the certain amount of the compound **H** with water solution of NaOH 11,2 cm³ of hydrogen is released. The products of the complete combustion of the same amount of the compound **H** react with the solution of Ca(OH)₂ to give 1,20 g of a white precipitate.

- a) Determine the formulas of the i) substance B (use calculations), ii) substance A (use calculations), iii) substance C, iv) substance E and v) substance D (check the molar mass).
- **b)** Write equation of the reaction $A + C \rightarrow D + E$.
- c) Write the abbreviated formulas of the possible products of the reaction between the compound **D** and *tret*-butanol (in abbreviated form $CH_3 = Me$; $C_2H_5 = Et$ etc).
- **d)** Determine the abbreviated formula of the compound **H**.
- **e)** Write equation of the reaction D + tret-butanol \rightarrow compound H + ...
- **f)** Write equation of the reaction: compound **H** + NaOH + $H_2O \rightarrow$.
- g) i) Determine the formula of compound I. ii) Why it is necessary to heat up the reaction mixture in order to obtain compound I?
- **5.** In a year 1828 the student of J.J. Berzelius decided to prepare salt **B** for the subsequent experiments. For this purpose he mixed solutions of ammonium chloride and salt **A** according to the equation of the reaction. After the end of the reaction he separated precipitate and decanted solution was dried to give transparent needle crystals, which weight was equal to that of calculated. As a big surprise the chemist found out, that at heating with the hydrated lime the product **X** does not yield a smell, that is characteristic for substance **B**. The consequent analyses has shown, that weight of a product **X** is 2,50 times less than a weight of salt **A** and the substance **X** contains 4 elements: 46,67% of nitrogen, 20,00% of

carbon and 26,67% of oxygen. Modern chemistry handbooks say that compound $\bf B$ is formed from the compound $\bf X$ at 60 $^{\circ}$ C.

- a) Determine the brutto formula of a product **X** and formulae of the compounds that correspond to this brutto formula.
- **b)** Determine the formula of salt **A** and give its name.
- c) Write the equations of the reactions: i) $A \rightarrow B$, ii) $B \rightarrow X$, iii) B + Ca (OH)₂ \rightarrow .
- d) i) Write a name of the author of the given experiment. ii) What phenomenon did he discover during this experiment? iii) Why this experiment is considered as turning point in chemical synthesis?
- 6. In a laboratory one little girl found a paper flower, which seven paper petals were coated with unknown substances of different colour. The petal A was white, B - violet, C - green, **D** - yellow-green, **E** - light-blue, **F** - orange-red and **G** - yellow. The weights of the substances A, B and C were equal to 1,00 g. Under the action of the sunlight the substance A has turned into reddish substance H, which mass was 0,333 g. The treatment of the substance B with a hydrochloric acid produced a light pink solution and also 354 cm³ of gas I was released. At heating of the substance **C** 0,72 g of black substance **J** were obtained. The light-blue solution of substance **K** was formed at the reaction of substance **J** with hydrochloric acid. The substances **D** and **E** are binary compounds of the same metal **L**. At the reaction with water both substances **D** and **E** form hydroxide **M** (58 g/mol), also tetratomic gas **N** and pentatomic gas **O** are released respectively. The gases **N** and **O** can burn in air, forming water and element P or water-insoluble acid oxide R respectively. The substance F can be viewed as an oxide and as ortho salt too. The percentage of oxygen in compound F is equal to 9,34%. The substance **G** can only be dissolved in agua regia, producing an acid **Q**. The reaction of 1,00 g of substance **G** with CsCl gives 2,40 g of the complex compound **S**, the number of atoms of which is the same as in the acid **H**.
- a) i) Identify substance H.
 - ii) Calculate the molar mass of an anion of substance A and identify substance A.
- **b) i)** Write the equation of the reaction of substance **B** with hydrochloric acid;
 - ii) Find the volume of the released gas and determine the substance **B**.
- c) i) Identify substance J; ii) Calculate the molar mass of the substance C and identify this substance C; iii) Write equations of the reactions $C \to J$ and iv) $J \to K$.
- d) i) Identify substances L and M; ii) write the equations of the reactions D + $H_2O \rightarrow$ and

 $\textbf{N}+O_2 \rightarrow$ and identify substances $\textbf{D},\,\textbf{N}$ and $\textbf{P};\,\textbf{iii})$ write equations of the reactions

 $\mathbf{E} + H_2 O \rightarrow$ and $\mathbf{O} + O_2 \rightarrow$ and identify substances \mathbf{E} , \mathbf{O} and \mathbf{R} .

- e) i) Identify substance F. Write the formulas of its oxide and salt,
 - ii) Calculate the percentage of oxygen in substance F.
- f) i) Identify substance G; ii) write equation of the reaction $Q \to S$ and identify substances Q and S; iii) calculate weight of the substance S.

Note: To identify substance means to write its formula and give its name.

48th CHEMISTRY OLYMPIAD Final National Competition

2001

ESTONIA

Solutions

Form IX

1. a) i) V(drop of water) =
$$\frac{3,00 \text{ cm}^3}{110 \text{ drops}} = 0,0273 \text{ cm}^3/\text{drop} = 2,73 \cdot 10^{-2} \text{ cm}^3/\text{drop}$$

ii) m(H₂O) =
$$\frac{2.73 \cdot 10^{-2} \text{ cm}^3}{drop} \cdot \frac{1.00 \text{ g}}{1 \text{ cm}^3} = 2.73 \cdot 10^{-2} \text{ g/drop}$$

iii)
$$n(H_2O) = \frac{2,73 \cdot 10^{-2} \text{ cm}^3}{drop} \cdot \frac{1 \text{ mole}}{18,0 \text{ g}} = 1,52 \cdot 10^{-3} \text{ mol/drop}$$

iv) N(H₂O)=
$$\frac{1,52 \cdot 10^{-3} \text{ mol}}{\text{drop}} \cdot \frac{6,02 \cdot 10^{23} \text{ molecules}}{mole} = 9,15 \cdot 10^{20} \text{ molecules/drop}$$

b) Molar concentration is defined as number of moles per one dm³: $c = \frac{mol}{dm^3}$. Abbreviation for $\frac{mol}{dm^3}$ is M.

$$\mathbf{c(H_2O)} = \frac{1,52 \cdot 10^{-3} \text{ mole}}{drop} \cdot \frac{1 \text{ drop}}{2,73 \cdot 10^{-2} \text{ cm}^3} \cdot \frac{10^3 \text{ cm}^3}{dm^3} = 55,7 \text{ mol/dm}^3 = 55,7 \text{ M}$$

c)
$$I(H_2O) = \frac{9,15 \cdot 10^{20} \text{ molecules}}{drop} \cdot \frac{1,50 \text{ Å}}{molecules} \cdot \frac{1 \text{ m}}{10^{10} \text{ Å}} \cdot \frac{1 \text{ km}}{10^3 \text{ m}} = 1,37 \cdot 10^8 \text{ km} = 137 \text{ mil.km}$$

2. a) i) m(C) =
$$45 \text{ g} \cdot 0.15 \cdot 0.80 = 5.4 \text{ g}$$

ii) %(C) =
$$\frac{5.4}{45} \cdot 100 = 12$$

b)
$$2KNO_3 + 3C + S = K_2S + 3CO_2 + N_2$$

c) i)
$$C + O_2 = CO_2$$

15 g m
 $C \Leftrightarrow O_2$
12 g/mol 32 g/mol

$$m(O_2, necessary) = \frac{1}{1} \cdot 15 \text{ g} \cdot \frac{1 \text{ mol}}{12 \text{ g}} \cdot 32 \text{ g/mol} = 40 \text{ g}$$

$$\begin{array}{ccc} 75 \text{ g} & \text{m} \\ 2\text{KNO}_3 & \Leftrightarrow & 3\text{O}_2 \\ 101 \text{ g/mol} & 32 \text{ g/mol} \end{array}$$

$$m(O_2,obtained) = \frac{3}{2} \cdot 75 \text{ g} \cdot \frac{1 \text{ mol}}{101 \text{ g}} \cdot 32 \text{ g/mol} = 35,6 ≈ 36 \text{ g}$$

The amount of oxygen is insufficient, some amount of carbon will remain unburned.

ii)
$$2K + S = K_2S$$

 $10 g$
 $2K \Leftrightarrow S$
 $39 g/mol \quad 32 g/mol$
 $m(K,necessary) = \frac{2}{1} \cdot 10 g \cdot \frac{1 mol}{32 g} \cdot \frac{39 g}{mol} = 24,3 g \approx 24 g$

75 g m
KNO₃
$$\Leftrightarrow$$
 K
101 g/mol 39 g
m(K,obtained) = $\frac{1}{1}$ · 75 g · $\frac{1 \text{ mol}}{101 \text{ g}}$ · 39 g / mol = 29 g

All the sulfur takes part in the reaction.

3. a) i)
$$Q - H$$
, hydrogen (element)

- ii) $A H_2O$, water
 - $\mathbf{B} H_2O_2$, hydrogen peroxide
 - **C** KOH, potassium hydroxide
 - D NaOH, sodium hydroxide
 - **X** H₂, hydrogen (element)
 - $\mathbf{Y} O_2$, oxygen
 - $\mathbf{Z} \mathbf{I}_2$, iodine

b) i)
$$2H_2 + O_2 = 2H_2O$$

X Y A
ii) $H_2O + CaO = Ca(OH)_2$
A
iii) $H_2O + SO_3 = H_2SO_4$
A
iv) NaOH + HCl = NaCl + H_2O
D A
v) $2NaOH + CO_2 = Na_2CO_3 + H_2O$
D A

-I 0 -II

c) i)
$$2H_2O_2 \xrightarrow{MnO_2} O_2 + H_2O$$

B Y A

I 0 0 I

ii) $2H_2O + 2Na = H_2 + 2NaOH$

A X D

-I -I 0 -II

iii) $H_2O_2 + 2KI = I_2 + 2KOH$

- 4. a) A CO₂, carbon dioxide
 - **B** H₂O, water
 - C N₂, nitrogen
 - D MgO, magnesium oxide

The molecule of the oxide is diatomic, so the atomic mass of the element that forms this oxide is 40.3 - 16 = 24.3. This corresponds to the atomic mass of magnesium.

b)
$$n(C) = n(CO_2) = 2420 \text{ g} \cdot \frac{1 \text{ mol}}{44,0 \text{ g}} = 55 \text{ mol}$$

 $n(H) = 2n(H_2O) = 2.648 \text{ g} \cdot \frac{1 \text{ mol}}{18,0 \text{ g}} = 72 \text{ mol}$
 $n(N) = 2n(N_2) = 2.44,8 \text{ dm}^3 \cdot \frac{1 \text{ mol}}{22,4 \text{ dm}^3} = 4 \text{ mol}$
 $n(Mg) = n(MgO) = 40,3 \text{ g} \cdot \frac{1 \text{ mol}}{40.3 \text{ g}} = 1 \text{ mol}$

- c) M(chlorophyll,calculated) = (55 mol·12,0 g/mol + 72 mol·1,0 g/mol +
 - + 4 mol ·14,0 g/mol + 1 mol·24,3 g/mol) · $\frac{1}{\text{mol}}$ = 812,3 g/mol ≈ 812 g/mol

M(chlorophyll,real)-M(chlorophyll,calculated) = (892 - 812) g/mol = 80 g/mol $n(O,calculated) = (2 \cdot 55 + 0.5 \cdot 72 + 1.1) mol = 147 mol$

n(O,real) = 2 · 71 mol = 142 mol, this means that molecule of chlorophyll contains 5 moles of oxygen.

Bruto formula of the molecule of chlorophyll is C₅₅H₇₂N₄O₅Mg

5. a) Compound E contains 6 fluoride ions and 3 sodium ions. It means that the molecule contains one +3-charged cation or three +1-charged cations.

$$M(X^{3+})=(3 \text{ mol}\cdot 23,0 \text{ g/mol}+6 \text{ mol}\cdot 19,0 \text{ g/mol})\cdot \frac{1}{\text{mol}}\cdot \frac{1}{0.871}\cdot 0,129=27,1 \text{ g/mol}$$

$$M(X^+) = 27.1 \text{ g/mol} \cdot \frac{1}{3} = 9.0 \text{ g/mol}$$

$$X^{3+} - AI^{3+}$$
 fits

X⁺ – Be⁺ doesn't fit (because of valence and also of chemical properties)

- **b)** Elemental Al is obtained at the reduction of the melt Al₂O₃ during electrolysis.
- c) i) corund
 - ii) abrasive material

d) i)
$$4AI + 3O_2 = 2AI_2O_3$$

ii)
$$2AI + 6HCI = 2AICI_3 + 3H_2$$

iv)
$$2AI(OH)_3 \xrightarrow{\circ_t} AI_2O_3 + 3H_2O\uparrow$$
D A

- e) $A Al_2O_3$, aluminium oxide
 - C AlCl₃, aluminium chloride
 - **D** Al(OH)₃, aluminium hydroxide
 - **E** Na₃AIF₆, cryolite, sodium aluminium fluoride
- **6. a)** If the percentage content of the dissolved substance is greater than the percentage of the substance in the saturated solution, then some amount of this substance will precipitate out and the solution remains saturated at given temperature.

%(KNO₃,10°C, saturated solution) =
$$\frac{20,9}{100 + 20,9} \cdot 100 = 17,3$$

%(KNO₃,in the mixture) =
$$\frac{200,0 \cdot 0,150 + 50,0}{200,0 + 50,0} \cdot 100 = 32,0$$

 $%(KNO_3, obtained solution) = 17,3$

b) m(H₂O,initial solution) = 200,0 g· 0,850 = 170 g

m(KNO₃ solution,10°C) =
$$17\underline{0}$$
 g (water) $\cdot \frac{120.9 \text{ g (solution)}}{100 \text{ g (water)}} = 205,53 \text{ g} \approx 206 \text{ g}$

Form X

- **1. a)** i) $K_2SO_4 + Ba(NO_3)_2 = 2KNO_3 + BaSO_4 \downarrow$
 - ii) At 60 °C the solubility of the KNO₃ is higher than the mass of KNO₃ remained in solution, it means that the insoluble precipitate consists of BaSO₄.
 - b) i) BaSO₄

ii) 380 g·0,185 m

$$K_2SO_4 \Leftrightarrow BaSO_4$$

174 g/mol 233 g/mol
 $m(BaSO_4) = \frac{1}{1} \cdot 380 \text{ g} \cdot 0,185 \cdot \frac{1 \text{ mol}}{174 \text{ g}} \cdot 233 \text{ g/mol} = 94,1 \text{ g}$

c) i)
$$380 \text{ g} \cdot 0.185 \text{ m}$$
 $K_2SO_4 \Leftrightarrow 2KNO_3$
 174 g/mol
 101 g/mol

$$m(KNO_3, \text{before}) = \frac{2}{1} \cdot 380 \text{ g} \cdot 0.185 \cdot \frac{1 \text{ mol}}{174 \text{ g}} \cdot 101 \text{ g/mol} = \textbf{81,6 g}$$

ii) m(H₂O) = 380,0 g · 0,815 = 309,7 g
m(KNO₃,after) = 309,7 g ·
$$\frac{20,9}{100}$$
 = **64,7 g**

- **d) i)** m(KNO₃, precipitated) = 81,6 g 64,7 g = **16,9 g**
 - ii) m(lsolution,before) = 309,7 g + 81,6 g = 391,3 g
- 2. a) $A H_2O$, water

B – SO₃, sulfur trioxide

C - Hg, mercury

D – H₂SO₄, sulfuric acid

E – Hg₂SO₄, mercury(I) sulfate

F - SO₂, sulfur dioxide

b) i)
$$H_2O + SO_3 = H_2SO_4$$

A B D

ii) m(H₂SO₄) = 0,0240 mol
$$\cdot$$
 98,1 g/mol = 2,3544 g m(H₂O,final) = (0,0556 - 0,0240) mol \cdot 18,09 g/mol = 0,5716g %(H₂SO₄) = $\frac{2,3544}{2,9260} \cdot 100 = \textbf{80,5}$

c) i) $n(Hg,reacted) = 0.0672 \text{ mol} \cdot 0.357 = 0.02399 \approx 0.0240 \text{ mol}$

$$n(SO_3) = 0.0240 \text{ mol}$$

$$n(H_2SO_4) = 0.0240 \text{ mol}$$

$$n(salt E) = 0.0120 mol$$

$$n(SO_2) = 0.0120 \text{ mol}$$

The obtained salt must be Hg₂SO₄

ii)
$$2H_2SO_4 + 2Hg = Hg_2SO_4 + SO_2^+ + 2H_2O$$

D C E F

d)
$$n(H_2O,final) = [(0,0556 - 0,0240) + \frac{2}{2} \cdot 0,0240] \text{ mol} = \mathbf{0,0556} \text{ mol}$$

unreacted in the reaction c) ii)

- **e) i)** At the reaction of sulfur trioxide with water the large quantity of heat is released, it raises the temperature of the reaction mixture and so increases the reaction rate (in geometric progression).
 - ii) In a case of excess of the mercury the compounds of Hg(I) are formed.

3. a) n(Fe) =
$$34.85 \text{ g} \cdot \frac{1 \text{ mol}}{55.85 \text{ g}} = 0.624 \text{ mol}$$

$$n(S) = 13,34 \text{ g} \cdot \frac{1 \text{ mol}}{32,08 \text{ g}} = 0,417 \text{ mol}$$

$$n(H) = 1,89 \text{ g} \cdot \frac{1 \text{ mol}}{1,008 \text{ g}} = 0,1875 \text{ mol}$$

$$n(O) = 49,92 \text{ g} \cdot \frac{1 \text{ mol}}{16,0 \text{ g}} = 3,12 \text{ mol}$$

By dividing by the smaller amount (0,417 mol) we get ratio

n(Fe) : n(S) : n(H) : n(O) = 1,5 : 1 : 4,5 : 7,5

By multiplying by two we get ratio

3:2:9:15

Fe₃S₂H₉O₁₅

b) If the oxidation number of sulfur in this mineral is equal to VI, then the oxidation number (o.n.) of iron - o.n.(Fe) = [2·6+9·1+15·(-2)]:3 = III If the oxidation number of sulfur in this mineral is equal to IV or II, then the oxidation numbers of iron will be non-typical for iron.

c)
$$(H_3O)Fe_3(SO_4)_2(OH)_6$$

1 +9 -4 -6 = 0

- d) H₃O⁺ hydroxonium ion, oxonium ion
- **4. a)** M{[Ca₅(PO₄)₃]⁻} = 485 g/mol M(**X**) = 485 g/mol $\cdot \frac{3,77}{96,23}$ = 19,0 g/mol

b) i)
$$2F_2 + 2H_2O = 4HF + O_2$$

X
B
Y
ii) $2F_2 + SiO_2 = SiF_4 + O_2$
X
A
Y
iii) $2F_2 + Si = SiF_4$
X
A
iv) $F_2 + H_2 = 2HF$
X
B
v) $3SiF_4 + 4H_2O = H_4SiO_4 + 2H_2SiF_6$

vi)
$$H_2SiF_6 = SiF_4 + 2HF$$

C A B

- c) X F₂, fluorine
 - Y O₂, oxygen
 - A SiF₄, silicon fluoride
 - **B** HF, hydrogen fluoride
 - C H₂SiF₆, fluosilicic acid
- 5. a) At the ignition of the gaseous mixture the formed gases were absorbed to give only one compound, it means that one of the initial gases was oxygen and the another initial gas was an oxide with the low oxidation number, that was oxidized to give an oxide with a higher oxidation number third gas. Hydrocarbons do not fit, because no water was produced. NO and also SO₂ do not fit because the final mixture was colourless and the oxidation of the SO₂ requires a catalyst. The probable candidates are CO and CO₂.

Initial mixture may contain O₂, CO and CO₂; Final mixture may contain CO₂ and CO or CO₂ and O₂.

b) i)
$$2CO + O_2 = 2CO_2$$

ii) $CO_2 + 2NaOH = Na_2CO_3 + H_2O$

c) i) According to the equation of the reaction b)i) the volume of the obtained CO₂ is equal to the volume of CO that took part in the reaction. Accordingly to the given data of this problem the V(CO₂,product) causes the increase of the mass of the NaOH solution.

$$V(CO_2, product) = 1,375 \text{ g} \cdot \frac{1 \text{ mol}}{44,0 \text{ g}} \cdot 22,4 \text{ dm}^3 / \text{mol} = 0,700 \text{ dm}^3$$

The change in total volume is equal to the volume of the oxygen that participated in reaction (0,100 dm³).

 $\frac{2}{1}$ ·0,100 dm³ = 0,200 dm³ of carbon monooxide took part in the reaction and it is only

known CO₂ volumes in the initial and final mixtures.

$$V(CO_2, initial mixture) = 0.700 dm^3 - 0.200 dm^3 = 0.500 dm^3 V(CO_2, final mixture) = 0.700 dm^3$$

The volumes of the hydrogen and carbon monooxide can posess two different values, that depend on the different composition.

- **6. a)** Compound **D** is a rombic sulfur (S₈); if the liquid sulfur is cooled slowly, then the compound **E** is formed (monoclinic sulfur) (S₈); if the liquid sulfur is poured into water then the compound **F** is formed plastic sulfur (S_n).
 - **b) i) G** + $2HCI = GCI_2 + H_2$ (in the inert atmosphere the compound with the lower oxidation number is formed)

oxidation number is formed)

ii)
$$2,00 ext{ g } 803 ext{ cm}^3$$
 $G ext{ } + H_2$
 $M ext{ } 22,4 ext{ dm}^3/\text{mol}$
 $2,00 ext{ g } = \frac{1}{1} \cdot 0,803 ext{ dm}^3 \cdot \frac{1 ext{ mol}}{22,4 ext{ dm}^3} \cdot M(G)$
 $M(G) = 2,00 ext{ g} \cdot \frac{1}{0,803 ext{ dm}^3} \cdot \frac{22,4 ext{ dm}^3}{1 ext{ mol}} = 55,8 ext{ g/mol}$
 $G ext{ } - \text{Fe, iron}$

c) i) FeS + 2HCl = FeCl₂ + H₂S
A, iron sufide B, hydrogen disulfide
ii)
$$2H_2S + 3O_2 = 2H_2O + 2SO_2$$

B C, sulfur dioxide
iii) in water solution
 $2H_2S + H_2SO_3 = 2H_2O + 3S$
B C D
iv) in gaseous phase
 $2H_2S + SO_2 = 2H_2O + 3S$
steam liquid

v)
$$S + H_2 = H_2S \uparrow$$

D B
vi) $S + O_2 = SO_2 \uparrow$
C
vii) $2S + C = CS_2$
carbon disulfide

Form XI

1. a) i)
$$X + Pb^{2+} = X^{2+} + Pb \downarrow$$

ii) ii) $X + Cu^{2+} = X^{2+} + Cu \downarrow$

b) M(Pb) = 207,29 g/mol and M(Cu) = 63,5 g/mol; M(X) – molar mass of metal, m – mass of the metal plate, n – the amount of metal and ions that took place in the reaction.

(II)

Solution 1 $\Delta m_1=207.2$ g/mol·n-M(X)·n; [207,2 g/mol·n-M(X)·n]/m=0,190 Solution 2 $\Delta m_2=M(X)\cdot n-63,5$ g/mol·n; [M(X)·n-63,5 g/mol·n]/m=0,098 207,2 g/mol - M(X) = 0,190 m/n (I)

M(X) - 63.5 g/mol = 0.098 m/n

Summarizing (I) and (II) we get

 $143,7 \text{ g/mol} = 0,288 \text{ m/n}, \implies \text{m/n} = 498,9 \text{ g/mol}$

Substitution of the obtained result into equation I gives

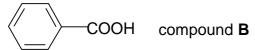
M(X) = 207,2 g/mol - 0,190.498,9 g/mol = 112 g/mol

X - Cd, cadmium

- c) $3600 ext{ s·1,000 A}$ 2,097 g $2e^- \Leftrightarrow X$ 96485 m $2,097 ext{ g} = \frac{1}{2} \cdot 3600 ext{ s·1,000 A} \cdot \frac{1 ext{ mol}}{96485 ext{ A·s}} \cdot M(X)$ $M(X) = 2,097 ext{ g·2·96485 A·s} \cdot \frac{1}{\text{mol}} \cdot \frac{1}{3600 ext{ A·s}} = 112,4 ext{ g/mol}$
- d) Cd + H_2SO_4 (diluted)= CdSO₄ + H_2 (for the formation of electrolyte) anode Cd = Cd²⁺ + 2e⁻ catode Cd²⁺ + 2e⁻ = Cd Electrodes are Cd plates.
- **2.** a) i) Compound ${\bf C}$ is an ester that contains two phenyl groups.

ii) $C_{15}H_{14}O_2 + NaOH = C_7H_5O_2Na + C_8H_9OH$ **C D A**

b) Compound **B** should be an acid that contains phenyl group (C₆H₅–) and carboxyl groop (–COOH), because it was obtained as a product of an oxidation reaction of compound **A** and the compound **D** is a salt of the compound **A**.



Compound **A** is an alcohol, (>CHOH) C_8H_9OH , that contains phenyl group (C_6H_5-) and methyl group (CH_3-). 1-methyl-1-phenylmethanol is an optically active, because one of its carbon atoms contains four different substituents (hydrogen, hydroxyl, methyl and phenyl groups). The molar mass of the group [-CH(CH₃)OH] is equal to a molar mass of the carboxyl group (-COOH).

c) i)
$$\leftarrow$$
 CHOH compound A \rightarrow COOH + CO₂ + H₂O \rightarrow COOH + CO₂ + H₂O

A B

ii)
$$\leftarrow$$
 CHOH + HOC \rightarrow CH₃ \rightarrow C

A B \leftarrow C

d)
$$1 \sqrt{\frac{0}{\text{CHOH} + 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4}} = 1 \sqrt{\frac{\text{III}}{\text{COOH} + 1\text{CO}_2}} + \frac{1}{1\text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 5\text{H}_2\text{O}}}$$

0 III

$$C - 3e^{-} = C$$

-III IV
 $C - 7e^{-} = C$
VII II
 $Mn + 5e^{-} = Mn + 5$ 2

3. a)
$$n(C) = n(CO_2) = 1,15 \text{ dm}^3 \cdot \frac{1 \text{ mol}}{22,4 \text{ dm}^3} = 0,05134 \text{ mol}$$
 $m(C) = 0,05134 \text{ mol} \cdot 12,0 \text{ g/mol} = 616 \text{ mg}$ $n(H) = 2n(H_2O) = 2 \cdot 1,15 \text{ g} \cdot \frac{1 \text{ mol}}{18,0 \text{ g}} = 0,1278 \text{ mol}$ $m(H) = 0,1278 \text{ mol} \cdot 1,008 \text{ g/mol} = 128,8 \text{ mg} \approx 129 \text{ mg}$ $m(O) = (949 \cdot 616 \cdot 129) \text{ mg} = 204 \text{ mg}$ $n(O) = 0,204 \text{ g} \cdot \frac{1 \text{ mol}}{16,0 \text{ g}} = 0,01275 \text{ mol}$

Lets assume, that 1 molecule of this compound contains 1 atom of oxygen

$$n(C) = 0.05134 \text{ mol} \cdot \frac{1 \text{ mol}}{0.01275 \text{ mol}} = 4 \text{ mol}$$

$$n(H) = 0.1278 \text{ mol} \cdot \frac{1 \text{ mol}}{0.01275 \text{ mol}} = 10 \text{ mol}$$

$C_4H_{10}O$

1-butanol

$$H_3C$$
 O CH_3

ethoxyethane

$$H_3C$$
 CH_3 CH_3

2-methyl-2-propanol

$$H_3C$$
 OH

2-butanol

methoxypropane

2-methoxypropane

2-methylpropanol

R-2-butanol

S-2-butanol

4. a)
$$B - CH_3CH_3$$
, ethane

C - NaOH, sodium hydroxide

D – CO₂, carbon dioxide

E – H₂, hydrogen

F – Na₂CO₃, sodium carbonate

G - NaHCO₃, sodium bicarbonate

 $\mathbf{H} - \mathbf{CH}_2 = \mathbf{CH}_2$, ethene

I - BrCH₂CH₂Br, 1,2-dibromoethene

J - CH≡CH, ethyne

b) i)
$$CH_3CH_3$$
 (**B**) = $CH_2=CH_2$ (**H**) + H_2 ii) $CH_2=CH_2$ (**H**) + $Br_2 = BrCH_2CH_2Br$ (**I**)

iii)
$$BrCH_2CH_2Br(I) + 2KOH = CH \equiv CH(J) + 2KBr + 2H_2O H_2O$$

iv)
$$CO_2$$
 (excess) (**D**) + NaOH (**C**) = Na₂ CO_3 (**F**) + H₂O H₂O

v) CO_2 (**D**) + NaOH (**C**) = NaH CO_3 (**G**)

5. a) i)
$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

 $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$
ii) $K_1 = \frac{[H^+] \cdot [HCO_3^-]}{[H_2CO_3]}$ $K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$

b) i) pH = pK -
$$\lg \frac{[H_2CO_3]}{[HCO_3^-]} = 6.10 - \lg \frac{1}{20} = 7.40$$

ii) $[H^+] = 10^{-pH} = 10^{-7.4} = 3.98 \cdot 10^{-8} \text{ M}$

c) For the obtaining of the initial value of pH this value must be increased, it means that the value of $-lg \frac{[H_2CO_3]}{[HCO_3^-]}$ should increase. If the value of the equation member $\frac{[H_2CO_3]}{[HCO_3^-]}$ is increased then its negative logarythm value gets larger. The equilibrium concentration of the metacarbonic acid decreases at the fast breathing, because CO_2 became removed from the gaseous phase. Initial pH value is recovered at faster inhalation.

b) i)
$$Sn + S = SnS$$
 $_{0}^{0}t$
 $SnS + S = SnS_{2}$
A
ii) $Pb(NO_{3})_{2} + 2KI = PbI_{2} + 2KNO_{3}$
B
iii) $3Sn + 8HNO_{3}$ (diluted) = $3Sn(NO_{3})_{2} + 2NO + 4H_{2}O$

d) i) catode reaction:
$$Pb^{4+} + 2e^- = Pb^{2+}$$

ii) anode reaction: $Pb = Pb^{2+} + 2e$
iii) $Pb + PbO_2 + 2H_2SO_4 = 2PbSO_4 \downarrow + 2H_2O$

e) IV II IV
$$H_2SnO_3$$
 $Pb_2PbO_4 \Leftrightarrow Pb_3O_4$ E

Form XII

1. a) Aqua regia dissolves Au and does not dissolve Ag, because it became coated with a layer of AgCl.

Au + HNO₃ + 3HCl = AuCl₃ + NO
$$\uparrow$$
 + 2H₂O
HCl + AuCl₃ = H[AuCl₄]

- **b)** HNO₃ (conc.) + 3HCl (conc.) = NOCl + 2Cl* + 2H₂O The active agent that dissolves gold is atomic chlorine.
- c) i) catode: tetrachloroaurate(III) ions are unstable and as a result Au³⁺– ions are formed and they are reduced

$$Au^{3+} + 3e^{-} = Au$$

Sum:
$$[AuCl_4]^{-} + 3e^{-} = Au + 4Cl^{-}$$

ii) anode: $2Cl^{-} - 2e^{-} = Cl_{2}^{\uparrow}$

The same reaction take place in a case of AlCl₃ solution.

m(Au,electrolyte)=
$$\frac{1}{3} \cdot 20 \text{ A} \cdot 4 \cdot 3600 \text{ s} \cdot 0.9 \cdot \frac{1 \text{ mol}}{96485} \cdot 196,97 \text{ g/mol} = =176,38 \text{ g}$$

m(medal) =
$$\frac{176,38 \text{ g}}{0.9} \cdot \frac{24}{23} = 204,50 \text{ g}$$

c) i)
$$(COOH)_2 \cdot 2H_2O = CO_2 + CO + 3H_2O$$

ii)
$$5(COOH)_2 + 2KMnO_4 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O$$
D

d) 0,153 dm³

$$5(gases) \Leftrightarrow F$$

 $22,4 \text{ dm}^3 / \text{mol} \cdot \frac{373}{273}$
 $n(F) = \frac{1}{5} \cdot 1,53 \text{ dm}^3 \cdot \frac{1 \text{ mol}}{22,4 \text{ dm}^3 \cdot \frac{373}{273}} = 0,009998 \text{ mol} \approx 0,0100 \text{ mol}$

e)
$$0.0100 \text{ mol} \cdot \frac{1}{0.1 \text{ dm}^3} \cdot 10 \text{ cm}^3$$
 $5(F) = 2(KMnO_4)$ $c \cdot 13.2 \text{ cm}^3$

$$c(KMnO_4) = \frac{2}{5} \cdot 0,100 \text{ mol/dm}^3 \cdot 10 \text{ cm}^3 \cdot \frac{1}{13,2 \text{ cm}^3} = 0,0303 \text{ mol/dm}^3$$

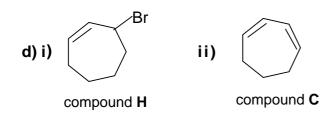
b) The brutto formula for the compounds **A, B** and **C** (isomers) should be C_7H_{10} . In all 7 isomers of the compound **B** the location of carbon atoms must be the same as in the methylcyclohexane (C_7H_{14}), it means that all these molecules must be dienes.

c) i)
$$\longrightarrow$$
 O_2 + O_2 + O_2 Compound E

HOOC
$$\xrightarrow{\text{KMnO}_4/\text{H}^+}$$
 CO₂ + HOOC $\xrightarrow{\text{H}}$ Compound **E** compound **F**

HOOC $\xrightarrow{\text{KMnO}_4/\text{H}^+}$ HOOC COOH

compound **G**1 1,5-pentadicarboxylic acid



4. a) i) M(B) = 44,01 g/mol·1,611 = 70,90 g/mol

 $B-Cl_2$

ii) From 1 mole of compound $\bf A$ there was obtained 1,5 moles of Cl_2 , ie the oxidation number of metal $\bf X$ in the compound $\bf A$ should be equal to III. So the formula of the compound shoul be XCl_3

 $M(X) = 3.35,45 \text{ g/mol} \cdot 20,24/79,76 = 26,99 \text{ g/mol}$

$$\mathbf{X} - \mathsf{AI}$$

iii) C - LiH

- iv) ${\bf E}$ LiCl. According to the data the oxidation number of metal in compound ${\bf E}$ is equal to I.
- v) D LiAlH₄

 $M(AICI_3) = 133,35 \text{ g/mol}$

 $M(D) = 133,35 \text{ g/mol} \cdot 0,285 = 38,0 \text{ g/mol}$

 $M(LiAIH_4) = 6.94+26.98+4\cdot1.008 = 37.95 \text{ g/mol} \approx 38.0 \text{ g/mol}$

b) AlCl₃ + 4LiH = LiAlH₄ + 3LiCl

A C D E

c) LiAlH₄ + Me₃COH the hydrogen is released as a reaction product and other products are formed in the case if the compound LiAlH₄ contains the different number of substituted hydrogen atoms

Li[AlH₃(OCMe₃)] **F**

Li[AlH₂(OCMe₃)₂] G

Li[AlH(OCMe₃)₃] H

Li[Al(OCMe₃)₄]

d) $n(H_2) = 0.0112 \text{ dm}^3 \cdot \frac{1 \text{ mol}}{22.4 \text{ dm}^3} = 0.0005 \text{ mol} = 0.5 \text{ mmol}$

 $C \Leftrightarrow CaCO_3$

$$n(C) = 1,20 \text{ g} \cdot \frac{1 \text{mol}}{100 \text{ g}} = 0,012 \text{ mol} = 12 \text{ mmol}$$

Compound H is Li[AlH(OCMe₃)₃]

- **e)** LiAlH₄ + 3(Me₃COH) = Li[AlH(OCMe₃)₃] + 3H₂ **D**
- f) Li[AlH(OCMe₃)₃] + 3NaOH + 4H₂O \rightarrow 3Me₃COH + LiOH + Na₃[Al(OH)₆] + 0,5H₂
- g) i) Li[Al(OCMe₃)₄], ii) any steric hindrances caused by Me₃C-groups can be overcome at heating.
- **5. a)** The desired salt $\bf A$ should give the characteristic smell (NH₃) upon the treatment with the hydrated lime. It indicates, that compound $\bf X$ contains hydrogen as a fourth element 6,66%.

$$\begin{aligned} \text{N}:\text{C}:\text{O}:\text{H} &= \frac{46,67}{14,0} : \frac{20,00}{12,0} : \frac{26,67}{16,0} : \frac{6,66}{1,01} = 3,33 : 1,67 : 1,67 : 6,60 &= 2 : 1 : 1 : 4 \\ \text{N}_2\text{COH}_4 & \text{NH}_4\text{OCN} - \text{ammonium cyanate} - \textbf{B} \\ & (\text{NH}_2)_2\text{CO} - \text{urea} & -\textbf{X} \end{aligned}$$

- **b)** $Y(OCN)_n + nNH_4CI = nNH_4OCN + YCI_n$ $M(NH_4OCN) = M(X) = 60.0 g/mol$ $M(A) = 60.0 \text{ g/mol} \cdot 2.50 = 150 \text{ g/mol} = M[Y(OCN)_n]$ If n=1, then M(Y) = 150 - 42 = 108 g/mol $\mathbf{Y} - \mathsf{A}\mathsf{a}$
 - A AgOCN, silver cyanate
- c) i) AgOCN + NH₄CI = NH₄OCN + AgCI↓

 A
 B
 ii) >60 °C

 NH₄OCN = (NH₂)₂CO

 B
 X
 iii) 2NH₄OCN + Ca(OH)₂ = 2NH₃↑ + Ca(OCN)₂ + 2H₂O
- d) i) Friedrich Wöhler
 - ii) Isomerism
 - iii) For the first time in history the organic compound was obtained using the inorganic compounds.
- **6. a) i) A** \xrightarrow{hv} Under the action of sunlight halogenides of Ag⁺ and Cu⁺ decompose. the petal changed red then the salt must be CuHal.

$$2CuHal \xrightarrow{h \cdot v} 2Cu + Hal_2$$

H – Cu,

ii) $n(\mathbf{A}) = 2n(Hal)$

$$\frac{1,00 \text{ g}}{63,5 \text{ g/mol} + \text{M(Hal)}} = 2 \cdot \frac{0,667 \text{ g}}{2 \cdot \text{M(Hal)}}$$

 $M(Hal) = 42.4 \text{ g/mol} + 0.667 \cdot M(hal)$

M(Hal) = 127.3 g/mol

A - Cul, copper(I) iodide, white

- b) 1,00 g
 - i) $2KMnO_4 + 16HCI = 2KCI + 2MnCl_2 + 5Cl_2 + 8H_2O$

ii)
$$V(Cl_2) = \frac{5}{2} \cdot 1,00 \text{ g} \cdot \frac{1 \text{ mol}}{158 \text{ g}} \cdot 22,4 \text{ dm}^3 / \text{mol} = \mathbf{0,354 \text{ dm}}^3$$

- **B** KMnO₄, potassium permanganate, violet; **I** Cl₂, chlorine
- c) i) C $\stackrel{\circ_t}{\longrightarrow}$ J + HCl \rightarrow light blue colour, that is typical for Cu²⁺– ions. J CuO, copper(II) oxide, black

ii) if
$$n(\mathbf{C}) = n(\mathbf{J})$$
, then $M(\mathbf{C}) = \frac{m(\mathbf{C})}{n(\mathbf{C})} = 1,00 \text{ g} \cdot \frac{79,5 \text{ g/mol}}{0,720 \text{ g}} = 110,4 \text{ g/mol}$

if $n(\mathbf{C}) = 2n(\mathbf{J})$, then $M(\mathbf{C}) = 221$ g/mol

C – (CuOH)₂CO₃, copper(II) hydroxycarbonate, malachite, green

iii)
0
t $(CuOH)_{2}CO_{3} = 2CuO + CO_{2} + 2H_{2}O$

iv)
$$CuO + 2HCI = CuCl_2 + H_2O$$

K - CuCl₂, copper(II) chloride, light blue

d) i) L- Mg, magnesium

M - Mg(OH)₂, magnesium hydroxide

ii)
$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2\downarrow + 2NH_3\uparrow 4NH_3 + 3O_2 = 2N_2\uparrow + 6H_2O$$

D – Mg₂N₃, magnesium nitride, yellow-green

N - NH₃, ammonia

P - N₂, nitrogen

iii)
$$Mg_2Si + 4H_2O = 2Mg(OH)_2 \downarrow + SiH_4 \uparrow$$

 $SiH_4 + 2O_2 = SiO_2 + 2H_2O$

E – Mg₂Si, magnesium silicide, light blue

O - SiH₄, silane

R - SiO₂, silicon dioxide

e) i) $\mathbf{F} - Pb_3O_4$, trilead tetraoxide, lead(II,IV) oxide, orange-red

F - Pb₂PbO₄, dilead(II) orthoplumbate

ii) %(O) =
$$\frac{64.0}{685} \cdot 100 = 9.34$$

f) i) G – Au, gold, yellow

ii) $H[AuCl_4] + CsCl = Cs[AuCl_4]$

Q – H[AuCl₄], hydrogen tetrachloroaurate(III)

S– Cs[AuCl₄], cesium tetrachloroaurate(III)

iii) 1,00 g

 $Au \Leftrightarrow Cs[AuCl_4]$

197 g/mol 472 g/mol

$$m\{Cs[AuCl_4]\} = \frac{1}{1} \cdot 1,00 \text{ g} \cdot \frac{1 \text{ mol}}{197 \text{ g}} \cdot 472 \text{ g / mol} = 2,40 \text{ g}$$