**UNIVERSITY OF TARTU**

**THE GIFTED AND TALENTED DEVELOPMENT CENTRE**

# 56TH ESTONIAN NATIONAL CHEMISTRY OLYMPIAD

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# CONTENTS

## National Theoretical Examination

## National Theoretical Examination: 10th grade

**1. a)** Draw constitutional formulas for the following compounds: HCHO, $CO_2$, $H_2O_2$, $COCl_2$, $(COCl)_2$, $CH_3CN$, $HClO_4$.

**b)** The density of heavy water $D_2O$ at 20°C is 1.106 g $cm^{-3}$. The density of normal water is 0.9982 g $cm^{-3}$. Calculate the values of molar mass and molar volume of $H_2O$ and $D_2O$ with a precision of four significant figures. What volume (in litres) does one water molecule occupy in average in both liquids? [$A_r$(H) = 1.008, $A_r$(D) = 2.014, and $A_r$(O) = 15.999]

**c)** The following assumptions are made: cytoplasm of bacterium cell contains 900 different enzymes (by type) in equal quantities. The molecular mass of each enzyme is 90 000; bacterium cell is a cylinder 1.0 μm in diameter and 2.0 μm in height; the mass of enzymes is 25% of the cytoplasm mass (density is 1.2 g/$cm^3$). Calculate the volume ($m^3$) of such hypothetical bacterium cell and molar concentration of enzymes (μmol/$dm^3$) in bacterium cytoplasm.

Hint: $V_{cylinder} = h\pi r^2$

**2.** Gas **B** is obtained in the reaction of substance **A** with $MnO_2$ under acidic condition. During the oxidation of gas **B** by the substance **C** substances **D** and **E** are formed. During the hydrolysis of substance **D** binary compound **F** and compound **G** are formed. Compound **G** is unstable and decomposes when exposed to light into compounds **H**, **I** and **J**. One of the decomposition products (**J**) also forms in the reaction of substance **I** with sulphur dioxide.

Hints: Substances **A**, **B**, **D**, **E**, **G–J** contain element **X**. Substance **A** is long known as a flavor additive as well as preservative. Element contained in elementary substance **C** is located in the same group as element **X**. Compounds **D** and **E** are binary, consist of the same elements, and oxidation state of one of the elements in compound **D** is three times higher than oxidation tate of this element in compound **E**. The molecular mass of compound **J** is 95% of molecular mass of substance **B**.

**a)** Write the formulas for the substances **A**–**J**.

**b)** Write the equations of the reactions:

**A** + $MnO_2$ + $H_2SO_4$ → **B** + ...

**B** + **C** → **D** + **E**

**D** + $H_2O$ → ...

**I** + $SO_2$ →

**c)** According to electronic balance method find the coefficients of the equation of the decompotion reaction of compound **G**.

**d)** Arrange the aqueous solutions of **G**, **H**, **I** in order of increasing acids' strength.

**3.** Molar mass of helium is 4.00 g/mol, molar mass of air is 29.0 g/mol.
**a)** Determine the mass of precisely 1 litre of helium and 1 litre of air under normal conditions (1 atm, 0°C)?
**b)** How high should be the pressure of helium for its density be equal to the density of air at normal pressure (both gases are at the same temperature)?
**c)** How high should be the temperature of air (°C) for its density at normal pressure be equal to the density of helium (under normal conditions).
**d)** There are 5.2 ppm of helium in the air (by volume). Determine the amount of helium in ppm by mass? (ppm = Parts per million)

**4.** Metal **M** plays an important role in contemporary energetics. Due to its high chemical activity it is spread in nature only in the form of compounds in which oxidation state is always the same. Already at room temperature metal **M** in the air gets covered by the oxide, hydroxide, carbonate and nitride layer. During heating it combines, for instance, with hydrogen, forming a hydride. Throughout the reaction of 1 mole of hydride with water 1 mole of hydrogen is evolved. Metal **M** and its oxide react with water forming a hydroxide which is a strong base. Hydroxide, as well as carboname of **M**, is thermally unstable and under heating it decomposes into oxide.
**a)** Calculate the oxidation number of metal **M** in compounds. Determine the metal **M.**
**b)** Write the equation of the reaction of hydride **M** with water. Which element acts as an oxidant and which is a reducer? How many litres of hydrogen (under normal conditions) are formed in the reaction of 1.0 gramme of hydride with water?
**c)** Write equations for the reactions: of metal **M** with oxygen, hydrogen, water and nytrogen; of metal **M** oxide with water; of thermal decomposition of carbonate **M**. Give names for the compounds of metal **M** that take part in reactions.

**5.** Liquefied or natural gas can be used as a fuel for gas heater. The AGASOL® balloon contains 33.0 kg of liquefied butane. Natural gas contains approximately 98% of methane by volume and the rest 2% is a mixture of $C_2H_6$, $C_3H_8$, $C_4H_{10}$, $H_2$, $N_2$, He, $CO_2$. Enthalpies of combustoin: $C_4H_{10}$: −2655 kJ/mol, $CH_4$: −802 kJ/mol.
Hints: In order to simplify calculations, assume that natural gas contains 98% of $CH_4$ and 2% $N_2$. Assume that pressure is constant.
**a)** Write equation for the combustion reaction of butane and calculate the energy released during the combustion of 33.0 kg of butane.

**b)** Write equation for the combustion reaction of methane. Calculate the volume of natural gas needed to be combusted to produce as much energy as one balloon of butane does **i)** in winter (−10°C) and **ii)** in summer (+20°C).

**6.** Elements **A**, **B**, **C**, **D**, **E** are the closest neighbours of element **F**. Let us examine the periodic table. The atomic mass of element **B** is bigger than the atomic masses of elements **A** and **C**. Atomic number of element **D** is bigger by 31 than the atomic number of element **F** and imore by 49 than the atomic number of element **B**. The difference in atomic masses of elements **D** and **E** is 2,0 a.m.u. Elements **B** and **E** are located in the same group. Elements **A** and **C** are present in **C−A** accumulators, in which the elementary substance **C** reacts with hydroxide of element **A** and as a result two hydroxides are formed.

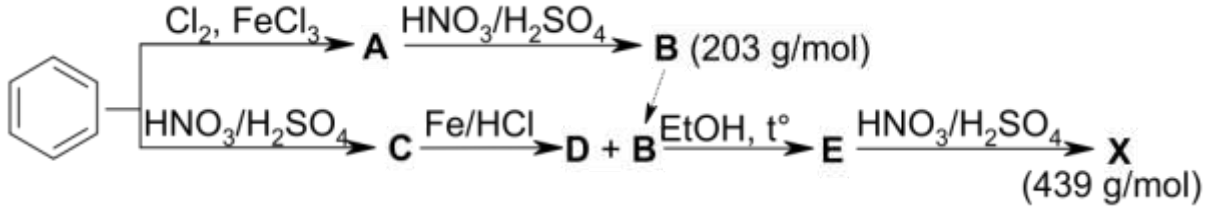
**a)** Write symbols for the elements **A−F**.

**b)** Write equation for the reaction of elementary substance **C** with hydroxide of element **A**.

**c)** Justify the logic of elements' determination.

# National Theoretical Examination: 11th Grade

**1.** Substance **X** was first synthesized by German chemist Peter Austen in 1874. Due to its interesting properties its commercial production was soon started. Substance **X** is used in detonators as it has a considerable blasting power. Substance **X** is obtained according to the following scheme:




**a)** Write structural formulas for substances **A**–**E** and **X**.

Substance **X** is also used for qualitative and quantitative determination of $K^+$, $Rb^+$ и $Cs^+$ ions: these ions form a bright red salt with substance **X**.

**b)** Write the structural formula of this product indicating the ion of metal $M^+$.

**2.** Tom, a medic to be, decided to analyze hemolysis—the breaking of the membrane of red blood cells. In order to do it he had to prepare 0.90% and 0.30% solutions starting from the 1.0% solution of NaCl and distilled water. The mass of both solutions had to be 5.0 grammes.

**a)** Calculate how many grammes of both initial components: 1.0% aqueous NaCl solution ($\rho$ = 1.0 g/cm$^3$) and water, should be taken for the preparation of both solutions. Calculate the molar concentration (1 M = 1 mol/dm$^3$) of both solutions.

Hemolysis happens when blood cells are added into hypotonic solution. In hypotonic solution the osmotic pressure π is less than in blood cells; thus, water overflows through the cell wall into the blood cell and cell breaks. This happens when osmotic pressure in the solution surrounding the cell is less than 3 atm.

**b)** Tom added 2–3 drops of blood in both prepared solutions. Prove with your calculations in which of the solutions hemolysis may take place at room temperature.

Osmotic pressure $\pi = icRT$, where $i$ – isotonic coefficient (in NaCl solution $i$ = 2), $c$ – molar concentration of solution (M), $T$ – temperature (K), and $R$ = 0,082 dm$^3$·atm/(K·mol).

**3.** Probably there is no carbon on the planet Grelzak (the sixth planet in the constellation of Bob). What does Zerblat— inhabitant of the planet Grelzak — consist of? It is believed that Zerblat has his carbon replaced by element **X**. In contrast to carbon, in oxidation of element **X** a solid oxide **A** is obtained which forms alien's skeleton. This substance is chemically inert and reacts only with

one specific acid **B**. Element **X** itself does not react with that acid; however, it reacts with alkaline solution. Zerblat's bones are able to change their shape under force. This ability is used by alien to move hands and legs. Due to this fact he absolutely does not need muscles. **C** is an element **X**'s analogue of propane which easily inflames in the air. This explains why Zerblat glows in the darkness. Instead of enzymes and cell membranes, Zerblat has microporous compounds; for example, $Na_4Al_4X_4H_{18}O_{25}$. On the Earth similar compounds are used for oil cracking and water purification. Zerblat has very hard teeth consisting of compound $\mathbf{X_3Z_4}$. Unfortunately, in the course of time they corrode under the influence of consumption of 40% acid **B** (delightful drink that replaces ethanol for Zerblat). Decomposition products are a complex acid of element **X** (%(**X**) = 19,5) and a simple salt of acid **B** (%(**Z**) = 37,8). On the Earth Zerblat becomes soft and sticky because by the inhale of carbon dioxide by means of complicated transformations, substance **D** is produced, which contains carbon, oxygen, hydrogen and element **X**. Similar substances are used on the Earth for the production of spacers and hoses. Electroconductivity of substance **X** depends on the impurities. This peculiarity is used for alien's information storage and processing (similar to human's brain). Along with big head this explains Zerblat's unbelievable intellectuality (IQ = 12735 and 57 zetaflops).

**a)** Write formulae and names for **X**, **A**-**D**, $Na_4Al_4\mathbf{X}_4H_{18}O_{25}$ (write in the form of oxides), $\mathbf{X_3Z_4}$.

**b)** Write the equations of the reactions:

$\mathbf{X} + O_2 \rightarrow$ ...

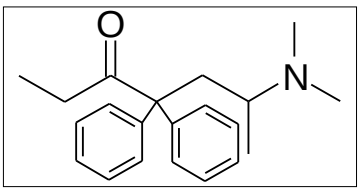
$\mathbf{A} + \mathbf{B} \rightarrow$ ...

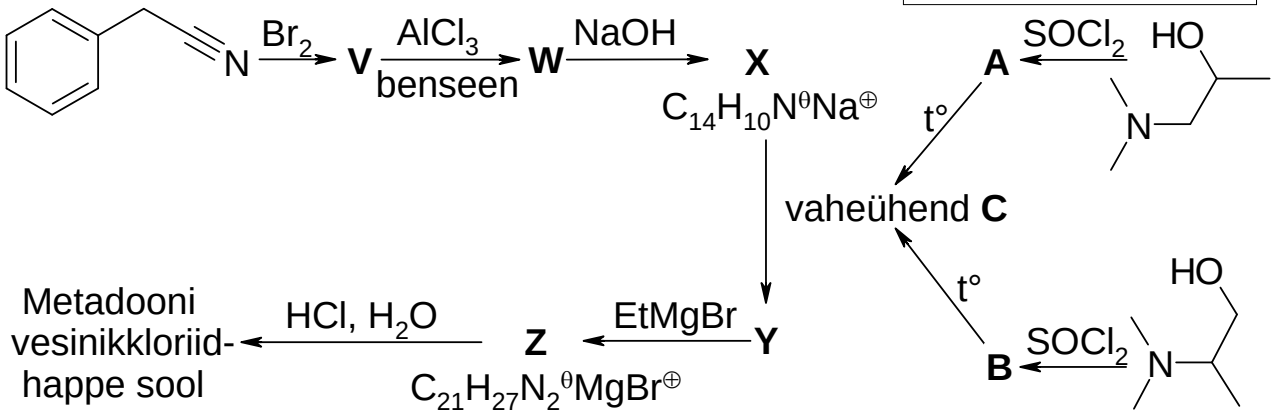
$\mathbf{X} + H_2O + NaOH \rightarrow$ ...

$\mathbf{C} + O_2 \rightarrow$ ...

$\mathbf{X_3Z_4} + \mathbf{B}$(in excess) $\rightarrow$ ...

**4.** Methadone (in the picture) is an opioid, used as an anelgetic and also in substitution treatment of morphinism. It may be prepared as a hydrochloride salt accroding to the following scheme:





It is known that intermediate compound **C** is a salt containing a chloride-ion.

**a)** Write structural formulas for substances **A**–**C**, **V**–**Z**, and for hydrochloride salt of methadone.

Only methadone's (*R*)-enantiomer is biologically active.

**b)** Write structural formula for methadone's *R*-isomer.

**5.** Gout is a disease hallmarked by elevated levels of uric acid in bloodstream (hyperuricaemia) and by formation of its salts' crystals, sodium urates, in the body tissues. The formation of such crystals in finger joints cause heavy state of illness and their swelling.

**a)** The solubility product of sodium urate ($C_5H_3N_4O_3Na$) is $6.04 \cdot 10^{-5}$ and of disodium urate ($C_5H_2N_4O_3Na_2$) is $7.8 \cdot 10^{-7}$. Calculate the solubilities (M) of both salts in pure water.

In order to facilitate disease it is recommended to exclude table salt (NaCl) from diet or replace it by another salt that does not contain sodium.

**b)** Calculate how many times solubility of sodium urate and disodium urate will decrease if poured together $8\underline{0}$ $cm^3$ of saturated solution of each salt with $2\underline{0}$ $cm^3$ 0.25 M solution of NaCl. The contraction may be neglected.

**6.** Dick and Harry play a game. In turns they name natural nonradioactive elements according to their characteristic oxidation state (o.s.) from +I to +VIII, then again from +I to +VIII, etc. For instance, 1st move: Harry – Li (o.s. = +I, $Li_2O$), Dick – Be (o.s. = +II, BeO); 2nd move: Harry – B (o.s. = +III, $B_2O_3$), Dick – C (o.s. = +IV, $CO_2$); 3rd move: etc. Each element can be named only once. Wins the one who cannot name any element that may have the compounds with corresponding oxidation state. Dick started the game first.

**a)** Write the last nonradioactive element in the periodic table and also all the radioactive elements that precede it.

**b)** Write the two most rare oxidation states of the periodic table.

**c)** Which is the minimal number of moves needed for Dick's victory? Give one example of oxygen-containing compound for each element (in corresponding oxidation state), which will certainly be named by Dick in this case.

**d)** Which is the minimal number of moves needed for Harry's victory? Give one example of oxygen-containing compound or fluoride for each element (in corresponding oxidation state) that in this case will certainly be named by Harry?

**e)** How many moves may be required in order to finish the game if Dick and Harry play passively?

# National Theoretical Examination: 12th Grade

**1.** Stirlitz attempted to poison Müller*. He added 0.21 moles of sodium salt Na**A** into a glass of water (250 $cm^3$). Weak acid H**A** ($pK_a$ = 9.22), which comes from drupes, causes poisoning. It is formed during the hydrolysis of amygdalin ($C_{20}H_{27}NO_{11}$) as well as glucose and benzaldehyde.

**a)** Write the equation of the hydrolysis of amygdalin.

**b)** Write the formula of H**A** acid and give its trivial name.

**c)** Calculate the concentration of HA acid in the glass ($K_W = 10^{-14}$).

**d)** How many cherries should have Stirlitz fed to Müller (the latter one is obviously not really smart and swallows the stones) in order to accumulate the amount of HA in Müller's body as high as in the glass. The content of amygdalin in cherry stone is 0.8% and the mass of stone is ca. 2 g.

* Max Otto von Stirlitz and Heinrich Müller is a character of a popular Russian book series written by novelist Julian Semyonov and of the television series "Seventeen Moments of Spring".

**2.** H—protium—is an isotope of hydrogen which has the atomic mass of 1, D—deuterium—is an isotope with the atomic mass of 2, T—tritium—is an isotope with the atomic mass of 3. In aqueous medium the atoms of protium and deuterium exchange between water molecules due to the dissociation of water.

**a)** 80 moles of $H_2O$ and 20 moles of $D_2O$ are mixed. Which is the final composition of the mixture after it stands for a while?

"Hot" tritium atoms obtained in the nuclear reaction replace the atoms of protium in butane molecules.

**b)** How many monosubstituted products are there in the mixture of butane and "hot" tritium? Estimate and justify the ratio of products.

Due to adsorption on metal surface the exchange of protium atoms by deuterium atoms in propane molecules takes place. In order to determine the mechanism of exchange reaction, assume that propane reacts according to the following scheme (M is the atom of the metal on the surface; R is $C^1H_3$; on stage **I** both $^1H_2$, and $D_2$ adsorb on the metal surface and then react with propane $C^1H_3C^1H_2R$):

$$H\text{-}H + 2M \rightleftarrows 2MH \qquad (\textbf{I})^*$$

$$CH_3CH_2R + 4M \rightarrow CMH_2CMHR + 2MH \qquad (\textbf{II})$$

$$MH + CMH_2CMHR \rightleftarrows 2M + CMH_2CH_2R \qquad (\textbf{III})^*$$

$$MH + CMH_2CH_2R \rightarrow 2M + CH_3CH_2R \qquad (\textbf{IV})$$

* Reactions (**I**) and (**III**) are reversible: hydrogen atoms may exchange for several times.

**c)** How many products of propane can be produced according to given scheme? Draw constitutional formulas of these products; mark the position of protium and deuterium.

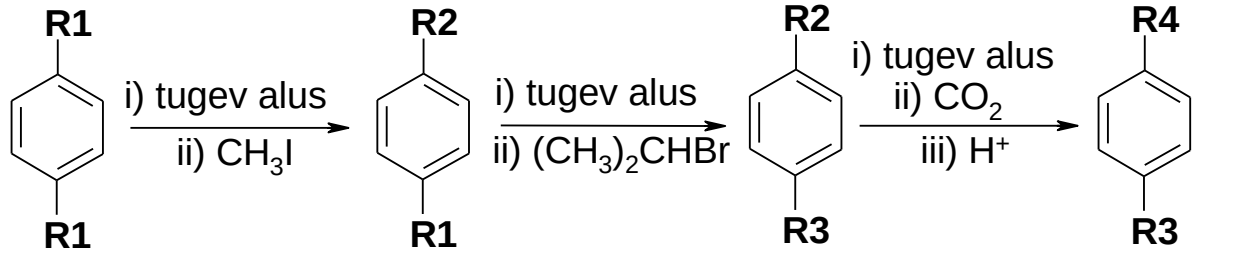
**3.** Chlorine compound **A**, a reddish-yellow gas, was the first chlorine oxide to be discovered (%(Cl) = 52.6%). Nowadays it is produced on a very large scale for the bleaching of wood pulp and for water treatment. Humphry Davy obtained gas **A** by the disproportionation reaction of chlorine-containing acid **B**. Acid **B** was synthesized in the reaction of concentrated sulphuric acid and solid $KClO_3$. The rest products of disproportionation reaction are water and acid **C** (**1**). For safety reasons gas **A** is produced where it is to be used. For pulp bleaching it is obtained by the partial reduction of $NaClO_3$ by sulphur dioxide under acidic conditions (**2**). In the laboratory gas **A** is made in the reaction between $NaClO_3$ and $(COOH)_2$ in the presence of sulphuric acid (**3**). Compound **A** can also be produced by oxidising $NaClO_2$ with chlorine gas (**4**).

**a)** Determine the oxidation numbers of chlorine in substances **A**, **B** and **C**.

**b)** What is the structure of **A** and **C** molecules? Estimate the angles between bonds.

**c)** Write the equations of the aforementioned reactions of substance **A** production.

**4.** The C–H bond has very weak acidic properties and can be deprotonated by strong bases. Nucleophilicity of obtained carbanions is used in synthesis routes. One of the elegant examples is the sythesis of ibuprofen (206 g/mol), which is done in three stages, in one flask, without separation and purification of intermediate products, and using as initial reagent a hydrocarbon with a simple structure:




Ibuprofeen

The structure of ibuprofen contains a chiral centre. Only one equivalent of each reagent is used.

**a)** Draw structural formulas for the **R1**–**R4** groups.

**b)** Draw structural formula for the *R*-isomer of the final product.

**c)** What is the yield of the synthesis if the yield on each of the three-stages of the synthesis is in average 80%?

**d)** Butyllithium ($C_4H_9Li$) is one of the strongest bases used in organic synthesis. Write and balance the equation of the reaction of acetic acid with one equivalent of butyllithium.

**5.** In 1783 a French scientist, A. Lavoisier, has descovered that in the reaction of combustible gas (phlogiston) with phlogiston free air water is produced. Immediately there has been launched a number of studies aimed at finding the appropriate industrial method of production of this gas, in order to use it in aeronautics. The found method was based on the fact that water vapour deflated from boiler was let through the red hot gun barrel.

**a)** Write the equation of the reaction for this method.

**b)** How many cubic meters of hydrogen can be theoretically obtained from the gun tube of 2.0 kg (15°C and 1.0 bar)?

| | Fe | FeO | $H_2O$ | $H_2$ |
|---|---|---|---|---|
| $H_f^0$, kJ mol$^{-1}$ | 0 | −217 | −204 | 0 |
| $S^0$, J mol$^{-1}$ K$^{-1}$ | 78 | 141 | 243 | 174 |

**c)** Calculate the reaction equilibrium constant at 1000°C. In order to do that calculate the values of $\Delta H^0$, $\Delta S^0$ и $\Delta G^0$ for the reaction. Use the data provided in the table.

**d)** In which dirrection will the equilibrium shift if **i)** pressure increases and **ii)** temperature rises?

**e)** Find how many gun barrels are needed to fill the balloon and make it rise. (15°C and 1.0 bar). Total weight of the balloon shell, basket, and scientist is 200 kg.

**f)** Calculate the volume of this quantity of hydrogen at a height of 2 km if the atmospheric pressure equals 0.78 bar and temperature 2.0°C.

1 bar = 100 kPa, $R$ = 8,314 J mol$^{-1}$ K$^{-1}$, $M_r$(air) = 29

**6.** Once an opossum saw an issue of a sports magazine and started to dream: “What if I could be a sprinter?”. Having imagined how fabulously he might have looked in tight-fitting training suit, he firstly decided to test his hypothesis. In *Nature* magazine he found a suitable method to find out whether his muscles were good for sprint or marathon.

Following this method, opossum made an attempt to determine the activity of the enzyme of ATPase, which provides energy for muscle fibers. ATP dissociates into ADP and anion **A**. Anion **A** is treated with $CaCl_2$ under base conditions, which results in salt **B** and anion **C**. Then, Chloride **D** (pale pink solution), containing 45.39% of metal **Y**, is added to salt **B**. Salt **E** and $CaCl_2$ are produced. During the reaction of $(NH_4)_2S$ with substance **E,** a dark-coloured spot of the finial insoluble product **M** appears. The spot of **M** indicates the activity of ATPase.

**a)** Write the formulae and names for ions **A**, **C**, and substances **B**, **D**, **E**, **Y**. Determine the substance **D**. Show your calculations.

**b)** Write equations for the following reactions:

$ATP^{4-} \xrightarrow{\text{ATP-aas}} ADP^{3-}$ + **A**

**A** + $CaCl_2 \rightarrow$ **B**

**B** + **D** $\rightarrow$ **E**

**E** $\rightarrow$ **M**

According to the aforementioned method one part of muscular fibers becomes dark and another remains light in colour. Opossum found out that during the analysis of his muscles the amount of light-coloured fibers was higher.

**c)** Explain whether opossum has the right type of muscles to make his dream of being a sprinter become true?