

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

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

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formed were collected into two upside-down beakers that were filled with water. In one beaker, the amount of water displaced by the gas was two times the amount displaced in the other beaker.

- a) Write the equations for the half-reactions for both the anode and cathode. Write the equation for the overall reaction.
- b) Calculate: i) the masses of the substances formed during electrolysis, ii) the amounts of the substances formed during electrolysis.
- c) What products would form (give formulas and names) under the same conditions if  $\text{Na}_2\text{SO}_4$  would be replaced with  $\text{CuSO}_4$ ?

3. A laboratory assistant needed to prepare 500 mL of a solution that contains 0,25 M sulfate ions ( $\text{SO}_4^{2-}$ ). For that, she could use 37,4 g  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ . The solubility of anhydrous aluminium sulfate at 5 °C is 31,7 g/100 ml water and at 20 °C it is 36,4 g/100 ml water.

- a) Give the systematic name for  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ . To which sub-class of salts does this compound belong?
- b) How many grams of  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  should the assistant take to prepare a solution of sulfate ions at the desired concentration? How many grams of salt will be left unused?
- c) How many moles of aluminium sulfate should the assistant dissolve in 0,25 dm<sup>3</sup> water in order to get a saturated solution of  $\text{Al}_2(\text{SO}_4)_3$  at 20 °C? How many grams of salt will precipitate upon cooling this solution to 5 degrees?

4. The molecules of the explosive **X** contain the elements **A** (37,8%), **B** (16,2%), **C** (43,2%) and **D**. A molecule consisting only of **A** is the main component of air. **B** can be found in every organic compound. **C** is the most abundant element in the crust. The molar mass of **X** is 222,1 g/mol.

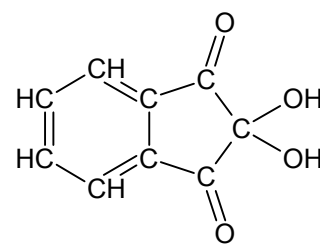
There are only bonds between **A-A**, **A-B**, **B-D** and **A-C** in a molecule of **X**; each atom of **A** bonds to three other atoms and there is one ring comprising of six atoms. The decomposition of **X** can be described with a simplified chemical equation with three products. Two of the products are diatomic gases, one of which consists of the element **A** and the other of the elements **B** and **C**. The third product is a triatomic fluid (at room temperature).

- a) Give the symbols and names for the elements **A**, **B**, **C** and **D**.
- b) Find by calculation i) the empirical formula of **X** and ii) the molecular formula of **X**.
- c) Write the balanced chemical equation for the decomposition of **X**.
- d) Draw the structural formula for **X**.

5. Precisely half a litre of a mixture of gases (at standard conditions) comprised of two substances: **A** and **B**. **A** is an acyclic alkane and there is 8,93 mmol of **A** in the mixture. **B** does not contain hydrogen. The mixture was ignited after adding 1,857 g of oxygen. When the reaction was complete, only two substances were left in the mixture: 0,804 g of water and 2,16 g of carbon dioxide.

- a) Calculate the molecular formula of **A**.
- b) Draw all possible structural formulas that correspond to the molecular formula for **A**.
- c) Give the formula for **B**. Explain your reasoning.
- d) Calculate the ratio of the density of the original mixture (**A+B**) and the density of helium.

6. Ninhydrin is a colourless organic substance (structural formula given on the figure) that reacts easily with primary amines giving a product that is coloured dark blue. For this reason, solutions of ninhydrin are used in criminal investigations for revealing fingerprints on surfaces.



- a) In which biological macromolecules (biopolymers) inside the human body can primary amine groups be found?
- b) Give two reasons for using solutions of ninhydrin in ethanol or acetone instead of aqueous solutions.
- c) Mari, an investigator, uses a solution of ninhydrin for revealing fingerprints. This solution can be produced by dissolving 0,50 grams of ninhydrin in exactly 100 ml of ethanol (the density of ethanol is 0,789 g/cm<sup>3</sup>). In this solution, calculate for ninhydrin: **i)** the mass percentage; **ii)** the molar concentration; **iii)** the mole fraction. Assume that the densities of the solution and the solvent are equal.
- d) What kind of protection equipment must Mari use when she is spraying the solution of ninhydrin onto a surface under investigation?



3. a)  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  – aluminium sulfate-water (1/18) or aluminium sulfate octadecahydrate

Sub-class of salts – hydrates

$$\text{b) } n(\text{SO}_4^{2-}) = 500 \text{ ml} \cdot \frac{1 \text{ dm}^3}{1000 \text{ ml}} \cdot 0,25 \text{ mol/dm}^3 = 0,125 \text{ mol}$$

$$n[\text{Al}_2(\text{SO}_4)_3] = \frac{0,125 \text{ mol}}{3} = 0,0417 \text{ mol}$$

$$M[\text{Al}_2(\text{SO}_4)_3] = 2 \cdot 27,0 + 3 \cdot 32,1 + 3 \cdot 4 \cdot 16,0 = 342,3 \text{ g/mol}$$

$$M[\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}] = 342,3 + 18 \cdot (2 \cdot 1,01 + 16,0) = 666,7 \text{ g/mol}$$

$$m[\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}] = 0,0417 \text{ mol} \cdot 666,7 \text{ g/mol} = 27,8 \sim \mathbf{28 \text{ g}}$$

$$m[\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O, unused}] = 37,4 - 27,8 = \mathbf{9,6 \text{ g}}$$

$$\text{c) } m[\text{Al}_2(\text{SO}_4)_3] = 0,25 \text{ dm}^3 \cdot \frac{1000 \text{ ml}}{1 \text{ dm}^3} \cdot \frac{36,4 \text{ g}}{100 \text{ ml}} = 91 \text{ g}$$

$$n[\text{Al}_2(\text{SO}_4)_3] = \frac{91 \text{ g}}{342,3 \text{ g/mol}} = \mathbf{0,27 \text{ mol}}$$

$$m[\text{Al}_2(\text{SO}_4)_3, \text{ precipitated}] = 91 \text{ g} - 0,25 \text{ dm}^3 \cdot \frac{1000 \text{ ml}}{1 \text{ dm}^3} \cdot \frac{31,7 \text{ g}}{100 \text{ ml}} = 11,75 \sim \mathbf{12 \text{ g}}$$

4. a) **A** – N, nitrogen; **B** – C, carbon; **C** – O, oxygen; **D** – H, hydrogen.

b) i) If we take precisely 100 g of **X**, it contains

$$n(\text{N}) = 100 \text{ g} \cdot 0,378 \cdot \frac{1 \text{ mol}}{14,01 \text{ g}} \approx 2,70 \text{ mol}$$

$$n(\text{C}) = 100 \text{ g} \cdot 0,162 \cdot \frac{1 \text{ mol}}{12,01 \text{ g}} \approx 1,35 \text{ mol}$$



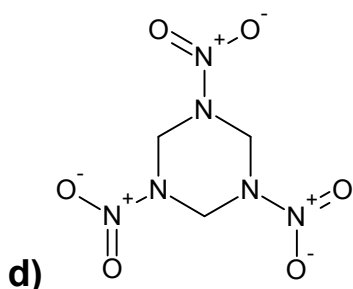
$$n(\text{O}) = 100 \text{ g} \cdot 0,432 \cdot \frac{1 \text{ mol}}{16,00 \text{ g}} = 2,70 \text{ mol}$$

$$n(\text{H}) = 100 \text{ g} \cdot (1 - 0,378 - 0,162 - 0,432) \cdot \frac{1 \text{ mol}}{1,008 \text{ g}} \approx 2,78 \text{ mol}$$

$$\frac{n(\text{N})}{n(\text{C})} \approx \frac{n(\text{O})}{n(\text{C})} \approx \frac{n(\text{H})}{n(\text{C})} \approx 2, \text{ thus the empirical formula is } \text{CH}_2\text{N}_2\text{O}_2.$$

ii) Since  $\frac{222,1 \text{ g/mol}}{(12,01 + 2 \cdot 1,008 + 2 \cdot 14,01 + 2 \cdot 16,00) \text{ g/mol}} \approx 3$ , the molecular

formula must be  $\text{C}_3\text{H}_6\text{N}_6\text{O}_6$ .



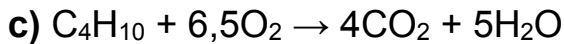
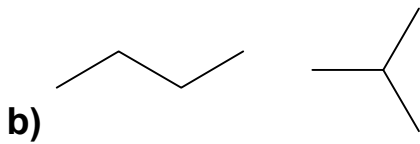
5. a) Since B does not contain hydrogen, all of the water was produced from A.

$$n(\text{H-atoms}) = (0,804 \text{ g} / 18,0 \text{ g/mol}) \cdot 2 = 89,3 \text{ mmol}$$

The amount of H-atoms in a molecule of A:

$$n(\text{H-atoms}) / n(\text{A}) = 89,3 \text{ mmol} / 8,93 \text{ mmol} = 10$$

Since the alkane is acyclic, 4 carbon atoms correspond to 10 hydrogen atoms:  **$\text{C}_4\text{H}_{10}$** .



The oxygen added to the mixture:  $n(O_2) = 1,857 \text{ g} / 32,0 \text{ g/mol} = 58,0 \text{ mmol}$

The oxygen used for the combustion of A:

$$n(O_2) = 8,93 \text{ mmol} \cdot 6,5 = 58,0 \text{ mmol}$$

Therefore all of the oxygen was used for the combustion of the alkane, thus B is incombustible. Since after the reaction was complete only carbon dioxide was left in addition to water, B must be carbon dioxide - **CO<sub>2</sub>**.

d)  $n(\text{gas}) = 0,500 \text{ L} / 22,4 \text{ L/mol} = 22,3 \text{ mmol}$

$$X(C_4H_{10}) = 8,93 \text{ mmol} / 22,3 \text{ mmol} = 0,400$$

$$X(CO_2) = (22,3 \text{ mmol} - 8,93 \text{ mmol}) / 22,3 \text{ mmol} = 0,600$$

$$M(A+B \text{ mixture}) = 0,400 \cdot 58,1 \text{ g/mol} + 0,600 \cdot 44,0 \text{ g/mol} = 49,6 \text{ g/mol}$$

$$M(\text{He}) = 4,00 \text{ g/mol}$$

$$\text{Relative density of the original mixture: } 49,6 \text{ g/mol} / 4,00 \text{ g/mol} = \mathbf{12,4}.$$

## 6. a) Protein

b) Ninhydrin does not solve to a great extent in water at room temperature (max. 0,1-0,5 g / 100 ml water). In addition, the image of the fingerprint should be as sharp as possible, however many proteins are soluble in water.

$$w = \frac{0,50 \text{ g}}{0,50 \text{ g} + 100 \text{ cm}^3 \cdot 0,789 \text{ g/cm}^3} \cdot 100\% = 0,63\%$$

c) i)

**ii)**  $M(\text{ninhydrin}) = 9 \cdot 12,0 + 6 \cdot 1,01 + 4 \cdot 16,0 = 178 \text{ g/mol}$

$$c = \frac{0,50 \text{ g}}{178 \frac{\text{g}}{\text{mol}} \cdot 100 \text{ ml}} \cdot 1000 \frac{\text{ml}}{\text{l}} = 0,028 \frac{\text{mol}}{\text{l}}$$

**iii)**  $n(\text{ninhydrin}) = 0,50 \text{ g} : 178 \text{ g/mol} = 0,0028 \text{ mol}$

$$M(\text{ethanol}) = 2 \cdot 12,0 + 6 \cdot 1,01 + 16,0 = 46,1 \text{ g/mol}$$

$$n(\text{ethanol}) = 100 \text{ cm}^3 \cdot 0,789 \text{ g/cm}^3 : 46,1 \text{ g/mol} = 1,71 \text{ mol}$$

$$x = 0,0028 \text{ mol} : (0,0028 + 1,71 \text{ mol}) = 0,0016$$

**d)** Gloves, coat, goggles.

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

### Problems

- a)** Draw all possible isomers of  $C_3H_2BrCl$ .

**b)** The molar mass of **X** is 104. Find the molecular formula and spatial structure for **X** if it has been established that it contains no double bonds and it has three planes of symmetry.
- The structures of alcohols can be derived by replacing one or more hydrogens with hydroxyl groups in hydrocarbons. The simplest alcohol is methanol, which is produced by reducing carbon monoxide with hydrogen at the presence of a catalyst (**reaction 1**). Another common alcohol is ethanol. The main production methods for ethanol are hydration of ethene (**reaction 2**) and fermenting sacharides. The hydroxyl group of alcohols is weakly acidic and reacts with active metals (**reaction 3**). Reactions between carboxylic acids and alcohols produce esters.

**a)** Write the reactions for the complete combustion of **i)** methanol and **ii)** ethanol.

**b)** Write and balance **reactions 1-3**. For **reaction 3**, pick the alcohol and a suitable metal yourself.

**c)** Write and balance the reaction for the fermentation of glucose.

**d)** Using structural formulas, write the reaction between 3,3-dimethylpentanoic acid and 2-methylpropan-2-ol. Give the name of the product.
- Element **X** is one of the most abundant chemical elements in the nature and it is found in substances **A-G**. Oxide **A** is a colourless gas that forms oxide **B** upon reacting with oxygen (**i**). **B** can react with ozone (**ii**) and form oxide **C**. Upon solving oxide **D** in water (**iii**), a weak acid **E** is formed. **A**

does not form acids, however **B** reacts with water (**iv**), producing a mixture of two acids **E** and **F**. Oxides **A** and **B** can react (**v**), producing one of the aforementioned oxides. Acid **F** can be produced from a reaction (**vi**) of one of the aforementioned oxides, water and oxygen. Finally, the fifth oxide **G** of element **X** is used as a stimulant of the nervous system.

a) Write the names and formulas of all substances **A-G**.

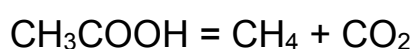
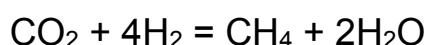
b) Write the balanced equations for reactions **i-vi**.

4. **A** is a soft grey metal that produces a dark red colour in a flame test. The oxide **B** of metal **A** is a white solid that can be found in cement. Oxide **B** can also be produced by heating the main component **C** of limestone at more than 825°C (**reaction 1**). **B** reacts with water, producing the base **D** (**reaction 2**). **D** reacts with the gaseous substance **E<sub>2</sub>**, producing two salts of the metal **A** – **F** (the oxidation number of **E** is 1) and **G** (the ox. number of **E** is -1) – and water (**reaction 3**). **E<sub>2</sub>** is a gas that is 2,45 times more dense than air. **F** is used as bleach and as disinfectant. If the strong acid **H** (which contains **E**) is added to **F**, salt **G**, water and gas **E<sub>2</sub>** are formed (**reaction 4**).

a) Write i) the formulas and names for substances **A-H**; ii) the common names for substances **B**, **D** and **H**.

b) Write and balance reactions **1-4**.

5. Methanogens are micro-organisms that obtain the energy necessary to support their life from enzyme-catalyzed reactions that produce methane:



Methanogens can be found in the digestive systems of ruminant animals;

a cow can emit 200 litres of methane in a day, for example. Methanogens are also thought to live in the digestive systems of fire-emitting dragons. There is a special methane container in a dragon's body; the expulsion and ignition of the methane from that container causes the emission of fire.

- a) Which elements in the given formation reactions of methane are reducing and which are oxidising agents?
- b) Calculate the enthalpy change for both formation reactions of methane. The enthalpy of formation for water is  $-286 \text{ kJ/mol}$ , the enthalpy of combustion is  $-890 \text{ kJ/mol}$  for methane and  $-875 \text{ kJ/mol}$  for ethanoic acid.
- c) Write the equation for the combustion of methane. Calculate the amount of heat released upon the combustion of 200 litres of methane ( $25 \text{ }^\circ\text{C}$ ,  $R = 8,314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ).
- d) Compare methanol and methane with respect to the heat released upon the combustion of the same amount (in moles) of each substance.

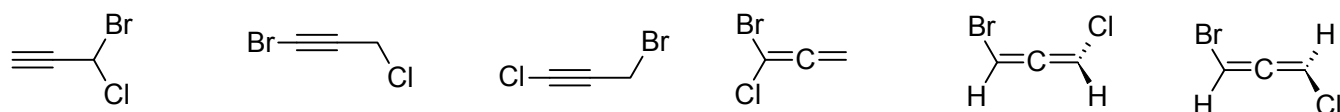
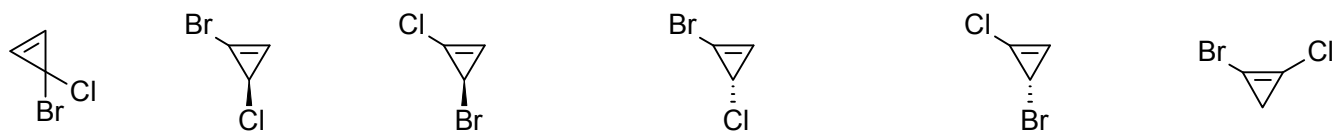
6. Phenol ( $\text{C}_6\text{H}_5\text{OH}$ ) is a weak acid in aqueous solutions and pyridine ( $\text{C}_5\text{H}_5\text{N}$ ) is a weak base. The equilibrium constant for the dissociation reaction of phenol is  $K_a = 1,3 \cdot 10^{-10}$  (**reaction 1**) and the equilibrium constant for the reaction between pyridine and hydrogen ion  $K_b = 1,5 \cdot 10^{-9}$  (**reaction 2**).

- a) Write **reactions 1 and 2** and expressions for the corresponding equilibrium constants.
- b) Write the reaction between pyridine and phenol. Write the corresponding expression for the equilibrium constant.
- c) Find the value of the equilibrium constant for the reaction between pyridine and phenol.
- d) When  $9,4 \text{ g}$  of phenol is solved in  $1 \text{ litre}$  of water, a weakly basic solution results. Find the pH of this solution.
- e) This solution is mixed with  $1 \text{ litre}$  of  $0,1 \text{ M}$  pyridine solution. Find the con-

centrations of the pyridinium ion ( $C_5H_5NH^+$ ) and phenolate ion ( $C_6H_5O^-$ ). Assume that no volume contraction occurs upon mixing solutions.

## Solutions

1. a)



b) Since a hydrocarbon consists of only hydrogen and carbon and a saturated hydrocarbon with  $x$  atoms ( $C_xH_{2x+2}$ ) contains a maximum of  $2x+2$  atoms of hydrogen, we get the following system of equations:

$$12x + y = 104$$

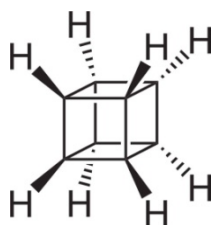
$$y \leq 2x + 2$$

$$104 - 12x \leq 2x + 2$$

$$102 \leq 14x$$

$$x \geq 7.3$$

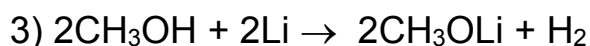
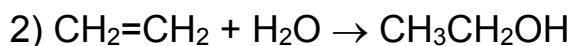
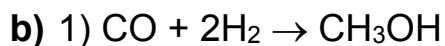
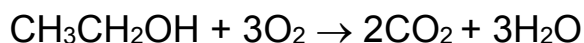
Therefore the hydrocarbon must contain exactly 8 atoms of carbon – for 9 carbons, the molar mass would be greater than 104 and for 7 carbons, there would not be enough hydrogen atoms to have a molar mass of 104.



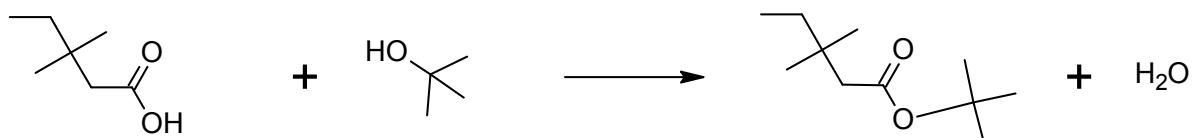
Since there are three planes of symmetry, the shape of the molecule must be highly symmetric and a molecule with cubic structure, cubane,



fits all the criteria.



d) (1,1-dimethyl)ethyl-3,3-dimethylpentanoate, (2-methylprop-2-yl)-3,3-dimethylpentanoate or tert-butyl-3,3-dimethylpentanoate



3. a) **A** – NO – nitric oxide

**B** – NO<sub>2</sub> – nitrogen dioxide

**C** – N<sub>2</sub>O<sub>5</sub> – dinitrogen pentoxide

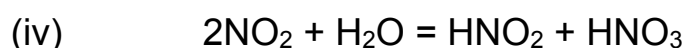
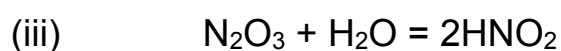
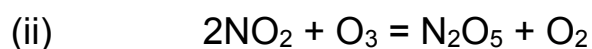
**D** – N<sub>2</sub>O<sub>3</sub> – dinitrogen trioxide

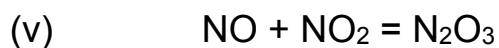
**E** – HNO<sub>2</sub> – nitrous acid

**F** – HNO<sub>3</sub> – nitric acid

**G** – N<sub>2</sub>O – nitrous oxide

b)





**4. a) i)**

**A** = Ca, calcium

**B** = CaO, calcium oxide

**C** = CaCO<sub>3</sub>, calcium carbonate

**D** = Ca(OH)<sub>2</sub>, calcium hydroxide

**E**<sub>2</sub> = Cl<sub>2</sub>, chlorine

**F** = Ca(OCl)<sub>2</sub>, calcium hypochlorite

**G** = CaCl<sub>2</sub>, calcium chloride

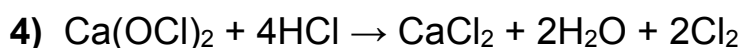
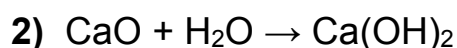
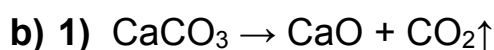
**H** = HCl, hydrochloric acid

ii)

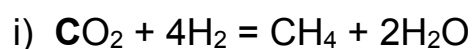
**B** – quicklime or burnt lime

**D** – slaked lime

**H** – [Estonian synonym for hydrochloric acid – TP]



**5. a) oxidising agents and reducing agents:**



**b)** Calculate through enthalpies of combustion (since upon the combustion of hydrogen one mole of hydrogen produces one mole of water, the enthalpy of formation of water is equal to the enthalpy of combustion of hydrogen).



reaction i:  $\Delta H^\circ = 4 \cdot (-286 \text{ kJ/mol}) - (-890 \text{ kJ/mol}) = \mathbf{-254 \text{ kJ/mol}}$

reaction ii:  $\Delta H^\circ = -875 \text{ kJ/mol} - (-890 \text{ kJ/mol}) = \mathbf{15 \text{ kJ/mol}}$

**c)**  $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$

$n = 101325 \text{ Pa} \cdot 0,200 \text{ m}^3 / (8,314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \cdot 298 \text{ K}) = 8,18 \text{ mol}$  of methane

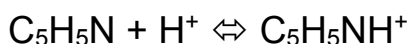
$\Delta H = 8,18 \text{ mol} \cdot (-890 \text{ kJ/mol}) = \mathbf{-7280 \text{ kJ}}$

**d)** Since carbon is more oxidised in methanol than it is in methane and the amounts of carbon are equal for both substances, the heat released upon the burning of methanol is smaller (the enthalpy of combustion of gaseous methanol is -764 kJ/mol).

**6. a)**



$$K_1 = \frac{[\text{C}_6\text{H}_5\text{O}^-] \cdot [\text{H}^+]}{[\text{C}_6\text{H}_5\text{OH}]}$$



$$K_2 = \frac{[\text{C}_5\text{H}_5\text{NH}^+]}{[\text{C}_5\text{H}_5\text{N}] \cdot [\text{H}^+]}$$

**c)**  $\text{C}_5\text{H}_5\text{N} + \text{C}_6\text{H}_5\text{OH} \rightleftharpoons \text{C}_5\text{H}_5\text{NH}^+ + \text{C}_6\text{H}_5\text{O}^-$

$$K_3 = \frac{[\text{C}_5\text{H}_5\text{NH}^+] \cdot [\text{C}_6\text{H}_5\text{O}^-]}{[\text{C}_5\text{H}_5\text{N}] \cdot [\text{C}_6\text{H}_5\text{OH}]}$$

$$K_3 = \frac{[C_5H_5NH^+][C_6H_5O^-] \cdot [H^+]}{[C_5H_5N][C_6H_5OH] \cdot [H^+]} = \frac{[C_5H_5NH^+][C_6H_5O^-] \cdot [H^+]}{[C_5H_5N][H^+][C_6H_5OH]} = K_2 \cdot K_1 = 1.95 \cdot 10^{-19}$$

d)  $n(\text{phenol}) = m(\text{phenol}) / M(\text{phenol}) = 9.4 \text{ g} / 94 \text{ g/mol} = 0.1 \text{ mol}$

$$c(\text{phenol}) = n/V = 0.1 \text{ M}$$

Assume that upon the dissociation of phenol the amount of  $H^+$  ions generated is  $x$  (the unit of  $x$  is M):  $[H^+] = x$

$[C_6H_5OH] = 0.1 - x$  and  $[C_6H_5O^-] = [H^+] = x$ , thus

$$K_1 = \frac{[C_6H_5O^-][H^+]}{[C_6H_5OH]} = \frac{x \cdot x}{0.1 - x} = 1.3 \cdot 10^{-10}$$

$$x^2 + 1.3 \cdot 10^{-10} \cdot x - 1.3 \cdot 10^{-11} = 0$$

$$x = 3.6 \cdot 10^{-6}$$

$$pH = -\log[H^+] = 5.44$$

e) After mixing the solutions:

$$c(\text{phenol}) = c(\text{pyridine}) = 0.05 \text{ M}$$

Stoichiometry of the reaction:  $[C_5H_5NH^+] = [C_6H_5O^-] = x$  and

$$[C_5H_5N] = [C_6H_5OH] = 0.05 - x$$

$$K_3 = \frac{[C_5H_5NH^+][C_6H_5O^-]}{[C_5H_5N][C_6H_5OH]} = \frac{x \cdot x}{(0.05 - x) \cdot (0.05 - x)} = 1.95 \cdot 10^{-19}$$

$$x^2 = 1.95 \cdot 10^{-19} \cdot x^2 - 1.95 \cdot 10^{-20} \cdot x + 4.875 \cdot 10^{-22}$$

$$x = 2.21 \cdot 10^{-11} \text{ M}$$

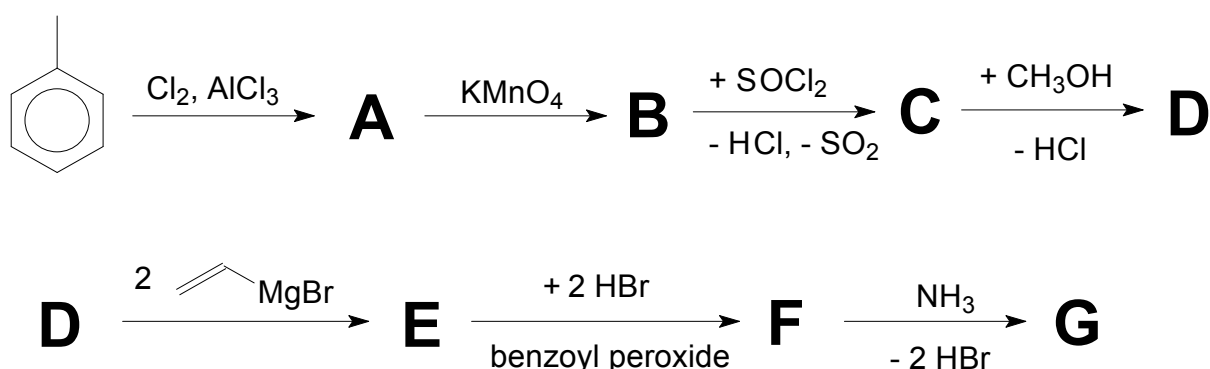
## 11<sup>th</sup> grade

### Problems

1. a) Which element forms compounds with itself and with the elements that lie right and left of it in the periodic table? The oxidation number of the element ranges ten different values in these compounds.
- b) Write the corresponding structural formulas and names for these compounds. Each compound may consist of atoms of all three elements.

2. Haloperidol is a well-known medication used for treating mental disorders. It is also used in drug rehabilitation treatments.

One of the reagents for the synthesis of haloperidol is obtained according to the following scheme:



In order to solve this scheme, the following hints have been provided:

- <sup>1</sup>H-NMR data for compound **A**: s(3H)  $\delta = 2.35$  ppm, d(2H) 6.95 ppm, d(2H) 7.2 ppm.
- molecular formula for **B**: C<sub>7</sub>H<sub>5</sub>ClO<sub>2</sub>.
- **D** (M = 170.5) consists of the following elements: 56.3% C, 4.11% H, 20.8% Cl, the rest is O.
- stage **D** – **E**: Grignardi reaction with 2 mol ethenylmagnesium bromide

- stage **E – F**: 2 mol HBr addition according to anti-Markovnikov
- molecular formula for **F**:  $C_{11}H_{13}Br_2ClO$
- stage **F – G**: cyclisation reaction with  $NH_3$ -gas, resulting in a derivative of piperidine

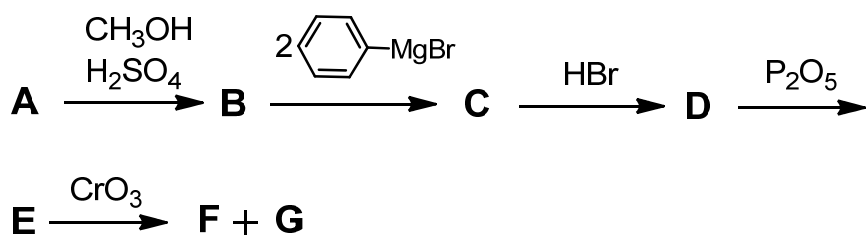
- Write the structural formulas for compounds **A-G**.
- Why is benzoyl peroxide used in stage **E – F**?
- Draw the structural formula of the compound that would be produced in stage **E – F**, had benzoyl peroxide not been used.
- What properties should the solvent used in stage **D – E** have?

3. In the 1920s, the engineer Thomas Midgely and a team of scientists developed an additive **A** ( $M = 323,4$  g/mol, consists of 64,1% of element **X**, 29,7% of element **Y** and 6,2% of element **Z**). The toxicity of **A** caused numerous illnesses and deaths among the workers handling it, however the dangers of the compound was undisclosed. Since the usage of **A** led to a worldwide contamination with the element **X** and at the same time intoxicated the catalytic converters of cars, using **A** in fuels is prohibited since the end of the 20<sup>th</sup> century.

**A** is produced industrially using a compound **B** that comprises of atoms of three elements (37,2% **Y** and 7,8% **Z**) and the alloy of metal **X** with sodium; metallic **X** and a Na salt form as by-products. In a laboratory, **A** can be prepared in a reaction of **B** with Mg and metal **X** in diethyl ether. In conditions of high temperature, **A** decomposes. In the first step of the decomposition, radicals **C** and **D** are formed. In further steps, **C** decomposes and after several steps produces the metal **X**. It is thought that an oxide **E** that forms upon the oxidation of **X** causes an increase in the detonation resistance by reacting with some of the radicals that take part in fuel combustion. **E** reacts **F** (3,0% **Z**), producing compound **G** and radical **H** (5,9%

**Z**). Upon the addition of **H** to oxide **E**, compound **I** forms. **I** in turn reacts with the radical **H** producing **G** and the oxide **J** (water). Upon the reduction of **G**, compound **E** forms.

- a) Write the symbols for elements **X**, **Y** and **Z** and the formulas for compounds **A-G**.
- b) Write balanced equations for the following reactions: i)  $\text{NaX} + \text{B} \rightarrow \text{A} + \text{X} + \dots$ ; ii)  $\text{B} + \text{X} + \text{Mg} \rightarrow \text{A} + \dots$ ; iii)  $\text{A} \rightarrow \text{C} + \text{D}$ ; iv)  $\text{E} + \text{F} \rightarrow \text{G} + \text{H}$ ; v)  $\text{H} + \text{E} \rightarrow \text{I}$ ; vi)  $\text{I} + \text{H} \rightarrow \text{J} + \text{G}$
- c) Two molecules of **D** can react and give stable products by two different processes (reactions). Write equations for those two possible reactions.
- d) Another important discovery Thomas Midgley made was related to using a new type of compounds as refrigerants. These compounds, too, caused large-scale environmental problems in the atmosphere. Name the group of compounds.
4. The abundance of carboxylic acids with an even number of C atoms differs from the abundance of those with an odd number of C atoms. Caprylic acid (C8), for example, can be produced from coconut oil, however there is not as much acid with seven carbon atoms in the nature. To synthesize this 7-carbon acid, the method of Barbier-Wieland degradation for aliphatic acids (shown on the scheme) can be used. The acid **F** (24,6% O) has an unbranched carbon chain. Upon reaction with  $\text{CrO}_3$ , the oxidative dissociation of multiple bonds takes place (in both **F** and **G**, the oxidation number of carbon grows as much as possible). **G** contains 8,8% O.



- a) Find the structure of **F**.
- b) Write i) the structural formulas for compounds **A-G** and ii) the systematic name for **A, D, F** and **G**.

5. Among of the most important metal-organic compounds are Grignard reagents with general formula R-Mg-X (the actual structure is more complicated). They are named after the scientist who discovered the reagents. Victor Grignard (1871-1935), a French chemist, received the Nobel prize in 1912 for discovering magnesium-organic reagents of this kind. Great care must be taken when making a Grignard reagent, since the reagent is a strong base. For this reason, it is synthesized immediately before using and often the following reaction is conducted in the same flask where the reagent was synthesized.

- a) i) Write the equation for the synthesis of  $\text{CH}_3\text{CH}_2\text{MgBr}$ . ii) Should the reaction be conducted in an inert environment? Give reasons.
- b) Grignard reagents react well with carbons in carbonyl groups. Write the mechanism for a reaction where a Grignard reagent (use  $\text{CH}_3\text{CH}_2\text{MgBr}$ ) reacts with the carbon in the acetone carbonyl group.
- c) What should you add to the reaction mixture in order to get a stable product? What would happen if the last step was conducted right after the Grignard reagent has been produced (write the equation for this reaction)?
- d) What would be the product of the reaction in which a solution of  $\text{CH}_3\text{CH}_2\text{MgBr}$  is added to dry ice?



**6.** 0,247 grams of a pure alkane was burned. The gases that formed were piped into 100 mL of 5%  $\text{Ba}(\text{OH})_2$  solution. A white precipitate formed. After filtering and drying the precipitate was found to weigh 3,356 grams.

**a)** Which alkane was it?

Three consecutive gaseous alkenes (i.e. with the amount of carbon atoms in consecutive alkenes differing by one) were burned. The volume of the gas produced was three times the volume of the original mixture of the alkanes.

**b)** Which alkenes were in the mixture? Find the mass percentages of the gases in the mixture.

## Solutions

1.

I  $\text{N}_2\text{O}$  nitrous oxide

II  $\text{N}=\text{O}$  nitric oxide

III  $\text{C}(\text{NO}_2)_4$  tetranitromethane or  $\text{N}_2\text{O}_3$  dinitrogen trioxide

IV  $\text{NO}_2$  nitrogen dioxide

V  $\text{N}_2\text{O}_5$  dinitrogen pentoxide

0  $\text{N}_2$  dinitrogen

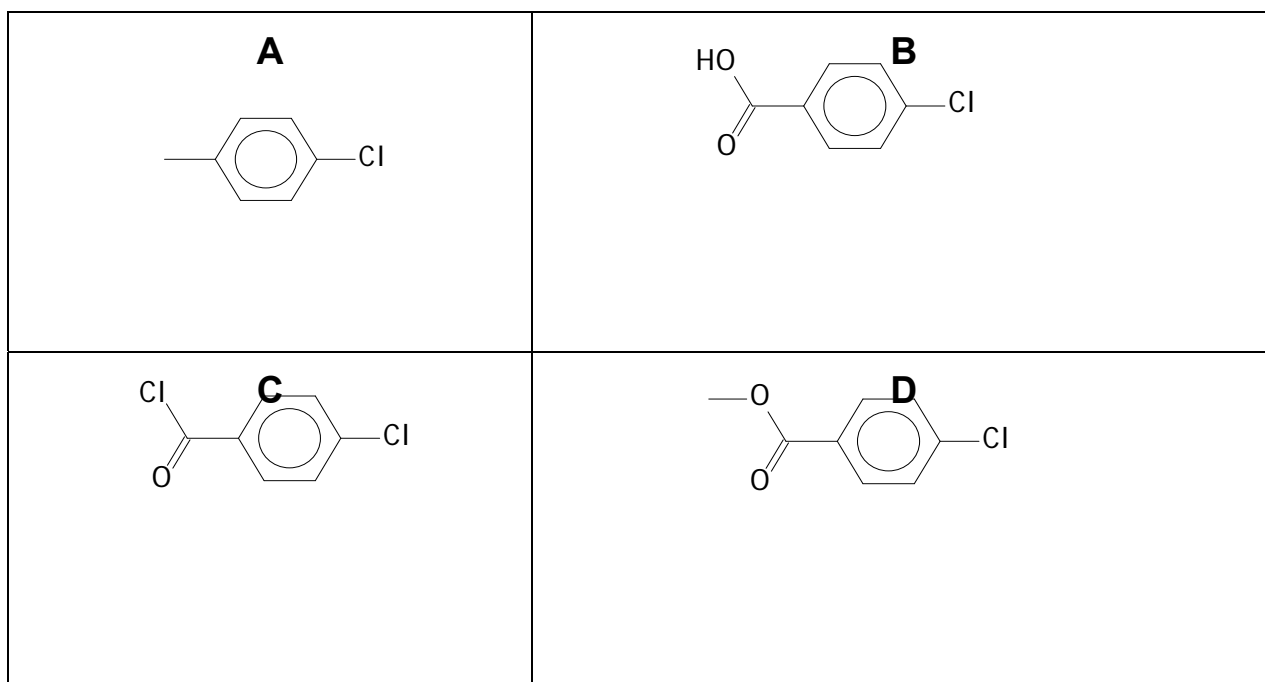
-1/3  $\text{C}(\text{N}_3)_4$  tetraazidomethane

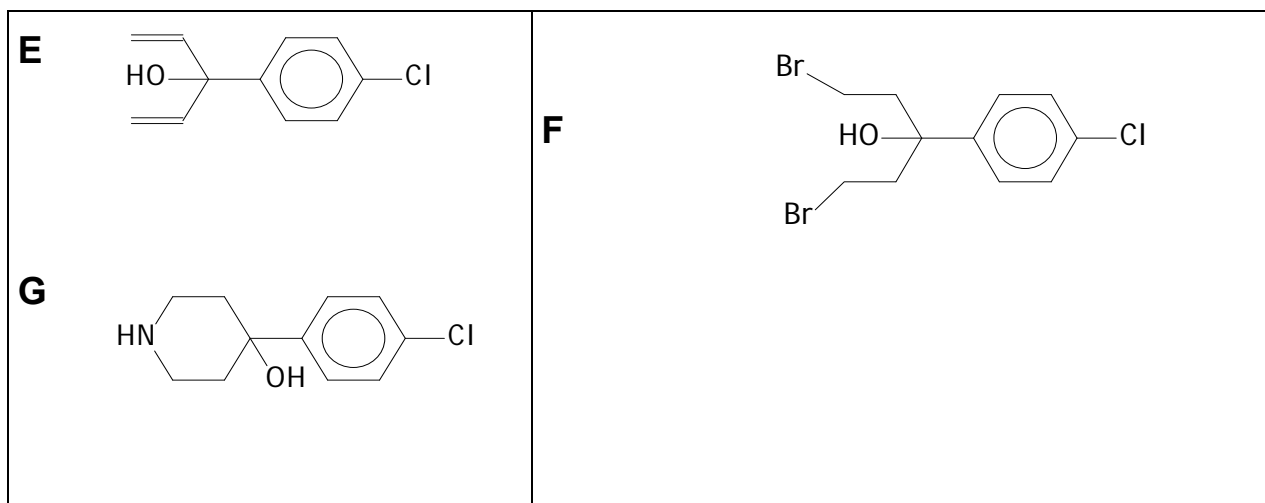
-I  $-\text{O}-\text{CO}-\text{N}=\text{N}-\text{CO}-$  (cyclic compound)

-II  $\text{O}=\text{C}=\text{N}-\text{N}=\text{C}=\text{O}$  diisocyanate

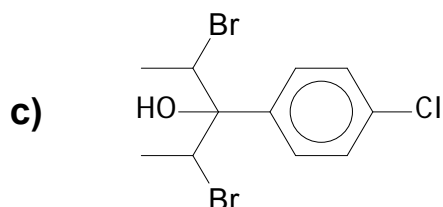
-III  $\text{N}\equiv\text{C}-\text{C}\equiv\text{N}$  dicyan

2. a)



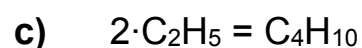
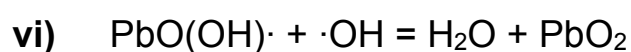
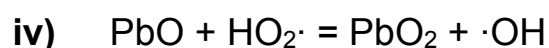
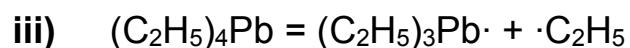
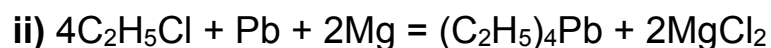
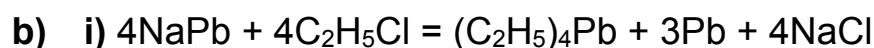


**b)** Benzoyl peroxide is a radical initiator that directs the reaction according to the anti-Markovnikov rule only over radicals.



**d)** The solvent must be an ether solvent and as dry as possible.

**3. a)** **X** – Pb, **Y** – C, **Z** – H, **A** – (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>Pb, **B** – C<sub>2</sub>H<sub>5</sub>Cl, **C** – (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Pb·, **D** – ·C<sub>2</sub>H<sub>5</sub>, **E** – PbO, **F** – HO<sub>2</sub>·, **G** – PbO<sub>2</sub>, **H** – ·OH, **I** – PbO(OH)·, **J** – H<sub>2</sub>O

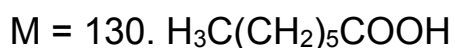




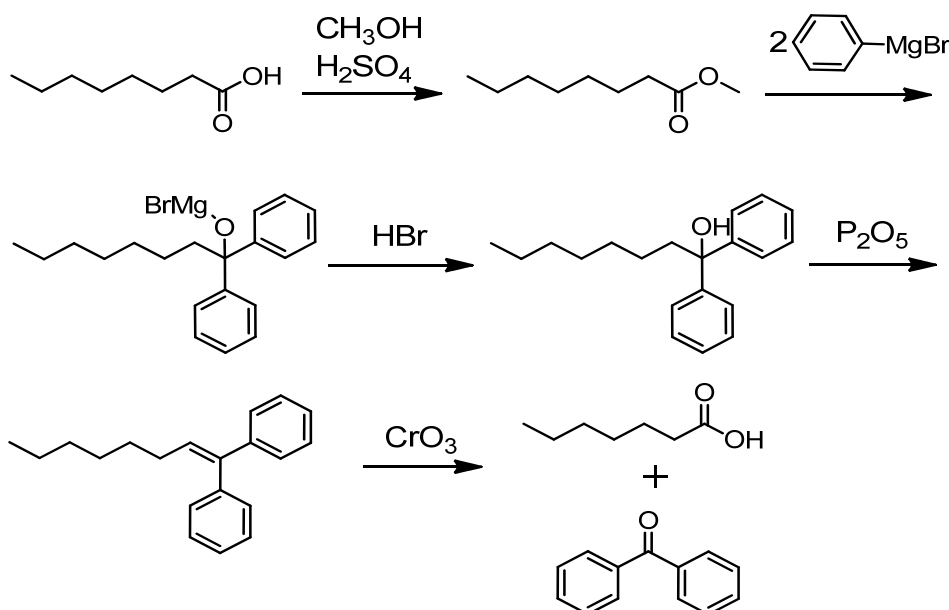
c) Chlorofluorocarbons (freons)

4.

a) Since F is an acid, there must be at least two O in the structure. Therefore

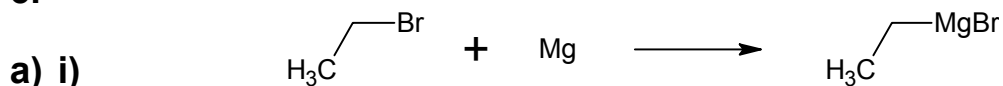


b) i)



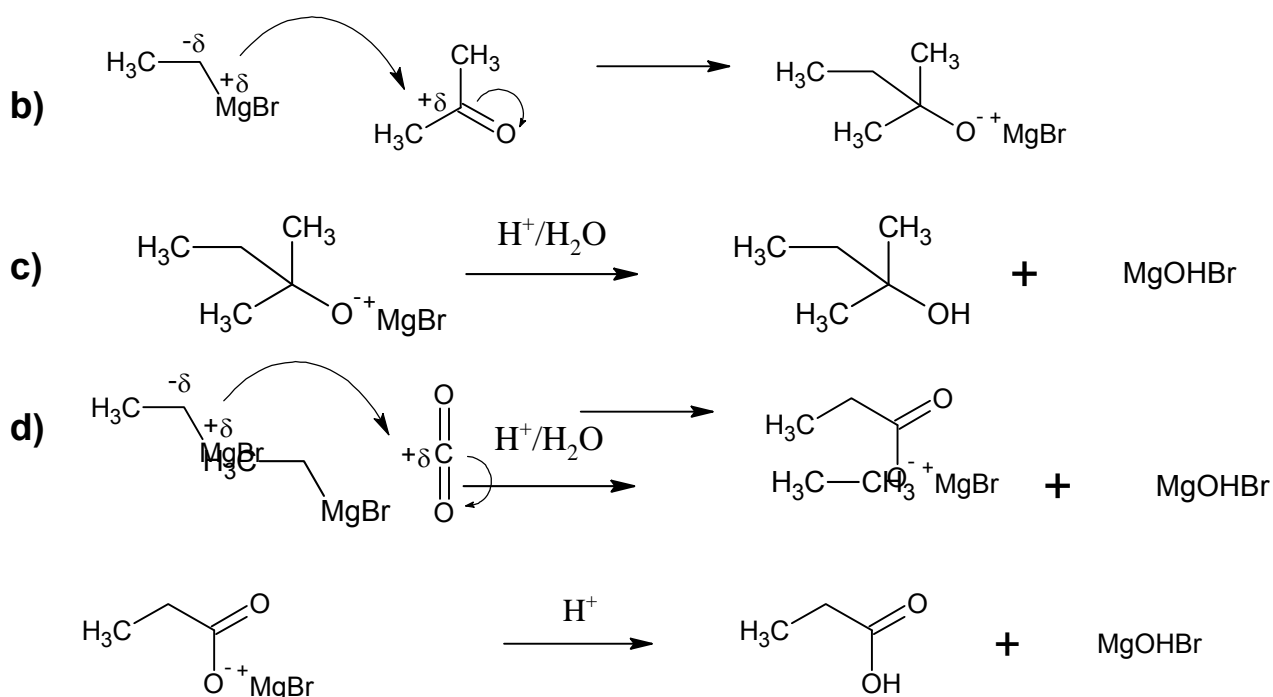
ii) A – octanoic acid, D – 1,1-diphenyloctan-1-ol, F – heptanoic acid, G – diphenylmethanone.

5.



ii) An aprotic solvent that contains no electrophilic centres (for example an ether) should be used. Since the Grignard reagent is a strong base, it would react with protic solvents (acid-base reaction), and with electrophiles like acetone.

iii) The reaction should be conducted in an inert environment since the Grignard reagent reacts with both water and oxygen in air. If small amounts are used, an inert environment is even more important.

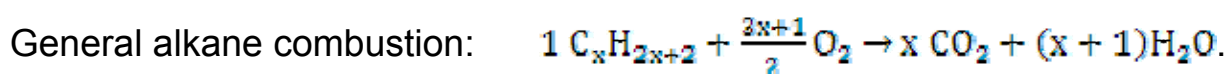


6.

a) The precipitate was  $\text{BaCO}_3$ . Let's prove with calculation that  $\text{Ba(OH)}_2$  was in excess and the amount of precipitate was determined by the amount of  $\text{CO}_2$ . The density of  $\text{Ba(OH)}_2$  5% solution is probably larger than the density of water, thus:

$$n(\text{Ba(OH)}_2) > \frac{100 \text{ g} \cdot 5\%}{100\%} \times \frac{1 \text{ mol}}{(137 + 2 \times (1,01 + 16,00)) \text{ g}} = 29,2 \text{ mmol}$$

$$n(\text{BaCO}_3) = 3,356 \text{ g} \times \frac{1 \text{ mol}}{(137 + 12,0 + 16,0 \times 3) \text{ g}} = 17,04 \text{ mmol} = n(\text{CO}_2)$$



Thus  $n(\text{alkaan}) = \frac{17,04 \times 10^{-3}}{x} \text{ mol}$  (alkaan (ET) = alkane (EN))

$$\text{and } M(\text{alkaan}; \text{g/mol}) = \frac{m}{n} = 0,247; \frac{17,04 \times 10^{-3}}{x} = 12x + (2x + 2).$$

Upon solving the equation we get  $x = 4$ , butane.



Since  $V = \text{konst} \times n$ , (konst (ET) = constant (EN)) the amount of  $\text{CO}_2$  formed must be three times larger than the total amount of gases in the original mixture. Let the total amount of gases in the original mixture be  $n$  mol (therefore  $\frac{n}{3}$  mol of each alkene, because the mixture was equimolar), then the amount of  $\text{CO}_2$  produced was  $3n$  mol. Since upon the combustion of 1 mol  $\text{C}_q\text{H}_{2q}$  the amount of  $\text{CO}_2$  produced is  $q$  mol, we get:

$$n(\text{CO}_2) = 3n = \frac{n}{3}x + \frac{n}{3}y + \frac{n}{3}z$$

Since the alkenes are consecutive:  $x + (x + 1) + (x + 2) = 9$ , thus  $x = 2$ , ethene, propene, butene. Finally, since the mixture is equimolar, the mass ratio is equal to the molar mass ratio (  $28:42:56$  ). Result:  $\frac{28}{126} \times 100\% = 22,2\%$  ethene,  $\frac{42}{126} \times 100\% = 33,3\%$  propene and  $44,4\%$  butene.

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

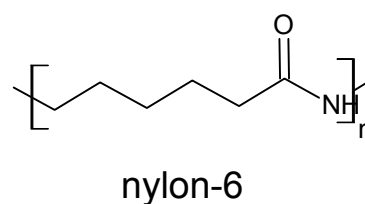
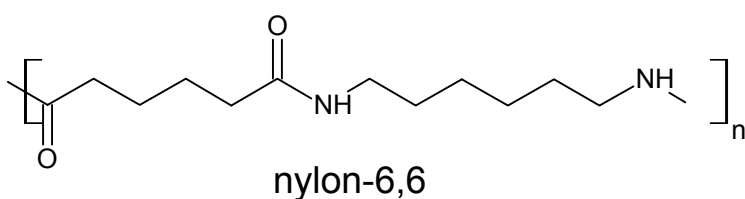
### Problems

1. Mass spectrometry allows us to measure the mass-to-charge ratio of ions. With a good spectral resolution, it's possible to discern ions with different isotopic composition. Upon ionization by bombardment with electrons, bromobenzene produces  $C_6H_5Br^+$ . The natural isotopic occurrence of bromine, carbon and hydrogen are:

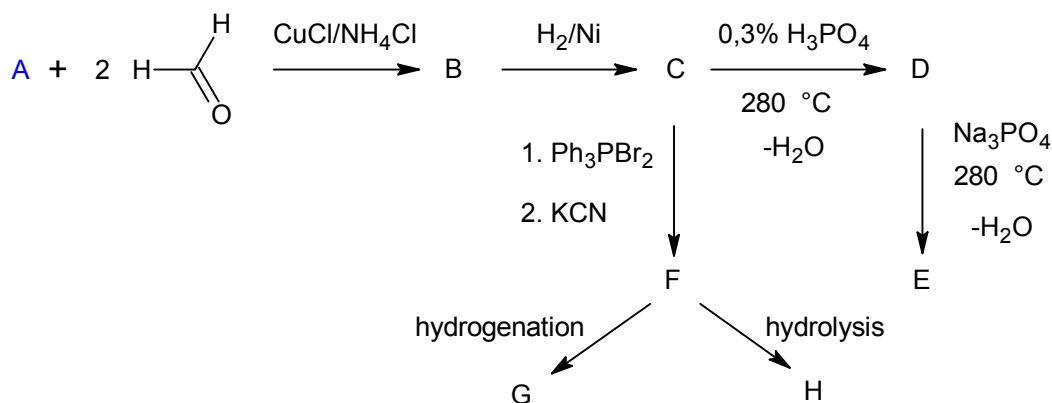
Br: 50,7%  $^{79}Br$  and 49,3%  $^{81}Br$ ; C: 98,9%  $^{12}C$  and 1,1%  $^{13}C$ ; H: 99,99%  $^1H$  and 0,01%  $^2H$ .

- a) How many ions with different isotopic compositions can bromobenzene produce upon ionization? Do not count two ions different if they only differ in geometric configuration.
- b) Which four ions (give the isotopic compositions) are the most abundant if the isotopic composition of each element in the original bromobenzene is the same as in nature?

2. Of polymer fibers, nylons are used the most:



The scheme for the synthesis of nylon-6,6 is:



The polycondensation of **G** and **H** produces nylon-6,6. From **C**, it's possible to produce the cyclic ether **D**, which is often used as a solvent. **E** is a precursor to synthetic rubber. Benzene forms upon the trimerization of **A**. The solution of 2,00 g **C** in 100 grams of water freezes at  $-0,413\text{ }^\circ\text{C}$  [ $K_{kr}(\text{H}_2\text{O}) = 1,86\text{ K}\times\text{kg/mol}$ ]. The compound **C** contains 53,3% carbon and 11,2% hydrogen. **F** contains 66,7% carbon.  $\text{Ph}_3\text{PBr}_2$  is a brominating reagent.

a) By calculation, find the empirical formula for **C**.

b) Draw the structural formulas for compounds **A** - **H**.

Nylon-6 can be produced upon the polymerization of **J**. For the production of **J**, cyclohexanone is reacted with hydroxylamine, producing **I** ( $\text{C}_6\text{H}_{11}\text{NO}$ ). Reacting **I** with oleum, the lactam **J** ( $\text{C}_6\text{H}_{11}\text{NO}$ ) forms.

c) Draw the structural formulas for compounds **I** and **J**.

d) Draw structural formulas for products from the reaction **E** with  $\text{Br}_2$  in carbon tetrachloride.

3. Preparing for an approaching ski marathon, Juku decided to find out in what form he should carry the energy needed to ski 63 kilometres.

a) i) Calculate the heat of combustion (MJ/kg) for i) carbohydrates (glucose), ii) fats (hexadecanoic acid) and iii) proteins (alanine).



Hexadecanoic acid:  $\Delta H_f^0 = -848 \text{ kJ/mol}$  and  $S^0 = 452 \text{ J/(mol K)}$ ;

Glucose:  $\Delta H_f^0 = -1271 \text{ kJ/mol}$  and  $S^0 = 209 \text{ J/(mol K)}$ ;

Alanine ( $\text{C}_3\text{H}_7\text{NO}_2$ )  $\Delta H_f^0 = -560 \text{ kJ/mol}$  and  $S^0 = 119 \text{ J/(mol K)}$ ;

$\text{CO}_2$ :  $\Delta H_f^0(\text{CO}_2) = -394 \text{ kJ/mol}$  and  $S^0 = 214 \text{ J/(mol K)}$ ;

$\text{H}_2\text{O}$ :  $\Delta H_f^0 = -286 \text{ kJ/mol}$  and  $S^0 = 189 \text{ J/(mol K)}$ .

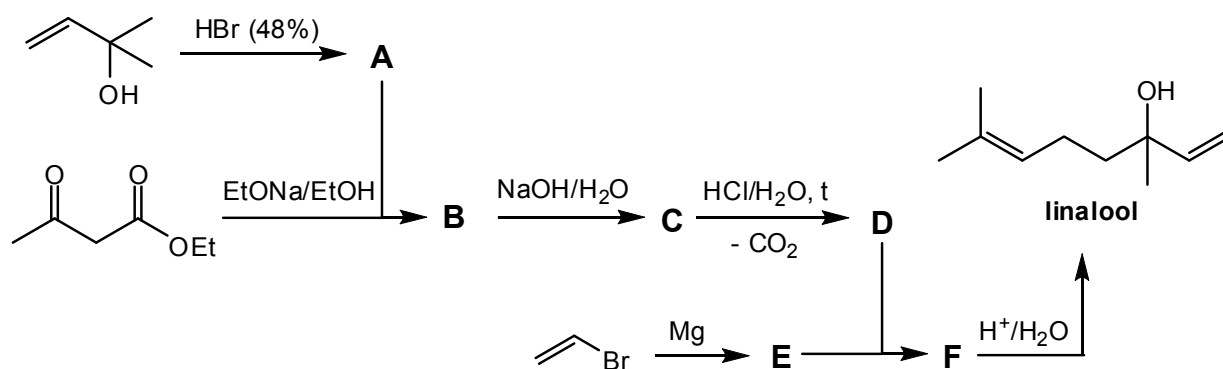
- b) i)** How much energy did Juku use if, over the course of a month, he worked with an average power of  $200 \text{ W}$  (24 % efficiency)? **ii)** How many loafs of bread (320 g, 60% carbohydrates); **iii)** how much lard, **iv)** how much beef jerky should he take? Assume all carbohydrates to be glucose, all fat to be hexadecanoic acid and beef jerky to be 100% alanine.

„To be, or not to be,“ thought Juku to himself after the marathon and calculated the standard entropy change  $\Delta S^0$  and equilibrium constant  $K$  for the complete oxidation of himself.

- c)** Calculate, for the reaction  $\text{Juku} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$ , **i)**  $\Delta S^0$ , **ii)**  $\Delta H^0$ , **iii)**  $\Delta G^0$  and **iv)**  $K$  if Juku weighs 75 kg and consists of approximately 12% fat, 20% protein and 0,4 % carbohydrates. **v)** Why doesn't Juku spontaneously combust?

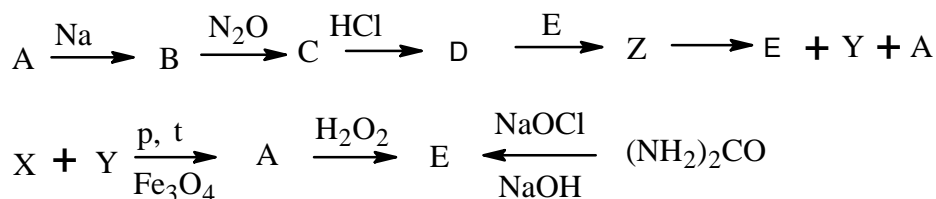
$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = -RT\ln K$$

- 4.** Linalool is a natural ly occurring terpene found, for example, in lemons, grapes and orange oil. Linalool is widely used in the production of per-fumes. The compound can be synthesized using the following scheme:



- Write the structural formulas for compounds **A-F**.
- Write the mechanism for the reaction that produces **A**.
- The class of compounds that contains **E** was named after which famous chemist?

5. Solve the following cascades of reactions. Upon the decomposition of 1.00 mol **Z**, 35,5 litres (standard conditions) of gaseous **Y** is produced. **A** and **E** are weak bases; **X** and **Y** consist of only one element.



- Write the names and formulas for **A-E**, **X**, **Y** and **Z**.
- Write the equations for all of the reactions.

6. A student in Germany studied reactions catalyzed by transition metals. Due to the high price of these catalysts, she had to prepare them herself. To do this, she used the golden-coloured **X** that is insoluble in ordinary acids. She dissolved **X** in a mixture of HCl and HNO<sub>3</sub>, producing **A** and a diatomic gas **B**. **X** reacts with gaseous **C** (density relative to air **2,45**) in an aqueous solution of HCl, producing **A** again. **A** reacts with **2** molecules of dimethyl sulfide at the presence of water (the oxidation number of one sul-

fur increases by two) producing **D**. The complex cation of **D** contains both sulfur and **66,87%** of the metal **X**. In addition, 1 mol of a common organic solvent and 3 mol of a common inorganic acid are produced for every mole of **A**. **D** is the most common precursor for the synthesis of coordination complexes of the metal **X** because the ligand substitution reactions are fast. In order to produce the necessary coordination complex **E**, the student also had to conduct a reaction with triphenylphosphane (**C<sub>6</sub>H<sub>5</sub>**)<sub>3</sub>**P**. Since she was tired, she decided to conduct it the next day and left **D** in a solution overnight. However, in the morning she discovered that there was a yellow precipitate in the solution of **D** and she had to carry out all the reactions again.

- a) Calculate the molar mass and write the formula and name for **C**.
- b) Write names for the metal **X** and the gas **B**.
- c) Write equations for each reaction mentioned above.

## Solutions

1.

a) There is one atom of Br in each molecule, thus there are 2 possible isotopic compositions with respect to bromine. Six carbons can occur in 7 different ways:  $^{12}\text{C}:^{13}\text{C}$  – 6:0, 5:1, 4:2, 3:3, 2:4, 1:5, 0:6. 5 hydrogens can similarly occur in 6 different configurations. So with respect to all three elements there are  $2 \cdot 7 \cdot 6 = 84$  ions with different isotopic configurations.

$$\text{b) } ^{79}\text{Br}-^{12}\text{C}_6^1\text{H}_5^+ \quad m/z=157 \quad p=0.507 \cdot (0,989)^6 \cdot (0,9999)^5 = 0,474$$

$$^{79}\text{Br}-^{12}\text{C}_5^{13}\text{C}_1^1\text{H}_5^+ \quad m/z=158$$

$$p=0,507 \cdot (0,989)^5 \cdot 6 \cdot (0,011)^1 \cdot (0,9999)^5 = 0,032$$

$$^{81}\text{Br}-^{12}\text{C}_6^1\text{H}_5^+ \quad m/z=159 \quad p=0.493 \cdot (0,989)^6 \cdot (0,9999)^5 = 0,461$$

$$^{81}\text{Br}-^{12}\text{C}_5^{13}\text{C}_1^1\text{H}_5^+ \quad m/z=160$$

$$p=0,493 \cdot (0,989)^5 \cdot 6 \cdot (0,011)^1 \cdot (0,9999)^5 = 0,031$$

Therefore the most abundant ion is  $^{79}\text{Br}-^{12}\text{C}_6\text{H}_5^+$  (47,4% of all ions).

$$2. \text{ a) } 0,413 \text{ K} = 1,86 \text{ K} \times \text{kg/mol} \times 2 \text{ g/M}(\text{compound C}) \times 1/0,1 \text{ kg}$$

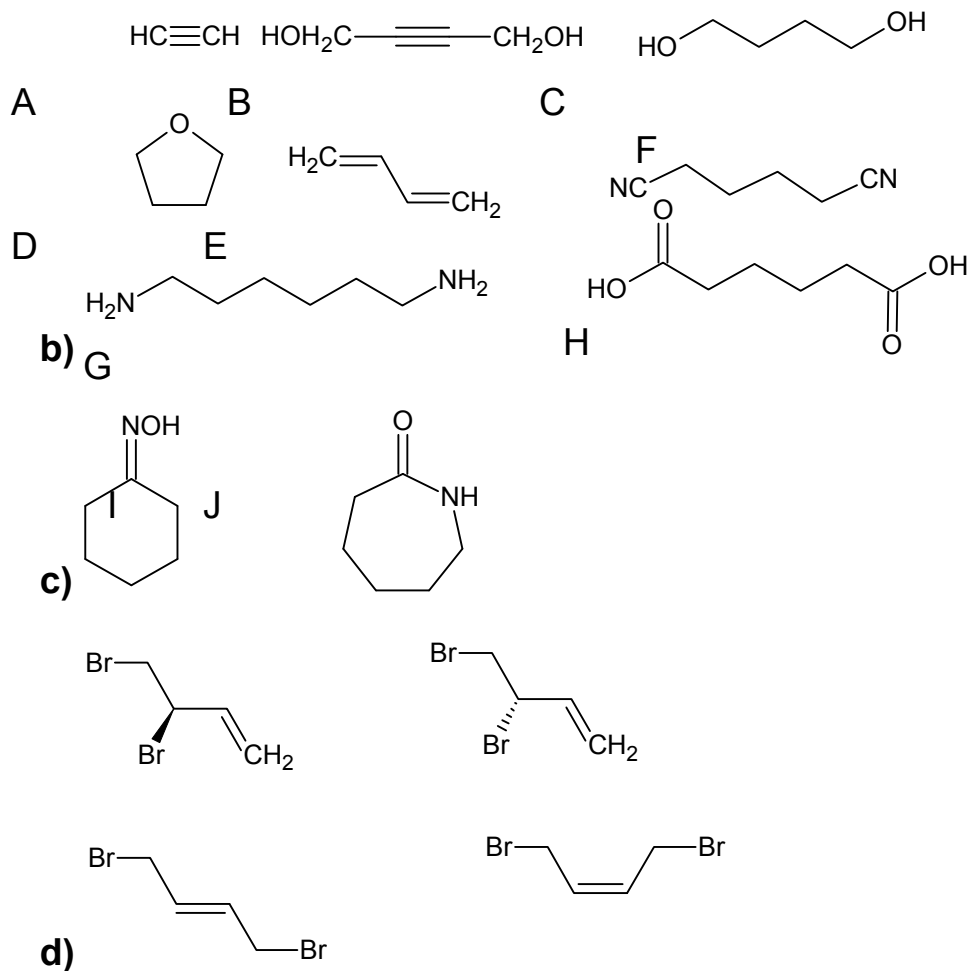
$$M(\text{compound C}) = 1,86 \text{ K} \times \text{kg/mol} \times 2 \text{ g} \times 1/0,1 \text{ kg} \times 1/0,413 \text{ K} = 90,1 \text{ g/mol}$$

$$n(\text{C}) = 90,1 \text{ g} \times 0,533 \times 1 \text{ mol} / 12 \text{ g} = 4 \text{ mol}$$

$$n(\text{H}) = 90,1 \text{ g} \times 0,112 \times 1 \text{ mol} / 1 \text{ g} = 10 \text{ mol}$$

$$n(\text{O}) = 90,1 \text{ g} \times (1 - 0,533 - 0,112) \times 1 \text{ mol} / 16 \text{ g} = 2 \text{ mol}$$

Compound C is  $\text{C}_4\text{H}_{10}\text{O}_2$



**3. a) i) Glucose/carbohydrates:**  $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}$

$$\Delta H_c^0 = 6 \cdot (-286) + 6 \cdot (-394) - (-1271) = -2809 \text{ kJ mol}^{-1} / 180 \text{ g mol}^{-1} \cdot 10^3 \text{ g/kg} = -15,6 \text{ MJ kg}^{-1}$$

**ii) Hexadecanoic acid/fats:**  $\text{C}_{16}\text{H}_{32}\text{O}_2 + 23\text{O}_2 \rightarrow 16\text{CO}_2 + 16\text{H}_2\text{O}$

$$\Delta H_c^0 = 16 \cdot (-286) + 16 \cdot (-394) - (-848) = -10032 \text{ kJ mol}^{-1} / 256,4 \text{ g mol}^{-1} \cdot 10^3 \text{ g/kg} = -39,2 \text{ MJ kg}^{-1}$$

**iii) Alanine/protein:**  $\text{C}_3\text{H}_7\text{NO}_2 + 3,75\text{O}_2 \rightarrow 3\text{CO}_2 + 3,5\text{H}_2\text{O} + 0,5\text{N}_2$

$$\Delta H_c^0 = 3,5 \cdot (-286) + 3 \cdot (-394) - (-560) = -1623 \text{ kJ mol}^{-1} / 89 \text{ g mol}^{-1} \cdot 10^3 \text{ g/kg} = -18,2 \text{ MJ kg}^{-1}$$

The metabolism of fats and protein actually isn't fast enough to provide the necessary energy for doing sports, which is why carbohydrates must be used for this purpose.

**b) i) Expended energy:**  $200 \text{ W (J s}^{-1}) \cdot 1/0,24 \cdot 3600 \text{ sek h}^{-1} \cdot 5,5 \text{ h} \cdot 10^{-6} \text{ MJ J}^{-1}$

**= 16 MJ**

ii) bread loafs:  $16,5 \text{ MJ} / ((15,6 \text{ MJ kg}^{-1} * 0.6) / 320 \text{ g} * 10^{-3} \text{ kg/g}) = \mathbf{5,5}$  loafs of bread

iii) lard:  $16,5 \text{ MJ} / 39,4 \text{ MJ kg}^{-1} = \mathbf{420 \text{ g}}$

iv) beef jerky:  $16,5 \text{ MJ} / 18,2 \text{ MJ kg}^{-1} = \mathbf{910 \text{ g}}$

c) i) Glucose:  $\Delta S^0 = 6*(189) + 6*(214) - 209 = 2209 \text{ J K}^{-1} \text{ mol}^{-1} / 180 \text{ g mol}^{-1} * 10^3 \text{ g/kg} = -12300 \text{ J K}^{-1} \text{ kg}^{-1}$

Hexadecanoic acid:  $\Delta S^0 = 16*(189) + 16*(214) - 452 = 5996 \text{ J K}^{-1} \text{ mol}^{-1} / 256,4 \text{ g mol}^{-1} * 10^3 \text{ g/kg} = 23400 \text{ J K}^{-1} \text{ kg}^{-1}$

Alanine:  $\Delta S^0 = 3,5*(189) + 3*(214) - 119 = 1184,5 \text{ J K}^{-1} \text{ mol}^{-1} / 89 \text{ g mol}^{-1} * 10^3 \text{ g/kg} = 13309 \text{ J K}^{-1} \text{ kg}^{-1}$

Juku has  $75 \text{ kg} * 0,4\%/100\% = 0,3 \text{ kg}$  carbohydrates,  $9 \text{ kg}$  lard and  $15 \text{ kg}$  protein.

$\Delta S^0 = 0,3 \text{ kg} * 12300 \text{ J K}^{-1} \text{ kg}^{-1} + 9 \text{ kg} * 23600 \text{ J K}^{-1} \text{ kg}^{-1} + 15 \text{ kg} * 13310 \text{ J K}^{-1} \text{ kg}^{-1} = \mathbf{414000 \text{ J K}^{-1}}$

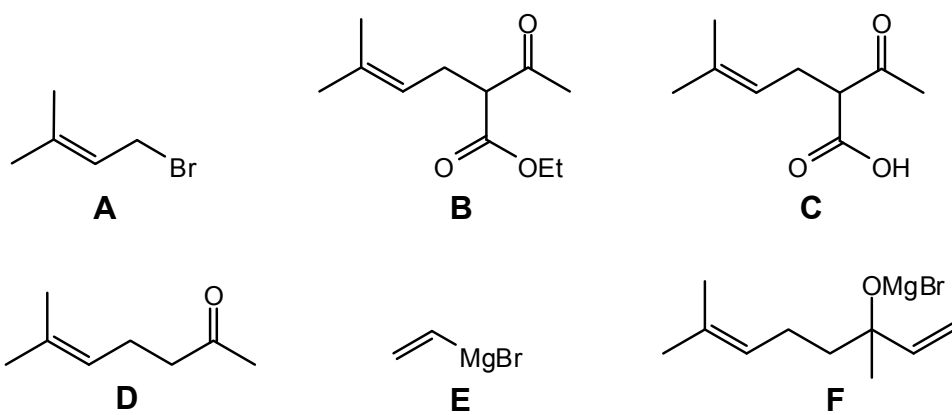
ii)  $\Delta H^0 = 0,3 \text{ kg} * (-15,6 \text{ MJ kg}^{-1}) + 9 \text{ kg} * (-39,2 \text{ MJ kg}^{-1}) + 15 \text{ kg} * (-18,2 \text{ MJ kg}^{-1}) = \mathbf{-630 \text{ MJ}}$

iii)  $\Delta G = -630 * 10^6 \text{ J} - 310 \text{ K} * 414000 \text{ J K}^{-1} = \mathbf{-759 \text{ MJ} \Rightarrow -800 \text{ MJ}}$

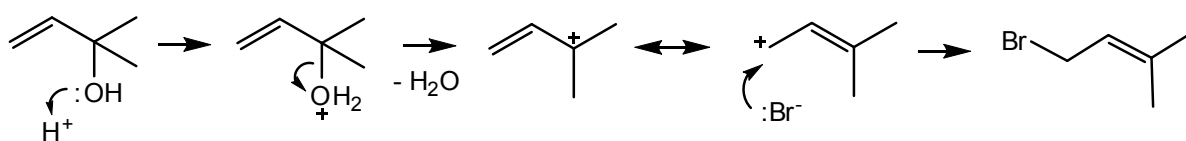
iv)  $K = e^{-\Delta G/RT} = e^{310000} = \infty$

v) Considering the large positive entropy, negative Gibbs energy and infinite equilibrium constant, Juku should spontaneously decompose. However, these are just thermodynamic values; in reality, the rates of these reactions are low at body temperature and they do not take place spontaneously in practice.

**4. a)**



**b)**



**c) Victor Grignard**

**5. a) A – NH<sub>3</sub> – ammonia**

B – NaNH<sub>2</sub> – sodium amide

C – NaN<sub>3</sub> – sodium azide

D – HN<sub>3</sub> – hydrogen azide

E – H<sub>2</sub>N-NH<sub>2</sub> – hydrazine

X – H<sub>2</sub> – hydrogen

Y – N<sub>2</sub> – nitrogen

Z – [N<sub>2</sub>H<sub>5</sub><sup>+</sup>][N<sub>3</sub><sup>-</sup>] – hydrazine azide

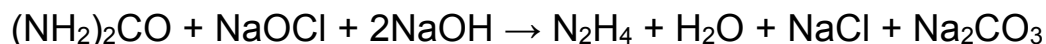
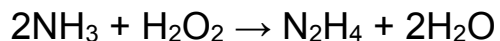
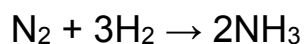
**b) 2NH<sub>3</sub> + 2Na → 2NaNH<sub>2</sub> + H<sub>2</sub>**

2NaNH<sub>2</sub> + N<sub>2</sub>O → NaN<sub>3</sub> + NaOH + NH<sub>3</sub>

NaN<sub>3</sub> + HCl → NaCl + HN<sub>3</sub>

N<sub>2</sub>H<sub>4</sub> + HN<sub>3</sub> → [N<sub>2</sub>H<sub>5</sub><sup>+</sup>][N<sub>3</sub><sup>-</sup>]

12[N<sub>2</sub>H<sub>5</sub><sup>+</sup>][N<sub>3</sub><sup>-</sup>] → 3N<sub>2</sub>H<sub>4</sub> + 16NH<sub>3</sub> + 19N<sub>2</sub>

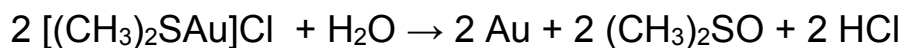
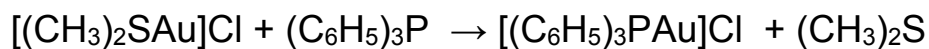
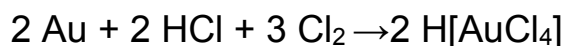
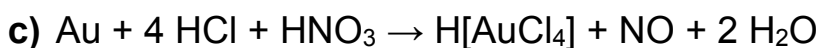


**6. a)**  $M(\text{C}) = 29 \times 2,45 = 71$

**C** –  $\text{Cl}_2$ , chlorine

**b)** X – Au, gold. The metallic form is stable, does not react with most substances and is different in colour from other metals.

B – NO, nitric oxide





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

### **Gold medal**

Vladislav Ivaništšev 2003

Taavi Pungas 2009

Gleb Široki 2010

### **Silver medal**

Ain Uustare 1996

Valerija Sizemskaja 1997

Tavo Romann 2001

Pavel Starkov 2002

Vladislav Ivaništšev 2002

Kaur Adamson 2003

Kaur Adamson 2004

Andres Laan 2006; 2007; 2008

Andi Kipper 2007

Taavi Pungas 2008

Gleb Široki 2009

Julia Tšeglakova 2011

### **Bronze medal**

Jaak Suurpere 1994; 1995

Ain Uustare 1995

Artur Jõgi 1996

Aleksei Lulla 1996

Olga Tšubrik	1996; 1997
Anton Samussenko	1997
Valerija Sizemskaja	1998
Erkki Tempel	1999
Kirill Vassilkov	2000
Tavo Romann	2000
Pavel Starkov	2001
Jevgenia Tamjar	2003
Anneli Kruve	2003
Olga Knjazeva	2004
Jasper Adamson	2004
Viktoria Prostakova	2004
Andres Laan	2005
Olga Jasnovidova	2005
Konstantin Ossipov	2005
Irina Tarassova	2006
Eliko Töldsepp	2006
Taavi Pungas	2007
Ivan Ogibalov	2007
Jörgen Metsik	2008
Svetlana Tšupova	2008
Kadi-Liis Saar	2009; 2010
Maksim Mišin	2010

Ivan Jakovlev	2010
Taivo Pungas	2011; 2012
Katrina Sepp	2011
Eva-Lotta Käsper	2011; 2012
Jaan Toots	2012
Lona-Liisa Sutt	2012

### **Honorable mention**

Ain Uustare	1994
Mati Möttus	1994
Kaido Viht	1997
Aleksei Bredihhin	2000
Jevgenia Kozevnikova	2000
Mikk Eelmets	2001
Siim Karus	2002
Jevgenia Tamjar	2002
Maksim Mišin	2009

### **Participants**

Ave Sarapuu	1994
Artur Jõgi	1995
Aleksei Lulla	1995
Ivo Antsi	1998
Ruslan Svetlitski	1998
Jan Klaasen	1998

Tavo Romann	1999
Jevgenia Kozevnikova	1999
Oksana Travnikova	1999
Indrek Koppel	2001
Mikk Müraus	2005
Elo Sõnajalg	2006

### **Participated four times**

Andres Laan	2005; 2006; 2007; 2008
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### **Participated three times**

Ain Uustare	1994; 1995; 1996
Tavo Romann	1999; 2000; 2001
Taavi Pungas	2007; 2008; 2009

### **Participated twice**

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

Kadi Liis Saar 2009; 2010

Maksim Mišin 2009; 2010

Gleb Široki 2009; 2010

Taivo Pungas 2011, 2012

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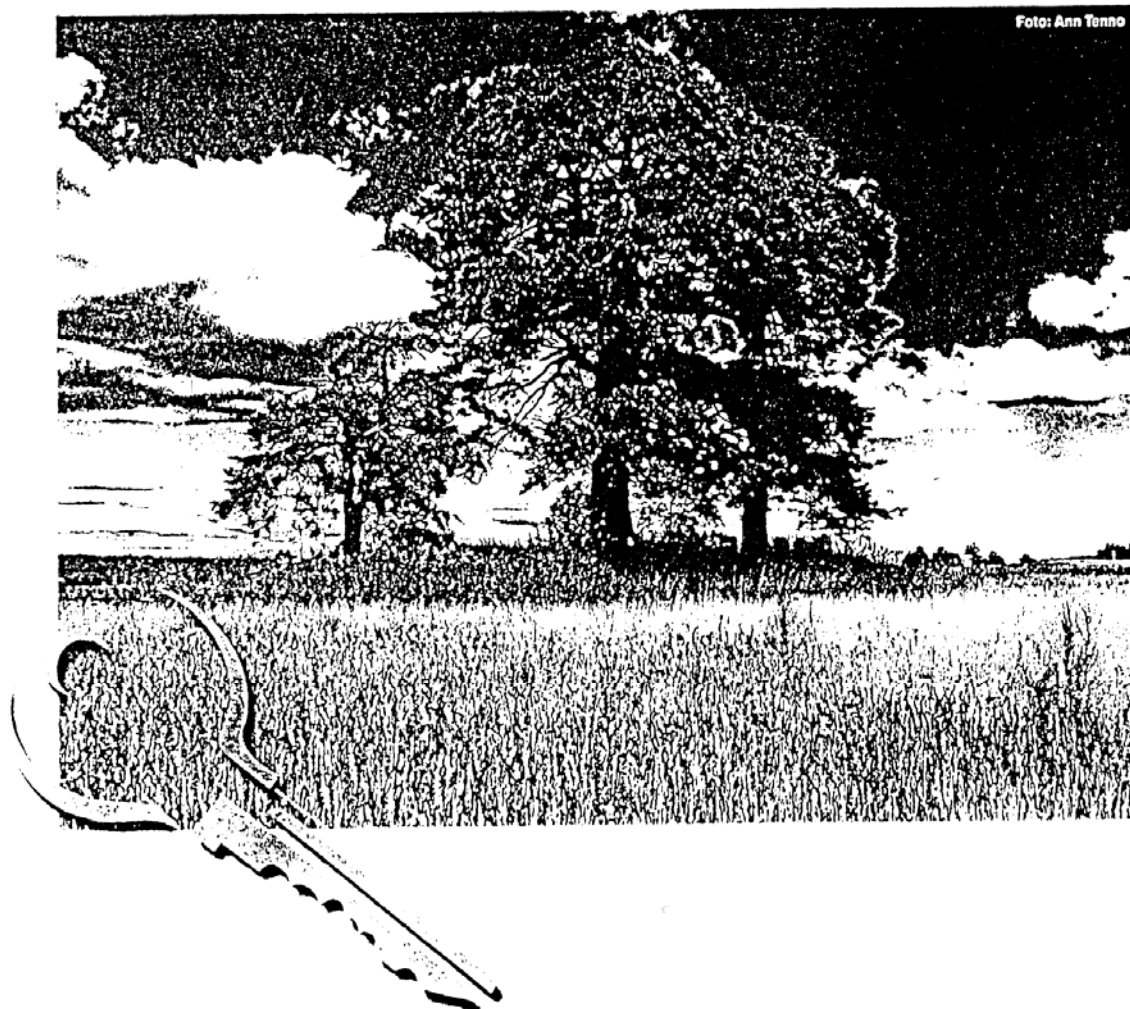
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# Võti puhtasse keskkonda



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