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26th CHEMISTRY OLYMPIAD OF THE BALTIC STATES

Riga, Latvia
April 13th-15th, 2018

PRACTICAL EXAMINATION

Riga Technical University
https://www.rtu.lv/en

JSC OlainFarm
http://olainfarm.lv/

Biosan
https://www.biosan.lv/en

Bapeks
http://www.bapeks.com/

Bauskas alus
https://bauskasalus.lv/en/products/non-alcoholic-drinks

"Back to where it all began"

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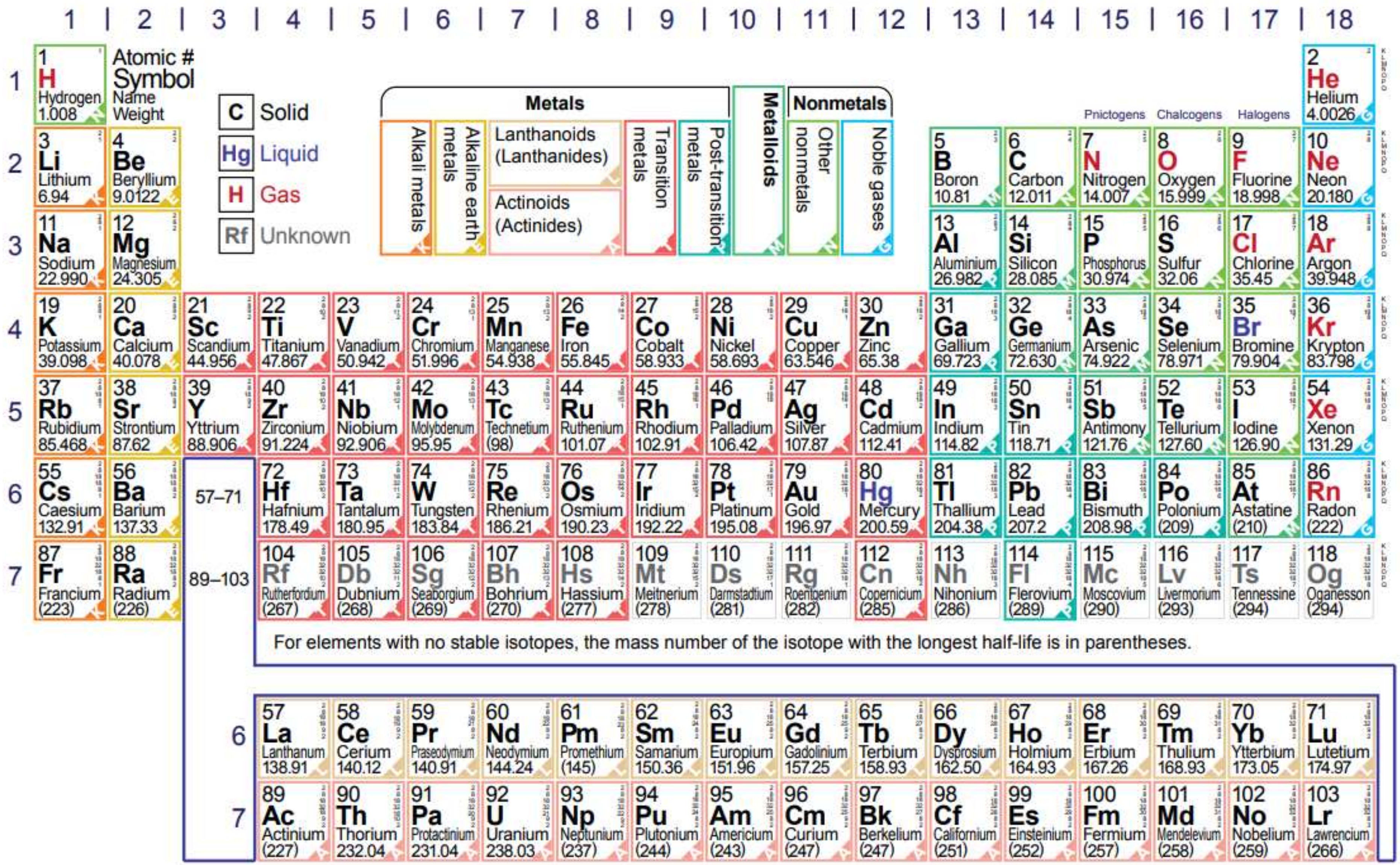
Ķīmisko elementu periodiskā tabula



avots: https://ptable.com/

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General information

This exam contains 11 pages for practical exam tasks (including the answer sheets). There are a total of 2 Tasks:

- Problem 1 - Determining the concentration of sodium hypochlorite solution;
- Problem 2 - Synthesis of cyclohexanone and its isolation as a 2,4-dinitrophenylhydrazone derivative

- Follow safety rules while working in laboratory! It is forbidden to eat and drink in lab. While you are in lab you must wear lab suit and protective glasses. Gloves are not mandatory, but you can ask for them.
- Write your code on each answer sheet.
- You will have a total of 5 hours to complete two practical tasks. You must begin as soon as the **"Start Command"** is given.
- You must start the practical examination with Problem 1 – determination of NaOCl concentration. This task will be held in analytical chemistry lab on 3rd floor. Write **sample number** on the answer sheet. After your calculations are finished show your results to lab assistant.
- The second practical task (Problem 2) will be held in organic chemistry labs on 4th floor. After you finish Problem 1 – take your lab report and go to other lab as designated by lab assistant.
- Some of the plastic and glass equipment will be used more than once. Wash them carefully.
- All answers should be written in answer boxes provided. Answer written in other places will not be graded. You can use other side of page as a draft paper.
- When it is necessary, provide your calculations in the answer boxes. You will get full marks for correct answers (numbers and units) only if the calculations will be shown.
- You must stop your work immediately (including filling answer sheets) when the **"Stop Command"** is announced.
- Do not leave laboratory before lab assistant allows to do it.
- Chemicals and labwares, unless noted, are not supposed to be refilled or replaced. Chemical and labwares will be refilled or replaced without penalty only for the first incident. Each further incident will result in the deduction of 1 point from your 40 practical exam points.

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PROBLEM 1 (18 POINTS)

Determining the concentration of sodium hypochlorite

In order to perform problem 2 – the oxidation of the cyclohexanol, you will need to know the concentration of the aqueous sodium hypochlorite solution. In this problem the concentration of the sodium hypochlorite solution will be determined by titration.

Reagents

- 0.100 M $Na_2S_2O_3$ aqueous solution
- 10% KI aqueous solution
- 5% CH_3COOH aqueous solution
- 1% starch aqueous solution
- Distilled water
- The sample to be analyzed (aqueous solution of sodium hypochlorite)

Glassware and equipment

- 100.0 mL measuring flask
- 5.00 mL pipette
- 10.00 mL pipette
- 100 mL conical flasks
- Burette
- Pipette for the starch solution
- Kipp dispensers for KI and CH_3COOH solutions:
    - 1 mL nominal for KI solution
    - 10 mL nominal for CH_3COOH solution

Analytical procedure

1. Transfer the sample (5.00 mL) into the 100.0 mL measuring flask and dilute it with distilled water to the mark.

2. Transfer part of the obtained solution (10.00 mL) into the conical flask, add 10 % KI solution (2 mL) and 5 % acetic acid solution (10 mL).

3. Titrate the obtained mixture with 0.100 M $Na_2S_2O_3$ solution until a pale yellow colour. Add 1% starch solution (1–2 mL) and continue the titration until the colour disappears. The blue colour should not reappear for at least 30 seconds.

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During the analysis the following reactions occur:

$2H^+ + OCl^- + 2I^- \rightarrow I_2 + Cl^- + H_2O$

$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

Results of the titrations **Sample Nr .______________**

Nr.	Volume of $Na_2S_2O_3$ (aq)		
1			
2			
3			

Calculations:	*Points: (filled by jury)*
The concentration of the NaOCl in the sample Nr_______ is: _________________________	

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Comments and signature by lab assistant:	
Total points for Problem 1:	

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PROBLEM 2 (22 POINTS)

The synthesis of cyclohexanone and its isolation as a 2,4-dinitrophenylhydrazone derivative

Cyclohexanone is the starting material in the synthesis of nylon, and it is manufactured in industry in large quantities. One of the most economical and nature friendly methods is the oxidation of cyclohexanol by sodium hypochlorite. The oxidation reaction is conducted in water and in industry cyclohexanone is isolated by steam distillation. In this problem you will synthesize cyclohexanone and part of it you will isolate as its derivative.

Reagents

- Aqueous solution of sodium hypochlorite (concentration to be determined by titration)
- Acetic acid
- Cyclohexanol
- Na_2CO_3
- NaCl
- Methyl tert-butyl ether (MTBE)
- 2,4-Dinitrophenylhydrazine reagent ($EtOH/H_2O/H_2SO_4$ solution)
- Ethanol
- Toluene
- Distilled water
- Cyclohexanone 2,4-dinitrophenylhydrazone standard

Glassware and equipment

- Magnetic stirrer hotplate
- Water bath
- Two-neck round-bottom flask, 250 mL
- Dropping/separating funnel, 100 ml
- Thermometer
- Measuring cylinders, 100 mL, 20 mL, 10 mL
- Beakers, conical flasks
- Dephlegmator (Vigreux column)
- Büchner funnel, Bunsen flask
- Petri dish
- Spatula
- Glass rod
- Funnels
- Universal indicator
- Drying oven, 60 °C (for communal use)
- Balance (for communal use)
- TLC plates, glass capillary tubes, TLC jar

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The oxidation of cyclohexanol

1. Clamp the 250 mL two-neck round-bottom flask and put it in the water bath on the magnetic stirred hotplate. Pour in 5.2 mL of cyclohexanol (d = 0.962 g/cm^3). *(The necessary amount of cyclohexanol is precisely measured and provided to each student).*
Attach the 100 mL dropping funnel to one neck of the flask, attach the thermometer to the other. Heat the water bath to 40–45 °C.

2. Pour the calculated volume of aqueous NaOCl solution in the 100 mL beaker. NaOCl should be taken in excess – **1.5 equiv. per 1 equiv. of cyclohexanol**. The concentration of NaOCl should be calculated from the titration.
Slowly add glacial acetic acid (5 mL, d = 1.049 g/cm^3) to the NaOCl solution, while slowly stirring with the glass rod. *(Should be done in the fume hood! Do not breathe the vapour!)* Transfer the resulting mixture into the dropping funnel.

3. Slowly add the oxidative mixture from the dropping funnel to the cyclohexanol over a period of 15 minutes, while stirring. Keep the internal temperature of the reaction mixture between 40–50 °C. After the addition, keep stirring at 45–50 °C for 15 min. Usually, to achieve this, the water bath must be heated to 60–70 °C.

4. Change the hot water in the water bath to cold water, and, while stirring, add sodium carbonate until pH 7–8 (roughly 1–2 g). In order to decrease the solubility of the product in water, the mixture should be saturated with NaCl.

5. Cool the mixture to 15–20 °C and transfer it to the separating funnel. Extract the mixture twice with 6–8 mL of methyl *tert*-butyl ether (MTBE). Combine the organic extracts and measure the volume.

The synthesis of cyclohexanone 2,4-diphenylhydrazone

1. Pour 70 mL (*calculated so that it would be in excess*) of the 2,4-dinitrophenylhydrazine reagent into a 100 mL beaker. While stirring, add a specific volume (approximately 1/5 of the total volume) of the obtained cyclohexanone solution in MTBE. Transfer the rest of the cyclohexanone solution into a 20 mL bottle and leave it aside

2. Filter the obtained slurry, wash the precipitate on the filter with water, and after that with ethanol (2×5 mL). Transfer the precipitate into a Petri dish and dry it in the drying oven at 60 °C (10–15 min). After drying, weigh the precipitate. Calculate the yield of the crude product. Leave couple of milligrams aside for the TLC analysis.

3. **Crystallization.** Transfer the obtained crude product into a 200 mL conical flask, connect the flask with dephlegmator and recrystallize the substance from ethanol. Approximately 75 mL of ethanol are needed for 1 g of the product. After recrystallization, filter the crystalline solid, dry it, weigh it and calculate the yield of the recrystallization.

Thin Layer Chromatography

By performing the TLC analysis, compare the crude product, crystallized product and the given standard of cyclohexanone 2,4-diphenylhydrazone. The samples (2–3 mg) should be dissolved in toluene. Use toluene as the eluent.
Calculate the R_f of the obtained cyclohexanone 2,4-diphenylhydrazone.

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Answer sheets

1. Write the reaction equations for the cyclohexanone synthesis and its reaction with 2,4-dinitrophenylhydrazine.	*Points (filled by jury)*

2. Calculate the necessary volume of the aqueous NaClO solution. Concentration of the sodium hypochlorite: ____________________________ Necessary volume (mL): _________________________ **3.** The volume of the cyclohexanone solution after the extraction with methyl *tert*-butyl ether (MTBE) (mL) _______________________	*Points*

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4. The volume of the solution taken for the reaction with 2,4-dinitrophenylhydrazine: ___________________________	

5. Calculate the **theoretical yield** of the product. Since the cyclohexanone was not isolated, you should calculate the yield of its 2,4-dinitrophenylhydrazone derivative	*Points*
6. Estimate the yield for the oxidation reaction "cyclohexanol → cyclohexanone" based on the mass of the crude cyclohexanone 2,4-dinitrophenylhydrazone. Doing calculation please consider that: a) the formation of cyclohexanone 2,4-dinitrophenylhydrazone is quantitative; b) only a fraction of whole cyclohexanone solution in MTBE was used. Mass of the crude cyclohexanone 2,4-dinitrophenylhydrazone: _______________ g Calculation: Estimated yield for the oxidation reaction "cyclohexanol → cyclohexanone": __________%	*Points*

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7. Crystallization of cyclohexanone 2,4-dinitrophenylhydrazone Mass of the crude product: ___________ g Mass of the crystallized product: ___________ g Yield of the crystallization: _______________ %	
8. Thin Layer Chromatography: (see table below) Conclusion:	*Points*
Total points for Problem 2:	

Sample name	**R_f**