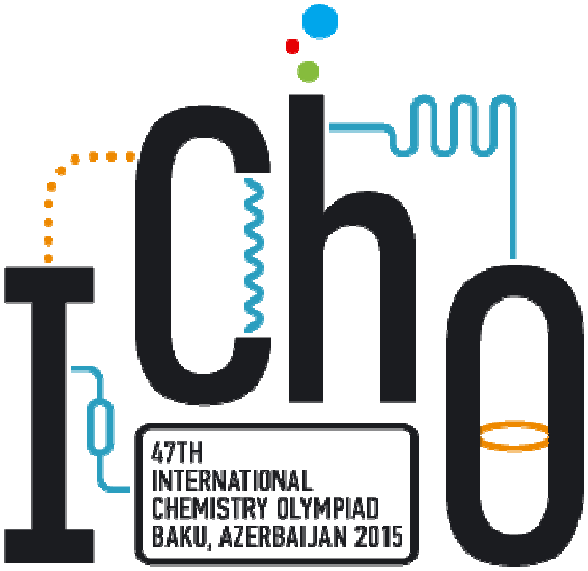
Life is a huge lab



PRACTICAL EXAMINATION

JULY 23, 2015
BAKU, AZERBAIJAN

General Directions

- **Safety rules: follow ones given in the Preparatory problems booklet**
- **No eating or drinking in the lab**.
- **Always wear your lab coat and safety goggles** when being in the lab. Ask your lab assistant for the gloves of your size.
- **Violating safety rules:** you will get one warning only; offend again: you are disqualified.
- **Problems and answers booklet: XX** pages (incl. the cover sheet and Periodic table of elements) with 3 tasks.
- **Time:** 5 h; you will have 30 min for reading before the start. 30 min notification before the end.
- **Your student code:** write it down on **every page!**
- **Answers:** Write down your answers only in the answer boxes in the booklet and cells in the file on the memory stick. Answers written elsewhere will not be graded. Relevant calculations have to be shown.
- **Use only the pen, pencil, and calculator provided.**
- **Take the reading of the burette** as accurately as possible.
- **More chemicals or glassware** needed? Ask your lab assistant. Replacement of **each** item will be **penalized** with 1 point of 40 for the Practical examination. This does not refer to the distilled water, ice and napkins. No replacement of manometer, set-up for Task 3 and the memory stick.
- **Questions re:** safety, apparatus, chemicals, toilet break, drinking water: **ask your lab assistant.**
- **Liquid chemical waste:** put it only in the designated 1 L bottle labeled “WASTE”.
- **Official English version available** on request **for clarification only.** Ask your lab assistant.
- **After the stop signal** put your booklet in the envelope (do not seal), leave at your table.
- **Do not leave the lab** until you are allowed so by your lab assistant.
- **You must stop your work immediately after the stop signal. A 1 min delay will result in zero points for the current task.**
- **During the Practical exam, some of the glassware and plastics are expected to be used several times. Clean it carefully.**
- **We do not recommend overlapping Task 1 with either Task 2, or Task 3.**

List of Chemicals

Name	State	Concentration	Quantity	Placed in	Labeled
Task 1					
3-Methyl-thiophene	Solution in CCl_4	4g/8 mL	4 g	Plastic vial, 30 ml	3-methylthiophene in CCl_4
1-Bromo-2,5-pyrrolidinedione (NBS)	Solid	-	7.3g	Plastic vial, 30 ml	NBS 7,3 g
Carbon tetrachloride	Liquid	-	24 mL	Plastic vial, 125 mL	CCl_4
Unknown catalyst	in CCl_4			Plastic vial, 4 mL	Catalyst
Potassium carbonate	Solid	-	0.02 g	Plastic vial, 4 mL	K_2CO_3
Task 2					
Test solution containing VO^{2+} and Cr^{3+}	Aqueous solution	To be determined	100 mL	Plastic bottle, 100 mL	Test solution
Sulfuric acid	Aqueous solution	1 M	~ 500 mL	Glass bottle, 1000 mL	1M H_2SO_4
Potassium permanganate	Aqueous solution	0.03 M	15 mL	Plastic bottle, 30 mL	0.03 M $KMnO_4$
Oxalic acid	Aqueous solution	0.03 M	30 mL	Plastic bottle, 50 mL	0.03 M $H_2C_2O_4$
Phenylanthranilic acid	Aqueous solution	0.1 %	5 mL	Dropper, 6 mL	Indicator
Ammonium iron(II) sulfate	Aqueous solution	Read from the label	100 mL	Glass bottle, 100 mL	Mohr's salt
Silver nitrate	Aqueous solution	0.3 %	5 mL	Dropper, 8 mL	0.3 % $AgNO_3$
Ammonium persulfate	Aqueous solution	10 %	70 mL	Plastic bottle, 100 mL	10 % $(NH_4)_2S_2O_8$
Task 3					
Diclofenac containing medicine	Aqueous solution	To be determined	5 mL	Plastic vial, 30 mL	Control
Potassium permanganate	Aqueous solution	6×10^{-3} M	~ 30 mL	Reagent bottle, 100 mL	$KMnO_4$ 6×10^{-3} M
Sulfuric acid (in the same bottle as for Task 2)	Aqueous solution	1 M	~ 500 mL	Reagent bottle with glass stopper, 1L	1M H_2SO_4
Diclofenac sodium salt	Aqueous solution	~ 600 mg/L	~ 20 mL	Reagent bottle, 100 mL	DCF 600 mg/L

List of labware and equipment

Item	Quantity	Located
On the tables for common use		
Refractometer Refracto 30GS	1-2 / 1 lab	Under the hood
Napkins for refractometer cleaning		Under the hood
Wash bottle "Cleaning solvent" for the refractometer		Under the hood
Aluminum foil for wrapping	1-2 rolls / 1 lab	On lab assistants' table
Balances	1-3/ 1 lab	On separate tables
Gloves (S, M, L)		On lab assistants' table
Large bottle labeled "H_2O dist."		Near the sink
Napkins for general purposes	1 Pack / 1 row	Near the sink
Item	**Quantity**	**As labeled on Fig. 1, 2, 5**
On each working place, to be used in more than one task		
Hot-plate magnetic stirrer	1	
Waste bottle labeled "Waste"	1	
Cotton gloves	1 pair	
Wash bottle, 500 mL, labeled "H_2O distilled"	1	
Pipette pump, 10 mL, green	1	
Pipette pump, 2 mL, blue	1	
Graduated cylinder, 25.0 mL for H_2SO_4 only	1	
Safety goggles	1	
Napkins for general purposes	1 pack	
Task 1		
Laboratory stand	2	**1**
Round-bottom three-necked flask, 100 mL	1	**2**
Reflux condenser, connected to water supply	1	**3**
Glass ground joint stopper	6 (one labeled with your student code)	**4**
Dropping funnel, 50 mL	1	**5**
Oval magnetic stir-bar (big)	1	**6**
Pear-shaped round-bottom flask for distillation, 50 mL	1	**7**
Claisen distillation adapter	1	**8**
Thermometer with fixed ground joint tube	1	**9**

Buchner type fritted glass filter	1	**10**
Rubber spacer for vacuum filtration	1	**11**
Liebig (downward) condenser	1	**12**
Distilling receiver cow	1	**13**
Receiver flask, 10 mL	4 (one labeled with your student code)	**14**
Receiver flask, 50 mL	1	**15**
Adjustable lab jack lift support	1	**16**
Oval magnetic stir-bar (small)	1	**17**
Plastic beaker, 50 mL, labeled "For the receiver with the product"	1	
Teflon sleeves for ground tapered joints	12	
Large funnel, 65 mm, with short stem	1	
Joint clips	5	**18**
Grey clamp	1	**19**
Red clamp	1	**20**
Permanent marker	1	
Glass beaker, 25 mL	1	
Plastic container labeled "Used glassware"	1	
Plastic container labeled "Ice bath"	1	
Digital manometer	1	
Cotton wool	3	
Spatula	1	
Glass rod	1	
Ruler	1	
Pencil	1	
Task 2		
Laboratory stand	1	
Clamp for burette	1	
Plastic beaker, 100 mL, labeled "Waste"	1	
Glass beaker, 150 mL	1	
Volumetric flask with a stopper, 100 mL	1	
Small funnel, 45 mm	1	
Medium-size funnel, 55 mm	1	
Watch glass	1	
Burette, 25.00 mL, clamped in the stand	1	
Volumetric pipette, 10.00 mL	1	
Graduated pipette, 5.00 mL	1	
Erlenmeyer flask, 150 mL	2	
Graduated cylinder, 100.0 mL	1	
Pasteur pipette	2	
White paper sheet	1	

Task 3		
Photometer, 525 nm	1	**1**
Thermostat with adaptor	1	**2**
Spectrophotometer cell with 3.5 cm optical path length	2	**3**
Magnetic stirrer	1	**4**
Magnetic stir-bar (medium-size)	1	
Netbook with adaptor and mouse	1	
Volumetric flask with a stopper, 100 mL	1	
Graduated pipette, 2 mL	2	
Memory stick 8 Gb labeled with your student code	1	
Black magnet	1	

Hazard codes, provided by Globally Harmonized System of Classification and Labelling of Chemicals

Substance	Name	GHS Hazard Statement
C_5H_6S	3-methylthiophene	H225, H302, H332
$C_4H_4BrNO_2$	1-Bromo-2,5-pyrrolidinedione	H302, H314
CCl_4	Carbon tetrachloride	H301, H331, H311, H317, H351, H372, H402, H412
$HClO_4$	Perchloric acid	H271, H302, H314
$C_8H_{12}N_4$	2,2'-Azobis(2-methylpropionitrile)	H242, H302, H332 H412
$C_{14}H_{10}O_4$	Dibenzoyl peroxide	H241, H317, H319, H400
K_2CO_3	Potassium carbonate	H315, H319
Test solution	Test solution containing VO^{2+} and Cr^{3+}	H302, H312, H314, H332
H_2SO_4	Sulfuric acid	H314, H290
$KMnO_4$	Potassium permanganate	H272, H302, H400, H410
$H_2C_2O_4$	Oxalic acid	H314, H318
$C_{13}H_{11}NO_2$	Solution of N-phenylanthranilic acid in sodium carbonate	H302, H315, H319, H335
$(NH_4)_2Fe(SO_4)_2$	Mohr's salt	H315, H319, H335
$AgNO_3$	Silver nitrate	H272, H302, H314, H410
$(NH_4)_2S_2O_8$	Ammonium persulfate	H272, H302, H315, H317, H319, H334, H335
$C_{14}H_{10}Cl_2NNaO_2$	Diclofenac sodium salt	H301
H_2SO_4	Sulfuric acid	H290, H302, H314, H332, H351
$KMnO_4$	Potassium permanganate	H272, H302, H400, H410

Hazard statements description

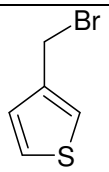
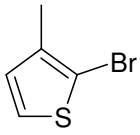
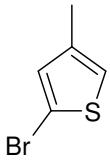
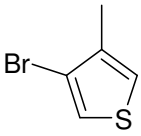
Code	Hazard Statement
Physical Hazards	
H225	Highly flammable liquid and vapour
H241	Heating may cause fire or explosion
H242	Heating may cause a fire
H271	May cause fire or explosion; strong oxidizer
H272	May intensify fire; oxidizer
H290	May be corrosive to metals
Health hazards	
H301	Toxic if swallowed
H302	Harmful if swallowed
H311	Toxic in contact with skin
H312	Harmful in contact with skin
H314	Causes severe skin burns and eye damage
H315	Causes skin irritation
H317	May cause an allergic skin reaction
H318	Causes serious eye damage
H319	Causes serious eye irritation
H331	Toxic if inhaled
H332	Harmful if inhaled
H334	May cause allergy or astma simpthoms or breating difficulties if inhalted
H335	May cause respiratory irritation
H351	Suspected of causing cancer
H372	Causes demage to organs through prolonged or repeated exposure
Environmental hazards	
H400	Very toxic to aquatic life
H402	Harmful to aquatic life
H410	Very toxic to aquatic life with long lasting effects
H412	Harmful to aquatic life with long lasting effects

TASK 1. Tuning bromination selectivity by catalysis (15 points).

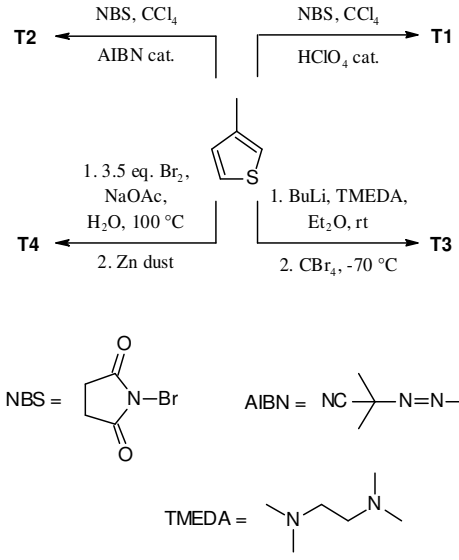
Quest. #	Q1	Q2	Q3	Q4	Q5	Q6	Total
Marks	2	39	4	2	1	2	50

Selectivity of chemical reactions is one of the most challenging problems of contemporary research. In many cases, reaction conditions and the catalysts applied are keys to achieving high selectivity of organic reactions. In this task, you will study one of such cases. 3-Methylthiophene can theoretically be transformed into four monobrominated derivatives **T1-T4**, which have been actually synthesized and characterized in detail. Structures of **T1-T4** and the values of refractive indexes are given in Table 1.

Table 1. Structures and refractive indexes of monobrominated thiophenes.

Designation	**A**	**B**	**T3**	**T4**
Structure				
n_D^{20}	1.5961	1.5706	1.5786	1.5795

The selective synthesis of each of **T1-T4** can be performed using 3-methylthiophene as the starting material. **T1** and **T2** can be obtained by direct bromination using different catalysts, whereas **T3** and **T4** are the products of "one pot" multistep synthesis (see Scheme 1).



Scheme 1. Selective synthesis of monobrominated thiophenes.

Q1. Assign the structures given in Scheme 1 with **T1, T2** to the structures given in the Table 1. Fill in the boxes below with one of A-B.

B	T1	A	T2

2 marks

In this task, you will:

- Synthesize a monobrominated thiophene derivative using one of the catalysts from the list below;
- Measure the product refractive index (n_D)
- Compare the results obtained with literature data and decide on the product structure and the catalysts given.

List of possible catalysts

- $HClO_4$ in CCl_4
- AIBN in CCl_4

PROCEDURE

Note!

- ***Apparatuses used in this task are shown in Fig. 1 and 2.***
- ***Always equip every joint with the Teflon sleeve. Immediately place every piece of the used glassware in the corresponding container. Always keep the container tightly closed.***
- ***You can use cotton gloves when handling hot things!***

Step 1. Clamp the three-necked flask on the laboratory stand on top of the hot-plate magnetic stirrer. (Fig.1). Apply the dropping funnel and the reflux condenser to the corresponding necks and put the big magnetic stir-bar into the flask through the open neck. Ask your lab assistant to switch on water supply in the reflux condenser (**Do not do it yourself!**). Transfer NBS quantitatively into the flask using spatula and big plastic funnel. Transfer ~15 mL of CCl_4 into the 25 mL glass beaker. Pour ~2/3 of the solvent volume from the beaker into the flask. Shake the Catalyst and quantitatively add it through the same plastic funnel into the flask. Add the rest of the solvent from the beaker to the flask. Close the open neck with the stopper. Put the flask into the ice bath filled with water and ice to ~ 2/3 of its volume. Start stirring the mixture.

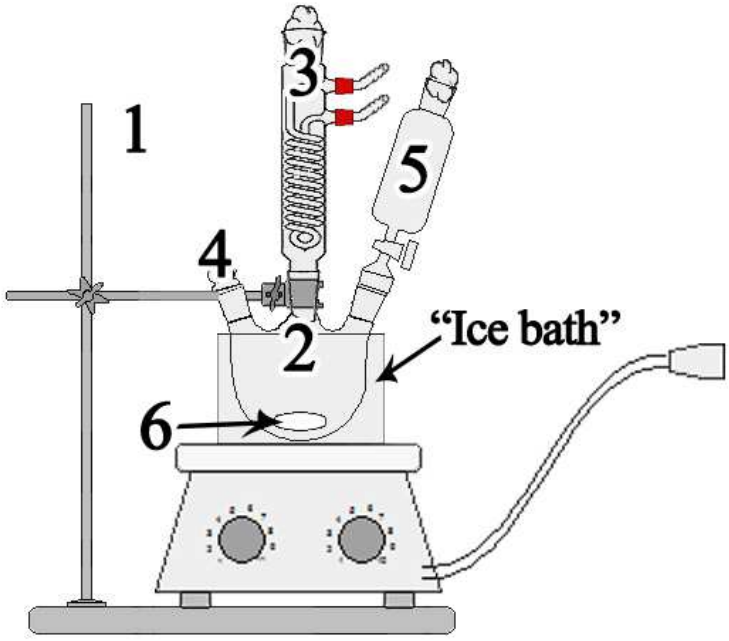


Fig. 1. Set up needed to implement Steps 1-4 of the synthesis. Refer to page 4-5 for the numbers

Step 2. Using the big plastic funnel quantitatively transfer the solution of 3-methylthiophene to the dropping funnel with **tap closed**. Apply a piece of the cotton wool to the open end of the dropping funnel and reflux condenser. Under vigorous stirring, add the solution of 3-methylthiophene dropwise during ~ 3 min. Replace the dropping funnel by a glass stopper. Use the Teflon sleeve. Remove the ice bath. Dry the plate and bottom of the flask with napkin.

Step 3. Wrap up the flask with aluminum foil. Switch on the heater (position 3). Bring up the mixture to boiling and boil it for 10 min. Prepare the ice bath (~2/3 of the volume) while the mixture boils.

Step 4. Switch off the heater and carefully **(hot!)** remove the hot-plate magnetic stirrer aside. Dip the flask equipped with the condenser and stoppers into the ice bath for 3-5 min. Keep gently swirling the flask from time to time to provide the faster cooling. Then remove the reflux condenser and load 0.02 g of K_2CO_3 using the big funnel applied to the open neck. Close the neck with a glass stopper and shake the flask several times. Turn off the water supply and unscrew the adaptors of the tubings from the reflux condenser. Let the residual water leak out of the condenser and immediately place it into the container for the used glassware. Remove the clamp keeping the flask in the ice bath.

Step 5. Weigh the 10 mL receiver flask for product with the glass stopper, both marked with your student code. Write down the value in the answer sheet. Put the small magnetic stir-bar in the 50 mL pear-shaped distillation flask. Screw on the adaptors with tubings to the Liebig condenser and fix it on the stand with the red clamp. Turn on the water supply yourself and make sure there is no water leakage.

Step 6. Assemble the distillation apparatus as shown on Fig. 2 supplying all the joints with the teflon sleeves and clips. First, attach two 10 mL and one 50 mL receiver flasks to the distilling receiver cow. Then connect the vacuum hose to the cow and complete assembling. Fix the apparatus over the magnetic stirrer to adjust it on height. Use the adjustable lab jack lift support.

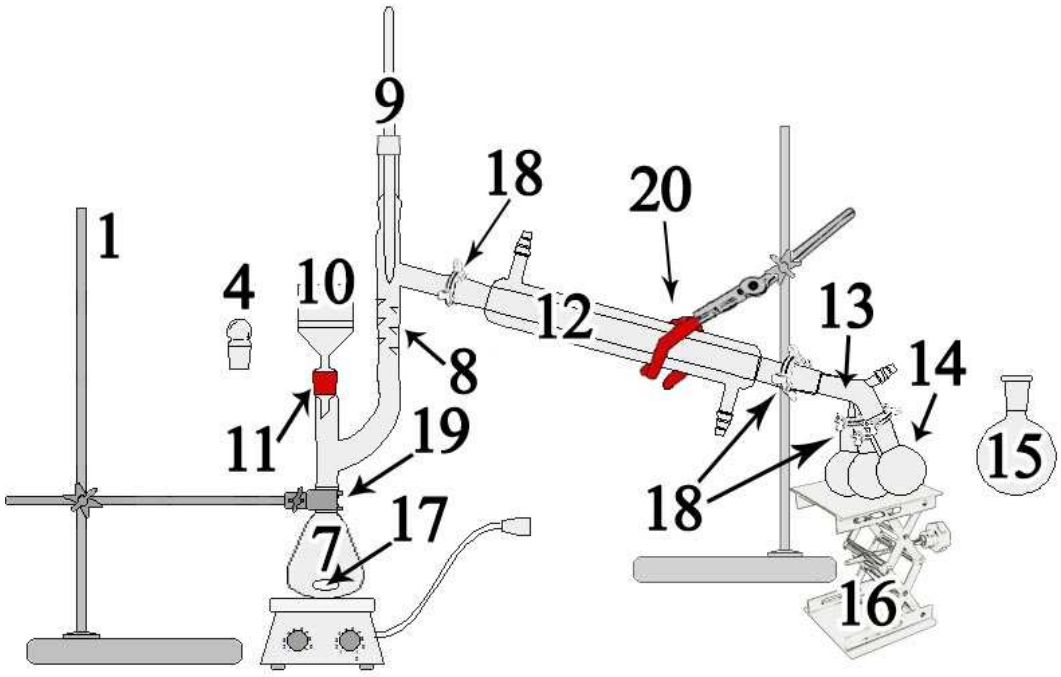


Fig. 2. Set up needed to implement Steps 5-10 of the synthesis. Refer to page 4-5 for the numbers

Step 7. Remove the hot-plate magnetic stirrer aside. Insert the fritted glass filter into the Claisen distillation adapter using the rubber spacer. Turn on the water-jet pump and switch on the digital manometer. Remove the three-necked flask from the ice bath and dry it with a napkin. Carefully transfer the reaction mixture from the three-necked flask to the filter (**Attention! If you do it too fast, the mixture can be partially sucked into the curved part of the adaptor**). When finished, turn off the pump and replace the filter with a glass stopper, use the teflon sleeve.

Step 8. Tightly wrap up the flask and distillation adaptor with aluminum foil up to the thermometer joint. Bring back the magnetic stirrer and turn on stirring and heating (position 6). **Do not turn on the water-jet pump!** Collect the distilled solvent into the 50 mL receiver. When the solvent distillation is over, turn off heating and stirring and carefully **(hot!)** remove the hot-plate magnetic stirrer aside. Replace the receiver flask containing the distilled solvent by a new 10 mL receiver. Close the 50 mL flask with a glass stopper and deliver it to your lab assistant.

Step 9. Remove the foil and put the pear-shaped bottom flask into the ice bath for 2-3 min to bring the temperature below ambient. Remove the ice bath; dry the flask with a napkin. Bring back the magnetic stirrer under the flask **(Attention! The hot-plate may be still hot!).** Turn on stirring. Wrap up the flask tightly with aluminum foil. Switch on the water-jet pump. When vacuum is stabilized (follow the reading of the digital manometer), turn on the heater (position 6). Observe the initial stage of the targeted product distillation and collect the first 3-5 drops into an attached receiver flask not labeled with your student code. Then rotate the cow and collect the targeted product into the receiver flask with your student code. Write down the product boiling point and pressure reading from the digital manometer into the answer sheet.

Step 10. When the targeted product is collected, turn off the heater, remove the foil and carefully **(hot!)** remove the hot-plate magnetic stirrer aside. Cool down the apparatus to ambient temperature using the ice bath. **Ask your lab assistant to disconnect the vacuum line.** Disconnect the receiver flask with the targeted product and **immediately** close it with the glass stopper labeled with your student code. Do not attempt to drag the teflon sleeve out if it remains in the receiver. Place the flask into the 50 mL plastic beaker labeled "For the receiver with the product". Immediately attach a new receiver instead of the removed one and apply the joint clip. **Leave the apparatus as it is.**

Step 11. Measure the refraction index **(before weighing)** following the instruction below. Record the temperature from the refractometer.

Weigh the receiver with the targeted product closed with the labeled stopper. Calculate the mass and yield of the product (take the mass of the teflon sleeve equal to 149 mg). The molar masses of 3-metylthiophene and the product equal 98 and 177 g mol^{-1}, respectively.

Q2. Write down all the result in the hereunder Table.

#	Parameter /Characteristics	Value	Units
1	Mass of the receiver flask with the glass stopper, both marked with student code		g
2	Mass of the product		g
3	Yield of the product		%
4	Refraction index for the product		-
5	Temperature recorded from the refractometer		°C
6	Boiling point of the product		°C
7	Pressure at the Boiling point		mmHg

Deliver the product to your lab assistant and get it signed.

The targeted product delivered: _____

Student signature _____ Lab assistant signature _____

The grading scheme takes into account two values re-measured by the Science Committee: mass of the Product (m, g) and its refraction index (n_D) (Fig. 1).

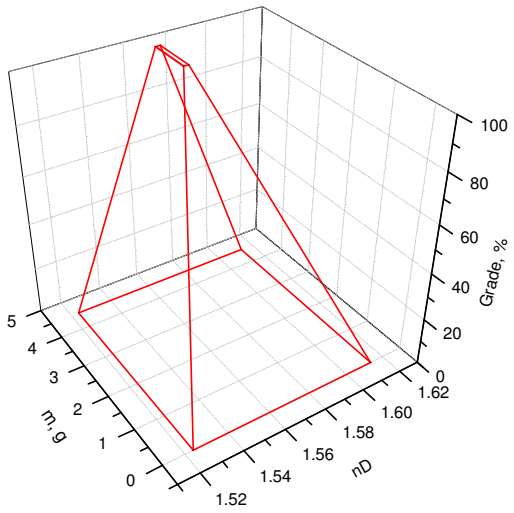


Fig. 1. The 3D diagram.

There are several regions (A-D) on the hereunder projection of the 3D diagram (Fig. 2).

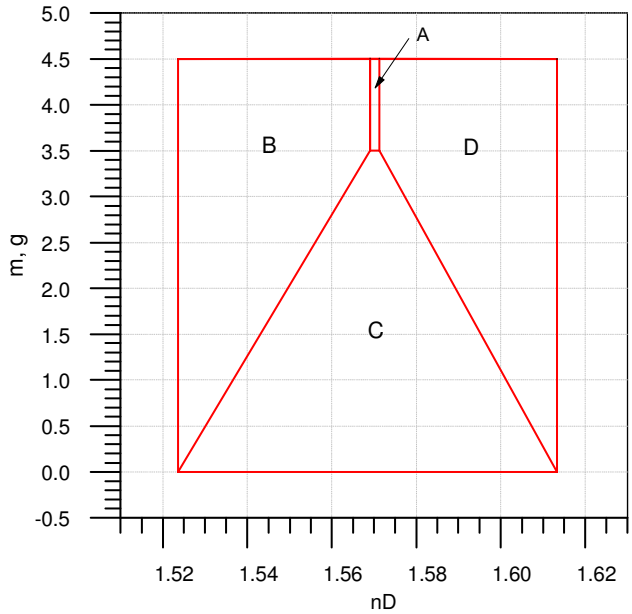


Figure 2. Mass-n_D plot.

- If the value obtained is within region A, 100% of 30 marks
- If the value obtained is within region B, 2202.643*n_D-3355.95 % of 30 marks
- If the value obtained is within region C, 28.57143*m % of 30 marks
- If the value obtained is within region D, -2380.95*n_D+3841.1905 % of 30 marks

Refraction index measurement skills: 4 marks if a student's result differs from the re-measured value not more than by 0.4 %.

Weighing skills: 2 marks if a student's result differs from the re-weighed value not more than by 0.02%.
Correct calculation of mass: 1 mark.
Correct calculation of yield: 1 mark.
Measurement of the Boiling point: 1 mark

REFRACTO 30GS – OPERATING INSTRUCTIONS

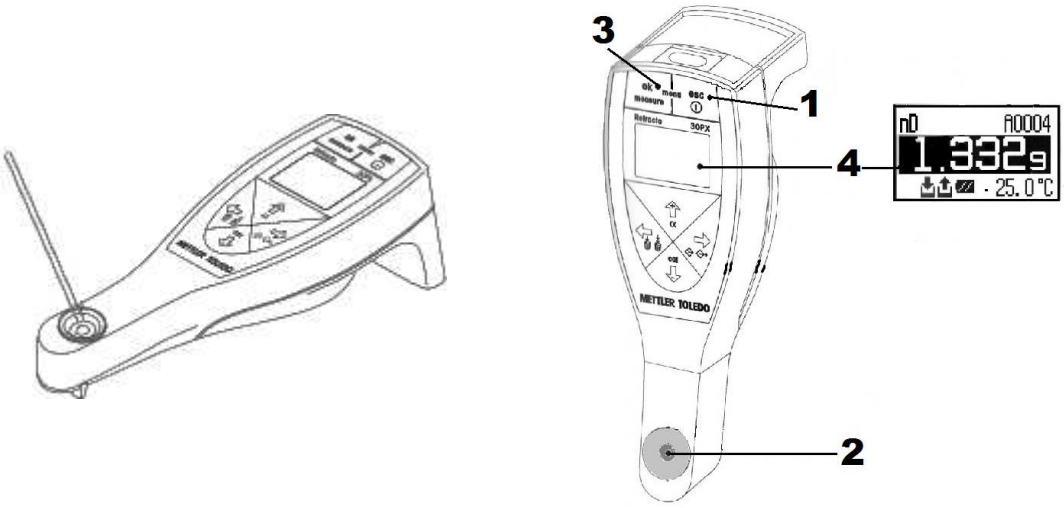
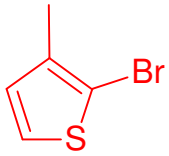


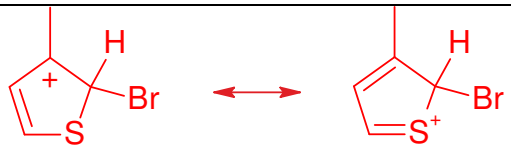
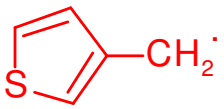
Fig. 3. Using the Refracto 30GS

1. To switch Refracto 30GS on, press and hold "ESC" button (1) until the display appears. The instrument is ready for operation. It switches off automatically if not operated for 10 min.
2. Clean the cell and glass rod with a napkin wetted with the solvent from the washing bottle labeled "cleaning solvent". Dry both with another napkin.
3. Make sure the sample to be measured has reached ambient temperature and is homogeneous.
4. Apply 2-3 drops of the sample onto the measuring cell (2) using the glass rod.
5. To start the measurement press and hold the ok button (3) until the beep.
6. Take the value of the refraction index and the temperature from digital display (4) and write down the result in the answer sheet.
7. Clean up the cell and the glass rod.

Q3. By comparing the obtained and literature data, draw the structure of the product and catalyst given.

The Product obtained	**The Catalyst given**
 3 marks	$HClO_4$ 1 mark 0 mark, if inconsistent with Q1

Q4. Draw the structure of the 3-methylthiophene-based reactive intermediates behind the selectivity in the case of **T1** and **T2**.

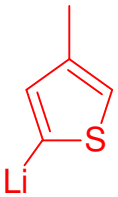
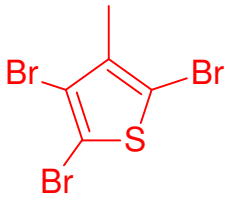
T1	**T2**
 1 mark for any of the structures	 1 mark

Q5. Write down the product (**T1** or **T2**) formed as a result of direct bromination of 3-methylthiophene with NBS under the given conditions / catalyst used.

$ZnBr_2$	T1
Dibenzoyl peroxide	T2
LiBr in AcOH	T1
Visible light or UV light	T2

0.25 marks each, 1 mark in total

Q6. In the synthetic pathways to **T3** and **T4**, draw the structures of the compounds formed in the first steps of each pathways shown on Scheme 1.

T3	**T4**
 1 mark	 1 mark

TASK 2. Analysis of the solution of a chromium – vanadium alloy (12 points)

Quest. #	Q1	Q2	Q3a	Q3b	Q4a	Q4b	Q5a	Q5b	Q6	Total
Marks	32	32	1	1	3	2	4	10	5	90

Antiferromagnetic materials show a good prospect in the development of memory devices for ultra-high-density data storage, the world's smallest magnetic memory bit using only 12 atoms being one of prime examples. Vanadium – chromium alloys exhibit antiferromagnetic properties at subzero temperatures. It is obvious that composition of alloys used in various hi-tech applications should be accurately controlled.

In this task, you will analyze an aqueous solution simulating the product of digestion of vanadium – chromium alloy sample. The task consists of two parts:

I. Oxidation of vanadyl (VO^{2+}) to vanadate (VO_3^-) in the test solution using potassium permanganate, followed by determination **of vanadium** (note that chromium (III) is not oxidized under these conditions).

II. Oxidation of the test solution with ammonium persulfate, followed by titrimetric determination of the **total content of vanadium and chromium** with Mohr's salt (Ammonium iron(II) sulfate).

Procedure

Note!

- ***The amount of vanadium and chromium should be calculated and reported in mg per 100 mL of the test solution.***
- ***Start doing this task with Part A, since you will need time to oxidize the test solution to be analyzed in Part C.***
- ***The 10.00-mL volumetric pipette has two graduation lines. You should pipette a volume between the two lines.***

Part A. Preparation of the solution for determination of vanadium and chromium total content

1. Transfer a 10.00-mL aliquot of your **test solution** into the 150-mL beaker and add 20 mL of 1M sulfuric acid using the 25-mL graduated cylinder.
2. Add 6–8 drops of the 0.3% solution of silver nitrate (the catalyst) and heat the mixture on the hotplate to 70–80°C (position 3), until condensate on the beaker wall appears.

3. Add 20 mL of the 10% ammonium persulfate solution to the heated mixture using the 100-mL graduated cylinder.
4. Continue heating and observe the appearance of **yellow** color, indicating the formation of dichromate.

Note! ***You can perform the determination of vanadium (Part B, 1 – 6), while the mixture is being heated.***

5. Keep heating the mixture for 10-15 min (position 3) after appearance of the yellow color to decompose the excess of ammonium persulfate (the decomposition is over when you see no small bubbles in the solution).
6. Cool the solution **to ambient temperature**.
7. Transfer **quantitatively** the solution from the 150-mL beaker into the **100-mL volumetric flask**, dilute to the mark with distilled water, stopper the flask and mix thoroughly.

Part B. Titrimetric determination of Vanadium

1. Transfer a 5.00-mL aliquot of the test solution into an Erlenmeyer flask using the graduated pipette.

Note! ***The 5.00-mL graduated pipette is self-draining.***

2. Carefully add 0.03 M potassium permanganate solution dropwise, shaking the flask after adding each drop until light pink color appears. Make sure that the light pink color is stable. Remove the excess of potassium permanganate by adding 0.03 M oxalic acid solution dropwise. Shake the flask after each drop until the light pink color changes to **pale blue**. Let the solution stand for about 1 min to make sure that the pink color has disappeared completely.
3. Transfer 10 mL of the 1M H_2SO_4 solution into the Erlenmeyer flask using the 25-mL graduated cylinder.
4. Add 2–3 (**not more!**) drops of the indicator into the Erlenmeyer flask and shake it vigorously. Let the flask stand for 2–3 min and observe the **purple** color appearance.
5. Fill the burette with the Mohr's salt solution. Use the 100-mL plastic beaker labeled "Waste" to drain the excess of Mohr's salt solution from the burette, record the initial reading.
6. Titrate the solution in the Erlenmeyer flask with the Mohr's salt solution until the color changes to **pure light green** through brownish-grey one.
7. Take the final reading of the burette. Repeat as necessary.

Q1. Fill in Table 2.

Table 2. Determination of vanadium

Titration №	1	2	3			
Initial reading of the burette, mL						
Final reading of the burette, mL						
Consumed volume, mL						

Accepted volume, V_1 _____mL

Part C. Titrimetric determination of vanadium and chromium total content in the test solution

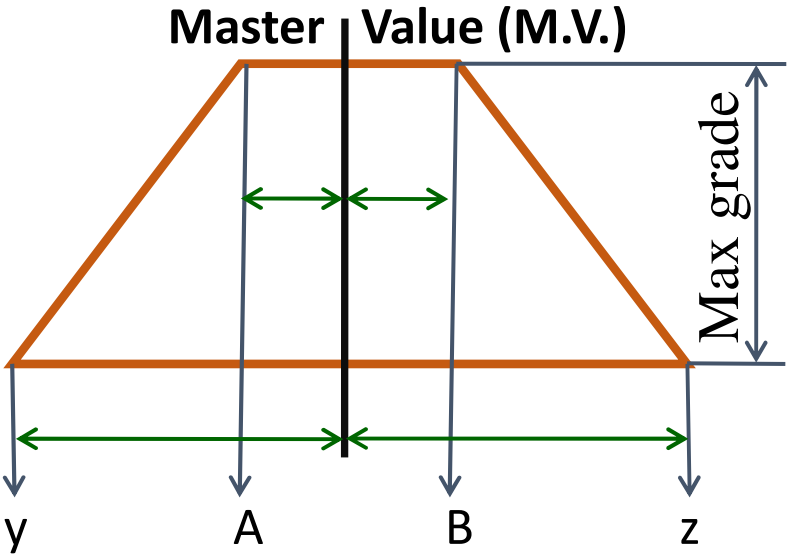
1. Wash the 10.00-mL volumetric pipette with distilled water, rinse with the solution prepared in 100-mL volumetric flask (obtained in part A).
2. Pipette a 10.00-mL aliquot into an Erlenmeyer flask, add 10 mL of 1M H_2SO_4 solution using the 25-mL graduated cylinder.
3. Add 3–4 drops of the indicator. Vigorously shake the flask and let it stand for 3–4 min. Observe appearance of **red** color.
4. Fill the burette with the Mohr's salt solution. Use the 100-mL plastic beaker labeled "Waste" to drain the excess of Mohr's salt solution from the burette, record the initial reading.
5. Titrate the solution in the flask with the Mohr's salt solution until the color changes to **light yellow-green**.
6. Take the final reading of the burette. Repeat as necessary.

Q2. Fill in Table 3.

Table 3. Determination of vanadium and chromium total content

Titration No	1	2	3			
Initial reading of the burette, mL						
Final reading of the burette, mL						
Consumed volume, mL						

Accepted volume, V_2 _____mL



If $A <$ Value $< B$, then Grade = *Maxgrade*

If Value $< y$, then Grade = 0, If Value $> z$, then Grade = 0

If $y <$ Value $< A$, then Grade = $Maxgrade * \frac{Value - y}{A - y}$

If $B <$ Value $< z$, then Grade = $Maxgrade * \frac{z - Value}{z - B}$

For Parts B and C (max marks 32 for each titration)

Parameter	Part B	Part C
A	M.V.-2.5%	M.V.-3.5%
B	M.V.+2.5%	M.V.+3.5%
y	M.V.-7.5%	M.V.-10%
z	M.V.+7.5%	M.V.+10%

Part D. Questions and Data Analysis

Q3. Write down the balanced chemical equations for the reactions that take place upon**:**

a) oxidation of the test solution with **potassium permanganate**

b) titration of vanadate with Mohr's salt

a) $2KMnO_4 + 10VOSO_4 + 12H_2O = 2MnSO_4 + 10HVO_3 + K_2SO_4 + 7H_2SO_4$	1 mark
b) $2HVO_3 + 2FeSO_4 + 3H_2SO_4 = 2VOSO_4 + Fe_2(SO_4)_3 + 4H_2O$	1 mark

Q4. Write down the balanced chemical equations for the reactions that take place upon**:**

a) oxidation of the test solution with **ammonium persulfate**

b) titration of the oxidized test solution with Mohr's salt

a) $Cr_2(SO_4)_3 + 3(NH_4)_2S_2O_8 + 7H_2O = H_2Cr_2O_7 + 3(NH_4)_2SO_4 + 6H_2SO_4$	1.5 mark
$2VOSO_4 + (NH_4)_2S_2O_8 + 4H_2O = 2HVO_3 + (NH_4)_2SO_4 + 3H_2SO_4$	1.5 mark
b) $H_2Cr_2O_7 + 6FeSO_4 + 6H_2SO_4 = Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$	1.5 mark
$2HVO_3 + 2FeSO_4 + 3H_2SO_4 = 2VOSO_4 + Fe_2(SO_4)_3 + 4H_2O$	0.5 mark

Q5. Calculate the a) V(IV) and b) Cr(III) concentrations in the test solution. Calculate the amount of the metals in mg **<u>per 100 mL of test solution</u>**.

a) Your work: Vanadium:

a) $C(VO^{2+}) = \frac{V_1(Fe^{2+}) * C(Fe^{2+}) * 1000}{1000 * V_{2,1}}$, mol L^{-1} 3 marks

b) $m(V) = 0{,}1 * C(VO^{2+}) * M(V) * 1000$, mg 1 mark

b) Your work: Chromium:

a) $n(Fe^{2+} on\ Cr_2O_7^{2-}) = \frac{V_2(Fe^{2+}) * C(Fe^{2+})}{1000} - 2 * \frac{V_1(Fe^{2+}) * C(Fe^{2+})}{1000} * \frac{10}{100}$, mol L^{-1} 4 marks

b) $n(Cr_2O_7^{2-}) = \frac{1}{6} n(Fe^{2+} on\ Cr_2O_7^{2-})$, mol L^{-1} 2 marks

c) $C(Cr^{3+}) = 2 * \frac{n(Cr_2O_7^{2-}) * 100}{10} * \frac{1000}{100}$, mol L^{-1} 2 marks

d) $m(Cr) = 0{,}1 * C(Cr^{3+}) * M(Cr) * 1000$, mg 2 marks

Q6. This protocol can not be applied to the determination of vanadium and chromium in steels, if the steel was digested by conc. HCl. Give equations of two reactions to explain the reasons behind.

$Fe + 2HCl \rightarrow FeCl_2 + H_2\uparrow$
$2FeSO_4 + (NH_4)_2S_2O_8 \rightarrow Fe_2(SO_4)_3 + (NH_4)_2SO_4$
$2Cl^- + S_2O_8^{2-} \rightarrow Cl_2 + 2SO_4^{2-}$
(decrease of the amount of ammonium persulfate due to its reaction with excess of iron(II) in steels)

2.5 marks

$Ag^+ + Cl^- \rightarrow AgCl\downarrow$; $AgCl + Cl^- \rightarrow AgCl_2^-$
(reaction between the catalyst and chloride)

2.5 marks

TASK 3. Kinetic determination of Diclofenac (DCF) (13 points)

Quest. #	Q1	DCF curves	DCF Control	Reaction order	Total
Marks	10	40	20	10	80

Kinetic methods with spectrophotometric detection for assaying drugs have been intensively developed during the last decade due to a number of obvious advantages, including inherent simplicity, cost-effectiveness, availability in most quality control laboratories, and improved selectivity. In this task you will:

- Perform kinetic determination of Diclofenac (DCF) in a medicine by following the progress of the drug oxidation reaction.
- Determine the reaction order with respect to DCF

Q1. Spectral changes in the course of DCF oxidation with $KMnO_4$ are given in Fig. 4, (1 to 10 reflects the reaction progress). Complete the table below suggesting which wavelengths can be applied for photometric kinetic determination of DCF. In each case, indicate the direction of the absorbance changes (denote increasing with ↑ and decreasing with ↓).

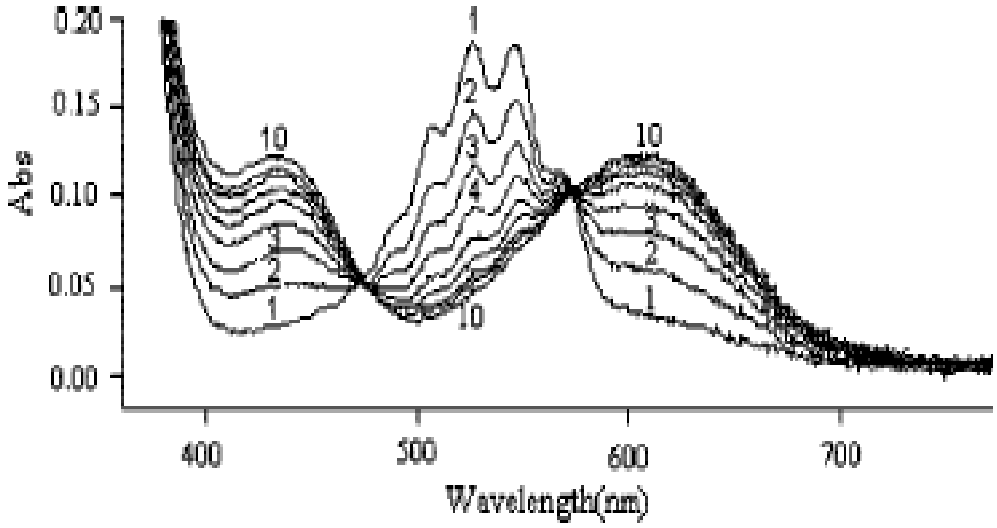


Fig. 4. DCF oxidation with $KMnO_4$

#	Wavelength, nm	Yes or No and direction
1	420	Yes ↑ 2 marks
2	480	No 2 marks
3	520	Yes ↓ 2 marks
4	580	No 2 marks
5	610	Yes ↑ 2 marks

Procedure

Part A. Assembling of laboratory equipment

Assemble the laboratory equipment as shown in Fig. 5. Connect the photometer (1), 525 nm (fixed wavelength) and thermostat (2) to the Netbook via USB slots. Connect the thermostat to the cable labeled “Thermo” to the power supply at your work place via the power adapter. Put the optical cuvette (3) on top of the magnetic stirrer (4), pass the cuvette through the photometer from aside (not possible from top down) and place the thermostat over the cuvette from top down (Fig. 5b).

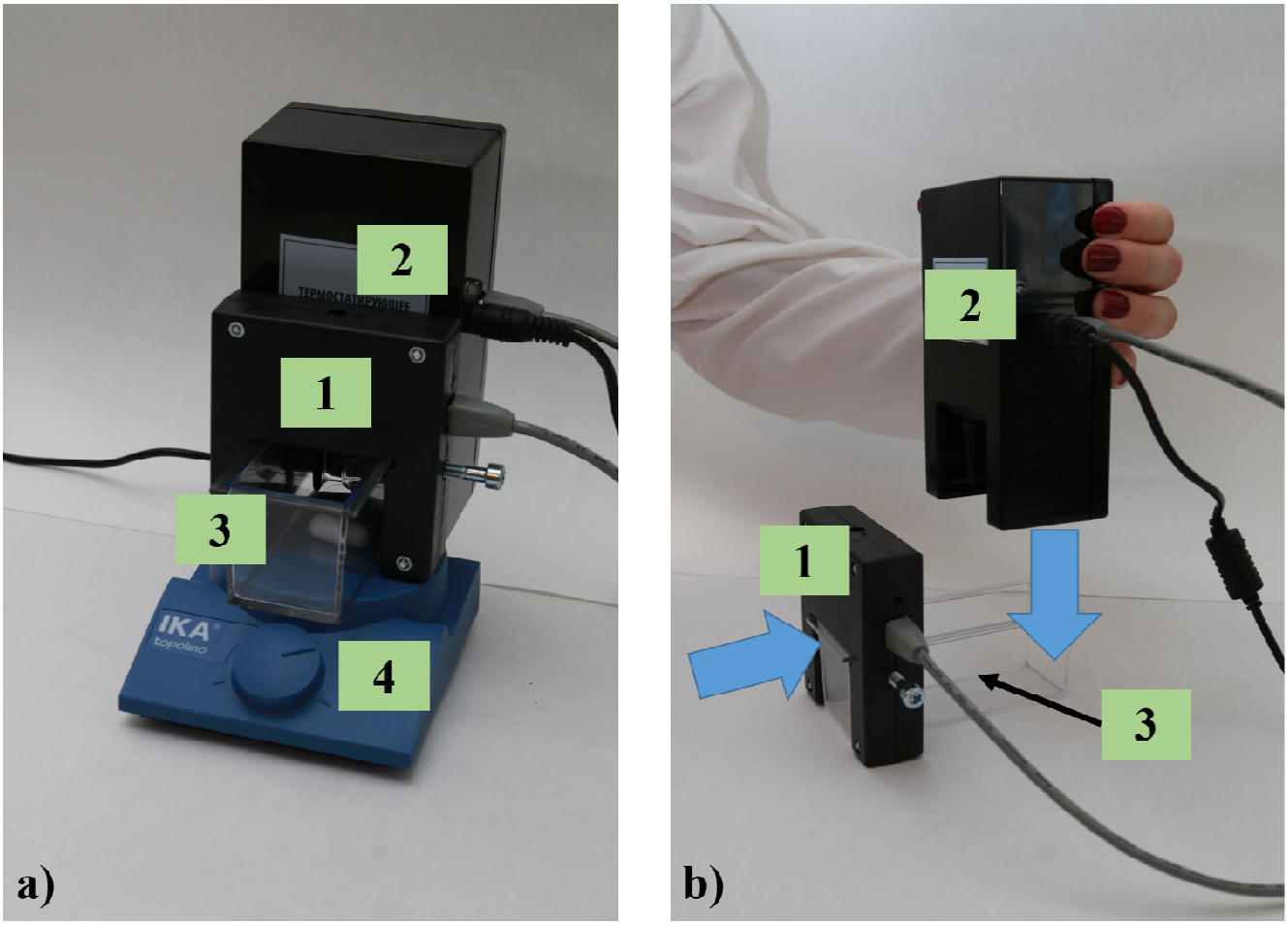


Fig. 5. Laboratory equipment

Hints!

- ***Plug in your Netbook to the mains before switching on.***
- ***Plug in all the equipment (the photometer and thermostat) before switching on the Netbook. Switch on the mouse.***
- ***If only one window (hereafter referred to as Pattern) instead of two appears after launching the software, quit and re-launch the program.***

- ***Do not unplug ANY device from the USB slot while carrying out the measurements. If it still happens, you will see a warning on the screen. Quit and re-launch the program.***
- ***If your Netbook falls asleep, click the «Setup» button in the Measurements window on the absorbance plot pattern when reverting to the measurements.***
- ***In case you see chaotic temperature changes on the screen, stop and re-start the measurement.***

Part B. Plotting of the calibration curve

All measurements needed to plot the calibration curve are carried out at 30 °C with constant $KMnO_4$ and H_2SO_4 initial concentrations. The DCF concentration is varied by using 4 different aliquots (of 0.2, 0.4, 0.6, and 0.8 mL) of the DCF stock solution.

1) Transfer 5 mL of 1M H_2SO_4 solution using the graduated cylinder and 0.2 mL of DCF stock solution using the 2 mL pipette into the 100 mL volumetric flask, dilute to the mark with distilled water, stopper the flask and mix thoroughly.
2) Carry over the flask contents into the cuvette, put the medium-size stir-bar and switch on the magnetic stirrer. Adjust the stirring speed regulator to the mark shown on Fig. 5a to provide for intensive mixing.
3) Launch the «Chemistry-Practicum» software on the Netbook. The software will detect the external devices (sensors) automatically. You will see two plot patterns (that of absorbance/extinction/optical density, D *vs.* t, s; and that of temperature, T °C *vs.* t, s) on the display.
4) Set the following parameters in the Menu bars of the corresponding plot patterns (Fig. 6):

- Click the  icon next to the  button («Fixes X-axis maximum on screen») on the absorbance plot pattern. The entire plot will always fit to the screen;
- Click the  button («Sets the Y range») on the absorbance plot pattern and set the absorbance range (the ordinate axis) from -0.1 to 1.1.
- Type "2" (instead of "1") in the box of the measurements interval on the absorbance plot pattern.
- Choose «Precisely» in the «Precisely/Roughly» window on the temperature plot pattern, then click on the «T = X» button and set the required temperature of 30 °C in the pop-up window.
- Calibrate the photometer by clicking the «Setup» button in the Measurements window on the absorbance plot pattern.

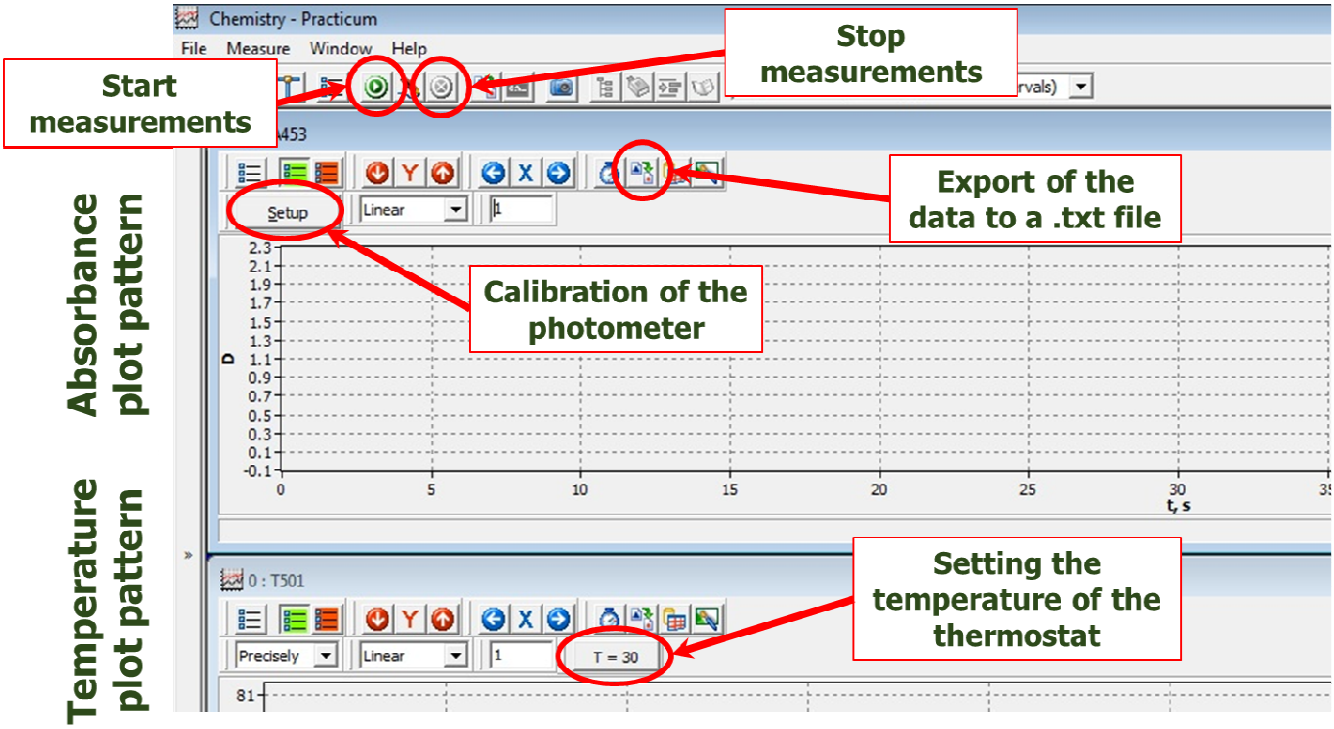


Fig. 6. "Chemistry-Practicum" software interface

Note! ***Setting the parameters (step 4) is needed only prior to the first measurement.***

5) Click the  button («Start measure for chosen sensors») to switch on the thermostat and observe the lamp heating up the solution in the cuvette. Follow the current temperature reported in the line above the plot. Wait until the thermostat lamp switches off, reflecting the set up temperature is attained. Stop the measurements by clicking  button (is activated and turns to red-orange when the measurement is on).
6) Click any part of the absorbance plot pattern to activate it. Take 2 mL of the $KMnO_4$ solution using the 2 mL pipette. Click the  button («Start measure for chosen sensors») in the Menu bar of the Measurements window and quickly blow out (press the pipette piston) the permanganate solution from the pipette into the cuvette.

Note! ***Make sure the temperature in the cuvette equals 30 ℃ before adding the $KMnO_4$ solution!***

7) Observe the progress of the kinetic curve on the screen. Continue measurement for 50 s after adding the $KMnO_4$ solution, then terminate the measurement by clicking the «Stop measurements»  button.

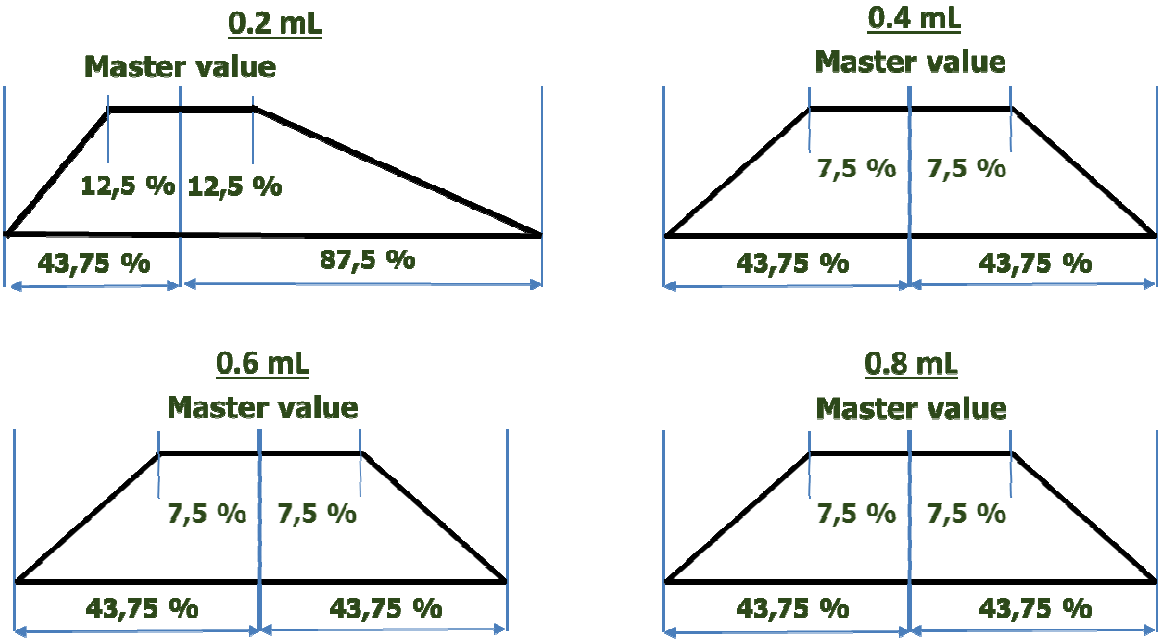
8) Save the data by clicking the  button («Export all the data collected in an external file») in the Menu bar of the absorbance plot pattern, choose the **Desktop** and type the file name "DCF2" (change the name to "DCF4", or "DCF6", or "DCF8" in the subsequent experiments).

Note!

- ***Use only the names of the given format!***
- ***Always save the data on your Desktop before starting the next experiment, otherwise the current data set will be lost after the next click on the***  ***button.***
- ***Make sure absorbance plot pattern is active when exporting the data. Otherwise, you will export invalid results. In case no pattern is chosen, you will get a warning.***

9) Empty the cuvette into the Waste bottle, wash thoroughly the cuvette with distilled water. Use black magnet from the outer side of the cuvette to avoid your stir-bar being dropped into the Waste bottle while washing. Wipe carefully the external surfaces of the cuvette with the napkin. Also, use the napkin to dab the thermostat lamp.

10) Repeat the steps 1), 2) 5)-9) with the other volumes of the DCF stock solution.



10 marks maximum for each of 4 measurements. Students data will be recalculated by Science Committee. 40 marks in total.

Part C.

1. Studying of the DCF containing medicine ("Control")

1) Wash the volumetric flask and prepare the mixture as described above using a 0.4 mL aliquot of the medicine ("Control") instead of the DCF stock solution.
2) Repeat the steps 1), 2), 5)-9) described in Part B. When saving the data, name the file "DCFmed".
3) Repeat the measurement of the "Control" as necessary.

2. Experimental data analysis

1) Open the Excel file on your memory stick in Excel. One by one open your saved data files in Notepad by double clicking on them on Desktop. Choose Edit/Select All in the Menu bar, then right click and copy the selected data into the Excel sheet with the corresponding name (the volume of DCF added or "DCFmed") and choose Edit/Paste in the Menu bar. You will see the experimental data on the Excel sheet (time, s, in column A, and absorbance in column B).

2) Ignore the values before the maximum. Select columns A and B, and plot the data. Use the "Insert Scatter" icon shown on Fig. 7.

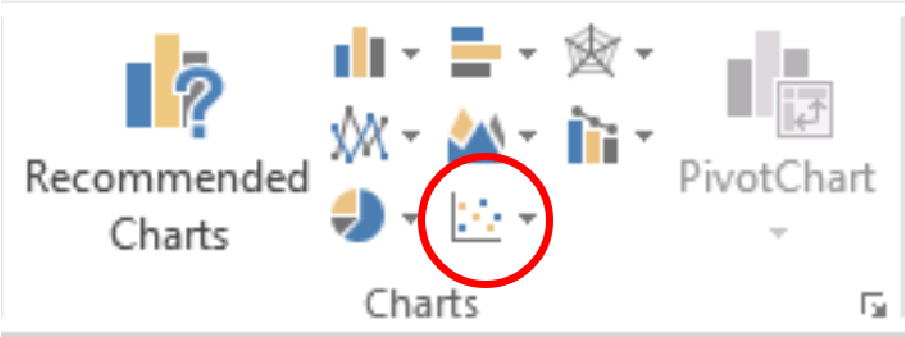
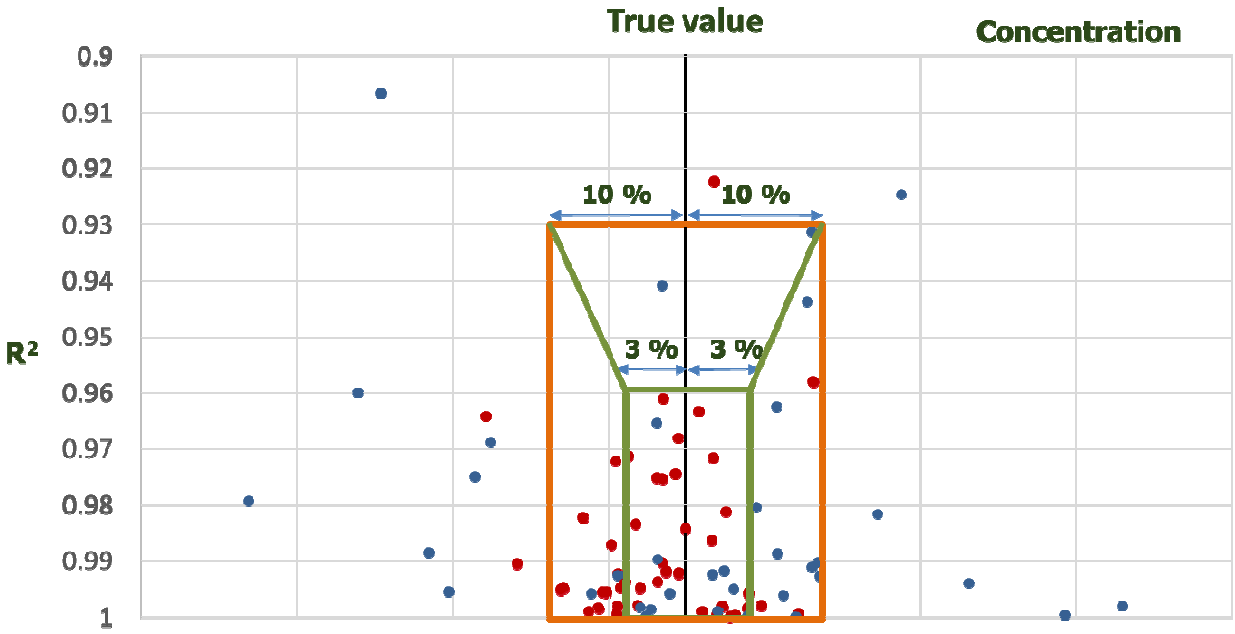


Figure 7. Position of the "Insert Scatter" icon

3) Choose the initial linear section of the remaining curve (15 to 20 data points), apply linear approximation by adding the linear trend line and bring the parameters to the chart area. Make sure that the R^2 value exceeds 0.98. If needed, decrease the number of the experimental data points plotted removing later data points. Still always search for the most wide range of the experimental data providing for the target R^2 value. Determine the value of the initial rate of absorbance change, v_0.

Note! ***You will get zero point for this part of the task if less than 12 values are included in the plotted data range.***

4) Analyze similarly the experimental data obtained with the other DCF concentrations and with the medicine solution "Control" ("DCFmed" file).
5) Calculate the DCF concentrations in the reaction mixtures (in mg/L). Write down the DCF concentrations and initial rates in appropriate cells of the "Results" Excel sheet.
6) Plot the calibration graph on the "Results" sheet and use it to determine the DCF concentration in the analyzed mixture prepared from the medicine ("Control"). Fill in the appropriate cells of the "Results" Excel sheet with the coefficients of linear approximation of the calibration graph. Calculate the DCF concentration in the medicine.



20 marks maximum (including 8 marks for data obtained and calculations). To be graded similarly to the procedure in Task 1.

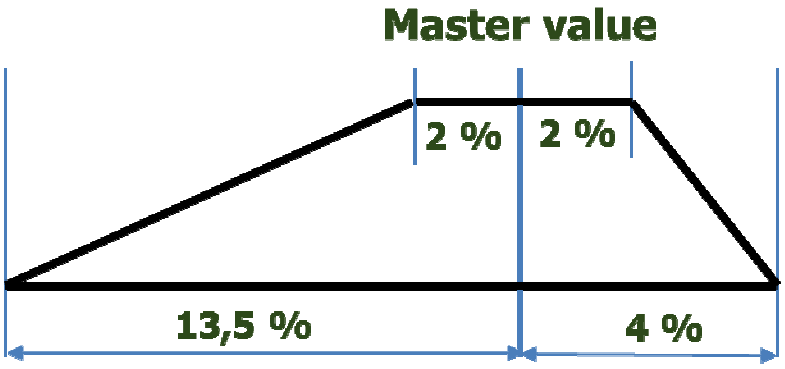
The grading scheme takes into account two values re-measured by the Science Committee: R-squared value (R^2) and obtained concentration of the control solution (Conc).

- If the value obtained is within region A, 100% of 12 marks
- If the value obtained is within region B, 0.1926*Conc-154.2857 (%) of 12 marks
- If the value obtained is within region C, 400*R^2-372 (%) of 12 marks
- If the value obtained is within region D, -0.1926*Conc+188.5714 (%) of 12 marks

Master value – 890.1 mg/L

7) Write down the accepted value in the cell F10 of the "Results" sheet.

8) On the "Results" Excel sheet, graphically determine the reaction order with respect to DCF and write down the exact obtained value in the cell I3.



10 marks for the determination of the reaction order

9) Once finished, save your file and invite your Lab assistant to demonstrate that you have got experimental data in the Excel file. Sign and get the Lab assistant's signature.

Note! ***Only the data saved on the memory stick will be considered as the result of the Task.***

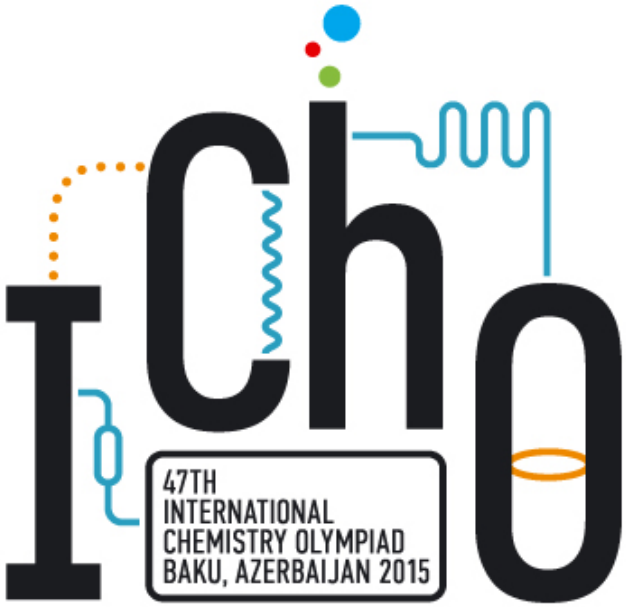
Data present in Excel on the memory stick (to be ticked by the Lab assistant)

☐ Yes	☐ No	Student	Lab assistant
		_____	_____

REPLACEMENTS WITH PENALTY

Item	Quantity	Student's signature	Lab assistant's signature

Life is a huge lab



THEORETICAL EXAMINATION

ANSWERS and GRADING SCHEMES

JULY 25, 2015

BAKU, AZERBAIJAN

General Directions

- Write down your name and code number on each page.

- You have 5 hours to fulfill the tasks. Failure to stop after the STOP command may result in zero points for the current task.

- Write down answers and calculations within the designated boxes. Give your work where required.

- Use only the pen and calculator provided.

- If you need draft paper use the back side of the paper. It will not be marked.

- There are **40** pages in the booklet including the answer boxes, Cover Sheet and Periodic Table.

- The official English version is available on demand for clarification only.

- Need to go to the restroom – raise your hand. You will be guided there.

- **After the STOP signal** put your booklet in the envelope (don't seal), leave at your table. Do not leave the room without permission.

- You have additional 15 minutes to read the whole set.
-
- Formulas necessary for solution of some problems can be found on the next page.

Physical Constants, Units, Formulas and Equations

Universal gas constant	$R = 8.3145\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
Standard pressure	$p^\circ = 1\ \mathrm{bar} = 10^5\ \mathrm{Pa} = 750\ \mathrm{mmHg}$
Atmospheric pressure	$1\ \mathrm{atm} = 1.013 \times 10^5\ \mathrm{Pa} = 760\ \mathrm{mmHg}$
Zero of the Celsius scale	273.15 K

Reversible adiabatic process for an ideal gas	$pV^{1+R/C_V} = \mathrm{const}$
Work made on an ideal gas in an adiabatic process	$W = nC_V(T_2 - T_1)$
Dependence of internal energy on temperature	$U(T_2) = U(T_1) + C_V(T_2 - T_1)$
Relation between molar isobaric and isochoric heat capacities for an ideal gas	$C_p = C_V + R$
Gibbs energy	$G = H - TS$
Relation between equilibrium constant and standard Gibbs energy	$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right)$
Dependence of Gibbs energy of reaction on concentration or pressure	$\Delta G = \Delta G^\circ + RT \ln \frac{a_{\mathrm{prod}}}{a_{\mathrm{reag}}}$, $a = c$ / (1 mol/L) for the substances in solution, $a = p$ / (1 bar) for gases
Change of Gibbs energy per unit volume in time for the system with two chemical reactions 1 and 2 with rates r_1 and r_2	$\frac{\Delta G_{\mathrm{Syst}}}{\Delta t} = \Delta G_1 r_1 + \Delta G_2 r_2$

Problem 1. New and well-forgotten old refrigerants
(8 points)

Question	1			2			3	4				**Total**
	1.1	1.2	1.3	2.1	2.2	2.3		4.1	4.2	4.3	4.4	
Marks	4	2	2	1	1	1	3	10	2	6	1	**33**

The problem of choosing a refrigerant for refrigeration and air conditioning systems attracted the attention of scientists and technologists throughout the last century. It has been suggested that during this time refrigerants progressed through four generations. Ammonia, which was ascribed to the first generation, had been used in most of the oldest refrigeration units. It was later replaced by chlorofluorocarbons (CFCs) – derivatives of methane and ethane with the hydrogen atoms replaced by fluorine and chlorine.

In Baku, at "Bakkonditsioner" factory, production of the first Soviet serial household air conditioners BK-1500 had been launched. A second-generation refrigerant chlorodifluoromethane CHF_2Cl was used in them. In this problem, we compare various refrigerants in terms of thermodynamics.

First air conditioner of Baku factory in a souvenir shop in the Old City ("Icheri Sheher")

Thermodynamic properties of various refrigerants

Refrigerant	"Generation"	ΔH_{vap} / kJ·mol^{-1} (at 280 K)	$C_{V(gas)}$ / J·K^{-1}·mol^{-1}
NH_3	1	21.3	26.7
CHF_2Cl	2	20.0	48.8
CF_3CH_2F	3	22.1	79
$CF_3CF{=}CH_2$	4	19.1	120

Consider a model refrigeration cycle consisting of 4 steps schematically shown below in the pressure (p) – internal energy (U) coordinates.

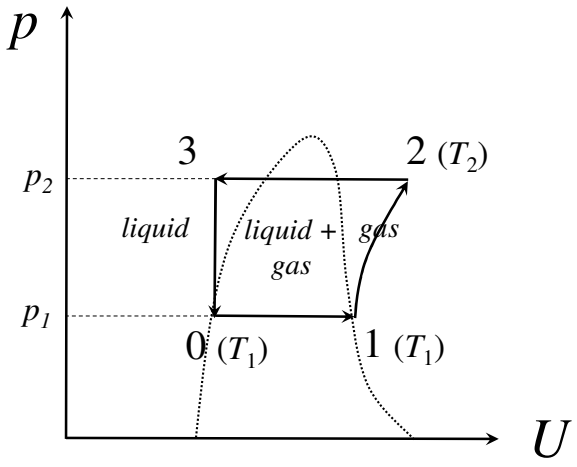


Diagram 1. Dashed line indicates the phase boundaries

During the first step of the cycle (line 0-1 in diagram 1), a liquid refrigerant is boiling at constant pressure p_1 and temperature T_1 (boiling temperature) until it completely evaporates. At this step, the refrigeration unit absorbs heat from surrounding objects. At the second step, the refrigerant undergoes reversible adiabatic compression and heats up to temperature T_2 (line 1-2). After that the compressed refrigerant is cooled in a condenser at constant pressure p_2 (line 2-3) and then returns to the initial state (line 3-0).

Let the cycle involve 1 mole of refrigerant, which is initially (point 0) completely liquid, T_1 = 280 K, T_2 = 380 K, assume that the vapor of any refrigerant behaves like an ideal gas. The thermodynamic characteristics of refrigerants are listed in the table above.

1.1. For each of refrigerants, ammonia and chlorodifluoromethane, calculate the amount of heat Q absorbed by refrigeration unit during heat exchange (line 0-1) and the work W required to compress its vapor adiabatically (line 1-2).

Calculations

Note: here and below in this problem, only correct VALUES are marked except 4.1, 4.3

Ammonia

$Q = \nu\Delta H_{vap}$ = 21.3 kJ; **1p**

$W = \nu C_{V(gas)}(T_2 - T_1)$ = 2.67 kJ. **1p**

Q = 21.3 kJ

W = 2.67 kJ

Chlorodifluoromethane

$Q = \nu\Delta H_{vap}$ = 20.0 kJ; **1p**

$W = \nu C_{V(gas)} \cdot (T_2 - T_1)$ = 4.88 kJ. **1p**

Q = 20.0 kJ

W = 4.88 kJ

1.2. Which quantity(ies) remain(s) constant during the adiabatic compression step? Indicate by the circle(s).

U *H* (*S*) *G* *V*

2p for the correct answer
Minus 1p for every incorrect option, total – no less than 0.

To compare the energy efficiency of refrigeration cycles with different parameters and refrigerants, the coefficient of performance (*COP*) is used, which is defined as a ratio of heat removed from a cooled system to the work of compressor: $COP = Q/W$.

1.3. Calculate the values of *COP* in a considered cycle for ammonia and chlorodifluoromethane.

Calculations

Ammonia
$COP = Q/W = 7.98$ **1p**

COP = 7.98

Chlorodifluoromethane
$COP = Q/W = 4.10$ **1p**

COP = 4.10

2.1. Why was ammonia replaced by CFCs in household refrigeration units? (Choose only one option)

a) to increase the energy efficiency of refrigeration cycles
b) because the density of ammonia is less than that of air under the same conditions
c) for user safety reasons

c

1p

A search for replacement of CFCs as refrigerants started when it was shown that their use can cause irreparable damage to the protective ozone layer of the atmosphere. The third, ozone-friendly generation of refrigerants came on the scene. Its typical representatives are fluoroalkanes.

2.2. What is the cause of the damage made by CFCs to the ozone layer? (Choose only one option)

a) ozone molecule easily adds to C–F bond
b) C–F bond is easily broken by radiation, which leads to the formation of free radicals
c) ozone molecule easily adds to C–Cl bond
d) C–Cl bond is easily broken by radiation, which leads to the formation of free radicals

d

1p

However, under the 1997 Kyoto Protocol, fluoroalkanes also had to be replaced because they accumulate in the atmosphere and rapidly absorb infrared radiation, causing a rise in temperature of the atmosphere (the greenhouse effect). The refrigerants of the fourth generation such as 2,3,3,3-tetrafluoropropene $CF_3CF{=}CH_2$ have been suggested and are coming into use.

2.3. Why does this compound enhance the greenhouse effect less than fluoroalkanes? (Choose only one option)

a) it is more reactive and easier to decompose
b) it easily reacts with ozone
c) it is better soluble in water

a

1p

3. Calculate the values of the *COP* in the refrigeration cycle considered above for two refrigerants of the third and fourth generations – CF_3CH_2F and $CF_3CF{=}CH_2$. Did the energy efficiency improve in comparison with CHF_2Cl? Choose "Yes" or "No".

Calculations

CF_3CH_2F

$COP = \Delta H_{vap} / (C_{V(gas)}(T_2 - T_1)) = 2.80$ **1p**

$COP = 2.80$

Yes **No** **0.5p**

$CF_3CF{=}CH_2$

$COP = \Delta H_{vap} / (C_{V(gas)}(T_2 - T_1)) = 1.59$ **1p**

$COP = 1.59$

Yes **No** **0.5p**

Unlike household appliances, industrial refrigeration systems are often still using ammonia. It does not contribute to the greenhouse effect nor does it destroy the ozone layer. Industrial units can have a huge size and a large cost. Prior to their construction, they should be carefully modeled taking into account many different factors. In real systems, some part of the refrigerant at the start of the heat exchange with the environment is in the vapor phase (point 0 in the diagram below), and at the end (point 1) it is always overheated above the boiling point.

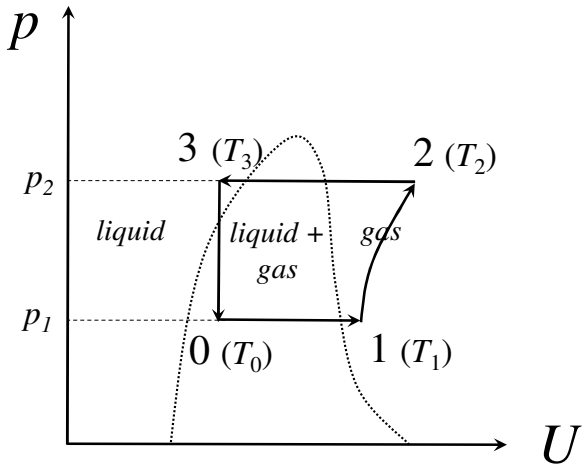


Diagram 2. Dashed line indicates the phase boundaries

Consider a cycle with 1 mole of ammonia. Its thermodynamic properties are the following: enthalpy of vaporization ΔH_{vap} = 23.35 kJ·mol^{-1} at T_{vap} = 239.8 K (boiling temperature at 1 bar pressure). Heat capacity of the liquid phase $C_{V(liq)}$ = 77 J·K^{-1}·mol^{-1}, of the gas phase $C_{V(gas)}$ = 26.7 J·K^{-1}·mol^{-1}. Assume that the heat capacities are temperature-independent and the vapor behaves like an ideal gas. The temperature dependence of the saturated vapor pressure of ammonia can be described by the empirical equation:

$$\log (p/\text{bar}) = 4.87 - 1114 / (T/\text{K} - 10.4).$$

During the first step of the cycle (line 0-1 in diagram 2), the equilibrium mixture of liquid refrigerant and its vapor receives heat from the environment at constant pressure p_1 = 3.0 bar. The refrigerant completely evaporates and overheats up to the temperature T_1 = 275 K. In the beginning of the process (point 0), the molar fraction of gaseous ammonia is x = 0.13.

4.1. Calculate the initial temperature of refrigerant T_0, its volume change ΔV and the amount of heat Q absorbed by refrigeration unit during this step. Take into account that the dependence of ΔH_{vap} from the temperature **cannot** be neglected.

Calculations:

$T_0 = 10.4 + 1114 / (4.87 - \log p_1) = 264$ K **2p**

$T_0 = 264$ K

$\Delta V = (\nu R T_1 / p_1) - (x\nu R T_0 / p_1) = 6.7$ L **3p**

$\Delta V = 6.7$ L

$Q = \Delta H = \Delta U + p_1 \Delta V = \Delta U$(liquid fraction)$+ \Delta U$(gas fraction) $+ p_1 \Delta V =$

$= \Delta U$(vaporization of liquid fraction at T_0) $+ \Delta U$(heating evaporated liquid fraction up to T_1) $+$

$+ \Delta U$(gas fraction) $+ p_1 \Delta V =$

$= \nu (1-x)(\Delta H_{vap} - RT_{vap} + (C_{V(gas)} - C_{V(liq)})(T_0 - T_{vap})) + \nu C_{V(gas)} (T_1 - T_0) + p_1 \Delta V = 19.8$ kJ

or

$Q = \nu (1-x)(\Delta H_{vap} + (C_{V(gas)} + R - C_{V(liq)})(T_0 - T_{vap})) + \nu (C_{V(gas)} + R)(T_1 - T_0) = 19.8$ kJ

5p

(3p for a correct equation for calculation and 2p for correct value)

$Q = 19.8$ kJ

Then the refrigerant is reversibly and adiabatically compressed. It heats up to the temperature $T_2 = 393$ K (line 1-2).

4.2. Find the work W required for compression and the COP of the system. If you were not able to find Q in 4.1, use $Q = 20.15$ kJ.

Calculations:

$W = \nu C_{V(gas)} (T_2 - T_1) = 3.15$ kJ **1p**

$W = 3.15$ kJ

$COP = Q/W = 6.3$ **1p**

$COP = 6.3$

At the next step corresponding to the line 2-3 in diagram, the compressed refrigerant is cooled in a condenser at constant pressure. Then it returns to the initial state through adiabatic expansion with zero work (line 3-0).

4.3. Determine the temperature T_3 at point 3 to which the refrigerant is cooled in a condenser.

Calculations:

The internal energies of the refrigerant are equal in points 0 and 3. Thus,

$x \cdot (\Delta H_{vap} - RT_{vap} + (C_{V(gas)} - C_{V(liq)})(T_0 - T_{vap})) + C_{V(liq)} (T_0 - T_3) = 0,$

$T_3 = 298$ K.

6p

(3p for a correct equation and 3p for correct value)

$T_3 = 298$ K

In the production of refrigeration units it is necessary to consider climatic factors. If a condenser is cooled by atmospheric air, the temperature T_3 increases as the air temperature increases.

4.4. How will the *COP* change if T_3 increases while T_0, T_1, T_2 remain the same?

a) Increase

b) Remain the same

c) Decrease

c

1p

Comment: It will decrease because the length of 0-1 line decreases or because x (see 4.3) increases and less liquid is in the equilibrium mixture at T_0, so less heat Q is necessary to evaporate it!

Problem 2. Coupling of chemical reactions
(7 points)

Question	1			2		3	**Total**
	1.1	1.2	1.3	2.1	2.2		
Marks	4	6	4	3	6	2	**25**

I.Prigogine (left)


N. Shilov


W. Ostwald

When in the system one reaction allows another one to proceed they say that these two reactions are coupled. Ilya Prigogine, Nobel prize winner in chemistry (1977) in his books widely used the concept of "coupled reactions". Coupling of reactions is an essential feature of living systems, including human body.

How one reaction makes another one to occur? In this problem we are going to discuss several possible mechanisms of coupling.

(I) "Chemical coupling"

"On Chemical coupling" was the title of the dissertation defended by Russian chemist N.Shilov in 1905. N. Shilov was the graduate student of famous professor W. Ostwald. Dr. Shilov described the following set of reactions.
The substance ***A*** does not react with ***Ac***. In the presence of the third reagent (called inductor), ***In***, however, the reaction of ***A*** with ***Ac*** takes place:

$$A + Ac \xrightarrow{\text{In the absence of In}} \text{no reaction!} \qquad (1)$$

$$A + Ac \xrightarrow{\text{In the presence of In}} P_1 \qquad (2)$$

In is not a catalyst! Its concentration decreases in the course of the reactions.

According to the scheme proposed by Shilov, ***Ac*** reacts not with ***A*** itself, but with the intermediate product ***R*** of the reaction of ***A*** with ***In***. There is another, competing reaction of ***R*** that forms P_2.

$$(a)\quad \alpha \boldsymbol{A} + \beta \boldsymbol{In} \xrightarrow{k(3a)} \boldsymbol{R}$$

$$(b)\quad \boldsymbol{R} \xrightarrow{k(3b)} \boldsymbol{P_2} \qquad (3)$$

$$(c)\quad \boldsymbol{R} + \boldsymbol{Ac} \xrightarrow{k(3c)} \boldsymbol{P_1}$$

α and β are stoichiometric coefficients. Other stoichiometric coefficients and **reaction order with respect to all reactants in all three reactions are unity.**

In the Shilov's experiments the ratio of the consumed amounts of ***Ac*** and ***In***, $I = \frac{\Delta n_{Ac}}{\Delta n_{In}}$ increased up to the constant value with the increasing initial concentration $[\boldsymbol{Ac}]_0$ at $[\boldsymbol{In}]_0$ = const.

1.1. What was this limiting constant value of I at $[\boldsymbol{Ac}]_0 \to \infty$, $[\boldsymbol{In}]_0$ = const?

Brief explanation

The value of I should increase with the increase of $[\boldsymbol{Ac}]_0$ at $[\boldsymbol{In}]_0$ = const, because the larger fraction of the intermediate product ***R*** will enter the reaction (3c). The maximum value of I will be achieved if all ***R*** reacts in (3c), therefore $I_\infty = 1/\beta$.

$I_\infty = 1/\beta$ **4 points** (**2 points** if only $I_\infty = 1/\beta$ is given!)

1.2. Derive an expression for I using the steady-state approximation if necessary. Plot the graph of I vs $[\boldsymbol{In}]_0$ at $[\boldsymbol{Ac}]_0$ = const. Assume that ***In*** was completely consumed and ***Ac*** was in excess..

Calculations

Shilov's mechanism includes the initial reaction

$\alpha \boldsymbol{A} + \beta \boldsymbol{In} \to \boldsymbol{R}$ (3a)

and two competitive reactions

$\boldsymbol{R} + \boldsymbol{Ac} \to \boldsymbol{P_1}$ (3c)

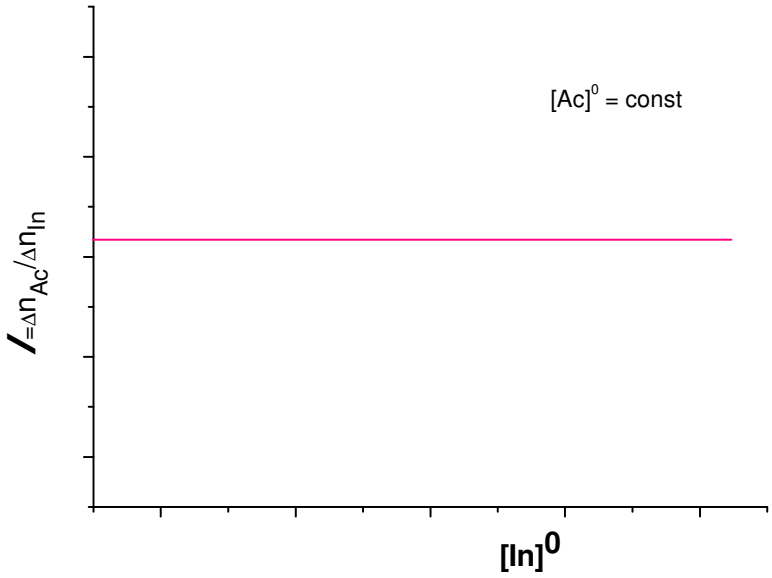
$\boldsymbol{R} \to \boldsymbol{P_2}$ (3b)

The rates of conversion of ***In*** and ***Ac*** are determined by the rates of the reactions (3a) and (3c), respectively:

$$\frac{r(3c)}{r(3a)}=\frac{k(3c)[R][Ac]}{k(3a)[A][In]}=\frac{k(3c)[Ac]\times\dfrac{k(3a)[A][In]}{k(3c)[Ac]+k(3b)}}{k(3a)[A][In]}=\frac{k(3c)[Ac]}{k(3c)[Ac]+k(3b)}$$

in steady-state approximation for [***R***]. We see that the ratio of two rates does not depend on the initial concentration $[\boldsymbol{In}]_0$ and I will also not depend on it. This gives the straight line parallel to the $[\boldsymbol{In}]_0$ axis on the graph.

Graph



6 points (**2 points** for the graph + **4 points** for the steady-state equations)

What if Shilov's mechanism is not valid and ***In*** is a conventional catalyst of the reaction (2)? Simultaneously ***In*** reacts with ***A*** and its concentration decreases. The reaction scheme in this case is

$$(a)\quad \alpha\boldsymbol{A}+\beta\boldsymbol{In}\longrightarrow \boldsymbol{P}_2$$
$$(b)\quad \boldsymbol{A}+\boldsymbol{Ac}\xrightarrow{\boldsymbol{In},\ \text{catalysis}}\boldsymbol{P}_1 \qquad (4)$$

1.3. What is the limiting value of I for the reaction scheme (4) at $[\boldsymbol{Ac}]_0 \to \infty$, $[\boldsymbol{In}]_0$ = const?

Brief explanation

In this case I will permanently increase with the increase of $[\boldsymbol{Ac}]_0 \to \infty$ at $[\boldsymbol{In}]_0$ = const. The rate of the reaction (4b) may be so high that conversion of ***In*** in reaction (4a) will be negligible. Hence $I \to \infty$ if $[\boldsymbol{Ac}]_0 \to \infty$ at $[\boldsymbol{In}]_0$ = const.

$I_\infty = \infty$ (infinity) **4 points** (**2 points** if only $I_\infty = \infty$ (infinity) is given).

(II) «Kinetic coupling»

The standard Gibbs energy of the gas-phase reaction

$$Br + H_2 \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} HBr + H \qquad (5)$$

is positive, $\Delta G^\circ(5) = 66$ kJ·mol^{-1} at $T = 600$ K.

2.1. What is the ratio of the rates of forward and reverse reactions, $\frac{r_5}{r_{-5}}$, at this temperature, standard pressures of H_2 and HBr and equal pressures of H and Br?

Calculations

The standard Gibbs energy of reaction (5) at 600K is 66 kJ/mol. The equilibrium constant is

$K = e^{-66000/8.314/600} = 1.8 \cdot 10^{-6} = k_5 / k_{-5}$. **1 point**

Reaction is considered at standard pressures of all the reactants and products. The ratio of the rates of forward and reverse reactions is

$$\frac{r_5}{r_{-5}} = \frac{k_5[Br][H_2]}{k_{-5}[HBr][H]} = \frac{k_5}{k_{-5}} = 1.8 \cdot 10^{-6}$$

$$\frac{r_5}{r_{-5}} = 1.8 \cdot 10^{-6}$$ **2 points**

Total – **3 points**

If you could not answer this question, for further calculations use reference value $r_5/r_{-5} = 3.14 \cdot 10^{-7}$.

Reaction (5) proceeds in the forward direction due to the reaction (6) which simultaneously occurs in the system:

$$Br + H_2 \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} HBr + H \qquad (5)$$

$$H + Br_2 \xrightarrow{k_6} HBr + Br \qquad (6)$$

k_5, k_{-5}, k_6 are rate constants of forward and reverse reaction (5) and forward reaction (6), respectively.

This is the *kinetic coupling* of two reactions.

Let pressures of neutral molecules keep standard values $p(H_2) = p(Br_2) = p(HBr) = 1$ bar, and pressures of radicals $p(H)$, $p(Br)$ reach steady-state values. Rate constant k_6 is 10 times larger than k_{-5}.

2.2. Calculate $\Delta G(5)$ and $\frac{r_5}{r_{-5}}$ under such conditions.

Calculations

The steady-state condition is the same for both radicals, e.g. for radical H

$$\frac{d[H]}{dt} = k_5[Br][H_2] - k_{-5}[HBr][H] - k_6[H][Br_2] = 0$$

$$\frac{[H]}{[Br]} = \frac{k_5[H_2]}{k_{-5}[HBr] + k_6[Br_2]}$$

The concentrations of all the neutral molecules are the same (they correspond to the pressure of 1 bar), therefore

$$\frac{[H]}{[Br]} = \frac{k_5}{k_{-5} + k_6} = \frac{k_5 / k_{-5}}{1 + k_6 / k_{-5}} = \frac{1.8 \cdot 10^{-6}}{1 + 10} = 1.6 \cdot 10^{-7}$$ **2 points**

The Gibbs energy of reaction (5) under such conditions is:

$$\Delta G = \Delta G^\circ + RT \ln \frac{[H][HBr]}{[Br][H_2]} = 66 + 8.314 \cdot 10^{-3} \cdot 600 \cdot \ln\left(1.6 \cdot 10^{-7}\right) = -12\,\text{kJ} \cdot \text{mol}^{-1}$$

2 points

The ratio of rates is:

$$\frac{r_5}{r_{-5}} = \frac{k_5[Br][H_2]}{k_{-5}[HBr][H]} = \frac{k_5}{k_{-5}} \frac{[Br]}{[H]} = \frac{k_5}{k_{-5}} \frac{1 + k_6 / k_{-5}}{k_5 / k_{-5}} = 1 + \frac{k_6}{k_{-5}} = 11$$ **2 points**

$\Delta G(5) = -12$ kJ·mol^{-1}

$\frac{r_5}{r_{-5}} = 11$

Total – **6 points**

(III) "Second law of thermodynamics restricts coupling"

According to the Second Law of thermodynamics, two simultaneously occurring chemical reactions should decrease the system's Gibbs energy G_{Syst}, $\frac{\Delta G_{\text{Syst}}}{\Delta t} < 0$.

One of these reactions may have positive Gibbs energy and still proceed in the forward direction due to the coupling with the second reaction. This second reaction must have negative Gibbs energy and the requirements of the Second law must be fulfilled! Consider the example.

The synthesis of urea under specific conditions

$$2NH_3 + CO_2 \rightarrow (NH_2)_2CO + H_2O \qquad (7)$$

$\Delta G(7) = 46.0\ \text{kJ}\cdot\text{mol}^{-1}$

is supposed to be coupled with the complete oxidation of glucose (under the same conditions)

$$1/6\ C_6H_{12}O_6 + O_2 \rightarrow CO_2 + H_2O \qquad (8)$$

$\Delta G(8) = -481.2\ \text{kJ}\cdot\text{mol}^{-1}$,
$r(8) = 6.0\cdot10^{-8}\ \text{M}\cdot\text{min}^{-1}$.

Both reactions are presented schematically. No other reactions are considered.

3. What is the maximum rate of the reaction (7) permitted by the Second Law if this reaction is coupled to reaction (8)?

Calculations

According to the Second law the following condition has to be met:

$$\frac{\Delta G_{\text{Syst}}}{\Delta t} = \Delta G(7) \times r_7 + \Delta G(8) \times r_8 \le 0$$

therefore

$$r_7 \le \frac{-\Delta G(8)}{\Delta G(7)} r_8 = \frac{481.2}{46.0} \cdot 6.0 \cdot 10^{-8} = 6.3 \cdot 10^{-7}\ \text{M} \cdot \text{min}^{-1}$$

This is the maximum possible rate of the coupled reaction.

$r_7(\text{max}) = 6.3\cdot10^{-7}\ \text{M}\cdot\text{min}^{-1}$ **2 points**

Problem 3. Two binding centers – competition or cooperation?
(7 points)

Question	1		2				Total
	1.1	1.2	2.1	2.2	2.3	2.4	
Marks	3	2	8	3	6	6	**28**

Many chemical reactions in living organisms include the formation of "host-guest" complexes where the host molecule reversibly binds one or several guest molecules. Consider a host molecule ***H*** with two binding centers – say, *a* and *b* which have different affinities for the guest molecules ***G***:

$$\boldsymbol{H} + \boldsymbol{G} \rightleftarrows \boldsymbol{HG_a} \qquad K_a = \frac{[\boldsymbol{HG_a}]}{[\boldsymbol{H}][\boldsymbol{G}]}$$

$$\boldsymbol{H} + \boldsymbol{G} \rightleftarrows \boldsymbol{HG_b} \qquad K_b = \frac{[\boldsymbol{HG_b}]}{[\boldsymbol{H}][\boldsymbol{G}]} \qquad K_b \neq K_a.$$

where $\boldsymbol{HG_a}$ and $\boldsymbol{HG_b}$ denote a complex where guest is bound to *a* center and *b* center, respectively. K_a and K_b are the binding constants for the centers *a* and *b*, brackets denote molar concentrations.

Attachment of one ***G*** molecule to ***H*** can change the binding ability of the second centre. This change is described by the "interaction factor" β which reflects the influence of one binding center on another and is defined as follows:

$$\boldsymbol{HG_a} + \boldsymbol{G} \rightleftarrows \boldsymbol{HG_2} \qquad \frac{[\boldsymbol{HG_2}]}{[\boldsymbol{HG_a}][\boldsymbol{G}]} = \beta K_b$$

where $\boldsymbol{HG_2}$ is the completely bound complex.

1.1. Determine the range of values (or one value, if necessary) of β which correspond to three possible ways of interaction between binding centers: a) cooperation (binding by one center facilitates subsequent binding); b) competition (first binding complicates the second); c) independence (no interaction).

Cooperation: $\beta > 1$	**1 pt** (**0.5 pt** – for value, not range)
Competition: $0 < \beta < 1$	**1 pt** (**0.5 pt** without zero; **0.5 pt** – for value, not range)
Independence: $\beta = 1$	**1 pt**
	Total **3 pts**

1.2. Find the equilibrium constant for the process: $\boldsymbol{HG_b} + \boldsymbol{G} \rightleftarrows \boldsymbol{HG_2}$ in terms of binding constant(s) and interaction factor.

Calculations:

$$K = \frac{[HG_2]}{[HG_b][G]} = \frac{[HG_2]}{[HG_a][G]} \cdot \frac{[HG_a]}{[HG_b]} = \beta K_b \cdot \frac{K_a}{K_b} = \beta K_a$$

$\boldsymbol{K} = \beta K_a$ **2 pts**

2.1. The solution was prepared with the initial concentrations $[\boldsymbol{H}]_0 = 1$ M and $[\boldsymbol{G}]_0 = 2$ M. After the reactions were completed, the concentration of ***H*** decreased by 10 times and that of ***G*** by 4 times. For these host and guest, $K_b = 2K_a$. Determine the concentrations of all other species in the solution and find the binding constant K_a and the factor β.

Calculations:

From $K_b = 2K_a$ it follows: $[\boldsymbol{HG_b}] = 2[\boldsymbol{HG_a}]$ **1 pt**

Material balance with respect to ***H***: $[\boldsymbol{H}] + [\boldsymbol{HG_a}] + [\boldsymbol{HG_b}] + [\boldsymbol{HG_2}] = [\boldsymbol{H}]_0 = 1$ M, or

$0.1 + 3[\boldsymbol{HG_a}] + [\boldsymbol{HG_2}] = 1$ M **0.5 pt**

Material balance with respect to ***G***: $[\boldsymbol{G}] + [\boldsymbol{HG_a}] + [\boldsymbol{HG_b}] + 2[\boldsymbol{HG_2}] = [\boldsymbol{G}]_0 = 2$ M, or

$0.5 + 3[\boldsymbol{HG_a}] + 2[\boldsymbol{HG_2}] = 2$ M. **0.5 pt**

Solving the system of two equations, we find: $[\boldsymbol{HG_a}] = 0.1$ M, $[\boldsymbol{HG_2}] = 0.6$ M, hence $[\boldsymbol{HG_b}] = 0.2$ M.

$$K_a = \frac{[HG_a]}{[H][G]} = \frac{0.1}{0.1 \cdot 0.5} = 2$$

$$\beta = \frac{[HG_2]}{[HG_a][G]K_b} = \frac{0.6}{0.1 \cdot 0.5 \cdot 4} = 3$$

$[\boldsymbol{HG_a}] = 0.1$ M $[\boldsymbol{HG_b}] = 0.2$ M $[\boldsymbol{HG_2}] = 0.6$ M

(**1 pt** for $[\boldsymbol{HG_a}]$, **2 pts** for $[\boldsymbol{HG_2}]$, and $[\boldsymbol{HG_b}]$ is not marked if $[\boldsymbol{HG_b}] = 2[\boldsymbol{HG_a}]$ was given 1 pt, otherwise **1 pt**)

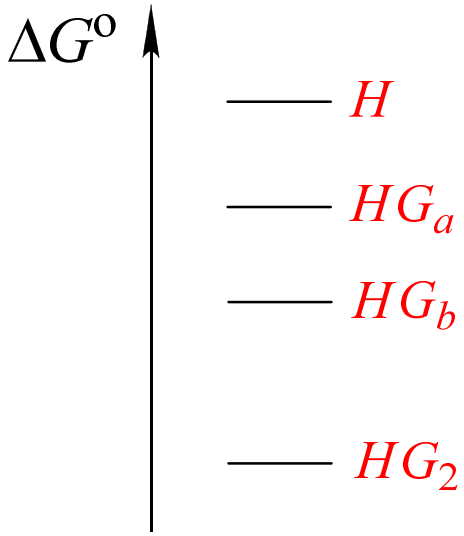
$K_a = 2$ **1 pt**

$\beta = 3$ **2 pts**

Total **8 pts**

If you could not answer this question, for further calculations use reference values $K_a = 3.14$ and $\beta = 2.72$.

2.2. Find the correct order of standard molar Gibbs energies of formation of host ***H*** and all host-guest complexes from ***H*** and ***G***. In the scheme below, write the corresponding chemical formula near every line.



1 pt – for the highest $\Delta G°(\boldsymbol{H})$,
1 pt – for the lowest $\Delta G°(\boldsymbol{HG_2})$
1 pt – for $\Delta G°(\boldsymbol{HG_a}) > \Delta G°(\boldsymbol{HG_b})$

Total **3 pts**

2.3. Some amount of ***G*** was added to 1 mole of ***H*** and the mixture was dissolved in water to obtain 1 liter of the solution. The number of the totally bound molecules $\boldsymbol{HG_2}$ in the solution is equal to the total number of single-bound molecules ***HG***. Find the initial amount of ***G*** (in mol). The constants K_a and K_b and the factor β are the same as in question 2.1.

Calculations:

1) $[HG_2] = [HG_a] + [HG_b] = 3[HG_a]$

$$\frac{[HG_2]}{[HG_a][G]} = \beta K_b = 12, \qquad \frac{3}{[G]} = 12, \qquad [G] = 0.25 \text{ M}$$

2) Material balance with respect to H: $[H] + 3[HG_a] + [HG_2] = 1$ M

$[H] + 6[HG_a] = 1$ M

$[H] + 12[H][G] = 1$ M

$[H] = 0.25$ M.

3) $[HG_a] = K_a[H]\,[G] = 0.125$ M.

$[HG_2] = 3[HG_a] = 0.375$ M.

4) Material balance with respect to G: $[G]_0 = [G] + 3[HG_a] + 2[HG_2] = 1.375$ M

$n_0(G) = 1.375$ mol

Correct determination of $[G]$, $[H]$, $[HG_a]$, $[HG_2]$ – **1 pt** for each concentration

$n_0(G)$ – **2 pts**

Total **6 pts**

2.4. What would be the equilibrium composition of the solution if: a) β = 0; b) β is very large (β → ∞). The constants K_a and K_b as well as the initial concentrations of ***H*** and ***G*** are the same as in question 2.1.

β = 0

Calculations:

In this case, no $\boldsymbol{HG_2}$ is formed.

Material balance with respect to ***H***: $[\boldsymbol{H}] + [\boldsymbol{HG_a}] + [\boldsymbol{HG_b}] = 1$ M, or

$$[\boldsymbol{H}] + 3[\boldsymbol{HG_a}] = 1 \text{ M}$$

Material balance with respect to ***G***: $[\boldsymbol{G}] + [\boldsymbol{HG_a}] + [\boldsymbol{HG_b}] = 2$ M, or

$$[\boldsymbol{G}] + 3[\boldsymbol{HG_a}] = 2 \text{ M}$$

Equilibrium constant: $K_a = \dfrac{[HG_a]}{[H][G]} = 2$

Solving the system of three equations, we get:

$[\boldsymbol{H}] = 0.129$ M $[\boldsymbol{G}] = 1.129$ M $[\boldsymbol{HG_a}] = 0.290$ M $[\boldsymbol{HG_b}] = 0.580$ M

$[\boldsymbol{HG_2}] = 0$

1 pt for each concentration except $\boldsymbol{HG_b}$, maximum – **4 pts**

β → ∞

Calculations (or arguments):

In this case, formation of $\boldsymbol{HG_2}$ is practically irreversible, so only $\boldsymbol{HG_2}$ is present in the solution.

$[\boldsymbol{H}] = 0$ $[\boldsymbol{G}] = 0$ $[\boldsymbol{HG_a}] = 0$ $[\boldsymbol{HG_b}] = 0$

$[\boldsymbol{HG_2}] = 1$ M

2 pts

(any calculation which gives similar result – full mark)

Total **6 pts**

Problem 4. From one yellow powder to another: A simple inorganic riddle
(6 points)

Question	1	2	3	4	Total
Marks	8	8	3	5	24

The yellow binary compound $\mathbf{X_1}$ was completely dissolved in concentrated nitric acid by heating, the gas evolved is 1.586 times denser than air. Upon adding an excess of barium chloride to the solution formed a white solid $\mathbf{X_2}$ precipitates. It was filtered. The filtrate reacts with an excess of silver sulfate solution forming a precipitate of two solids $\mathbf{X_2}$ and $\mathbf{X_3}$, also separated from solution by filtration. To the new filtrate the solution of sodium hydroxide was being added drop-wise until the solution became nearly neutral (about pH 7). At this time a yellow powder $\mathbf{X_4}$ (77.31 wt.% of Ag) crystallized from the solution. The mass of $\mathbf{X_4}$ is nearly 2.4 times larger than that the mass of the first portion of $\mathbf{X_2}$.

1. Determine the chemical formulae of $\mathbf{X_1}$ – $\mathbf{X_4}$.

Calculations:
The precipitate $\mathbf{X_2}$ formed by addition of barium chloride in acidic medium is barium sulfate $BaSO_4$. **1 pt**
The precipitate $\mathbf{X_3}$ formed by addition of silver sulfate is silver chloride AgCl **1 pt**

The yellow precipitate $\mathbf{X_4}$ formed by addition of alkali can be mercury oxide HgO or silver phosphate Ag_3PO_4. The ratio of molar masses $\mathbf{X_4}$: $\mathbf{X_2}$ is 0.931 for HgO : $BaSO_4$ which is not valid and 1.798 for Ag_3PO_4 : $BaSO_4$ which gives 2.4 being multiplied by 4/3. So, the molar ratio is $4Ag_3PO_4 : 3BaSO_4$ which corresponds to P : S = 4:3, i.e. to formula of $\mathbf{X_1}$ P_4S_3.

$\mathbf{X_1}$ = P_4S_3 $\mathbf{X_2}$ = $BaSO_4$ $\mathbf{X_3}$ = AgCl $\mathbf{X_4}$ = Ag_3PO_4
2 pts for Ag_3PO_4
4 pts for P_4S_3 (**0 pts** without calculations)
Total – **8 pts**

2. Determine the chemical formula of the gas and provide equations for all reactions in ionic or non-ionic form.

Calculation
The gas evolved has a molar mass 1.586 × 29 = 46 g/mol, that is NO_2. **1 pt**
Chemical formula of the gas _____

Dissolution of $\mathbf{X_1}$
$P_4S_3 + 38HNO_3 = 4H_3PO_4 + 3H_2SO_4 + 38NO_2 + 10H_2O$ **2 pt**

Formation of **X_2**

$H_2SO_4 + BaCl_2 = BaSO_4\downarrow + 2HCl$ **1 pt**

Formation of **X_2** and **X_3**

$Ag_2SO_4 + 2HCl = 2AgCl\downarrow + H_2SO_4$ **1 pt**

$BaCl_2 + Ag_2SO_4 = BaSO_4\downarrow + 2AgCl\downarrow$ **1 pt**

Addition of NaOH and formation of **X_4**

$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O$ **1 pt**

$2H_3PO_4 + 6NaOH + 3Ag_2SO_4 = 2Ag_3PO_4\downarrow + 3Na_2SO_4 + 6H_2O$ **2 pts**

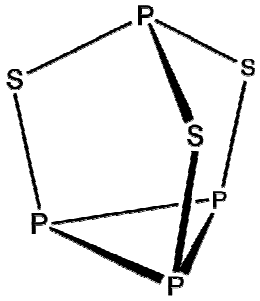
(neutralization of H_3PO_4 and subsequent reaction with Ag_2SO_4 will also be accepted)

(50% of points for non-balanced reactions with correct products)

Total – **8 pts**

3. In the structural unit of **X_1** all atoms of only one element are in equivalent positions. Draw the structure of **X_1**.

Phosphorus sulfide P_4S_3 is a molecular cage



3 pts

(Any reasonable structures with correct valencies of sulfur and phosphorus will also be accepted.

1 pt for the structure with non-equivalent atoms of both elements)

4. Predict the products of **X_1** interaction with:

a) excess oxygen;

b) excess of hot concentrated sulfuric acid;

c) solid $KClO_3$ with grinding.

Write down the reaction equations.

a) $P_4S_3 + 8O_2 = 2P_2O_5 + 3SO_2$ **1 pt**

b) $P_4S_3 + 16H_2SO_4 = 4H_3PO_4 + 19SO_2 + 10H_2O$ **2 pts**

(oxidation of sulfide to S instead of SO_2 is full mark)

c) $3P_4S_3 + 16KClO_3 = 16KCl + 6P_2O_5 + 9SO_2$ **2 pts**

(50% of points for non-balanced reactions with correct products)

Total – **5 pts**

Problem 5. Indispensable glucose

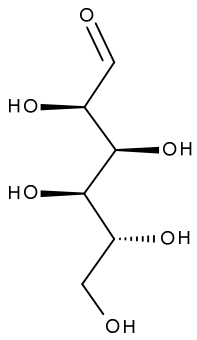
(8 points)

Question	1						2					**Total**
	1.1	1.2	1.3	1.4	1.5	1.6	2.1	2.2	2.3	2.4	2.5	
Marks	2	3	6	4	6	1	2	2	4	2	2	34

Carbohydrates are the most important providers of energy for living cells. Monosaccharide glucose is a source of energy for the living cell, but for persons who suffer from diabetes glucose may be dangerous. High level of glucose may lead to cardiovascular diseases and even death. That is why people avoid consuming too much carbohydrates and glucose particularly.

1. Determination of reducing sugars in fruit juice

One of the technique for determination of reducing sugars in different samples includes the use of Fehling's reagent. A 10.00-mL aliquot of fruit juice (assuming the initial sample contained only glucose and fructose) was transferred into a titration flask and Fehling's reagent was added. This reagent was prepared by mixing 50.00 mL of 0.04000 M copper sulfate (solution A) and potassium-sodium tartrate and sodium hydroxide (solution B). Solution C thus obtained, was then heated and red precipitate was formed.



Glucose

1.1. Write the balanced ionic equation of chemical reaction occurring upon heating of the solution C. Use Cu^{2+} for initial copper solution.

$C_6H_{12}O_6 + 2\ Cu^{2+} + 5OH^- = C_6H_{11}O_7^- + Cu_2O + 3H_2O$ If $C_6H_{12}O_7$ instead of $C_6H_{11}O_7^-$ Hereinafter if an equation is not balanced, then points/2.	**2 points** **1 point**

After that 10 mL of 10% solution of potassium iodide and 1 M sulfuric acid were added to the flask. The mixture was covered with watch glass and was then placed in a dark place. An excess of iodine was then titrated with 0.05078 M sodium thiosulphate solution. 11.87 mL of the titrant was required to reach the endpoint.

1.2. Write the balanced equation(s) in molecular or ionic form for all the reactions taking place in the flask.

$2CuSO_4 + 4KI = 2CuI + I_2 + 2K_2SO_4$ or $2Cu^{2+} + 4I^- = 2CuI + I_2$ $KI + I_2 = KI_3$ or $I^- + I_2 = I_3^-$ $C_6H_{11}O_7^- + H_2SO_4 = C_6H_{12}O_8 + HSO_4^-$ $2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$ or $2S_2O_3^{2-} + I_2 = 2I^- + S_4O_6^{2-}$	**2 points** not marked not marked **1 point**

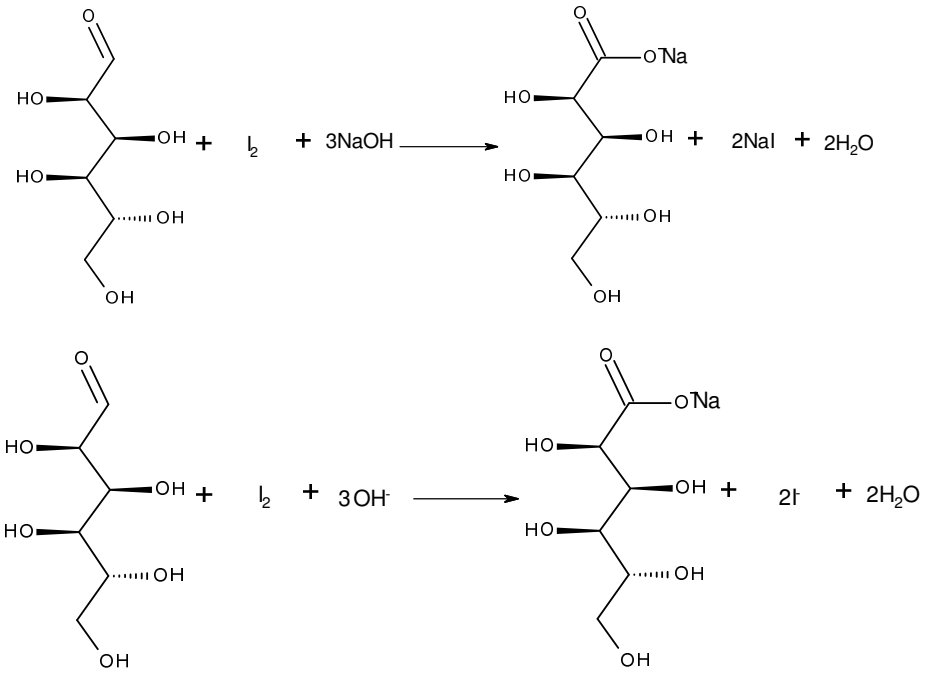
1.3. Consider all fructose was transformed into glucose under the experimental conditions; calculate the total mass content of sugars (in g/L) in a fruit juice. Mw = 180.16 g/mol.

Total amount of copper(II) is 50.00 mL * 0.04000 M = 2.0000 mmol. Obviously, there is an excess of iodine and the remaining iodine was titrated with sodium thiosulphate: 11.87 mL * 0.05078 M = 0.6028 mmol. 2.0000 – 0.6028 mmol = 1.3972 mmol of copper(II) was required to oxidize the sugars. $\nu(sugars) = \nu(Cu^{2+})/2 = 0.6986$ mmol in 10.00 mL C(sugars) = 0.6986 mmol/10.00 mL = 0.06986 M mass content = 180.16 g/mol * 0.06986 M = 12.6 g/L	**6 points**

A new 10.00-mL aliquot of the same juice was treated with a 10.00-mL portion of acidified potassium iodate(V) solution (0.01502 M) and 10 mL of 10 % solution of potassium iodide. After the mixture turned brown, an excess of sodium hydroxide solution was added. The flask was then covered with a watch glass and put into a dark place. The obtained solution was acidified and titrated with 0.01089 M solution of sodium thiosulphate. The average titrant volume used for titration was 23.43 mL. Note that fructose is not converted into glucose under these conditions.

1.4. Write all the balanced equations for the described reactions in molecular or ionic form.

$KIO_3 + 5KI + 3H_2SO_4 = 3I_2 + 3K_2SO_4 + 3H_2O$ $IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O$	**2 points**
Only glucose was oxidized with iodine	**2 points**

 or	
$H^+ + OH^- = H_2O$	not marked
$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$	not marked

1.5. Calculate the mass content of each sugar (in g/L) in the juice.

Total amount $\nu(I_2) = 3\nu(IO_3^-) = 3*0.01502$ M * 10 mL = 0.4506 mmol	**1 pt**	
$\nu(S_2O_3^{2-}) = 23.43$ mL*0.01089 M = 0.2552 mmol	**1 pt**	
$\nu(S_2O_3^{2-})/2 = \nu(I_2) = 0.1276$ mmol	**1 pt**	
0.4506 mmol – 0.1276 mmol = 0.3230 mmol of iodine was used to oxidize glucose		**6 points**
C(glucose) = 0.3230 mmol/10.00 mL = 0.03230 M	**1 pt**	
mass content of glucose = 180.16 g/mol *0.03230 M = 5.82 g/L	**1 pt**	
mass content of fructose = 12.6 – 5.82 = 6.78 g/L	**1 pt**	

1.6. One bread exchange unit (1 BEU) corresponds to the content of 12 g of digestible carbohydrates in product. How many BEU are in one glass (200 mL) of juice?

0.2 L*5.82 g/L = 1.16 g of digestible carbohydrates, it is 0.1 BEU	**1 point**
Or 0.2 L*12.6 g/L = 2.52 g, it is 0.2 BEU	**1 point**

2. Diagnosis of diseases

The derivative of glucose, 2-deoxy-2-(^{18}F)fluoro-D-glucose (FDG), is the most common radiopharmaceuticals for diagnosis of cancer using positron emission tomography. The first step of FDG preparation is to produce a radionuclide fluoro-18 by nuclear reaction in a cyclotron. The next step is the radiochemical synthesis. Fluorine-18 is introduced into D-glucose molecule by

nucleophilic substitution. 2-deoxy-2-(^{18}F)fluoro-D-glucose once injected into the patient actively accumulates in cells of malignant tumors; this process is accompanied by decomposition of fluorine-18. This radionuclide is a β^+ emitter – nucleus emits a positron (anti-electron). Positron interacts with an electron and after that annihilation occurs, which can be detected. This allows determining precisely the tumor sizes and type.

2.1. Complete the nuclear reactions leading to various fluorine isotopes.

a)	$^{18}O + {}^{1}_{1}H \rightarrow \ldots + {}^{18}F$	n	**0.5 points**
b)	$\ldots + {}^{2}_{1}D \rightarrow {}^{18}F + \alpha$	^{20}Ne	**0.5 points**
c)	$^{19}F + {}^{2}_{1}D \rightarrow {}^{20}F + \ldots$	${}^{1}_{1}H$	**0.5 points**
d)	$^{16}O + \ldots \rightarrow {}^{18}F + {}^{1}_{1}H + n$	α or ${}^{4}_{2}He$	**0.5 points**

2.2. The decay mode of unstable light nuclei depends on the ratio between the number of neutrons and protons in them. If this ratio is greater than that for a stable isotope then the nucleus decays in a β^--mode, if it is smaller – in a β^+-mode.

Determine the type of decay for the nuclei in the table:

Nucleus	^{11}C	^{20}F	^{17}F	^{14}C
Decay mode	β^+	β^-	β^+	β^-
	0.5 points	**0.5 points**	**0.5 points**	**0.5 points**

When nuclear reaction (a) is used for fluorine-18 preparation, the target material is presented as water enriched with $H_2{}^{18}O$. The presence of usual water $H_2{}^{16}O$ leads to a side nuclear reaction with ^{16}O, leading to the formation of isotope ^{17}F.

2.3. It is known that within five minutes after completion of irradiation of the target the ratio of radioactivities of ^{18}F and ^{17}F is 10^5. Assuming that irradiation time is short, the radioactivity of each isotope is proportional to the nuclear reaction yield and the mole fraction of a component in the irradiated target, **calculate** the mass fraction of $H_2{}^{18}O$ in the target. $t_{1/2}(^{18}F)$ = 109.7 minutes, $t_{1/2}(^{17}F)$ = 65 seconds. The ratio between nuclear reactions yields is $\eta_{18_O-18_F} / \eta_{16_O-17_F} = 144.7$.

Radioactivity is:

$A = \lambda N$, where N is the number of atoms, $\lambda = \ln 2 / t_{1/2}$ **1 point**

The initial ratio of radioactivities:

$$\frac{A_0(^{18}\mathrm{F})}{A_0(^{17}\mathrm{F})} = \frac{\lambda(^{18}\mathrm{F})}{\lambda(^{17}\mathrm{F})} \cdot \frac{\eta(^{18}\mathrm{O} \to {}^{18}\mathrm{F})}{\eta(^{16}\mathrm{O} \to {}^{17}\mathrm{F})} \cdot \frac{\chi(\mathrm{H_2}{}^{18}\mathrm{O})}{\chi(\mathrm{H_2}{}^{16}\mathrm{O})} = \frac{65/60}{109.7} \cdot 144.7 \cdot \frac{\chi(\mathrm{H_2}{}^{18}\mathrm{O})}{\chi(\mathrm{H_2}{}^{16}\mathrm{O})} = 1.43 \frac{\chi(\mathrm{H_2}{}^{18}\mathrm{O})}{\chi(\mathrm{H_2}{}^{16}\mathrm{O})}$$

After 5 minutes the ratio changed due to radioactive decay of fluorine:

$$\frac{A_{300}(^{18}\mathrm{F})}{A_{300}(^{17}\mathrm{F})} = \frac{A_0(^{18}\mathrm{F}) \cdot \exp\left(-\frac{\ln 2}{109.7} \cdot 5\right)}{A_0(^{17}\mathrm{F}) \cdot \exp\left(-\frac{\ln 2}{65} \cdot 300\right)} = 23.75 \cdot \frac{A_0(^{18}\mathrm{F})}{A_0(^{17}\mathrm{F})} = 33.94 \cdot \frac{\chi(\mathrm{H_2}{}^{18}\mathrm{O})}{\chi(\mathrm{H_2}{}^{16}\mathrm{O})} = 10^5$$

1 point

$$\frac{\chi(\mathrm{H_2}{}^{18}\mathrm{O})}{\chi(\mathrm{H_2}{}^{16}\mathrm{O})} = 2947$$ **1 point**

Mass fraction of $\mathrm{H_2}{}^{18}\mathrm{O}$ is:

$$\omega(\mathrm{H_2}{}^{18}\mathrm{O}) = \frac{2947 \cdot 20}{2947 \cdot 20 + 18} = 0.9997$$ **1 point**

$\omega(\mathrm{H_2}{}^{18}\mathrm{O}) = 0.9997 = 99.97\%$.

Total – **4 points**

2.4. Calculate the yield of labeling D-glucose with fluorine-18, if initial radioactivity of a fluorine-18 sample was 600.0 MBq and radioactivity of the obtained 2-deoxy-2-(^{18}F)fluoro-D-glucose is 528.2 MBq. Synthesis time is 3.5 minutes.

During the synthesis, the radioactivity will decrease:

$$A_{3.5} = A_0 \cdot \exp\left(-\frac{\ln 2}{109.7} \cdot 3.5\right) = 586.9 \text{ MBq}$$ **1 point**

$\eta = 528.2 / 586.9 = 0.900 = 90.0\%$ **1 point**

2.5. Biological half-life (through the excretory organs) of 2-deoxy-2-(^{18}F)fluoro-D-glucose is 120.0 minutes. How much radioactivity (in MBq) will remain in the patient ten hours after injection of FDG with the initial radioactivity of 450.0 MBq.

Radioactivity is excreted by radioactive decay and through the excretory organs (e.g. kidneys). The excretion process may be considered as two competitive first-order reactions. Activity after one hour is:

$$A_{60} = A_0 \exp\left(-(\lambda_1 + \lambda_2)t\right) = 450 \cdot \exp\left(-\left(\frac{\ln 2}{109.7} + \frac{\ln 2}{120}\right) \cdot 600\right) = 0.32 \text{ MBq}$$ **2 points**.

Problem 6. Bread is the stuff of life

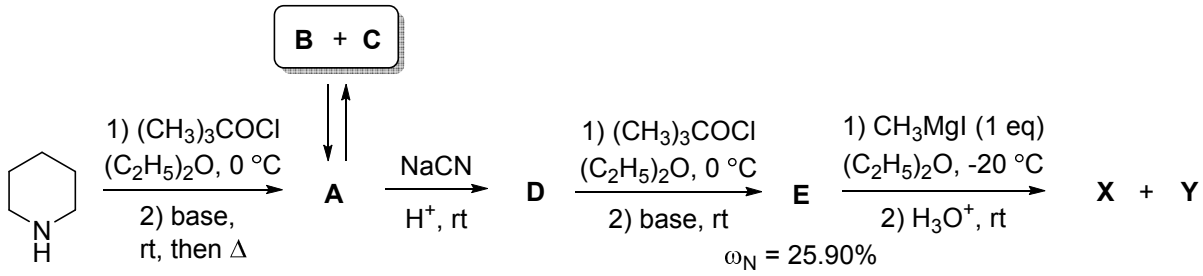
(8 points)

Question	1	2	3	**Total**
Marks	28	4	8	**40**

When you pass by the bakery, you are stopped by the smell of freshly baked bread. The hero of one of the novels said on a similar occasion: "If you tell me that this is not perfect, you are my enemy forever." The principle bread flavour component was identified in 1969 as compound **X** which occurs in equilibrium with its tautomer **Y** in a 2:1 ratio. Unfortunately, both forms are labile, and after some hours bread has no the same nice smell.

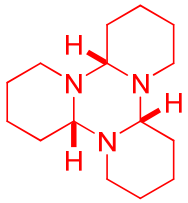
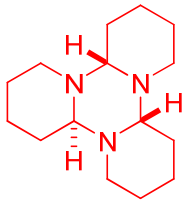
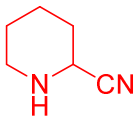
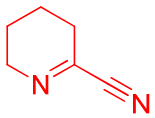
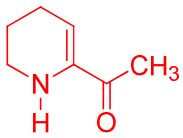
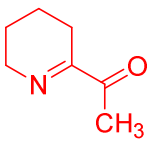
This tautomeric mixture of **X** and **Y** was synthesized in 1993 from piperidine by the reaction sequence given in Scheme 1. It is noteworthy that the initial ratio of **X** and **Y** was 1:4; on standing this ratio gradually changed to an equilibrium one.

Scheme 1.



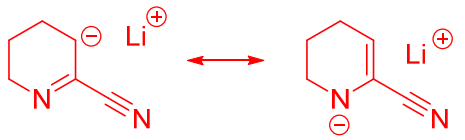
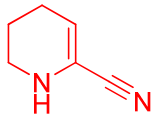
Compound **B** which is characterized by 3-fold axis of symmetry (*i.e.*, rotation by 120° results in a molecule indistinguishable from the original) occurs in equilibrium with its diastereomer **C**. The interconversion of these two forms proceeds *via* intermediate **A** which is also intermediate in **B** and **C** formation as well as their transformation to **D**. Compounds **A**, **B**, and **C** have the same elemental composition: $\omega_C = 72.24\%$, $\omega_H = 10.91\%$, $\omega_N = 16.85\%$.

1. Write down the structural formulae of compounds **A-E**, **X**, **Y**.

A  **4 pts** (**1pt** for any reasonable isomer)	**B**  **4 pts** (Other reasonable structures with molecular formula $(C_5H_9N)_n$ but without 3-fold axis of symmetry – **2 pts**)	**C**  **4 pts**
D  **4 pts**	**E**  **4 pts** (**1 pt** for any reasonable isomer)	**X**  **4 pts** (other structures will be estimated only if they are consistent with both reaction schemes, **3 pts** if in cell Y)
Y  **4 pts** (other structures will be estimated only if they are consistent with both reaction schemes, **3 pts** if in cell X)		

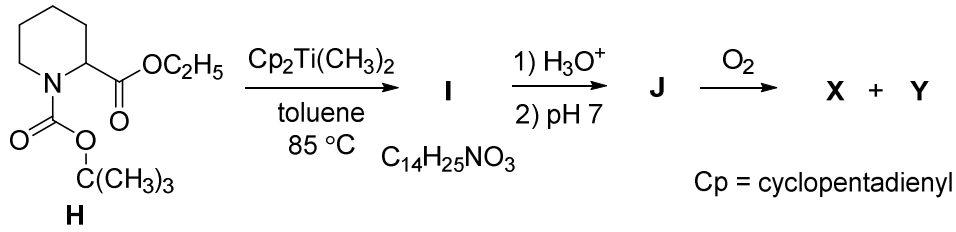
Treatment of compound **E** with $CH_3Li \cdot LiBr$ complex in $(C_2H_5)_2O$ at 0 °C failed to produce the target products **X** and **Y**. Instead, a yellow precipitate **F** was initially formed. Aqueous workup of this precipitate led to the mixture of compound **E** and its tautomer **G.**

2. Write down the structural formulae of compounds **F** and **G**.

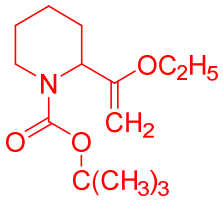
F	**G**
 **2 pts**	 **2 pts**

Another approach to compound **X** is based on the use of pipecolinic acid derivative **H**. It was shown that **X** can be synthesized by reaction sequence presented in Scheme 2.

Scheme 2.



3. Write down the structural formulae of compounds **I** and **J**.

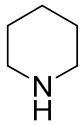
I	**J**
 **4 pts** (**2 pts** for product of substitution of another carbonyl oxygen)	 **4 pts** (other structures will be estimated only if they are consistent with both previous compound **I** and products **X** and **Y**)

Problem 7. Not by bread alone

(8 points)

Question	1	2	3	4	**Total**
Marks	8	24	2	16	**50**

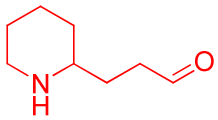
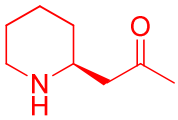
Pomegranate is called in Azerbaijan, which is famous for its vegetables, as the "king of all fruits". Pomegranate is honored in various religions as a "fruit of Paradise", symbol of righteousness, wealth, hope for eternal life.



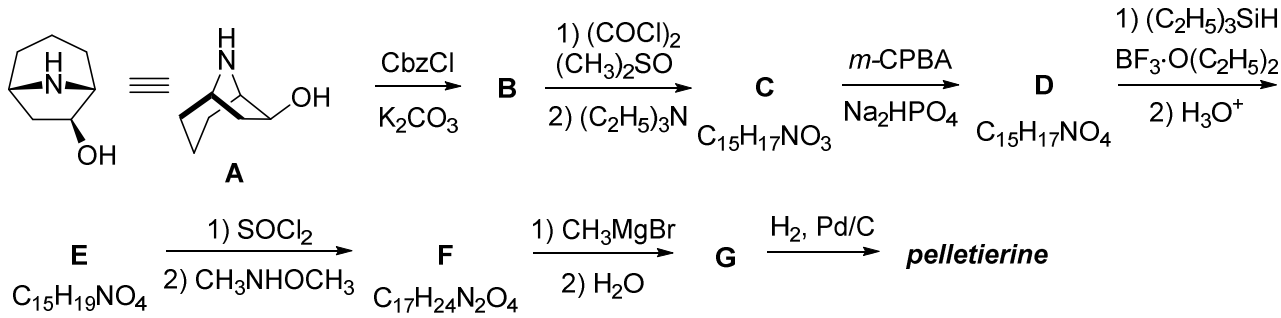
piperidine

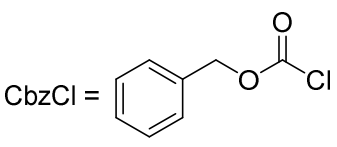
In 1878 alkaloid ***pelletierine*** was isolated from the bark of pomegranate tree (*Punica granatum* L., *Lythraceae*). This alkaloid is traditionally used as an anti-helminthic drug. Initially $\mathbf{X_W}$ (3-(piperidin-2-yl)propanal) was incorrectly proposed for pelletierine. But now it is accepted that natural pelletierine is (*S*)-1-(piperidin-2-yl)propan-2-one ($\mathbf{X_S}$).

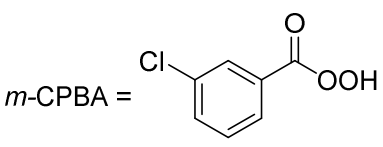
1. Write down the structural formulae of $\mathbf{X_W}$ and $\mathbf{X_S}$ (the latter – with the stereochemical information).

$\mathbf{X_W}$	$\mathbf{X_S}$
(3-(piperidin-2-yl)propanal)	(*S*)-1-(piperidin-2-yl)propan-2-one
	
4 pts	**4 pts**
	(**2 pts** without stereochemistry)

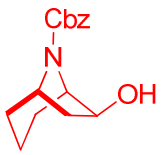
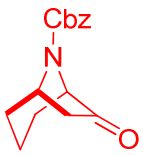
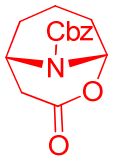
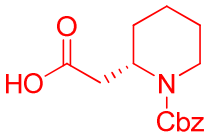
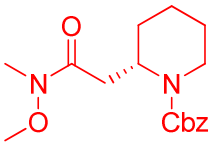
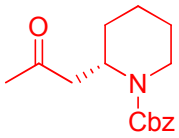
The synthesis of natural pelletierine ($\mathbf{X_S}$) based on the transformation of nortropanol **A** was recently described.







2. Write down the structural formulae of compounds **B-G** with the stereochemical information.

B	**C**	**D**
 **4 pts**	 **4 pts**	 **4 pts**
E	**F**	**G**
 **4 pts**	 **4 pts**	 **4 pts**

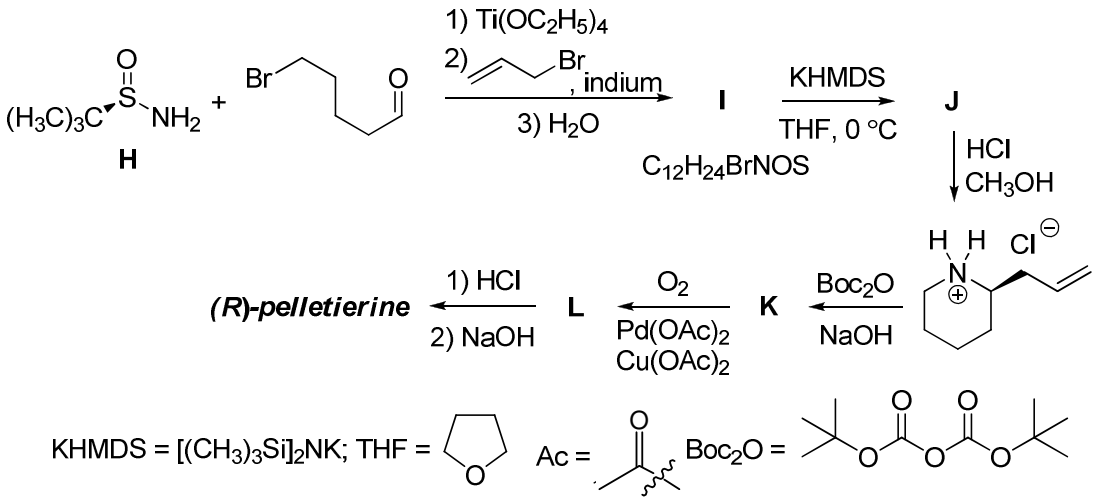
(For the structural formulae without stereochemistry (or with bad stereochemistry): 3 pts for each. Comments: a) for compound **B**, product of hydroxyl group acylation in **A** is estimated by 2 pts; b) for wrong isomeric structures of compounds **C–F** the mark will be in the range of 0-2 pts depending on the credibility of answer; c) for the wrong structures of compound **G** the mark will be in the range of 0-4 pts depending on the credibility of answer (4 pts will be given if under the specified conditions compound **G** can be obtained from **F** and can be transformed into (*S*)-1-(piperidin-2-yl)propan-2-one.)

3. Nortropanol **A** was used in this reaction as a single stereoisomer. How many stereoisomers can exist for compound **A** (including **A**)? Ignore nitrogen chirality.

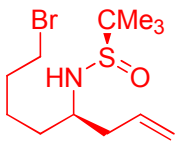
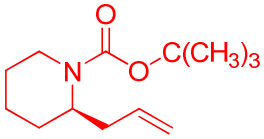
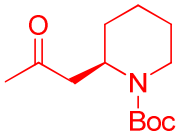
The number of possible stereoisomers of **A**: 4 .

2 pts (0.5 pts for 8)

Enantiomer of $\mathbf{X_S}$ was synthesized using chiral *tert*-butanesulfinamide (**H**):



4. Write down the structural formulae of compounds **I-L** with the stereochemical information.

I  **4 pts**	**J**  **4 pts**
K  **4 pts**	**L**  **4 pts**

(For the structural formulae without stereochemistry (or with bad stereochemistry): 3 pts for each. Wrong structures will be estimated depending on the credibility of answer.)

Problem 8. Oil for Life and Life after Oil
(8 points)

Question	1					2	3	4	**Total**
	1a	1b	1c	1d	1e				
Marks	1	4	4	3	12	5	13	13	**55**

Azerbaijan is known for its vast oil and gas fields. The first drilling for oil was done in Bibi-Heybat in 1846, 13 years before establishment of the first commercial oil well in Pennsylvania (USA). This remarkable date in the history of Azerbaijan is regarded as a starting point of contemporary oil industry, the leading sector of today's world economy. Currently, on-land and shelf sea oil production is being developed in Azerbaijan. Though serious precautions are taken, there is always a risk of hydrocarbon pollution of the environment during production, transportation, and processing of oil. In this task we will consider diverse technologies of oil spills clean up and specific features of metabolic pathways involved.

Application of complex solvents (dispersants) leading to capture of marine oil spills is among most promising clean up approaches. Organic substance **X** (11.94% of H by mass) is a typical component of such dispersants. Safety of **X** to human is fiercely debated. **X1** (54.53% of carbon by mass) composed of three elements and excreted with urine is the major metabolite of **X** in humans. The numbers of atoms of different elements in **X1** are three consecutive terms of a geometric progression (n, nq, nq^2), whereas the sum of these numbers does not exceed 25.

1a. Decide on the relationship (tick the correct variant) between the numbers of carbon and oxygen atoms in **X1**.

$n(C) > n(O)$	$n(C) < n(O)$	$n(C) = n(O)$	Data insufficient
☑ **1 p**	☐	☐	☐

1b. Derive the empirical formula of **X1** (hereafter always show your work where required). Be sure you prove the answer by calculations.

Your work

With regard to 1a, three variants (n(H)>n(C)>n(O), n(C)>n(H)>n(O), and n(C)>n(O)>n(H)) are possible for **X1**. For each inequality, one can write down the corresponding formula using elements of a geometric progression (q is the progression common ratio), equations for calculation of mass fractions of carbon and its roots

Inequality	Formula	Equation	The first root (q_1)	The second root (q_2)
n(H)>n(C)>n(O)	$C_{qn}H_{q2n}O_n$	$\frac{12.01qn}{12.01qn+1.008q^2n+16.00n}=0.5453$	2.00	7.93
n(C)>n(H)>n(O)	$C_{q2n}H_{qn}O_n$	$\frac{12.01q^2n}{12.01q^2n+1.008qn+16.00n}=0.5453$	–1.21	1.32
n(C)>n(O)>n(H)	$C_{q2n}H_nO_{qn}$	$\frac{12.01q^2n}{12.01q^2n+1.008n+16.00qn}=0.5453$	–0.06	1.66

There is only one positive integer root, thus the empirical formula is C_2H_4O.

problem formulation – **1p**

derivation – **1p**

result – **2p**

Total **4 pts**

(alternative approaches are possible)

Empirical formula of **X1**: C_2H_4O

The biotransformation of **X** into **X1** occurs in two enzymatically catalyzed steps according to the hereunder reaction balanced equations (NAD^+ and NADH are the oxidized and reduced forms of nicotinamide adenine dinucleotide, respectively):

$$\mathbf{X} + NAD^+ \rightarrow \mathbf{X0} + NADH + H^+ \qquad (1)$$

$$\mathbf{X0} + NAD^+ + H_2O \rightarrow \mathbf{X1} + NADH + H^+ \qquad (2)$$

1c. Derive the molecular formula of **X**.

Your work

Since (1) and (2) are the reaction equations, one can write down the formula of **X** as: $C_{2n}H_{4n}O_n$ + 2H − 1O = $C_{2n}H_{4n+2}O_{n-1}$. With an account for the known mass fraction of hydrogen: $\frac{1.008(4n+2)}{12.01\cdot 2n+1.008(4n+2)+16.00(n-1)}=0.1194$. Finally, n = 3, and the molecular formula of **X** is $C_6H_{14}O_2$.

derivation – **2p**

result – **2p**

Total **4 pts**

Molecular formula of **X**: $C_6H_{14}O_2$

A minor metabolic transformation of **X** is catalyzed by cytochrome P450-dependent monooxygenase. This reaction leads to two compounds **X2** (51.56% of oxygen and 9.74% of hydrogen by mass) and **X3**.

1d. Derive the molecular formula of **X2** and draw its structure.

Your work

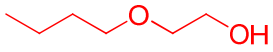
X2 is formed from **X** composed of three elements (C, H, and O) via a monooxygenase catalyzed reaction: $n(\mathrm{C}):n(\mathrm{H}):n(\mathrm{O})=\frac{100-51.56-9.74}{12}:\frac{9.74}{1.008}:\frac{51.56}{16.00}=1:3:1.$ **1p**

Since the number of hydrogen atom is necessarily even, the molecular formula of **X2** is $C_2H_6O_2$. Other variants with a higher even number of hydrogen are not valid. Ethylene glycol $HOCH_2CH_2OH$ is the only stable substance with the molecular formula deciphered above.

Molecular formula of **X2**: $C_2H_6O_2$ **1p**	Structure of **X2:** $HO–CH_2–CH_2–OH$ **1p**

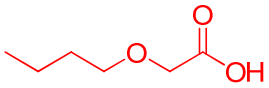
X contains only primary and secondary carbon atoms. **X0** and **X3** contain common functional group.

1e. Draw the structural formulae of **X**, **X1**, and **X3**.



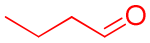
X **4p**

If incorrect, but
saturated **0.5p**
no branch **0.5p**
alcohol and ether **0.5p**



X1 **4p**

If incorrect, but
molecular formula **0.5p**
carboxyl **1p**

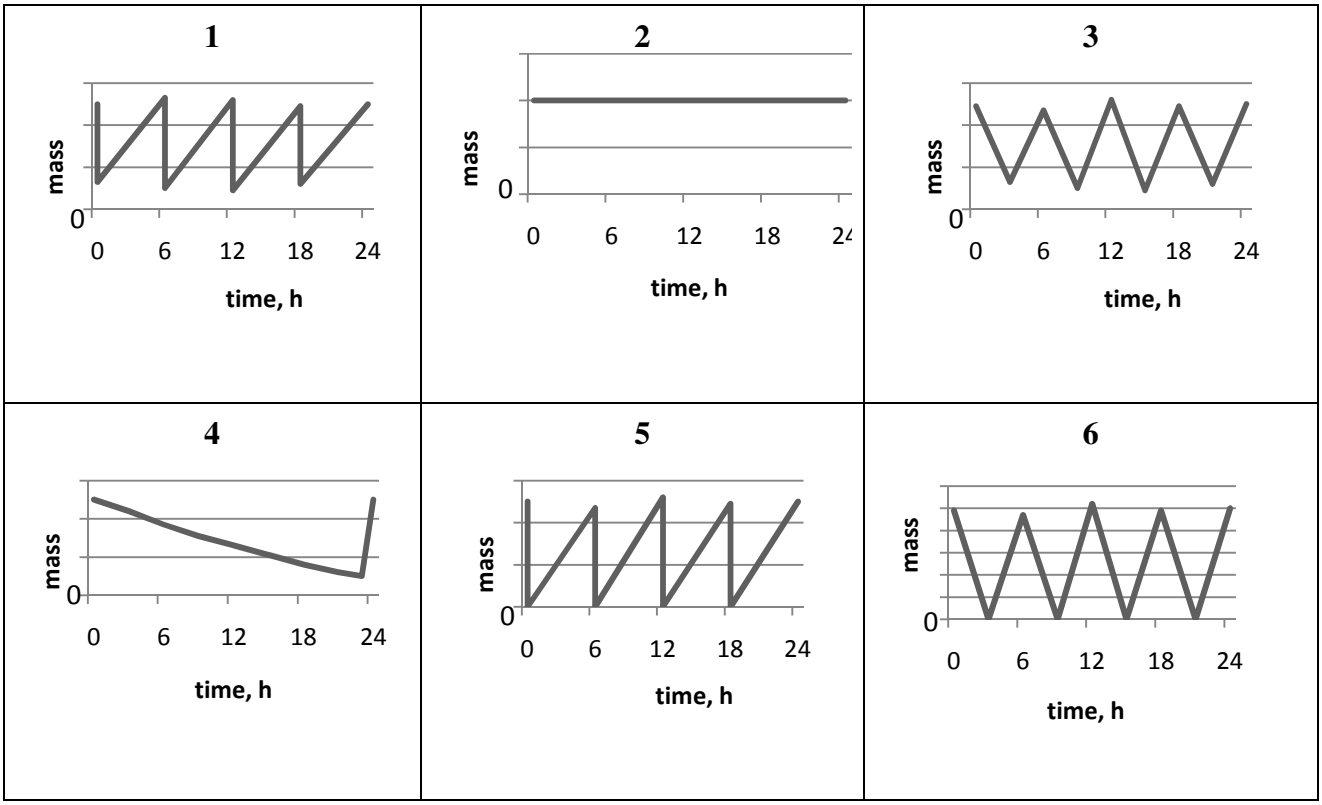


X3 **4p**

If incorrect, but
molecular formula **0.5p**
aldehyde **1p**

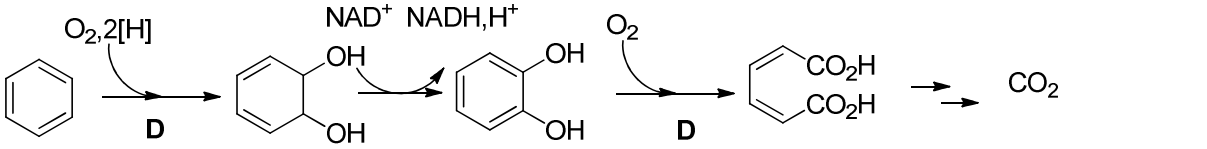
In a medical study, personnel permanently exposed to **X**-based solvents without proper protection was found to have a stationary concentration of **X** in blood.

2. **X1** is excreted with urine. Choose the graph of **X1** daily mass content in the body of a volunteer participated in this experiment. Write down the number of the correct graph.

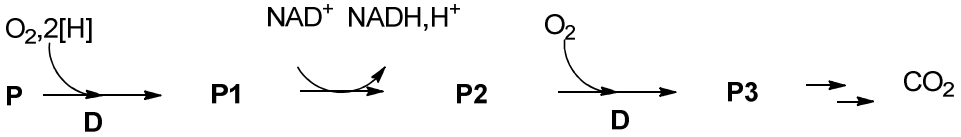


Number of graph: **1 (5 pts), if 5 (2.5 pts)**

The use of different bacteria is also considered as a promising way for the removal of hydrocarbon (even aromatic) contaminants from sea water and soil. Under aerobic conditions, benzene undergoes biodegradation as follows (first three steps are balanced):



Under the same conditions, a monocyclic aromatic hydrocarbon **P** (91.25% of carbon by mass) undergoes the following transformation (first three steps are balanced):



P3 gives a positive iodoform test. A 100 mg sample of **P3** requires 6.41 mL of 0.100 M KOH solution for complete neutralization.

3. Derive the structures of **P–P3**. Give the most stable tautomer of **P3**.

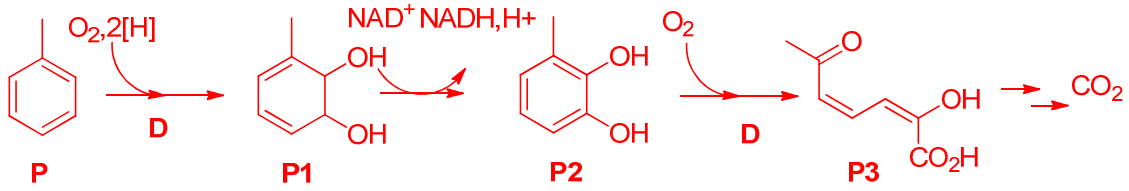
Your work

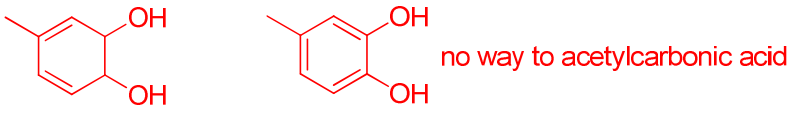
Dioxygenase incorporates two oxygen atoms in vicinal positions of the substrate, which can be followed by chemical bonds reorganization. The empirical formula of the hydrocarbon **P** is C_7H_8 ($C : H = \frac{91.25}{12.01} : \frac{100-91.25}{1.008} = 7:8$). Thus, it is toluene. **1p**

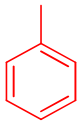
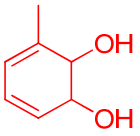
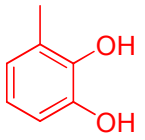
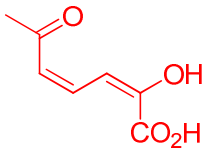
The molar mass of **P3** equivalent containing acidic group(s) is $\frac{100}{6.41 \cdot 0.100} = 156$ g/mol. **1p**

Two dioxygenase steps suggest the composition of $C_7H_8O_4$. **1p**

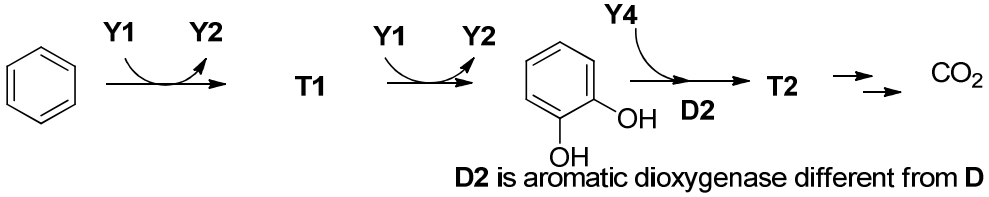
P3 must be a monocarboxylic acid if it still contains seven carbon atoms. Fragments containing a $CH_3CO–$ group (or a $CH_3CH(OH)–$ group further transforming into $CH_3CO–$ one) **(1p)** are involved into the iodoform reaction. This suggests splitting of the benzene moiety during the second oxygenase step at the carbon connected to the methyl group.





P	P1	P2	P3
			
1p	**3p** (**1p** for isomer)	**3p** (**1p** for isomer)	**2p** (**1 p** for tautomer)

Microorganisms *Alicycliphilus* are capable of biodegradation of aromatic hydrocarbons even in soil. The process requires a suitable electron acceptor such as inorganic anion **Y1** (first three steps are balanced).



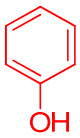
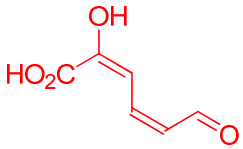
D2 is aromatic dioxygenase different from D

The intermediate anion **Y2** is enzymatically decomposed according to the balanced reaction equation:

Y2(aq) → **Y3**(aq) + **Y4**(g),

wherein each of **Y3** and **Y4** is composed of atoms of only one element. **T2** does not contain two identical oxygen-containing functional groups. **T2** gives a precipitate when treated with the ammonia solution of Ag_2O, whereas **Y3** does not.

4. Deduce and give formulas of **Y1-Y4**. Draw the structures of **T1-T2**. Give the most stable tautomer of **T2**.

Y1 ClO_3^- **1.5p** (wrong central atom **0.5p**)	**Y2** ClO_2^- **1.5p** (wrong central atom **0.5p**)	**Y3** Cl^- **1.5p** (wrong element **0.5p**)
Y4 O_2 **1.5p**	**T1**  **2p**	**T2**  **5p** If incorrect, but molecular formula **1p** aldehyde **1p** no identical **0.5p** (**5p** for hemiacetal, **3p** for other tautomers)

The Periodic Table of the Elements

1 **H** Hydrogen 1.00794																	2 **He** Helium 4.003
3 **Li** Lithium 6.941	4 **Be** Beryllium 9.012182											5 **B** Boron 10.811	6 **C** Carbon 12.0107	7 **N** Nitrogen 14.00674	8 **O** Oxygen 15.9994	9 **F** Fluorine 18.9984032	10 **Ne** Neon 20.1797
11 **Na** Sodium 22.989770	12 **Mg** Magnesium 24.3050											13 **Al** Aluminum 26.981538	14 **Si** Silicon 28.0855	15 **P** Phosphorus 30.973761	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.4527	18 **Ar** Argon 39.948
19 **K** Potassium 39.0983	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.955910	22 **Ti** Titanium 47.867	23 **V** Vanadium 50.9415	24 **Cr** Chromium 51.9961	25 **Mn** Manganese 54.938049	26 **Fe** Iron 55.845	27 **Co** Cobalt 58.933200	28 **Ni** Nickel 58.6934	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.92160	34 **Se** Selenium 78.96	35 **Br** Bromine 79.904	36 **Kr** Krypton 83.80
37 **Rb** Rubidium 85.4678	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.90585	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.90638	42 **Mo** Molybdenum 38.696	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.90550	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.8682	48 **Cd** Cadmium 112.411	49 **In** Indium 114.818	50 **Sn** Tin 118.710	51 **Sb** Antimony 121.760	52 **Te** Tellurium 127.60	53 **I** Iodine 126.90447	54 **Xe** Xenon 131.29
55 **Cs** Cesium 132.90545	56 **Ba** Barium 137.327	57 **La** Lanthanum 138.9055	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.9479	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.217	78 **Pt** Platinum 195.078	79 **Au** Gold 196.96655	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.3833	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.98038	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)
87 **Fr** Francium 52.147	88 **Ra** Radium (226)	89 **Ac** Actinium (227)	104 **Rf** Rutherfordium (261)	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (263)	107 **Bh** Bohrium (262)	108 **Hs** Hassium (265)	109 **Mt** Meitnerium (266)	110 (269)	111 (272)	112 (277)	113	114				

58 **Ce** Cerium 140.116	59 **Pr** Praseodymium 140.90765	60 **Nd** Neodymium 144.24	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.964	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.92534	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.93032	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.93421	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.967
90 **Th** Thorium 232.0381	91 **Pa** Protactinium 231.03588	92 **U** Uranium 238.0289	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (262)