NATIONAL CHEMISTRY OLYMPIAD 2024

ASSIGNMENTS PRELIMINARY ROUND 2
To be conducted from 19 until 22 March 2024

- This preliminary round consists of 20 multiple choice questions divided over 8 topics and 3 problems with a total of 15 open questions as well as an answer sheet for the multiple choice questions and a worksheet.
- Use the answer sheet to answer the multiple choice questions.
- Use for each problem with open questions a separate answer sheet. Don't forget to write your name on it.
- Put your name on all pages of the worksheet.
- The maximum score for this work is 95 points.
- The preliminary round lasts a maximum of 3 clock hours.
- Required materials: (graphic) calculator and BINAS 6th or 7th edition or ScienceData 1st edition or BINAS 5th edition, English version. Green chemistry table in the back.
- For each question the number of points you can score are given.
- Unless otherwise stated, standard conditions apply: T = 298 K and $p = p_0$.

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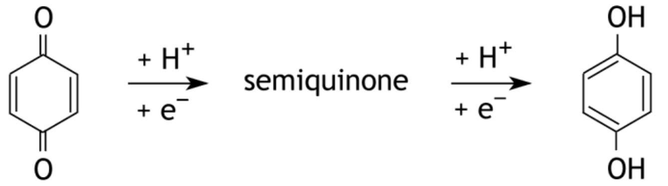
Problem 1 Multiple choice questions total 40 points

Write your answer (letter) for each question on the answer sheet. This answer sheet can be found at the end of this examination booklet.

Marks: 2 points for each correct answer.

Carbon chemistry

1 The conversion of quinone ($C_6H_4O_2$) to hydroquinone ($C_6H_6O_2$) is shown below. This conversion produces semiquinone ($C_6H_5O_2$) as an intermediate product. The molecule semiquinone is a radical.



$C_6H_4O_2$ $C_6H_5O_2^{\bullet}$ $C_6H_6O_2$

How many resonance structures, without formal charges, does a molecule of semiquinone have?

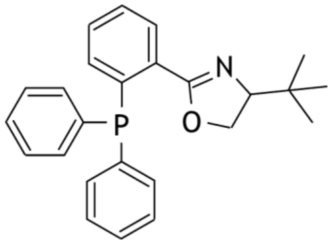
A 1
B 2
C 3
D 4
E 5
F 6
G 7
H 8

2 Below three-dimensional structural formulas of two molecules are given.

What is the relationship between these molecules?

A they are diastereomers
B they are enantiomers
C they are identical molecules
D they are structural isomers

3 How many chiral centers are there in the molecule below?



A 0
B 1
C 2
D 3
E 4
F 5

Reaction rate and equilibrium

4 For the reaction:

$O_2(g) + 4\ HBr(g) \rightarrow 2\ H_2O(g) + 2\ Br_2(g)$

the following mechanism is proposed:

$O_2\ (g) + HBr(g) \rightleftharpoons HOOBr(g)$	fast
$HOOBr(g) + HBr(g) \rightarrow 2\ HOBr(g)$	slow
$HOBr(g) + HBr(g) \rightarrow H_2O(g) + Br_2(g)$	fast

Which rate equation fits this mechanism?

A $s = k[HBr]$
B $s = k[O_2][HBr]$
C $s = k[O_2][HBr]^2$
D $s = k[O_2][HBr]^4$

5 Gas X dissociates when heated and the following equilibrium is reached:

$X(g) \rightleftharpoons Y(g) + Z(g)$

An amount of X is heated to a certain temperature at a constant pressure, *p*. After equilibrium is reached, the partial pressure of X turns out to be equal to $\frac{1}{7}p$.

What is the value of the equilibrium constant K_p of the above equilibrium at this temperature?

A $\frac{6}{7}p$

B $\frac{9}{7}p$

C $\frac{36}{7}p$

D $6p$

E $9p$

Structures and formulas

6 What are the approximate bond angles in a molecule of chloroisocyanate (Cl – N = C = O)?

	∠ClNC	∠NCO
A	109.5°	109.5°
B	109.5°	120°
C	109.5°	180°
D	120°	109.5°
E	120°	120°
F	120°	180°
G	180°	109.5°
H	180°	120°
I	180°	180°

7 For one electron of a Ge atom in the ground state that is in the gas phase, the set of quantum numbers 4, 1, 1, + ½ applies for *n*, *l*, m_l and m_s respectively.

Which set of the following sets of quantum numbers **cannot apply** for another electron of this atom?

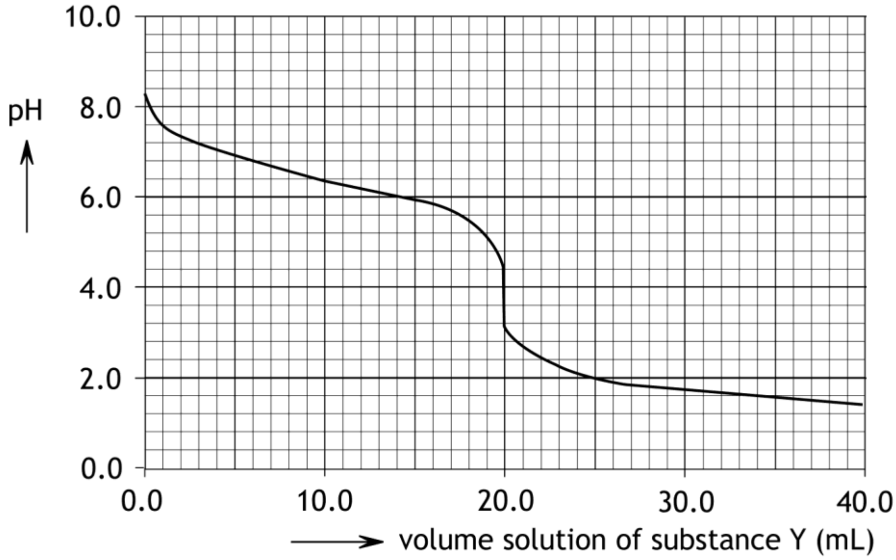
	n	*l*	m_l	m_s
A	3	2	1	– ½
B	4	0	0	+ ½
C	4	1	1	– ½
D	4	1	0	+ ½

8 How many σ-bonds and how many π-bonds are there in a molecule of cyanogen, N≡C−C≡N?

	number of σ bonds	number of π bonds
A	1	2
B	1	4
C	1	6
D	3	2
E	3	4
F	5	2
G	5	4

pH / acid-base

9 20 mL of a solution of substance X was pipetted into an Erlenmeyer flask. Then, a titration was performed from a burette containing a solution of substance Y. During the experiment, the pH was monitored using a pH meter. The results are displayed in the graph shown below.



What combination of X and Y is possible?

	X	Y
A	KOH	CH_3COOH
B	$NaHCO_3$	HCl
C	CH_3COOH	$NaHCO_3$
D	KOH	HCl
E	HCl	$NaHCO_3$

10 A 1.0 M NaOH solution is gradually added to 500 mL of a 0.200 M NaH_2PO_4 solution, until a buffer solution with pH = 6.90 is formed.

How many mL of the 1.0 M NaOH solution were added?

A 25 mL
B 33 mL
C 50 mL
D 67 mL
E 75 mL
F 100 mL

Redox and electrochemistry

11 Which half-reactions occur in the electrolysis of a zinc sulphate solution, using two zinc electrodes?

	at the negative electrode	at the positive electrode
A	$2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$	$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$
B	$2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$	$Zn \rightarrow Zn^{2+} + 2\ e^-$
C	$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$	$2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$
D	$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$	$Zn^{2+} + 2\ e^- \rightarrow Zn$
E	$Zn^{2+} + 2\ e^- \rightarrow Zn$	$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$
F	$Zn^{2+} + 2\ e^- \rightarrow Zn$	$Zn \rightarrow Zn^{2+} + 2\ e^-$
G	$Zn \rightarrow Zn^{2+} + 2\ e^-$	$2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$
H	$Zn \rightarrow Zn^{2+} + 2\ e^-$	$Zn^{2+} + 2\ e^- \rightarrow Zn$

12 For which of the following half-reactions is the electrode potential dependent on the pH?

I $NO_3^-(aq) + 3\ H^+(aq) + 2\ e^- \rightarrow HNO_2(aq) + H_2O(l)$

II $Ni(OH)_2(s) + 2\ e^- \rightarrow Ni(s) + 2\ OH^-(aq)$

A for neither
B only for I
C only for II
D for both I and II

13 During an investigation of a catalyst that can potentially be used for the electrolytic conversion of carbon dioxide into methanol, an electrolysis is performed for 200 minutes with a constant current of 0.370 A. After the electrolysis, the contents of the area around the negative electrode are analyzed and found to contain $5.30 \cdot 10^{-3}$ mol CH_3OH.

What percentage of the electric current was used for the conversion of carbon dioxide into methanol?

A 11.5 %
B 23.0 %
C 46.1 %
D 69.1 %
E 92.1 %

Analysis

14 In an acidified solution of potassium dichromate, the dichromate, $Cr_2O_7^{2-}$, can be converted into chromium(III), Cr^{3+}. Dichromate ions cause an orange colour in a solution and chromium(III) ions cause a green colour. Because of this colour change, an acidified potassium dichromate solution is a suitable reagent for identifying certain substances.

Aqueous solutions of the four substances listed below were made. Several drops of an acidified potassium dichromate solution were added to each solution. Only one solution turned orange.

Which solution was that?

A $Al_2(SO_4)_3$
B $H_2C_2O_4$
C KI
D $SnCl_2$

15 The absorbance of a $3.00 \cdot 10^{-4}$ M potassium permanganate solution is measured at a wavelength of 525 nm using a spectrophotometer: 0.600.
To 50.0 mL of this solution, 50.0 mL of a solution of sodium sulphite is added. The following reaction occurs:

$$2\ MnO_4^- + 5\ SO_3^{2-} + 6\ H^+ \rightarrow 2\ Mn^{2+} + 5\ SO_4^{2-} + 3\ H_2O$$

After the reaction has ended the absorbance of the resulting solution is measured, also at a wavelength of 525 nm: 0.100.

What was the molarity of the sodium sulphite solution?

A $8.00 \cdot 10^{-5}$ mol L^{-1}
B $1.00 \cdot 10^{-4}$ mol L^{-1}
C $2.50 \cdot 10^{-4}$ mol L^{-1}
D $5.00 \cdot 10^{-4}$ mol L^{-1}
E $6.25 \cdot 10^{-4}$ mol L^{-1}

Chemical calculations

16 Which noble gas has a density of 0.826 g dm^{-3} at 900 °C and 2.00 atm?

A He
B Ne
C Ar
D Kr
E Xe

17 On iron ships, blocks of zinc are often applied as sacrificial metal. Zinc prevents the rusting of iron because it is a stronger reducing agent than iron, so zinc reacts and iron does not react. In this reaction, zinc is converted into zinc hydroxide. Such a block with an initial mass of 113.0 g has a mass of 140.2 g after some time of use.

What is the ratio of Zn(0) : Zn(II) in this block? Assume that the block originally consisted of pure zinc and that the formed zinc hydroxide remains on the block.

A 0.0800 : 1.00
B 1.08 : 1.00
C 1.16 : 1.00
D 2.16 : 1.00
E 4.23 : 1.00
F 5.32 : 1.00
G 11.6 : 1.00

Thermochemistry and Green Chemistry

18 Elemental copper can be produced from chalcopyrite, $CuFeS_2$. The reaction equation for this process is shown below:

$$2\ CuFeS_2 + 5\ O_2 + 2\ SiO_2 \rightarrow 2\ Cu + 4\ SO_2 + 2\ FeSiO_3$$

The *E*-factor of this production is 6.5.

What is the percentage yield of this reaction?

A 7.0%
B 13%
C 32%
D 68%
E 87%
F 93%

19 Below standard reaction enthalpies for two reactions of hydrogen sulfide in the gas phase are given.

$H_2S(g) + 1.5\ O_2(g) \rightarrow SO_2(g) + H_2O(g)$ $\Delta_r H^0{}_1 = -518.2\ kJ\ mol^{-1}$

$2\ H_2S(g) + CO_2(g) \rightarrow CS_2(g) + 2\ H_2O(g)$ $\Delta_r H^0{}_2 = +67.8\ kJ\ mol^{-1}$

What follows for the standard reaction enthalpy $\Delta_r H^0{}_3$ for the combustion of carbon disulfide in the gas phase: $CS_2(g) + 3\ O_2(g) \rightarrow CO_2(g) + 2\ SO_2(g)$?

A $-450.4\ kJ\ mol^{-1}$

B $-586.0\ kJ\ mol^{-1}$

C $-968.6\ kJ\ mol^{-1}$

D $-1104.2\ kJ\ mol^{-1}$

20 For which reaction among the ones below is $\Delta_r G^0$ closest to $\Delta_r H^0$?

A $2\ CO_2(g) \rightarrow 2\ CO(g) + O_2(g)$

B $2\ HCl(g) \rightarrow H_2(g) + Cl_2(g)$

C $2\ H_2O(l) \rightarrow 2\ H_2(g) + O_2(g)$

D $2\ NaCl(s) \rightarrow 2\ Na(s) + Cl_2(g)$

Open questions total 55 points

Problem 1 Hydrogen for a fuel cell 15 points

For sustainable energy, hydrogen seems to be a suitable energy carrier. In a fuel cell, hydrogen can be efficiently used for the production of electrical energy. However, a drawback to using hydrogen is the storage of large quantities of this gas. Therefore, research is also being conducted to investigate whether hydrogen can be stored in the form of the solid substance sodium borohydride ($NaBH_4$).
Sodium borohydride is not toxic and reasonably stable under normal conditions.

By hydrolyzing $NaBH_4$ the hydrogen gas is released again:

$$BH_4^-(aq) + 2\ H_2O(l) \rightarrow BO_2^-(aq) + 4\ H_2(g)$$

This hydrolysis is a slow process at room temperature, which is why a catalyst is needed. Ruthenium (Ru) catalysts are highly active for this hydrolysis, even at room temperature. They ensure the complete conversion of $NaBH_4$ into H_2. Kinetic studies have shown that the catalytic hydrolysis of $NaBH_4$ is a zero-order reaction with respect to the concentration of BH_4^- and is directly proportional to the amount of Ru.
For each mole of Ru, 92 moles of H_2 are formed per minute at 298 K.

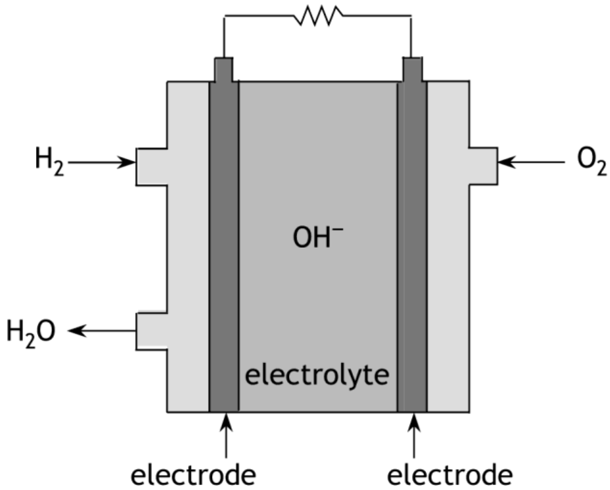
□1 Calculate the amount of Ru needed, in mg, for the production of 0.100 dm^3 H_2 per minute from 100 mL of a 1.0 M $NaBH_4$ solution, at 298 K and $p = p_0$. 3

□2 Calculate how many minutes this system can produce 0.100 dm^3 H_2 per minute, at 298 K and $p = p_0$. 4

The activation energy (E_a) for the catalytic hydrolysis of $NaBH_4$ is 42 kJ mol^{-1}.

□3 Calculate the temperature, in K, that is needed to produce hydrogen at the same rate (0.100 dm^3 H_2 per minute) with only half the amount of catalyst available as was used at 298 K. 4

To the right of this text a schematic diagram of an alkaline hydrogen fuel cell is provided.



The essential part of the fuel cell consists of three components: two electrodes with the electrolyte in between.
The following half-reactions occur at the electrodes:

$$O_2 + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$$

$$H_2 + 2\ OH^- \rightarrow 2\ H_2O + 2\ e^-$$

□4 Calculate the Gibbs energy for the formation of $H_2O(l)$ in the fuel cell under standard conditions. Use $\Delta G^0 = -nF\Delta E^0$. 4

Problem 2 A high-temperature superconductor 24 points

Superconductors are materials in which an electric current can flow without encountering resistance. Superconductivity was first discovered in 1911 by the Dutch (Leiden) scientist Heike Kamerlingh Onnes during his groundbreaking work in the field of extremely low temperatures. Superconductors are useful for various applications, such as in MRI, for example. However, a drawback is that most materials only become superconducting when cooled to near the absolute zero point. It was, therefore, a breakthrough when Georg Bednorz and Alex Müller discovered a class of ceramic materials that are already superconducting when cooled with liquid nitrogen. For this discovery of high-temperature superconductors, they were awarded the Nobel Prize in Physics in 1987.

Among the best known examples of these ceramic superconductors are substances that can be represented by YBCO. These are composed of ions of yttrium (Y), barium, copper, and oxygen. The ions of yttrium (Y), barium, and copper occur in a ratio of 1 : 2 : 3. The number of oxide ions in the empirical formula of YBCO depends on the amount of oxygen that reacts during the preparation of a YBCO compound but is at most 7. The empirical formula of a YBCO compound can then be represented as $YBa_2Cu_3O_{(7-x)}$.

In the preparation of $YBa_2Cu_3O_{(7-x)}$, yttrium(III) carbonate, barium carbonate and copper(II) carbonate are allowed to react with each other in the presence of oxygen. Besides $YBa_2Cu_3O_{(7-x)}$, only carbon dioxide is formed.

□5 Give the reaction equation for this preparation of $YBa_2Cu_3O_{(7-x)}$. 3

During the preparation of a YBCO compound in the presence of oxygen, a portion of the Cu^{2+} ions is converted into Cu^{3+} ions. Y^{3+} and Ba^{2+} ions remain unchanged.

□6 Calculate the value of *x* in $YBa_2Cu_3O_{(7-x)}$ if 20% of the Cu^{2+} ions have been converted into Cu^{3+} ions. 4

To determine the value of *x* in a YBCO compound, an iodometric titration can be performed. Initially, the YBCO compound is allowed to react with hydrochloric acid. This results in a solution in which no Cu^{3+} is present because it has reacted with water. This reaction of Cu^{3+} with water is a redox reaction that produces, among other things, Cu^{2+} and O_2.

□7 Give the equations of both half-reactions and the overall reaction equation for the reaction of Cu^{3+} with water. 2

Afterwards, an excess of potassium iodide is added to the solution, leading to the following reaction:

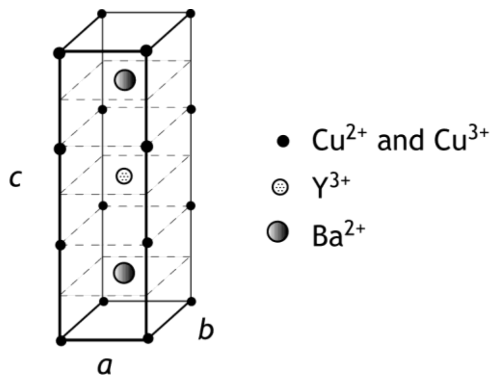
$2\ Cu^{2+} + 4\ I^- \rightarrow 2\ CuI + I_2$

Finally, the formed iodine is titrated with a solution of sodium thiosulfate, $Na_2S_2O_3$. The following reaction occurs in the titration:

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

In such a determination, 160 mg of YBCO compound was used. For the titration of the formed iodine, 21.8 mL of 0.0332 M sodium thiosulfate solution was required.

□8 Calculate the value of *x* in the examined YBCO compound. 7



The unit cell of the crystal lattice of a YBCO compound is shown on the left.

The barium ions and the yttrium ion are located inside the cell; dashed lines represent the horizontal planes in which these ions are situated.

The copper ions are located at the corners and on the edges of the unit cell.

The oxide ions are not depicted.

To complete the drawing of the unit cell of $YBa_2Cu_3O_7$ (YBCO with $x = 0$), 20 oxide ions need to be drawn. Some of these oxide ions are located on edges, while others are situated in exterior faces of the unit cell.

□9 Calculate how many oxide ions are located on edges and how many are situated in exterior faces in the unit cell of $YBa_2Cu_3O_7$. 4

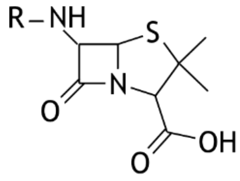
The lengths of the cell edges of the above unit cell are as follows: a = 0.382 nm, b = 0.389 nm and c = 1.168 nm.

□10 Calculate the density in $g\,cm^{-3}$ of $YBa_2Cu_3O_7$. 4

Problem 3 Penicillin 16 points

Penicillin is used as the collective term for the group of various types of penicillin. Penicillin has a bactericidal effect and is a commonly used antibiotic to combat infectious diseases.

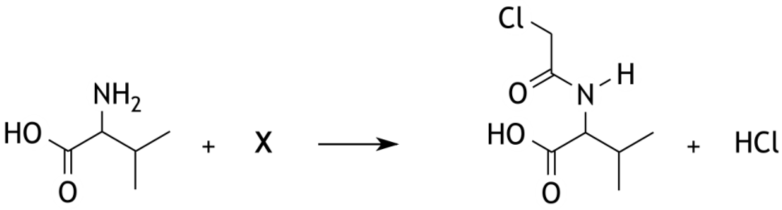
Below is a schematic representation of a penicillin molecule.



penicillin

The molecules of the various types of penicillin are characterized by the presence of two cyclic structures; they are distinguished from each other by the side group R.
Sir Alexander Fleming discovered penicillin (later called penicillin G) in 1928, as a product of the fungus *Penicillium notatum*. Fleming received the Nobel Prize in Medicine in 1945 for his discovery, along with Florey and Chain, who investigated the action of penicillin. Due to the highly useful properties of penicillin, many years have been spent developing its syntheses. In this problem, a part of the synthesis of a certain type of penicillin developed by Professor J.C. Sheenan is considered.

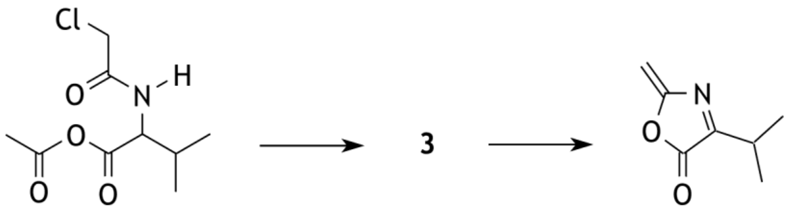
In the first reaction, the amino acid valine reacts with compound **X** to form compound **1**. In this conversion, HCl is released as a byproduct.



valine **1**

□11 Write the structural formula of **X**. 2

The synthesis route continues as follows:
1 is reacted with acetic anhydride; in this reaction **2** (see below) is formed.
By increasing the temperature, **2** is converted into an intermediate product **3**.
From **3**, after the splitting of ethanoate and HCl, compound **4** is formed.



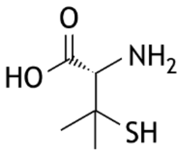
2 **4**

The mechanism of the conversion from **2** into **3** proceeds as follows:
- reaction of a base with the NH group;
- formation of a structure with a C = N bond;
- ring closure to form a structure with a five-membered ring.

On the worksheet with this test, the structural formula of **2** and B as formula for the base are represented.

▫12 On the worksheet, show the mechanism of the conversion of **2** into **3** by:
- drawing the structural formulas of the products;
- drawing non-bonding electron pairs in the structural formulas before and after the arrow;
- using curly arrows () to indicate how electron pairs shift during formation and breaking of bonds;
- placing formal charges at the appropriate positions. 4

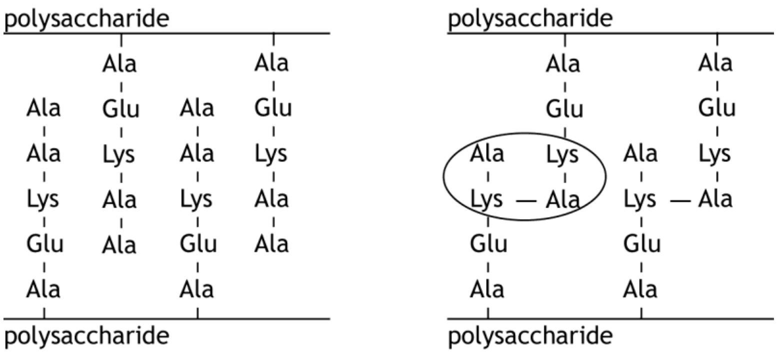
Through several reactions **4** is converted to compound **5**, an important intermediate in the synthesis of penicillin.



5

▫13 Explain whether compound **5** has the *R*- or *S*-configuration. Use a drawing in your explanation. 3

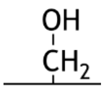
The bactericidal action of penicillin is based on the inhibition of bacterial cell wall formation. The cell wall of a bacterium consists, amongst other things, of a polysaccharide. Peptide chains, formed from a number of amino acids, are bound to this polysaccharide. The first amino acid bound to the polysaccharide is always alanine, with the amino group of alanine always linked to the polysaccharide. During the creation of the cell wall, two adjacent peptide chains are linked together. This linking is catalyzed by the enzyme transpeptidase. Two of such linkings are schematically shown below.



before linking   after linking

□14 Draw the structural formula of the 'encircled' part. From this structural formula, it should be clear how the four amino acid residues are linked. Use data from this problem and your data booklet. 4

Penicillin prevents the above mentioned linking of peptide chains because penicillin reacts with the enzyme transpeptidase. In this process, the penicillin molecule binds to the enzyme. This reaction is irreversible.
The resulting substance is not enzymatically active. Transpeptidase is a polypeptide.
A molecule of transpeptidase contains, amongst other things, a serine unit. In the reaction between penicillin and transpeptidase, the side chain of the serine unit reacts with the peptide bond in the core of a penicillin molecule. In this process that peptide bond is broken and an ester is formed.
On the worksheet with this test, the reaction equation of the reaction between penicillin and transpeptidase is partially shown. The molecule transpeptidase containing the side chain of the serine unit is schematically represented as follows:



□15 On the worksheet, complete the reaction equation between penicillin and transpeptidase. Show the product of this reaction as a structural formula, similar to the way it was done before the arrow for penicillin and transpeptidase. 3

Green Chemistry

The twelve principles of green chemistry are:

1. *Prevention* Preventing waste is better than treating or cleaning up waste after it is created.
2. *Atom economy* Synthetic methods should try to maximize the incorporation of all materials used in the process into the final product. This means that less waste will be generated as a result.
3. *Less hazardous chemical syntheses* Synthetic methods should avoid using or generating substances toxic to humans and/or the environment.
4. *Designing safer chemicals* Chemical products should be designed to achieve their desired function while being as non-toxic as possible.
5. *Safer solvents and auxiliaries* Auxiliary substances should be avoided wherever possible, and as non-hazardous as possible when they must be used.
6. *Design for energy efficiency* Energy requirements should be minimized, and processes should be conducted at ambient temperature and pressure whenever possible.
7. *Use of renewable feedstocks* Whenever it is practical to do so, renewable feedstocks or raw materials are preferable to non-renewable ones.
8. *Reduce derivatives* Unnecessary generation of derivatives — such as the use of protecting groups — should be minimized or avoided if possible; such steps require additional reagents and may generate additional waste.
9. *Catalysis* Catalytic reagents that can be used in small quantities to repeat a reaction are superior to stoichiometric reagents (ones that are consumed in a reaction).
10. *Design for degradation* Chemical products should be designed so that they do not pollute the environment; when their function is complete, they should break down into non-harmful products.
11. *Real-time analysis for pollution prevention* Analytical methodologies need to be further developed to permit real-time, in-process monitoring and control *before* hazardous substances form.
12. *Inherently safer chemistry for accident prevention* Whenever possible, the substances in a process, and the forms of those substances, should be chosen to minimize risks such as explosions, fires, and accidental releases.

atom economy $$\frac{\text{mass of desired product}}{\text{total mass of all reactants}} \times 100\%$$

percentage yield $$\frac{\text{experimental yield}}{\text{theoretical yield}} \times 100\%$$

E-factor $$\frac{\text{total mass of all reactants} - \text{mass of desired product}}{\text{mass of desired product}}$$

45th National Chemistry Olympiad 2024 preliminary round 2
Answer sheet multiple choice questions

name:

no.	choice letter	(score)
1		
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