NATIONAL CHEMISTRY OLYMPIAD 2023

ASSIGNMENTS PRELIMINARY ROUND 1
To be conducted from 11 until 27 January 2023

SCHEIKUNDE OLYMPIADE

Universiteit Leiden

- **This preliminary round consists of 20 multiple choice questions divided over 8 topics and 2 problems with a total of 14 open questions as well as an answer sheet for the multiple-choice questions.**
- **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 put your name on it.**
- **The maximum score for this work is 77 points.**
- **The preliminary round takes up to two full hours.**
- **Required materials: (graphic) calculator and BINAS 6th edition or ScienceData 1st edition or BINAS 5th edition, English version.**
- **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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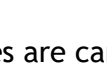
Problem 1 Multiple-choice questions (total 40 points)

For each question, write your answer (letter) 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 hydrolysis of a molecule of trehalose produces two molecules of glucose. What is the molecular formula of trehalose?

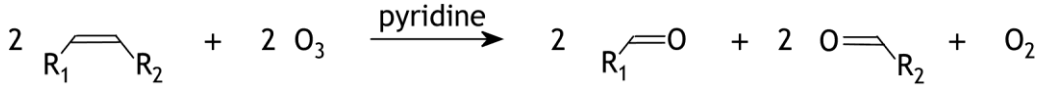
A $C_{11}H_{22}O_{11}$
B $C_{11}H_{22}O_{12}$
C $C_{11}H_{24}O_{12}$
D $C_{12}H_{22}O_{11}$
E $C_{12}H_{22}O_{12}$
F $C_{12}H_{24}O_{12}$

2 Epoxides are carbon compounds with the group  in the molecule.

How many epoxides with molecular formula C_4H_8O exist? Take stereoisomerism into account.

A 2
B 3
C 4
D 5
E 6
F 7

3 An alkene can react with ozone in a so-called ozonolysis reaction. During this reaction, the C = C bond is broken. When pyridine is used as a catalyst, aldehydes and/or ketones are formed. See reaction equation below, where two aldehydes are formed.



The alkenes pent-2-ene, hex-3-ene and cyclopentene, among others, can be used in this reaction.

Which of the three alkenes above produces only **one** other substance, besides O_2, in the above reaction?

A none of them
B only pent-2-ene
C only hex-3-ene
D only cyclopentene
E only pent-2-ene and hex-3-ene
F only pent-2-ene and cyclopentene
G only hex-3-ene and cyclopentene
H all three

Reaction rate and equilibrium

4 In an investigation into the following reaction

$CO\,(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

four tests have been carried out in a reactor where the volume is kept constant and no matter can escape. The following data was obtained:

temperature	equilibrium constant
298 K	$9.9 \cdot 10^4$
500 K	$1.2 \cdot 10^2$
750 K	4.5
1000 K	0.86

Is the reaction to the right endothermic or exothermic? And at high temperature is there more or less H_2 present at equilibrium than at low temperature?

	reaction to the right	amount of H_2
A	endothermic	more
B	endothermic	less
C	exothermic	more
D	exothermic	less

5 In which of the following equilibria does the position of the equilibrium shift to the right when the volume of the reactor is increased?

I $C(s) + CO_2(g) \rightleftharpoons 2\,CO(g)$

II $H_2(g) + F_2(g) \rightleftharpoons 2\,HF(g)$

III $2\,NO_2(g) \rightleftharpoons 2\,NO(g) + O_2(g)$

A in none of them
B only in I
C only in II
D only in III
E only in I and II
F only in I and III
G only in II and III
H in all three

6 In the reaction $N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)$ the rate at which H_2 reacts is equal to $1.2 \cdot 10^{-3}$ mol s^{-1}.

What is the rate of formation of NH_3?

A $8.0 \cdot 10^{-4}$ mol s^{-1}
B $1.2 \cdot 10^{-3}$ mol s^{-1}
C $1.8 \cdot 10^{-3}$ mol s^{-1}
D $2.4 \cdot 10^{-3}$ mol s^{-1}

Structures and formulas

7 Which type(s) of bond(s) is/are present in solid magnesium sulphite?

A only covalent bonds
B only covalent bonds and ionic bonds
C only covalent bonds and metallic bonds
D only covalent bonds, ionic bonds and metallic bonds
E only ionic bonds
F only ionic bonds and metallic bonds
G only metallic bonds

8 Which of the following statements about a molecule of oxygen difluoride, OF_2, is/are correct?

I A molecule of oxygen difluoride is linear.
II A molecule of oxygen difluoride is a dipole molecule.

A none of them
B only I
C only II
D both

9 How many electrons are represented in the Lewis structure of a persulfate ion, SO_5^{2-}?

A 32
B 34
C 36
D 38

pH / acid-base

10 Some sodium hydroxide solution is added to a solution of ammonium chloride (NH_4Cl). The resulting solution has a pH of 9.50.

What % of the NH_4^+ has been converted to NH_3?

A 23%
B 36%
C 44%
D 56%
E 64%
F 77%

11 200 mL of 0.0657 M sodium hydroxide solution, 140 mL of 0.107 M hydrochloric acid and 160 mL of water are mixed.

What is the pH of the resulting solution?

A 2.27
B 2.43
C 2.74
D 3.04

Redox and electrochemistry

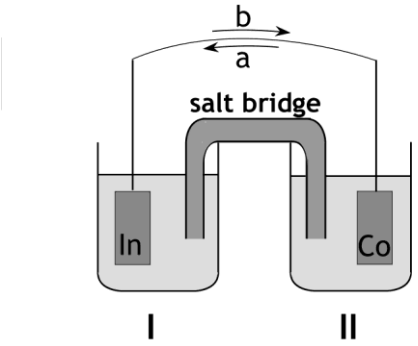
12 In a basic solution, chlorine dioxide reacts according to the incomplete reaction equation below. In this incomplete reaction equation only the coefficients are missing.

$ClO_2(aq) + OH^-(aq) \rightarrow ClO_2^-(aq) + ClO_3^-(aq) + H_2O(l)$

What is the ratio between the coefficients of ClO_2 and ClO_3^- in the balanced reaction equation of this reaction?

A $ClO_2 : ClO_3^- = 1 : 1$
B $ClO_2 : ClO_3^- = 2 : 1$
C $ClO_2 : ClO_3^- = 3 : 1$
D $ClO_2 : ClO_3^- = 3 : 2$
E $ClO_2 : ClO_3^- = 4 : 1$

13 In the electrochemical cell below, half-cell I contains a 1.0 M solution of indium(III) nitrate with an indium electrode and half-cell II contains a 1.0 M solution of cobalt(II) nitrate with a cobalt electrode.



The following standard electrode potentials apply:

$In^{3+} + 3\ e^- \rightleftharpoons In \qquad V^0 = -0{,}34\ V$
$Co^{2+} + 2\ e^- \rightleftharpoons Co \qquad V^0 = -0{,}28\ V$

Which arrow shows the correct direction in which the electrons move when the cell is supplying current and what is the cell potential of this electrochemical cell?

	direction of electron flow	cell potential
A	arrow a	0.06V
B	arrow a	0.62V
C	arrow b	0.06V
D	arrow b	0.62V

Chemical calculations

14 A certain kind of vinegar contains 5.00% by mass of acetic acid, CH_3COOH (M = 60.0 g mol^{-1}).

What is the molarity of acetic acid in this vinegar? The density of the vinegar is 1.00 g mL^{-1} .

A 0.833 mol L^{-1}
B 1.00 mol L^{-1}
C 1.20 mol L^{-1}
D 3.00 mol L^{-1}

15 3.00 g of an alloy of copper and silver is added to excess of diluted nitric acid. A solution is formed. An excess of sodium phosphate solution is then added to the formed solution. The resulting suspension is filtered and the residue dried and weighed. The residue consists of silver phosphate (M = 418.58 g mol^{-1}) and copper(II) phosphate (M = 380.59 g mol^{-1}). The mass of the dried residue is 4.25 g.

What is the mass percentage of silver in the alloy?

A 10% à 11%
B 17% à 18%
C 82% à 83%
D 89% à 90%

Thermochemistry and Green chemistry

16 Epoxyethane is prepared industrially from the reaction of ethene with oxygen:

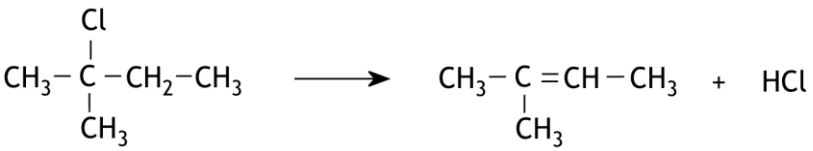
$2\ C_2H_4(g)\ +\ O_2(g)\ \rightarrow\ 2\ C_2H_4O(g)$

The enthalpy change (at 298 K, $p = p_0$) of this synthesis is − 148 kJ per mole of ethene.

What is the enthalpy of formation (at 298 K, $p = p_0$) of epoxyethane? Given: the enthalpy of formation (at 298 K, $p = p_0$) of ethene is + 52 kJ mol^{-1}.

A − 200 kJ mol^{-1}
B − 148 kJ mol^{-1}
C − 96 kJ mol^{-1}
D + 96 kJ mol^{-1}
E + 148 kJ mol^{-1}
F + 200 kJ mol^{-1}

17 An example of an elimination reaction is shown below:



The yield of the production of 2-methylbut-2-ene is 77%.

What is the *E*-factor of this process (see information on page 15)?

A 0.17
B 0.51
C 0.52
D 0.97
E 1.9

18 We compare the absolute values of the enthalpies of combustion, expressed in different units, of the following gases: methane, methanal and hydrogen.

Which gas has the greatest enthalpy of combustion (at 298 K, $p = p_0$) expressed in J kg^{-1} and which gas has the greatest enthalpy of combustion (at 298 K, $p = p_0$) expressed in J m^{-3}?

Use Binas tables 56 and 57A or ScienceData tables 8.7 and 9.2.

	greatest enthalpy of combustion in J kg^{-1}	greatest enthalpy of combustion in J m^{-3}
A	methane	methane
B	methane	methanal
C	methane	hydrogen
D	methanal	methane
E	methanal	methanal
F	methanal	hydrogen
G	hydrogen	methane
H	hydrogen	methanal
I	hydrogen	hydrogen

Analysis

19 Gerrit examines a solution of an unknown salt in water.
He performs two tests:

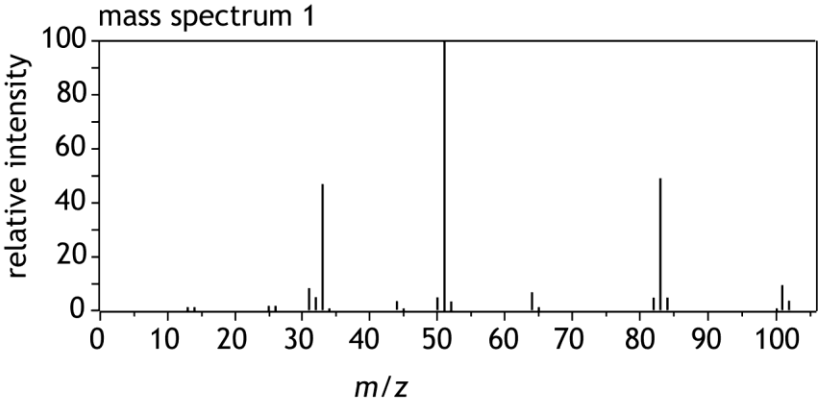
Test 1: He adds hydrochloric acid to a part of the solution of the unknown salt. A gas and a solution are formed.

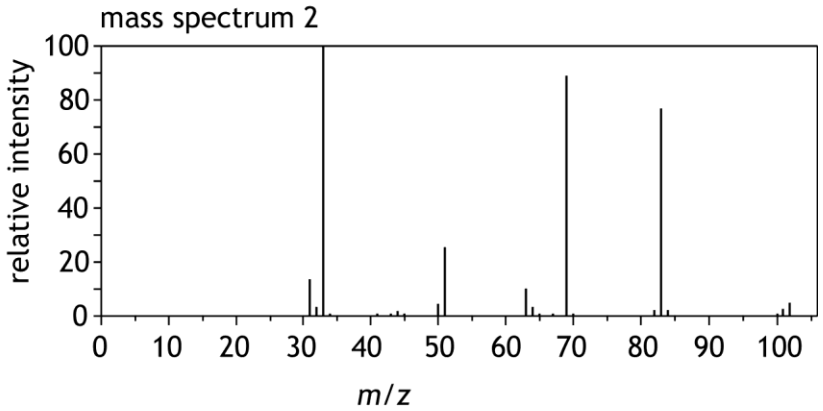
Test 2: He adds a solution of barium iodide to a part of the solution of the unknown salt. A solution is formed.

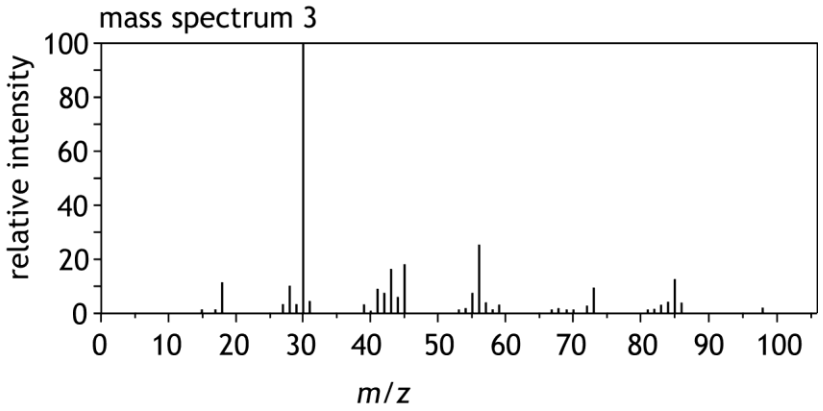
Which of the following salts could be the unknown salt?

A $Ba(OH)_2$
B K_2CO_3
C $Mg(HCO_3)_2$
D NaOH
E $Pb(HCO_3)_2$

20 Below are the mass spectra of 1,1,1,2-tetrafluoroethane, pentane-1,5-diamine and 1,1,2,2-tetrafluoroethane.







Which spectrum belongs to which substance?

	mass spectrum 1	mass spectrum 2	mass spectrum 3
A	pentane-1,5-diamine	1,1,1,2-tetrafluoroethane	1,1,2,2-tetrafluoroethane
B	pentane-1,5-diamine	1,1,2,2-tetrafluoroethane	1,1,1,2-tetrafluoroethane
C	1,1,1,2-tetrafluoroethane	pentane-1,5-diamine	1,1,2,2-tetrafluoroethane
D	1,1,1,2-tetrafluoroethane	1,1,2,2-tetrafluoroethane	pentane-1,5-diamine
E	1,1,2,2-tetrafluoroethane	pentane-1,5-diamine	1,1,1,2-tetrafluoroethane
F	1,1,2,2-tetrafluoroethane	1,1,1,2-tetrafluoroethane	pentane-1,5-diamine

Open questions (total 37 points)

Problem 2 Gold in solution (19 points)

Gold is a noble metal; there are almost no acids that will react with it. One of the few liquids that gold will react with is aqua regia. Aqua regia is a mixture of concentrated hydrochloric acid and concentrated nitric acid in a volume ratio of 3.0 : 1.0. The molarity of concentrated hydrochloric acid is 12 mol L^{-1} and the molarity of concentrated nitric acid is 15 mol L^{-1}.

Aqua regia has a very low pH.

▫1 Calculate the pH of aqua regia. Provide your answer in the correct number of significant figures. Assume that both acids are fully ionised. 3

When gold reacts with aqua regia, the gold is mainly converted into $AuCl_4^-$ ions. Nitrogen dioxide is also produced. This is a redox reaction.

▫2 Provide the equations of both half-reactions for this redox reaction and the complete reaction equation. 3

When you only account for the V^0 values of these half-reactions, which are listed in Binas or ScienceData, you could conclude that this redox reaction cannot take place.

▫3 Provide a possible explanation for why this redox reaction takes place anyway. 1

Besides $AuCl_4^-$ ions, there are also $AuCl_2^-$ ions. However, $AuCl_2^-$ ions are instable; at room temperature they are converted into solid gold and $AuCl_4^-$. This is an equilibrium reaction. The incomplete reaction equation for this conversion is:

$AuCl_2^-(aq) \rightleftharpoons Au(s) + AuCl_4^-(aq) + Cl^-(aq)$ equilibrium I

The only thing missing from this equation are the coefficients.

▫4 Copy the equation above to your answer sheet and complete it. 3

In order to determine the equilibrium constant for equilibrium I, a mixture is investigated in which equilibrium I has been established. In this equilibrium mixture, the only negative ions present are $AuCl_4^-$, $AuCl_2^-$ and Cl^-. The only positive ions present in the mixture are H_3O^+.

First, the equilibrium mixture is filtered. Afterwards, the [$AuCl_4^-$] in the filtrate is determined. For this, an excess of potassium iodide solution is added to a 10.00 mL sample of the filtrate, which causes the following reactions:

$AuCl_4^-(aq) + 2\ I^-(aq) \rightarrow AuCl_2^-(aq) + I_2(aq) + 2\ Cl^-(aq)$

and

$AuCl_2^-(aq) + I^-(aq) \rightarrow AuI(s) + 2\ Cl^-(aq)$

The iodine which is produced, is then titrated with a solution of sodium thiosulphate, which causes the following reaction:

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

This titration required 5.34 mL of a 0.0100 M sodium thiosulphate solution.

It can be assumed that the filtration, addition of potassium iodide solution, and the titration do not cause a shift of equilibrium I.

▫5 Calculate the $[AuCl_4^-]$ in mol L^{-1} of the investigated equilibrium mixture. 3

After the $[AuCl_4^-]$ is known, more has to be determined in order to be able to calculate the equilibrium constant.

The $[AuCl_2^-]$ in the equilibrium mixture can be calculated by filtering the mixture that was created after the titration and determining the mass of the residue. With this, and the amount of mmol of $AuCl_4^-$ in the 10.00 mL sample, you can calculate how many mmol of $AuCl_2^-$ were present in the 10.00 mL sample.

▫6 Explain how you can calculate the amount of mmol of $AuCl_2^-$ in the 10.00 mL sample, using the amount of mmol of AuI in the residue and the amount of mmol of $AuCl_4^-$ in the 10.00 mL sample. 2

By determining the pH of the equilibrium mixture, the $[Cl^-]$ in the equilibrium mixture can be calculated. This is because the $[H_3O^+]$, the $[AuCl_4^-]$, the $[AuCl_2^-]$ and the $[Cl^-]$ are related.

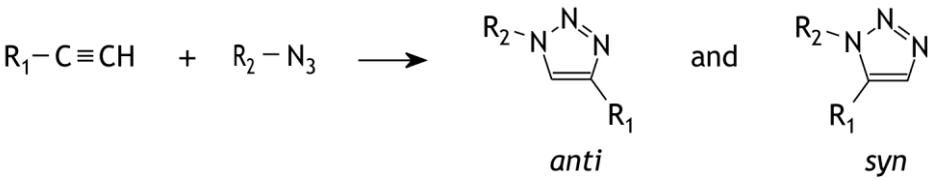
▫7 What is the relation between the $[H_3O^+]$, the $[AuCl_4^-]$, the $[AuCl_2^-]$ and the $[Cl^-]$ in the equilibrium mixture? Explain your answer. 2

▫8 Does the concentration of Au still need to be determined in order to calculate the equilibrium constant of equilibrium I? Explain your answer. 2

Problem 3 Click Chemistry (18 points)

The Nobel prize for chemistry was won by Carolyn Bertozzi, Barry Sharpless and Morten Meldal in 2022 for thinking of and developing the concept of click chemistry. During click chemistry one takes two molecules and basically "clicks" them together, like you would Lego bricks.

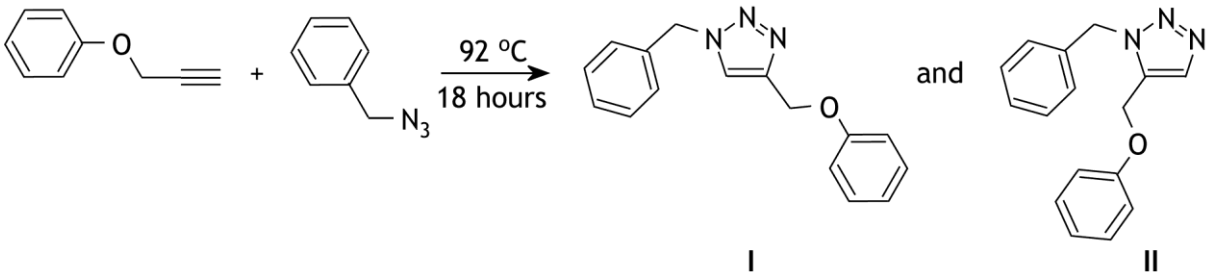
An example of a click reaction is the one between an alkyne ($R_1-C\equiv CH$) and an organic azide (R_2-N_3), for the forming of a so-called triazole. If one does not utilise a specific catalyst, a mixture of two compounds is formed: the so-called *anti* product and the so-called *syn* product.



In many cases equal amounts of the *anti* and *syn* product are formed.

□9 Is the *anti* product a stereoisomer of the *syn* product? Please explain. 2

When R_1 and/or R_2 are big groups (and no catalyst is used), there appears to be a preference for the forming of the *anti* product. This is because the large groups are in each other's way (steric hindrance). An example of one such reaction where the *anti* and *syn* products are not formed in equal amounts, is the conversion below:



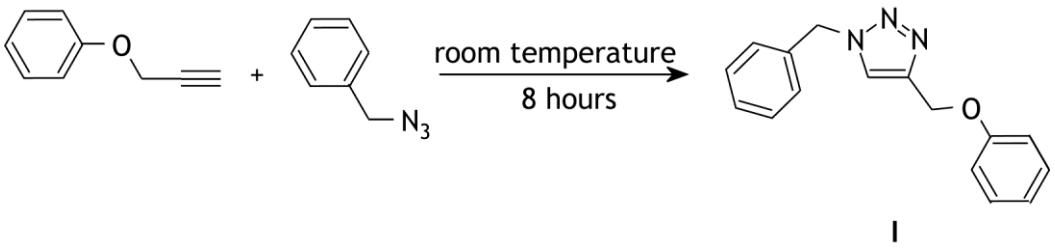
Here the *anti* product (**I**) and the *syn* product (**II**) are formed in a molar ratio of 1.6 : 1.0.

In an experiment in which 10 grams of the alkyne reacted with the appropriate amount of the azide, 11 grams of the *anti* product (**I**) had formed.

□10 Calculate the percentage of the alkyne that was in total converted to both products **I** and **II**. 5

The work that was awarded with the Nobel Prize contained, among other things, the research into catalysts that helped form specifically the *anti* or *syn* product. They discovered that by the use of a copper(I) catalyst only the *anti* product was formed and by the use of a ruthenium catalyst only the *syn* product was formed.

The production of compound **I** with a copper(I) catalyst is shown below.

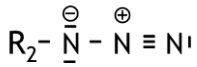


I

If one only wants to produce the *anti* product **I**, the reaction with the use of the copper(I) catalyst better suits the principles of Green Chemistry than the reaction without the use of a catalyst.

▫11 Explain for principles 2 and 6 why the reaction with the use of the copper(I) catalyst is 'greener' than the reaction without a catalyst (see BINAS-table 97F or ScienceData table 38.6 or the information on page 15 of this booklet). Use information given to you in this exercise. 2

For the azide-group of a molecule R_2-N_3 two mesomeric structures can be drawn that comply with the octet rule. One of those structures is shown below.

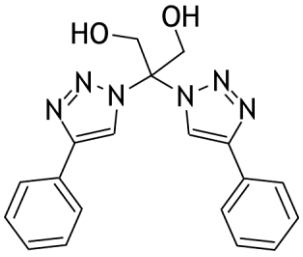


▫12 Draw the other mesomeric structure. If applicable, also give the formal charges. 2

▫13 Give a possible reaction mechanism for the forming of the *anti* product from $R_1-C\equiv CH$ and R_2-N_3.

- Use the mesomeric structure of the azide given above.
- Clarify how the electron pairs move with the forming and breaking of bonds by using curved arrows ( ).
- Show all the non-bonding electron pairs in the product. 4

Click reactions are used to make many different chemicals. Below is given the product of a reaction that was used as a part of a study to the medicinal properties of such chemicals. To prepare this chemical, two other chemicals were used: an alkyne and a chemical which had azide groups in its molecules. A catalyst was also used for this reaction.



▫14 Provide the structural formula of the two chemicals used to synthesise the chemical with the above structural formula. Write the azide group using N_3. Also mention what catalyst was used during this reaction, a copper(I) catalyst or a ruthenium catalyst. 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 $\frac{m_{\text{product}}}{m_{\text{starting materials}}} \times 100\%$

rendement $\frac{\text{practical yield}}{\text{theoretical yield}} \times 100\%$

E-factor $\frac{m_{\text{starting materials}} - m_{\text{real product yield}}}{m_{\text{real product yield}}}$

44th National Chemistry Olympiad 2023 preliminary round 1

Answer sheet Multiple choice questions

name:

no.	choice letters	(score)
1		
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