NATIONAL CHEMISTRY OLYMPIAD 2024

ASSIGNMENTS PRELIMINARY ROUND 1

To be conducted from 15 until 31 January 2024

SCHEIKUNDE OLYMPIADE

Maastricht University

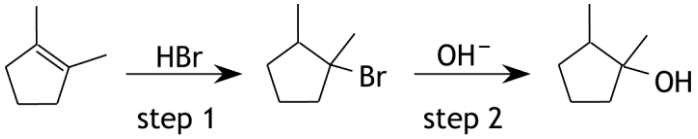
- **This preliminary round consists of 25 multiple choice questions divided over 9 topics and 2 problems with a total of 8 open questions as well as an answer sheet for the multiple choice questions.**
- **Use the answer sheet to answer the multiple choice questions.**
- **Use for each problem with open 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 lasts up to two full hours.**
- **Required materials: (graphic) calculator and BINAS 6th or 7th edition, 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 $p = p_0$.**

Problem 1 Multiple choice questions total 50 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 Look at the reaction scheme below.



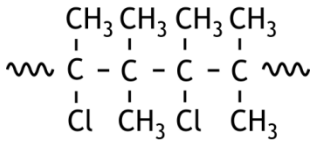
Below are two statements about this reaction scheme:

I step 1 is an addition reaction
II step 2 is a substitution reaction

Which of the above statements is/are correct?

A none
B only I
C only II
D both

2 Below is a fragment from the middle of a polymer molecule.



What is the name of the monomer used to form this polymer?

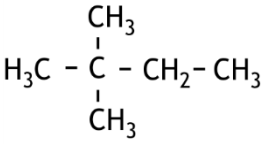
A 2-chloro-3-methylbutane
B 2-chloro-3-methylbut-2-ene
C 2-chloropentane
D 2-chloropent-2-ene

3 A hydrocarbon X has the molecular formula C_6H_{14}. Substance X reacts with a limited amount of chlorine gas under the influence of light.

The resulting reaction mixture contains only three different monochloroalkanes with the molecular formula $C_6H_{13}Cl$. Two of these three monochloroalkanes have the same boiling point.

What is the structural formula of substance X?

A



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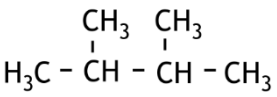

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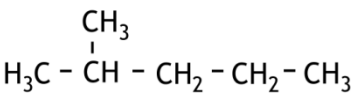

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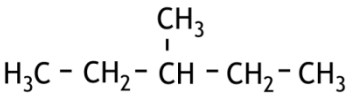
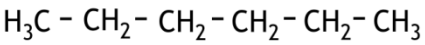


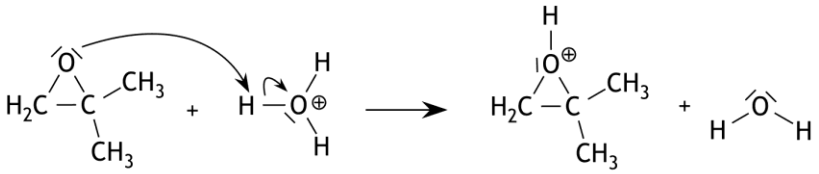
E



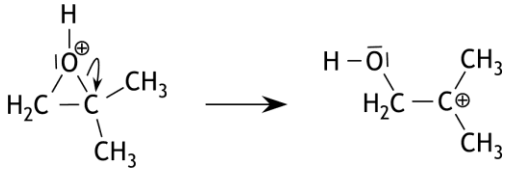
4 A four-step reaction mechanism is given below. The movements of electron pairs are indicated by curly arrows.

In one of the steps one or more arrow(s) is/are drawn incorrectly.

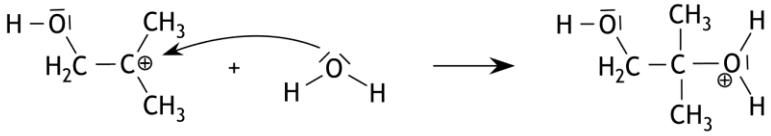
step 1



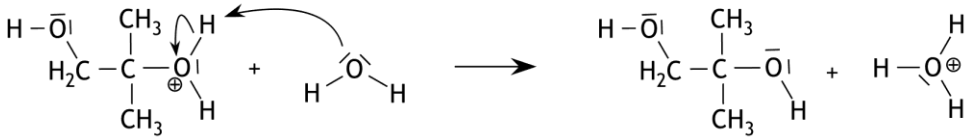
step 2



step 3



step 4



In which step is/are one or more arrow(s) drawn **incorrectly ?**

A step 1
B step 2
C step 3
D step 4

Reaction rate and equilibrium

5 Given the homogeneous equilibrium in a HAc solution in water:

$HAc + H_2O \rightleftharpoons Ac^- + H_3O^+$

The HAc solution is diluted with water. The new equilibrium is installed.

What applies to the number of moles of H_3O^+ ions in the solution and what applies to the pH of the solution?

	number of moles of H_3O^+ ions	pH
A	has become smaller	has become lower
B	has become smaller	has become higher
C	has become larger	has become lower
D	has become larger	has become higher

6 Fenton's reagent is a solution of an iron(II) salt and hydrogen peroxide in water. Such a solution is used to convert polluting organic substances in the soil to other less harmful substances.

MTBE, with molecular formula $C_5H_{12}O$, is a substance that can leak into the ground when refueling gasoline. During an experiment, 1.0 mg of MTBE reacts with a large excess of Fenton's reagent. It takes 4.0 minutes to convert 98% of the MTBE.

What is the average reaction rate during these 4.0 minutes for this conversion of MTBE?

A $4.6 \cdot 10^{-8}$ mol s^{-1}
B $4.7 \cdot 10^{-8}$ mol s^{-1}
C $1.9 \cdot 10^{-7}$ mol s^{-1}
D $2.8 \cdot 10^{-6}$ mol s^{-1}
E $4.1 \cdot 10^{-6}$ mol s^{-1}

7 $Ba(IO_3)_2$ is a poorly soluble salt. In a saturated solution of $Ba(IO_3)_2$ in water the following equilibrium is established:

$Ba(IO_3)_2(s) \rightleftharpoons Ba^{2+}(aq) + 2\ IO_3^-(aq)$

To determine the equilibrium constant of the above equilibrium, 0.2000 grams of $Ba(IO_3)_2$ (M = 487.1 g mol^{-1}) is weighed out and mixed with 100 mL of water. After reaching equilibrium, the suspension is filtered and the residue is weighed. The residue was found to contain 0.1513 grams of solid $Ba(IO_3)_2$.

What is the value of the equilibrium constant of the above equilibrium?

A $4.00 \cdot 10^{-12}$
B $1.00 \cdot 10^{-9}$
C $4.00 \cdot 10^{-9}$
D $1.20 \cdot 10^{-7}$
E $1.00 \cdot 10^{-6}$
F $2.00 \cdot 10^{-6}$

8 An experiment measures the rate of the following reaction:

$Zn(s) + 2\ H_3O^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g) + 2\ H_2O(l)$

The rate of this reaction is defined as the amount of $H_2(g)$ formed per second at the start of the reaction.

In the first test, 5.0 g of zinc granules and 100 mL of 1.0 M hydrochloric acid are used. The reaction takes place at room temperature.

Which adjustment will **not** lead to an acceleration of the reaction?

A Replace the zinc granules with 5.0 g zinc powder.
B Replace the hydrochloric acid with 50 mL of 2.0 M hydrochloric acid.
C Replace the hydrochloric acid with 200 mL of 1.0 M hydrochloric acid.
D Heat the hydrochloric acid before adding the zinc granules.

Thermochemistry

9 When dinitrogen pentoxide decomposes, the following reactions occur consecutively:

$2\ N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2(g)$ reaction 1

and

$2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$ reaction 2

Reaction 1 goes to completion, reaction 2 does not go to completion. Eventually a mixture of nitrogen dioxide, nitrogen monoxide and oxygen is produced. Dinitrogen pentoxide is no longer present in the reaction mixture.

The conversion of N_2O_5 to NO_2, NO and O_2 was found to have an enthalpy change of $+0.725 \cdot 10^5$ J per mol N_2O_5.

What percentage of the NO_2 produced in reaction 1 was converted in reaction 2?

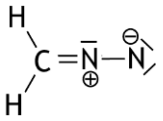
- the enthalpy of formation of N_2O_5 is $+0.133 \cdot 10^5$ J mol^{-1};
- assume that under these conditions, the data from BINAS table 57 and ScienceData table 9.2 can be used.

A 16.7%
B 33.4%
C 45.5%
D 91.0%

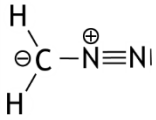
Structures and formulas

10 What is the Lewis structure of diazomethane, CH_2N_2?

A



B



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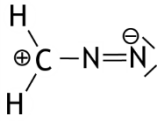

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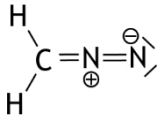


11 Which of the following atoms has/have an electron domain geometry of 3?

A the C atom in CH_2Cl_2
B the C atom in $COCl_2$
C the N atom in NH_3
D the N atoms in N_2H_4

12 Which of the following ions has the most electrons?

A Cu^+
B Hg^+
C I^-
D Ni^{2+}
E Zn^{2+}

pH / acid-base

13 A 0.15 M solution of an unknown weak base has a pH of 12.50.

What is the K_b of this unknown base?

A $6.7 \cdot 10^{-25}$
B $6.7 \cdot 10^{-3}$
C $8.4 \cdot 10^{-3}$
D $1.2 \cdot 10^{-2}$
E $1.0 \cdot 10^{-1}$

14 150 mL 0.150 M sodium hydroxide solution is mixed with 250 mL 0.100 M hydrochloric acid.

What is the pH of the final solution?

A 1.30
B 2.00
C 2.20
D 11.80
E 12.00
F 12.70

15 Linde needs a buffer solution with a pH of 7.41 for her biology experiment with enzymes. She asks the laboratory assistant of the chemistry department for a vial with disodium hydrogen phosphate (Na_2HPO_4) and a vial with sodium dihydrogen phosphate (NaH_2PO_4).

In what mass ratio should Linde dissolve the Na_2HPO_4 and NaH_2PO_4 in demineralized water to obtain a buffer solution with a pH of 7.41?

	NaH_2PO_4	Na_2HPO_4
A	1.0 g	0.29 g
B	1.0 g	0.53 g
C	1.0 g	0.62 g
D	1.0 g	0.74 g
E	1.0 g	1.6 g
F	1.0 g	1.9 g
G	1.0 g	3.5 g

Redox and electrolysis

16 Two electrolysis experiments are carried out: one with molten aluminum fluoride and one with molten lithium fluoride, using the same current. After *t* seconds,1.0 g of lithium is formed during the electrolysis of lithium fluoride.

After how many seconds will 1.0 g of aluminum be produced during the electrolysis of the aluminum fluoride?

A 0.26*t* s
B 0.33*t* s
C 0.77*t* s
D 1.3*t* s

17 An electrochemical cell is made for electrical energy production.

Which of the following not balanced reaction equations correspond(s) to a cell that could be used for this purpose? Assume all dissolved particles have a concentration of 1.00 mol L^{-1}.

I $Cr_2O_7^{2-} + Mn^{2+} + H^+ \rightarrow Cr^{3+} + MnO_4^- + H_2O$

II $NO_3^- + SO_2 \rightarrow NO_2 + SO_4^{2-}$

A none
B only I
C only II
D both

Analysis

18 For a titration of a solution of ammonia with hydrochloric acid, the ammonia solution needs to be diluted. During the titration of 25.00 mL of this diluted ammonia solution, the equivalence point should be reached when between 12.00 mL and 25.00 mL of hydrochloric acid is added. In a rapid titration of 1.0 mL of the undiluted ammonia solution, it is found that 8.5 mL of hydrochloric acid is required.

Which of the following dilutions can be applied to ensure that the amount of the hydrochloric acid that is added lies between 12.00 mL and 25.00 mL?

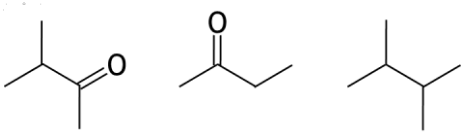
A 10.00 mL of the ammonia solution is diluted to 250 mL
B 10.00 mL of the ammonia solution is diluted to 500 mL
C 25.00 mL of the ammonia solution is diluted to 100 mL
D 25.00 mL of the ammonia solution is diluted to 250 mL
E 25.00 mL of the ammonia solution is diluted to 500 mL

19 In an experiment to determine the molarity of sodium chloride in a solution, the Mohr method was used. In this determination, 10.00 mL of the sodium chloride solution was pipetted into a volumetric flask with a capacity of 250.00 mL. It was then filled with distilled water to the mark. From the solution in the volumetric flask, 10.00 mL was titrated with a 0.00850 M silver nitrate solution. This titration yields a white solid, silver chloride. During the determination, 14.36 mL of silver nitrate solution was required to convert all the chloride ions into silver chloride.

What was the molarity of sodium chloride in the original solution?

A $6.10 \cdot 10^{-3}$ mol L^{-1}
B $1.22 \cdot 10^{-2}$ mol L^{-1}
C $1.53 \cdot 10^{-1}$ mol L^{-1}
D $3.05 \cdot 10^{-1}$ mol L^{-1}

20 Below are the structural formulas of three substances.



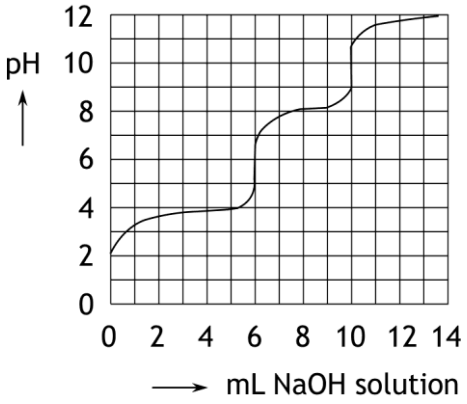
I II III

Mass spectra are generated for substances I, II and III.

In which mass spectrum/spectra does a peak appear at m/z = 43?

A only in the mass spectrum of I
B only in the mass spectrum of II
C only in the mass spectrum of III
D only in the mass spectra of I and II
E only in the mass spectra of I and III
F only in the mass spectra of II and III
G in the mass spectra of I, II and III

21 An acidic solution containing two monoprotic weak acids with different concentrations is titrated with a solution of sodium hydroxide. The image below is the titration curve of this titration.



Below are two statements about this titration.

I The molarity of the weaker acid in the examined solution is higher than the molarity of the stronger acid.

II If you do not have a pH meter, you can determine the equivalence points using the indicators dimethyl yellow and thymolphtalein.

Which of these statements is/are true?

A none
B only I
C only II
D both

Chemical calculations

22 Concrete corrosion, known as concrete decay, occurs when the iron present in reinforced concrete, known as reinforcement, starts to rust. Rust (Fe_2O_3) occupies more space than the iron from which it originates. Consequently, the reinforcement expands and leads to damaged concrete.

Rust is formed when iron comes into contact with water and oxygen through the following reaction:

$$4\ Fe\ +\ 3\ O_2\ \rightarrow\ 2\ Fe_2O_3$$

The density of iron is 7.87 g cm^{-3} and the density of Fe_2O_3 is 5.25 g cm^{-3}.

What is the increase in volume (in cm^3) of the reinforcement when 16.0 grams of iron is completely converted to rust according to the reaction equation above?

A 0.87 cm^3
B 1.16 cm^3
C 2.03 cm^3
D 2.14 cm^3
E 2.33 cm^3
F 4.36 cm^3

23 Which of the following fuels, listed below, releases the greatest amount of CO_2 per gram of fuel during complete combustion?

A CH_4
B C_3H_8
C C_6H_6
D C_8H_{18}

Green chemistry and industry

24 What happens to the atom economy and *E*-factor of a reaction when the percentage yield of the reaction increases?

	atom economy	*E*-factor
A	decreases	decreases
B	decreases	stays the same
C	decreases	increases
D	stays the same	decreases
E	stays the same	stays the same
F	stays the same	increases
G	increases	decreases
H	increases	stays the same
I	increases	increases

25 Researchers from a university in Iraq have been looking for the ideal conditions to produce zinc, having ZnO react with pure carbon at different temperatures. The researchers found that, under optimal conditions, 15 grams of powder containing 98 mass% of ZnO produced 8.0 grams of zinc.

What is the percentage yield of this zinc production?

A 42%
B 44%
C 54%
D 65%
E 66%
F 68%

Open questions total 27 points

Problem 2 Determining manganese levels in tea leaves 11 points

Tea leaves contain small amounts of manganese; less than 0.1 percent by mass. The manganese exclusively occurs in the form of Mn^{2+} ions. The content of manganese in tea leaves can be determined using colorimetry. Because Mn^{2+} does not produce any colour in aqueous solutions, it should first be converted into permanganate (MnO_4^-). Permanganate ions cause a purple coloration in water. For this conversion, periodate (IO_4^-) is used, which is converted to iodate (IO_3^-):

$$2\ Mn^{2+} + 5\ IO_4^- + 3\ H_2O \rightarrow 2\ MnO_4^- + 5\ IO_3^- + 6\ H^+$$

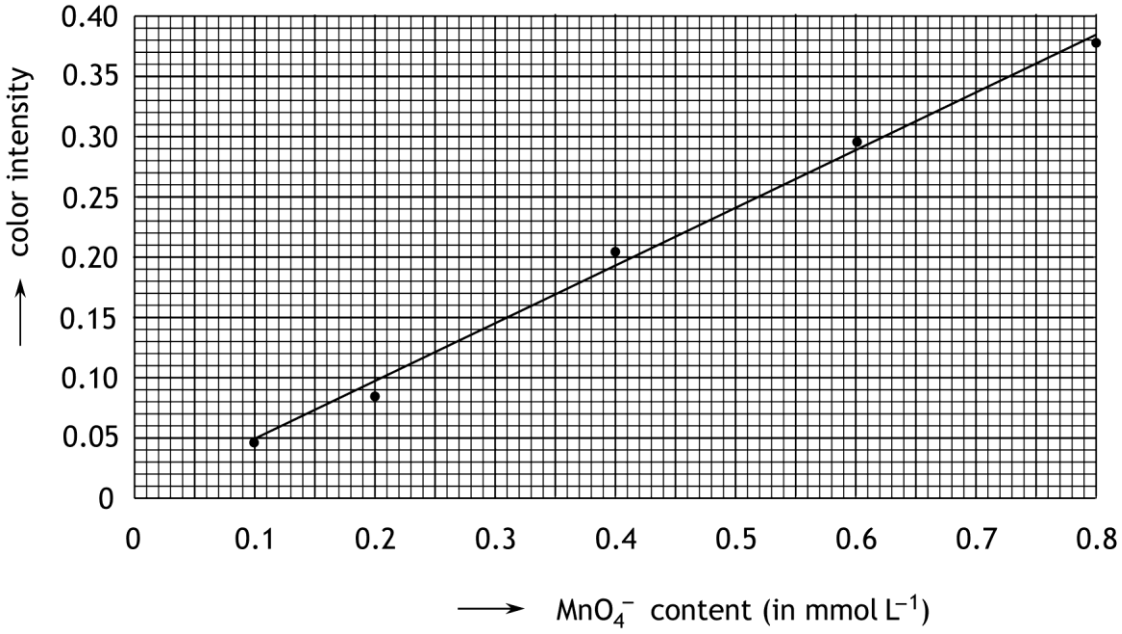
▫1 Give the equation of the half-reaction for the conversion of periodate to iodate. 3

For the determination of the Mn^{2+} content of tea leaves, the periodate must be added in excess. In such a determination, 2 to 3 grams of tea leaves and roughly 0.5 g of potassium periodate are used.

▫2 Show by calculation that adding 0.5 g of potassium periodate is more than enough to get all the Mn^{2+} in tea leaves to react. Assume that the tea leaves contain 0.1 percent Mn^{2+} by mass. 4

For a colorimetric determination of the manganese content of tea leaves, a series of solutions is first made with MnO_4^- contents of 0.800, 0.600, 0.400, 0.200 and 0.100 mmol L^{-1}.

For each of these solutions, the color intensity is measured using a colorimeter. These color intensities are then graphed against the MnO_4^- content in mmol L^{-1}. This graph is shown below.



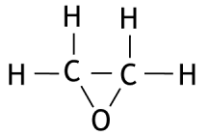
For the determination of the mass percentage of Mn^{2+} in Earl Grey tea leaves the following steps were taken:

1. 2.580 g of tea leaves were heated in a porcelain crucible.
2. The resulting ashes were heated with an amount of 4 M sulfuric acid solution.
3. Afterwards, the mixture was filtered.
4. 0.50 g potassium periodate was added to the filtrate.
5. When the reaction was complete, the entire mixture was transferred into a 50 mL volumetric flask. In the flask, demineralized water was added up to the mark.
6. Finally, the intensity of the purple colour of this solution was measured: 0.140.

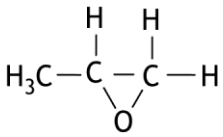
▫3 Calculate the mass percentage of Mn^{2+} in the examined tea leaves. 4

Problem 3 Vasa 16 points

Epoxyalkanes are compounds that can be thought of as being derived from alkanes by replacing per molecule two H atoms on two different C atoms with one O atom. Examples of epoxyalkanes are:



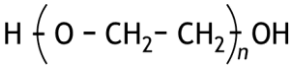
epoxyethane



1,2-epoxypropane

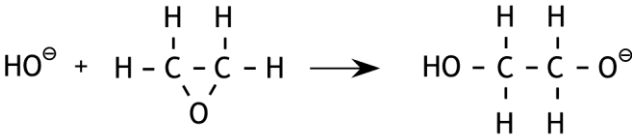
Epoxyalkanes in which the oxygen atom in the molecules is bonded to two adjacent carbon atoms can easily polymerize under the influence of sodium hydroxide. This produces polyepoxyethane from epoxyethane. This polymer is often used to preserve wooden ships that have been under water for a very long time. This happened, among other things, with the Swedish warship Vasa, which capsized in the Stockholm harbor on its maiden voyage in 1628. From April 1961, when the ship resurfaced, it was treated with polyepoxyethane for 17 years.

A molecule of polyepoxyethane can be represented as follows:



The value of *n* in this formula can vary from less than 10 to more than 100. The formation of such a polymer molecule follows a mechanism with a number of successive steps.

The first step (initiation) is the attachment of a hydroxide ion to an epoxyethane molecule:



ion A

Then, starting from ion A, a number of successive propagation steps take place. A negative ion is formed again and again.

▫4 Starting from ion A, show the first two successive propagation steps in structural formulas. 3

1,2-epoxypropane can also polymerize under the influence of sodium hydroxide. This polymerization proceeds by the same mechanism as the polymerization of epoxyethane.

▫5 Show a part of the middle of a polymer molecule of poly-1,2-epoxypropane in structural formula. This part must be composed of three monomer units. 3

In polymerizations of epoxyalkanes, a series of successive propagation steps is terminated by a reaction with a water molecule (termination reaction). Research into the polymerization of epoxyethane under the influence of sodium hydroxide showed that, depending on the conditions under which the polymerization is carried out, different types of polyepoxyethane with different melting ranges can be obtained.

In one of the experiments in this study, an amount of polyepoxyethane with a mass of 92 grams was formed from 88 grams of epoxyethane. In this experiment there was no epoxyethane left at the end.

▫6 Give the reaction equation for the mentioned termination reaction. Use the formula $H\left(O-CH_2-CH_2\right)_nOH$ for the end product. 3

▫7 Calculate the average value of *n* in the polyepoxyethane molecules $H\left(O-CH_2-CH_2\right)_nOH$ that are formed during the experiments described above. 4

Two other experiments from this study are described below.

fabric used			
	epoxyethane (mol)	NaOH (mol)	H_2O (mol)
experiment 1	1.0	0.036	0.33
experiment 2	1.0	0.036	0.10

Both experiments took place at the same temperature and pressure.
After polymerization of all epoxyethane, the polyepoxyethane was separated from the resulting reaction mixture. One of the experiments showed that polyepoxyethane was formed with a melting range of +2 °C to +4 °C , while in the other experiment the melting range of the resulting polyepoxyethane was +31 °C to +33 °C.

▫8 Explain which of the two experiments produced polyepoxyethane with the highest melting range. 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 $\dfrac{\text{mass of desired product}}{\text{total mass of all reactants}} \times 100\%$

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

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

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45th National Chemistry Olympiad 2024 preliminary round 1

Answer sheet multiple choice questions

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