DUTCH NATIONAL CHEMISTRY OLYMPIAD 2025

Assignments and Marking schemes

Preliminary round 1

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Final round

SCHEIKUNDE OLYMPIADE

Symeres
Making Molecules Matter. Together.

57th INTERNATIONAL CHEMISTRY OLYMPIAD UNITED ARAB EMIRATES 2025

Contents

NATIONAL CHEMISTRY OLYMPIAD 2025

ASSIGNMENTS PRELIMINARY ROUND 1

To be held between 13th and 31st January 2025

SCHEIKUNDE OLYMPIADE

Symeres
Making Molecules Matter. Together.

- **This preliminary round consists of 25 multiple choice questions divided over 9 topics and 2 problems, with a total of 8 open questions, in addition to an answer sheet for the multiple choice questions.**
- **Use the answer sheet to answer the multiple choice questions.**
- **For the open questions, use a separate answer sheet for each of the two problems. Remember to include your name on each sheet.**
- **The maximum score for this paper is 76 points.**
- **The preliminary round lasts two hours in total.**
- **Required materials: (graphic) calculator and BINAS 6th or 7th edition, ScienceData 1st edition or BINAS 5th edition, English version. “Green chemistry” table is included.**
- **The total number of points available for each question is stated.**
- **Unless otherwise stated, standard conditions apply: T = 298 K and $p = p_0$.**

This test was made possible with the support of the following people:

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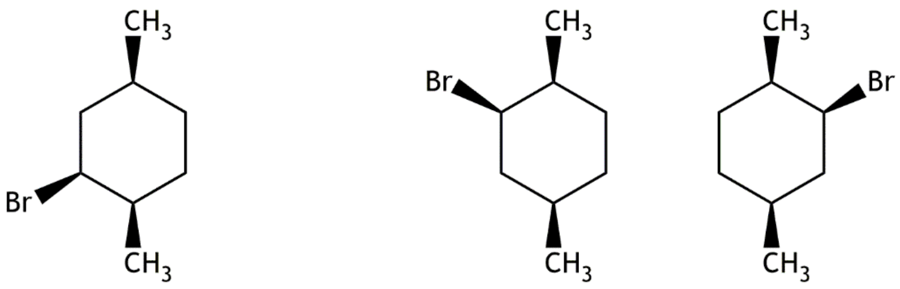
Problem 1 Multiple choice questions total 50 points

For each question, write your answer (letter) on the answer sheet. The answer sheet can be found at the end of this examination booklet.
Marks: 2 points for each correct answer.

Carbon chemistry

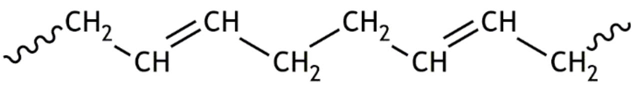
1 Which of the substances, I and II, shown below is a stereoisomer / are stereoisomers of substance X?



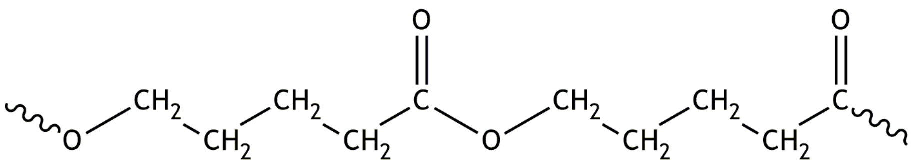
X I II

- **A** none
- **B** only I
- **C** only II
- **D** both

2 Fragments of two polymer chains are shown below.



polymer I



polymer II

What are the molecular formulas of the monomers from which the above polymer chains could have been formed?

	polymer I	polymer II
A	C_2H_4	$C_5H_{10}O_2$
B	C_2H_4	$C_5H_{10}O_3$
C	C_4H_6	$C_5H_{10}O_2$
D	C_4H_6	$C_5H_{10}O_3$
E	C_4H_8	$C_5H_{10}O_2$
F	C_4H_8	$C_5H_{10}O_3$

3 How many alcohols with the molecular formula $C_5H_{12}O$ are there? Take stereoisomerism into account.

A 6
B 7
C 8
D 9
E 10
F 11
G 12

Thermochemistry

4 Sodium perchlorate, $NaClO_4$, is a solid at room temperature. When heated, it melts and thermolysis occurs:

$NaClO_4(l) \rightarrow NaCl(s) + 2\ O_2(g)$ (reaction 1)

What is the reaction enthalpy of reaction 1?

Use, among others, the following thermodynamic data for sodium perchlorate :

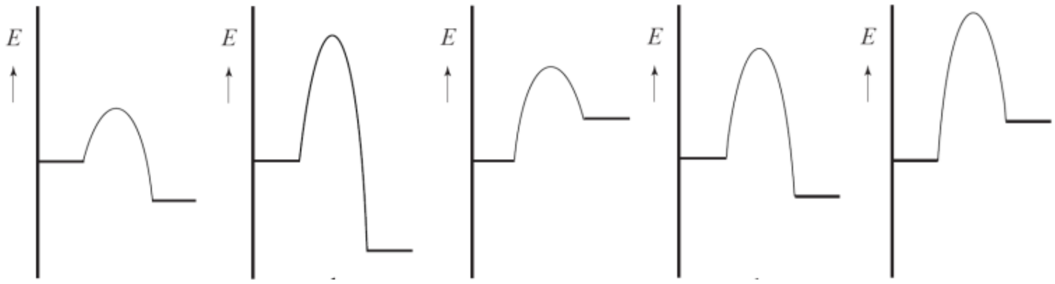
- The enthalpy of formation of $NaClO_4$ (s) is -382.75 kJ mol^{-1}.
- The amount of energy required to melt 1 mole of $NaClO_4(s)$ is 14.7 kJ.
- Assume that data valid at 298 K is also valid under the conditions of reaction 1.

A -809 kJ mol^{-1}
B -779 kJ mol^{-1}
C -43 kJ mol^{-1}
D -13 kJ mol^{-1}
E +13 kJ mol^{-1}
F +43 kJ mol^{-1}
G +779 kJ mol^{-1}
H +809 kJ mol^{-1}

5 Electrolysis of water produces hydrogen and oxygen:

$2\ H_2O(l) \rightarrow 2\ H_2(g) + O_2(g)$ (reaction 1)

Five energy diagrams (I, II, III, IV and V) are shown below. In these diagrams, the left level corresponds to the energy level of the reactants and the right level to the energy level of the products. One of the diagrams shows the course of reaction 1 without a catalyst and one of the other diagrams shows the course of reaction 1 with a catalyst. In all diagrams, the vertical axis has the same scale.



I II III IV V

Which of the diagrams above shows the progress of reaction 1 without a catalyst and which of the diagrams shows the progress of reaction 1 with a catalyst?

	without catalyst	with catalyst
A	I	IV
B	I	II
C	II	I
D	II	IV
E	III	V
F	IV	I
G	IV	II
H	V	III

Reaction rate and equilibrium

6 10 mL of 0.50 M potassium sulfate solution and 10 mL of 0.50 M silver nitrate solution are combined.

A heterogeneous mixture is formed and equilibrium is achieved.

What is the correct order of the concentrations of the ions in this mixture?

A $[K^+] = [NO_3^-] > [Ag^+] > [SO_4^{2-}]$
B $[K^+] = [NO_3^-] > [SO_4^{2-}] > [Ag^+]$
C $[K^+] > [NO_3^-] > [Ag^+] > [SO_4^{2-}]$
D $[K^+] > [NO_3^-] > [SO_4^{2-}] > [Ag^+]$
E $[K^+] > [NO_3^-] > [SO_4^{2-}] = [Ag^+]$
F $[K^+] > [NO_3^-] = [SO_4^{2-}] = [Ag^+]$

7 Consider the following equilibrium:

$2\ NO_2(g) \rightleftharpoons N_2O_4(g)$ with equilibrium constant K.

Extra NO_2 is added. The new equilibrium is reached. During the addition of the NO_2 and the reaching of the equilibrium, the volume and temperature are kept constant.

After reaching equilibrium, did the value of K decrease, remain the same, or increase?

After reaching equilibrium, did the rate of reaction to the left decrease, remain the same, or increase?

	value of K	reaction rate to the left
A	decreased	decreased
B	decreased	remained the same
C	decreased	increased
D	remained the same	decreased
E	remained the same	remained the same
F	remained the same	increased
G	increased	decreased
H	increased	remained the same
I	increased	increased

8 In a closed space of 250 cm^3 2.50 g of calcium carbonate is heated to a constant temperature. The following equilibrium results:

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

When equilibrium is reached, 1.70 g of $CaCO_3$ is still present.

What is the value of the equilibrium constant, K_c, of this equilibrium at this temperature?

A 0.0080
B 0.015
C 0.032
D 0.068
E 31
F 66
G $1.3 \cdot 10^2$

9 Consider the following equilibrium:

$$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$$

For the reaction to the right, $\Delta H = -196\ \text{kJ mol}^{-1}$.

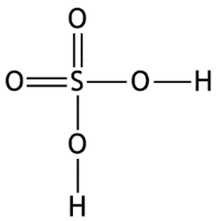
Under constant temperature, how should the pressure be changed to favour the reaction to the right?

Under constant pressure, how should the temperature be changed to favour the reaction to the right?

	pressure (under constant T)	temperature (under constant p)
A	decrease	decrease
B	decrease	increase
C	increase	decrease
D	increase	increase

Structures and formulas

10 The structural formula for sulfuric acid is:



What are the partial charges of the atoms in this molecule?

	H atom	S atom	double-bonded O atoms (O══)	O atoms in O—H groups
A	δ^+	δ^+	δ^-	δ^+
B	δ^+	δ^+	δ^-	δ^-
C	δ^+	δ^-	δ^-	δ^+
D	δ^+	δ^-	δ^-	δ^-
E	δ^-	δ^+	δ^+	δ^+
F	δ^-	δ^+	δ^+	δ^-
G	δ^-	δ^-	δ^+	δ^+
H	δ^-	δ^-	δ^+	δ^-

11 An atom of ^{232}Th is transformed into an atom of ^{208}Pb after emitting a number of alpha particles. An alpha particle is the nucleus of a He-4 atom. During this transformation, a number of neutrons in the atomic nucleus are also converted into protons. Electrons are not considered during this process.

How many alpha particles are emitted during this transformation?

How many neutrons are converted into protons?

	number of emitted alpha particles	number of neutrons converted into protons
A	4	4
B	4	8
C	6	4
D	6	12
E	8	8
F	8	12

12 How many valence electrons does a ClO_3^- particle contain?

A 24
B 25
C 26
D 31
E 32
F 33

13 How many resonance structures can be drawn for the oxalate ion ($C_2O_4^{2-}$)? Assume that all atoms follow the octet rule.

A 1
B 2
C 3
D 4
E 5
F 6

pH and acid-base

14 0.320 mol of the monoprotic weak acid HA is dissolved in water and diluted with water to a volume of 1.00 L.

In this solution, 10.2% of the acid is ionized.

What is the K_a of HA?

A $3.33 \cdot 10^{-3}$
B $3.71 \cdot 10^{-3}$
C $1.16 \cdot 10^{-2}$
D $3.26 \cdot 10^{-2}$

15 A 100 mL solution of sodium hydroxide (NaOH) has a pH of 9.20.

How many mL of 0.10 M HCl solution must be added to reduce the pH to 8.20?

A 0.00014 mL
B 0.0016 mL
C 0.014 mL
D 0.016 mL
E 0.10 mL

16 Four solutions are made by dissolving 0.1 mol of the following substances in water: K_2CO_3, K_2O, NaOH, Na_2SO_4. The final volume of each solution was 1 L.

Which of these solutions has the highest pH?

A the solution with 0.1 mol of K_2CO_3
B the solution with 0.1 mol of K_2O
C the solution with 0.1 mol of NaOH
D the solution with 0.1 mol of Na_2SO_4

Redox and electrochemistry

17 To launch space shuttles into space, two 'solid rocket boosters' were used. These worked based on a redox reaction between ammonium perchlorate and aluminium.

The incomplete reaction equation, where only the coefficients are missing, is shown below.

$NH_4ClO_4 + Al \rightarrow Al_2O_3 + NO + HCl + H_2O$

What is the ratio between the coefficients of Al and HCl in the balanced equation for this reaction?

	Al	:	HCl
A	8	:	3
B	2	:	1
C	1	:	1
D	1	:	2
E	2	:	3

18 In an electrochemical cell, one of the half-cells contains a 1 M solution of lead(II) nitrate and an electrode.

The half reaction that occurs in this half-cell during current flow is:

$Pb^{2+} + 2e^- \rightarrow Pb$

What material could be used for the electrode?

Would this be the positive or negative electrode during discharging?

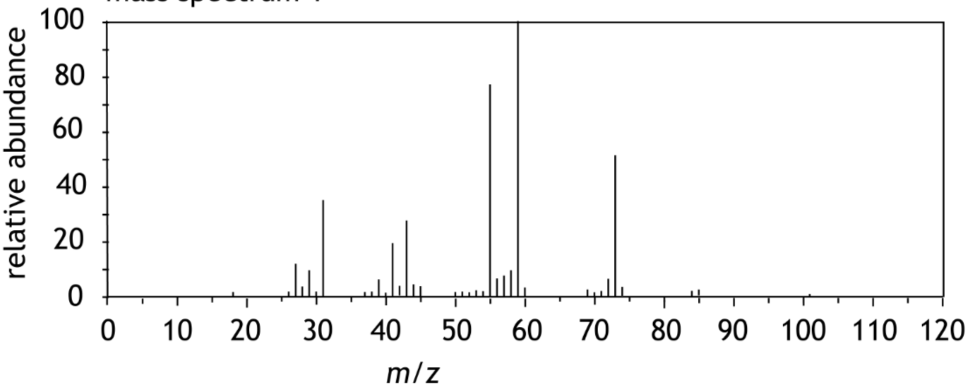
	material	electrode is
A	copper	positive
B	copper	negative
C	zinc	positive
D	zinc	negative

Analysis

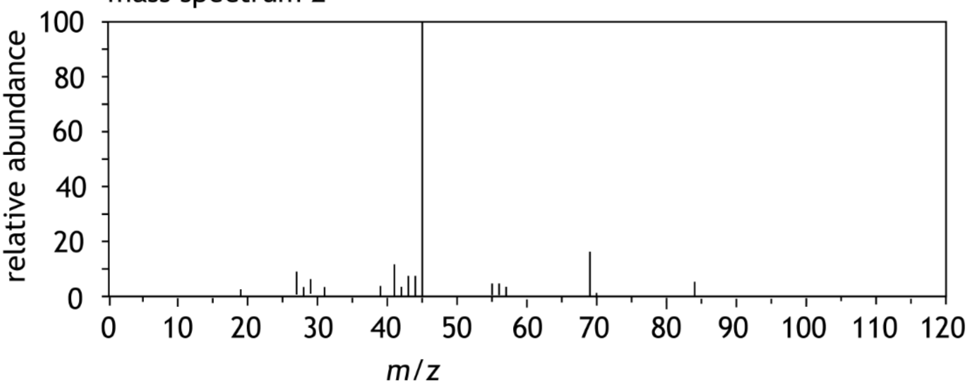
19 There are three isomeric unbranched hexanols: hexan-1-ol, hexan-2-ol and hexan-3-ol.

The mass spectra of two of these structural isomers are shown below.

mass spectrum 1



mass spectrum 2



It is known that in alcohols, a C — C bond adjacent to the alcohol group can be broken. One of these two C atoms is attached to the O atom of the alcohol group.

In the mass spectra above, in both cases, the peak with the highest abundance can be attributed to a fragment that is formed when a C — C bond adjacent to an alcohol group is broken.

To which substance does mass spectra 1 belong and to which substance does mass spectra 2 belong?

	mass spectrum 1	mass spectrum 2
A	hexan-1-ol	hexan-2-ol
B	hexan-1-ol	hexan-3-ol
C	hexan-2-ol	hexan-1-ol
D	hexan-2-ol	hexan-3-ol
E	hexan-3-ol	hexan-1-ol
F	hexan-3-ol	hexan-2-ol

20 Which salt below is sparingly soluble in water, but gives a clear solution in a solution containing sufficient hydrogen iodide?

A lead(II) chloride
B lead(II) oxide
C magnesium chloride
D magnesium oxide

21 In gas chromatography, a mixture of the following substances I, II and III is separated in a non-polar column.

Which substance has the shortest retention time and which has the longest?

$H_3C—CH_2—CH_3$	$H_3C—CH_2—CH_2—CH_3$	$H_3C—CH_2—CH_2—CH_2—CH_3$
I	II	III

	shortest retention time	longest retention time
A	I	II
B	I	III
C	II	I
D	II	III
E	III	I
F	III	II

Chemical calculations

22 Sodium cyanide (NaCN) is used to extract gold from ore according to the reaction equation below.

$$4\ Au(s) + 8\ CN^{-}(aq) + O_2(g) + 2\ H_2O(l) \rightarrow 4\ Au(CN)_2^{-}(aq) + 4\ OH^{-}(aq)$$

How many litres of a 0.0100 M sodium cyanide solution are needed to completely convert 11.8 g of gold according to the above reaction equation?

A 0.749 L
B 1.50 L
C 2.99 L
D 5.99 L
E 12.0 L

23 Ethanol (C_2H_5OH) is converted by dichromate in an acidic environment to ethanal (CH_3CHO) according to the reaction equation below.

$$3\ C_2H_5OH(aq) + Cr_2O_7^{2-}(aq) + 8\ H^+(aq) \rightarrow 3\ CH_3CHO(aq) + 2\ Cr^{3+}(aq) + 7\ H_2O(l)$$

At what rate does the [CH_3CHO] change if the [Cr^{3+}] increases by 0.18 mol $L^{-1}\ s^{-1}$ according to the above reaction equation?

A the [CH_3CHO] decreases by 0.12 mol $L^{-1}\ s^{-1}$
B the [CH_3CHO] decreases by 0.27 mol $L^{-1}\ s^{-1}$
C the [CH_3CHO] increases by 0.12 mol $L^{-1}\ s^{-1}$
D the [CH_3CHO] increases by 0.27 mol $L^{-1}\ s^{-1}$

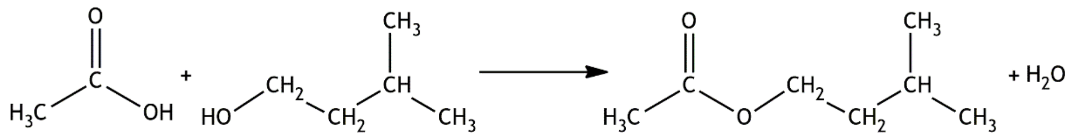
24 A spoon is coated with silver by electrolysis of a 1.0 M solution of silver nitrate at a current of 0.10 A.

How many minutes of electrolysis are required to ensure that 0.10 g of silver is coated on the spoon?
1 A is 1 C s^{-1} and the charge on 1 mole of electrons is $9.65 \cdot 10^4$ C.

A 1.5 min
B 5.0 min
C 10 min
D 15 min
E 30 min

Green chemistry

25 The following reaction occurs in the production of the banana-scented ester:



The water produced in this reaction is considered waste.

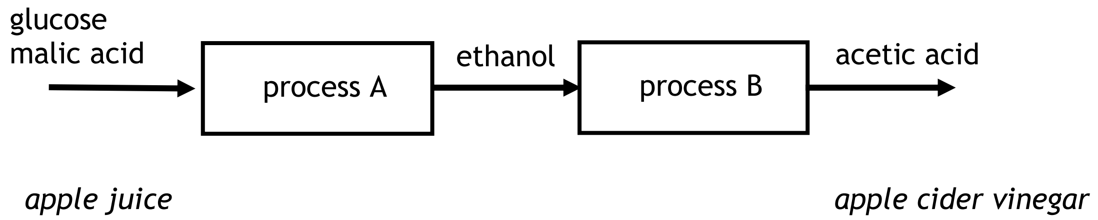
What is the percentage yield of this process if the *E*-factor is 0.34?

A 34%
B 66%
C 75%
D 85%

Open questions total 26 points

Problem 2 Apple cider vinegar 12 points

Apple cider vinegar is used as a salad dressing and as a food preservative. Apple cider vinegar is made from apple juice by performing two processes. This is shown in simplified form in the block diagram below.



In process A, glucose and malic acid (2-hydroxybutanedioic acid, $C_4H_6O_5$) from apple juice are converted to ethanol. The reaction equations of the two reactions that take place in process A are shown below.

$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2$ (reaction 1)

$C_4H_6O_5 \rightarrow C_2H_5OH + 2\ CO_2$ (reaction 2)

In process B, ethanol is converted with oxygen from the air to, among others, acetic acid (ethanoic acid).

The resulting solution is apple cider vinegar.

□1 Draw the structural formula of malic acid. 2

□2 Give the equation for the reaction that takes place in process B. Use molecular formulas. 2

The dissolved malic acid content of apple juice from which apple cider vinegar is produced was determined by an acid-base titration. For this purpose, 10.00 mL of apple juice was titrated with 0.1000 M sodium hydroxide solution and phenolphthalein as an indicator. The malic acid content was determined as 7.382 g L^{-1}.

□3 Calculate how many mL of 0.1000 M sodium hydroxide solution were needed for this titration. 4

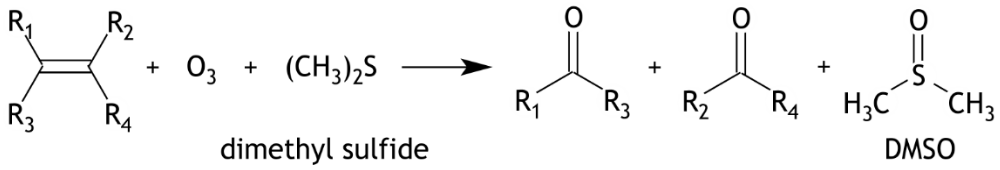
The acetic acid content of the produced apple cider vinegar was 1.086 mol L^{-1}.

□4 Calculate the glucose content in the apple juice in g L^{-1}.
Assume the following:

- The volume of the solution does not change during processes A and B.
- The percentage yield of processes A and B is 100%. 4

▌Problem 3 Ozonolysis 14 points

Ozonolysis is a chemical reaction in which an alkene reacts with ozone. In this reaction, the C = C bond is broken to form carbonyl groups. When an alkene reacts with ozone and then with dimethyl sulfide, aldehydes and/or ketones and DMSO are formed. These reactions can be represented in one equation (reaction 1):



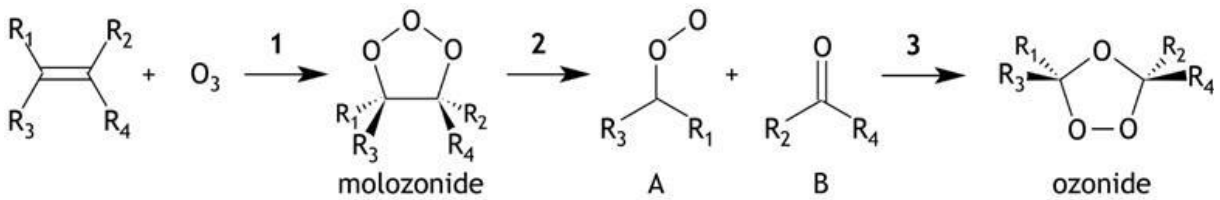
(reaction 1)

Here, R1 up to R4 represent hydrocarbon groups and/or H atoms.

▫5 Give the structural formulas of the two carbonyl compounds formed when 2-methylhex-2-ene reacts according to reaction 1. 2

In ozonolysis, the alkene first reacts with ozone to form a so-called ozonide. This reaction proceeds in three steps via a number of intermediate products. These steps are shown in figure 1. The structural formula of A is not complete in this figure.

figure 1



In step 1, an alkene molecule reacts with an ozone molecule to form a molozonide molecule. In step 2, electron pairs in the molozonide molecule are shifted to form A and B. One covalent bond is missing from the structural formula of A. Both oxygen atoms in molecule A have a formal charge. All atoms in molecule A follow the octet rule .

▫6 Complete the following assignments:

- Copy the incomplete structural formula of A from figure 1 and draw the missing covalent bond and complete the Lewis structure of A. Also indicate the formal charges.
- Copy the structural formula of the molozonide from figure 1 and draw the lone pairs in it.
- Use curly arrows to show how electron pairs in a molozonide molecule moved to create A and B. 4

Finally, in step 3, the ozonide molecule is formed.

Dimethyl sulfide is then added to the formed ozonide to convert the ozonide to carbonyl compounds. This is a redox reaction.

□7 Complete the following assignments:

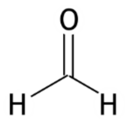
- Give the equation of the half-reaction for the conversion of ozonide shown above. Use the formula $C_2H_4O_3$ for ozonide . Here R_1 to R_4 are H atoms. This conversion produces only one carbonyl compound. H_2O and H^+ are also present in this equation.
- Using this equation, explain whether dimethyl sulfide is acting as an oxidizing agent or as a reducing agent. 3

Unsaturated compounds containing more than one C = C bond per molecule can also be ozonolyzed. Such ozonolysis occurs in the same way as described above: each individual C = C bond reacts in the way described.

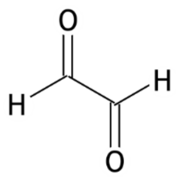
Ozonolysis was formerly used in the structural analysis of organic compounds. An example of such an analysis is the following:

A given amount of hydrocarbon X, containing more than one C = C bond per molecule, undergoes complete ozonolysis.

The only carbonyl compounds formed in this process are formaldehyde and glyoxal.



formaldehyde



glyoxal

Complete ozonolysis of a given amount of substance X produces 4.8 mg of formaldehyde and 14 mg of glyoxal.

□8 Determine the structural formula of X, showing your calculation 5

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

46th National Chemistry Olympiad 2025 preliminary round 1

Answer sheet: multiple choice questions

name:

no.	Answer letter	(score)
1		
2		
3		
4		
5		
6		
7		
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10		
11		
12		
13		
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23		
24		
25		
	Total	

NATIONAL CHEMISTRY OLYMPIAD 2025

ASSIGNMENTS PRELIMINARY ROUND 2
To be held between 17th and 25th March 2025

SCHEIKUNDE OLYMPIADE

Symeres
Making Molecules Matter. Together.

- **This preliminary round consists of 20 multiple choices questions divided over 8 topics, and 3 problems with a total of 16 open questions, in addition to an answer sheet for the multiple choice questions.**
- **Use the answer sheet to answer the multiple choice questions.**
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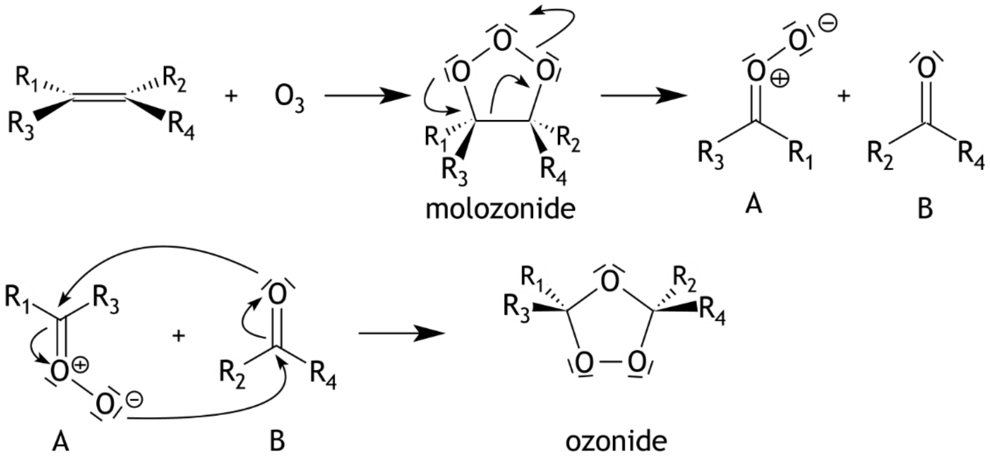
Problem 1 Multiple choice questions total 40 points

For each question, write your answer (letter) on the answer sheet. The answer sheet can be found at the end of this examination booklet.
Marks: 2 points for each correct answer.

Carbon chemistry

The next two questions are about the ozonolysis of alkenes.

Alkenes can react with ozone, O_3, forming a so-called ozonide. The reaction proceeds via a so-called molozonide and two intermediates A and B as follows:



In this reaction stereoisomers can be formed.

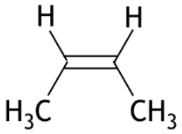
1 How many molozonides can be formed in the following two cases?

I R_1 to R_4 are different.
II $R_1 = R_2$ and $R_3 = R_4$

Assume that the ozone molecule reacts with the alkene molecule in one step.

	I	II
A	1	1
B	1	2
C	2	1
D	2	2
E	4	1
F	4	2

2 How many ozonides can be formed in the ozonolysis of the alkene below?



Consider stereoisomerism.

A 1
B 2
C 3
D 4

3 There is a large number of possible structures with the molecular formula C_6H_{10}.

How many of these structures contain both a cyclobutane ring and a double bond? Consider stereoisomerism.

- **A** 2
- **B** 3
- **C** 4
- **D** 5
- **E** 6
- **F** 7
- **G** 8
- **H** 9
- **I** 10

Reaction rate and equilibrium

4 5.00 g of nitrogen dioxide is introduced in a closed reaction vessel with a fixed volume of 1.00 dm^3. The following equilibrium is reached:

$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$

The temperature of the equilibrium mixture is 310 K and the pressure is $1.71 \cdot 10^5$ Pa.

What is the K_p of the equilibrium under these conditions?

- **A** 0.35
- **B** 0.57
- **C** 2.28
- **D** 2.92

5 Nitrous oxide in the gas phase can decompose as follows:

$2\ N_2O(g) \rightarrow 2\ N_2(g) + O_2(g)$

Chlorine gas can act as a catalyst in this process.

The following mechanism has been proposed for this catalyzed reaction:

$Cl_2 \rightleftharpoons 2\ Cl$	fast
$Cl + N_2O \rightarrow N_2 + ClO$	slow
$ClO + N_2O \rightarrow N_2 + ClO_2$	fast
$ClO_2 + Cl \rightarrow Cl_2 + O_2$	fast

Which equation for the reaction rate, r, is consistent with this mechanism?

- **A** $r = k[N_2O]$
- **B** $r = k[N_2O]^2$
- **C** $r = k[N_2O][Cl_2]$
- **D** $r = k[N_2O][Cl_2]^{1/2}$
- **E** $r = k[N_2O][Cl_2]^2$

6 Using the equilibrium constants, K_1, K_2, and K_3, of the following equilibria

$N_2(g) + O_2(g) \rightleftharpoons 2\ NO(g)$ K_1

$2\ NO(g) + O_2 \rightleftharpoons 2\ NO_2(g)$ K_2

$NO(g) + NO_2(g) \rightleftharpoons N_2O_3(g)$ K_3

the equilibrium constant K of the equilibrium

$2\ N_2O_3(g) \rightleftharpoons 2\ N_2(g) + 3\ O_2(g)$ K

can be calculated.

What is the relationship between K and K_1, K_2 and K_3?

A $K = K_1 \times K_2 \times K_3$

B $K = \dfrac{1}{K_1 \times K_2 \times K_3}$

C $K = K_1^2 \times K_2 \times K_3^2$

D $K = \dfrac{1}{K_1 \times K_2^2 \times K_3^2}$

E $K = \dfrac{1}{K_1^2 \times K_2 \times K_3^2}$

Structures and formulas

7 Which of the following particles have the same electron configuration in the ground state?

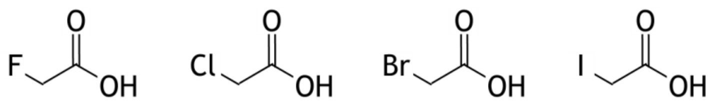
A Co^{3+} and Ni^{2+}

B Ni and Pd

C V^+ and Cr

D Zn and Ga^+

8 Which of the following halogenated ethanoic acids is the strongest acid?



I II III IV

A I

B II

C III

D IV

pH / acid-base

9 Equal volumes of 0.10 M solutions of H_3PO_4 and Na_3PO_4 are mixed.

What is the pH of the resulting solution?

A 4.69

B 7.21

C 9.77

D 12.32

10 20 mL of a solution of sodium hydroxide is added to 20 mL of a solution containing calcium chloride and magnesium chloride, both with a concentration of 0.10 M. The pH is measured and found to be 10.00.

Has a precipitate formed in the solution?

A no precipitate has formed
B only a precipitate of calcium hydroxide has formed
C only a precipitate of magnesium hydroxide has formed
D a precipitate of both calcium hydroxide and magnesium hydroxide has formed

Redox and electrochemistry

11 A pigment often used by the "Old Masters" to obtain a blue colour is the mineral vivianite. Vivianite can be represented by the formula $Fe_3(PO_4)_2 \cdot 8H_2O$. Vivianite is itself colourless, but turns blue after oxidation. Rembrandt and Vermeer, among others, used vivianite in their paintings.
When vivianite is oxidized, the $Fe_3(PO_4)_2$ reacts with oxygen and water to form iron(III) phosphate and iron(III) hydroxide. The incomplete reaction equation is shown below; only the coefficients are missing.

$$Fe_3(PO_4)_2 + O_2 + H_2O \rightarrow FePO_4 + Fe(OH)_3$$

What is the coefficient for O_2 in the balanced reaction equation?

A 1
B 2
C 3
D 4
E 5
F 6

12 A solution contains equal moles of $NiCl_2$ and $CuBr_2$. The solution is electrolyzed with graphite electrodes.

Which products are produced first ?

	at the negative electrode	at the positive electrode
A	$Br_2(aq)$	Cu(s)
B	$Br_2(aq)$	Ni(s)
C	$Cl_2(aq)$	Cu(s)
D	$Cl_2(aq)$	Ni(s)
E	Cu(s)	$Br_2(aq)$
F	Cu(s)	$Cl_2(aq)$
G	Ni(s)	$Br_2(aq)$
H	Ni(s)	$Cl_2(aq)$

1 3 What is the E^0 for the half-reaction $PbO_2(s) + 4\ H^+(aq) + 4\ e^- \rightarrow Pb(s) + 2\ H_2O(l)$?

Data:

$PbO_2(s) + 4\ H^+(aq) + 2\ e^- \rightarrow Pb^{2+}(aq) + 2\ H_2O(l)$ $\quad E^0 = 1.468$ V

$Pb^{2+}(aq) + 2\ e^- \rightarrow Pb(s)$ $\quad E^0 = -0.126$ V

Use the formula $\Delta G = -nF\Delta E$.

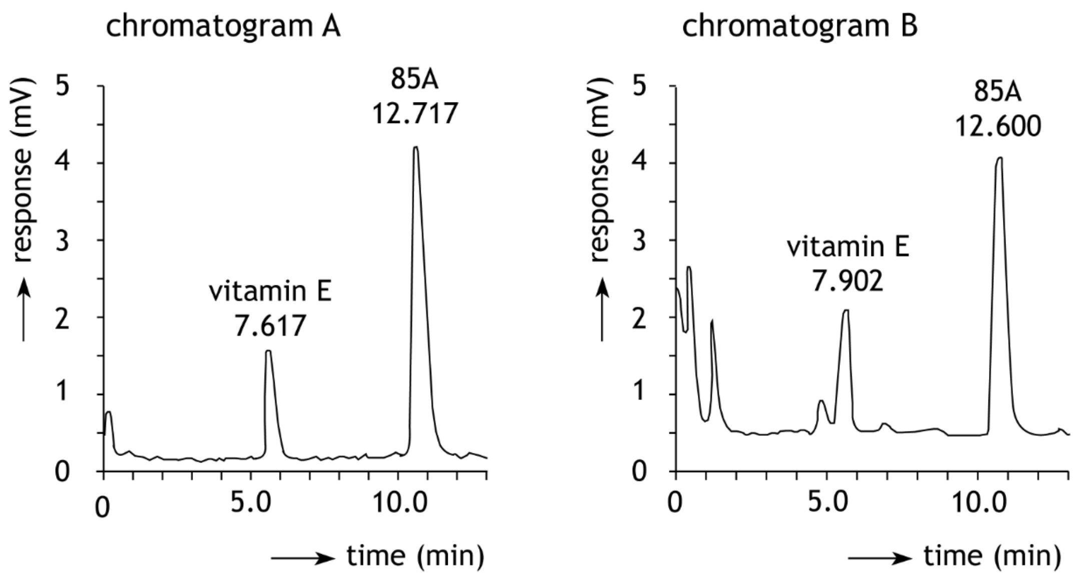
A 0.671 V
B 0.797 V
C 1.342 V
D 1.594 V

Analysis

14 The vitamin E content of blueberry juice can be determined using gas chromatography. Often an internal standard is used, indicated by the code 85A. This substance does not occur naturally in blueberry juice.

Two chromatograms are then recorded. The results of such a determination are shown below.

Chromatogram A is of a mixture, in which the concentration of vitamin E is $4.50\cdot10^{-4}$ mol L^{-1} and that of 85A is $1.00\cdot10^{-3}$ mol L^{-1}.
Chromatogram B is of a sample of blueberry juice where enough 85A has been added to ensure that the concentration of 85A in that sample is also $1.00\cdot10^{-3}$ mol L^{-1}.



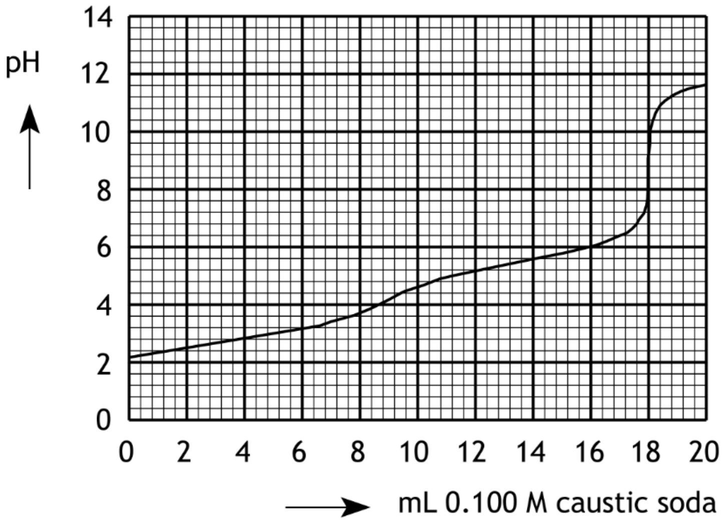
The peak areas are shown above the peaks in arbitrary units.

What was the concentration of vitamin E in the blueberry juice tested?

A $4.09\cdot10^{-4}$ mol L^{-1}
B $4.30\cdot10^{-4}$ mol L^{-1}
C $4.71\cdot10^{-4}$ mol L^{-1}
D $4.93\cdot10^{-4}$ mol L^{-1}

The next two questions are about the titration of a solution of a diprotic acid.

In a 250 mL volumetric flask, 1.494 g of the diprotic acid H_2A is dissolved. The solution is filled up to the mark. 25.00 mL of this solution is transferred to an conical flask and titrated with 0.100 M sodium hydroxide solution (caustic soda). The pH during the titration is monitored with a pH meter, and the following diagram is obtained.



15 The equivalence point of this titration could also be determined using an indicator. Which of the following indicators would be suitable for this?

I phenolphthalein
II thymol blue

A neither
B only phenolphthalein
C only thymol blue
D both

16 What is the molar mass of the examined diprotic acid ?

A 21.0 g mol^{-1}
B 42.0 g mol^{-1}
C 83.0 g mol^{-1}
D 166 g mol^{-1}
E 332 g mol^{-1}

Calculations and Green Chemistry

17 During the combustion of magnesium in air, in addition to magnesium oxide (MgO), magnesium nitride (Mg_3N_2) is formed.
1.000 g of magnesium is combusted. The mass of the produced mixture of magnesium oxide and magnesium nitride is 1.584 g.

What is the mass percentage of magnesium nitride in the mixture?

A 9.0%
B 11%
C 24%
D 90%

18 The metal vanadium can be obtained through the following reaction of vanadium(V) oxide with calcium:

$V_2O_5 + 5\ Ca \rightarrow 2\ V + 5\ CaO$

Under certain conditions, this production of vanadium proceeds with a yield of 85 percent.

What is the *E*-factor of this process?

A 2.7
B 2.8
C 3.2
D 3.4
E 7.8

Thermochemistry

19 An uncatalyzed reaction has an activation energy, E_a, of + 50 kJ mol^{-1} and a reaction enthalpy, ΔH_r, of – 10 kJ mol^{-1}.

Which of the following shows possible values for E_a and ΔH_r in the presence of a catalyst?

	E_a	ΔH_r
A	– 10 kJ mol^{-1}	– 50 kJ mol^{-1}
B	+ 30 kJ mol^{-1}	– 15 kJ mol^{-1}
C	+ 30 kJ mol^{-1}	– 10 kJ mol^{-1}
D	+ 30 kJ mol^{-1}	– 5 kJ mol^{-1}
E	+ 60 kJ mol^{-1}	– 10 kJ mol^{-1}
F	+ 60 kJ mol^{-1}	+ 5 kJ mol^{-1}
G	+ 60 kJ mol^{-1}	+ 10 kJ mol^{-1}
H	+ 60 kJ mol^{-1}	+ 15 kJ mol^{-1}

20 What is the bond enthalpy per mole of water for the hydration of copper sulphate?

$CuSO_4(s) + 5\ H_2O(l) \rightarrow CuSO_4{\cdot}5H_2O(s)$

A –297 kJ mol^{-1}
B –77.0 kJ mol^{-1}
C –59.4 kJ mol^{-1}
D –15.4 kJ mol^{-1}

Open questions total 58 points

Problem 2 The decomposition of dinitrogen pentoxide 21 points

The kinetics of the decomposition reaction of dinitrogen pentoxide in the gas phase have been studied extensively. The reaction equation is:

$2\ N_2O_5 \rightleftharpoons 4\ NO_2 + O_2$

Although it can be expected that an equilibrium will be established, the reaction can be considered to proceed to completion at fairly low temperatures.

□1 Show this by calculating the equilibrium constant at 50 °C. The enthalpy of formation of N_2O_5 is + 11.3 kJ mol^{-1} and the absolute entropy of N_2O_5 is + 355.6 J mol^{-1} K^{-1}; use your Data Booklet for additional data. 8

Scientists from the University of Managua (Nicaragua) have investigated the kinetics of the decomposition reaction of dinitrogen pentoxide, dissolved in carbon tetrachloride. Both dinitrogen pentoxide and nitrogen dioxide are soluble in carbon tetrachloride, but oxygen is not. When carried out in carbon tetrachloride, the decomposition reaction is still found to go to completion.

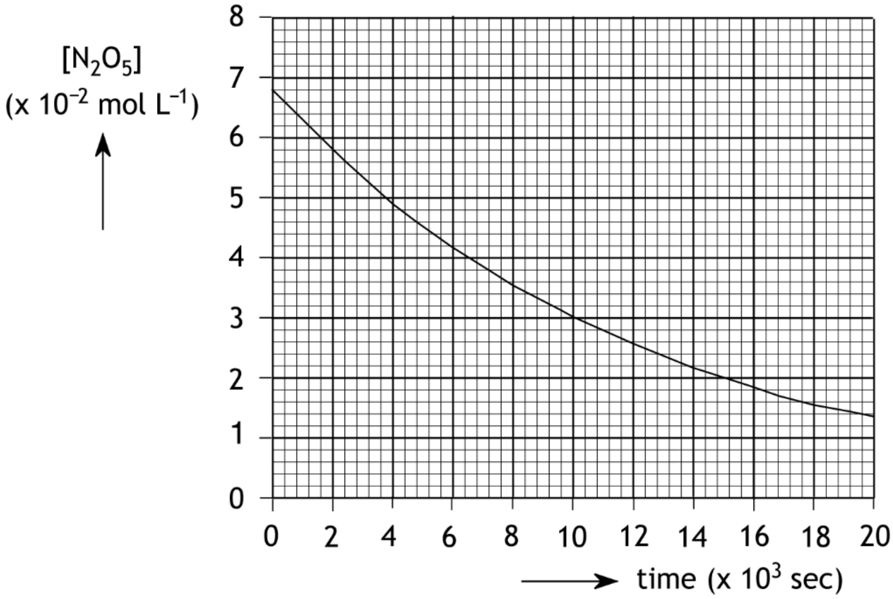
□2 Give an explanation for why the decomposition of dinitrogen pentoxide goes to completion under these circumstances. 1

The researchers dissolved a certain amount of N_2O_5 in 100 mL carbon tetrachloride and followed the progress of the reaction by measuring the volume of oxygen, V_t (in cm^3) produced at various times, t. When the reaction is complete (at time $t = \infty$), V_∞ cm^3 of oxygen has been formed.
The experiment was conducted at 30 °C and $p = p_0$.

From the collected data, the concentration of $[N_2O_5]_t$ at each time, t, during the reaction can be calculated. The following formula can be used for this calculation:
$[N_2O_5]_t = (V_\infty - V_t) \times F$, where F is a multiplication factor.

□3 Derive this formula and calculate the value of F. 4

When the calculated concentrations of N_2O_5 are plotted against time, the following diagram is produced.



From this diagram, the half-life of the decomposition of dinitrogen pentoxide in carbon tetrachloride under these conditions can be determined, and the reaction can be shown to be a first-order reaction.

□4 Using the diagram, determine the half-life of the decomposition of dinitrogen pentoxide in carbon tetrachloride under these conditions, and explain why it is a first-order reaction. 4

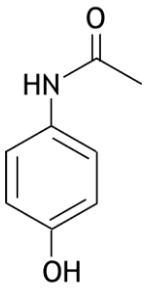
□5 Calculate the rate constant, *k*, under these conditions. 2

The Nicaraguans determined the rate constant in a different way, without calculating the concentrations of N_2O_5 through *F*. Instead, they plotted $\ln \frac{V_\infty}{(V_\infty - V_t)}$ against time.

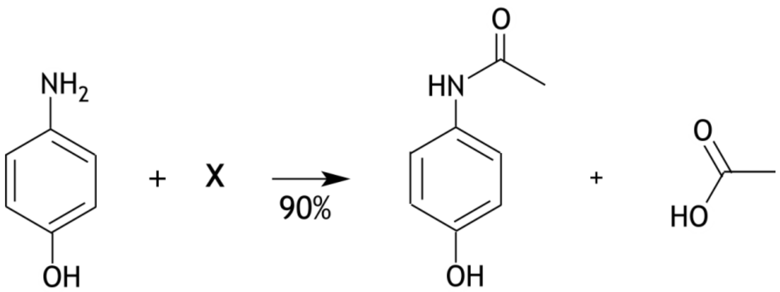
□6 Explain why this is an appropriate method for determining the rate constant. 2

Problem 3 Paracetamol 19 points

Paracetamol is the most commonly used painkiller worldwide. The skeletal structural formula of paracetamol is:

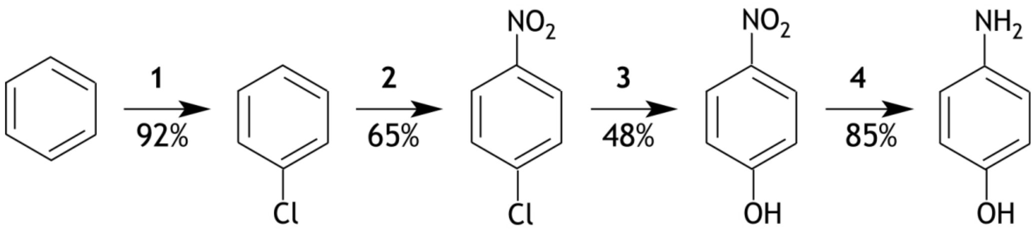


Paracetamol is made by reacting *para*-aminophenol with a substance **X**. In the process, another substance, ethanoic acid, is also formed. The reaction has a yield of 90%:



□7 Give the structural formula of substance **X**. 1

Para-aminophenol can be produced in various ways. One method involves four conversions with benzene as the initial reactant:



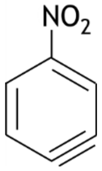
□8 Give the reaction equations for conversions 1, 2, and 4. Use structural formulas for the organic compounds. 7

In this synthesis route for *para*-aminophenol, the benzene ring is first chlorinated and then nitrated.

□9 Could there be a synthesis route for *para*-aminophenol that starts with the nitration of benzene? If you think there is, explain how that synthesis route should proceed.
If you think there is not such a synthesis route, explain why not. 3

In conversion 3, severe conditions must be applied, as nucleophilic substitution reactions generally do not occur on benzene rings. The *para*-nitrochlorobenzene first reacts with molten sodium hydroxide at a high temperature, and the reaction product is then treated with hydrochloric acid.

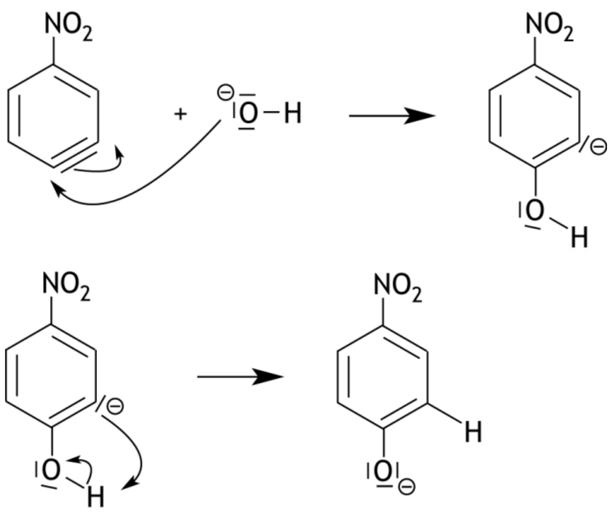
It is assumed that in the first step of the mechanism of this conversion, an OH^- ion binds to an H^+ ion from a *para*-nitrochlorobenzene molecule, resulting in a molecule with the following structure:



□10 Show the formation of this intermediate in a reaction equation with structural formulas;

- draw all relevant lone pairs;
- place any formal charges correctly;
- indicate the movement of electron pairs with curly arrows (). 3

Next, a second OH^- ion reacts, leading to the formation of a *para*-nitrophenolate anion in two steps:



Finally, after acidification, *para*-nitrophenol is formed.

Para-nitrophenol is not the only organic product formed according to this mechanism in this reaction.

□11 Give the structural formula for the other organic product formed. 1

In the reaction schemes above, the yield of the listed conversions is shown.

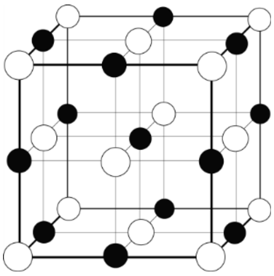
□12 Using this data, calculate how many tons of paracetamol can be produced from 1.00 ton of benzene. 4

Problem 4 Wüstite 18 points

Wüstite is a mineral with the formula Fe_xO. The value of x is dependent on the formation process of the mineral and ranges from 0.85 to 0.95. The fact that x is less than 1 is due to the presence of both Fe^{2+} and Fe^{3+} ions in wüstite.

▫13 Calculate the molar ratio between Fe^{2+} and Fe^{3+} in wüstite with the formula $Fe_{0.87}O$. Write down your answer as $Fe^{2+} : Fe^{3+}$ = … : 1.0. 3

Wüstite crystallises in the same way as NaCl. The unit cell of NaCl is shown below.



In the NaCl crystal, all positions in the crystal lattice are occupied, but in wüstite crystals, 'gaps' are present: on some positions in the crystal lattice ions are missing.

▫14 Give an explanation for this. 1

A certain type of wüstite has a density of $5.71 \cdot 10^3$ kg m^{-3}. Using X-ray diffraction, it is determined that the shortest distance between the nuclei of two ions is 214 pm.

▫15 Calculate the value of x in this type of wüstite. 6

The value of x in Fe_xO can also be determined by means of a titration with a potassium permanganate solution.

To determine the value of x in a second, different type of wüstite, 250 mg of wüstite is dissolved in an excess of dilute sulphuric acid. The resulting solution is titrated with a 0.0200 M potassium permanganate solution. The following reaction occurs:

$5\ Fe^{2+} + MnO_4^- + 8\ H^+ \rightarrow 5\ Fe^{3+} + Mn^{2+} + 4\ H_2O$

For the titration, 26.41 mL 0.0200 M potassium permanganate solution is required.

▫16 Calculate the value of x in this type of wüstite. 8

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

46th National Chemistry Olympiad 2025 preliminary round 2
Answer sheet: multiple choice questions

name:

no.	answer (letter)	(score)
1		
2		
3		
4		
5		
6		
7		
8		
9		
10		
11		
12		
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14		
15		
16		
17		
18		
19		
20		
Total		

46th National Chemistry Olympiad

Symeres, Nijmegen

THEORY TEST

Question booklet

Wednesday June 4 2025

- This test consists of 7 problems with 32 open questions and a worksheet.
- Use a separate answer sheet for each problem, making sure to write your name on each sheet. Maintain a 2 cm margin on all sides of the page.
- The maximum score for this test is 120 points.
- The test will last a maximum of 4 hours.
- Required resources: (graphic) calculator and Binas 6th or 7th edition or BINAS 5th edition, English version or ScienceData 1st edition.
- The number of points available for each question is given.
- Unless otherwise stated, standard conditions apply: T = 298 K and $p = p_0$.

This test was made possible with the support of the following people:

Leon van Berkom
Sander Brugman
Sam Ceusters
Roel Dullens
Rutger Folmer
Gydo van der Heijden
Dennis Hetterscheid
Hans Meissner
Jan Sadownik
Jean-Paul Seerden
Martijn Slagt

The final editing was done by:
Kees Beers, Martin Groeneveld, Dick Hennink and Piet Mellema

The NSO comittee
Marijn Jonker and Emiel de Kleijn

The exam was translated into English by:
Riëtte Pienaar, Jan Rombach, Lauren Rutherford and Alex Schaeffers

Problem 1 Carbide shooting 13 points

In the northern, eastern, and southern provinces of the Netherlands, it is a tradition around New Year's to 'shoot' carbide using milk churns. Carbide is the common name for calcium carbide, with the formula CaC_2. The negative ion in this salt has the formula C_2^{2-}.

On the worksheet accompanying this test, you will find an incomplete MO diagram for the formation of C_2^{2-} from C^- ions; the 2*s* and 2*p* levels of one of the C^- ions have already been drawn.

▫1 In the diagram on the worksheet:
- draw the 2*s* and 2*p* levels of the other C^- ion;
- draw the molecular orbitals of the C_2^{2-} ion, using the standard labels for 'bonding' and 'antibonding';
- fill the atomic and molecular orbitals with electrons according to the Aufbau principle. 6

▫2 Calculate the bond order of the C_2^{2-} ion. 2

When shooting, carbide reacts with water in a milk churn. The following reaction occurs:

$CaC_2(s) + 2\ H_2O(l) \rightarrow C_2H_2(g) + Ca(OH)_2(s)$

The resulting ethyne gas is ignited and explodes with a loud bang. The goal is to produce the loudest possible bang. To achieve this, oxygen and ethyne must be present in the correct ratio. As it turns out, in order to get the loudest bang, the volume ratio of ethyne to oxygen should be approximately **1 : 1**.

A manual for carbide shooting recommends using a 30 L milk churn, adding about 200 g of carbide chunks, pouring in 60 mL of water, and sealing the churn with a football. After about 45 seconds, enough ethyne gas will have formed to produce a satisfying bang, which also launches the football. The churn is then resealed, and after another 45 seconds, the ethyne gas can be ignited again. With 200 g of carbide and 60 mL of water, you can produce five bangs at 45-second intervals; after that, the water is used up and the churn must be refilled with new carbide and water.

▫3 Verify, using a calculation, whether the ideal volume ratio of ethyne : oxygen = 1 : 1 is met for each bang. In your calculation, use a water density of 1.0 g mL^{-1} and 21% as the volume percentage of oxygen in air.
Assume the following:
- no gas escapes from the milk churn before ignition;
- at the start of the reaction, T = 273 K and $p = p_0$;
- after each bang, the milk churn is immediately refilled with air. 5

Problem 2 The NO_2 – N_2O_4 equilibrium 30 points

An experiment often used in schools to demonstrate how the position of an equilibrium shifts with a change in temperature, is based on the dimerisation equilibrium

$2\ NO_2(g) \rightleftharpoons N_2O_4(g)$.

In a molecule of NO_2, the nitrogen atom is bonded to both oxygen atoms; the molecule is not cyclic.

□4 Give a Lewis structure for NO_2 and explain, based on this structure, why NO_2 molecules dimerise readily. 5

In the demonstration, two tubes are filled with nitrogen dioxide and sealed. One tube is then immersed in cold water, the other is immersed in warm water. Since nitrogen dioxide is a brown gas and dinitrogen tetroxide is colourless, the gas mixture in one tube appears lighter in colour than the mixture in the other tube, once an equilibrium has been established in both tubes.

The teacher often produces the nitrogen dioxide by reacting copper with warm concentrated nitric acid.

□5 Calculate the maximum volume (in cm^3) of nitrogen dioxide that can be formed when 100 mg of copper reacts with 10.0 mL of concentrated nitric acid at 80 °C and $p = p_0$. The density of the concentrated nitric acid is 1.40 g mL^{-1} and it contains 65.0 mass percent HNO_3. 6

The nitrogen dioxide produced cools to room temperature and is collected in a test tube, which is then sealed.

□6 Explain whether, when collecting the nitrogen dioxide, the test tube should be held upside down, right side up, or whether it makes no difference. 4

For the equilibrium constant, K_p, of a gas-phase equilibrium, the following formula applies:

$$K_p = e^{-\frac{\Delta_r G}{RT}}.$$

At a certain temperature T_1, the K_p of the above equilibrium has a value of 12.5.

□7 Calculate the temperature T_1 in K. Assume that the data from your information booklet, which apply at 298 K and $p = p_0$, can also be used under these conditions. 5

The teacher fills two test tubes with 0.35 mmoles of pure nitrogen dioxide gas. After sealing the tubes, the volume of the gas (mixture) in each test tube is 10.0 cm^3. One of the tubes is immersed in cold water so that the temperature reaches 5 °C. At this temperature, K_p = 15.8.

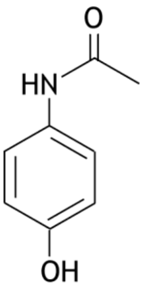
□8 Calculate the total pressure (in Pa) in the test tube once equilibrium has been established. 7

The other test tube is immersed in water at a temperature of 50 °C.

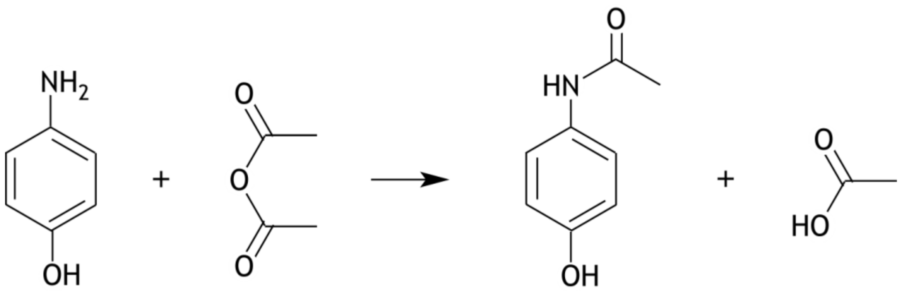
□9 In which of the two test tubes will the gas mixture appear lighter in colour? Explain your answer. 3

Problem 3 Paracetamol from lignin 25 points

Paracetamol (also known as acetaminophen) is the most widely used painkiller worldwide. The structural formula of paracetamol is:

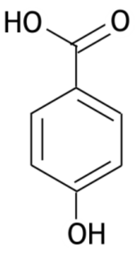


Paracetamol is produced by reacting *para*-aminophenol with acetic anhydride:



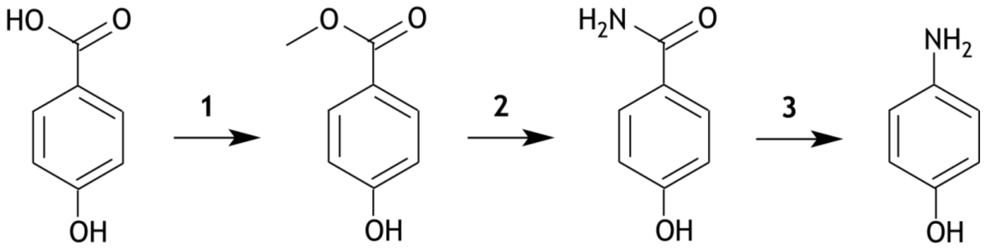
▫10 What type of reaction is this? 2

Until now, the *para*-aminophenol required for the production of paracetamol has mainly been obtained, through a series of steps, from benzene. The disadvantage of this route is that benzene is derived from crude oil. Recently, researchers have discovered a new synthesis method that uses a renewable raw material: lignin. Lignin is a complex organic compound which gives wood its strength. When lignin is reacted with dilute sodium hydroxide, a mixture of simple organic compounds is formed. From this mixture, the substance *para*-hydroxybenzoic acid (**I**) can be isolated. The structural formula of *para*-hydroxybenzoic acid is depicted below:



I

Through three conversion steps, *para*-hydroxybenzoic acid (**I**) can be transformed into *para*-aminophenol (**IV**) via intermediate compounds **II** and **III**:



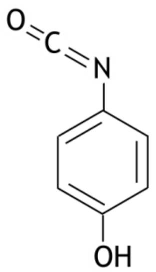
I **II** **III** **IV**

▫11 Give the structural formula of the substance that reacts with *para*-hydroxybenzoic acid in conversion step **1**. 1

To form compound **III** from compound **II**, an ammonia solution is used. Direct formation of **III** from **I** using an ammonia solution is not feasible, as an undesirable side reaction might occur.

▫12 Which side reaction might take place? 2

In conversion step **3**, a Hofmann rearrangement takes place. In this reaction, a C – C bond in the molecule is replaced by a C – N bond. The reaction proceeds with bromine in a basic medium. During the process, the following isocyanate is formed:



For the formation of the isocyanate, the following reaction mechanism is often proposed:

- an OH^- ion binds a H^+ ion attached to the nitrogen atom;
- next, a Br^+ ion from a Br_2 molecule binds to the nitrogen atom, with formation of a Br^- ion;
- then, a second OH^- ion binds the other H^+ ion attached to the nitrogen atom; at the same time, a double bond forms between the N atom and the C atom, and a single bond forms between the C atom and the O atom;
- finally, a Br^- ion is eliminated and the N atom becomes bonded to the benzene ring.

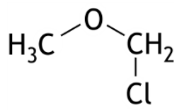
▫13 Represent this mechanism using chemical equations with structural formulas.

- Draw all relevant lone pairs;
- use curly arrows () to indicate how electron pairs shift during bond formation and bond breaking;
- place all formal charges in the correct positions. 6

Through the addition of a water molecule to a molecule of the isocyanate, followed by the elimination of a molecule **X**, a molecule of *para*-aminophenol is formed.

▫14 Give the structural formula of the addition product of water and the isocyanate, and give the molecular formula of **X**. 3

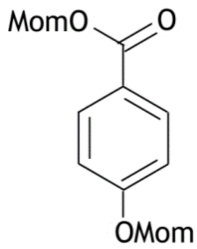
One disadvantage of this synthetic route to *para*-aminophenol is that the yield of the Hofmann rearrangement is rather low, resulting in an overall yield of less than 20%. This can be improved by replacing conversion step **1** with a reaction in which

para-hydroxybenzoic acid is reacted with chloromethoxymethane, 

,

(methoxymethyl chloride, commonly abbreviated as Mom-Cl).

This reaction protects both OH groups of the *para*-hydroxybenzoic acid molecule against side reactions.

The resulting product **V** can be represented as 

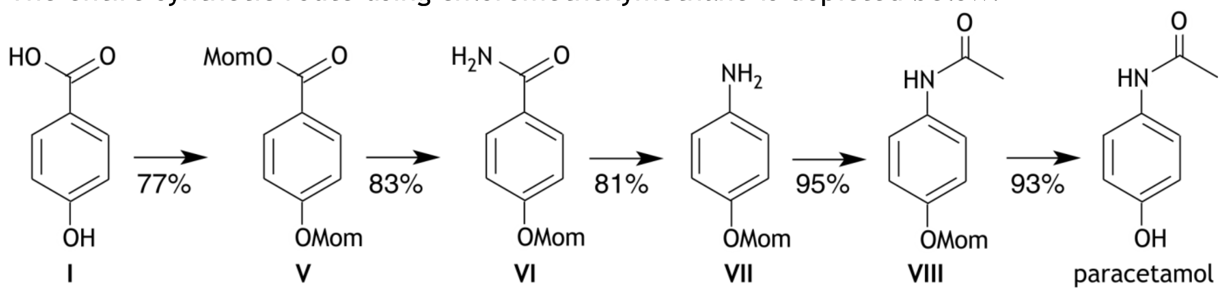
V

The reaction between chloromethoxymethane and *para*-hydroxybenzoic acid begins with the elimination of a chloride ion from a molecule of chloromethoxymethane. The resulting positively charged ion is ‘stabilised by resonance’.

▫15 Draw the resonance structures of the positive ion. 4

▫16 Give the full structural formula of compound **V**. 1

The entire synthetic route using chloromethoxymethane is depicted below:



The percentage yield of each conversion step is indicated in the figure.

Poplar wood is often used as a source of lignin. If you want to know how much poplar wood is required to synthesise a given number of kilograms of paracetamol, you must multiply that amount of kg of paracetamol by a factor *F*:

amount of poplar wood (kg) = amount of paracetamol (kg) × *F*.

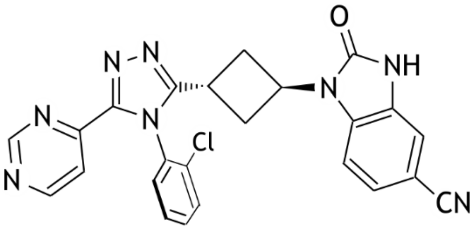
▫17 Calculate the value of *F*. In addition to the given conversion percentages, use the following data:

- poplar wood consists of 20 percent by mass lignin;
- from lignin, 1.2 percent by mass *para*-hydroxybenzoic acid can be obtained. 6

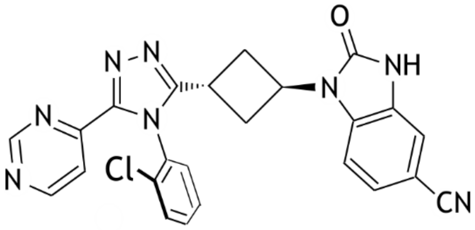
▌Problem 4 Tankyrase inhibitors 8 points

Tankyrase is an enzyme capable of attaching small chemical tags, known as ADP-ribose chains, to proteins. These tags may serve as signals indicating that a protein should be broken down, or they may alter the way a protein functions. Overexpression of tankyrase, that is the production of excessive amounts of this enzyme, has been linked to the development of cancer, as it disrupts the normal regulation of cell growth. Inhibiting tankyrase is therefore considered a promising strategy for the treatment of such conditions. Researchers at Symeres are actively engaged in the development of compounds that can act as tankyrase inhibitors.

Shown below are the structures of two compounds (**I** and **II**) that have been synthesised and investigated for their ability to inhibit tankyrase activity.



I



II

Due to the presence of the Cl atoms, rotation around the relevant C – N bonds is hindered at room temperature. As a result, **I** and **II** are stereoisomers

▫18 Explain whether **I** and **II** are enantiomers or diastereomers. 2

Aside from **II**, two other stereoisomers of **I** exist.

▫19 Explain why, aside from **II**, two other stereoisomers of **I** exist. 3

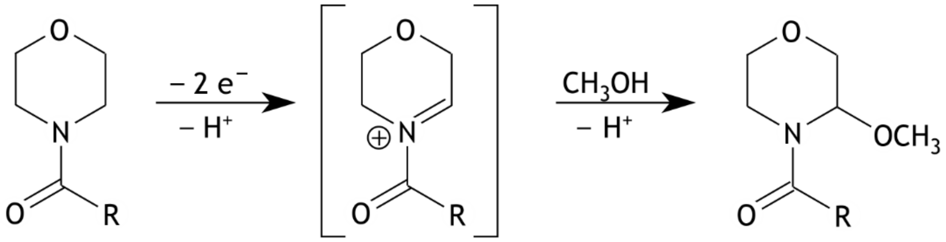
At elevated temperatures, the stereoisomers **I** and **II** gradually convert into one another due to the fact that rotation around the relevant C – N bonds becomes possible. This isomerisation follows first-order kinetics. Starting from compound **I**, after 72 hours at a temperature of 70 °C, 10 percent has been converted into compound **II**.

▫20 Calculate how many hours it will take to convert 1.0 percent of compound **I** to compound **II**, at 70 °C. Assume that the reverse conversion from **II** to **I** is negligible. 3

Problem 5 Shono oxidation 11 points

The synthesis of compounds by means of electrolysis is referred to as electrosynthesis. At Symeres, a research group specialises in the use of electrosynthesis to introduce functional groups into simple molecules, with the aim of using the introduced groups as 'scaffolds' for the construction of complex molecules.

An example of this type of electrosynthesis, a so-called Shono oxidation, is schematically represented below:



I intermediate **II**

I is a model molecule in which the nitrogen atom of a morpholine ring is bound to a protecting group (– COR). During the electrolysis, a highly selective methoxylation of the morpholine ring takes place.

▫21 Explain whether the conversion of compound **I** to the intermediate takes place at the positive electrode or at the negative electrode. 2

▫22 Verify, on the basis of the diagram, whether the methoxylation is regioselective. 2

▫23 Verify, on the basis of the diagram, whether the methoxylation is stereoselective. 2

The following is a representative example of the way in which this Shono oxidation can be carried out:
0.41 mol of compound **I** is dissolved in 400 mL of methanol. An inert electrolyte is added.
The solution is electrolysed using graphite electrodes. The electrolysis lasts for 15 hours, during which a current of 1.7 A is maintained.
The yield of the conversion of compound **I** to compound **II** is 92 percent.
The efficiency of the current usage (the percentage of the electric current used for the formation of the product) in this Shono oxidation is high.

▫24 Calculate what percentage of the electric current was used for the formation of compound **II**. 5

Problem 6 Cobalt complexes 22 points

Cobalt is a transition metal. In nature, it is primarily found in compounds containing Co^{2+} ions. Cobalt ions with a 3+ charge can also exist, but do not occur naturally, as Co^{3+} is a very strong oxidising agent.

Both cobalt ions, Co^{2+} and Co^{3+}, can form stable complexes with ammonia molecules.

Below is an overview of half-reactions of various forms of cobalt. The standard electrode potential is included for several of them.

$Co^{3+} + 3\,e^- \rightarrow Co$	$E^0 = +\,0.46$ V
$Co^{3+} + e^- \rightarrow Co^{2+}$	
$Co^{2+} + 2\,e^- \rightarrow Co$	$E^0 = -\,0.29$ V
$Co(NH_3)_6^{3+} + 3\,e^- \rightarrow Co + 6\,NH_3$	
$Co(NH_3)_6^{3+} + e^- \rightarrow Co(NH_3)_6^{2+}$	$E^0 = +\,0.1$ V
$Co(NH_3)_6^{2+} + 2\,e^- \rightarrow Co + 6\,NH_3$	$E^0 = -\,0.42$ V

To find the change in Gibbs free energy in a redox (half) reaction, the following formula can be applied: $\Delta G = -\,n \times F \times \Delta E$.

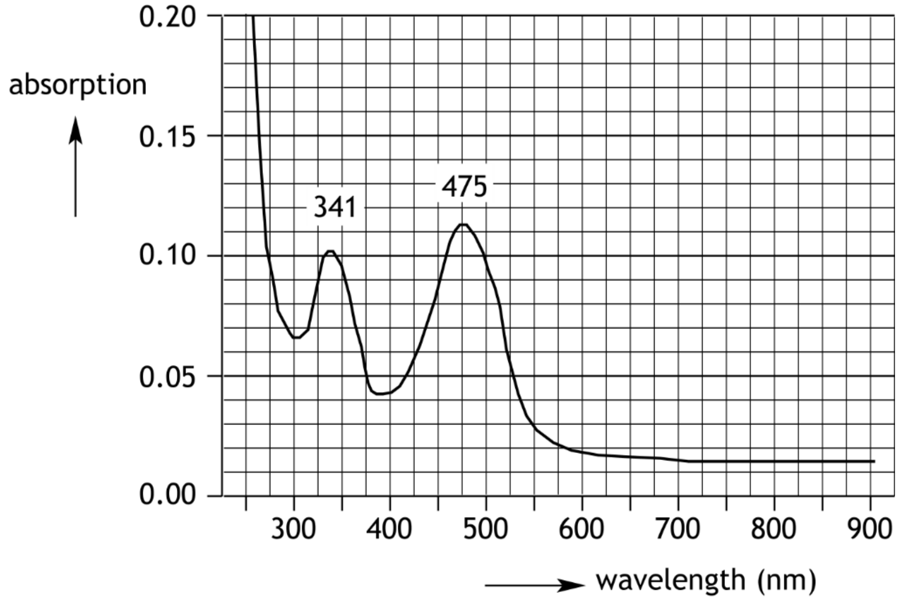
□25 Calculate, based on data from the overview above, the value of the standard electrode potential for the half-reaction $Co^{3+} + e^- \rightarrow Co^{2+}$. 4

The stability of the $Co(NH_3)_6^{3+}$ complex is related to the following equilibrium:

$Co^{3+} + 6\,NH_3 \rightleftharpoons Co(NH_3)_6^{3+}$ equilibrium 1 with $K = 1.0 \cdot 10^{33}$

□26 Calculate, based on data provided in this question, the value of the standard electrode potential for the half-reaction $Co(NH_3)_6^{3+} + 3\,e^- \rightarrow Co + 6\,NH_3$. 4

Complex cobalt ions give a characteristic colour to solutions. For example, a solution of the salt complex $Co(NH_3)_6Cl_3$ exhibits a dark purple colour. The graph below shows the UV–VIS spectrum of a $1.00 \cdot 10^{-3}$ M solution of $Co(NH_3)_6Cl_3$.



A cuvette with an optical path length of 1.00 cm was used when recording the spectrum.

□27 Calculate, based on this UV–VIS spectrum, the molar extinction coefficient, ε, of $Co(NH_3)_6^{3+}$ at 475 nm. Assume that only $Co(NH_3)_6^{3+}$ absorbs light in the solution. 3

The compound $Co(NH_3)_6Cl_3$ is formed in four steps:

$CoCl_2.6H_2O + NH_4Cl \rightarrow Co(H_2O)_6^{2+} + NH_4^+ + 3\ Cl^-$
$Co(H_2O)_6^{2+} + 6\ NH_3 \rightarrow Co(NH_3)_6^{2+} + 6\ H_2O$
$Co(NH_3)_6^{2+} + \frac{1}{2}\ H_2O_2 \rightarrow Co(NH_3)_6^{3+} + OH^-$
$Co(NH_3)_6^{3+} + 3\ Cl^- \rightarrow Co(NH_3)_6Cl_3$

The starting point is red cobalt(II) chloride hexahydrate. This is dissolved in boiling water, and ammonium chloride is added, resulting in the formation of the blue complex $Co(H_2O)_6^{2+}$. Concentrated ammonia is then added, producing brown $Co(NH_3)_6^{2+}$. Subsequently, this complex is oxidised with hydrogen peroxide to the dark purple complex $Co(NH_3)_6^{3+}$, which then precipitates with chloride as $Co(NH_3)_6Cl_3$.

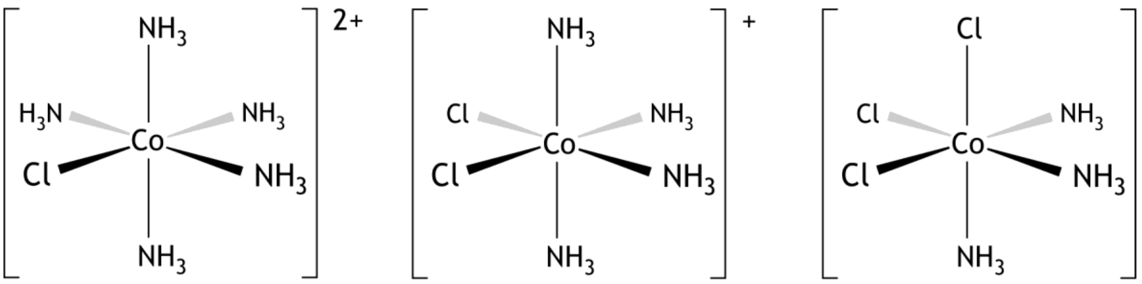
During an experiment, $Co(NH_3)_6Cl_3$ is synthesised via the above reactions, starting with 6.0065 g of cobalt(II) chloride hexahydrate. Ultimately, 5.4543 g of impure product is obtained. From this impure product, 30.0 mg is dissolved in a 100.0 mL volumetric flask. The absorbance of this solution is measured at 475 nm and found to be 0.122. The optical path length of the cuvette used was 1.00 cm.

□28 Calculate the yield of this synthesis. Assume that the impurities do not absorb light at 475 nm. 8

Complexes of Co^{3+} with ammonia also exist in which one or more ammonia molecules are replaced by one or more chloride ions. The general formula of these complexes can be represented as $[Co(NH_3)_{6-x}Cl_x]^{n+}$, where x is an integer.

□29 What is the relationship between n and x? 1

Below are the spatial structures of three of these complexes, for which x equals 1, 2, and 3, respectively.



complex I complex II complex III

An isomer exists for complex II and complex III.

The worksheet accompanying this test, contains outlines for the isomers of the complexes II and III.

□30 Draw the isomer of complex II and the isomer of complex III on your worksheet. 2

Problem 7 Permanganometry 11 points

Solutions of potassium permanganate ($KMnO_4$) are widely used in analytical chemistry to determine the content of reducing agents. An example is the determination of the tin(II) sulphate content in a sample.

In an Erlenmeyer flask, 200 mg of a sample containing tin(II) sulphate is dissolved. To this solution, 25.0 mL of 0.0200 M potassium permanganate solution is added. The solution is then made alkaline with sodium hydroxide. A redox reaction occurs in which Sn^{2+} is converted to $Sn(OH)_6^{2-}$ while the MnO_4^- is converted to a precipitate of Mn_3O_4. In this reaction, Sn^{2+} and MnO_4^- react with each other in a molar ratio of 13 : 6.

▫31 Give the equation for the half-reaction of the MnO_4^-. 4

The Mn_3O_4 precipitate is filtered off, and the filtrate is acidified and titrated with a 0.100 M solution of iron(II) sulphate. A volume of 6.26 mL was required.

The equation for the reaction that occurs during the titration is:

$$5\ Fe^{2+} + MnO_4^- + 8\ H^+ \rightarrow 5\ Fe^{3+} + Mn^{2+} + 4\ H_2O$$

▫32 Calculate the mass percentage of tin(II) sulphate in the examined sample. 7

46th National Chemistry Olympiad

Symeres, Nijmegen

THEORY TEST

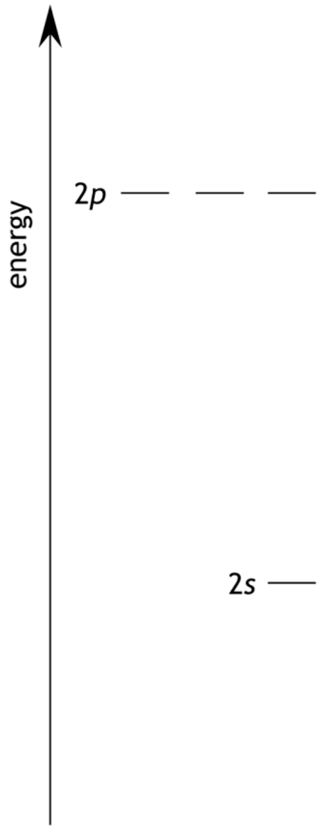
Worksheet

Wednesday June 4 2025

Name: ______________________________

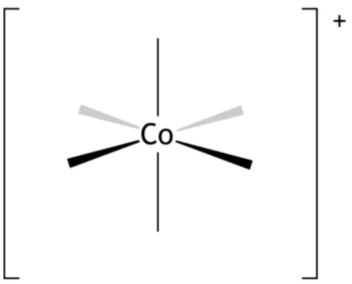
N.B.: Don't forget to write your name on the front!

Question 1

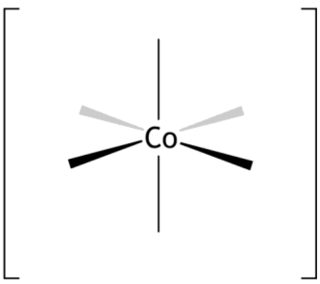


C^- (AO's) C_2^{2-} (MO's) C^- (AO's)

Question 30



isomer of complex II



isomer of complex III

46th National Chemistry Olympiad

Symeres, Nijmegen

PRACTICAL TEST

Assignment booklet

Thursday June 5 2025

The experiments for this test were prepared by:
Leon van Berkom
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The final editing was done by:
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The NSO committee:
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The exam was translated into English by:
Riëtte Pienaar, Jan Rombach, Lauren Rutherford and Alex Schaeffers

Instructions/resources

- This practical test consists of two parts:
  - The cracking of PET.
  - The determination of the amount of $NaBO_3.H_2O$ in a sachet of Bikosan.

- The practical test ends after 4 hours. During this time:
  - the attached answer sheets need to be completed;
  - all questions must be answered.

- After the practical test, when you have handed everything in, the glassware still needs to be cleaned and tidied up.

- The maximum score for the practical test is 80 points.

- The score is determined by:
  - practical skills, working cleanly, safety — maximum 20 points
  - results of the determinations and answers to the questions — maximum 60 points

- Required tools: (graphical) calculator, ruler/protractor triangle and Binas or ScienceData.

- First read the introduction and all the assignments before you start working.

- Write your answers to the questions in the boxes on the answer sheets provided. If you don't have enough space, you can request additional paper.

Additional:

- This is a test; it is not permitted to consult with other participants.
- If you have any questions, you can ask the supervisor.
- If there is anything wrong with your glassware or equipment, please report it to the supervisor as soon as you discover it. Don't borrow equipment from others!

Order of the experiments

This test consists of two experiments.

Start with **Experiment 1** (The cracking of PET).
During this experiment, the reaction mixture has to boil for 1.5 hours.
Use this time to perform **Experiment 2** (the titration).

The questions in **Experiment 2** can be answered after both experiments are finished, if necessary.

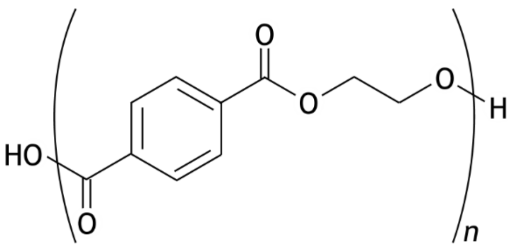
Experiment 1 The cracking of PET 40 points

Introduction

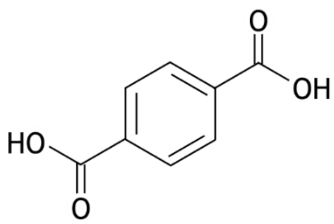
Many bottles for mineral water, soft drinks, liquid detergents and cleaning products are made of polyester PET, **P**oly**E**thylene **T**erephthalate.
It is recognizable by the ‘1’ symbol on the packaging. PET is also used for clothing (‘*fleece*’).
The environmental impact of PET is a major issue.
The advantages of plastic packaging are primarily attributable to its light weight, versatility in applications, and sustainability with regard to food preservation.
The disadvantages primarily relate to production and recycling. PET is easily recycled, better than other plastics, but the disposal of plastic as a separate waste stream could be significantly improved.

PET is primarily recycled by melting it down.
Another, advanced, chemical method for PET recycling could begin with the hydrolysis of PET in a basic environment (saponification). After processing and acidifying the reaction mixture, terephthalic acid can be isolated.

In this experiment you will perform this hydrolysis of PET and determine the yield of terephthalic acid.



PET



terephtalic acid

Chemicals

- piece of PET
- butan-1-ol
- KOH
- demineralized water
- 4 M hydrochloric acid
- ethanol

Butan-1-ol ▪ Formula: $C_4H_{10}O$ ▪ Density: 0.8098 g mL^{-1} ▪ Boiling point: 119 °C ▪ H226, H302, H315, H318, H335, H336 ▪ P261, P280, P302+P352, P304+P340, P305+P351+P338	Potassium hydroxide ▪ Formula: KOH ▪ H290, H302, H314 ▪ P280, P303+P361+P353, P305+P351+P338, P310
Hydrochloric acid 4 M ▪ Formula: HCl solution ▪ H290, H315, H319, H335 ▪ P302+P352, P304+P340, P305+P338+P351, P312	Ethanol (absolute) ▪ Formula: C_2H_6O ▪ Density: 0.789 g mL^{-1} ▪ Boiling point: 78 °C ▪ H225, H319 ▪ P210, P233, P305+P351+P338
Terephthalic acid ▪ Formula: $C_8H_6O_4$ ▪ H315, H319, H335 ▪ P261, P305+P351+P338	

Safety

- wear safety glasses
- if your skin comes into contact with any of the chemicals, rinse immediately with tap water

Materials

- scissors
- a spatula
- two measuring cylinders (25 mL and 50 mL)
- a magnetic stirrer
- a round-bottom flask
- a reflux condenser
- a magnetic bar
- a powder funnel
- a funnel
- a cotton pad
- an oil bath
- an ice bath
- a thermometer
- a lifting platform
- stand with clamp(s) (for separatory funnel)
- a separatory funnel
- two 100 mL Erlenmeyer flasks
- pH paper
- Pasteur pipette
- pipette teat
- glass filter
- a sample jar with a screw lid
- a sample jar with a crimp cap
- a highlighter pen
- a cork ring

Procedure

1. Prepare the setup for a reflux experiment.
2. Cut the PET piece into small pieces and accurately weigh it to approximately 1 g. Record the mass on your answer sheet.
3. Transfer these PET pieces to the round-bottom flask.
4. Add a magnetic bar.
5. Measure out approximately 30 mL of butan-1-ol and add it to the flask.
6. Weigh 0.88 g of potassium hydroxide and add it to the flask.
7. Place the reflux condenser on the flask.
8. Have your setup checked by a supervisor.
9. Place the oil bath on the magnetic stirrer and turn up the lifting platform. Ensure that the oil level remains below the solvent level in the flask.
10. Turn on the magnetic stirrer.
11. Put the thermometer in the oil bath and set the temperature to 120 °C.
12. Turn on the heat and let the reaction mixture reflux for 1.5 hours.
13. **Caution: Be extra careful from now on. The oil is hot!**

Now perform Experiment 2.
After performing Experiment 2, finish the rest of the steps of Experiment 1.

14. After 1.5 hours, turn off the heating, lower the lifting platform, and let the flask cool in the ice bath for about 5 minutes. Do not handle the flask with your hands; use the clamp.
15. Prepare your workspace for an extraction.
16. Add about 20 mL of water to the reaction mixture.
17. Filter the suspension through a funnel with a cotton pad and rinse with approximately 5 mL of water.
18. Transfer the filtrate to a separatory funnel, shake well and collect the aqueous layer in a clean Erlenmeyer flask.
19. Extract the organic layer again with 20 mL of water and collect the aqueous layer in the Erlenmeyer flask containing the aqueous layer from the previous step.
20. Using a Pasteur pipette, acidify the collected aqueous layers with 4 M hydrochloric acid to a pH of approximately 2.
21. Filter the obtained suspension over the glass filter using vacuum suction.
22. Turn off the vacuum suction.
23. Wash the residue as follows: add 5 mL of ethanol to the residue on the glass filter and stir the residue into the ethanol using the spatula. Work carefully.
24. Filter off the ethanol using vacuum suction.
25. Repeat steps 22, 23, and 24 two more times.
26. Turn off the vacuum suction and transfer the filtrate from the vacuum flask into a clean Erlenmeyer flask.
27. Further dry the residue on the glass filter under vacuum suction.
28. When the residue (= terephthalic acid) is dry (it no longer sticks to your spatula when you stir it), you can determine the mass.
29. Take the sample container with the screw cap, mark it with your name + PET, weigh it and record the mass.
30. Transfer the dry residue to this sample container and weigh the contents. Record the mass of the container and its contents.
31. Place approximately 20.0 to 25.0 mg (accurately weighed) of your product in the sample jar with a crimp cap, record the exact mass on the container and on your answer sheet, and sign the container with your name.
32. Close this jar with a crimp cap using the crimping pliers, a supervisor can help you with this.
33. Hand in both sample containers and their contents. The purity of your product will be determined by recording an NMR spectrum. In addition, if necessary, a Karl Fisher determination will be performed on the approximately 20 mg of product to determine the water content. This will be done for you after the practical exam. You do not need to wait for the results.

Tip 1: If the suspension is difficult to filter in step 20, add approximately 5 mL of ethanol first.

Tip 2: If the residue forms a hard lump or multiple lumps during drying in step 25, carefully break it up with the spatula and dry it some more.

Questions – write the answers on the answer sheets

1 Record:
- the mass of the PET
- the mass of the empty sample container
- the mass of the sample container with contents 3

2 Calculate the mass of your product. 1

To ensure complete hydrolysis of PET in alkali conditions, an excess of KOH was used.

3 Write the reaction equation for the complete hydrolysis of PET in alkali conditions. Use structural formulas for the organic compounds and write the structural formula for PET as shown in the introduction. 6

4 Show by calculation that an excess of KOH was used.
- Assume that the piece of PET consists exclusively of polyethylene terephthalate.
- Do not take into account the ends of the PET molecules. 5

Polyethylene terephthalate is the main component of the material used to make PET bottles. Besides polyethylene terephthalate, it also contains a plastisizer, for example.

5 Calculate the mass percentage of polyethylene terephthalate in the PET piece. Assume your product is pure terephthalic acid. Ignore the ends of the PET molecules. 5

Experiment 2 The determination of the amount of sodium perborate monohydrate in one sachet of Bikosan 40 points

Introduction

Bikosan is a solid mixture used as a mouth disinfectant in dissolved form. It consists of two substances. One of these substances is sodium perborate monohydrate ($NaBO_3.H_2O$). When one mole of $NaBO_3.H_2O$ is dissolved in water, one mole of hydrogen peroxide (H_2O_2) is produced. Hydrogen peroxide is the active ingredient in a Bikosan solution.

Bikosan is available in packages containing ten sachets of powder. It is used by dissolving the contents of one sachet in a cup of warm water (approximately 30 mL), and rinsing the mouth with the resulting solution.

In this experiment, the amount of $NaBO_3.H_2O$ in a single sachet of Bikosan is determined. An excess of sulfuric acid and an excess of potassium iodide solution are added to a precisely measured amount of Bikosan solution. The following reaction occurs:

$$H_2O_2 + 2\ H^+ + 2\ I^- \rightarrow I_2 + 2\ H_2O$$

This redox reaction, however, is slow. To speed up the reaction, a catalyst solution is added.

The amount of iodine formed is determined by titration with a sodium thiosulfate solution. The following reaction occurs:

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

The titration is performed in duplicate.

Chemicals

- Bikosan
- demineralized water
- approximately 0.050 M sodium thiosulfate solution (precise molarity is given)
- 0.3 M potassium iodide solution
- ammonium molybdate solution (catalyst)
- 2 M sulfuric acid solution
- starch solution

Sodium thiosulfate solution 0.050 M ▪ Formula: $Na_2S_2O_3$ solution ▪ No H and P phrases	Potassium iodide solution 0.3 M ▪ Formula: KI solution ▪ H372 ▪ P260, P264, P270, P314
Sulphuric acid solution 2 M ▪ Formula: H_2SO_4 solution ▪ H314 ▪ P280, P303+P361+P353, P310, P305+P351+P338.	Starch solution ▪ Formula: $(C_6H_{10}O_5)_n$ solution ▪ No H and P phrases
Ammonium molybdate solution ▪ Formula: $H_8Mo_2N_2O_7$ ▪ No H and P phrases	

Safety

- wear safety glasses
- if your skin comes into contact with any of the chemicals, rinse immediately with tap water

Materials

- a 100 mL volumetric flask
- a funnel
- a 50 mL burette
- a funnel for the burette
- four beakers
- a 10 mL graduated cylinder
- a 25 mL graduated cylinder
- a pipette filler
- a 10 mL pipette
- two 100 mL Erlenmeyer flasks with suitable rubber stoppers
- a magnetic stirrer
- a magnetic bar

Procedure

- ▫1 Weigh the total contents of one sachet of Bikosan. Record the mass on your answer sheet.
- ▫2 Weigh approximately 0.7 g of Bikosan accurately and record the mass on your answer sheet.
- ▫3 Transfer this Bikosan quantitatively into the 100 mL volumetric flask and fill up to the mark with demineralized water.
- ▫4 Transfer 10.00 mL of the Bikosan solution from the volumetric flask to each Erlenmeyer flask.
- ▫5 Add 15 mL of 2 M sulfuric acid solution and 10 mL of 0.3 M potassium iodide solution to both Erlenmeyer flasks.
- ▫6 Add 1 mL of catalyst solution (ammonium molybdate solution) to both Erlenmeyer flasks.
- ▫7 Close both Erlenmeyer flasks with a rubber stopper and wait at least 5 minutes. Swirl the solution occasionally.
- ▫8 While waiting, fill the burette with the sodium thiosulfate solution.
- ▫9 Place the magnetic bar into the solution in one of the Erlenmeyer flasks and begin stirring (do not heat).
- ▫10 Titrate the contents of the Erlenmeyer flask with the sodium thiosulfate solution until the liquid is light yellow.
- ▫11 Then add about 2 mL of starch solution.
- ▫12 Continue titrating until a clear color change occurs.
- ▫13 Remove the magnetic bar from the solution and repeat steps 9 through 12 with the solution in the other Erlenmeyer flask.

Questions – write the answers on the answer sheets

6 Record:

- the mass of the total contents of the Bikosan sachet
- the mass of the Bikosan sample
- all burette readings 8

7 Calculate the amount of $NaBO_3.H_2O$ (in g) in one sachet of Bikosan. 14

8 Closing the Erlenmeyer flask with the rubber stopper is important. Oxygen in the air can convert the iodide into iodine. Give the equation for this reaction and explain whether the calculated amount of $NaBO_3.H_2O$ in a sachet of Bikosan becomes higher or lower. 4

9 Could you also perform the determination by titrating with a solution of the oxidizing agent potassium permanganate?
If you think not, explain why it is not possible.
If you think so, give an outline of how such a determination should be performed. 4

Name:

46th National Chemistry Olympiad

Symeres, Nijmegen

PRACTICAL TEST

Answer sheets

Thursday June 5 2025

Name:

Answer sheets practical test
Experiment 1
Questions 1 and 2
mass PET: ………. mass of the sample container and its contents **:** ………. mass of the empty sample container: ………. mass of the product: ………. mass of the contents of the jar with crimp closure : ……….
Question 3

Name:

Question 4
Question 5

Name:

Answer sheets practical test

Experiment 2

Question 6

mass of the contents of a Bikosan sachet : ………..

mass of the weighed amount of Bikosan : ………..

burette readings

1.	final volume	……….	2.	final volume	……….
	initial volume	……….		initial volume	……….
	volume used	……….		volume used	……….

Question 7

Name:

Question 8
Question 9

NATIONAL CHEMISTRY OLYMPIAD 2025

MARKING SCHEME PRELIMINARY ROUND 1

To be held between 13th and 31st January 2025

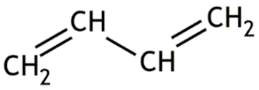
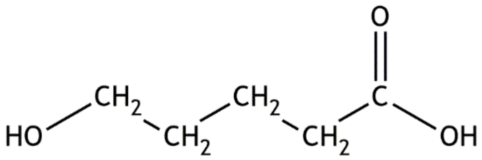
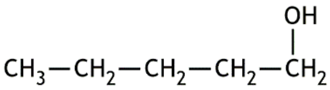
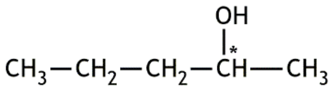
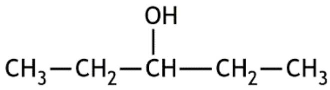
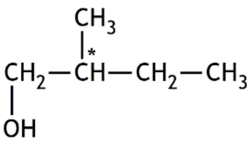
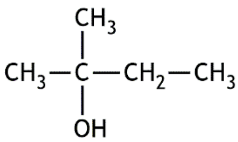
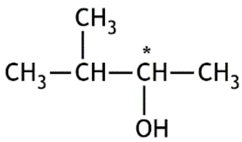
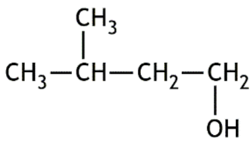
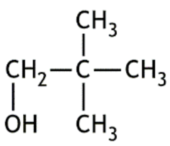
- **This preliminary round consists of 25 multiple choice questions divided over 9 topics and 2 problems, with a total of 8 open questions, in addition to an answer sheet for the multiple choice questions.**
- **Use the answer sheet to answer the multiple choice questions.**
- **For the open questions, use a separate answer sheet for each of the two problems. Remember to include your name on each sheet.**
- **The maximum score for this paper is 76 points.**
- **The preliminary round lasts two hours in total.**
- **Required materials: (graphic) calculator and BINAS 6th or 7th edition, ScienceData 1st edition or BINAS 5th edition, English version. “Green chemistry” table is included.**
- **The total number of points available for each question is stated.**
- **Unless otherwise stated, standard conditions apply: T = 298 K and $p = p_0$.**

Problem 1 Multiple choice questions total 50 points

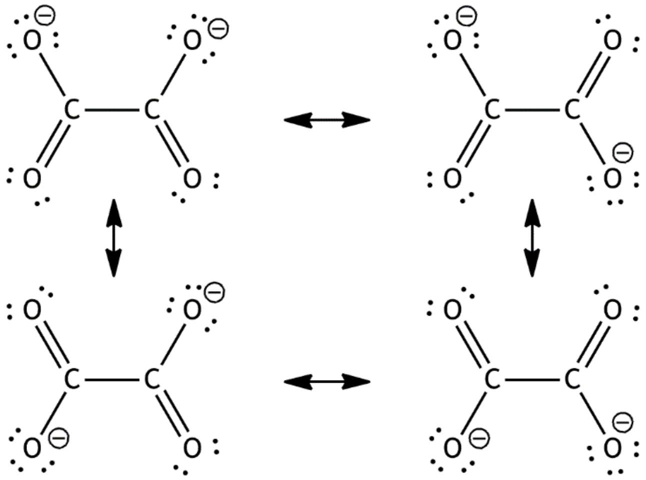
For every correct answer: 2 points

Brief summary

nr.	answer
1	B
2	D
3	F
4	C
5	H
6	D
7	F
8	C
9	C
10	B
11	C
12	C
13	D
14	B
15	C
16	B
17	C
18	A
19	F
20	D
21	B
22	E
23	D
24	D
25	D

		Carbon Chemistry
1	B	Compound I is a mirror image isomer of substance X, compound II is the same substance as substance X (rotated 180^0).
2	D	Polymer I is formed from the 1,4-addition of buta-1,3-diene:  Polymer II is formed from the condensation of 5-hydroxypentanoic acid. 
3	F	Below are all the structures. The asymmetric carbon atoms are indicated with *. Therefore, these structures have two stereoisomers.  **1**  **2+3**  **4**  **5+6**  **7**  **8+9**  **10**  **11**
		Thermochemistry
4	C	reaction enthalpy $= -E_{\text{initial}} + E_{\text{final}}$ $= -\Delta H_{\text{formation NaClO}_4\text{(s)}} - \Delta H_{\text{melting NaClO}_4\text{(s)}} + \Delta H_{\text{formation NaCl(s)}}$ $= --382.75 \text{ kJ mol}^{-1} - 14.7 \text{ kJ mol}^{-1} + -411 \text{ kJ mol}^{-1} = -43 \text{ kJ mol}^{-1}$
5	H	Electrolysis is an endothermic reaction and a catalyst lowers the activation energy, so diagram V is without a catalyst and diagram III is with a catalyst."

		Rate of reaction and equilibrium
6	**D**	10 mL of a 0.50 M K_2SO_4 solution and 10 mL of a 0.50 M $AgNO_3$ solution contain, respectively, 10 mmol K^+ and 5.0 mmol SO_4^{2-}, and 5.0 mmol Ag^+ and 5.0 mmol NO_3^-. The following heterogeneous equilibrium is established: $2\ Ag^+(aq) + SO_4^{2-}(aq) \rightleftharpoons Ag_2SO_4(s)$ The number of mmoles of K^+ and NO_3^- in the solution does not change. The numbers of mmoles of Ag^+ and SO_4^{2-} in the solution decrease, where the decrease in the number of mmoles of Ag^+ is twice as large as the decrease in the number of mmoles of SO_4^{2-}. Thus: $[K^+] > [NO_3^-] > [SO_4^{2-}] > [Ag^+]$
7	**F**	The value of *K* changes only with a change in temperature. The reaction rate in both directions increases at the new equilibrium due to the higher concentrations of all particles.
8	**C**	$2.50 - 1.70 = 0.80$ g $CaCO_3$ has reacted. This is equal to $\frac{0.80}{100.09} = 0.0080$ mol $CaCO_3$. Thus, 0.0080 mol CO_2 has been formed in 0.250 L. $K_c = [CO_2] = \frac{0.0080}{0.250} = 0.032$
9	**C**	On the left, there are more gas particles, so the reaction to the right is temporarily favoured at higher pressure. The reaction to the right is exothermic and is temporarily favoured at lower temperatures.
		Structures and formulas
10	**B**	The electronegativity of H is 2.1, of O is 3.5 and of S is 2.6. This means that every H — O bond, S — O bond and S = O bond is polar with the δ^+ on H and S and the δ^- on O.
11	**C**	$232 - 208 = 24$ nuclear particles are emitted. A helium nucleus consists of 4 nuclear particles, so $\frac{24}{4} = 6$ **alpha particles** are emitted. The atomic number of Th (Thorium) is 90, and that of Pb (Lead) is 82. The 6 emitted alpha particles contain 12 protons, so $82 + 12 - 90 = 4$ protons are added. Thus 4 neutrons are converted.
12	**C**	7 (one Cl atom) + 3×6 (three O atoms) + 1(charge 1—) = 26 valence electrons.

13	**D**	
		pH and acid-base
14	**B**	$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(0.102 \times 0.320)^2}{0.898 \times 0.320} = 3.71 \cdot 10^{-3}$
15	**C**	In the calculation, the increase in volume due to the addition of the HCl solution can be neglected. The initial pOH is $14.00 - 9.20 = 4.80$ so $\left[OH^-\right] = 10^{-4.80} = 1.58 \cdot 10^{-5}$ mol L^{-1} The pOH after the reaction is $14.00 - 8.20 = 5.80$ so $\left[OH^-\right] = 10^{-5.80} = 1.58 \cdot 10^{-6}$ mol L^{-1} Then $\left(1.58 \cdot 10^{-5} - 1.58 \cdot 10^{-6}\right) \times 100 = 1.43 \cdot 10^{-3}$ mmol OH^- must react. This reacts with an equal amount of H_3O^+ originating from the same amount of HCl. Then $\frac{1.43 \cdot 10^{-3}}{0.10} = 0.014$ mL 0.10 M HCl solution must be added.
16	**B**	From 0.1 mol K_2O, 0.2 mol OH^- is produced when the reaction proceeds to completion: $K_2O + H_2O \rightarrow 2\ K^+ + 2\ OH^-$ From 0.1 mol KOH, 0.1 mol dissolved OH^- is produced. K_2CO_3 and Na_2SO_4 both contain a weak base, so less than 0.1 mol OH^- per litre is produced. The higher the $[OH^-]$, the higher the pH.
		Redox and electrochemistry
17	**C**	The reaction equation is: $2\ NH_4ClO_4 + 2\ Al \rightarrow Al_2O_3 + 2\ NO + 2\ HCl + 3\ H_2O$

18	**A**	Zn can react with Pb^{2+} in a redox reaction because Zn is a stronger reducing agent than Pb. Cu will not react. During discharging, the electrode where the oxidizing agent reacts is always the positive electrode, and Pb^{2+} acts as the oxidizing agent here.
		Analysis
19	**F**	Mass spectrum 1 has the highest peak at an *m/z* value of 59. This corresponds to the fragment **$C_3H_7O^+$**, originating from **hexan-3-ol.** Mass spectrum 2 has the highest peak at an *m/z* value of 45. This corresponds to the fragment **$C_2H_5O^+$,** originating from **hexan-2-ol**.
20	**D**	Magnesium chloride is highly soluble in water. When a solution of the strong acid HI is added, lead(II) oxide and magnesium oxide will react in an acid-base reaction, releasing lead(II)ions and magnesium ions. Lead(II) ions form a precipitate with iodide ions, while magnesium ions do not. Lead(II) chloride does not react with the HI solution in an acid-base reaction. Lead(II) chloride is moderately soluble, and the lead(II) ions form a precipitate of lead(II)iodide with the I^- ions.
21	**B**	In gas chromatography, the substance whose molecules form the strongest interactions with the column will remain in the column the longest. All three substances are non-polar, so London dispersion forces are the determining factor. Molecules of **substance III** form the strongest London dispersion forces with the stationary phase of the column, meaning **substance III** has the longest retention time. **Substance I** consists of the smallest molecules, which form the weakest London dispersion forces, resulting in the **shortest retention time.**
		Chemical calculations
22	**E**	$n_{Au} = \frac{11.8}{197} = 0.0599$ mol $n_{NaCN} = n_{CN^-} = 0.0599 \times \frac{8}{4} = 0.120$ mol $V_{NaCN} = \frac{0.120}{0.0100} = 12.0$ L
23	**D**	When the amount of Cr^{3+} increases, the amount of CH_3CHO also increases, in the molar ratio of Cr^{3+} : CH_3CHO = 2 : 3. $0.18 \times \frac{3}{2} = 0.27$ mol L^{-1} s^{-1}

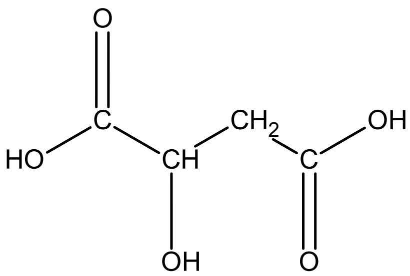
24	**D**	Silver is formed according to the half-reaction: $Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$ $n_{e^-} = n_{Ag} = \frac{0.10}{107.9} = 9.3 \cdot 10^{-4}$ mol charge $= 9.3 \cdot 10^{-4} \times 9.65 \cdot 10^{4} = 89$ C $t = \frac{89}{0.10} = 890$ s $\frac{890}{60} = 15$ min
		Green chemistry
25	**D**	$E\text{-factor} = \frac{\text{total mass of all reactants} - \text{mass of desired product}}{\text{mass of desired product}}$ The molar masses of the acid, alcohol, ester and water are respectively: 60.05 g mol^{-1}, 88.15 g mol^{-1}, 130.18 g mol^{-1}, and 18.02 g mol^{-1}. When starting with one mole of acid and one mole of alcohol: $m_{\text{reactants}} = 60.05 + 88.15 = 148.20$ g $m_{\text{theoretical yield}}$=130.18 g If x is the actual yield, the following applies: $0.34 = \frac{148.20 - x}{x}$ and $0.34x = 148.20 - x$ and $1.34x = 148.20$, thus $x = \frac{148.20}{1.34} = 110.60$ g percentage yield = $\frac{m_{\text{experimental yield}}}{m_{\text{theoretical yield}}} \times 100\% = \frac{110.60}{130.18} \times 100\% = 85\%$

Open questions total 26 points

Problem 2 Apple cider vinegar 12 points

□**1** **maximum score 2**

A correct answer can be given as follows:



- carbon skeleton with four carbon atoms and two carboxyl groups correctly drawn 1
- rest of the structural formula correctly drawn 1

□2 **maximum score 2**

$C_2H_6O + O_2 \rightarrow C_2H_4O_2 + H_2O$

- $C_2H_4O_2$ after the arrow 1
- H_2O after the arrow and elements balanced with correct molecular formulas before and after the arrow 1

Note

When the answer $C_2H_5OH + O_2 \rightarrow CH_3COOH + H_2O$ *is given, award full marks.*

□**3** **maximum score 4**

An example of a correct calculation is:

7.382 g malic acid per L is 7.382 mg malic acid per mL is $\frac{7.382}{134.09}$ = 0.05510 mmol per mL.

In 10.00 mL malic acid there is $\frac{7.382}{134.09} \times 10.00$ = 0.5510 mmol malic acid.

This reacts with $2 \times \frac{7.382}{134.09} \times 10.00$ = 1.101 mmol OH^-

and that is in $\frac{2 \times \frac{7.382}{134.09} \times 10.00}{0.1000} = 11.01$ mL 0.1000 M sodium hydroxide.

- calculation of the number of mmoles of malic acid per mL 1
- calculation of the number of mmoles of malic acid in 10.00 mL 1
- calculation of the number of mmoles of OH^- that reacted 1
- conversion to the number of mL of 0.1000 M sodium hydroxide 1

□4 **maximum score 4**

An example of a correct calculation is:

Per litre of apple juice applies:

From $\frac{7.382}{134.09}$ = 0.05510 mol malic acid, 0.05510 mol ethanol are formed and finally also 0.05510 mol ethanoic acid.

From glucose, therefore $1.086 - \frac{7.382}{134.09}$ = 1.031 mol ethanoic acid are formed and that is ultimately formed from $\frac{1.086 - \frac{7.382}{134.09}}{2}$ = 0.5155 mol glucose and that is

$\frac{1.086 - \frac{7.382}{134.09}}{2} \times 180.16 = 92.87$ g glucose per litre apple juice.

- calculation of the number of moles of ethanoic acid that is produced per L of malic acid 1
- conversion to the number of moles of ethanoic acid that is formed per L from the glucose 1
- conversion to the number of moles of glucose that is converted per L 1
- conversion to the number of grams of glucose per L 1

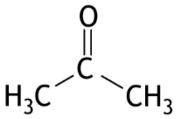
Note

When an incorrect answer to question 4 is the consequent result of an incorrect reaction equation in question 2, this answer to question 4 should be considered correct.

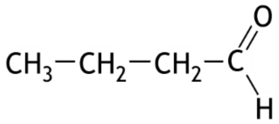
Problem 3 Ozonolysis 14 points

5 maximum score 2

A correct answer can be given as follows:



and

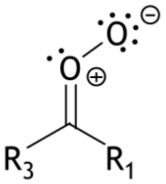


· correct structural formula of propanone 1

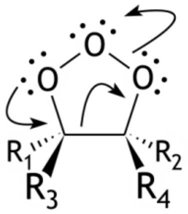
· correct structural formula of butanal 1

6 maximum score 4

A correct answer can be given as follows:



A



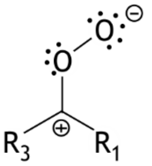
· correct Lewis structure of A 1

· correct formal charges in A 1

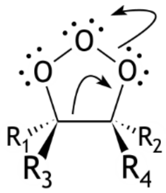
· lone pairs in molozonide correct 1

· curly arrows consistently drawn with the structural formula of A 1

If the following answer is given: 3



A



7 maximum score 3

$C_2H_4O_3$ + 2 H^+ + 2 e^- $\rightarrow$ 2 CH_2O + H_2O

The ozonide acts as an oxidizing agent, so dimethyl sulfide acts as a reducing agent.

· $C_2H_4O_3$, H^+ and e^- before the arrow and CH_2O and H_2O after the arrow 1

· correct coefficients 1

· consistent explanation and conclusion regarding the function of dimethyl sulfide 1

□8 maximum score 5

An example of a correct answer is:

$$n_{\text{formaldehyde}} = \frac{4.8 \cdot 10^{-3}}{30.0} = 1.6 \cdot 10^{-4} \text{ mol}$$

$$n_{\text{glyoxal}} = \frac{14 \cdot 10^{-3}}{58.0} = 2.4 \cdot 10^{-4} \text{ mol}$$

$$\frac{n_{\text{formaldehyde}}}{n_{\text{glyoxal}}} = \frac{1.6 \cdot 10^{-4}}{2.4 \cdot 10^{-4}} = \frac{2}{3}$$

This corresponds to the structure $H_2C{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH_2$

- calculation of the molar masses of formaldehyde and glyoxal 1
- calculation of the number of moles of formaldehyde and glyoxal 1
- conversion to the molar ratio of formaldehyde and glyoxal 1
- correct structural formula of X 2

If an otherwise correct answer contains an incorrect structural formula, from which only formaldehyde and glyoxal can be formed, for example, hexane-1,3,5-triene. 4

NATIONAL CHEMISTRY OLYMPIAD 2025

MARKING SCHEME PRELIMINARY ROUND 2

To be held between 17th and 25th March 2025

- **This preliminary round consists of 20 multiple choice questions divided over 8 topics, and 3 problems with a total of 16 open questions.**
- **The maximum score for this paper is 98 points.**
- **Required materials: (graphic) calculator and BINAS 6th or 7th edition or ScienceData 1st edition or BINAS 5th edition, English version.**
- **The total number of points available for each question is stated.**
- **The attached marking scheme must be used when grading the work. In addition, the general rules for the Dutch Central Exams apply.**

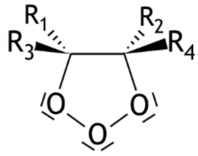
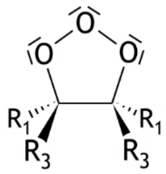
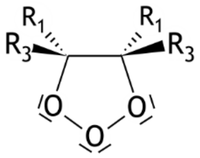
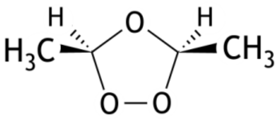
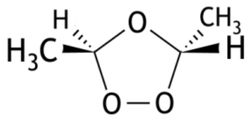
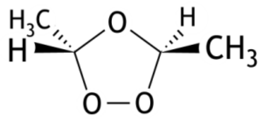
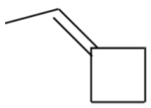
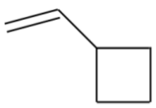
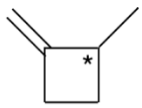
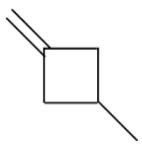
Problem 1 Multiple choice questions total 40 points

For every correct answer: 2 points

Brief summary

nr.	answer
1	**C**
2	**C**
3	**D**
4	**A**
5	**D**
6	**E**
7	**D**
8	**A**
9	**B**
10	**C**
11	**C**
12	**E**
13	**A**
14	**C**
15	**D**
16	**D**
17	**C**
18	**D**
19	**C**
20	**D**

Carbon chemistry

1	C	If the ozone molecule approaches from 'above' in case I, the molozonide depicted in the question is formed. If the ozone molecule approaches from ‘below’,  is formed and that is the mirror image of the molozonide drawn in the question. Also in case II, the ozone molecule can approach from two sides, and then it forms  and  These formulas are identical.
2	C	  
3	D	    The C atom indicated with an asterisk is asymmetric, so there are two variants of this structure.

Rate of reactions and equilibrium

4	A	5.00 g NO_2 is $\frac{5.00}{46.006}$ mol; at 310 K and a volume of 1.00 dm^3, the pressure is $p_{NO_2} = \frac{5.00}{46.006} \times \frac{8.314 \times 310}{1.00 \cdot 10^{-3}} = 2.80 \cdot 10^5$ Pa. $\begin{array}{lll} & N_2O_4 \rightleftharpoons & 2\ NO_2 \\ \text{initial} & 0 & 2.80 \cdot 10^5 \text{ Pa} \\ \text{change} & +x \text{ Pa} & -2x \text{ Pa} \\ \text{equilibrium} & x \text{ Pa} & (2.80 \cdot 10^5 - 2x) \text{ Pa} \end{array}$ The equilibrium pressure is $2.80 \cdot 10^5 - 2x + x = 2.80 \cdot 10^5 - x = 1.71 \cdot 10^5$ Pa. Thus $x = 1.09 \cdot 10^5$ Pa. Thus $p_{NO_2} = 2.80 \cdot 10^5 - 2 \times 1.09 \cdot 10^5 = 0.62 \cdot 10^5$ Pa and $p_{N_2O_4} = 1.09 \cdot 10^5$ Pa. Thus $K_p = \frac{(p_{NO_2} / p_0)^2}{p_{N_2O_4} / p_0} = \frac{(0.62 \cdot 10^5 / 10^5)^2}{1.09 \cdot 10^5 / 10^5} = 0.35$.

5	**D**	The rate of the total reaction is determined by the slowest (second) step, therefore $r = k_2[Cl][N_2O]$. For the first step, it applies that $K = \frac{[Cl]^2}{[Cl_2]}$, thus $[Cl]=\sqrt{K \times [Cl_2]}$, thus $r = k_2[N_2O]\sqrt{K \times [Cl_2]}$, or $r = k_2K^{1/2}[N_2O][Cl_2]^{1/2} = k[N_2O][Cl_2]^{1/2}$.
6	**E**	$K_1 = \frac{[NO]^2}{[N_2][O_2]}$ $K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]}$ $K_3 = \frac{[N_2O_3]}{[NO][NO_2]}$ $K = \frac{[N_2]^2[O_2]^3}{[N_2O_3]^2} = \frac{[N_2]^2[O_2]^2}{[NO]^4} \times \frac{[NO_2]^2[O_2]}{[NO_2]^2} \times \frac{[NO]^2[NO_2]^2}{[N_2O_3]^2} = \frac{1}{K_1^2 \times K_2 \times K_3^2}$

Structures and formulae

7	**D**	They both have the configuration $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}$.
8	**A**	F is the most electronegative halogen atom and makes the OH bond the most polar at a distance.

pH / acid-base

9	**B**	The following equilibrium reaction takes place: $H_3PO_4^- + PO_4^{3-} \rightleftharpoons H_2PO_4^- + HPO_4^{2-}$ A buffer solution is produced with $H_2PO_4^-$ as acid and HPO_4^{2-} as conjugated base, for which applies : $pH = pK_a - \log\frac{\text{number of moles of acid}}{\text{number of moles of conjugated base}} =$ $7.21 - \log\frac{\text{number of moles of } H_2PO_4^-}{\text{number of moles of } HPO_4^{2-}}$ Because the same amount of $H_2PO_4^-$ as HPO_4^{2-} is produced, the pH= pK_a = 7.21.
10	**C**	After adding the 20 mL of the solution of sodium hydroxide, $[Ca^{2+}]$ and $[Mg^{2+}]$ have been reduced by half to 0.050 mol L^{-1}. At pH = 10.00, $[OH^-] = 1.0 \cdot 10^{-4}$, thus, the ion products of $Ca(OH)_2$ and $Mg(OH)_2$ are $0.050 \times (1.0 \cdot 10^{-4})^2 = 5.0 \cdot 10^{-10}$. This is smaller than the solubility product of $Ca(OH)_2$, $5.0 \cdot 10^{-6}$, so $Ca(OH)_2$ does not precipitate. The ion product of $Mg(OH)_2$ is larger than the solubility product of $Mg(OH)_2$, $5.6 \cdot 10^{-12}$, so $Mg(OH)_2$ will precipitate.

Redox and electrolysis

11	**C**	The three Fe^{2+} ions donate a total of three electrons. The oxygen molecule gains four electrons. To make them equal to each other, the coefficient of $Fe_3(PO_4)_2$ is multiplied by 4 and that of O_2 by 3. The reaction equation becomes: $4\ Fe_3(PO_4)_2 + 3\ O_2 + 6\ H_2O \rightarrow 8\ FePO_4 + 4\ Fe(OH)_3$
12	**E**	At the negative electrode, the strongest oxidizing agent reacts first, that is Cu^{2+}. At the positive electrode, the strongest reducing agent reacts first, that is Br^-.
13	**A**	$\Delta G_{total} = \Delta G_1 + \Delta G_2$ or $-4 \times F \times \Delta E = -2 \times F \times 1.468 + \{-2 \times F \times (-0.126)\}$, thus $\Delta E = \frac{-1.468 + 0.126}{-2} = 0.671\ V$.

Analysis

14	**C**	When the peak area of 85A in chromatogram B is equal to that in chromatogram A, the peak area of vitamin E in chromatogram B is $\frac{12.717}{12.600} \times 7.902 = 7.975$. The concentration of vitamin E in blueberry juice is $\frac{7.975}{7.617} \times 4.50 \cdot 10^{-4} = 4.71 \cdot 10^{-4}\ mol\ L^{-1}$.
15	**D**	The pH transition range of an indicator must fit on a steep part of the pH curve.
16	**D**	There is 0.1494 g H_2A in the titrated 25.00 mL. After the addition of 18.0 mL 0.100 M sodium hydroxide solution, all of the H_2A has been converted. Therefore $\frac{1}{2} \times 18.0 \times 0.100 \times 10^{-3}$ mol H_2A has reacted. The molar mass is therefore $\frac{0.1494}{\frac{1}{2} \times 18.0 \times 0.100 \times 10^{-3}} = 166\ g\,mol^{-1}$.

Calculations and Green Chemistry

17	**C**	Suppose x g of Mg reacts to form MgO and y g of Mg reacts to form Mg_3N_2, Then $\frac{x}{24.31}$ mol MgO is formed, which is $\frac{x}{24.31}\times 40.305 = 1.658x$ g MgO and $\frac{1}{3}\times\frac{y}{24.31}$ mol Mg_3N_2, which is $\frac{1}{3}\times\frac{y}{24.31}\times 101.0 = 1.385y$ g Mg_3N_2. This produces the following system of two equations with two variables: $x + y = 1.000$ and $1.658x + 1.385y = 1.584$ Solving this gives $y = 0.27$. The mass percentage of Mg_3N_2 is $\frac{0.27\times 1.385}{1.584}\times 100\% = 24\%$.
18	**D**	$E-\text{factor} = \frac{\text{total mass of all reactants} - \text{mass of desired product}}{\text{mass of desired product}} =$ $\frac{181.88 + 5\times 40.08 - 0.85\times 101.88}{0.85\times 101.88} = 3.4$

Thermochemistry

19	**C**	A catalyst lowers the activation energy and does not influence the reaction enthalpy.
20	**D**	The reaction enthalpy is given by $\Delta H_r = -\Delta H_f(CuSO_4(s)) - 5\times\Delta H_f(H_2O(l)) + \Delta H_f(CuSO_4.5H_2O(s))$ $= -(-7.71\cdot 10^5) - 5\times(-2.86\cdot 10^5) + (-22.78\cdot 10^5) = -0.77\cdot 10^5$ J per 5 mol H_2O. That is $\frac{-0.77\cdot 10^5}{5} = -0.154\cdot 10^5$ J per mol H_2O or -15.4 kJ mol^{-1}.

Open questions total 58 points

Problem 2 The decomposition of dinitrogen pentoxide 21 points

□1 Maximum score 8

An example of a correct answer is:

$\Delta H_r = -11.3 + 2 \times 33.2 = +55.1$ kJ mol^{-1}

$\Delta S_r = -355.6 + 2 \times 240 + ½ \times 205 = +227$ J mol^{-1} K^{-1}

Thus $\Delta G_r = \Delta H_r - T\Delta S_r = 55.1 \times 10^3 - 323 \times 227 = -1.82 \cdot 10^4$ J mol^{-1}

It is also true that $\Delta G_r = -RT\ln K$, thus $K = e^{-\frac{\Delta G}{RT}} = e^{-\frac{-1.82.10^4}{8.314 \times 323}} = 8.78 \cdot 10^2$.

That is very large, so the equilibrium lies far to the right and the reaction can be considered as to proceed to completion.

- in the calculation of ΔH_r, the formation enthalpy of N_2O_5 with a negative sign 1
- in the calculation of ΔH_r, 2 × formation enthalpy of NO_2 with a positive sign 1
- correct summation of the formation enthalpies 1
- in the calculation of ΔS_r, the absolute entropy of N_2O_5 with a negative sign 1
- in the calculation of ΔS_r, 2 × the absolute entropy of NO_2 and ½ × the absolute entropy of O_2 with a positive sign 1
- correct summation of the absolute entropies 1
- calculation of ΔG_r 1
- calculation of K, and noting that it is very large (meaning the equilibrium lies far to the right) 1

□2 Maximum score 1

Since the oxygen escapes, the reverse reaction cannot take place.

□3 Maximum score 4

An example of a correct answer is:

At completion, $\frac{1.01 \cdot 10^5 \times V_\infty \times 10^{-6}}{8.314 \times 303} = 4.01 \cdot 10^{-5} \times V_\infty$ mol O_2 is formed.

There was initially $2 \times 4.01 \cdot 10^{-5} \times V_\infty$ mol N_2O_5 present in 0.100 L solution, thus

$[N_2O_5]_0 = \frac{2 \times 4.01 \cdot 10^{-5} \times V_\infty}{0.100} = 8.02 \cdot 10^{-4} \times V_\infty$ mol L^{-1}.

At time t, V_t cm^3 of O_2 has formed, so $8.02 \times 10^{-4} \times V_t$ moles of N_2O_5 per litre have been converted.

Thus $[N_2O_5]_t = 8.02 \cdot 10^{-4} \times V_\infty - 8.02 \cdot 10^{-4} \times V_t = (V_\infty - V_t) \times 8.02 \cdot 10^{-4}$ mol L^{-1}, thus $F = 8.02 \cdot 10^{-4}$.

- correct conversion from cm^3 to m^3 and °C to K 1
- calculation of the number of moles of O_2 in V_∞ cm^3 and V_t cm^3 respectively 1
- calculation of the number of moles of N_2O_5 initially present and the number of moles of N_2O_5 converted in t sec 1
- calculation of the decrease of $[N_2O_5]$ in t sec and of F 1

□4 Maximum score 4

An example of a correct answer is:

At $t = 0$ s, $[N_2O_5]$ is equal to $6.80 \cdot 10^{-2}$ mol L^{-1} , at $t = 8.5 \cdot 10^3$ s, $[N_2O_5]$ has decreased to $3.40 \cdot 10^{-2}$ mol L^{-1} and again $8.5 \cdot 10^3$ s later, at $t = 17 \cdot 10^3$ s, to $1.70 \cdot 10^{-2}$ mol L^{-1}.

The half-life is therefore $8.5 \cdot 10^3$ s and is independent of concentration, which is the case for a first order reaction.

- choice of (at least) two concentrations that differ by a factor of 2 — 1
- reading the corresponding times — 1
- calculation of the half-life — 1
- observation that the half-life is independent of concentration (so it is a first order reaction) — 1

□5 Maximum score 2

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{8.5 \cdot 10^3} = 8.2 \cdot 10^{-5}\ \text{s}^{-1}$$

- calculation of k — 1
- correct unit — 1

Note

If an incorrect answer to question 5 is the consequential result of an incorrect answer to question 4, mark the answer to question 5 as correct.

□6 Maximum score 2

An example of a correct answer is:

For this first order reaction we have $\ln\frac{[N_2O_5]_0}{[N_2O_5]_t} = kt$. Substituting $[N_2O_5]_0 = V_\infty \times F$ and $[N_2O_5]_t = (V_\infty - V_t) \times F$ gives $\ln\frac{V_\infty \times F}{(V_\infty - V_t) \times F} = \ln\frac{V_\infty}{(V_\infty - V_t)} = kt$.

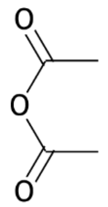
So if you plot $\ln\frac{V_\infty}{(V_\infty - V_t)}$ versus time in a diagram, you get a straight line. The slope of this line is k.

- demonstrate that $\frac{[N_2O_5]_0}{[N_2O_5]_t} = \frac{V_\infty}{(V_\infty - V_t)}$ — 1
- rest of the answer — 1

Problem 3 Paracetamol 19 points

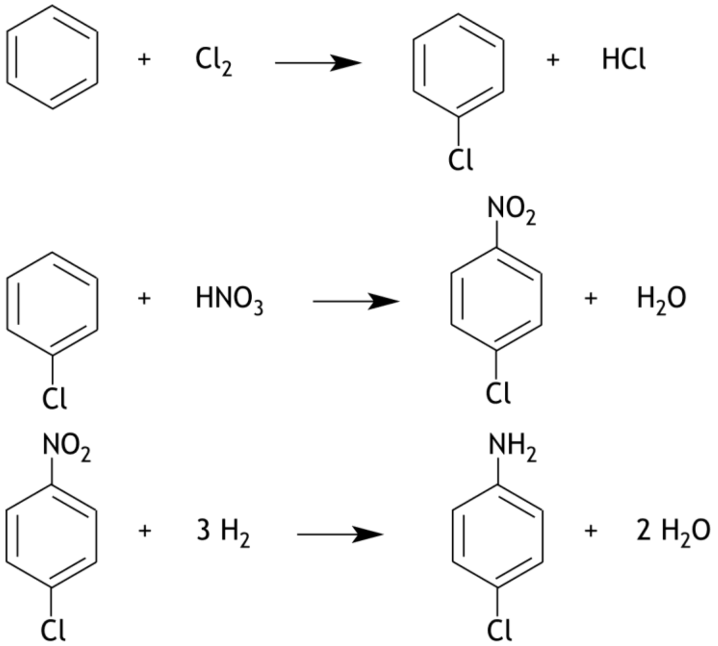
▫7 Maximum score 1

An example of a correct answer is:



▫8 Maximum score 7

An example of a correct answer is:



- in the first equation correct formulas before the arrow 1
- in the first equation correct formulas after the arrow 1
- in the second equation correct formulas before the arrow 1
- in the second equation correct formulas after the arrow 1
- in the third equation correct formulas before the arrow 1
- in the third equation correct formulas after the arrow 1
- correct coefficients in the third equation 1

Note:

When HCl and/or HNO_3 are written as $H^+ + Cl^-$ and $H^+ + NO_3^-$ respectively, mark this as correct.

□9 Maximum score 3

An example of a correct answer is:

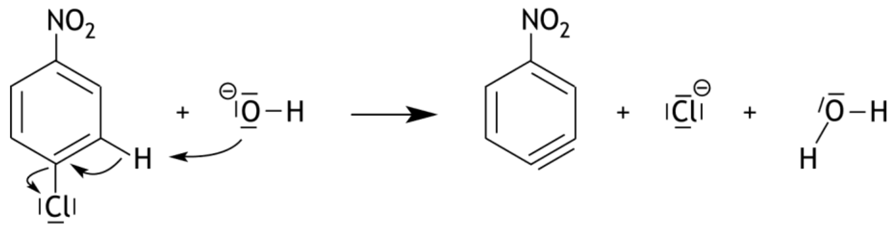
A synthesis route that starts with the nitration of benzene is possible. After the nitration, the nitro group must first be converted into an amino group, followed by chlorination, and then the chlorine atom is replaced by an OH group.

- (a synthesis route that starts with the nitration of benzene is possibe) after nitration, the nitro group must be converted into an amino group — 1
- followed by chlorination — 1
- then replacement of Cl with OH — 1

If an answer is given as: „It is not possible because the nitro group is a meta-directing group, and therefore, chlorination will (mainly) result in *meta*-chloronitrobenzene”. — 2

□10 Maximum score 3

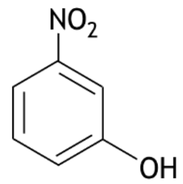
An example of a correct answer is:



- the structural formula of *para*-chloronitrobenzene and OH^- before the arrow and the structural formulas of the nitrobenzyne, Cl^- and H_2O after the arrow — 1
- all charges and relevant electron pairs correctly represented — 1
- the curly arrows correctly represented — 1

□11 Maximum score 1

An example of a correct answer is:



▫12 Maximum score 4

An example of a correct calculation is:

The yield of the total conversion of benzene to paracetamol is

$0.90 \times 0.92 \times 0.65 \times 0.48 \times 0.85 = 0.22$.

That means that per Mmol benzene ultimately 0.22 Mmol paracetamol can be formed.

1.00 ton benzene is $\frac{1.00}{78.11}$ Mmol, thus, from that $0.22 \times \frac{1.00}{78.11}$ Mmol paracetamol can be formed, that is $0.22 \times \frac{1.00}{78.11} \times 151.17 = 0.43$ ton paracetamol.

- calculation of the yield of the total conversion of benzene to paracetamol 1
- calculation of the number of Mmoles of benzene in 1.00 ton of benzene 1
- calculation of the number of Mmoles of paracetamol that can be formed from this 1
- calculation of the number of tons of paracetamol that can be formed 1

Problem 4 Wüstite 18 points

□13 Maximum score 3

Examples of a correct calculation are:

Suppose that wüstite contains p mol Fe^{2+} and q mol Fe^{3+} per mol O^{2-}, then it follows that:

$p + q = 0.87$ and $2p + 3q = 2$.

Solving this system of two equations with two unknowns results in $p = 0.61$ and $q = 0.26$.

Thus $p : q = 2.3 : 1.0$.

- formulation of the equation $p + q = 0.87$ 1
- formulation of the equation $2p + 3q = 2$ 1
- rest of the calculation 1

and

The average charge of the iron ions is $\frac{2}{0.87} = +2.3$. Suppose there are p moles Fe^{2+} in one mol of iron ions with an average charge of +2.3, then there are $(1 - p)$ moles Fe^{3+}, and the following equation applies $2p + 3(1 - p) = 2.3$. This results in $p = 0.7$.

Thus per mol of iron ions, there is 0.7 mol Fe^{2+} and 0.3 mol Fe^{3+}.

Thus the molar ratio $Fe^{2+} : Fe^{3+} = 0.7 : 0.3 = 2.3 : 1.0$.

- calculation of the average charge of the iron ions 1
- (supposing that there are p moles of Fe^{2+} per mol of iron ions) notion that $2p + 3(1 - p) = 2.3$ 1
- rest of the calculation 1

□14 maximum score 1

Examples of a correct answer are:

- If all positions of positive ions in the lattice were occupied by Fe^{2+} and Fe^{3+} ions, the substance would not be neutral.
- If two Fe^{3+} ions are present in the lattice, one Fe^{2+} ion must be missing.

□15 Maximum score 6

An example of a correct answer is:

The volume of the unit cell is $(2 \times 214)^3 = 7.84 \cdot 10^7$ pm^3 or $7.84 \cdot 10^{-29}$ m^3.

The unit cell contains 4 oxide ions and (on average) 4x iron ions.

The (average) mass of the unit cell is thus $4 \times 16.00 + 4x \times 55.85$ u, or

$(4 \times 16.00 + 4x \times 55.85) \times 1.66 \cdot 10^{-27}$ kg.

Thus, for the density applies $\frac{(4 \times 16.00 + 4x \times 55.85) \times 1.66 \cdot 10^{-27}}{7.84 \cdot 10^{-29}} = 5.71 \cdot 10^3$ kg m^{-3}.

From this it follows that $x = 0.92$.

- notion that the edge length of the unit cell is 2×214 pm 1
- calculation of the volume of the unit cell 1
- notion that the unit cell contains 4 oxide ions and (on average) 4x iron ions 1
- calculation of the mass of the unit cell 1
- dividing the calculated mass of the unit cell by the calculated volume of the unit cell and equating this to the given density 1
- calculation of x 1

□16 Maximum score 8

Examples of a correct calculation are:

26.41 mL 0.0200 M potassium permanganate solution contains 26.41 × 0.0200 mmol MnO_4^-.
This has reacted with 5 × 26.41 × 0.0200 = 2.64 mmol Fe^{2+}.
Because Fe_xO can be interpreted as a mixture of FeO and Fe_2O_3, the 250 mg Fe_xO must have contained 2.64 mmol FeO and this is 2.64 × 71.844 = 190 mg FeO.

Then it contained 250 – 190 = 60 mg Fe_2O_3 and this contains $2 \times \frac{60}{159.69} = 0.75$ mmol Fe^{3+}.

Thus, 250 mg Fe_xO contained 2.64 + 0.75 = 3.39 mmol iron ions and

$2.64 + \frac{3}{2} \times 0.75 = 3.77$ mmol oxide ions.

Thus, the formula of the examined wüstite is $Fe_{3.39}O_{3.77}$ or $Fe_{0.90}O$.
Thus, x = 0.90.

- calculation of the number of mmoles of MnO_4^- used for the titration 1
- calculation of the number of mmoles of Fe^{2+} that reacted with this 1
- calculation of the number of mg of FeO that the 250 mg Fe_xO contained 1
- calculation of the number of mg of Fe_2O_3 that the 250 mg Fe_xO contained 1
- calculation of the number of mmoles of Fe^{3+} that the 250 mg Fe_xO contained 1
- calculation of the total number of mmoles of iron ions in the 250 mg Fe_xO 1
- calculation of the total number of oxide ions in the 250 mg Fe_xO 1
- calculation of x 1

and

26.41 mL 0.0200 M potassium permanganate solution contains 26.41 × 0.0200 mmol MnO_4^-.
This has reacted with 5 × 26.41 × 0.0200 = 2.64 mmol Fe^{2+}.
Thus, the 250 mg Fe_xO contained 2.64 × 55.85 = 147 mg Fe^{2+}
and in total 250 – 147 = 103 mg Fe^{3+} and O^{2-}.
Suppose it contains p mmol Fe^{3+} and q mmol O^{2-} than the following applies
$55.85p + 16.00q = 103$ (equation 1).
Because the substance is electrically neutral, the following also applies
$3p - 2q + 2 \times 2.64 = 0$ (equation 2).

Solving this system of two equations with two unknowns results in p = 0.76 and q = 3.78.
Thus, the 250 mg Fe_xO contained 2.64 + 0.76 = 3.40 mmol iron ions and 3.78 mmol oxide ions.
Thus, the formula of the examined wüstite is $Fe_{3.39}O_{3.77}$ or $Fe_{0.90}O$.
Thus, x = 0.90.

- calculation of the number of mmoles of MnO_4^- used for the titration 1
- calculation of the number of mmoles of Fe^{2+} that reacted with this 1
- calculation of the number of mg of Fe^{2+} in the 250 mg Fe_xO and of the total number of mg of Fe^{3+} and O^{2-} in the 250 mg Fe_xO 1
- formulating equation 1 1
- formulating equation 2 1
- solving the system of equations 1
- calculation of the total number of mmoles of iron ions in the 250 mg Fe_xO 1
- rest of the calculation 1

46th National Chemistry Olympiad

Symeres, Nijmegen

THEORY TEST

Marking scheme

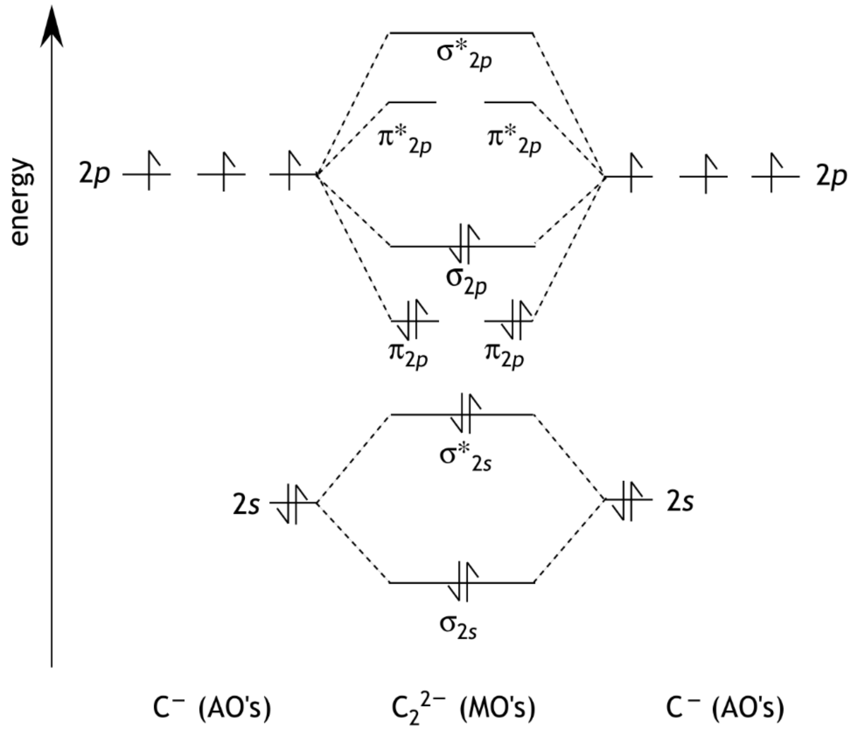
Wednesday June 4 2025

- This test consists of 7 problems with 32 open questions and a worksheet.
- The maximum score for this test is 120 points.
- The test will last a maximum of 4 hours.
- Required resources: (graphic) calculator and Binas 6th or 7th edition or BINAS 5th edition, English version or ScienceData 1st edition.
- The number of points available for each question is given.

Problem 1 Carbide shooting 13 points

□1 maximum score 6

A correct answer could look like this:



- one 2*s* and three 2*p* orbitals drawn in the other C^- ion and at the same height 1
- the two 2*s* atomic orbitals split into one σ and one σ* molecular orbital, including labels 1
- the six 2*p* atomic orbitals split into one σ and one σ* and two π and two π* molecular orbitals, including labels 1
- the σ_{2p} orbital lies above both π_{2p} orbitals 1
- correct filling of the atomic orbitals (AO's) of both C^- ions 1
- correct filling of the molecular orbitals (MO's) of C_2^{2-} 1

□2 maximum score 2

An example of a correct answer is:

The number of (drawn) electrons in bonding orbitals is 8, and the number of electrons in anti-bonding orbitals is 2. So the bond order is $\frac{8-2}{2} = 3$.

- correct number of electrons in bonding and anti-bonding orbitals 1
- correct calculation of bond order 1

Notes

- *When the answer is given as* $\frac{6-0}{2} = 3$ *, accept it as correct.*
- *When an incorrect answer to question 2 is the logical consequence of an incorrect answer to question 1, accept this answer to question 2 as correct.*

□3 maximum score 5

An example of a correct answer is:

60 mL water is $\frac{60 \times 1.0}{18.015} = 3.33$ mol. From that $\frac{1}{2} \times \frac{60 \times 1.0}{18.015} = 1.66$ moles of ethyne can be formed. In every interval of 45 seconds $\frac{1}{5} \times \frac{1}{2} \times \frac{60 \times 1.0}{18.015} = 0.33$ moles of ethyne ihave been formed.

The 30-litre milk churn contains $\frac{0.21 \times 30}{22.4} = 0.28$ moles of oxygen.

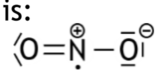
The mole ratio of ethyne : oxygen is therefore 0.33 : 0.28, and that is equal to the volume ratio, which is indeed approximately equal to the ideal volume ratio.

- calculation of the number of moles of water in 60 mL 1
- calculation of the number of moles of ethyne that can be produced from it 1
- calculation of the number of moles of ethyne that can be produced in each 45-second interval 1
- calculation of the number of moles of oxygen in 30 L 1
- rest of the calculation and conclusion 1

Problem 2 The NO_2 – N_2O_4 equilibrium 30 points

4 maximum score 5

An example of a correct answer is:

The Lewis structure of NO_2 is: 

A NO_2 molecule has one unpaired electron / is a radical, therefore, it can easily react with another molecule that also has an unpaired electron / is a radical.

- three bonding electron pairs correctly drawn 1
- five lone pairs correctly drawn 1
- one unpaired electron correctly drawn 1
- the formal charges in the correct places 1
- correct explanation why N_2O_4 molecules easily dimerize 1

5 maximum score 6

An example of a correct calculation is:

The reaction equation is:

$Cu + 4\,H^+ + 2\,NO_3^- \rightarrow Cu^{2+} + 2\,NO_2 + 2\,H_2O$

100 mg Cu is $\frac{100}{63.55}$ mmol and that can react with $4 \times \frac{100}{63.55} = 6.29$ mmol HNO_3.

In 10.0 mL concentrated nitric acid there is $\frac{10.0 \times 1.40 \times 0.650}{63.013} \times 10^3 = 144$ mmol HNO_3.

There is therefore a large excess of nitric acid, and the amount of copper determines how much nitrogen dioxide can be formed.

A maximum of $2 \times \frac{100}{63.55} = 3.15$ mmol NO_2 can be formed. At 80 °C and $p = p_0$ it has a volume of $V = \frac{3.15 \times 10^{-3} \times 8.314 \times (273+80)}{1.013 \cdot 10^5} \times 10^6 = 91.3$ cm^3.

- correct reaction equation 1
- calculation of the number of mmoles of Cu 1
- calculation of the number of mmoles of HNO_3 that can react with it 1
- calculation of the number of mmoles of HNO_3 in 10.0 mL concentrated nitric acid and the observation that (nitric acid is in excess and therefore) the amount of copper determines how much nitrogen dioxide can be formed 1
- calculation of the number of mmoles of NO_2 that can be formed 1
- calculation of the number of cm^3 of NO_2 that can be formed 1

Note

When instead of a reaction equation, it is stated that the molar ratio in which copper and nitric acid react with each other is 1 : 4, accept this as correct.

□6 maximum score 4

An example of a correct answer is:
You should not use the tube upside down. The (average) molar mass of air is about 28.8 g mol⁻¹ / lies somewhere between 28 g mol⁻¹ and 32 g mol⁻¹. This is less than the molar mass of NO_2 (46 g mol⁻¹), so the density of NO_2 is greater than the density of air. If you hold the tube upside down, the NO_2 will flow out again.

- correct estimation of the (average) molar mass of air 1
- the molar mass of NO_2 is greater than the (average) molar mass of air 1
- therefore, the density of NO_2 is greater than the density of air 1
- conclusion 1

Note
When an answer is given like: „You have to compare it with CO_2: the density of CO_2 is greater than the density of air. And because NO_2 has a greater molar mass than CO_2, the density of NO_2 is certainly greater than the density of air. So if you hold the tube upside down, the NO_2 will flow out again." accept this as correct.

□7 maximum score 5

An example of a correct calculation is:

$\Delta_r H = \Delta_f H_{N_2O_4} - 2 \times \Delta_f H_{NO_2} = 0.111 \cdot 10^5 - 2 \times 0.332 \cdot 10^5 = -0.553 \cdot 10^5 \text{ J mol}^{-1}$.

$\Delta_r S = S_{N_2O_4} - 2 \times S_{NO_2} = 304 - 2 \times 240 = -176 \text{ J mol}^{-1} \text{ K}^{-1}$.

So at a temperature T_1, the following applies:

$\Delta_r G = \Delta_r H - T_1 \Delta_r S = -0.553 \cdot 10^5 - T_1 \times (-176) = -0.553 \cdot 10^5 + T_1 \times 176 \text{ J mol}^{-1}$.

From $K_p = e^{-\frac{\Delta_r G}{RT}}$ follows $\ln K_p = -\frac{\Delta_r G}{RT}$ or $\ln 12{,}5 = -\frac{-0{,}553 \cdot 10^5 + T_1 \times 176}{8{,}314 \times T_1}$.

This gives T_1 = 281 K.

- calculation of $\Delta_r H$ 1
- calculation of $\Delta_r S$ 1
- calculation of $\Delta_r G$ 1
- $\ln 12.5 = -\frac{-0.553 \cdot 10^5 + T_1 \times 176}{8.314 \times T_1}$ 1
- calculation of T_1 1

□8 maximum score 7

An example of a correct calculation is:

Suppose x mmoles of N_2O_4 are formed, then 2x mmoles of NO_2 are converted.

	$2\ NO_2(g)$	$\rightleftharpoons$	$N_2O_4(g)$
start (mmol)	0.35		0
converted (mmol)	$-2x$		x
equilibrium (mmol)	$0.35-2x$		x

$$p_{NO_2} = \frac{(0.35-2x)\times 10^{-3}\times 8.314\times 278}{10.0\times 10^{-6}} = (0.35-2x)\times 2.31\cdot 10^{5} \text{ and}$$

$$p_{N_2O_4} = \frac{x\times 10^{-3}\times 8.314\times 278}{10.0\times 10^{-6}} = x\times 2.31\cdot 10^{5}$$

For K_p applies: $K_p = \dfrac{p_{N_2O_4}/p_0}{(p_{NO_2}/p_0)^2} = \dfrac{p_{N_2O_4}\times p_0}{(p_{NO_2})^2} = \dfrac{x\times 2.31\cdot 10^5\times 1.01\cdot 10^5}{\{(0.35-2x)\times 2.31\cdot 10^5\}^2} = 15.8$.

This gives x = 0.14.

Therefore $p_{NO_2} = (0.35-2\times 0.14)\times 2.31\cdot 10^5 = 1.6\cdot 10^4$ Pa and

$p_{N_2O_4} = 0.14\times 2.31\cdot 10^5 = 3.2\cdot 10^4$ Pa and the total pressure is $4.8\cdot 10^4$ Pa.

- notion that if x mmoles of N_2O_4 are formed, 2x mmoles of NO_2 are converted 1
- then (0.35 – 2x) mmoles of NO_2 remain 1
- expressing p_{NO_2} and $p_{N_2O_4}$ in terms of x 1
- notion that $K_p = \dfrac{p_{N_2O_4}/p_0}{(p_{NO_2}/p_0)^2}$ 1
- calculation of x 1
- calculation of p_{NO_2} and of $p_{N_2O_4}$ 1
- calculation of the total pressure 1

□9 maximum score 3

Examples of correct answers are:

From the calculation in question 7, it follows that the reaction to the right is exothermic. So, when the temperature decreases, the equilibrium position shifts to the right, which is towards the side of the colourless N_2O_4. The tube in the cold water therefore has the lightest colour.

- the reaction to the right is exothermic, follows from question 7 1
- correct conclusion about the shift in the position of equilibrium 1
- correct conclusion regarding the tube with the lightest colour 1

and

When the temperature decreases, the position of the equilibrium shifts to the side with the lowest entropy, which is the side with the fewest gas molecules, in this case to the right. That is towards the side of the colourless N_2O_4. The tube in the cold water therefore has the lightest colour.

- correct relation between temperature change and entropy change mentioned 1
- correct conclusion about the shift in the position of the equilibrium 1
- correct conclusion regarding the tube with the lightest colour 1

▌Problem 3 Paracetamol from lignin 25 points

▫10 maximum score 2

This is a condensation reaction.

If the answer „This is a substitution reaction.” is given 1

▫11 maximum score 1

A correct answer could look like this:

H_3C—OH or ——OH

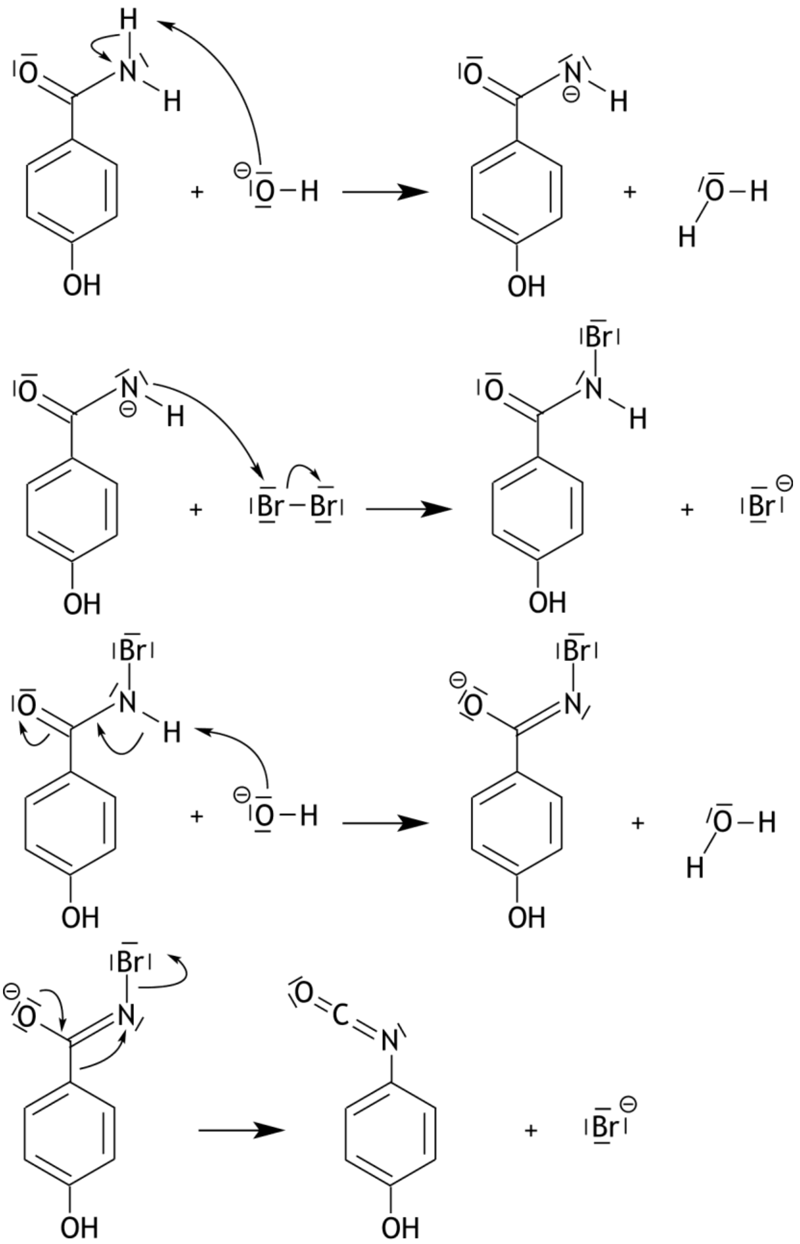
▫12 maximum score 2

A correct answer can be formulated as follows:
An acid-base reaction can occur with the carboxyl group.

If the answer given is that an acid-base reaction can occur with the phenolic OH group 1

▫13 maximum score 6

A correct answer could look like this:



- all relevant electron pairs shown 1
- the first equation correct 1
- the second equation correct 1
- the third equation correct 1
- the fourth equation correct 1
- all formal charges in the correct places 1

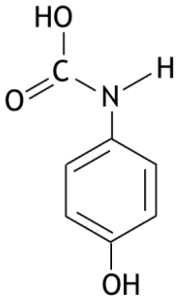
If in an otherwise correct answer one curly arrow is missing and/or incorrectly drawn 5

If in an otherwise correct answer two or more curly arrows are missing and/or incorrectly drawn 4

□14 maximum score 3

A correct answer could look like this:

The structural formula of the addition product is:

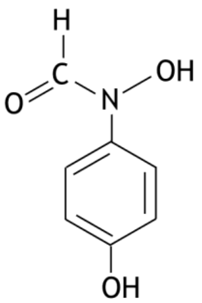


And substance **X** is CO_2.

· correct structual formula of the addition product 2

· substance **X** is CO_2 1

If in an otherwise correct answer the following structural formula is given as the structural formula of the addition product:



2

□15 maximum score 4

A correct answer could look like this:

· in the first structure, two lone pairs on the O atom 1

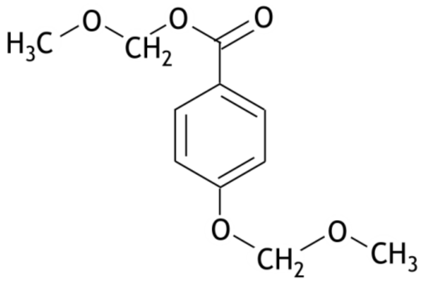
· in the first structure, the formal charge on the C atom 1

· in the second structure, one lone pair on the O atom and a double bond between O and C 1

· in the second structure, the formal charge on the O atom 1

▫16 maximum score 1

A correct answer could look like this:



▫17 maximum score 6

An example of a correct calculation is:

The total degree of conversion is: $0.77 \times 0.83 \times 0.81 \times 0.95 \times 0.93 = 0.46$.

Assume *m* kg paracetamol, that is $\dfrac{m}{151.17}$ kmol, therefore $\dfrac{m}{151.17} \times \dfrac{1}{0.46}$ kmoles of *para*-hydroxybenzoic acid must be converted and that is $\dfrac{m}{151.17} \times \dfrac{1}{0.46} \times 138.12$ kg.

That comes from $\dfrac{m}{151.17} \times \dfrac{1}{0.46} \times 138.12 \times \dfrac{100}{1.2}$ kg lignin and that is in

$\dfrac{m}{151.17} \times \dfrac{1}{0.46} \times 138.12 \times \dfrac{100}{1.2} \times \dfrac{100}{20} = m \times 8.3 \cdot 10^2$ kg poplar wood.

Therefore $F = 8.3 \cdot 10^2$.

- calculation of the total conversion rate 1
- calculation of the molar masses of paracetamol and *para*-hydroxybenzoic acid 1
- calculation of the number of kmoles of paracetamol 1
- calculation of the number of kmoles of *para*-hydroxybenzoic acid that must be converted 1
- conversion to the number of kg of poplar wood 1

Problem 4 Tankyrase inhibitors 8 points

□18 maximum score 2

A correct answer can be formulated as follows:
I and **II** are mirror images of each other, therefore they are enantiomers.

- **I** and **II** are mirror images of each other 1
- therefore: they are enantiomers 1

□19 maximum score 3

A correct answer can be formulated as follows:
In **I**, the two structural components on the cyclobutane ring are oriented *trans*. A *cis* orientation is also possible on the cyclobutane ring. In **II**, a *cis* orientation is also possible.

- in **I**, the two structural components on the cyclobutane ring are oriented *trans* 1
- a *cis* orientation is also possible 1
- in **II**, a *cis* orientation is also possible 1

□20 maximum score 3

An example of a correct calculation is:

For a first order reaction, the following applies: $\ln\frac{[\mathrm{I}]_0}{[\mathrm{I}]_t} = kt$.

When 10% of compound **I** has reacted in 72 hours, 90% remains, so $\ln\frac{100}{90} = k \times 72$. From this it follows that $k = \frac{\ln\frac{100}{90}}{72} = 1.5 \cdot 10^{-3}$ hours^{-1}.

When 1.0% is converted in *t* hours, the following applies $\ln\frac{100}{99} = 1{,}5 \cdot 10^{-3} \times t$, therefore

$t = \frac{\ln\frac{100}{99}}{1.5 \cdot 10^{-3}} = 6.9$ hours.

- use of $\ln\frac{[\mathrm{I}]_0}{[\mathrm{I}]_t} = kt$, possibly already (partially) filled in 1
- $\ln\frac{100}{90} = k \times 72$ and calculation of *k* 1
- $\ln\frac{100}{99} = 1.5 \cdot 10^{-3} \times t$ and calculation of *t* 1

Problem 5 Shono oxidation 11 points

□21 maximum score 2

A correct answer can be formulated as:
I donates electrons. This reaction therefore takes place at the positive electrode.

- **I** donates electrons 1
- therefore: the positive electrode 1

□22 maximum score 2

A correct answer can be formulated as follows:
The methoxylation takes place (at the position) next to the N atom. So the reaction is regioselective.

- the methoxylation takes place next to the N atom 1
- therefore: the reaction is regioselective 1

□23 maximum score 2

A correct answer can be formulated as follows:
The C atom to which the methoxy group attaches is sp^2 hybridized and can therefore react with a methanol molecule from above and from below. So the reaction is not stereoselective.

- the C atom to which the methoxy group attaches is sp^2 hybridized and can react from above and from below with a methanol molecule 1
- therefore: the reaction is not stereoselective 1

Note:
When an answer is given like: „In the diagram, it is not clear whether the methoxy group ends up below or above the six-membered ring. Therefore, the reaction is not stereoselective," accept this as correct.

□24 maximum score 5

An example of a correct calculation is:
A charge of $15 \times 60 \times 60 \times 1.7 = 9.18 \times 10^4$ C is delivered.
0.41 moles of compound **I** produce 0.92×0.41 moles of compound **II**.
For the conversion $2 \times 0.92 \times 0.41$ moles of e^- is needed.
That is $2 \times 0.92 \times 0.41 \times 9.649 \cdot 10^4$ C.

$$\frac{2 \times 0.92 \times 0.41 \times 9.649 \cdot 10^4}{9.18 \cdot 10^4} \times 100\% = 79\%$$

- $15 \times 60 \times 60 \times 1.7 = 9.18 \cdot 10^4$ C 1
- 0.41 moles of compound **I** yield 0.92×0.41 moles of compound **II** 1
- $2 \times 0.92 \times 0.41$ moles of e^- 1
- $2 \times 0.92 \times 0.41 \times 9.649 \cdot 10^4$ C 1
- calculation of the percentage 1

Problem 6 Cobalt complexes 22 points

▫25 maximum score 4

An example of a correct calculation is:

$Co^{3+} + e^- \rightarrow Co^{2+}$ with $E^0 = +x$ V and ΔG_1

$Co^{2+} + 2e^- \rightarrow Co$ with $E^0 = -0.29$ V and ΔG_2

$Co^{3+} + 3e^- \rightarrow Co$ with $E^0 = +0.46$ V and $\Delta G_3 = \Delta G_1 + \Delta G_2$

$\Delta G_1 = -1 \times F \times x$

$\Delta G_2 = -2 \times F \times (-0.29)$

$\Delta G_3 = -3 \times F \times 0.46$

Therefore $-3 \times F \times 0.46 = -1 \times F \times x + -2 \times F \times (-0.29)$. This produces $x = +1.96$.

The standard electrode potential of the half-reaction $Co^{3+} + e^- \rightarrow Co^{2+}$ is therefore +1.96V.

- correct calculation of ΔG_1, ΔG_2 and ΔG_3 2
- $\Delta G_3 = \Delta G_1 + \Delta G_2$ 1
- correct calculation of **x** 1

▫26 maximum score 4

The equation $Co^{3+} + 6\ NH_3 \rightleftharpoons Co(NH_3)_6^{3+}$ is obtained when the following two reactions are combined:

$Co^{3+} + 3e^- \rightarrow Co$ with $E^0 = +0.46$ V

$Co + NH_3 \rightarrow Co(NH_3)_6^{3+} + 3e^-$ with $E^0 = +x$ V

$\Delta E^0 = E^0_{oxidator} - E^0_{reductor} = (0.46 - x)$ V

The following applies: $\Delta_r G = -3 \times F \times \Delta E^0$ and $K = e^{-\frac{\Delta_r G}{RT}} = 1.0 \cdot 10^{33}$, therefore

$-\frac{\Delta_r G}{RT} = \ln 1.0 \cdot 10^{33}$.

This gives $x = -0.19$ V.

- correct half-reactions combined 1
- $\Delta_r G = -3 \times F \times \Delta E^0$ 1
- $K = e^{-\frac{\Delta_r G}{RT}} = 1.0 \cdot 10^{33}$ 1
- rest of the calculation correct 1

▫27 maximum score 3

$A = \varepsilon \times c \times l$

A at 475 nm is 0.112.

$\varepsilon = \frac{0.112}{1.0 \cdot 10^{-3} \times 1,0} = 112\ \text{L mol}^{-1}\ \text{cm}^{-1}$.

- correct formula for Lambert-Beer's law used 1
- absorbance correctly read as 0.112 1
- ε correctly calculated and given with the correct unit 1

Note

When an absorbance of 0.113 is read, accept this as correct.

□28 maximum score 8

An example of a correct calculation is:

In the measured solution there is $[Co(NH_3)_6{}^{3+}] = \frac{0.122}{0.112} \times 1.00 \cdot 10^{-3} = 1.09 \cdot 10^{-3}$ mol L^{-1}.

The 30.0 mg impure product contained $1.09 \cdot 10^{-3} \times 10^{3} \times \frac{100}{1000} = 0.109$ mmol $Co(NH_3)_6Cl_3$

and that is $0.109 \times 267.5 = 29.1$ mg.

The 5.4543 g impure product contained $5.4543 \times \frac{29.1}{30.0} = 5.30$ g $Co(NH_3)_6Cl_3$.

6.0065 g $CoCl_2.6H_2O$ is $\frac{6.0065}{237.9} = 0.02525$ mol and from that a maximum of

0.02525 mol $Co(NH_3)_6Cl_3$ is formed and that is $0.02525 \times 267.5 = 6.75$ g.

The yield is therefore $\frac{5.30}{6.75} \times 100\% = 78.4\%$.

- calculation of the molar masses of $Co(NH_3)_6Cl_3$ and of $CoCl_2{\cdot}6H_2O$: respectively 267.5 g mol^{-1} and 237.9 g mol^{-1} 1
- calculation of the $[Co(NH_3)_6]^{3+}$ in the measured solution 1
- conversion to the number of mmoles of formed $Co(NH_3)_6Cl_3$ in 30.0 mg impure product 1
- conversion to the number of mg of $Co(NH_3)_6Cl_3$ in 30.0 mg impure product 1
- conversion to the number of g of $Co(NH_3)_6Cl_3$ in 5.4543 g impure product 1
- calculation of the number of moles of $Co(NH_3)_6Cl_3$ that can be formed at most (is equal to the number of moles of $CoCl_2{\cdot}6H_2O$ in 6.0065 g $CoCl_2{\cdot}6H_2O$) 1
- conversion to the maximum number of grams of $Co(NH_3)_6Cl_3$ that can be formed 1
- conversion to the yield 1

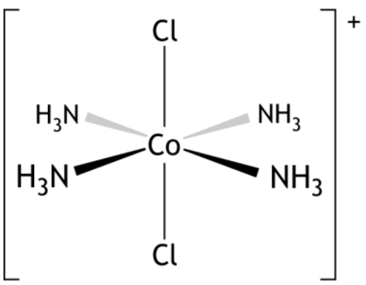
Note:
When an incorrect answer to question 28 is the logical consequence of an incorrect answer to question 27, accept this answer to question 28 as correct.

□29 maximum score 1

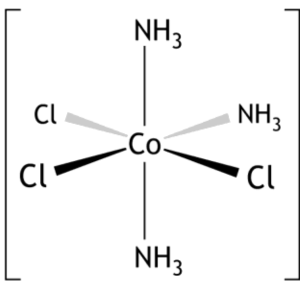
$n = 3 - x$

□30 maximum score 2

A correct answer could look like this:



isomer of complex II



isomer of complex III

per correctly drawn isomer 1

Problem 7 Permanganometry — 11 points

□31 maximum score 4

$3\ MnO_4^- + 8\ H_2O + 13\ e^- \rightarrow Mn_3O_4 + 16\ OH^-$

- MnO_4^- before the arrow and Mn_3O_4 after the arrow and Mn correctly balanced 1
- H_2O before the arrow and OH^- after the arrow 1
- O and H correctly balanced 1
- charge correctly balanced 1

□32 maximum score 7

An example of a correct calculation is:

$25.0 \times 0.0200 - \frac{6.26 \times 0.100}{5} = 0.375$ mmoles of MnO_4^- have reacted with Sn^{2+}.

Therefore the tested sample contained

$$\frac{25.0 \times 0.0200 - \frac{6.26 \times 0.100}{5}}{6} \times 13 = 0.812 \text{ mmoles of } Sn^{2+}$$

and that is $\frac{25.0 \times 0.0200 - \frac{6.26 \times 0.100}{5}}{6} \times 13 \times 214.8 = 174$ mg $SnSO_4$.

The mass percentage tin(II)sulfate in the tested sample is therefore

$$\frac{\frac{25.0 \times 0.0200 - \frac{6.26 \times 0.100}{5}}{6} \times 13 \times 214.8}{200} \times 100\% = 87.2\% .$$

- calculation of the number of mmoles of MnO_4^- in 25.0 mL of 0.0200 M $KMnO_4$ solution and of the number of mmoles of Fe^{2+} in 6.26 mL of 0.100 M $FeSO_4$ solution 1
- calculation of the number of mmoles of MnO_4^- that reacted during the titration 1
- calculation of the number of mmoles of MnO_4^- that reacted with Sn^{2+} 1
- calculation of the number of mmoles of $SnSO_4$ in the tested sample (is equal to the number of mmoles of Sn^{2+} that reacted with MnO_4^-) 1
- calculation of the molar mass of $SnSO_4$ 1
- calculation of the number of mg $SnSO_4$ in the sample 1
- calculation of the mass percentage 1

46th National Chemistry Olympiad

Symeres, Nijmegen

PRACTICAL TEST

Marking scheme

Thursday June 5 2025

Experiment 1 The cracking of PET 40 points

Maximum score 10
The following practical skills will be assessed:
- safety, working cleanly and independence
- handling of the glassware

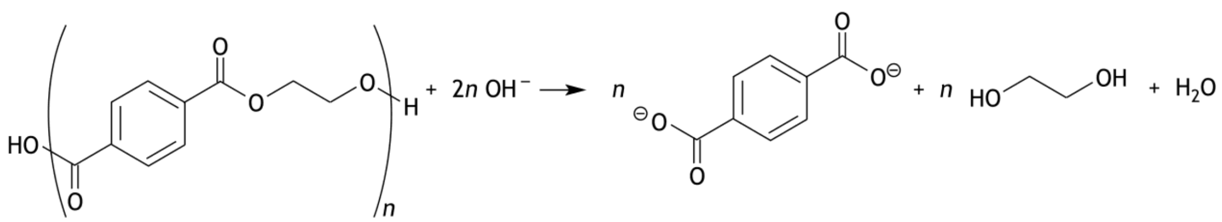
Maximum score 5
Assessment of terephthalic acid yield:
The score for yield is determined by comparing the yield (calculated by the organization) with the yield of an experiment performed by the organization.

Maximum score 5
Assessment of terephthalic acid purity:
The purity of the product is determined using an NMR spectrum, possibly in combination with a Karl-Fischer determination.
The score is determined by comparing the measured purity with the purity of the product obtained in an experiment performed by the organization.

□1 Maximum score 3
- numerical values of the masses noted 1
- accuracy of the numerical values in accordance with the accuracy of the balance used 1
- correct units noted 1

□2 Maximum score 1

□3 Maximum score 6
A correct answer can be expressed as follows:



- structure of PET and OH^- before the arrow 1
- structure of the terephthalate ion after the arrow 1
- structure of ethane-1,2-diol after the arrow 1
- H_2O after the arrow 1
- correct coefficients 2

If in an otherwise correct answer the coefficient 2 is used for OH^- and no coefficients are given after the arrow 5

▫4 Maximum score 5

An example of a correct answer is:

The repeating unit of PET is $C_{10}H_8O_4$. Its molar mass is 192.16 (g mol^{-1}).

Suppose 1000 mg of PET has been weighed, this is equal to $\frac{1000}{192.6} = 5.20$ mmol repeating units.

Therefore $2 \times \frac{1000}{192.16} = 10.4$ mmoles of KOH are needed.

Added were $\frac{0.88 \times 1000}{56.106} = 16$ mmoles of KOH, (an excess).

- the repeating unit of PET is $C_{10}H_8O_4$ (may be implicit from the correct molar mass) 1
- correct molar mass of the repeating unit of PET: 192.16 (g mol^{-1}) 1
- calculation of the number of mmoles of repeating unit in the number of mg of weighed PET 1
- calculation of the number of mmoles of KOH required for the complete conversion of PET 1
- calculation of the number of mmoles of KOH added (and conclusion) 1

▫5 Maximum score 5.

An example of a correct calculation is :

(This example assumes m g PET and a yield of p g terephthalic acid.)

p g terephthalic acid is $\frac{p}{166.13}$ mol.

Therefore, there were (on average) $\frac{p}{166.13}$ moles of repeating units in the PET molecules. That is $\frac{p}{166.13} \times 192.16$ g.

The mass percentage is therefore $\frac{\frac{p}{166.13} \times 192.16}{m} \times 100\,\%$.

- calculation of the molar mass of terephthalic acid 1
- calculation of the number of moles of terephthalic acid formed 1
- notion that the average number of moles of repeating units in the PET molecules is equal to the number of moles of terephthalic acid formed 1
- calculation of the number of grams of PET in the examined piece of PET 1
- calculation of the mass percentage 1

Note:
When the same incorrect value has been used in question 4 and question 5 for the molar mass of the PET repeating unit, do not penalize this in question 5.

Experiment 2 The determination of the amount of sodium perborate monohydrate in one sachet of Bikosan — 40 points

Maximum score 10
The following practical skills are assessed:

- safety, working cleanly and independence
- handling of glassware

□6 Maximum score 8

- the mass of the total contents of the Bikosan sachet and the mass of the Bikosan sample — 1
- burette readings read to two decimal places — 2
- difference between the duplicates of the titrations — 5

The scores for the differences between the duplicates are determined per titration as follows:
If the difference in volume between the duplicates is ≤ 0.10 mL — 5
If 0.10 mL < the difference in volume between the duplicates ≤ 0.20 mL — 4
If 0.20 mL < the difference in volume between the duplicates ≤ 0.30 mL — 3
If 0.30 mL < the difference in volume between the duplicates ≤ 0.50 mL — 2
If 0.50 mL < the difference in volume between the duplicates ≤ 0.70 mL — 1
If the difference in volume between the duplicates is > 0.70 mL — 0
The final score is the average of the scores for both titrations.

□7 Maximum score 14
If the average consumption of the titration with thiosulfate solution is *V* mL and the concentration of thiosulfate solution is *c* mol L^{-1}, then $V \times c$ mmoles of $S_2O_3^{2-}$ are added.

This corresponds to $\frac{V \times c}{2}$ mmol I_2.

Therefore 10.00 mL of the solution from the volumetric flask contained $\frac{V \times c}{2}$ mmol H_2O_2.

The Bikosan sample released $\frac{V \times c}{2} \times \frac{100.0}{10.00}$ mmol H_2O_2, and the Bikosan sample contained

$\frac{V \times c}{2} \times \frac{100.0}{10.00}$ mmol $NaBO_3.H_2O$.

This corresponds to $\frac{V \times c}{2} \times \frac{100.0}{10.00} \times 99.82$ mg $NaBO_3.H_2O$.

If the mass of the contents of the Bikosan sachet is m_1 g and the mass of the Bikosan sample is m_2 g, then the amount of $NaBO_3.H_2O$ in a Bikosan sachet is:

$$\frac{\frac{V \times c}{2} \times \frac{100.0}{10.00} \times 99.82 \times \frac{m_1}{m_2}}{1000} \text{ g.}$$

- calculation of the average consumption 2
- calculation of the number of mmoles of $S_2O_3^{2-}$ that reacted in the titrations 1
- conversion to the number of mmoles of H_2O_2 in the 10.00 mL solution (equals the number of mmoles of I_2 formed) 1
- conversion of the number of mmoles of H_2O_2 in the 10.00 mL solution to the total number of mmoles of H_2O_2 formed from the Bikosan sample 1
- calculation of the molar mass of $NaBO_3.H_2O$ (99.82 g mol^{-1}) 1
- conversion to the amount (in mg) of $NaBO_3.H_2O$. in the Bikosan sample 1
- conversion to the amount (in g) of $NaBO_3.H_2O$ in a Bikosan sachet 2
- result 5

The score for the result is determined by comparing the result (calculated by the organization) with the result of an experiment performed by the organization.

□8 Maximum score 4

An example of a correct answer is:

$4\,e^- + O_2 + 4\,H^+ \rightarrow 2\,H_2O \quad (\times 1)$

$2\,I^- \rightarrow I_2 + 2\,e^- \quad (\times 2)$

$O_2 + 4\,H^+ + 4\,I^- \rightarrow 2\,I_2 + 2\,H_2O$

The reaction with oxygen produces extra iodine. More thiosulfate is therefore used, resulting in a too high value for *V*. The calculated amount of $NaBO_3.H_2O$ in a Bikosan sachet will be too high.

- in the total reaction equation O_2 and H^+ before the arrow and H_2O after the arrow 1
- in the total reaction equation I^- before the arrow and I_2 after the arrow and correct coefficients 1
- correct explanation that a too high value of *V* is used in the calculation 1
- consistent conclusion 1

□9 Maximum score 4

A correct answer can be formulated as follows:
Hydrogen peroxide can also act as a reducing agent, and permanganate is a strong enough oxidizing agent (in an acidic environment) to react with it. Therefore, it is possible. You should then add the sulfuric acid solution to the (10.00 mL) Bikosan solution and titrate with the potassium permanganate solution.

- hydrogen peroxide can also react as a reducing agent 1
- permanganate (in an acidic environment) is a strong enough oxidizing agent to react with hydrogen peroxide (possibly with reference to the table of redox potentials from the data booklet) 1
- correct conclusion 1
- acidify the Bikosan solution and titrate with the potassium permanganate solution 1

If an answer is given such as: „It is not possible because two oxidizers cannot react with each other.” 1