

DUTCH NATIONAL CHEMISTRY OLYMPIAD

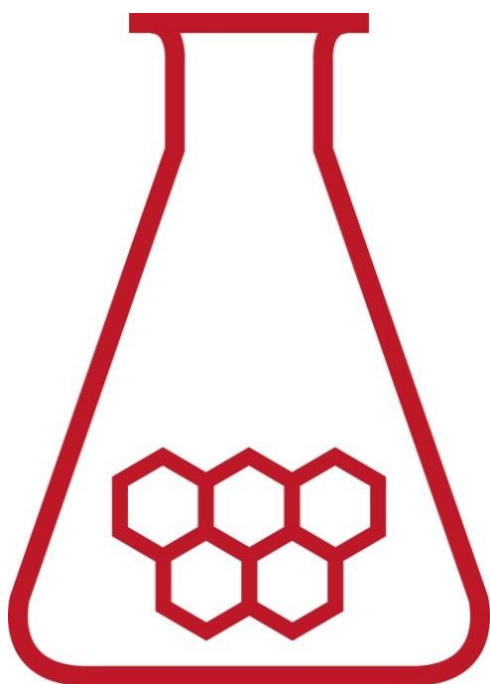
2023

Assignments and Marking schemes

Preliminary round 1

Preliminary round 2

Final round



**SCHEIKUNDE
OLYMPIADE**



55TH INTERNATIONAL
CHEMISTRY OLYMPIAD
SWITZERLAND 2023



Universiteit Leiden

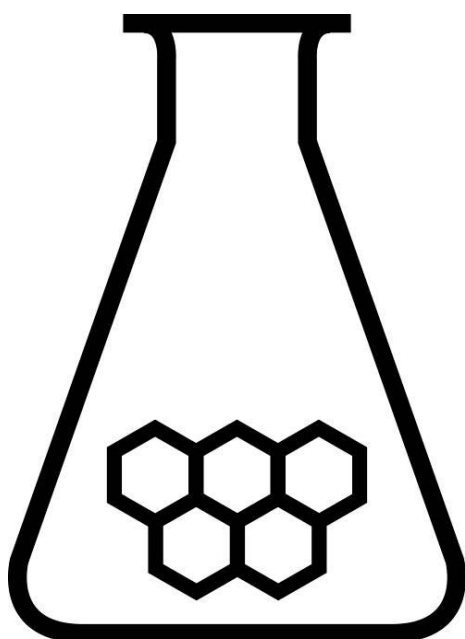
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NATIONAL CHEMISTRY OLYMPIAD 2023

ASSIGNMENTS PRELIMINARY ROUND 1

To be conducted from 11 until 27 January 2023



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- This preliminary round consists of 20 multiple choice questions divided over 8 topics and 2 problems with a total of 14 open questions as well as an answer sheet for the multiple-choice questions.
- Use the answer sheet to answer the multiple-choice questions. Use for each problem with open questions a separate answer sheet. Don't forget to write your name on it.
- The maximum score for this work is 77 points.
- The preliminary round takes up to two full hours.
- Required materials: (graphic) calculator and BINAS 6th edition or ScienceData 1st edition or BINAS 5th edition, English version.
- For each question the number of points you can score are given.
- Unless otherwise stated, standard conditions apply: $T = 298 \text{ K}$ and $p = p_0$.

This exam came about with the support of the following people:

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Problem 1 Multiple-choice questions

(total 40 points)

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

Marks: 2 points for each correct answer.

Carbon chemistry

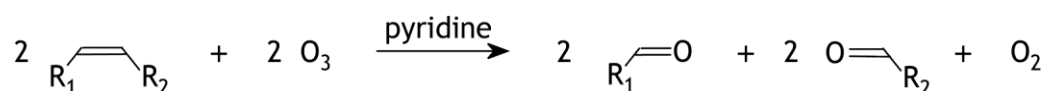
- 1 The hydrolysis of a molecule of trehalose produces two molecules of glucose. What is the molecular formula of trehalose?

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

- 2 Epoxides are carbon compounds with the group $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C} - \text{C} \end{array}$ in the molecule.
How many epoxides with molecular formula C_4H_8O exist? Take stereoisomerism into account.

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

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



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

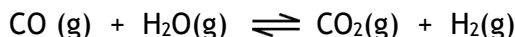
Which of the three alkenes above produces only **one** other substance, besides O_2 , in the above reaction?

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

Reaction rate and equilibrium

4

In an investigation into the following reaction



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

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

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

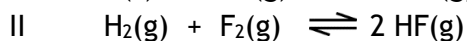
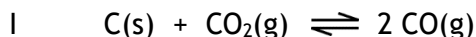
reaction to the right

amount of H_2

- | | | |
|----------|-------------|------|
| A | Endothermic | more |
| B | Endothermic | less |
| C | Exothermic | more |
| D | Exothermic | less |

5

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



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

6

In the reaction $\text{N}_2\text{(g)} + 3 \text{H}_2\text{(g)} \rightarrow 2 \text{NH}_3\text{(g)}$ the rate at which H_2 reacts is equal to $1.2 \cdot 10^{-3} \text{ mol s}^{-1}$.

What is the rate of formation of NH_3 ?

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

Structures and formulas

- 7 Which type(s) of bond(s) is/are present in solid magnesium sulphite?
- A only covalent bonds
 - B only covalent bonds and ionic bonds
 - C only covalent bonds and metallic bonds
 - D only covalent bonds, ionic bonds and metallic bonds
 - E only ionic bonds
 - F only ionic bonds and metallic bonds
 - G only metallic bonds
- 8 Which of the following statements about a molecule of oxygen difluoride, OF_2 , is/are correct?
- I A molecule of oxygen difluoride is linear.
 - II A molecule of oxygen difluoride is a dipole molecule.
- A none of them
 - B only I
 - C only II
 - D Both
- 9 How many electrons are represented in the Lewis structure of a persulfate ion, SO_5^{2-} ?
- A 32
 - B 34
 - C 36
 - D 38

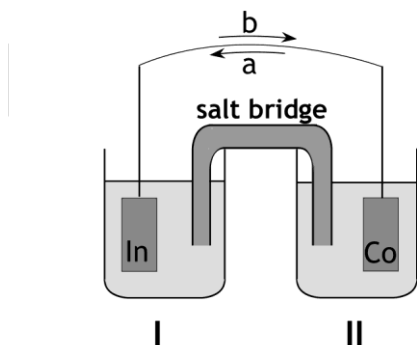
pH / acid-base

- 10 Some sodium hydroxide solution is added to a solution of ammonium chloride (NH_4Cl). The resulting solution has a pH of 9.50. What % of the NH_4^+ has been converted to NH_3 ?
- A 23%
 - B 36%
 - C 44%
 - D 56%
 - E 64%
 - F 77%

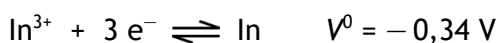
- 11 200 mL of 0.0657 M sodium hydroxide solution, 140 mL of 0.107 M hydrochloric acid and 160 mL of water are mixed.
What is the pH of the resulting solution?
- A 2.27
B 2.43
C 2.74
D 3.04

Redox and electrochemistry

- 12 In a basic solution, chlorine dioxide reacts according to the incomplete reaction equation below. In this incomplete reaction equation only the coefficients are missing.
 $\text{ClO}_2(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{ClO}_2^-(\text{aq}) + \text{ClO}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$
What is the ratio between the coefficients of ClO_2 and ClO_3^- in the balanced reaction equation of this reaction?
- A $\text{ClO}_2 : \text{ClO}_3^- = 1 : 1$
B $\text{ClO}_2 : \text{ClO}_3^- = 2 : 1$
C $\text{ClO}_2 : \text{ClO}_3^- = 3 : 1$
D $\text{ClO}_2 : \text{ClO}_3^- = 3 : 2$
E $\text{ClO}_2 : \text{ClO}_3^- = 4 : 1$
- 13 In the electrochemical cell below, half-cell I contains a 1.0 M solution of indium(III) nitrate with an indium electrode and half-cell II contains a 1.0 M solution of cobalt(II) nitrate with a cobalt electrode.



The following standard electrode potentials apply:



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

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

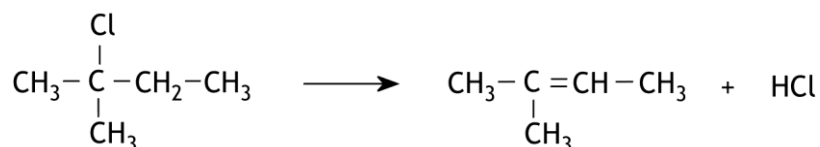
Chemical calculations

- 14 A certain kind of vinegar contains 5.00% by mass of acetic acid, CH_3COOH ($M = 60.0 \text{ g mol}^{-1}$).
- What is the molarity of acetic acid in this vinegar? The density of the vinegar is 1.00 g mL^{-1} .
- A 0.833 mol L^{-1}
B 1.00 mol L^{-1}
C 1.20 mol L^{-1}
D 3.00 mol L^{-1}
- 15 3.00 g of an alloy of copper and silver is added to excess of diluted nitric acid. A solution is formed. An excess of sodium phosphate solution is then added to the formed solution. The resulting suspension is filtered and the residue dried and weighed. The residue consists of silver phosphate ($M = 418.58 \text{ g mol}^{-1}$) and copper(II) phosphate ($M = 380.59 \text{ g mol}^{-1}$). The mass of the dried residue is 4.25 g.
- What is the mass percentage of silver in the alloy?
- A 10% à 11%
B 17% à 18%
C 82% à 83%
D 89% à 90%

Thermochemistry and Green chemistry

- 16 Epoxyethane is prepared industrially from the reaction of ethene with oxygen:
- $$2 \text{C}_2\text{H}_4(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{C}_2\text{H}_4\text{O}(\text{g})$$
- The enthalpy change (at 298 K, $p = p_0$) of this synthesis is -148 kJ per mole of ethene.
- What is the enthalpy of formation (at 298 K, $p = p_0$) of epoxyethane? Given: the enthalpy of formation (at 298 K, $p = p_0$) of ethene is $+52 \text{ kJ mol}^{-1}$.
- A -200 kJ mol^{-1}
B -148 kJ mol^{-1}
C -96 kJ mol^{-1}
D $+96 \text{ kJ mol}^{-1}$
E $+148 \text{ kJ mol}^{-1}$
F $+200 \text{ kJ mol}^{-1}$

- 17 An example of an elimination reaction is shown below:



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

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

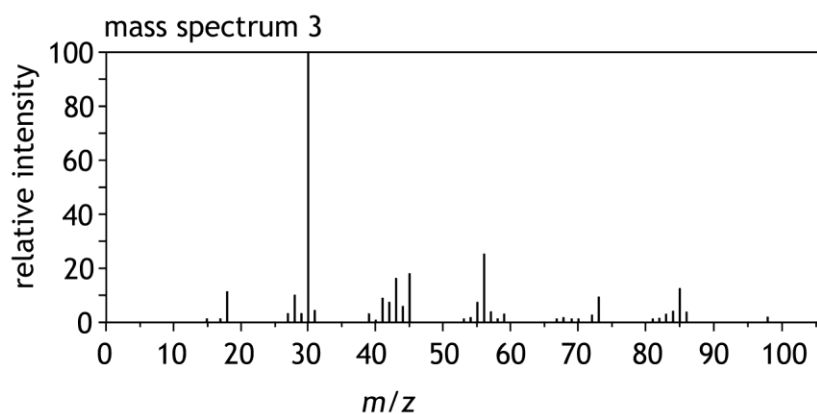
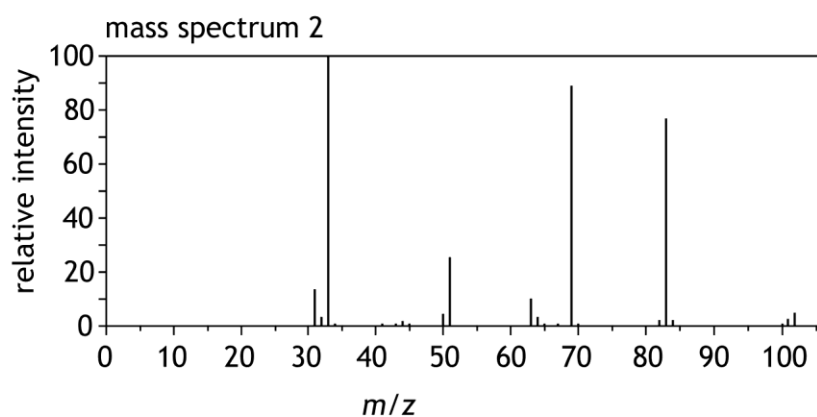
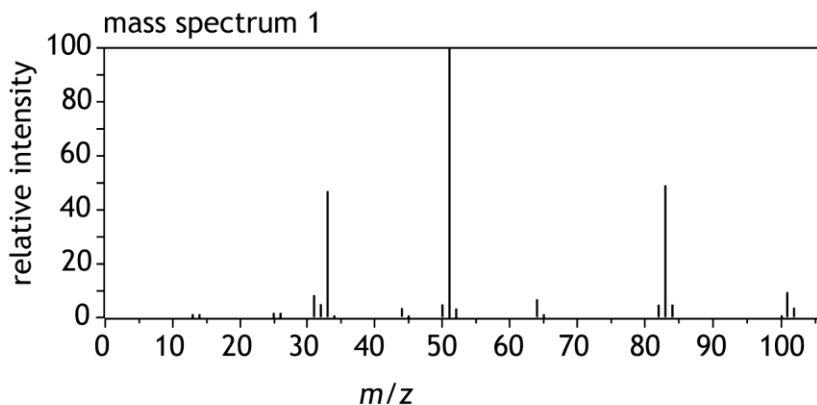
- A 0.17
B 0.51
C 0.52
D 0.97
E 1.9
- 18 We compare the absolute values of the enthalpies of combustion, expressed in different units, of the following gases: methane, methanal and hydrogen.
Which gas has the greatest enthalpy of combustion (at 298 K, $p = p_0$) expressed in J kg^{-1} and which gas has the greatest enthalpy of combustion (at 298 K, $p = p_0$) expressed in J m^{-3} ?
Use Binas tables 56 and 57A or ScienceData tables 8.7 and 9.2.
- | | greatest enthalpy of combustion in J kg^{-1} | greatest enthalpy of combustion in J m^{-3} |
|---|---|--|
| A | methane | methane |
| B | methane | methanal |
| C | methane | hydrogen |
| D | methanal | methane |
| E | methanal | methanal |
| F | methanal | hydrogen |
| G | hydrogen | methane |
| H | hydrogen | methanal |
| I | hydrogen | hydrogen |

Analysis

- 19 Gerrit examines a solution of an unknown salt in water.
He performs two tests:
Test 1: He adds hydrochloric acid to a part of the solution of the unknown salt.
A gas and a solution are formed.
Test 2: He adds a solution of barium iodide to a part of the solution of the unknown salt. A solution is formed.
Which of the following salts could be the unknown salt?
- A $\text{Ba}(\text{OH})_2$
B K_2CO_3
C $\text{Mg}(\text{HCO}_3)_2$
D NaOH
E $\text{Pb}(\text{HCO}_3)_2$

20

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



Which spectrum belongs to which substance?

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

Open questions

(total 37 points)

Problem 2 Gold in solution

(19 points)

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

Aqua regia has a very low pH.

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

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

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

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

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

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



The only thing missing from this equation are the coefficients.

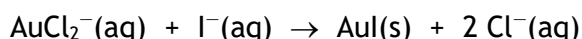
- 4 Copy the equation above to your answer sheet and complete it. 3

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

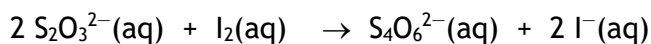
First, the equilibrium mixture is filtered. Afterwards, the $[\text{AuCl}_4^-]$ in the filtrate is determined. For this, an excess of potassium iodide solution is added to a 10.00 mL sample of the filtrate, which causes the following reactions:



and



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



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

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

- 5 Calculate the $[\text{AuCl}_4^-]$ in mol L^{-1} of the investigated equilibrium mixture. 3

After the $[\text{AuCl}_4^-]$ is known, more has to be determined in order to be able to calculate the equilibrium constant.

The $[\text{AuCl}_2^-]$ in the equilibrium mixture can be calculated by filtering the mixture that was created after the titration and determining the mass of the residue. With this, and the amount of mmol of AuCl_4^- in the 10.00 mL sample, you can calculate how many mmol of AuCl_2^- were present in the 10.00 mL sample.

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

By determining the pH of the equilibrium mixture, the $[\text{Cl}^-]$ in the equilibrium mixture can be calculated. This is because the $[\text{H}_3\text{O}^+]$, the $[\text{AuCl}_4^-]$, the $[\text{AuCl}_2^-]$ and the $[\text{Cl}^-]$ are related.

- 7 What is the relation between the $[\text{H}_3\text{O}^+]$, the $[\text{AuCl}_4^-]$, the $[\text{AuCl}_2^-]$ and the $[\text{Cl}^-]$ in the equilibrium mixture? Explain your answer. 2

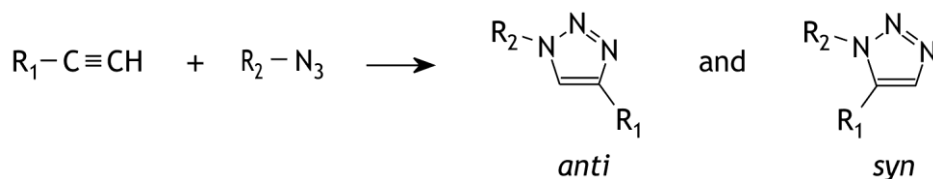
- 8 Does the concentration of Au still need to be determined in order to calculate the equilibrium constant of equilibrium I? Explain your answer. 2

Problem 3 Click Chemistry

(18 points)

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

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

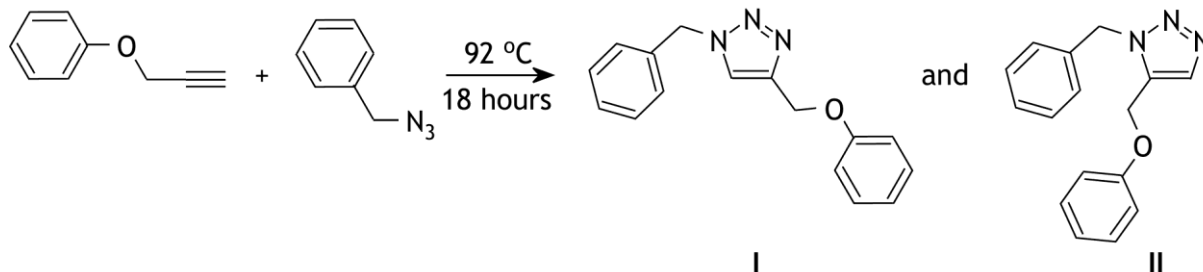


In many cases equal amounts of the *anti* and *syn* product are formed.

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

2

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



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

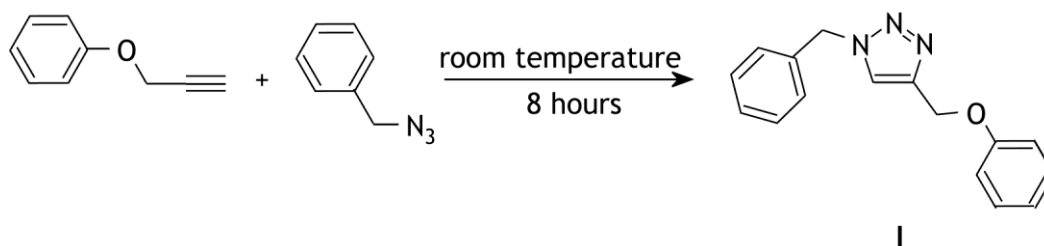
In an experiment in which 10 grams of the alkyne reacted with the appropriate amount of the azide, 11 grams of the *anti* product (I) had formed.

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

5

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

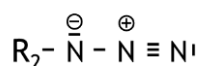
The production of compound I with a copper(I) catalyst is shown below.



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

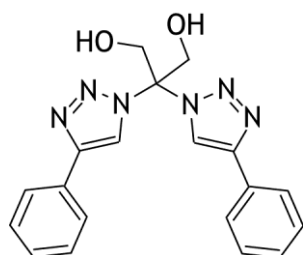
- 11 Explain for principles 2 and 6 why the reaction with the use of the copper(I) catalyst is 'greener' than the reaction without a catalyst (see BINAS-table 97F or ScienceData table 38.6 or the information on page 15 of this booklet). Use information given to you in this exercise. 2

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



- 12 Draw the other mesomeric structure. If applicable, also give the formal charges. 2
- 13 Give a possible reaction mechanism for the forming of the *anti* product from $R_1 - C \equiv CH$ and $R_2 - N_3$. 4
- Use the mesomeric structure of the azide given above.
 - Clarify how the electron pairs move with the forming and breaking of bonds by using curved arrows (\curvearrowright).
 - Show all the non-bonding electron pairs in the product.

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



- 14 Provide the structural formula of the two chemicals used to synthesise the chemical with the above structural formula. Write the azide group using N_3 . Also mention what catalyst was used during this reaction, a copper(I) catalyst or a ruthenium catalyst. 3

Green Chemistry

The twelve principles of green chemistry are:

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

atom economy
$$\frac{m_{\text{product}}}{m_{\text{starting materials}}} \times 100\%$$

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

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

44th National Chemistry Olympiad 2023 preliminary round 1

Answer sheet Multiple choice questions

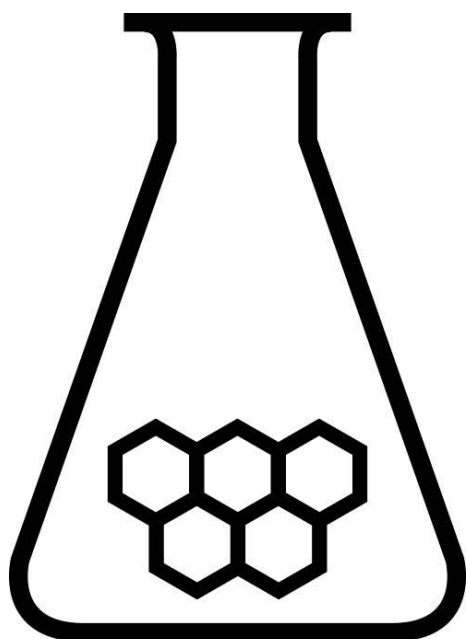
name:

no.	choice letters	(score)
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NATIONAL CHEMISTRY OLYMPIAD 2023

MARKING SCHEME PRELIMINARY ROUND 1

To be conducted from January 11 until Januari 27 2023



SCHEIKUNDE OLYMPIADE



Universiteit Leiden

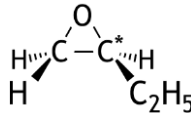
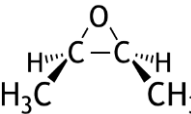
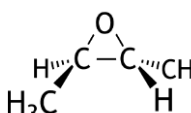
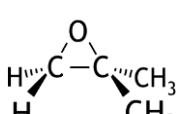
- This preliminary round consists of 20 multiple choice questions divided over 8 topics and 2 problems with a total of 14 open questions.
- The maximum score for this work is 77 points.
- Required materials: (graphic) calculator and BINAS 6th edition or ScienceData 1st edition or BINAS 5th edition, English version.
- For each question the number of points you can score are given.
- While assigning scores for the work, this marking scheme has to be used. Moreover the general rules for the Dutch Central Exams apply.

Problem 1 Multiple-choice questions

(total 40 points)

For every correct answer: 2 points

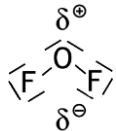
Carbon chemistry

1	D	Glucose has the molecular formula $C_6H_{12}O_6$. Together, the two glucose molecules have 12 C, 24 H and 12 O. During hydrolysis, H_2O is added to one molecule of trehalose. Therefore one molecule of trehalose contains 12 C, 22 H and 11 O.
2	E	 <p>1,2-epoxybutane C* is asymmetric, so two stereoisomers</p>  <p><i>cis</i>-2,3-epoxybutane the mirror image is identical to the original, so one stereoisomer</p>  <p><i>trans</i>-2,3-epoxybutane the mirror image is not identical to the original, so two stereoisomers</p>  <p>2-methylepoxypropane the mirror image is identical to the original, no asymmetrical carbon atom so one stereoisomer</p>
3	G	With cyclopentene, only pentanedial is formed. With pent-2-ene, ethanal and propanal is formed. With hex-3-ene, only propanal is formed.

Reaction rate and equilibrium

4	D	When the temperature is increased, the position of the equilibrium is shifted to the endothermic side, which in this case is to the left. The reaction to the right is therefore exothermic. At higher temperature, the equilibrium constant decreases and less H_2 is present during equilibrium at higher temperature when compared to lower temperature.
5	F	When the volume is increased, the position of the equilibrium, when gases are involved, will shift to the side with the largest amount of mol of gas. That is the case in I and III.
6	A	The rate at which NH_3 is produced, is $\frac{2}{3} \times 1.2 \cdot 10^{-3} = 8.0 \cdot 10^{-4} \text{ mol s}^{-1}$.

Structures and formulas

7	B	Magnesium sulfite is MgSO_3 . The compound is made up of Mg^{2+} ions and SO_3^{2-} ions. Between the Mg^{2+} and the SO_3^{2-} there is an ionic bond. In the SO_3^{2-} ions there are atomic bonds present.
8	C	An OF_2 molecule is bent, just like a H_2O molecule. The fluorine atom has a larger electronegativity than the oxygen atom. So: 
9	D	The number of valence electrons of an S atom is 6 and of the five O atoms $5 \times 6 = 30$. Two extra electrons are responsible for the $2-$ charge. So there will be 38 electrons represented in the Lewis structure.

pH / acid-base

10	E	From the K_z of NH_4^+ follows: $\frac{[\text{NH}_3]}{[\text{NH}_4^+]} = \frac{K_z}{[\text{H}_3\text{O}^+]} = \frac{5.6 \cdot 10^{-10}}{10^{-9.50}} = 1.77$ The percentage conversion of NH_4^+ = $\frac{1.77}{2.77} \times 100\% = 64\%$.
11	B	The caustic soda contains $200 \times 0.0657 = 13.14 \text{ mmol OH}^-$. The hydrochloric acid contains $140 \times 0.107 = 14.98 \text{ mmol H}^+$. After the reaction between OH^- and H^+ is completed, the amount of H^+ left over is $14.98 - 13.14 = 1.84 \text{ mmol}$. $\text{pH} = -\log \frac{1.84 \text{ (mmol)}}{200 \text{ (mL)} + 140 \text{ (mL)} + 160 \text{ (mL)}} = 2.43$

Redox and electrochemistry

12	B	The reaction equation is: $2 \text{ClO}_2(\text{g}) + 2 \text{OH}^-(\text{aq}) \rightarrow \text{ClO}_2^-(\text{aq}) + \text{ClO}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$
13	C	Indium has the lowest V^0 value and will therefore act as reducing agent. The electrons will move from the In electrode to the Co electrode through the wire, as indicated by arrow b. The EMF is $V_{\text{ox}} - V_{\text{red}} = -0.28 \text{ V} - (-0.34 \text{ V}) = 0.06 \text{ V}$.

Chemical calculations

14	A	$\frac{\frac{5.00 (\%)}{100 (\%)} \times 1.00 (\text{g mL}^{-1}) \times 10^3 (\text{mL L}^{-1})}{60.0 (\text{g mol}^{-1})} = 0.833 (\text{mol L}^{-1})$
15	C	<p>Two examples of a correct calculation are:</p> <p>Suppose there was x g silver and y g Cu in the 3.00 g alloy, then $x + y = 3.00$ (1).</p> <p>$\frac{1}{3} \times \frac{x}{107.9}$ mol Ag_3PO_4 arises and that is equal to $\frac{1}{3} \times \frac{x}{107.9} \times 418.58$ g Ag_3PO_4 and</p> <p>$\frac{1}{3} \times \frac{y}{63.55}$ mol $\text{Cu}_3(\text{PO}_4)_2$ and that is $\frac{1}{3} \times \frac{y}{63.55} \times 380.59$ g $\text{Cu}_3(\text{PO}_4)_2$.</p> <p>So $\frac{1}{3} \times \frac{x}{107.9} \times 418.58 + \frac{1}{3} \times \frac{y}{63.55} \times 380.59 = 4.25$ (2).</p> <p>(1) and (2) are a set of two equations with two unknowns. Solving this will produce $x = 2.47$.</p> <p>There was therefore 2.47 g silver in the 3.00 g alloy, which is $\frac{2.47}{3.00} \times 100\% = 82.3\%$.</p> <p>And</p> <p>If the sample was made up of 100% silver, the residue would have contained only Ag_3PO_4 and the mass would be $\frac{1}{3} \times \frac{3.00}{107.9} \times 418.58 = 3.88$ g.</p> <p>If the sample was made up of only copper, the residue would have contained only $\text{Cu}_3(\text{PO}_4)_2$ and the mass would be $\frac{1}{3} \times \frac{3.00}{63.55} \times 380.59 = 5.99$ g.</p> <p>The mass of the residue is 4.25 g.</p> <p>If the percentage mass of Ag is equal to y, interpolation will result in the following:</p> $\frac{4.25 - 3.88}{5.99 - 3.88} = \frac{100 - y}{100} \text{ and } y = 82\%.$

Thermochemistry and Green chemistry

16	C	$\Delta H_{\text{reaction}} = \Delta H_{\text{formation, epoxyethane}} - \Delta H_{\text{formation, ethene}}$ $\Delta H_{\text{formation, epoxyethane}} = \Delta H_{\text{reaction}} + \Delta H_{\text{formation, ethene}} = -148 + (+52) = -96 \text{ kJ mol}^{-1}$																
17	D	<p>From 1 mole of 2-chloro-2-methylbutane, 0.77 mole of 2-methylbut-2-ene is produced.</p> $m_{\text{reactant}} = 5 \times 12.01 + 11 \times 1.008 + 35.45 = 106.59 \text{ g}$ $m_{\text{product}} = 0.77 \times (5 \times 12.01 + 10 \times 1.008) = 0.77 \times 70.13 = 54.00 \text{ g}$ <p>So E-factor = $\frac{106.59 - 54}{54} = 0.97$.</p>																
18	G	<p>Absolute values of the combustion enthalpies:</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th></th> <th>in J mol^{-1}</th> <th>in J kg^{-1}</th> <th>in J m^{-3}</th> </tr> </thead> <tbody> <tr> <td>Methane, CH_4</td> <td>$8.90 \cdot 10^5$</td> <td>$\frac{8.90 \cdot 10^5}{16.0} \times 10^3 = 5.56 \cdot 10^7$</td> <td>largest</td> </tr> <tr> <td>Methanal, CH_2O</td> <td>$5.50 \cdot 10^5$</td> <td>$\frac{5.50 \cdot 10^5}{30.0} \times 10^3 = 1.83 \cdot 10^7$</td> <td></td> </tr> <tr> <td>Hydrogen, H_2</td> <td>$2.86 \cdot 10^5$</td> <td>$\frac{2.86 \cdot 10^5}{2.02} \times 10^3 = 1.42 \cdot 10^8$</td> <td></td> </tr> </tbody> </table> <p>So the largest.</p> <p>The enthalpy of combustion in J m^{-3} is proportionate to the enthalpy of combustion in J mol^{-1}, therefore that of methane is the largest.</p>		in J mol^{-1}	in J kg^{-1}	in J m^{-3}	Methane, CH_4	$8.90 \cdot 10^5$	$\frac{8.90 \cdot 10^5}{16.0} \times 10^3 = 5.56 \cdot 10^7$	largest	Methanal, CH_2O	$5.50 \cdot 10^5$	$\frac{5.50 \cdot 10^5}{30.0} \times 10^3 = 1.83 \cdot 10^7$		Hydrogen, H_2	$2.86 \cdot 10^5$	$\frac{2.86 \cdot 10^5}{2.02} \times 10^3 = 1.42 \cdot 10^8$	
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Analysis

19	C	<p>In test 1 a gas is produced. NaOH and Ba(OH)_2 are then eliminated because upon reaction with an acid, H_2O is produced instead of CO_2, which is produced in the following reactions:</p> $2 \text{H}_3\text{O}^+ + \text{CO}_3^{2-} \rightarrow 3 \text{H}_2\text{O} + \text{CO}_2(\text{g})$ $\text{H}_3\text{O}^+ + \text{HCO}_3^- \rightarrow 2 \text{H}_2\text{O} + \text{CO}_2(\text{g})$ <p>In test 2 no precipitate is produced, therefore $\text{Pb(HCO}_3)_2$ can be eliminated because a PbI_2 precipitate would be produced. K_2CO_3 can also be eliminated because it would produce a BaCO_3 precipitate.</p>
20	F	<p>In spectrum 2 the peak at $m/z = 69$ is an indication for CF_3^+ and this only occurs in 1,1,1,2-tetrafluoroethane.</p> <p>In spectrum 3 the peak at $m/z = 30$ is an indication for CH_2NH_2^+. This only occurs in pentane-1,5-diamine.</p> <p>The peak at $m/z = 51$ is also an indication for 1,1,2,2-tetrafluoroethane. Which is for CHF_2^+, which will most probably occur at 1,1,2,2-tetrafluoroethane.</p> <p>In spectrum 1 the peak at $m/z = 51$ is relatively the largest, it is therefore 1,1,2,2-tetrafluoroethane.</p>

Open questions

(total 37 points)

Problem 2 Gold in solution

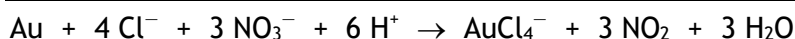
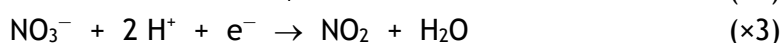
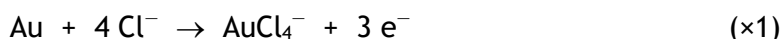
19 points

□1 Maximum score 3

$$\text{pH} = -\log \frac{3.0 \times 12 + 1.0 \times 15}{4.0} = -1.11$$

- calculation of the $[\text{H}_3\text{O}^+]$ in aqua regia (equals the average molarity): $\frac{3.0 \times 12 + 1.0 \times 15}{4.0}$ 1
- calculation of the pH 1
- correct significance 1

□2 Maximum score 3



- equation of the half-reaction of Au is correct 1
- equation of the half-reaction of NO_3^- is correct 1
- combination of both half-reaction equations into complete reaction equation 1

□3 Maximum score 1

An example of a correct answer is:

The V^0 values are for 1.00 M solutions. The molarity of nitric acid in aqua regia is much higher.

Note:

When an answer is given like: „The V^0 values are for a temperature of 298 K; the temperature during the reaction of gold with aqua regia could be different.‟, give full marks.

□4 Maximum score 3



- Au balance correct 1
- Cl balance correct 1
- charge balance correct 1

If the following equation is given:



□5 Maximum score 3

$$[\text{AuCl}_4^-] = \frac{(5.34 \times 0.0100)}{10.00} = 2.67 \cdot 10^{-3} \text{ (mol L}^{-1}\text{)}$$

- calculation of the amount of mmoles of $\text{S}_2\text{O}_3^{2-}$ that was used for the titration: multiply 5.34 (mL) with 0.0100 (mmol L^{-1}) 1
- calculation of the amount of mmoles of AuCl_4^- in the investigated solution (equals the amount of mmoles of I_2 produced): divide the amount of mmoles of $\text{S}_2\text{O}_3^{2-}$ that was used for the titration by 2 1
- calculation of the $[\text{AuCl}_4^-]$ in the investigated solution: divide the amount of mmoles of AuCl_4^- in the investigated solution by 10.00 (mL) 1

□6 Maximum score 2

An example of a correct answer is:

After the titration, all of the Au has ended up as AuI , so the amount of mmoles of AuI is the sum of the amount of mmoles of AuCl_2^- and the amount of mmoles of AuCl_4^- in the 10.00 mL sample.

- notion that after titration, all Au has ended up as AuI . 1
- conclusion 1

□7 Maximum score 2

An example of a correct answer is:

The solution has to be electrically neutral, therefore:

$$[\text{H}_3\text{O}^+] = [\text{AuCl}_2^-] + [\text{AuCl}_4^-] + [\text{Cl}^-]$$

- notion that solution must be electrically neutral 1
- conclusion 1

□8 Maximum score 2

An example of a correct answer is:

No, because gold is a solid and solids are not included in the reaction quotient / equilibrium condition.

- gold is a solid 1
- solids are not included in the reaction quotient / equilibrium condition and conclusion 1

If answer is given like: „No, because gold is a solid and solids are not included in the equilibrium constant.” 1

Note:

When an answer is given like: „No, because gold is a solid and you cannot determine the concentration of solids in a solution”, give full marks.

Problem 3 Click Chemistry

18 points

□9 Maximum score 2

An example of a correct answer is:

They are not stereoisomers because the R₁ is located on different positions in the two molecules.

- the R₁ group is located on different positions in the two molecules 1
- conclusion 1

□10 Maximum score 5

Examples of correct answers are:

$$\frac{11}{\frac{1.6}{2.6} \times \left(10 + \frac{133.16}{132.15} \times 10 \right)} \times 100\% = 89\%$$

- calculation of the molar masses of the alkyne (132.15 g mol⁻¹) and the azide (133.16 g mol⁻¹) 1
 - calculation of the amount of g of azide that reacts with 10 g of the alkyne: the molar mass of the azide divided by the molar mass of the alkyne, and the quotient multiplied by 10 (g) 1
 - calculation of the total mass of the products that are produced during 100% completion (is equal to the total mass of the starting materials): 10 (g) added to the amount of g of azide that reacts with 10 g alkyne 1
 - calculation of the amount of g of *anti*-product that is produced during 100% completion: the total mass of the products that are produced during 100% completion multiplied by 1.6 and divided by 2.6 1
 - calculation of the conversion percentage: 11 (g) divided by the amount of g of *anti*-product that is produced during 100% completion and multiplied by 100% 1
- and

$$\frac{11 + \frac{11}{1.6}}{10 + \frac{133.16}{132.15} \times 10} \times 100\% = 89\%$$

- calculation of the molar masses of the alkyne (132.15 g mol⁻¹) and the azide (133.16 g mol⁻¹) 1
 - calculation of the amount of g of azide that reacts with 10 g of the alkyne: the molar mass of the azide divided by the molar mass of the alkyne, and the quotient multiplied by 10 (g) 1
 - calculation of the total mass of the products that are produced during 100% completion (is equal to the total mass of the starting materials): 10 (g) added to the amount of g of azide that reacts with 10 g alkyne 1
 - calculation of the amount of g of *syn*-product that is produced experimentally: 11 (g) divided by 1.6 1
 - calculation of the conversion percentage: the amount of g of *syn*-product that is produced experimentally, added to 11 (g) and the sum divided by the total mass of the starting materials, and the quotient multiplied by 100% 1
- and

$\frac{10}{132.15}$ moles of alkyne react. So during 100% completion, a total of $\frac{10}{132.15}$ moles of *anti*-product and *syn*-product should be produced. Suppose that x moles of *syn*-product are produced, then $1.6x$ moles of *anti*-product are produced.

Therefore $\frac{10}{132.15} = 1.6x + x$, which produces $x = 0.0291$. During 100% completion

1.6×0.0291 moles of *anti*-product will be produced. Which is $1.6 \times 0.0291 \times 265.31 = 12.4$ g.

There is 11 g, therefore the conversion percentage was $\frac{11}{12.4} \times 100\% = 89\%$.

- calculation of the molar masses of the alkyne ($132.15 \text{ g mol}^{-1}$) and the product ($265.31 \text{ g mol}^{-1}$) 1
- calculation of the total amount of moles of *anti*- and *syn*-product that is produced (which is equal to the amount of moles of alkyne that has reacted): 10 (g) divided by the molar mass of the alkyne 1
- calculation of the amount of moles of *syn*-product that has been produced during 100% completion: solve for x from $\frac{10}{132.15} = 1.6x + x$ 1
- calculation of the amount of g of *anti*-product that is produced during 100% completion: the amount of moles of *syn*-product that is produced during 100% completion multiplied by 1.6 and by the molar mass of the product 1
- calculation of the conversion percentage: 11 (g) divided by the amount of g of *anti*-product that is produced during 100% completion and multiplied by 100% 1

□11 Maximum score 2

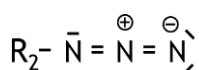
An example of a correct answer is:

Principle 2: Two products are formed in the reaction without a catalyst. In this case the atom economy is lower than 100%. In the reaction involving a catalyst all atoms end up in the product. In this case the atom economy is 100%.

Principle 6: The reaction involving a catalyst (is faster and) takes place at a lower temperature when compared to the reaction without a catalyst.

- argument for principle 2 is correct 1
- argument for principle 6 is correct 1

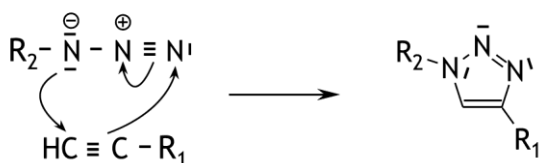
□12 Maximum score 2



- there is a double bond between the N atom on the left and the N atom in the middle and there is a double bond between the N atom in the middle and the N atom on the right 1
- non-bonding electron pairs and charges in the correct position 1

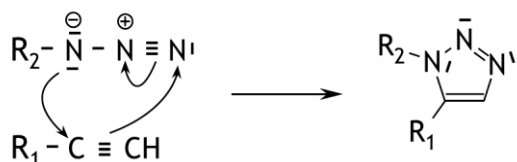
□13 Maximum score 4

An example of what a correct answer could look like:



- curved arrow from the nitrogen atom on the left (in the azide) to the carbon atom on the left (in the alkyne) 1
- curved arrow from the triple bond in the alkyne to the nitrogen atom on the right (in the azide) 1
- curved arrow from the N≡N to the nitrogen atom in the middle 1
- non-bonding electron pairs in the product are presented correctly 1

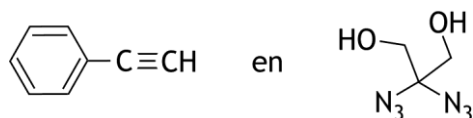
If in an otherwise correct answer, the mechanism for the formation of the *syn*-compound is provided, for example:



3

□14 Maximum score 3

The substances used are:

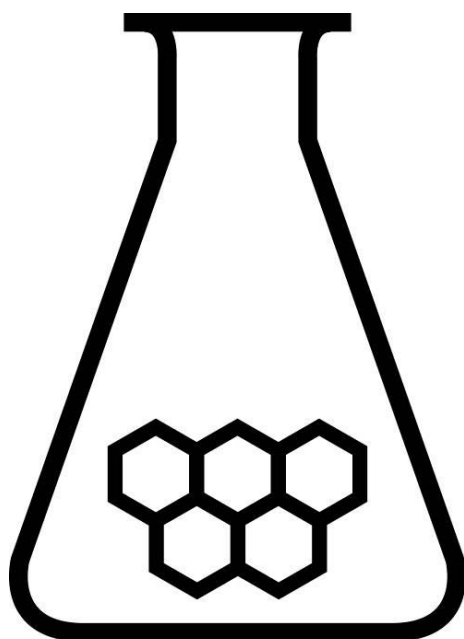


A copper(I) catalyst is used.

- correct structure of the alkyne 1
- correct structure of the diazide 1
- a copper(I) catalyst is used 1

NATIONAL CHEMISTRY OLYMPIAD 2023

ASSIGNMENTS PRELIMINARY ROUND 2
To be conducted from March 20 until March 24 2023



SCHEIKUNDE OLYMPIADE



Universiteit Leiden

- This preliminary round consists of 20 multiple choice questions divided over 8 topics and 3 problems with a total of 17 open questions as well as an answer sheet for the multiple choice questions.
- Use the answer sheet to answer the multiple choice questions.
- Use for each problem with open questions a separate answer sheet. Don't forget to write your name on it.
- The maximum score for this work is 94 points.
- The preliminary round lasts a maximum of 3 clock hours.
- Required materials: (graphic) calculator and BINAS 6th edition or ScienceData 1st edition or BINAS 5th edition, English version.
- For each question the number of points you can score are given.
- Unless otherwise stated, standard conditions apply: $T = 298 \text{ K}$ and $p = p_0$.

Problem 1 Multiple-choice questions

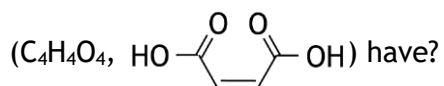
(total 40 points)

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

Score: 2 points for each correct answer.

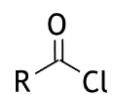
Carbon chemistry

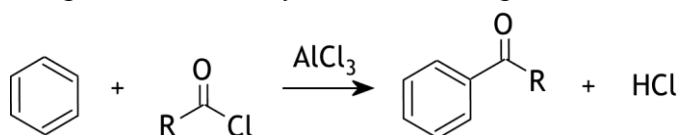
- 1 How many σ bonds and how many π bonds does a molecule of maleic acid



	number of σ bonds	number of π bonds
A	4	6
B	6	3
C	6	6
D	7	3
E	8	3
F	8	6
G	9	3
H	9	6
I	11	3
J	11	6

- 2

When an acyl chloride, , reacts with benzene using $AlCl_3$ as a catalyst, the following reaction occurs:

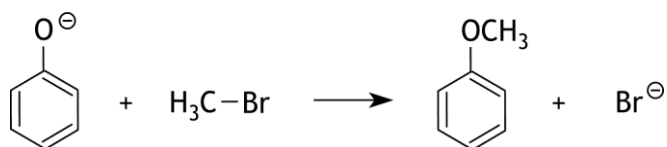


What kind of reaction is this?

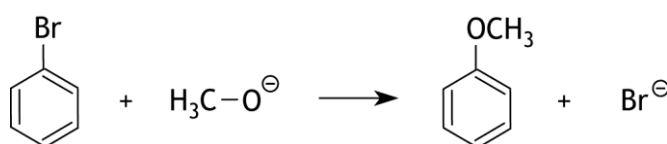
- A addition
- B condensation
- C elimination
- D substitution

- 3 Someone wants to make anisole (methoxybenzene). He has devised the following two methods for this:

Method I: a reaction of phenol (hydroxybenzene) with bromomethane in alkaline conditions. After the base has accepted a proton from a phenol molecule, the following reaction should occur:



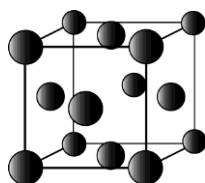
Method II: a reaction of bromobenzene with methanol under the influence of a very strong base. After the base has accepted a proton from a methanol molecule, the following reaction should occur:



Which method(s) is(are) suitable?

- A neither method
 - B method I only
 - C method II only
 - D both methods
- ### Structures and formulas
- 4 What is the formal charge of the sulfur atom in the Lewis structure of SO_2 in which all atoms follow the octet rule?
- A 4-
 - B 2-
 - C 1-
 - D 1+
 - E 2+
 - F 4+

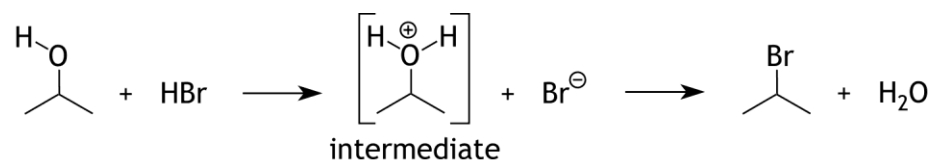
- 5 The unit cell of the metal gold is a face-centered cube, FCC, see figure below.



The density of gold is $19.3 \cdot 10^3 \text{ kg m}^{-3}$.

What is the smallest distance between the nuclei of two gold atoms?

- A $1.44 \cdot 10^{-10} \text{ m}$
 B $2.88 \cdot 10^{-10} \text{ m}$
 C $4.08 \cdot 10^{-10} \text{ m}$
 D $5.77 \cdot 10^{-10} \text{ m}$
- 6 In the reaction between propan-2-ol and hydrogen bromide, 2-bromopropane is formed. First, an alcohol molecule is protonated, creating an intermediate:



What is the hybridization of the O atom in a molecule of propan-2-ol and in the intermediate?

in a molecule of propan-2-ol

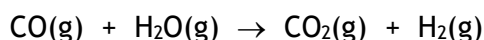
in the intermediate

- | | | |
|---|--------|--------|
| A | sp | sp |
| B | sp | sp^2 |
| C | sp | sp^3 |
| D | sp^2 | sp |
| E | sp^2 | sp^2 |
| F | sp^2 | sp^3 |
| G | sp^3 | sp |
| H | sp^3 | sp^2 |
| I | sp^3 | sp^3 |
- 7 Which set of quantum numbers can correspond to one of the valence electrons in an O atom in the ground state?

	n	l	m_l	m_s
A	1	0	0	$+\frac{1}{2}$
B	1	1	0	$-\frac{1}{2}$
C	2	0	-1	$+\frac{1}{2}$
D	2	1	-1	$-\frac{1}{2}$
E	3	0	0	$+\frac{1}{2}$
F	3	1	0	$-\frac{1}{2}$

Thermochemistry

- 8 In the water-gas shift reaction, carbon monoxide reacts with water vapor to form carbon dioxide and hydrogen:



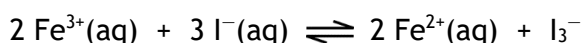
In this reaction the entropy change $\Delta S^\circ = -42 \text{ J mol}^{-1} \text{ K}^{-1}$. For this question, assume that ΔH and ΔS are independent of temperature and that the reaction occurs under standard pressure.

Two statements are made:

- I This reaction is an exothermic reaction.
II This reaction is spontaneous at temperatures above 1200 K.

Which of the above statements is/are true?

- A neither
B only I
C only II
D both
- 9 When a solution of potassium iodide is added to a solution of iron(III) chloride, the following equilibrium is reached:



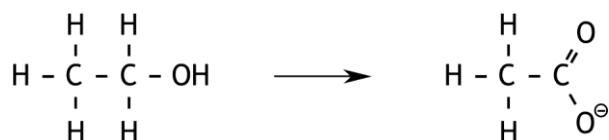
The change in the Gibbs energy can be calculated with: $\Delta G^\circ = -nF\Delta E^\circ$.

What is the value of the equilibrium constant at 298 K and $p = p_0$?

- A $1.7 \cdot 10^{-8}$
B $1.3 \cdot 10^{-4}$
C $7.8 \cdot 10^3$
D $6.0 \cdot 10^7$

Redox and electrochemistry

- 10 Given is the redox couple ethanol/ethanoate:



How many electrons (e^-) are in the equation of the half-reaction of this redox couple and on which side of the arrow are they?

- A $2 e^-$ to the left of the arrow
B $2 e^-$ to the right of the arrow
C $4 e^-$ to the left of the arrow
D $4 e^-$ to the right of the arrow
E $6 e^-$ to the left of the arrow
F $6 e^-$ to the right of the arrow

- 11 A solution containing equal amounts of moles of NiCl_2 and CuBr_2 is electrolyzed. The voltage of the power source used for the electrolysis is slowly increased.

Which products are formed first?

at the negative electrode

at the positive electrode

- | | | |
|---|--------------------------|--------------------------|
| A | $\text{Br}_2(\text{aq})$ | $\text{Cu}(\text{s})$ |
| B | $\text{Br}_2(\text{aq})$ | $\text{Ni}(\text{s})$ |
| C | $\text{Cl}_2(\text{aq})$ | $\text{Cu}(\text{s})$ |
| D | $\text{Cl}_2(\text{aq})$ | $\text{Ni}(\text{s})$ |
| E | $\text{Cu}(\text{s})$ | $\text{Br}_2(\text{aq})$ |
| F | $\text{Cu}(\text{s})$ | $\text{Cl}_2(\text{aq})$ |
| G | $\text{Ni}(\text{s})$ | $\text{Br}_2(\text{aq})$ |
| H | $\text{Ni}(\text{s})$ | $\text{Cl}_2(\text{aq})$ |

pH / acid-base

- 12 Amino acid molecules contain an amino group and a carboxylic acid group. The amino group can act as a base and the carboxylic acid group as an acid. For glycine, the $\text{p}K_{\text{b}}$ of the amino group is 4.22 and the $\text{p}K_{\text{a}}$ of the carboxylic acid group is 2.35.

In what form does glycine mainly exist in a solution where the pH has been adjusted to 4.60 with a solution of hydrochloric acid?

- A $\text{NH}_2\text{CH}_2\text{COO}^-$
B $\text{NH}_2\text{CH}_2\text{COOH}$
C $^+\text{NH}_3\text{CH}_2\text{COO}^-$
D $^+\text{NH}_3\text{CH}_2\text{COOH}$
- 13 0.020 mol NaOH is added to 1.50 L of a solution containing 0.100 mol lactic acid (2-hydroxypropanoic acid, $\text{CH}_3\text{CHOHCOOH}$) and 0.120 mol sodium lactate (lactate is the conjugate base of lactic acid).
What will the pH be?
- A 3.61
B 3.77
C 3.93
D 4.10
E 4.27

Chemical calculations

- 14 Weigh out 600 mg of iron(III) oxide. This reacts with hydrogen gas. Water vapor and a solid containing only iron ions and oxide ions are formed.
At a certain moment, 22.6 mg of water vapor was created.

What is the molar ratio between Fe and O in the remaining solid?

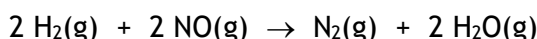
- | | | | |
|---|----|---|---|
| | Fe | : | O |
| A | 1 | : | 1 |
| B | 3 | : | 4 |
| C | 4 | : | 5 |
| D | 5 | : | 6 |
| E | 6 | : | 7 |
| F | 7 | : | 8 |

- 15 Which gas has a density of 2.16 g dm^{-3} at $200 \text{ }^\circ\text{C}$ and 3.00 atm ?

- A argon
- B krypton
- C neon
- D nitrogen
- E hydrogen
- F oxygen

Reaction rate and equilibrium

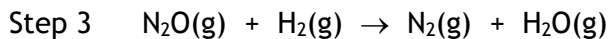
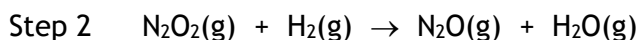
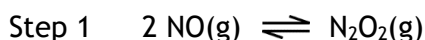
- 16 For the reaction



the rate equation is:

$$\text{rate} = k[\text{H}_2][\text{NO}]^2$$

The following mechanism is proposed:



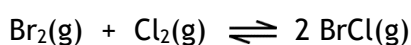
Which statement(s) about the rate equation and the proposed mechanism can be correct?

- I The mechanism is in agreement with the rate equation if step 1 is the rate determining step.
- II The mechanism is in agreement with the rate equation if step 2 is the rate determining step.

- A neither
- B only I
- C only II
- D both

- 17 0.015 M ZnF_2 solution is slowly added to 50 mL of a 0.010 M BaCl_2 solution. After adding 50 mL of this solution, a precipitate of BaF_2 forms for the first time. What is the solubility product of BaF_2 according to these data?
- A $2.8 \cdot 10^{-7}$
 - B $1.1 \cdot 10^{-6}$
 - C $9.0 \cdot 10^{-6}$
 - D $3.8 \cdot 10^{-5}$
 - E $7.5 \cdot 10^{-5}$
 - F $1.5 \cdot 10^{-4}$

- 18 A mixture of 1.00 mol bromine and 1.00 mol chlorine is heated to 190°C . The following equilibrium is reached:



The equilibrium constant K_c for this equilibrium at 190°C is 6.80.

What is the mass percentage of BrCl in the equilibrium mixture at 190°C ?

- A 28.3%
- B 32.4%
- C 36.1%
- D 56.6%
- E 64.8%
- F 72.3%
- G 77.2%

Analysis

- 19 A student is instructed to investigate whether a white solid is barium carbonate, zinc carbonate or calcium hydroxide.

The student proposes the following two designs:

Design 1: Add an excess of hydrochloric acid to part of the white solid.

Design 2: Add an excess of sulfuric acid solution to part of the white solid.

Which design(s) gives/give visible observations that enables the student to identify the white solid?

- A neither design
- B design 1 only
- C design 2 only
- D design 1 and design 2

20 A student determines the concentration of a colored salt solution by measuring the absorbance at the wavelength at which the absorbance is greatest (λ_{\max}) and calculates the concentration using Lambert-Beer's law.

In which action(s) below does she find a higher concentration than the actual concentration?

I She rinses the cuvette with water and then fills it with the salt solution.

II She sets the spectrophotometer at a wavelength higher than (λ_{\max}).

- A in neither
- B only in I
- C only in II
- D in both

Open questions

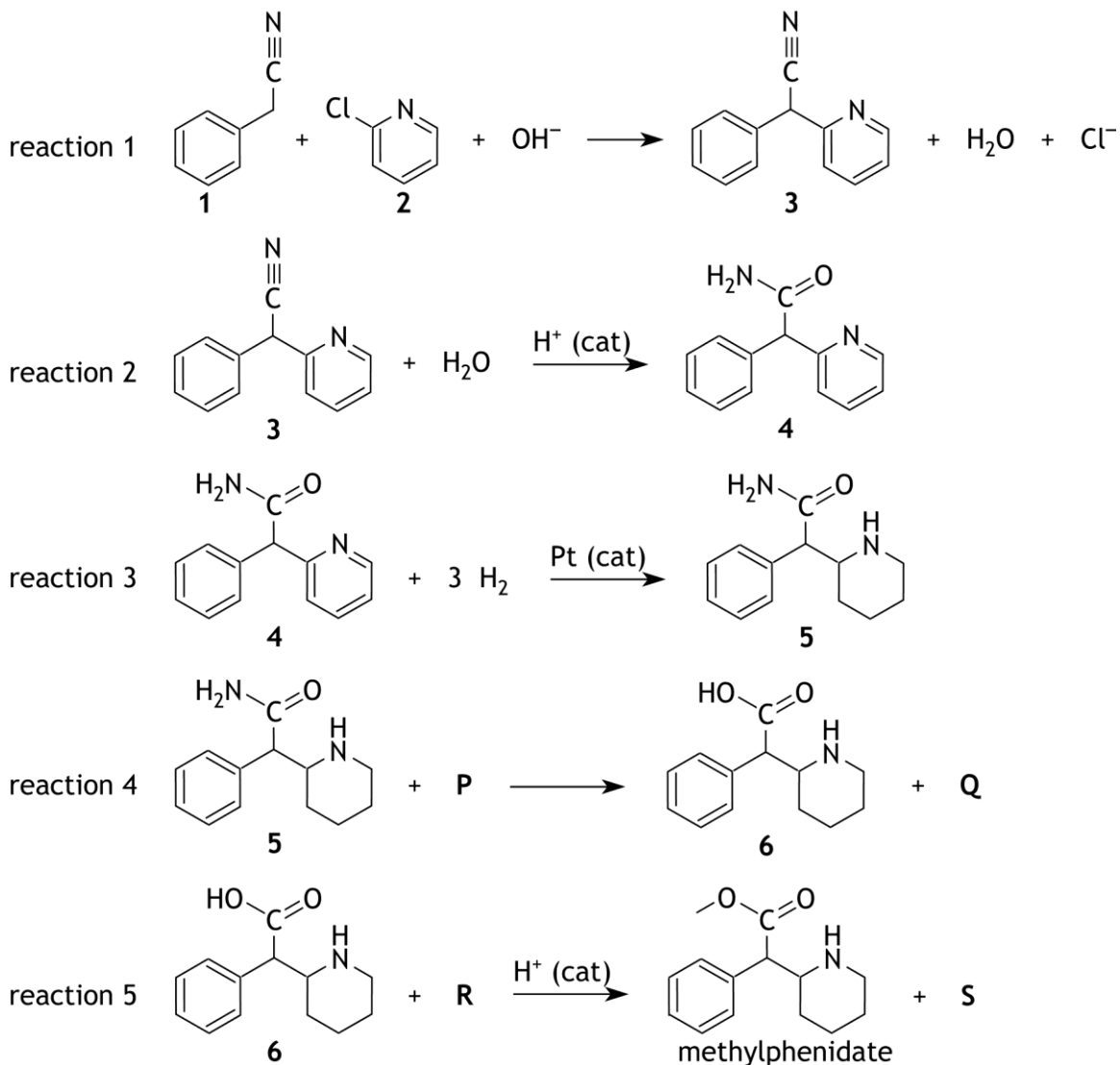
(total 54 points)

Problem 2 Methylphenidate

(25 points)

Methylphenidate is the active ingredient of the medicine Ritalin®.

Methylphenidate was first synthesized in 1944 by Panizzon. The synthesis route is shown below.

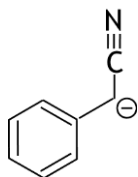


During this synthesis route reactions occur in which stereoisomers are formed. The mixtures of stereoisomers that are formed during this synthesis route, are not separated.

□1 In which reaction(s) does the number of stereoisomers increase?

2

In reaction 1, first a hydroxide ion reacts with a molecule 1 to form the negative ion below.



In this ion, the negative charge is not localized on one atom, but distributed over several atoms. This can be explained with the help of resonance (mesomerism).

- 2 Copy the structural formula of the negative ion and indicate with asterisks (*) which atoms, except the C atom in the formula shown above, are negatively charged. 2

The resultant negative ion reacts with a molecule 2.

- 3 Copy the sentence below and choose the correct option between the alternatives in cursive:

The reaction of the negative ion of 1 with a molecule 2 to form molecule 3 is *an addition reaction / an elimination reaction / a substitution reaction* in which the negative ion of 1 functions as *electrophile / nucleophile*. 2

In reaction 2, the formed molecule 3 reacts with water, with sulfuric acid acting as catalyst. The mechanism of the reaction is described step by step below.




Step 1: the lone pair on the N atom of the CN group of 3 bonds to the H⁺ of a H₃O⁺ ion.

Step 2: a water molecule is bonded to the C atom of the CN group, while also a neutral NH group is formed.

Step 3: exchange of a proton takes place between the formed OH₂⁺ group and the N atom.

Step 4: transfer of a proton takes place from the OH group to a water molecule, bonds also shift so that 4 is produced.

- 4 Show the steps 1 to 4 of the mechanism with structural formulas.

- Use the following notations for the side chains:  = R₁ and  = R₂.
- Draw all bonding and non-bonding electron pairs.
- Use curved arrows () to indicate how the electron pairs shift during the formation and breaking of bonds.
- Place all formal charges in the right place.

8

In reaction 3 the pyridine ring (R_2 in question 4) reacts with hydrogen. In this reaction, the benzene ring (R_1 in question 4) does not react with hydrogen. This is due to the so-called resonance energy (mesomeric energy) of both groups.

The resonance energy of the benzene ring ($1.50 \cdot 10^5 \text{ J mol}^{-1}$) is the difference between the energy released during the complete hydrogenation of three moles of $\text{C}=\text{C}$ bonds and the energy released during the complete hydrogenation of one mole of benzene rings.

The resonance energy of the pyridine ring ($1.07 \cdot 10^5 \text{ J mol}^{-1}$) is the difference between the energy released during the complete hydrogenation of two moles of $\text{C}=\text{C}$ bonds together with one mole of $\text{C}=\text{N}$ bonds and the energy released during the complete hydrogenation of one mole of pyridine rings.

As an explanation for the fact that in reaction 3 the pyridine ring is hydrogenated and the benzene ring is not, Gerrit assumes that more energy is released in the reaction of the pyridine ring with hydrogen than in the reaction of the benzene ring with hydrogen.

- 5 Control by means of a calculation whether during the hydrogenation of one mole of pyridine rings more energy is released than in the hydrogenation of one mole of benzene rings.
- Use information from Binas table 58 or ScienceData table 9.3.
 - The resonance energy of the pyridine ring is $1.07 \cdot 10^5 \text{ J mol}^{-1}$.
 - During the complete hydrogenation of one mole of benzene rings, $2.1 \cdot 10^5 \text{ J}$ is produced.

6

- 6 Give another possible explanation for the fact that the benzene ring in reaction 3 is not hydrogenated.

1

In reaction 4, substance **5** reacts with a solution of hydrochloric acid.

- 7 Give the formulas of **P** and **Q**. Record your answers as follows:

P is ...

Q is ...

2

- 8 Give the formulas of **R** and **S**. Record your answers as follows:

R is ...

S is ...

2

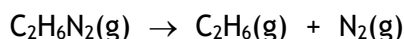
Problem 3 The decomposition of azomethane

(14 points)

Azomethane has the molecular formula $C_2H_6N_2$. In one molecule of azomethane, there are two nitrogen atoms bonded to each other and each nitrogen atom is bonded to a methyl group.

- 9 Give the Lewis structure of a molecule of azomethane. Indicate the methyl groups as CH_3 . 2
- 10 Explain whether stereoisomers of azomethane are possible. 3

Azomethane decomposes readily to form ethane and nitrogen:



During an investigation into the kinetics of the reaction, a certain amount of azomethane was placed in a reaction vessel with a fixed volume and the pressure in the vessel was measured a number of times. The temperature remained constant during the experiment. The following results were obtained:

t	10.0 min	21.0 min	35.0 min	∞
p_{total}	$0.656 \cdot 10^5 \text{ Pa}$	$0.732 \cdot 10^5 \text{ Pa}$	$0.813 \cdot 10^5 \text{ Pa}$	$1.144 \cdot 10^5 \text{ Pa}$

At $t = \infty$ all azomethane has been converted.

- 11 Show that the decomposition of azomethane is a first order reaction and calculate the rate constant k for the reaction at this temperature. 7
- 12 Indicate what you need to do if you want to determine the activation energy of this reaction. 2

Problem 4 Superphosphate

(15 points)

The fertilizer superphosphate is a mixture of mostly calcium hydrogen phosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2$) and calcium sulphate (CaSO_4). Superphosphate is prepared by reacting an ore, consisting mainly of fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$), with pure sulfuric acid at normal temperature and pressure. This reaction produces only gaseous hydrogen fluoride (HF), solid calcium dihydrogen phosphate and solid calcium sulfate.

- 13 Give the equation of the reaction between fluorapatite and sulfuric acid. Also indicate the states. 3
- 14 Calculate the mass percentage of calcium dihydrogen phosphate, rounded to a whole number, in superphosphate if it were prepared from pure fluorapatite and pure sulfuric acid. 3

Of the ingredients in superphosphate, only calcium dihydrogen phosphate is effective as fertilizer. Calcium dihydrogen phosphate is soluble in water at room temperature. The remaining ingredients of the superphosphate can be removed by adding water to the superphosphate and then filtering the obtained cloudy liquid at room temperature. When water is added to superphosphate, the following occurs:



and



Calcium sulfate is moderately soluble in water at room temperature. When water is added to superphosphate, less calcium sulfate dissolves per liter compared to adding water to calcium sulphate alone.

- 15 Explain why, when water is added to superphosphate, less calcium sulfate dissolves per liter compared to adding water to calcium sulphate alone. 2

Emmy wants to determine the amount of mmoles of calcium dihydrogen phosphate present in a small sample of superphosphate. Water is added to the sample until the volume of the solution is 100.0 mL. All calcium dihydrogen phosphate dissolves. After the non-dissolved components of the superphosphate have precipitated, two solutions are added in excess to 10.00 mL of the colourless solution: one of them is a solution of ammonia and the other is a solution of a molybdenum (Mo) complex. As a result, all H_2PO_4^- ions in solution react forming solid $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$. This solid compound is removed from the suspension by means of filtration. It is then added to a solution containing 10.0 mmol dissolved NaOH. This amount of NaOH is a small excess.

Upon adding the solid to the NaOH solution, all $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ reacts with OH^- . Only MoO_4^{2-} , HPO_4^{2-} , H_2O and NH_3 are formed. Finally, after adding a suitable indicator, the amount of unreacted OH^- is determined using a titration with a solution of hydrochloric acid. It turns out that 0.380 mmol H_3O^+ ions are needed. You can assume that H_3O^+ only reacts with OH^- .

To determine the amount of mmoles of calcium hydrogen phosphate in the sample of superphosphate one needs to know the molar ratio in which $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ and OH^- react. This (rather extreme) molar ratio can be found by setting up part of the reaction equation and looking at the charges left and right of the reaction arrow.

- 16 Set up part of the reaction equation and explain, based on charges left and right of the reaction arrow, how many moles of OH^- react with 1 mol $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$. 3
- 17 Calculate the amount of mmoles of calcium hydrogen phosphate in the superphosphate sample. 4

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44th National Chemistry Olympiad 2023 preliminary round 2

Answer sheet Multiple choice questions

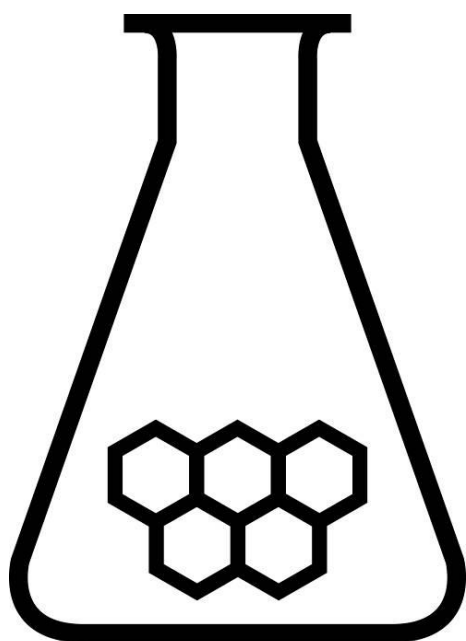
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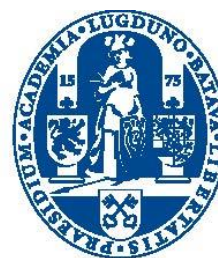
NATIONAL CHEMISTRY OLYMPIAD 2023

MARKING SCHEME PRELIMINARY ROUND 2

To be conducted from March 20 until March 24 2023




SCHEIKUNDE OLYMPIADE



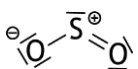
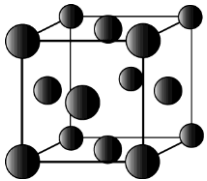
Universiteit Leiden

- This preliminary round consists of 20 multiple choice questions divided over 8 topics and 3 problems with a total of 17 open questions.
- The maximum score for this work is 94 points.
- Required materials: (graphic) calculator and BINAS 6th edition or ScienceData 1st edition or BINAS 5th edition, English version.
- For each question the number of points you can score are given.
- While assigning scores for the work, this marking scheme has to be used. Moreover the general rules for the Dutch Central Exams apply.

Problem 1 Multiple-choice questions**(total 40 points)****For every correct answer: 2 points****Carbon chemistry**

1	I	The single bonds between the C atoms and the H atoms are σ -bonds, as are the single bonds between two C atoms, between the C atoms and the O atoms of the OH groups, and between the O atoms and the H atoms. The double bond between the C atoms consists of a σ -bond and a π -bond. The double bonds between the C atoms and the O atoms consist of a σ -bond and a π -bond.
2	D	An H atom is replaced by a  group.
3	B	Method I is a nucleophilic substitution reaction of the phenolate on the bromomethane. Method II would also be a nucleophilic substitution reaction, of methanolate on the benzene ring, but in a benzene ring only electrophilic substitution would occur.

Structures and formulas

4	D	
5	B	The structure of the FCC unit cell is:  The unit cell contains $8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$ atoms. When the edge of the unit cell is set to a m, the density is $\frac{4 \times 197.0 \times 1.66 \cdot 10^{-27}}{a^3} = 19.3 \cdot 10^3 \text{ kg m}^{-3}$. That gives $a = 4.08 \cdot 10^{-10}$ m. The smallest distance between two gold nuclei is half of the diagonal of one face of the cube, so $\frac{4.08 \cdot 10^{-10}}{\sqrt{2}} = 2.88 \cdot 10^{-10}$ m.
6	I	The oxygen atom in the alcohol molecule has two bonds and two lone pairs, so it is sp^3 hybridised. The oxygen atom in the intermediate has three bonds and one lone pair, so it is also sp^3 hybridised.
7	D	Oxygen is in period 2, so $n = 2$ and $l = 0$ or $l = 1$. If $l = 0$ m_l can't be -1 .

Thermochemistry

8	B	$\Delta H = -(-1.105 \cdot 10^5) - (-2.42 \cdot 10^5) + (-3.935 \cdot 10^5) = -0.41 \cdot 10^5 \text{ J mol}^{-1}$, this is negative so the reaction is exothermic. When the reaction occurs spontaneously, it must be that $\Delta G < 0$, so $\Delta H - T\Delta S < 0$. At 1200 K $\Delta H - T\Delta S = -0,41 \cdot 10^5 - 1200 \times (-42) = 9,4 \cdot 10^3 \text{ J mol}^{-1}$. This is greater than zero and at even higher temperatures ΔG becomes even greater.
9	D	$\Delta G^0 = -nF\Delta E^0 = -RT \ln K$; $n = 2$ and $\Delta E^0 = (0.77 - 0.54) = 0.23 \text{ V}$, so $K = e^{\frac{nF\Delta E^0}{RT}} = e^{\frac{2 \times 9.649 \cdot 10^4 \times 0.23}{8.314 \times 298}} = 6.0 \cdot 10^7.$

Redox and electrochemistry

10	D	The equation of the half-reaction is: $\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H} - \text{C} - & \text{C} - \text{OH} \\ & \\ \text{H} & \text{H} \end{array} + 5 \text{OH}^- \longrightarrow \begin{array}{c} \text{H} & \text{O} \\ & // \\ \text{H} - \text{C} - & \text{C} \\ & \backslash \\ \text{H} & \text{O}^\ominus \end{array} + 4 \text{H}_2\text{O} + 4 \text{e}^-$
11	E	The strongest oxidising agent (Cu^{2+}) and the strongest reducing agent (Br^-) will react first.

pH / acid-base

12	C	At very high pH, glycine occurs as $\text{H}_2\text{NCH}_2\text{COO}^-$. As the pH drops, a H^+ binds to the most basic group, which is the NH_2 group ($\text{p}K_b = 4.22$, while the $\text{p}K_b$ of the COO^- group is equal to $14.00 - 2.35 = 11.65$). At pH = 4.60 there is the following equilibrium: ${}^+\text{NH}_3\text{CH}_2\text{COOH} \rightleftharpoons {}^+\text{NH}_3\text{CH}_2\text{COO}^- + \text{H}^+$ $\text{p}K_z = \text{pH} - \log \frac{\text{number of moles of } {}^+\text{NH}_3\text{CH}_2\text{COO}^-}{\text{number of moles of } {}^+\text{NH}_3\text{CH}_2\text{COOH}}$, filled out: $2.35 = 4.60 - \log \frac{\text{number of moles of } {}^+\text{NH}_3\text{CH}_2\text{COO}^-}{\text{number of moles of } {}^+\text{NH}_3\text{CH}_2\text{COOH}}$, so $\log \frac{\text{number of moles of } {}^+\text{NH}_3\text{CH}_2\text{COO}^-}{\text{number of moles of } {}^+\text{NH}_3\text{CH}_2\text{COOH}} = 4.60 - 2.35 = 2.25$ So, the number of moles of ${}^+\text{NH}_3\text{CH}_2\text{COO}^- \gg$ the number of moles of ${}^+\text{NH}_3\text{CH}_2\text{COOH}$. At even lower pH values, the COO^- group is also protonated. At $\text{pH} < 2.35$, glycine occurs primarily as ${}^+\text{NH}_3\text{CH}_2\text{COOH}$.
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13	D	<p>0.020 moles of OH⁻ react with 0.020 moles of CH₃CHOHCOOH to form 0.020 moles of CH₃CHOHCOO⁻.</p> <p>After the reaction there are 0.100 – 0.020 = 0.080 moles of CH₃CHOHCOOH present and 0.120 + 0.020 = 0.140 moles of CH₃CHOHCOO⁻, so a buffer solution has formed.</p> <p>So, $[H_3O^+] = K_z \times \frac{\text{number of moles of CH}_3\text{CHOHCOOH}}{\text{number of moles of CH}_3\text{CHOHCOO}^-} = 1.4 \cdot 10^{-4} \times \frac{0.080}{0.140} = 8.0 \cdot 10^{-5}$</p> <p>and pH = –log8.0·10⁻⁵ = 4.10.</p>
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Chemical calculations

14	B	<p>600 mg Fe₂O₃ is $\frac{600}{159.69}$ mmol which contains $2 \times \frac{600}{159.69} = 7.51$ mmoles of Fe and</p> <p>$3 \times \frac{600}{159.69} = 11.27$ mmoles of O.</p> <p>In 22.6 mg H₂O there is $\frac{22.6}{18.015} = 1.25$ mmoles of O,</p> <p>so there is 11.27 – 1.25 = 10.02 mmoles of O remaining in the solid.</p> <p>Therefore, the ratio Fe : O is 7.51 : 10.02 = 3 : 4.</p>
15	D	<p>200 °C is 473 K, 3.00 atm is 3.00 × 1.01·10⁵ Pa and 2.16 g dm⁻³ is 2.16·10³ g m⁻³.</p> <p>Setting the molar mass to <i>M</i> g mol⁻¹, it follows that 1.00 m³ of the gas contains $\frac{2.16 \cdot 10^3}{M}$ mol.</p> <p>The ideal gas law states that $pV = nRT$ or $3.03 \cdot 10^5 \times 1.00 = \frac{2.16 \cdot 10^3}{M} \times 8.314 \times 473$ or</p> <p>$M = \frac{2.16 \cdot 10^3}{3.03 \cdot 10^5 \times 1.00} \times 8.314 \times 473 = 28.0 \text{ g mol}^{-1}$.</p> <p>This is the molar mass of nitrogen, N₂.</p>

Reaction rate and equilibrium

16	C	<p>When step 2 is rate determining, $rate = k_2[N_2O_2][H_2]$.</p> <p>From the equilibrium condition $\frac{[N_2O_2]}{[NO]^2} = K$ for step 1, it follows that $[N_2O_2] = K[NO]^2$.</p> <p>So $rate = k_2K[NO]^2[H_2]$, which is in agreement with the stated rate equation for $k = k_2K$.</p>
17	B	<p>$[Ba^{2+}] = \frac{50 \times 0.010}{50 + 50} = 0.0050 \text{ mol L}^{-1}$ and $[F^-] = \frac{2 \times 50 \times 0.015}{50 + 50} = 0.015 \text{ mol L}^{-1}$</p> <p>$K_s = [Ba^{2+}][F^-]^2 = 0.0050 \times (0.015)^2 = 1.1 \cdot 10^{-6}$</p>

18	D	$\text{Br}_2 + \text{Cl}_2 \rightleftharpoons 2 \text{BrCl}$																
		<table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 15%;"></td> <td style="width: 35%; text-align: center;">1.00 mol</td> <td style="width: 35%; text-align: center;">1.00 mol</td> <td style="width: 15%; text-align: center;">0.00</td> </tr> <tr> <td>start</td> <td></td> <td></td> <td></td> </tr> <tr> <td>converted/produced</td> <td style="text-align: center;">x mol</td> <td style="text-align: center;">x mol</td> <td style="text-align: center;">$2x$ mol</td> </tr> <tr> <td>equilibrium</td> <td style="text-align: center;">$(1.00 - x)$ mol</td> <td style="text-align: center;">$(1.00 - x)$ mol</td> <td style="text-align: center;">$2x$ mol</td> </tr> </table>		1.00 mol	1.00 mol	0.00	start				converted/produced	x mol	x mol	$2x$ mol	equilibrium	$(1.00 - x)$ mol	$(1.00 - x)$ mol	$2x$ mol
			1.00 mol	1.00 mol	0.00													
		start																
converted/produced	x mol	x mol	$2x$ mol															
equilibrium	$(1.00 - x)$ mol	$(1.00 - x)$ mol	$2x$ mol															
$K = \frac{[\text{BrCl}]^2}{[\text{Br}_2][\text{Cl}_2]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{1.00 - x}{V}\right)^2} = 6.80, \text{ or } \frac{(2x)^2}{(1.00 - x)^2} = 6.80, \text{ it follows that } x = 0.566.$																		
<p>So, 2×0.566 moles of BrCl are produced, which is $2 \times 0.566 \times 115.35$ g BrCl. The total mass is $1.00 \times 2 \times 79.90 + 1.00 \times 2 \times 35.45 = 230.7$ g, so the mass percentage BrCl is $\frac{2 \times 0.566 \times 115.35}{230.7} \times 100 = 56.6\%$.</p>																		

Analysis

19	C	<p>Adding hydrochloric acid causes gas production with the carbonates but not with the hydroxide. There is no precipitation when a solution of hydrochloric acid is added to barium carbonate or zinc carbonate.</p> <p>The negative SO_4^{2-} ion of sulphuric acid forms a precipitate with Ba^{2+} and Ca^{2+} but not with Zn^{2+}. Sulphuric acid causes gas formation with barium carbonate, while with calcium hydroxide it does not.</p>
20	A	<p>Because the cuvette is not rinsed with the solution that will be measured, dilution will cause a lower extinction to be measured and thus a lower concentration to be found.</p> <p>At a wavelength higher than λ_{max}, the extinction is lower. When calculations are then performed with the smaller ϵ (molar extinction coefficient), belonging to that higher wavelength, the student will find a similar concentration to the real one. If calculations are performed with the ϵ that belongs to λ_{max}, the student will find a lower concentration than the real one.</p>

Open questions

(total 54 points)

■ Problem 2 Methylphenidate

25 points

□1 Maximum score 2

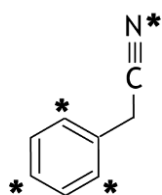
- in reaction 1 1
- in reaction 3 1

Note

When an incorrect reaction is listed, deduct 1 point - the minimum score for this question is 0 points.

□2 Maximum score 2

A correct answer might look as follows:



- asterisks at the three carbon atoms of the benzene ring correct 1
- asterisk at the N atom of the cyanide group 1

Notes

- When an asterisk is placed at an incorrect atom of the benzene ring, the first partial score is not to be assigned.
- When an asterisk is placed at the C atom of the cyanide group, the second partial score is not to be assigned.
- When an asterisk is placed at the C atom where the negative charge was drawn in the given structural formula, do not penalize this.

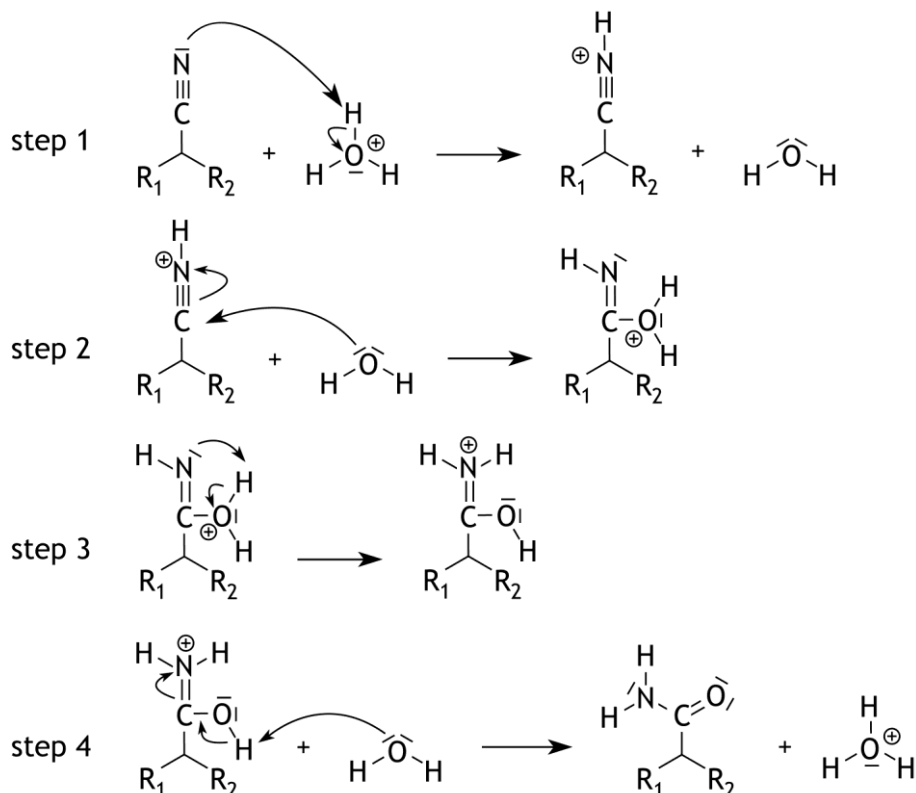
□3 Maximum score 2

The reaction of the negative ion of 1 with a molecule 2 to form molecule 3 is a substitution reaction in which the negative ion from 1 functions as nucleophile.

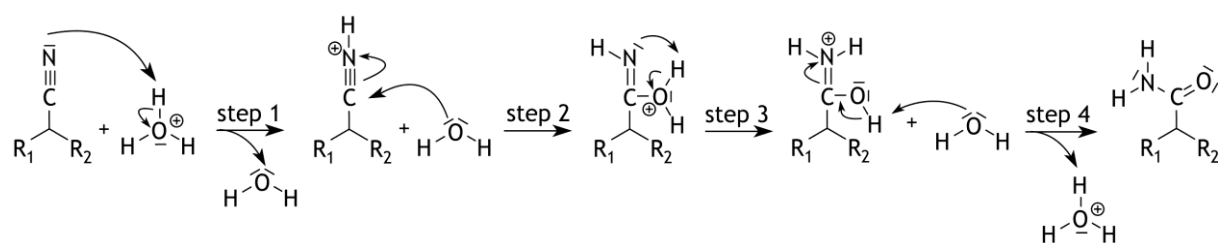
- substitution reaction 1
- nucleophile 1

□4 Maximum score 8

Examples of a correct answer are:



and



- in step 1, correctly drawn arrows 1
- in step 1, the Lewis structures and charges correct 1
- in step 2, correctly drawn arrows 1
- correct Lewis structure and charge after step 2 1
- in step 3, correctly drawn arrows 1
- correct Lewis structure and charge after step 3 1
- in step 4, correctly drawn arrows 1
- correct Lewis structure and charge after step 4 1

If, in an otherwise correct answer, one or more arrows are drawn 'wrong way around' 7

Note

When H₂O is not listed to the right of the arrow in step 1 and/or H₃O⁺ is not listed to the right of the arrow in step 4, do not penalize this.

□5 Maximum score 6

A correct answer might look as follows:

The change in energy for the hydrogenation of 2 moles of C = C bonds and 1 mole of C = N bonds is:

$$2 \times (-BE_{C=C} - BE_{H-H} + BE_{C-C} + 2 \times BE_{C-H}) + (-BE_{C=N} - BE_{H-H} + BE_{C-N} + BE_{C-H} + BE_{N-H}) = \\ 2 \times \{ -(-6.1 \cdot 10^5) - (-4.36 \cdot 10^5) + (-3.5 \cdot 10^5) + 2 \times (-4.1 \cdot 10^5) \} + \{ -(-6.2 \cdot 10^5) - (-4.36 \cdot 10^5) + \\ (-2.8 \cdot 10^5) + (-4.1 \cdot 10^5) + (-3.9 \cdot 10^5) \} = -2.7 \cdot 10^5 \text{ J.}$$

So, the hydrogenation energy of one mole of pyridine rings is

$$-2.7 \cdot 10^5 + 1.07 \cdot 10^5 = -1.6 \cdot 10^5 \text{ J.}$$

This is less than the $2.1 \cdot 10^5 \text{ J}$ released in the hydrogenation of a mole of benzene rings.

- notion that 2 moles of C = C bonds and 1 mole of C = N bonds are broken 1
- notion that 3 moles of H – H bonds are broken 1
- notion that 2 moles of C – C bonds and 1 mole of C – N bonds are formed 1
- notion that 5 moles of C – H bonds and 1 mole of N – H bonds are formed 1
- correct summation of bond energies 1
- calculation of the hydrogenation energy of a mole of pyridine rings and conclusion 1

□6 Maximum score 1

Examples of a correct answer are:

- The activation energy for the hydrogenation of benzene rings is greater than that for the hydrogenation of pyridine rings.
- The catalyst is specific for the hydrogenation of the pyridine ring.

□7 Maximum score 2

- P is H_3O^+ 1
 - Q is NH_4^+ 1
- If the answer P is H_2O and Q is NH_3 is given 1

□8 Maximum score 2

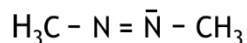
- R is CH_3OH 1
- S is H_2O 1

Problem 3 The decomposition of azomethane

14 points

□9 Maximum score 2

A correct answer might look as follows:



- single bonds between the N atoms and C atoms and double bond between both N atoms 1
- non-bonding electron pairs on both N atoms 1

Note

When the answer $\text{CH}_3 - \underline{\text{N}} = \bar{\text{N}} - \text{CH}_3$ is given, give full marks.

□10 Maximum score 3

The nitrogen atoms have a trigonal planar geometry.

There is no free rotation around the double bonds between the N atoms / the double bond is rigid, so there are two *cis-trans* isomers.

- the nitrogen atoms have a trigonal planar geometry 1
- there is no free rotation around the double bond between the N atoms / the double bond is rigid 1
- conclusion 1

Note

An answer like the following is also correct: „There are two stereoisomers / cis-trans

isomers namely

$$\begin{array}{c} \text{H}_3\text{C} \\ \diagdown \\ \text{N}=\text{N} \\ \diagup \\ \text{CH}_3 \end{array} \quad \text{and} \quad \begin{array}{c} \text{H}_3\text{C} \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{N}=\text{N} \end{array} .”$$

□11 Maximum score 7

An example of a correct calculation is as follows:

$$\text{For a first order reaction } \ln \frac{[\text{C}_2\text{H}_6\text{N}_2]_0}{[\text{C}_2\text{H}_6\text{N}_2]_t} = kt .$$

For gases, the partial pressure is proportional to the concentration, therefore

$$\ln \frac{(p_{\text{C}_2\text{H}_6\text{N}_2})_0}{(p_{\text{C}_2\text{H}_6\text{N}_2})_t} = kt \text{ or } k = \frac{\ln \frac{(p_{\text{C}_2\text{H}_6\text{N}_2})_0}{(p_{\text{C}_2\text{H}_6\text{N}_2})_t}}{t} .$$

From 1 mole of gas, 2 moles of gas are produced, therefore

$$(p_{\text{C}_2\text{H}_6\text{N}_2})_0 = \frac{(p_{\text{C}_2\text{H}_6\text{N}_2})_\infty}{2} = \frac{1.144 \cdot 10^5}{2} = 0.572 \cdot 10^5 \text{ Pa} .$$

If at time t during the reaction the partial pressure of $\text{C}_2\text{H}_6\text{N}_2$ has decreased by x Pa, the partial pressures of C_2H_6 and N_2 have increased by x Pa, and the total pressure is then $(0.572 \cdot 10^5 + x)$ Pa, thus

$$(p_{\text{C}_2\text{H}_6\text{N}_2})_t = 0.572 \cdot 10^5 - x .$$

After 10.0 min, $p_{\text{total}} = 0.656 \cdot 10^5$ Pa, thus $x = 0.656 \cdot 10^5 - 0.572 \cdot 10^5 = 0.084 \cdot 10^5$ Pa and

$$(p_{\text{C}_2\text{H}_6\text{N}_2})_{10.0} = 0.572 \cdot 10^5 - 0.084 \cdot 10^5 = 0.488 \cdot 10^5 \text{ Pa and}$$

$$\frac{\ln \frac{(p_{\text{C}_2\text{H}_6\text{N}_2})_0}{(p_{\text{C}_2\text{H}_6\text{N}_2})_{10.0}}}{10.0} = \frac{\ln \frac{0.572 \cdot 10^5}{0.488 \cdot 10^5}}{10.0} = 0.0159 .$$

After 21.0 min, $p_{\text{total}} = 0.732 \cdot 10^5$ Pa, thus $x = 0.732 \cdot 10^5 - 0.572 \cdot 10^5 = 0.160 \cdot 10^5$ Pa and

$$(p_{\text{C}_2\text{H}_6\text{N}_2})_{21.0} = 0.572 \cdot 10^5 - 0.160 \cdot 10^5 = 0.412 \cdot 10^5 \text{ Pa and}$$

$$\frac{\ln \frac{(p_{\text{C}_2\text{H}_6\text{N}_2})_0}{(p_{\text{C}_2\text{H}_6\text{N}_2})_{21.0}}}{21.0} = \frac{\ln \frac{0.572 \cdot 10^5}{0.412 \cdot 10^5}}{21.0} = 0.0156 .$$

After 35.0 min, $p_{\text{total}} = 0.813 \cdot 10^5$ Pa, thus $x = 0.813 \cdot 10^5 - 0.572 \cdot 10^5 = 0.241 \cdot 10^5$ Pa and

$$(p_{\text{C}_2\text{H}_6\text{N}_2})_{35.0} = 0.572 \cdot 10^5 - 0.241 \cdot 10^5 = 0.331 \cdot 10^5 \text{ Pa and}$$

$$\frac{\ln \frac{(p_{\text{C}_2\text{H}_6\text{N}_2})_0}{(p_{\text{C}_2\text{H}_6\text{N}_2})_{35.0}}}{35.0} = \frac{\ln \frac{0.572 \cdot 10^5}{0.331 \cdot 10^5}}{35.0} = 0.0156 .$$

Three times (almost) the same result for $\frac{\ln \frac{(p_{\text{C}_2\text{H}_6\text{N}_2})_0}{(p_{\text{C}_2\text{H}_6\text{N}_2})_t}}{t}$ is obtained, so this is a first order reaction.

$$k = \frac{0.0159 + 0.0156 + 0.0156}{3} = 0.0157 \text{ min}^{-1} .$$

$$\text{In SI units: } k = \frac{0.0157}{60} = 2.62 \cdot 10^{-4} \text{ s}^{-1} .$$

· notion that holds for the first order reaction $\ln \frac{(p_{\text{C}_2\text{H}_6\text{N}_2})_0}{(p_{\text{C}_2\text{H}_6\text{N}_2})_t} = kt$ or $k = \frac{\ln \frac{(p_{\text{C}_2\text{H}_6\text{N}_2})_0}{(p_{\text{C}_2\text{H}_6\text{N}_2})_t}}{t}$ 1

· calculation of $(p_{\text{C}_2\text{H}_6\text{N}_2})_0$: $1.144 \cdot 10^5$ Pa divided by 2 1

· notion that the increase in total pressure equals the decrease in $(p_{\text{C}_2\text{H}_6\text{N}_2})$ 1

· calculation of $(p_{\text{C}_2\text{H}_6\text{N}_2})_{10.0}$, $(p_{\text{C}_2\text{H}_6\text{N}_2})_{21.0}$ and $(p_{\text{C}_2\text{H}_6\text{N}_2})_{35.0}$ 1

· calculation of $\frac{\ln \frac{(p_{\text{C}_2\text{H}_6\text{N}_2})_0}{(p_{\text{C}_2\text{H}_6\text{N}_2})_t}}{t}$ for $t = 10.0$ min, $t = 21.0$ min and $t = 35.0$ min and concluding that it is a first order reaction 1

· calculation of k : the average of the results of $\frac{\ln \frac{(p_{\text{C}_2\text{H}_6\text{N}_2})_0}{(p_{\text{C}_2\text{H}_6\text{N}_2})_t}}{t}$ for $t = 10.0$ min, $t = 21.0$ min and $t = 35.0$ min 1

· correct unit of k provided 1

If in an otherwise correct answer k is calculated for only one moment (so not is proven that it is a first order reaction) 5

Notes

- If the unit is given in min^{-1} , do not penalize this.
- When by using the data at two points it is shown that the reaction is of the first

order, and for the calculation of k the average of the two results of $\frac{\ln \frac{(p_{\text{C}_2\text{H}_6\text{N}_2})_0}{(p_{\text{C}_2\text{H}_6\text{N}_2})_t}}{t}$ is used, do not penalize this.

□12 Maximum score 2

An example of a correct answer is:

The rate constant should be determined at one more temperature, and Arrhenius' law applied.

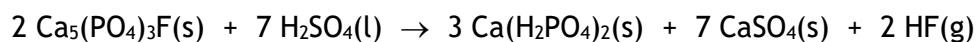
· the rate constant should be determined at one more temperature 1

· apply Arrhenius' law 1

Problem 4 Superphosphate

15 points

□13 Maximum score 3



- correct formulas with correct state symbols at the correct side of the arrow 1
- P and F balanced correctly 1
- Ca, H, S and O balanced correctly 1

□14 Maximum score 3

An example of a correct calculation is:

$$\frac{3 \times 234.05}{3 \times 234.05 + 7 \times 136.14} \times 10^2 = 42 \text{ (mass\%)}$$

- calculation of the molar mass of $\text{Ca}(\text{H}_2\text{PO}_4)_2$: $234,05 \text{ g mol}^{-1}$ 1
- calculation of the sum of the masses of 3 moles of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and 7 moles of CaSO_4 1
- rest of the calculation and answer rounded to the nearest whole number 1

Notes

- *When an incorrect answer to question 14 is a direct consequence of an incorrect answer to question 13 and the molar ratio $\text{Ca}(\text{H}_2\text{PO}_4)_2 : \text{CaSO}_4$ was not equal to 1:1, do not penalize this.*
- *When the molar ratio $\text{Ca}(\text{H}_2\text{PO}_4)_2 : \text{CaSO}_4 = 1 : 1$ was used in the answer to question 14, the second partial score is not to be assigned.*

□15 Maximum score 2

A correct answer can be formulated as follows:

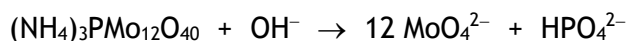
By dissolving $\text{Ca}(\text{H}_2\text{PO}_4)_2$, the $[\text{Ca}^{2+}]$ increases. Hence, the solution equilibrium of CaSO_4 shifts to the left (and less CaSO_4 dissolves).

- due to dissolving $\text{Ca}(\text{H}_2\text{PO}_4)_2$, the $[\text{Ca}^{2+}]$ increases 1
- so the solution equilibrium of CaSO_4 shifts to the left 1

If an answer is given such as: „Due to the dissolving of $\text{Ca}(\text{H}_2\text{PO}_4)_2$, the solution already contains many ions so that less Ca^{2+} and SO_4^{2-} can be added/dissolved.” 1

□16 Maximum score 3

A correct answer can be formulated as follows:



The amount of negative charges to right of the arrow is $12 \times 2 + 2 = 26$.

So 26 moles of OH^- react with 1 mole of $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$.

- each mole of $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ forms 12 moles of MoO_4^{2-} and 1 mole of HPO_4^{2-} 1
- calculation of the amount of negative charges to the right side of the arrow 1
- number of OH^- made equal to the amount of negative charges on the right side of the arrow 1

If an answer is given like: „To the right of the arrow MoO_4^{2-} and HPO_4^{2-} are listed, these have 4 negative charges, so 4 (moles of) OH^- react.” 1

Note

When the complete and correct reaction equation is given, give full marks.

□17 Maximum score 4

An example of a correct calculation is:

$$\frac{(10.00 - 0.380)}{26} \times \frac{1}{2} \times \frac{100.0}{10.00} = 1.85 \text{ (mmol)}$$

- calculation of the amount of mmoles of OH^- that reacted with $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$:
10.00 – 0.380 (mmol) 1
- calculation of the amount of mmoles of $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$: dividing the amount of mmoles of OH^- by 26 1
- calculation of the amount of mmoles of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ present in 10.00 mL solution: dividing the amount of mmoles of $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ by 2 1
- calculation of the amount of mmoles of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ present in 100.0 mL solution: dividing the amount of mmoles of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ by 10.00 (mL) and multiplying by 100.0 (mL) 1

Notes

- *When an incorrect answer to question 17 is a direct consequence of an incorrect answer to question 16 and the answer to question 16 was not equal to 1 mol OH^- , do not penalize this*
- *When the following molar ratio is used in question 17: „one mole of $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ reacts with one mole of OH^- (as answer to question 16)”, the second partial score is not to be assigned.*

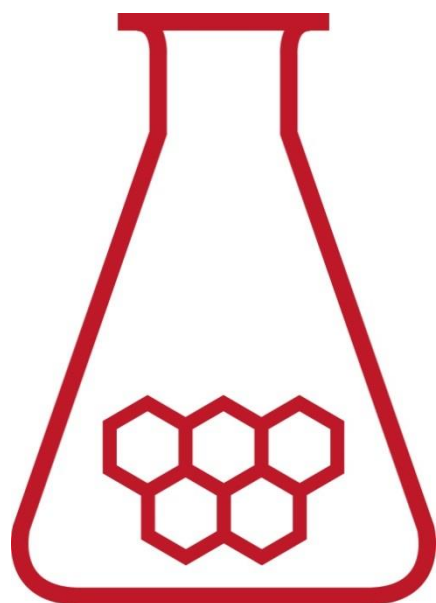
44th National Chemistry Olympiad

University Leiden

THEORY TEST

QUESTION BOOKLET

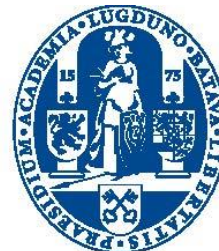
Monday 12 June 2023



**SCHEIKUNDE
OLYMPIADE**



55TH INTERNATIONAL
CHEMISTRY OLYMPIAD
SWITZERLAND 2023



Universiteit Leiden

- This test consists of 7 problems with 39 open questions and an answer booklet.
- Use a separate answer sheet for each problem, making sure to include 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 clock hours.
- Required resources: (graphic) calculator and Binas 6th edition or Sciencedata 1st print.
- Each question includes the number of points that a correct answer to that question will earn.

This test was created with thanks to the cooperation of the following people:

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Problem 1 Lithium-ion battery

(13 points)

In 2019, John B. Goodenough, M. Stanley Whittingham and A. Yoshino were awarded the Nobel Prize in chemistry for the development of the lithium-ion battery. A lithium-ion battery consists of a copper electrode covered with a layer of graphite containing lithium, represented by LiC_6 , and an aluminum electrode covered with a layer of LiCoO_2 . The equations for the half-reactions on which the operation of the cell relies, can be shown as follows, including the corresponding standard electrode potentials under standard conditions:



and



- 1 Write down the equation of the complete reaction when a lithium-ion battery provides a current. 2
- 2 Calculate the cell potential of a fully charged battery under standard conditions. 1
- 3 Give the charges of the particles in the CoO_2 and the LiCoO_2 . Indicate these charges in the sentences on the answer sheet. 3

An important characteristic of a battery is its capacity. This is measured in mAh.

- 4 Calculate the minimum amount of lithium in g that is required to be present in a lithium-ion battery to deliver a current of 200 mA over 2 days. 3

Based on the same principle of the lithium-ion battery, it should be possible to make a battery using magnesium instead.

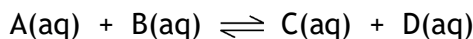
We compare such a magnesium-ion battery with a lithium-ion battery. When fully charged, there are equal amounts in gram of the metal in both batteries. We allow both batteries to provide the same constant current until they are fully discharged.

- 5 Explain which battery is able to provide power for the longest period of time and calculate the mathematical ratio between the times of the two different batteries (to full discharge). 4

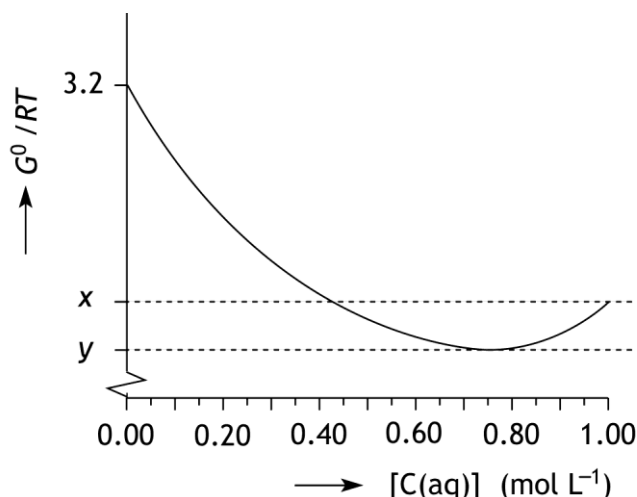
Problem 2 G and K

(13 points)

Consider the following general chemical reaction in aqueous environment:



A 1.00 liter solution containing 1.00 mol of substances A and B is prepared and the reaction is allowed to take place. The change in Gibbs free energy, G^0 (in units RT), of the system versus the concentration of C at 298 K is as follows:



With use of the diagram, the equilibrium constant K , at 298 K, can be calculated.

- 6 Calculate the equilibrium constant at 298K. 4
- 7 Calculate $\Delta_r G^0$ in J mol⁻¹. (The answer to question 6 is required. If you do not have an answer for question 6, use $K = 12$ - this is not the correct answer for question 6.) 2
- 8 Explain which values are represented by x and y on the vertical axes. 4

Another 1.00 mol of B is added to the solution at equilibrium. The temperature and the volume of the solution remain unaffected.

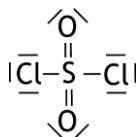
- 9 Comment on the values of [A], [B], [C] and [D] once equilibrium is re-established, when compared to the values of [A],[B], [C] and [D] in the initial equilibrium. Give your answer on the answer sheet by circling your choice from 'larger than', 'equal to', and 'smaller than'. 3

Problem 3 Sulfuryl chloride

(12 points)

Sulfuryl chloride is a compound consisting of sulfur, chlorine and oxygen. The molecular formula is SO_2Cl_2 .

The Lewis structure of sulfuryl chloride can be seen below:

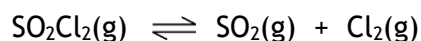


During the formation of the bonds within the molecule, the following excited state of the sulfur atom can be assumed: $3s^1, 3p^3, 3d^2$.

- 10 Give a description of a sulfuryl chloride molecule. Pay attention to the following:
- the shape of the molecule;
 - the type of hybridization of the sulfur atom and the oxygen atom;
 - the type of bonds in the molecule: π -bonds, σ -bonds; also describe how these bonds were formed.

6

Sulfuryl chloride decomposes readily at higher temperatures, leading to the formation of sulfur dioxide and chlorine. The following equilibrium is reached:



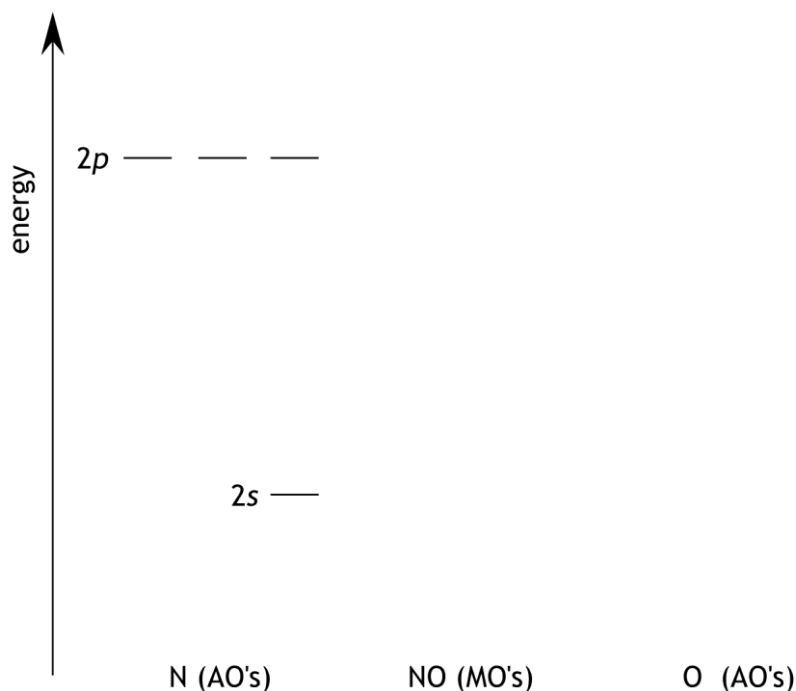
When 1.95 g of sulfuryl chloride is heated to $157\text{ }^\circ\text{C}$, the total volume of gas at equilibrium is 1.00 dm^3 and $p = p_0$.

- 11 Calculate the value of K_p for the equilibrium established at $157\text{ }^\circ\text{C}$.

6

Problem 4 NO**(24 points)**

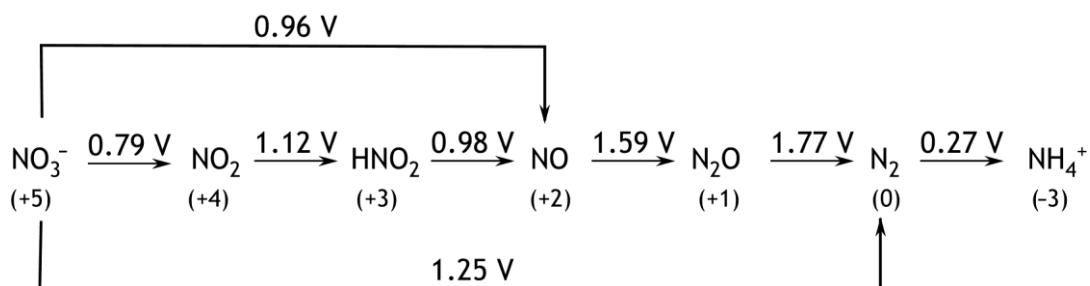
Below is the start for a MO diagram of nitrogen monoxide. The 2s and 2p levels of the nitrogen atom are already indicated in the diagram.



The above diagram is also present in the answer sheets of this test.

- 12 Draw the following on the diagram provided in the answer sheets:
- the 2s and 2p levels of the oxygen atom;
 - the molecular orbitals of the nitrogen monoxide molecule, including the common designations for 'bonding' and 'anti-bonding';
 - fill the atomic and molecular orbitals with electrons according to the Aufbau principle. 6
- 13 Calculate the bond order of the NO molecule. 2
- The strength of the bond between the N atom and the O atom in a nitrogen monoxide molecule can be calculated using the enthalpy of reaction of the reaction between NO(g) and H₂(g), whereby N₂(g) and H₂O(g) are formed.
- 14 Calculate the enthalpy of reaction of the reaction between NO(g) and H₂(g) whereby N₂(g) and H₂O(g) are formed. 3
- 15 Calculate the bond energy, in J mol⁻¹, of the bond between N and O in NO. 3

From a thermodynamic perspective, NO is an unstable compound at 298K. This can be concluded from the Latimer diagram of nitrogen, which is provided below. The conditions for the conversions shown in the diagram are 298 K, $p = p_0$ and $\text{pH} = 0.00$ ($[\text{H}^+] = 1.0 \text{ M}$).



In an aqueous solution at $\text{pH} = 0.00$, NO could be converted to HNO_2 and N_2O during a so-called auto redox reaction.

□16 Give the equation for this reaction. 3

□17 Calculate the equilibrium constant for this reaction. Use, among other things, the fact that for a redox reaction the change in free energy can be expressed as $\Delta G^0 = -nF\Delta V^0$. 4

For each conversion in the above Latimer diagram it holds that $\Delta G^0 = -nFV^0$.

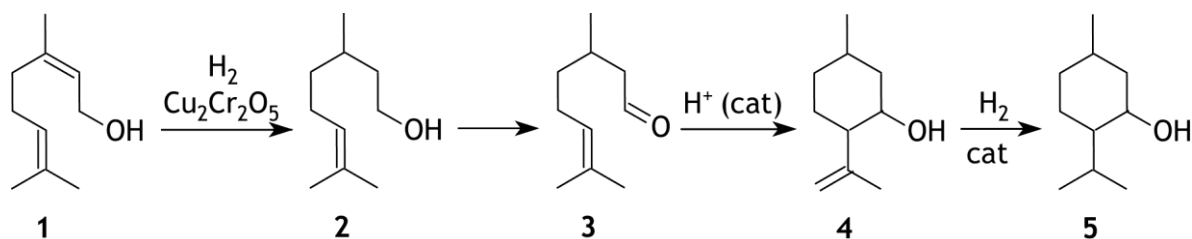
Using this relationship and data from the Latimer diagram above, the V^0 for the conversion of NO to NH_4^+ can be calculated as follows: $\frac{1.59 + 1.77 + 3 \times 0.27}{5}$.

□18 Derive this relationship. 3

Problem 5 Crazy scents

(27 points)

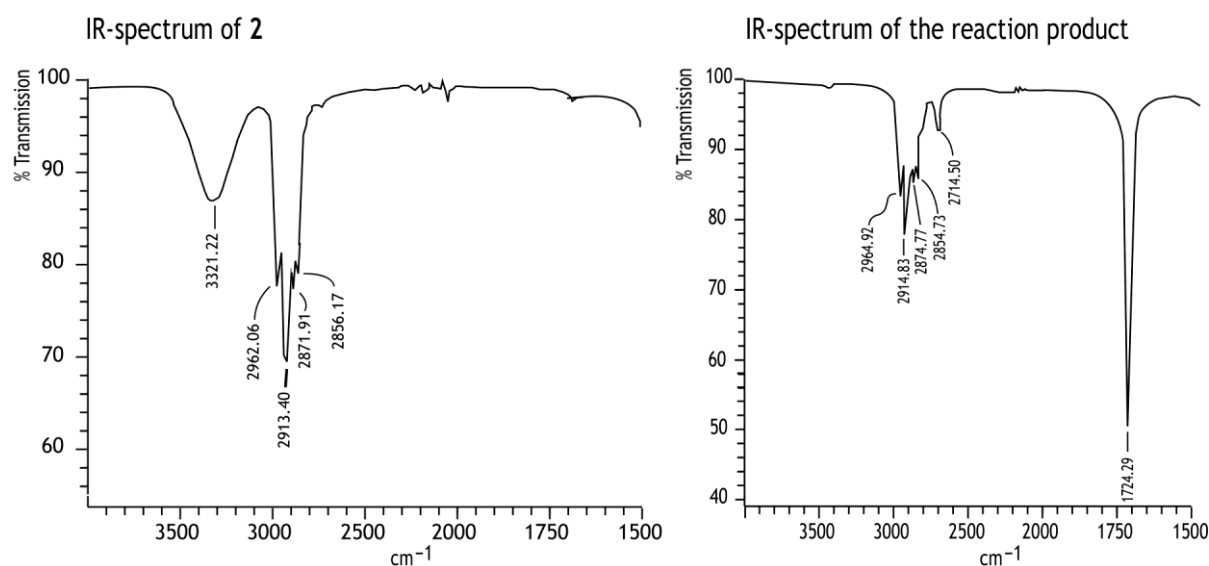
The structural formulas of fragrances found in plants are represented in the diagram below. They are widely applied, for example in the perfume industry.



These are nerol (1), citronellol (2), citronellal (3), isopulegol (4) and menthol (5). Isolating these compounds from plants is not always a simple process. Moreover, the quantities obtained are often insufficient. It is for this reason that synthetic conversions are also used during the production of these fragrances. These are also indicated in the diagram above.

- 19 Give the systematic name of nerol (1); make use of *E/Z* notation. 3
- 20 Use the diagram to determine if the conversion from 1 to 2 is chemo selective. 2
- 21 Use the diagram to determine if the conversion from 1 to 2 is stereo selective. 2
- 22 Which reagent(s) is/are suitable for the conversion from 2 to 3?
Choose from the following reagents: 4
- CrO_3 , pyridine
 - H_2 (Pd/C)
 - LiAlH_4
 - $\text{Na}_2\text{Cr}_2\text{O}_7$, H^+ , H_2O
 - O_3
 - PCC (pyridinium chlorochromate)

After the reaction that leads to the conversion of 2 to 3 is completed, the IR-spectrum is recorded for the product of the reaction. A section of that IR-spectrum is shown below. A section of the IR-spectrum for 2 is also shown.

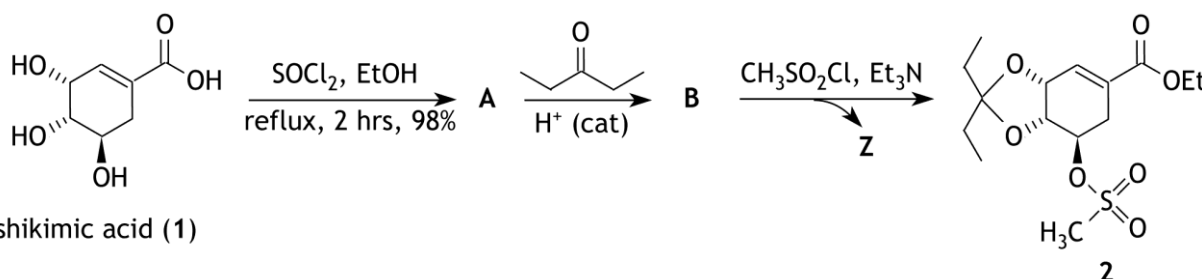


- From these IR-spectra, arguments that support the conversion from **2** to **3** can be derived.
- 23 Give two of these arguments and clarify how they support the desired conversion. 2
- For the structural formula drawn for isopulegol (**4**), multiple stereo-isomers are possible.
- 24 Explain how many stereo-isomers in total are possible for the structural formula that is drawn for isopulegol. 2
- In the molecules of menthol (**5**), the three side chains in the cyclohexane ring are in the equatorial position.
The chair conformation of the cyclohexane ring is drawn in the answer sheets.
- 25 In the answer sheets, draw the 3D structure of a molecule of menthol. 3
Make use of the cyclohexane ring that is already drawn. Draw the three side groups in the equatorial position.
- The synthesis of **4** from **3** can be carried out under the influence of H^+ (acidic solution) as catalyst. The ring closure that takes place can be thought of as an electrophilic addition reaction to a $C = C$ bond, followed by an $E1$ -elimination reaction.
The mechanism takes place according to the following steps:
- protonation of the carbonyl group;
 - electrophilic addition to the $C = C$ bond, where an intermediate carbocation is produced;
 - elimination of H^+ leading to the product.
- The structure of citronellal (**3**) is provided in the answer sheets.
- 26 Show the mechanism for the synthesis of **4** from **3** in the answer sheets. 6
- start with the structure of **3** that is already provided;
 - when representing the mechanism, use similar structures to those already given;
 - include the non-bonding electron pairs;
 - make use of curly arrows to indicate how electron pairs move when forming and breaking bonds;
 - include all formal charges in the appropriate places.
- Three 1H -NMR-spectra (in the area above 2.5 ppm) are provided in the answer sheets. These are spectra from the three compounds from series **1** - **5**. The conditions under which these spectra were recorded are identical (solvent $CDCl_3$, 300 MHz).
- 27 Write the number of the corresponding compound in each spectrum in your answer sheets. 3

Problem 6 Synthesis of Oseltamivir

(14 points)

Oseltamivir is a registered medicine (Tamiflu®) that is used to treat the influenza virus. Due to the importance of this medicine, multiple pathways for the synthesis of Oseltamivir have been developed. The first part of one of these pathways is provided below and begins with shikimic acid (1), that is isolated from star anise.



During the conversion of shikimic acid (1) to compound A, ethanol is both reagent and solvent. A limited amount of thionyl chloride (SOCl_2) is gradually added to a mixture of ethanol and shikimic acid.

The reaction between ethanol and thionyl chloride produces hydrogen chloride, which acts as a catalyst in the formation of A from shikimic acid and ethanol.

Then A reacts with pentane-3-one under the influence of an acid catalyst to form compound B.

Finally, $\text{CH}_3\text{SO}_2\text{Cl}$ is used to prepare compound 2 in the presence of triethylamine.

The reaction of ethanol with thionyl chloride produces two other compounds other than hydrogen chloride.

- 28 Give the formulas of these two compounds.

2

A procedure for the conversion of shikimic acid to A is described below:

In a 250 mL round-bottom flask, equipped with a reflux condenser and a magnetic stirrer, under an atmosphere of an inert gas, 19.90 g (= 0.114 mol) shikimic acid is suspended in 80 mL (= 1.4 mol) ethanol. To this mixture 4.16 mL (= 0.057 mol) thionyl chloride is added gradually over the course of 10 minutes. The mixture is refluxed for 2 hours, after which compound A is isolated with a 98% yield.

Due to the presence of OH groups in the shikimic acid molecule, thionyl chloride can react with ethanol as well as with shikimic acid. Whether that reaction affects the final yield of A depends on the type of OH groups in shikimic acid that react.

When the reaction takes place with the OH group of the COOH group, it has no influence on the yield of A.

When the reaction takes place with the alcoholic OH groups, it does have an influence on the yield of A.

- 29 Explain why the reaction between thionyl chloride with shikimic acid, via the OH of the COOH group, has no influence on the yield of A.

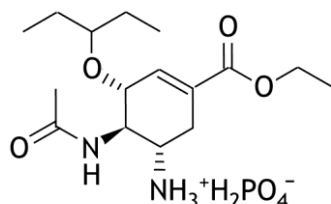
2

- 30 Explain that, for the reaction with thionyl chloride, it can be deduced from the data in the above description that the reactivity of the OH groups of ethanol is greater than the reactivity of the alcoholic OH groups of shikimic acid. 3
- 31 Give the formula of **Z**. 2
- 32 Explain, using the diagram, whether the reaction of **A** with pentan-3-one is regio selective. 2
- 33 Explain whether the 'lower' C atom (to which the $-\text{OSO}_2\text{CH}_3$ group is attached) in the six-membered ring of compound **2** has the *R*- or *S*-configuration. Use a sketch in your explanation. 3

Problem 7 Oseltamivir determination

(17 points)

Oseltamivir is sold as the water-soluble salt of phosphoric acid, oseltamivir phosphate:

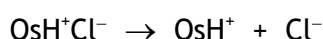


Oseltamivir phosphate

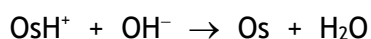
From here on, oseltamivir phosphate will be represented as $\text{OsH}^+\text{H}_2\text{PO}_4^-$.

In order to guarantee the quality of oseltamivir phosphate, the purity of the product must be checked regularly. This can be done, for example, by first converting the oseltamivir phosphate to oseltamivir chloride, OsH^+Cl^- . Excess caustic soda (a solution of NaOH) is added to a solution of this compound and finally a titration with hydrochloric acid is performed.

OsH^+Cl^- dissolves as follows:



OsH^+ is a weak acid, with $\text{p}K_a = 7.90$. When caustic soda is added, the following reaction occurs:



In such a determination, the oseltamivir phosphate from one 75.0 mg capsule is completely converted to oseltamivir chloride. This is dissolved in demineralized water and then the solution is filled to a final volume of 50.0 mL. Then 1,00 mL $5.00 \cdot 10^{-2}$ M caustic soda is added to 10.0 mL of this solution. The excess caustic soda is then back-titrated with $1.00 \cdot 10^{-3}$ M hydrochloric acid, of which 13.6 mL was required.

- 34 Calculate the mass percentage of the oseltamivir phosphate in the capsule. Assume that the ester bond does not react during the addition of the caustic soda and the titration process.

6

Phenolphthalein is used as indicator during the back-titration.

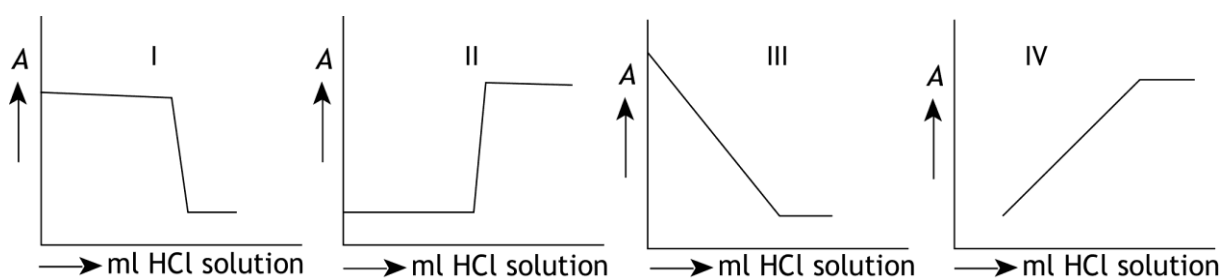
- 35 Would methyl orange also be a viable option to use, or would this result in a too high or too low result? Explain your answer.

3

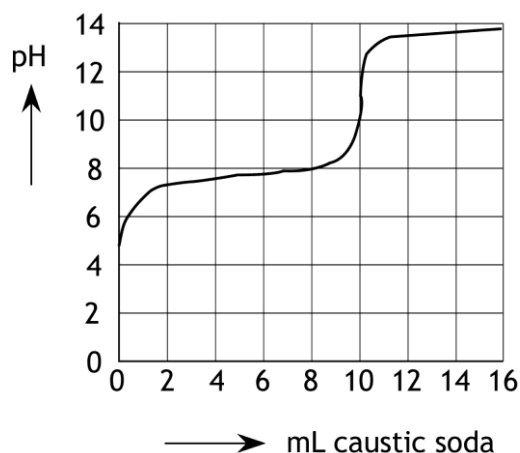
To accurately determine the equivalence point of the titration, you could perform the titration and follow the absorbance A caused by the presence of phenolphthalein.

- 36 Which of the following figures best indicates the progress of the absorbance during the titration? Explain your answer.

2



A titration curve for a solution of oseltamivir phosphate with caustic soda was established based on a pK_a of 7.90 for the OsH^+ to investigate if the determination could also be carried out by dissolving the capsule containing the oseltamivir phosphate in water and titrating the solution directly.



A peculiar aspect of this titration curve is that there is only one steep area, despite $OsH^+H_2PO_4^-$ being a triprotic acid.

- 37 Explain why there is only one steep area in the titration curve when oseltamivir phosphate is titrated with caustic soda, despite oseltamivir phosphate being a triprotic acid 2

The titration curve above shows that it is possible to titrate a solution of oseltamivir phosphate directly with caustic soda.

- 38 Using the titration curve above, explain that it is possible to titrate a solution of oseltamivir phosphate directly with caustic soda; also indicate which indicator you might use and give the color change of that indicator at the equivalence point. 3
- 39 Indicate the molar ratio for $OsH^+H_2PO_4^- : OH^-$ during the direct titration of a solution of oseltamivir phosphate with caustic soda. 1

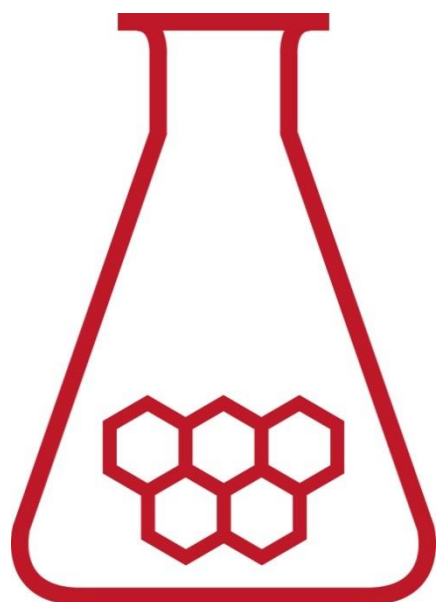
44^e National Chemistry olympiad

University Leiden

THEORY TEST

answer sheets

Monday 12 June 2023



**SCHEIKUNDE
OLYMPIADE**



55TH INTERNATIONAL
CHEMISTRY OLYMPIAD
SWITZERLAND 2023



Universiteit Leiden

Name: _____

N.B.: Do not forget to write your name on the first page!!

Question 3

In CoO_2 : the charge of Co is and the charge of O is

In LiCoO_2 : the charge of Li is, the charge of Co is and the charge of O is

Question 9

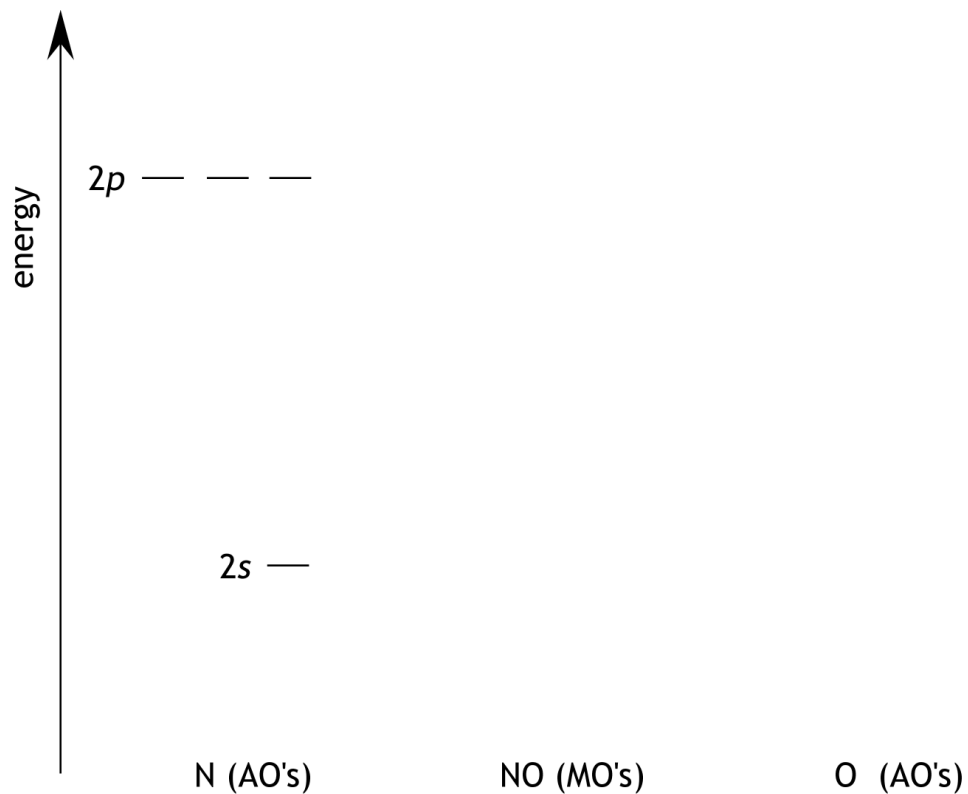
$[A]_{\text{new}}$ is larger than / equal to / smaller than $[A]_{\text{original}}$

$[B]_{\text{new}}$ is larger than / equal to / smaller than $[B]_{\text{original}}$

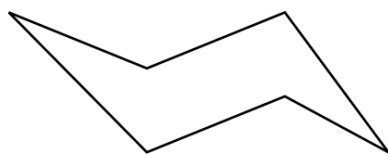
$[C]_{\text{new}}$ is larger than / equal to / smaller than $[C]_{\text{original}}$

$[D]_{\text{new}}$ is larger than / equal to / smaller than $[D]_{\text{original}}$

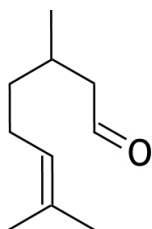
Question 12



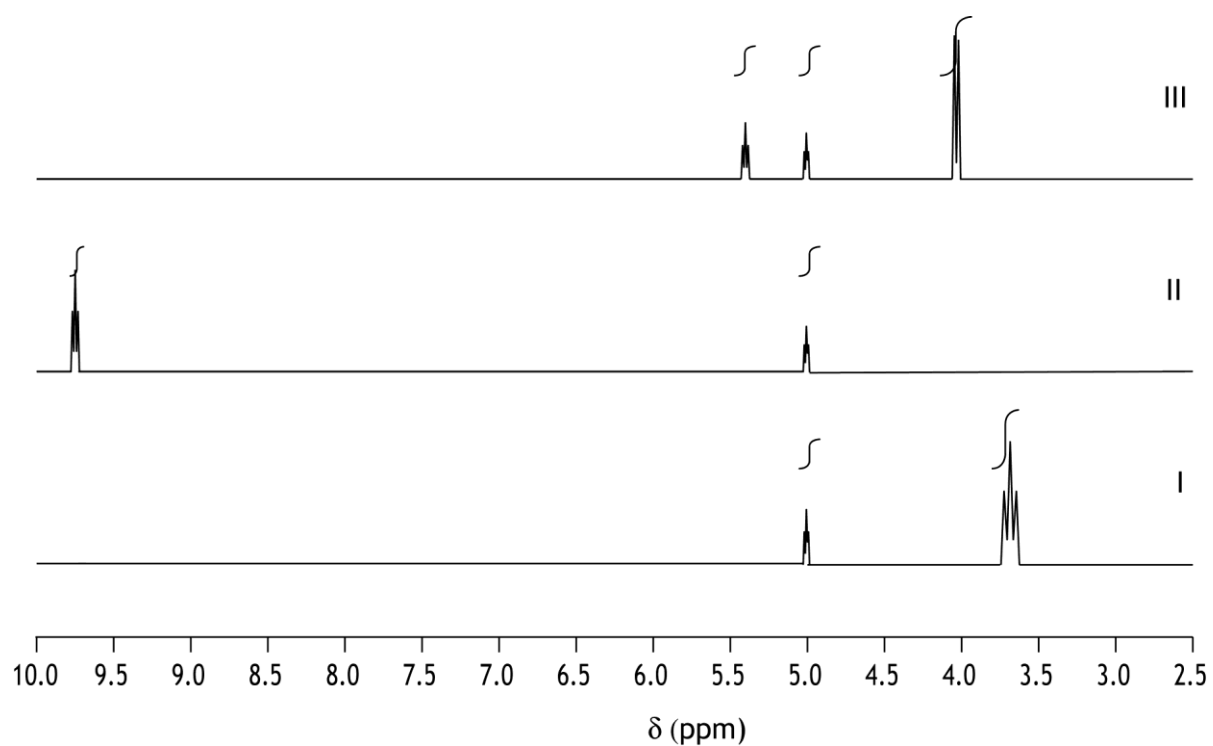
Question 25



Question 26



Question 27



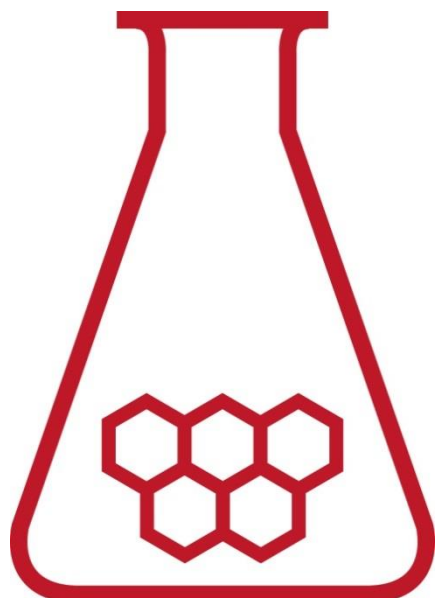
44th National Chemistry Olympiad

University Leiden

THEORY TEST

Marking scheme

Monday 12 June 2023



**SCHEIKUNDE
OLYMPIADE**



55TH INTERNATIONAL
CHEMISTRY OLYMPIAD
SWITZERLAND 2023



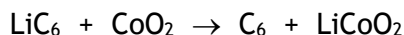
Universiteit Leiden

- This test consists of 7 problems with 39 open questions and a booklet with answer sheets.
- Use a separate piece of paper for each problem, making sure to include your name on it. 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 clock hours.
- Required resources: (graphic) calculator and Binas 6th edition or Sciencedata 1st print.
- Each question includes the number of points that a correct answer to that question will earn.

Problem 1 Lithium-ion battery

13 points

□1 Maximum score 2



· $\text{LiC}_6 + \text{CoO}_2$ before the arrow 1

· $\text{C}_6 + \text{LiCoO}_2$ after the arrow 1

If the chemical equilibrium sign is used instead of a single arrow 1

If the equation $\text{LiC}_6 + \text{CoO}_2 + \text{Li}^+ \rightarrow \text{Li}^+ + \text{C}_6 + \text{LiCoO}_2$ is given 1

If the equation $\text{C}_6 + \text{LiCoO}_2 \rightarrow \text{LiC}_6 + \text{CoO}_2$ is given 1

□2 Maximum score 1

$$E_{\text{cell}} = V_{\text{ox}}^0 - V_{\text{red}}^0 = +1.00 - (-3.05) = 4.05 \text{ V}$$

□3 Maximum score 3

In CoO_2 : the charge of Co is +4 and the charge of O is -2

In LiCoO_2 : the charge of Li is +1, the charge of Co is +3 and the charge of O is -2

· the charge of O in both cases is correct 1

· the charge of Co in CoO_2 is correct 1

· the charge of Li and Co in LiCoO_2 is correct 1

□4 Maximum score 3

An example of a correct calculation is:

$$\frac{200 \times 10^{-3} \times 2 \times 24 \times 60 \times 60}{9.649 \cdot 10^4} \times 6.941 = 2.49 \text{ g .}$$

· calculation of the amount of coulombs transported during two days: multiply 200 (mA) by 10^{-3} (A mA^{-1}) and by 2 (days) and by 24 (hours dag^{-1}) and by 60 (min uur^{-1}) and by 60 (sec min^{-1}) 1

· calculation of the amount of moles of electrons (equals the amount of moles of lithium): divide the amount of coulombs transported during two days by Faraday's constant 1

· calculation of the amount of g of lithium: multiply the amount of moles of lithium by 6.941 (g mol^{-1}) 1

□5 Maximum score 4

An example of a correct answer is:

A magnesium atom can supply two electrons and a lithium atom can supply one, so given an equal amount of atoms, the magnesium-ion battery could supply twice as much current as the lithium-ion battery. But the atomic mass of magnesium is more than twice the atomic mass of lithium, therefore, there are more than twice as many lithium atoms in the lithium-ion battery as magnesium atoms in the magnesium-ion battery. Therefore the

lithium-ion battery takes the longest time to be discharged, and that is $\frac{24.31}{2} = 1.75$ times longer.

- explanation that for an equal amount of atoms, the magnesium-ion battery can provide twice as much current as the lithium-ion battery 1
- explanation that there are more than twice as many lithium atoms in the lithium-ion battery as magnesium atoms in the magnesium-ion battery 1
- conclusion about which battery takes the longest time to discharge 1
- calculation of how many times longer the lithium-ion battery takes to discharge than the magnesium-ion battery 1

Problem 2 G and K**13 points**

□6 Maximum score 4

There is equilibrium when the curve is at its minimum. $[C] = 0.75 \text{ mol L}^{-1}$. Then $[D]$ is also equal to 0.75 mol L^{-1} . $[A] = [B] = 1.00 - 0.75 = 0.25 \text{ mol L}^{-1}$.

$$\text{Therefore } K = \frac{[C][D]}{[A][B]} = \frac{0.75 \times 0.75}{0.25 \times 0.25} = 9.0.$$

- notion that there is equilibrium at the minimum of the curve 1
- determining $[C]$ and $[D]$ set equal to $[C]$ 1
- calculation of $[A]$ and $[B]$ 1
- calculation of K 1

□7 Maximum score 2

$$\Delta_r G^0 = -RT \ln K = -8.314 \times 298 \times \ln 9.0 = -5.4 \cdot 10^3 \text{ J mol}^{-1}$$

- $\Delta_r G^0 = -RT \ln K$ 1
- calculation of $\Delta_r G^0$ 1

□8 Maximum score 4

$$\Delta_r G^0(\text{in units } RT) = \frac{-5.4 \cdot 10^3}{8.314 \times 298} = -2.2.$$

The distance between 3.2 and x is equal to $\Delta_r G^0(\text{in units } RT)$, therefore x is $3.2 - 2.2 = 1.0$.

The distance between 3.2 and x along the vertical axis is 2.8 cm. The distance between x

and y is 0.6 cm. The distance between between x and y , in RT units, is $\frac{0.6}{2.8} \times 2.2 = 0.47$.

Thus y will read $1.0 - 0.47 = 0.53$ (rounded to 0.5).

- calculation of $\Delta_r G^0(\text{in units } RT)$ 1
- conclusion regarding x 1
- calculation of the distance between x and y in RT units 1
- conclusion regarding y 1

□9 Maximum score 3

$[A]_{\text{new}}$ is smaller than $[A]_{\text{original}}$

$[B]_{\text{new}}$ is larger than $[B]_{\text{original}}$

$[C]_{\text{new}}$ is larger than $[C]_{\text{original}}$

$[D]_{\text{new}}$ is larger than $[D]_{\text{original}}$

- $[A]_{\text{new}}$ is smaller than $[A]_{\text{original}}$ 1
- $[B]_{\text{new}}$ is larger than $[B]_{\text{original}}$ 1
- $[C]_{\text{new}}$ is larger than $[C]_{\text{original}}$ and $[D]_{\text{new}}$ is larger than $[D]_{\text{original}}$ 1

Problem 3 Sulfuryl chloride

12 points

□10 Maximum score 6

A correct answer could look like the following:

The molecule is tetrahedral.

The sulfur atom has sp^3 hybridization and the oxygen atoms have sp^2 hybridization.

The bond between the sulfur atom and a chlorine atom is a σ -bond formed by overlap of an sp^3 orbital of the sulfur atom with a p orbital of the chlorine atom.

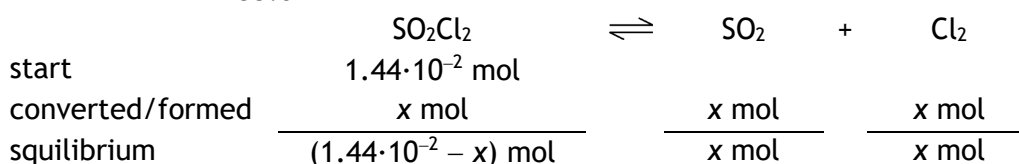
The bond between the sulfur atom and an oxygen atom is a σ -bond and a π -bond. The σ -bond between the sulfur atom and an oxygen atom is formed by overlap of an sp^3 orbital of the sulfur atom with an sp^2 orbital of the oxygen atom; the π -bond is formed by overlap of a d orbital of the sulfur atom and a p orbital of the oxygen atom.

- tetrahedral structure 1
- correct hybridization of the sulfur and oxygen atoms 1
- σ -bonds between S and Cl 1
- σ -bonds and π -bonds between S and O 1
- correct description of how σ -bonds in the molecule are formed 1
- correct description of how π -bonds in the molecule are formed 1

□11 Maximum score 6

An example of a correct calculation is:

$$1.95 \text{ g SO}_2\text{Cl}_2 \text{ is } \frac{1.95}{135.0} = 1.44 \cdot 10^{-2} \text{ mol.}$$



During equilibrium, there is $(1.44 \cdot 10^{-2} - x) + x + x = (1.44 \cdot 10^{-2} + x)$ mol gas present and this has a volume of 1.00 dm^3 at $157 \text{ }^\circ\text{C}$ and $p = p_0$, therefore, via $pV = nRT$:

$$1.013 \cdot 10^5 \times 1.00 \cdot 10^{-3} = (1.44 \cdot 10^{-2} + x) \times 8.314 \times (273 + 157)$$

This produces $x = 1.39 \cdot 10^{-2} \text{ mol}$.

During equilibrium there is $1.44 \cdot 10^{-2} + 1.39 \cdot 10^{-2} = 2.83 \cdot 10^{-2} \text{ mol gas}$.

Of which $1.44 \cdot 10^{-2} - 1.39 \cdot 10^{-2} = 0.05 \cdot 10^{-2} \text{ mol SO}_2\text{Cl}_2$ and $1.39 \cdot 10^{-2} \text{ mol SO}_2$ and Cl_2 .

The partial pressures are: $p_{\text{SO}_2\text{Cl}_2} = \frac{0.05 \cdot 10^{-2}}{2.83 \cdot 10^{-2}} \times 1.013 \cdot 10^5 = 2 \cdot 10^3 \text{ Pa}$ and

$$p_{\text{SO}_2} = p_{\text{Cl}_2} = \frac{1.39 \cdot 10^{-2}}{2.83 \cdot 10^{-2}} \times 1.013 \cdot 10^5 = 498 \cdot 10^4 \text{ Pa.}$$

$$\text{Therefore } K_p = \frac{\frac{p_{\text{Cl}_2} \times p_{\text{SO}_2}}{p_0}}{\frac{p_{\text{SO}_2\text{Cl}_2}}{p_0}} = \frac{p_{\text{Cl}_2} \times p_{\text{SO}_2}}{p_{\text{SO}_2\text{Cl}_2}} \times \frac{1}{p_0} = \frac{4.98 \cdot 10^4 \times 4.98 \cdot 10^4}{2 \cdot 10^3} \times \frac{1}{1.013 \cdot 10^5} = 1 \cdot 10^1.$$

- calculation of the amount of moles of SO_2Cl_2 1
- (in the case of $x \text{ mol}$ of converted SO_2Cl_2) calculation of the total amount of moles of gas during equilibrium: the amount of moles of SO_2Cl_2 plus x 1
- calculation of the amount of moles of SO_2 and Cl_2 during equilibrium (is equal to x) 1
- calculation of the amount of moles of SO_2Cl_2 during equilibrium 1
- calculation of the partial pressures 1
- calculation of K_p 1

Note

When K_p is calculated as follows: $K_p = \frac{p_{\text{Cl}_2} \times p_{\text{SO}_2}}{p_{\text{SO}_2\text{Cl}_2}} = \frac{4.98 \cdot 10^4 \times 4.98 \cdot 10^4}{2 \cdot 10^3} = 1 \cdot 10^6 \text{ (Pa)}$, accept

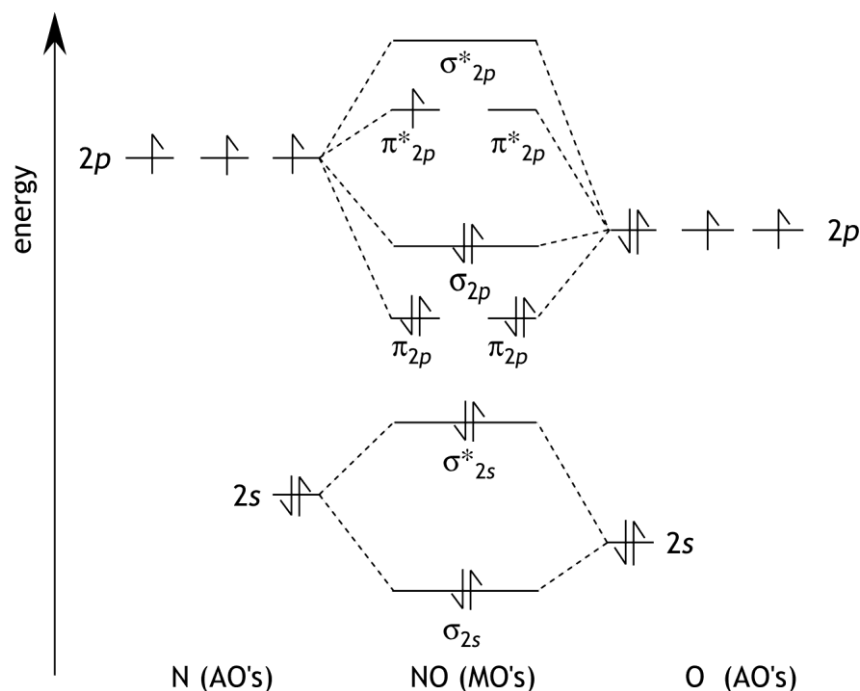
this as correct.

Problem 4 NO

24 points

□12 Maximum score 6

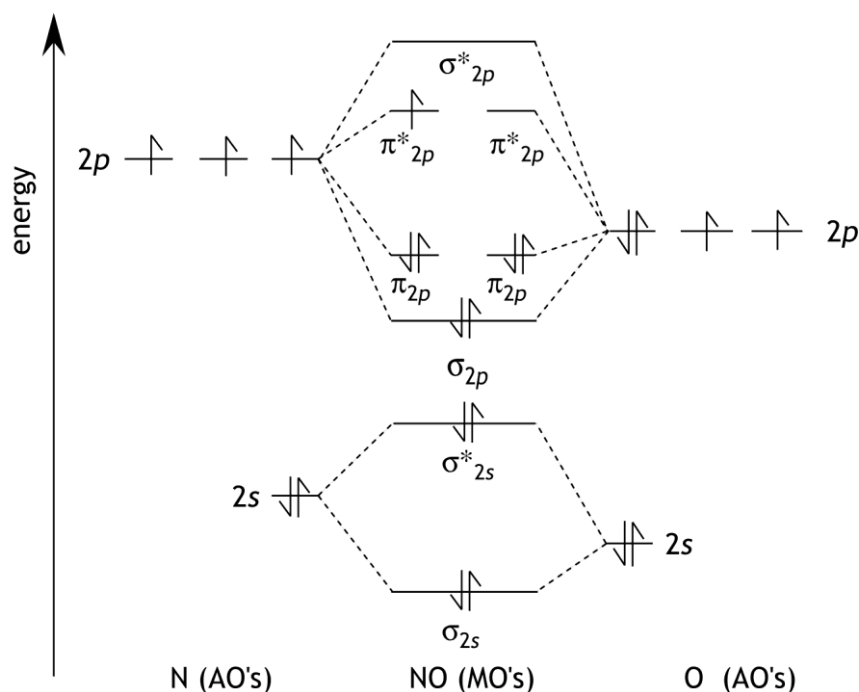
A correct answer can look as follows:



- 2s and 2p levels of the oxygen atom are drawn lower than the 2s and 2p levels of the nitrogen atom 1
- in the 2s level of the nitrogen atom there is one electron pair and in the 2s level of the oxygen atom there is one electron pair 1
- in the nitrogen atom there are three unpaired electrons in the 2p level 1
- in the oxygen atom there are one electron pair and two unpaired electrons in the 2p level 1
- the levels of all molecular orbitals are drawn in the correct manner and with the correct notation 1
- in the nitrogen monoxide molecule electron pairs in the σ_{2s} , σ^*_{2s} , the two π_{2p} 's and σ_{2p} and one unpaired electron in the π^*_{2p} 1

Note

When the following answer is provided, accept this as correct:



□13 Maximum score 2

$$\text{bond order} = \frac{8-3}{2} = 2.5$$

- number of electrons in the bonding and anti-bonding molecular orbitals are correct
- the rest of the calculation

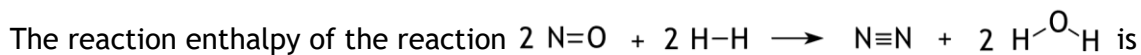
1
1

Notes

- When the answer for bond order is given as $= \frac{6-1}{2} = 2.5$, accept this as correct.
- When an incorrect answer to question 13 is consequently due to an incorrect answer to question 12, accept the answer to question 13 as correct.

□14 Maximum score 3

An example of a correct answer is:



$$\Delta_r H = -2 \times (+0.913 \cdot 10^5) + 2 \times (-2.42 \cdot 10^5) = -6.67 \cdot 10^5 \text{ J per 2 mol NO.}$$

- all heats of formation are correct
- all signs are correctly processed
- all coefficients are correctly processed

1
1
1

□15 Maximum score 3

An example of a correct answer is:

$\Delta_r H = -2 \times BE_{N=O} - 2 \times BE_{H-H} + BE_{N=N} + 4 \times BE_{O-H}$, so

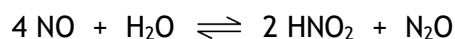
$$BE_{N=O} = \frac{-2 \times BE_{H-H} + BE_{N=N} + 4 \times BE_{O-H} - \Delta_r H}{2} =$$
$$\frac{-2 \times (-4.36 \cdot 10^5) + (-9.45 \cdot 10^5) + 4 \times (-4.635 \cdot 10^5) - (-6.67 \cdot 10^5)}{2} = -6.30 \cdot 10^5 \text{ J mol}^{-1}$$

- all bond enthalpies are correct 1
- all signs and $\Delta_r H$ are correctly processed 1
- all coefficients are correctly processed 1

Note

When an incorrect answer to question 15 is a consequence of an incorrect answer to question 14, mark the answer to question 15 as correct.

□16 Maximum score 3



- NO and H₂O on the left of the equilibrium sign 1
- HNO₂ and N₂O on the right of the equilibrium sign 1
- correct coefficients 1

If the following equation is given: $3 \text{ NO} + \text{H}^+ \rightleftharpoons \text{HNO}_2 + \text{N}_2\text{O}$ 1

Note

When a single arrow is used instead of the equilibrium sign, accept this as correct.

□17 Maximum score 4

An example of a correct answer is:

From $\Delta G^0 = -RT \ln K$ en $\Delta G^0 = -nF \Delta V^0$, follows:

$$K = e^{\frac{\Delta G^0}{RT}} = e^{\frac{-2 \times (1.59 - 0.98) \times 9.65 \cdot 10^4}{8.31 \times 298}} = 4.4 \cdot 10^{20}$$

- notion that $n = 2$ 1
- calculation of ΔV^0 1
- calculation of ΔG^0 1
- the rest of the calculation 1

□18 Maximum score 3

A correct answer can be formulated as follows:

The ΔG^0 for the conversion of NO to N₂O is equal to $-1 \times 9.65 \cdot 10^4 \times 1.59$.

The ΔG^0 for the conversion of N₂ to NH₄⁺ is equal to $-3 \times 9.65 \cdot 10^4 \times 0.27$.

Therefore the ΔG^0 for the conversion of NO to NH₄⁺ is equal to

$$-1 \times 9.65 \cdot 10^4 \times 1.59 + (-1 \times 9.65 \cdot 10^4 \times 1.77) + (-3 \times 9.65 \cdot 10^4 \times 0.27).$$

Then

$$\begin{aligned} V^0 &= -\frac{\Delta G^0}{n \times F} = -\frac{-1 \times 9.65 \cdot 10^4 \times 1.59 + (-1 \times 9.65 \cdot 10^4 \times 1.77) + (-3 \times 9.65 \cdot 10^4 \times 0.27)}{5 \times 9.65 \cdot 10^4} \\ &= \frac{1.59 + 1.77 + 3 \times 0.27}{5}. \end{aligned}$$

- calculation of the ΔG^0 for the conversion of NO to N₂O and the ΔG^0 for the conversion of N₂O to N₂ and the ΔG^0 for the conversion from N₂ to NH₄⁺ 1
- calculation of the ΔG^0 for the conversion from NO to NH₄⁺ 1
- the rest of the calculation 1

Problem 5 Crazy scents

27 points

- 19 Maximum score 3
(Z)-3,7-dimethylocta-2,6-diene-1-ol or 2-Z-3,7-dimethyl-2,6-octadien-1-ol
- dimethyloctadienol correct 1
 - the numbers correct 1
 - Z correct 1
- 20 Maximum score 2
A correct answer can be formulated as follows:
The hydrogenation takes place at the C = C of the allyl alcohol (and not at the other C = C).
Thus the conversion is chemo selective.
- the hydrogenation takes place at the C = C of the de allyl alcohol (and not at the other C = C) 1
 - correct conclusion 1
- 21 Maximum score 2
Examples of a correct answer could be:
The methyl group (on C atom 3) can be situated above or below the plane of the drawing.
The conversion is not stereo selective.
- and
- From the structure of **2** it is not possible to tell the position of the methyl group (on C atom 3).
So there is no way to check whether the conversion is stereo selective.
- the methyl group (on C atom 3) can be above or below the plane of the drawing / from the structure of **2** it is not possible to tell the position of the methyl group (on C atom 3). 1
 - correct conclusion 1
- 22 Maximum score 4
a and f
- per correct reagent 2
- Note*
For each incorrect reagent, subtract 2 points from the assigned partial score(s), up to a minimum score of 0.
- 23 Maximum score 2
A correct answer can be formulated as follows:
The peak at 3321 cm^{-1} (in the IR-spectrum of **2**) is no longer visible in the IR-spectrum of the product, therefore the OH group is no longer present.
The peak at 1724 cm^{-1} (in the spectrum of the product) indicates the presence of a carbonyl group / C = O group.
- the peak at 3321 cm^{-1} (in the IR-spectrum of **2**) is no longer visible in the IR-spectrum of the product, therefore the OH group is no longer present 1
 - the peak at 1724 cm^{-1} (in the spectrum of the product) indicates the presence of a carbonyl group / C = O group 1

□24 Maximum score 2

A correct answer can be formulated as follows:

In the structure there are three asymmetrical carbon atoms. So $2^3 = 8$ stereo-isomers are possible.

· correct amount of asymmetrical carbons

1

· calculation of the amount of stereo-isomers

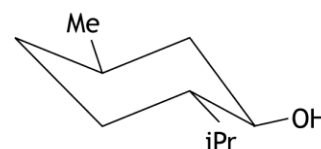
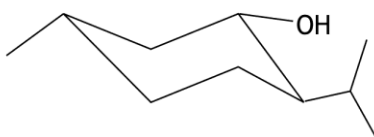
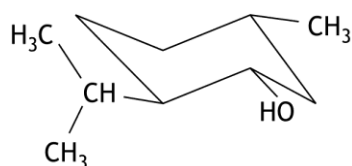
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If the following answer is given: „One asymmetric carbon atom occurs in the structure. So two stereo-isomers are possible.”

0

□25 Maximum score 3

Examples of correct answers are:

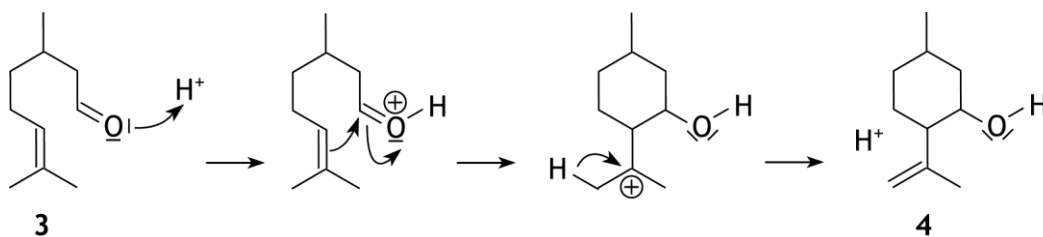


per correctly drawn side group

1

□26 Maximum score 6

A correct answer can be as follows:



· the structure with the protonated carbonyl group correct

1

· the structure with the carbocation correct

1

· the structure of 4 and H^+ correct

1

· the non-bonding electron pairs correct

1

· the formal charges correct

1

· the curly arrows correct

1

□27 Maximum score 3

I = 2, II = 3, III = 1

per correct spectrum

1

Problem 6 Synthesis of Oseltamivir

14 points

□28 Maximum score 2

SO₂ and CH₃CH₂Cl

· CH₃CH₂Cl

1

· SO₂

1

□29 Maximum score 2

A correct answer can be given as follows:

From the reaction of thionyl chloride with the COOH group, acyl chloride / acid chloride is produced. Ethanol reacts with acyl chloride to the desired ester **A**.

· from the reaction of thionyl chloride with the COOH group, acyl chloride / acid chloride is produced

1

· ethanol reacts with acyl chloride to the desired ester **A**

1

□30 Maximum score 3

A correct answer can be given as follows:

In the given amount of shikimic acid, there are ($3 \times 0.114 =$) 0.342 mol of OH groups. This is about a quarter of the OH groups in ethanol. If these were as reactive as the OH groups in ethanol, the yield of **A** would be (much) less than 98%. So the OH groups in ethanol are more reactive.

or

Suppose one OH group (per molecule of shikimic acid) would react. Then the mole ratio $\text{OH}_{\text{in shikimic acid}} : \text{OH}_{\text{in ethanol}} = 0.114 : 1.4$. If those different OH groups were equally reactive, the loss of **A** would be greater than 2 percent. So the OH groups in ethanol are more reactive.

· a correct comment regarding the ratio of the amount of alcoholic OH groups in the shikimic acid and the amount of OH groups in ethanol

1

· a correct comment about the yield of **A** / about the loss of **A** at equal reactivity

1

· the rest of the explanation

1

□31 Maximum score 2

(C₂H₅)₃NHCl or (C₂H₅)₃NH⁺Cl⁻

If the answer HCl is given

1

□32 Maximum score 2

A correct answer can be given as follows:

A molecule of pentane-3-one reacts with the two OH groups on the 'left' side of the hexagon and not with any other combination of two OH groups. Thus, the reaction is regio selective.

· a molecule of pentane-3-one reacts with the two OH groups on the 'left' side of the hexagon and not with any other combination of two OH groups

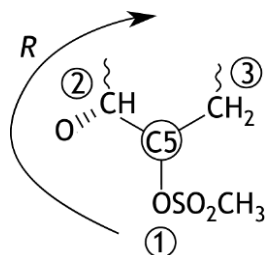
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· correct conclusion

1

□33 Maximum score 3

An example of a correct answer is as follows:



- a correct sketch 1
- correct priority 1
- correct indication of the configuration 1

Problem 7 Oseltamivir determination

17 points

□34 Maximum score 6

An example of a correct calculation is:

The amount of mmoles of OsH^+ that reacted is: $1.00 \times 5.00 \cdot 10^{-2} - 13.6 \times 1.00 \cdot 10^{-3}$.

In the 50,0 mL solution there was $\frac{50.0}{10.0} \times (1.00 \times 5.00 \cdot 10^{-2} - 13.6 \times 1.00 \cdot 10^{-3})$ mmol OsH^+

and that came from $\frac{50.0}{10.0} \times (1.00 \times 5.00 \cdot 10^{-2} - 13.6 \times 1.00 \cdot 10^{-3})$ mmol $\text{OsH}^+\text{H}_2\text{PO}_4^-$ and that

is $\frac{50.0}{10.0} \times (1.00 \times 5.00 \cdot 10^{-2} - 13.6 \times 1.00 \cdot 10^{-3}) \times 410.41$ mg $\text{OsH}^+\text{H}_2\text{PO}_4^-$. So the mass

percentage $\text{OsH}^+\text{H}_2\text{PO}_4^-$ in the capsule is

$$\frac{\frac{50.0}{10.0} \times (1.00 \times 5.00 \cdot 10^{-2} - 13.6 \times 1.00 \cdot 10^{-3}) \times 410.41}{75.0} \times 100\% = 99.6\%$$

- calculation of the amount of mmoles of added OH^- and the amount of mmoles of H^+ required for titration: multiply 1.00 (mL) by $5.00 \cdot 10^{-2}$ (mmol mL^{-1}) and multiply 13.6 (mL) by $1.00 \cdot 10^{-3}$ (mmol mL^{-1}) 1
- calculation of the amount of mmoles of OsH^+ in the 10.0 mL solution: subtract the amount of mmoles of H^+ needed for the titration from the amount of mmoles of added OH^- 1
- calculation of the amount of mmoles of $\text{OsH}^+\text{H}_2\text{PO}_4^-$ in the capsule (equals the amount of mmoles of OsH^+ in the 50.0 mL solution): multiply the amount of mmoles of OsH^+ in the 10.0 mL solution by 50.0 (mL) and divide by 10.0 (mL) 1
- calculation of the molar mass of $\text{OsH}^+\text{H}_2\text{PO}_4^-$: 410.41 (m)g (m) mol^{-1} 1
- calculation of the amount of mg of $\text{OsH}^+\text{H}_2\text{PO}_4^-$ in the capsule: multiply the amount of mmoles of $\text{OsH}^+\text{H}_2\text{PO}_4^-$ in the capsule by the molar mass of $\text{OsH}^+\text{H}_2\text{PO}_4^-$ 1
- calculation of the mass percentage: divide the amount of mg of $\text{OsH}^+\text{H}_2\text{PO}_4^-$ in the capsule by 75.0 mg and multiply by 100% 1

- 35 Maximum score 3
 An example of a correct answer is:
 Methyl orange changes colour at low pH. Then during the titration, some Os will also react with H⁺. Too much hydrochloric acid will then be added, making it appear that less OsH⁺ reacted with caustic soda. You will then get too low a result. (So it is better not to use methyl orange as an indicator).
- when using methyl orange, Os will also react with H⁺ 1
 - too much hydrochloric acid is then added 1
 - conclusion(s) 1
- 36 Maximum score 2
 An example of a correct answer is:
 Before the equivalence point (the solution keeps its color, that is) the absorbance remains almost the same. Only at the equivalence point does the phenolphthalein react and the absorbance drops rapidly. So Figure I shows the progress of the absorbance best.
- before the equivalence point, the extinction remains (nearly) constant 1
 - at the equivalence point the phenolphthalein reacts and the solution becomes colorless and conclusion 1
- 37 Maximum score 2
 An example of a correct answer is:
 The difference in the K_a values of the H₂PO₄⁻ and OsH⁺ is so small that no pH change can be seen at the first equivalence point.
 The K_a of the HPO₄²⁻ is so small that also the third equivalence point cannot be seen.
- explanation why the first equivalence point cannot be seen 1
 - explanation why the third equivalence point cannot be seen 1
- 38 Maximum score 3
 An example of a correct answer is:
 There is a steep region in the titration curve from pH = 10 to pH = 12. Alizarin yellow can then be used as an indicator; the color change is from pale yellow to red.
- there is a steep region in the titration curve 1
 - correct indicator identified 1
 - correct colour change given 1
- 39 Maximum score 1
 (OsH⁺H₂PO₄⁻ : OH⁻ =)1 : 2

44th National Chemistry Olympiad

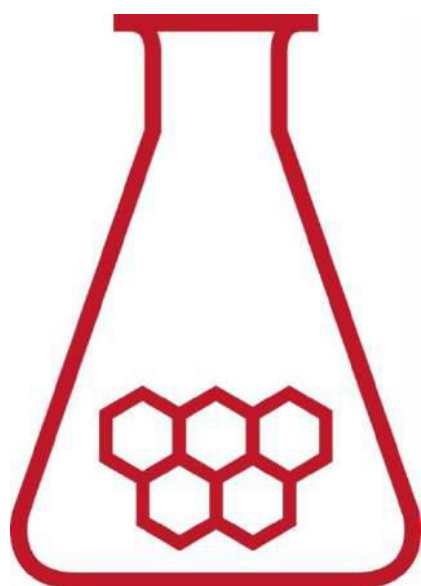
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Leiden

PRACTICAL TEST

Assignment booklet

Tuesday June 13, 2023



**SCHEIKUNDE
OLYMPIADE**



55TH INTERNATIONAL
CHEMISTRY OLYMPIAD
SWITZERLAND 2023



Universiteit Leiden

The experiments for this test were prepared by:

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Directions/resources

- This practical test consists of two integrated parts:
 - The synthesis of Hantzsch ester and Hantzsch pyridine;
 - The determination of the molar absorptivity (extinction coefficient) of Hantzsch ester at 400 nm.
- 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 in everything, 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 clean, safety maximum 20 points
 - results of the determinations and answers to the questions maximum 60 points
- Required tools: (graphic) calculator, ruler/protractor and Binas or ScienceData.
- First read the introduction and all assignments before you start working.
- Write the answers to the questions in the boxes on the answer sheets provided. If you don't have enough space, you can ask for extra paper.

Additional:

- This is a test; it is not permitted to consult with other participants.
- If you have a question, you can ask the supervisor.
- If something is wrong with your glassware or equipment, report it to the supervisor as soon as you discover it. Don't borrow someone else's things!

Sequence of experiments

This test consists of two experiments.

Experiment 1 consists of two parts: the preparation of the so-called Hantzsch ester (**synthesis part 1**) and the oxidation of Hantzsch ester to the pyridine form (**synthesis part 2**).

In **Experiment 2**, the molar absorptivity (extinction coefficient) of Hantzsch ester at 400 nm is determined.

To ensure that there is sufficient time in **Experiment 1** to synthesize, isolate and dry the crystalline Hantzsch pyridine and then measure everyone's NMR spectrum, you must start **synthesis part 2** immediately after starting **synthesis part 1**. You will receive pre-prepared Hantzsch ester for **synthesis part 2**. You will also receive pre-prepared Hantzsch ester for **Experiment 2**.

You will be asked several times to wait a few minutes, for example until crystals have formed. Make good use of this time by answering questions or starting **Experiment 2**. It is best to take a short break at step 13 of **synthesis part 2**.

Setups:

In the fumehood there are two setups ready for the two reactions and a setup for filtration. You can use the same Büchner flask several times for the three filtrations, each time with a clean filter.

Setup 1 is for **synthesis part 1** where a hot plate is used in combination with a magnetic stirrer. The temperature and stirring speed have already been set correctly, both the hot plate and the magnetic stirrer must be turned on.

Setup 2 is for **synthesis part 2**. This involves first stirring only at room temperature; the stirring speed is already set correctly. Only the hot plate is used in the recrystallization step; the temperature is already set correctly.

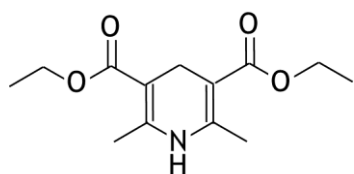
Experiment 1 Synthesis of Hantzsch ester and oxidation to the pyridine form

46 points

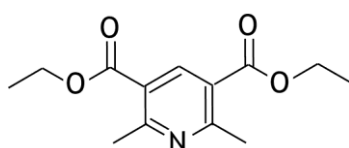
Introduction

Hantzsch ester is a particularly versatile molecule. It is an analogue of the biological reducing agent NADH and as such can be easily oxidized to a pyridine. It is used, among other things, as a hydride donor in hydrogenation transfer reactions. Derivatives of Hantzsch ester also find use as a drug for blocking Ca^{2+} ion channels, thereby lowering blood pressure.

The structural formulas of Hantzsch ester and the pyridine form are as follows:

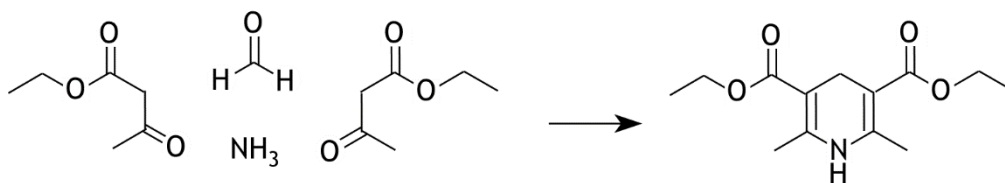


Hantzsch ester



Hantzsch pyridine

The synthesis of Hantzsch ester is a so-called multi-component condensation reaction: multiple reactants react simultaneously (at the same time) or sequentially (one after the other) in the same solution. Schematically this can be shown as follows:








multicomponent condensation reaction

In the synthesis performed in this experiment, the polymer paraformaldehyde is used as the source of the super-electrophilic methanal (formaldehyde) and ammonium acetate is used as the source of ammonia.

The synthesis proceeds via tautomerization of a β -keto ester (ethyl acetoacetate) to its nucleophilic enol form.

Chemicals and safety

<p style="text-align: center;"><u>Ethyl acetoacetate</u></p> <ul style="list-style-type: none"> ▪ Formula: $C_6H_{10}O_3$ ▪ CAS No.: 141-97-9 ▪ Molar mass: $130.14 \text{ g mol}^{-1}$ ▪ Density: 1.029 g mL^{-1} ▪ Boiling point: $181 \text{ }^\circ\text{C}$ ▪ No H/P sentences 	<p style="text-align: center;"><u>Sodium nitrite</u></p> <p style="text-align: center;"></p> <ul style="list-style-type: none"> ▪ Formula: $NaNO_2$ ▪ CAS No.: 7632-00-0 ▪ Molar mass: $69.00 \text{ g mole}^{-1}$ ▪ H272, H301, H319, H400 ▪ P210, P220, P264, P273, P301+P310, P305+P351+P338
<p style="text-align: center;"><u>Paraformaldehyde</u></p> <p style="text-align: center;"></p> <ul style="list-style-type: none"> ▪ Formula: $[CH_2O]_n$ ▪ CAS No.: 30525-89-4 ▪ Molar mass: 30.03 g mol^{-1} (monomer) ▪ Density: 0.984 g mL^{-1} ▪ H228, H302 + H332, H315, H317, H318, H335, H341, H350 ▪ P210, P280, P301+P312+P340, P305+P338+P351, P308+P313 	<p style="text-align: center;"><u>Ethanol (absolute)</u></p> <p style="text-align: center;"></p> <ul style="list-style-type: none"> ▪ Formula: C_2H_6O ▪ CAS No.: 64-17-5 ▪ Molar mass: 46.07 g mol^{-1} ▪ Density: 0.789 g mL^{-1} ▪ Boiling point: $78 \text{ }^\circ\text{C}$ ▪ H225, H319 ▪ P210, P233, P240, P241, P242, P305+P351+P338
<p style="text-align: center;"><u>Ammonium acetate (1.0 M aq.)</u></p> <ul style="list-style-type: none"> ▪ Formula: $C_2H_7NO_2$ ▪ CAS No.: 631-61-8 ▪ Molar mass: 77.08 g mol^{-1} ▪ No H/P sentences 	<p style="text-align: center;"><u>Hantzsch ester (product 1)</u></p> <ul style="list-style-type: none"> ▪ Formula: $C_{13}H_{19}NO_4$ ▪ CAS No.: 1149-23-1 ▪ Molar mass: $253.29 \text{ g mol}^{-1}$ ▪ No H/P sentences
<p style="text-align: center;"><u>Acetic acid</u></p> <p style="text-align: center;"></p> <ul style="list-style-type: none"> ▪ Formula: $C_2H_4O_2$ ▪ CAS No.: 64-19-7 ▪ Molar mass: 60.05 g mol^{-1} ▪ Density: 1.049 g mL^{-1} ▪ Boiling point: $118 \text{ }^\circ\text{C}$ ▪ H226, H314 ▪ P210, P233, P240, P280, P303+P361+P353, P305+P351+P338 	<p style="text-align: center;"><u>Hantzsch pyridine (product 2)</u></p> <p style="text-align: center;"></p> <ul style="list-style-type: none"> ▪ Formula: $C_{13}H_{17}NO_4$ ▪ CAS No.: 1149-24-2 ▪ Molar mass: $251.28 \text{ g mol}^{-1}$ ▪ H315, H319, H335 ▪ P261, P264, P271, P280, P302+P352, P305+P351+P338

Materials (synthesis part 1)

- 50 mL round bottom flask with stir bar and septum
- 25 mL measuring cylinder
- 5.0 mL measuring pipette + pipette balloon
- Büchner filter
- watch glass with filter paper
- 100 mL volumetric flask + stopper

Materials (synthesis part 2)

- 50 mL round bottom flask with stir bar
- 25 mL measuring cylinder (2x)
- 10 mL measuring cylinder (2x)
- 100 mL beaker
- 25 mL beaker
- watch glass
- glass filter (2x)
- weighing bottle containing 625 mg sodium nitrite

Materials (general)

- stir bar catcher (magnetic bar)
- tweezers
- spatula
- pH paper
- pan for ice bath
- squeezing bottle with demineralized water
- sample vial

Synthesis part 1

1. In the 50 mL round bottom flask with stir bar in setup 1, there is 450 mg paraformaldehyde (this yields 15.0 mmol methanal).
2. Measure approximately 18 mL of 1.0 M ammonium acetate (around 18 mmol) in a measuring cylinder and add it to the round bottom flask.
3. Using a measuring pipette, measure 4.0 mL of ethyl acetoacetate (32 mmol) and add it to the round bottom flask.
4. Turn on the magnetic stirrer and allow the reaction to stir for at least 1.5 hours at 65 °C with a rubber septum lightly placed on the flask.

Now perform synthesis part 2.

After you have completed synthesis part 2, do the following actions (from synthesis part 1) below.

5. After stirring for at least 1.5 hours:
 - switch off the magnetic stirrer;
 - remove the flask from the stand and place it in an ice bath;
 - let the flask sit on ice for 10 minutes.
6. Weigh the filter paper and write down the mass.
7. Filter the cold reaction mixture using a vacuum pump over a Büchner filter with filter paper. Rinse the flask with a small amount of demineralized water and use it to wash the solids on the filter. Allow the solid to dry on the filter for another 10 minutes with the pump switched on.
8. Remove the filter paper from the Büchner filter with tweezers and place it on the watch glass. Let this dry on air for as long as possible.

Now perform Experiment 2.

After running Experiment 2, perform the final steps (from Synthesis Part 1) below.

9. Determine the mass of the filter paper with product.
10. Accurately weigh approximately 10 mg of your self-prepared Hantzsch ester and record the exact weighed mass and transfer it to a 100 mL volumetric flask and fill it with ethanol. Shake vigorously to dissolve everything.
11. Now determine the absorbance (extinction) at 400 nm of this solution, as you did in Experiment 2, using holder '5' of the carousel.

Synthesis part 2

1. In the 50 mL round bottom flask with stir bar in setup 2, there is 1.14 g of Hantzsch ester.
2. Measure approximately 15 mL of acetic acid into a measuring cylinder and add it to the flask.
3. Place the flask in the stand and stir the reaction mixture.
4. While the reaction mixture is being stirred, add the 625 mg of sodium nitrite from the weighing bottle to the round bottom flask in small portions over a period of 5 minutes.
5. Place the round bottom flask on a cork ring and remove the stir bar from the flask with the stir bar catcher. Rinse the stir bar with demineralized water in a 100 mL beaker.
6. Add approximately 40 mL of demineralized water to the beaker and let it cool briefly in an ice bath. Also allow approximately 10 mL of demineralised water to cool in a measuring cylinder in the ice bath.
7. Pour the reaction mixture into the beaker and rinse the flask with a small amount of demineralized water from the squeezing bottle.
8. Neutralize the contents of the beaker with aqueous ammonia (25%). You need about 18 mL. Check with pH paper (pH 7 to 8).
9. Using vacuum filtration, filter the solid through a glass filter and rinse with cold water from the measuring cylinder. Allow the solid to dry for a few more minutes on the glass filter with the vacuum pump switched on.
10. Determine the mass of the 25 mL beaker, collect the solid in the beaker and determine the mass of the beaker filled with the solid.

Recrystallization:

11. Add 6 mL of ethanol and heat the beaker, with the hot plate at 120 °C, until the crystals have dissolved. Place a watch glass on the top of the beaker. Swirl occasionally to homogenize the mixture well.
12. Remove the beaker from the hot plate and let it cool to room temperature with the watch glass on top. Swirl the beaker occasionally.
13. Place the beaker on ice for another 10 minutes. Also place 10 mL of ethanol in a graduated cylinder on ice.
14. Filter the resulting crystals through a glass filter using vacuum filtration.
15. Rinse the beaker with cold ethanol and wash the crystals on the filter. Allow the vacuum pump to draw air through the crystals for a few more minutes.
16. Determine the mass of the empty sample vial, transfer the crystals to the sample vial and determine the mass of the sample vial filled with crystals.
17. Submit the sample vial for NMR analysis.

Questions for Experiment 1 - write the answers on the answer sheet

- 1 Write down:
 - The mass of the empty 25 mL beaker (**synthesis part 2**, point 10)
 - The mass of the 25 mL beaker filled with solid (Hantzsch pyridine) (**synthesis part 2**, point 10)
 - The mass of the empty sample vial (**synthesis part 2**, point 16)
 - The mass of the sample vial filled with crystals (**synthesis part 2**, point 16)
 - The mass of the clean filter paper (**synthesis part 1**, point 6)
 - The mass of the filter paper with product (Hantzsch ester) (**synthesis part 1**, point 9)
 - The mass of Hantzsch ester added to the 100 mL volumetric flask (**synthesis part 1**, point 10)
 - The absorbance of the solution of Hantzsch ester at 400 nm (**synthesis part 1**, point 11) 4
- 2 Calculate the percentage yield of Hantzsch pyridine after recrystallization. 9
- 3 Consider the ^1H NMR spectrum of Hantzsch pyridine made from your product. Assign all signals associated with Hantzsch pyridine and justify each one. 5
- 4 The conversion of Hantzsch ester to the pyridine form is a redox reaction. The equation of the half-reaction of the oxidizer is $\text{HNO}_2 + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2\text{O} + \text{NO}$.
Give the equation of the half-reaction of the reducing agent (Hantzsch ester), use molecular formulas for the organic substances, and give the total reaction equation. 2
- 5 Calculate the percentage yield of Hantzsch ester. 13
- 6 Calculate the purity of the synthesized Hantzsch ester in percent based on the absorbance. You can assume that any contaminants present will not absorb. 3

Experiment 2 Determination of the molar absorptivity (extinction coefficient) ϵ of Hantzsch ester at 400 nm

34 points

Introduction

Hantzsch ester contains a conjugated system that gives the compound a color. The absorption maximum of Hantzsch ester is at 371 nm. The Lambert-Beer law describes the absorbance (extinction) A of light of a certain wavelength according to:

$$A = \epsilon cl$$

Herein is:

- ϵ the molar absorptivity (extinction coefficient)
- c the concentration (in mol L⁻¹) of the solute
- l the length of the path of the light (in cm)

In this experiment the ϵ is determined at 400 nm using a calibration series.

Chemicals and safety

- absolute ethanol (see experiment 1)
- Hantzsch ester (see experiment 1)

Materials

- 100 mL volumetric flask
- 25 mL volumetric flask (4x)
- volumetric pipettes (4x)
- Pasteur pipettes with balloon
- 100 mL measuring cylinder
- funnel
- 50 mL beaker for liquid waste
- cuvettes, $l = 1.00$ cm

The determination of the molar absorptivity via UV-VIS

To determine the molar absorptivity of Hantzsch ester, a stock solution with an accurately determined concentration is first made. A dilution series is made from this stock solution. The absorbance (A) of each of the solutions from the dilution series at 400 nm is then determined against a blank. A calibration curve is created by plotting the measurement results in a diagram. We use the Genesys 10s spectrophotometer.

Preparation of the stock solution:

- Accurately weigh approximately 25 mg of the supplied Hantzsch ester on a weighing paper and record the exact weighed mass.
- Transfer this to the 100 mL volumetric flask and fill the volumetric flask to 100 mL with ethanol.
- Stopper the volumetric flask and shake vigorously until all the substance is dissolved.
Please note: this may take several minutes.

Dilution series:

Label the four 25 mL volumetric flasks '1' to '4'.

- Make four solutions according to the table below.
Use volumetric pipettes.
If necessary, pre-rinse the pipettes and empty them into the liquid waste beaker.
Fill the volumetric flask with ethanol to 25 mL each time and homogenize the solution.

Dilution no.	Volumetric flask (mL)	Volumetric pipette (mL stock solution)
1	25	1.00
2	25	4.00
3	25	7.00
4	25	10.0



Figure 1: the Genesys 10s spectrophotometer

Measuring the absorbances:

Use the Genesys 10s spectrophotometer. The correct setting has already been selected. You fill the cuvettes each time using Pasteur pipettes and fill them with one volume of a Pasteur pipette.

- To measure the blank, fill a cuvette with absolute ethanol only, place it in the spectrophotometer carousel at position 'B' and press 'Measure Blank'.
- Fill a new cuvette with the first dilution and place it in the spectrophotometer at position '1' of the carousel.
- Repeat the actions until the other three dilutions have also been placed in the correct position ('2' to '4').
- Press the buttons '1' to '4' in succession and copy the absorbances that appear on the screen.
- Leave the cuvettes in the carousel!

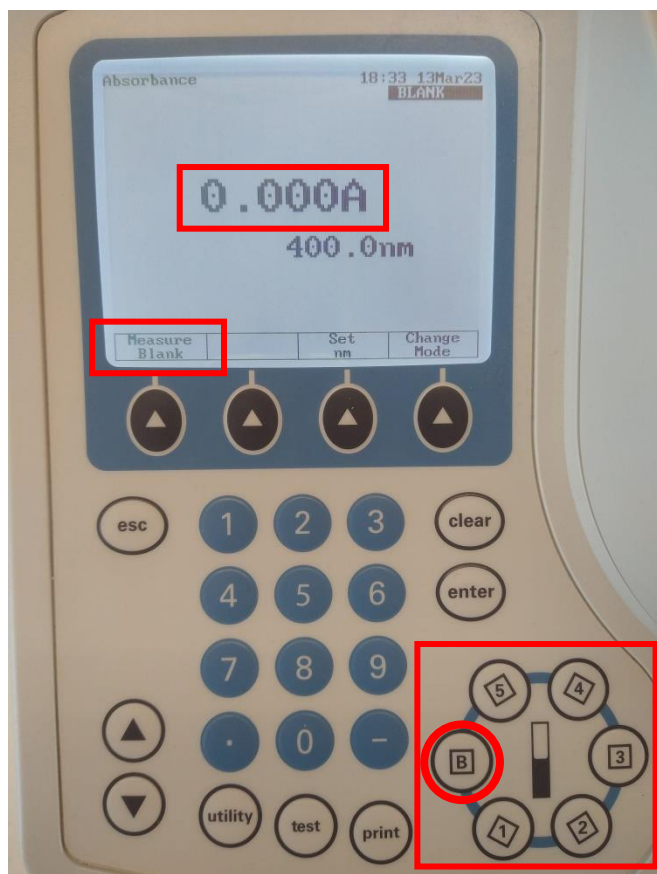


Figure 2: The screen and control buttons of the Genesys 10s.

Questions for Experiment 2 - write the answers on the answer sheet

- 7 Write down:
- the mass of Hantzsch ester used to make the stock solution
 - the measured absorbances. 2
- 8 Calculate the concentration in mol L⁻¹ of Hantzsch ester in the stock solution and in the four solutions of the dilution series. 6
- 9 Plot the measured absorbances at 400 nm against the concentrations in mol L⁻¹ of Hantzsch ester. 4
- 10 Calculate the molar absorptivity at 400 nm. 12

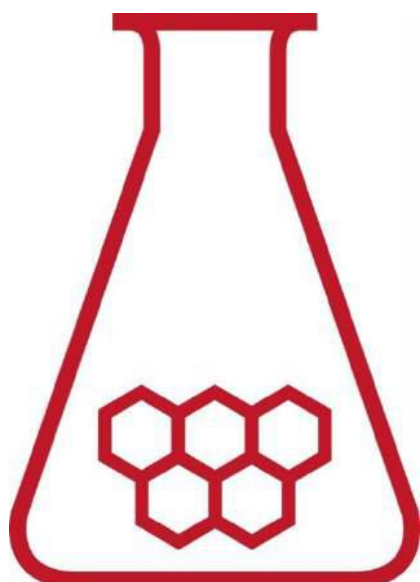
44th National Chemistry Olympiad

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Answer sheets

Tuesday June 13, 2023



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SWITZERLAND 2023



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NB.: Put your name at the top of every page!

Name:

**Practical test answer sheets
Experiment 1**

Question 1

mass of 25 mL beaker:

mass of 25 mL beaker with solid:

mass of sample vial:

mass of sample vial with crystals:

mass of filter paper:

mass of filter paper with product:

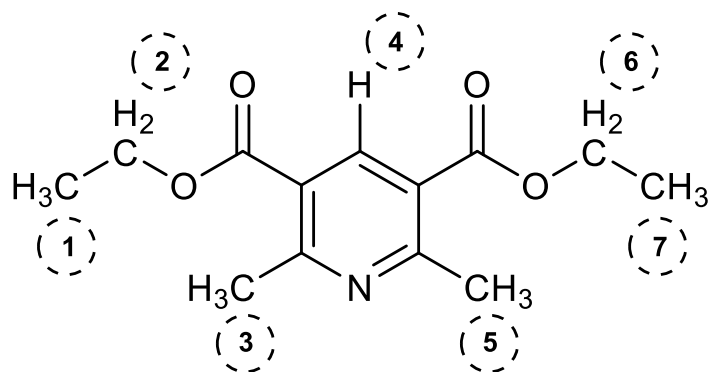
mass of Hantzsch ester added to the 100 mL volumetric flask:

absorbance (extinction) of the solution of Hantzsch ester:

Question 2

Name: _____

Question 3



Chemical shift (ppm)	Integral	Signal	Justification

Name:

Question 4

Question 5

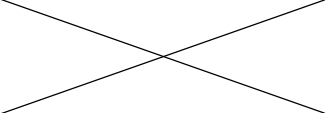
Question 6

Name: _____

**Practical test answer sheets
Experiment 2**

Questions 7 and 8

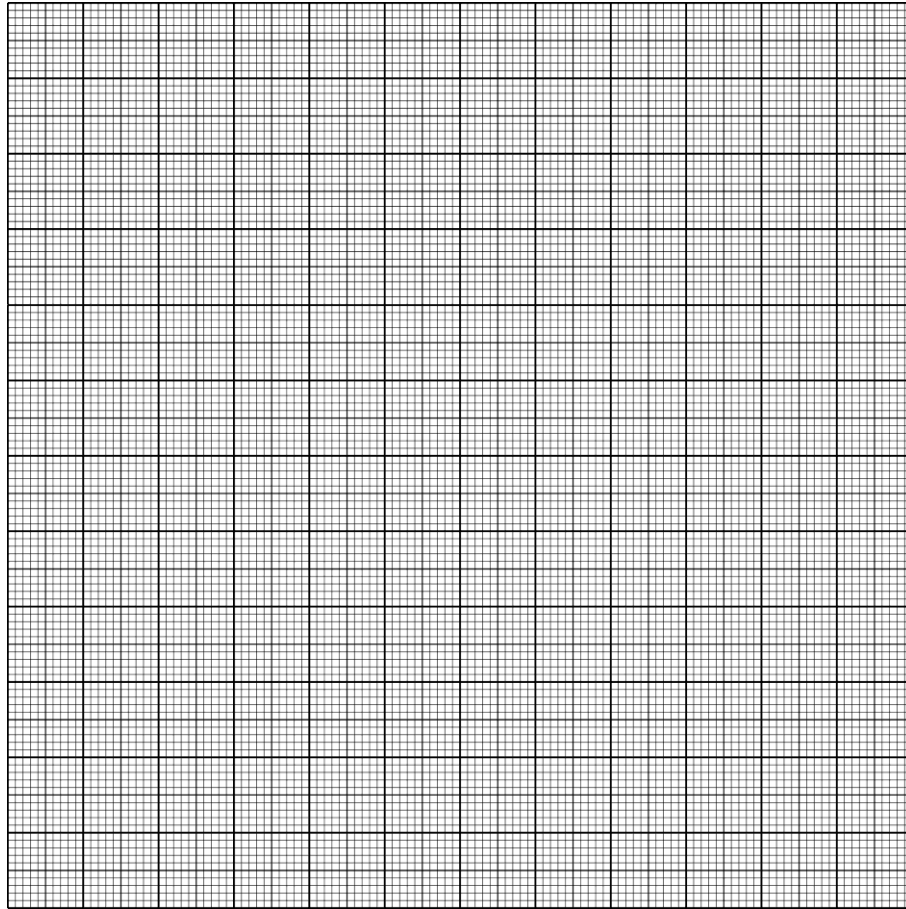
mass of Hantzsch ester used:

Dilution no.	Concentration (mol L ⁻¹)	Absorbance
0 (stock)		
1		
2		
3		
4		

Calculation

Name: _____

Question 9



Question 10

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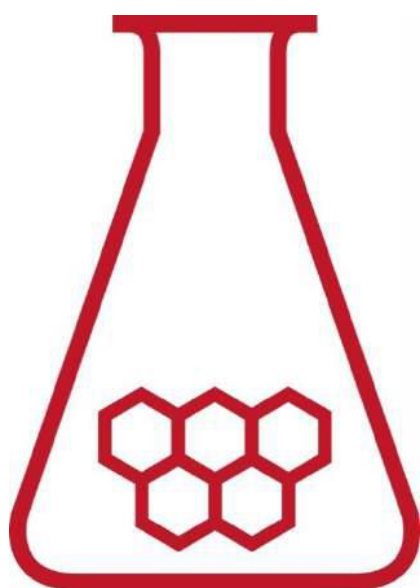
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PRACTICAL TEST

Marking scheme

Tuesday June 13, 2023



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SWITZERLAND 2023



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Experiment 1 Synthesis of Hantzsch ester and oxidation to the pyridine form

(46 points)

Maximum score 10

The following practical skills are assessed:

- safety, working clean and independence 5
- handling of the glassware 5

□1 Maximum score 4

per correctly noted mass, with unit, and absorbance 0.5

If the unit is not stated, penalize a maximum of twice.

□2 Maximum score 9

A correct calculation could be shown as follows:

The yield of Hantzsch pyridine after recrystallization is:

mass of filled sample vial - mass of empty sample vial

The maximum yield of Hantzsch pyridine is:

$$\text{max. yield of Hantzsch pyridine} = \frac{1.14}{253.29} \times 251.28$$

The percentage yield of Hantzsch pyridine after recrystallization is:

$$\frac{\text{amount of g of Hantzsch pyridine after recrystallisation}}{\text{max. yield of Hantzsch pyridine}} \times 100\%$$

- calculation of the yield of Hantzsch pyridine 1
 - calculation of the amount of moles of Hantzsch ester 1
 - calculation of the maximum amount of g of Hantzsch pyridine that can be formed 1
 - calculation of the percentage yield 1
- result maximum 5

□3 Maximum score 5

A correct answer could be stated as follows:

Chemical shift (ppm)	Integral	Signal	Justification
1.5	6	1 and 7	Triplet by 2 H's on the neighboring atom.
3.2	6	3 and 5	Singlet of six H's because there is no H on the neighboring atoms.
4.6	4	2 and 6	Quadruplet/quartet of four H's by 3 H's on the neighboring atoms. or Four identical H's. or The chemical shift belongs to that of H's next to an O.
8.7	1	4	Singlet of one H and no H on neighboring atoms.

· chemical shifts and integrals correct

1

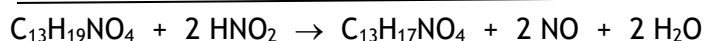
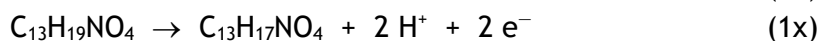
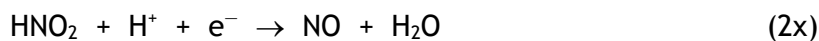
per correctly assigned signal with corresponding correct justification

1

Note

If a justification is given such as: „This remains after allocating three signals.“, do not award a score point.

□4 Maximum score 2



· half-reaction of the reducing species correct

1

· half-reactions with the correct multiplication factors added together and H⁺ before and after the arrow crossed out

1

□5 Maximum score 13

A correct calculation could be shown as follows:

The yield of Hantzsch ester is:

mass of the filter paper with product - mass of the clean filter paper

A maximum of $0.0150 \times 253.29 = 3.80$ g of Hantzsch ester can be formed.

The percentage yield is: $\frac{\text{amount of g of Hantzsch ester}}{3.80} \times 100\%$

- calculation of the yield of Hantzsch ester 1
- notion that a maximum of 15.0 mmol Hantzsch ester can be formed 1
- calculation of the maximum mass of Hantzsch ester that can be formed 1
- calculation of the percentage yield 1

result

maximum 9

□6 Maximum score 3

- calculation of the concentration of the solution of Hantzsch ester from the measured absorbance: divide the measured absorbance by the molar absorptivity from experiment 2 (and by 1.00 cm) 1
- calculation of the concentration of Hantzsch ester if the weighed mass were pure Hantzsch ester: divide the weighed amount of mg Hantzsch ester by 253.29 (mg mmol^{-1}) and by 100 (mL) 1
- calculation of the percentage purity: divide the concentration of the solution of Hantzsch ester from the measured absorbance by the concentration of Hantzsch ester if the weighed mass were pure Hantzsch ester and multiply the quotient by 100% 1

Experiment 2 Determination of the molar absorptivity (extinction coefficient) of Hantzsch ester at 400 nm

(34 points)

Maximum score 10

The following practical skills are assessed:

- safety, working clean and independent 5
- handling glassware and other materials 5

□7 Maximum score 2

- mass of Hantzsch ester used noted correctly 1
- absorbances noted correctly 1

□8 Maximum score 6

A correct calculation could be shown as follows:

$$\text{concentration of the stock solution} = \frac{\text{weighed mg of Hantzsch ester}}{100} \times \frac{253.29}{100} \text{ mol L}^{-1}.$$

Concentrations of dilutions 1 - 4: multiply the concentration of the stock solution

respectively by $\frac{1.00}{25.00}$, $\frac{4.00}{25.00}$, $\frac{7.00}{25.00}$ and $\frac{10.0}{25.00}$.

- calculation of the amount of mmoles of Hantzsch ester 1
- calculation of the concentration in mol L^{-1} of the stock solution 1
- per correct calculation of the concentrations in dilutions 1 - 4 1

□9 Maximum score 4

- concentration (mol L^{-1}) is correctly displayed as label on the x-axis and at least one numerical value is displayed 1
- A or absorbance (or E or extinction) shown as label on the y-axis and at least one number value shown 1
- optimal use of the graph paper/chart provided 1
- the four measuring points are shown correctly 1

□10 Maximum score 12

a justified straight line drawn based on the measuring points maximum 5

If the drawn straight line does not pass through the origin of the diagram maximum 4

- determination of the slope of the straight line drawn 1
- correct unit for the slope: $\text{L mol}^{-1} \text{ cm}^{-1}$ 1

result of the determination of ϵ maximum 5