

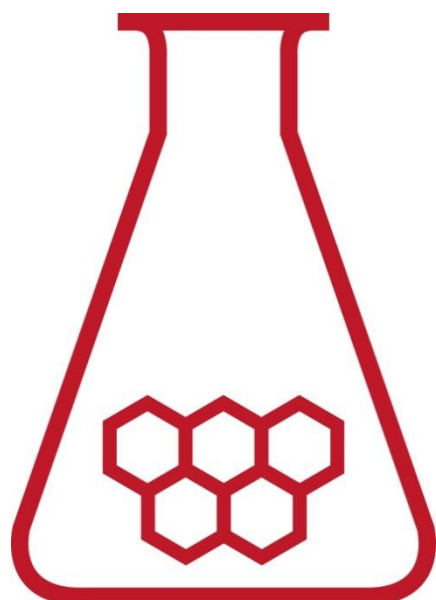
44th National Chemistry Olympiad

University Leiden

THEORY TEST

Marking scheme

Monday 12 June 2023



**SCHEIKUNDE
OLYMPIADE**



55TH INTERNATIONAL
CHEMISTRY OLYMPIAD
SWITZERLAND 2023



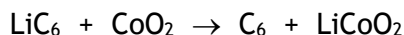
Universiteit Leiden

- This test is composed 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.

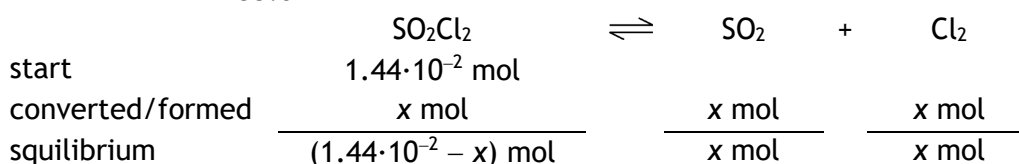
The bond between the sulfur atom and an oxygen atom is a σ -bond and a π -bond. The σ -bond between the sulfur atom and an oxygen atom is formed by overlap of an sp^3 orbital of the sulfur atom with an sp^2 orbital of the oxygen atom; the π -bond is formed by overlap of a d orbital of the sulfur atom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

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

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

- 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

Comment

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

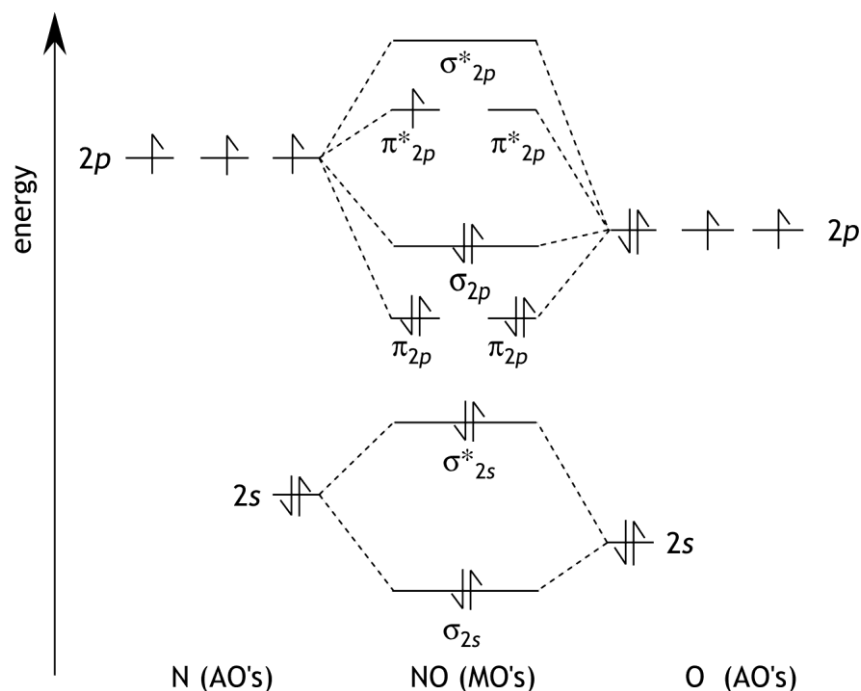
this as correct.

Problem 4 NO

24 points

□12 Maximum score 6

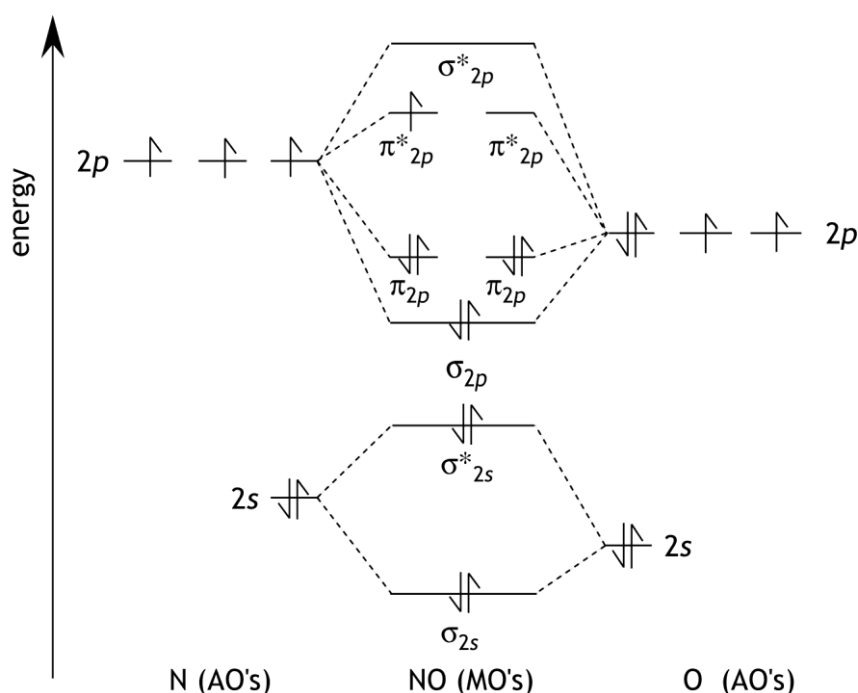
A correct answer can look as follows:



- 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

Comment

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



□13 Maximum score 2

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

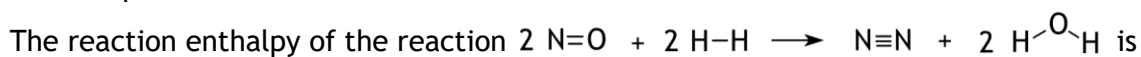
- number of electrons in the bonding and anti-bonding molecular orbitals are correct 1
- the rest of the calculation 1

Comments

- 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 1
- all signs are correctly processed 1
- all coefficients are correctly processed 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

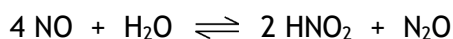
$$BE_{N=O} = \frac{-2 \times BE_{H-H} + BE_{N=N} + 4 \times BE_{O-H} - \Delta_r H}{2} =$$
$$\frac{-2 \times (-4.36 \cdot 10^5) + (-9.45 \cdot 10^5) + 4 \times (-4.635 \cdot 10^5) - (-6.67 \cdot 10^5)}{2} = -6.30 \cdot 10^5 \text{ J mol}^{-1}$$

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

Comment

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

Comment

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

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

- 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
- Comment*
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

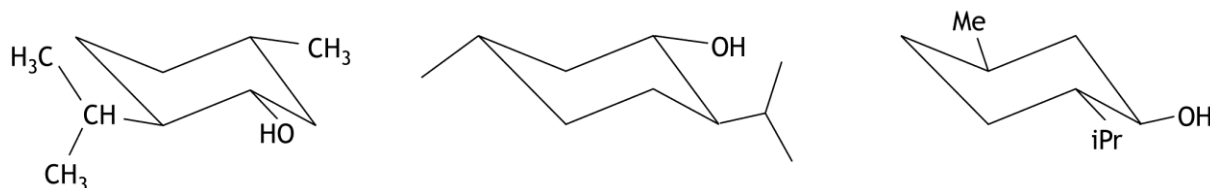
1

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:

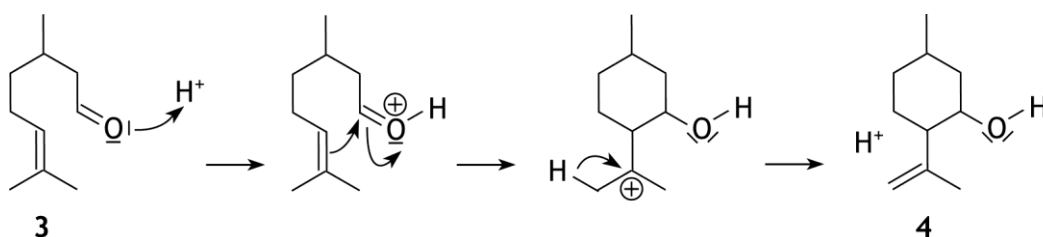


per correctly drawn side group

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 Syntheses 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

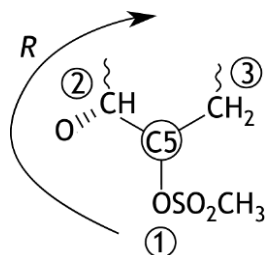
1

· 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 ($\text{m})\text{g}$ ($\text{m})\text{mol}^{-1}$ 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