

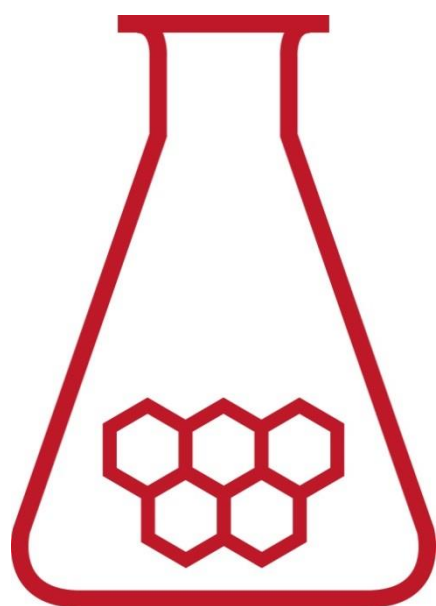
# 45<sup>e</sup> National Chemistry Olympiad

Maastricht University

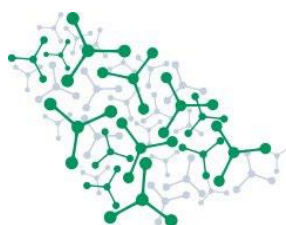
THEORETICAL TEST

Marking scheme

Wednesday June 5 2024



**SCHEIKUNDE  
OLYMPIADE**



56<sup>th</sup> IChO International  
Chemistry Olympiad  
Saudi Arabia 2024



**Maastricht University**

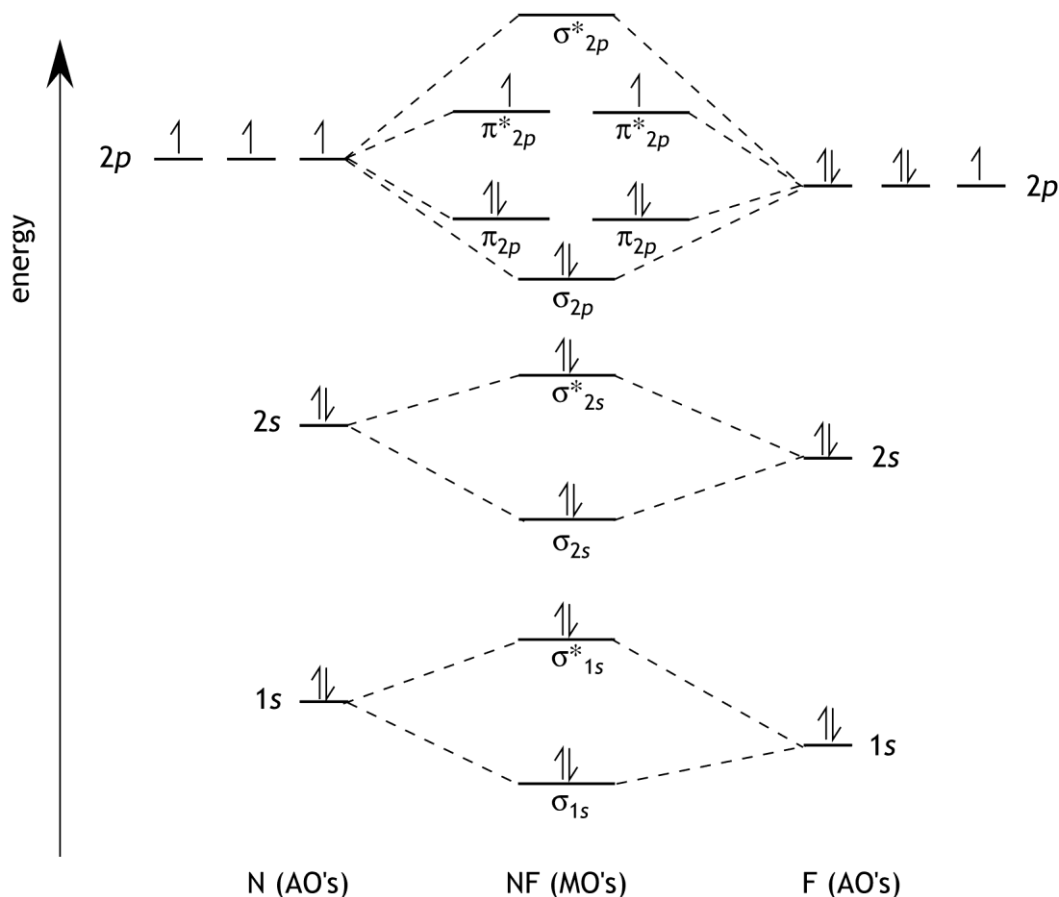
- This test consists of 7 problems with 32 open questions and an answer sheet..
- The maximum score for this test is 120 points.
- The test will last a maximum of 4 clock hours.
- Required resources: (graphic) calculator and BINAS 6<sup>th</sup> or 7<sup>th</sup> edition or ScienceData 1<sup>st</sup> edition.
- Each question includes the number of points that a correct answer to that question will earn.

# Problem 1 NF

12 points

□1 Maximum score 7

A correct answer can look as follows:



- the energy levels of the fluorine atom are drawn lower than the energy levels of the nitrogen atom 1
- one electron pair in the 1s en 2s levels of the nitrogen atom and the oxygen atom 1
- three unpaired electrons the 2p level of the nitrogen atom 1
- two electron pairs and one unpaired electron in the 2p level of the fluorine atom 1
- the levels of all molecular orbitals are correctly represented with the correct notations 1
- electron pairs in  $\sigma_{1s}$ ,  $\sigma_{1s}^*$ ,  $\sigma_{2s}$ ,  $\sigma_{2s}^*$  and in  $\sigma_{2p}$  and in both  $\pi_{2p}$ 's of the nitrogen fluoride molecule 1
- in each  $\pi_{2p}^*$  of the nitrogen fluoride molecule an unpaired electron 1

If in an otherwise correct answer the unpaired electrons in the 2p level of the nitrogen atom and/or the unpaired electrons in the  $\pi_{2p}^*$  levels of the nitrogen fluoride molecule are not parallel drawn 6

□2 Maximum score 2

An example of a correct answer is:

There are ten electrons in BMO's and six electrons in ABMO's, so bond order =  $\frac{10-6}{2} = 2$ .

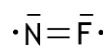
- ten electrons in BMO's and six electrons in ABMO's 1
- rest of the calculation 1

*Remarks*

- *When an incorrect answer to question 2 is consequently due to an incorrect answer to question 1, accept this answer to question 2 as correct.*
- *When the answer bond order =  $\frac{8-4}{2} = 2$  is given, accept this as correct.*

□3 Maximum score 3

A correct answer can look as follows:



- double bond 1
- double radical 1
- rest rest of the structure 1

If the answer to question 1 is correct and here the answer  $\ominus \text{N} = \text{F} \oplus$  is given 2

If the answer to question 1 is correct and here the answer  $\text{N} = \text{F}$  is given 1

*Remark*

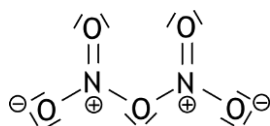
*When an incorrect answer to question 3 is consequently due to an incorrect answer to question 1 and/or question 2, accept this answer to question 3 as correct.*

## Problem 2 Dinitrogen penta-oxide

19 points

□4 Maximum score 3

A correct Lewis structure can be represented as follows:



- single bonds and double bonds between the the N atoms and O atoms correct 1
- non-bonding electron pairs correct 1
- formal charges correct 1

□5 Maximum score 3

A correct answer can be formulated as follows:

Each N atom with the attached O atoms lie in one plane. There is free rotation around the bonds between the central O atom and the N atoms. So it is possible that all seven atoms lie in one plane.

- each N atom with the attached O atoms lie in one plane 1
- there is free rotation around the bonds between the central O atom and the N atoms 1
- correct conclusion 1

□6 Maximum score 3

An example of a correct answer is:

(By multiplying the first and third reaction equation by two and adding these to the second reaction equation, one obtains  $2 \text{ N}_2(\text{g}) + 5 \text{ O}_2(\text{g}) \rightarrow 2 \text{ N}_2\text{O}_5(\text{g})$ .)

$$2 \times (-116,2) + (-106,2) + 2 \times (+182,6) = (+) 26,6 \text{ kJ per 2 moles of N}_2\text{O}_5$$

$$\Delta_f H^0 \text{ of N}_2\text{O}_5 = (+) 26,6 : 2 = (+) 13,3 \text{ (kJ mol}^{-1}\text{)}$$

- $\Delta_f H^0_1$ ,  $\Delta_f H^0_2$  and  $\Delta_f H^0_3$  are used in the summation 1
- multiplication factors are correctly used in the summation 1
- rest of the calculation is correct 1

□7 Maximum score 5

An example of a correct calculation is:

$$\Delta G = \Delta H - T\Delta S = + 94,83 \cdot 10^3 - 600 \times (269 + 293 - 426) = (+) 13,23 \cdot 10^3 \text{ (J mol}^{-1}\text{)}$$

$$\Delta G = -RT \ln K_p$$

$$\ln K_p = -\frac{\Delta G}{RT} = -\frac{13,23 \cdot 10^3}{8,314 \times 600} \quad K_p = e^{-\frac{13,23 \cdot 10^3}{8,314 \times 600}} = 0,0705$$

- calculation of  $\Delta S$  1
- calculation of  $\Delta G$  1
- $\Delta G = -RT \ln K_p$ , possibly already partly completed 1
- calculation of  $\ln K_p$  1
- calculation of  $K_p$  1

□8 Maximum score 5

An example of a correct calculation is:

$$\frac{p_{\text{NO}_2} \times p_{\text{NO}_3}}{p_{\text{N}_2\text{O}_5}} = K_p, \text{ because the pressure is given in bar, this can be written as}$$
$$\frac{p_{\text{NO}_2} \times p_{\text{NO}_3}}{p_{\text{N}_2\text{O}_5}} = K_p.$$

In the equilibrium are  $(1-x)$  moles of  $\text{N}_2\text{O}_5$ ,  $x$  moles of  $\text{NO}_2$ ,  $x$  moles of  $\text{NO}_3$  present per original mole of  $\text{N}_2\text{O}_5$ . So there are in total  $(1+x)$  moles of gas present.

$$p_{\text{NO}_2} = p_{\text{NO}_3} = \left(\frac{x}{1+x}\right) \times p_{\text{total}} \text{ and } p_{\text{N}_2\text{O}_5} = \left(\frac{1-x}{1+x}\right) \times p_{\text{total}}$$
$$\frac{\left(\frac{x}{1+x}\right)^2 \times p_{\text{total}}}{\left(\frac{1-x}{1+x}\right)} = K_p \quad \frac{\left(\frac{x}{1+x}\right)^2 \times 0.10}{\left(\frac{1-x}{1+x}\right)} = 0.0705$$

Solving this equation yields  $x = 0.64$  (mol).

$$\frac{p_{\text{NO}_2} \times p_{\text{NO}_3}}{p_{\text{N}_2\text{O}_5}} = K_p \quad 1$$

· in the equilibrium  $(1-x)$  moles of  $\text{N}_2\text{O}_5$ ,  $x$  moles of  $\text{NO}_2$  and  $x$  moles of  $\text{NO}_3$  are present, so  $(1+x)$  moles of gas in total 1

$$\cdot p_{\text{NO}_2} = p_{\text{NO}_3} = \left(\frac{x}{1+x}\right) \times p_{\text{total}} \text{ and } p_{\text{N}_2\text{O}_5} = \left(\frac{1-x}{1+x}\right) \times p_{\text{total}} \quad 1$$

$$\cdot \frac{\left(\frac{x}{1+x}\right)^2 \times p_{\text{total}}}{\left(\frac{1-x}{1+x}\right)} = K_p, \text{ possibly already partly completed} \quad 1$$

$$\cdot \text{Solving of the equation } \frac{\left(\frac{x}{1+x}\right)^2 \times 0.10}{\left(\frac{1-x}{1+x}\right)} = 0.0705 \quad 1$$

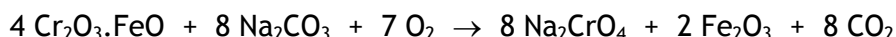
#### Remark

When an incorrect answer to question 8 is consequently due to an incorrect answer to question 7, accept this answer to question 8 as correct.

## Problem 3 Chromium

21 points

□9 Maximum score 4



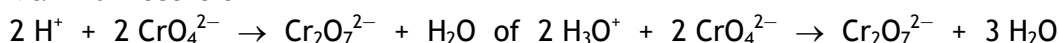
- all formulas correct and at the correct side of the reaction arrow 1
- chromium balance and iron balance correct 1
- sodium balance and carbon balance correct 1
- the oxygen balance correct 1

□10 Maximum score 3

Add water (and heat or stir). Filter the resulting mixture and evaporate the filtrate.

- add water (and heat or stir) 1
- filtrate 1
- evaporate 1

□11 Maximum score 3



- $\text{H}^+$  (of  $\text{H}_3\text{O}^+$ ) and  $\text{CrO}_4^{2-}$  before the arrow 1
- $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{H}_2\text{O}$  after the arrow 1
- correct coefficients 1

□12 Maximum score 4

In the conversion of  $\text{Cr}_2\text{O}_7^{2-}$  to Cr, 12 moles of electrons per mole of  $\text{Cr}_2\text{O}_7^{2-}$  are involved. In the conversion of  $\text{Cr}_2\text{O}_7^{2-}$  to  $\text{Cr}^{3+}$ , 6 moles of electrons per mole of  $\text{Cr}_2\text{O}_7^{2-}$  are involved. So, in the conversion of 100 moles of  $\text{Cr}_2\text{O}_7^{2-}$ , totally  $95,0 \times 12 + 5,0 \times 6$  moles of electrons are involved.

So, the percentage of the electron current that is used for the conversion to Cr is

$$\frac{95,0 \times 12}{95,0 \times 12 + 5,0 \times 6} \times 100\% = 97,4\%$$

- notion that in the conversion of  $\text{Cr}_2\text{O}_7^{2-}$  to Cr, 12 moles of electrons per mole of  $\text{Cr}_2\text{O}_7^{2-}$  are involved 1
- notion that in the conversion of  $\text{Cr}_2\text{O}_7^{2-}$  to  $\text{Cr}^{3+}$ , 6 moles of electrons per mole of  $\text{Cr}_2\text{O}_7^{2-}$  are involved 1
- calculation of the total amount of electrons that is involved in the conversion of 100 moles of  $\text{Cr}_2\text{O}_7^{2-}$  1
- rest of the calculation 1

□13 Maximum score 7

An example of a correct calculation is:

The density of chromium is  $\frac{2 \times 51,996 \times 1,66 \cdot 10^{-27}}{\left(\frac{4 \times 125 \cdot 10^{-12}}{\sqrt{3}}\right)^3} = 7,18 \cdot 10^3 \text{ kg m}^{-3}$  and that is in good

agreement with the value of  $7,15 \cdot 10^3 \text{ kg m}^{-3}$  that is listed Binas/ScienceData.

- notion that there are two atoms in a bcc unit cell 1
- calculation of the mass of the unit cell in u 1
- calculation of the mass of the unit cell in kg 1
- notion that the length of the body diagonal is four times the atomic radius 1
- calculation of the length of the edge of the unit cell 1
- calculation of the volume of the unit cell 1
- calculation of the density and conclusion 1

## Problem 4 Methyl isocyanide

15 points

□14 Maximum score 7

An example of a correct answer is:

For the steady state approximation applies:

$$\frac{d[\text{CH}_3\text{NC}^*]}{dt} = 0$$

$\text{CH}_3\text{NC}^*$  is created in the forward reaction of equilibrium (1) and is converted in the return reaction of equilibrium (1) as well as in reaction (2). For this applies respectively

$$s_1 = k_1[\text{CH}_3\text{NC}]^2, \quad s_{-1} = k_{-1}[\text{CH}_3\text{NC}^*][\text{CH}_3\text{NC}] \quad \text{and} \quad s_2 = k_2[\text{CH}_3\text{NC}^*].$$

$$\text{So } \frac{d[\text{CH}_3\text{NC}^*]}{dt} = k_1[\text{CH}_3\text{NC}]^2 - k_{-1}[\text{CH}_3\text{NC}^*][\text{CH}_3\text{NC}] - k_2[\text{CH}_3\text{NC}^*] = 0.$$

$$\text{From this it follows that } [\text{CH}_3\text{NC}^*] = \frac{k_1[\text{CH}_3\text{NC}]^2}{k_{-1}[\text{CH}_3\text{NC}] + k_2}.$$

$$\text{So, for the formation of } \text{CH}_3\text{CN} \text{ applies } \frac{d[\text{CH}_3\text{CN}]}{dt} = k_2[\text{CH}_3\text{NC}^*] = \frac{k_1 k_2 [\text{CH}_3\text{NC}]^2}{k_{-1}[\text{CH}_3\text{NC}] + k_2}.$$

$$\cdot s_1 = k_1[\text{CH}_3\text{NC}]^2 \quad 1$$

$$\cdot s_{-1} = k_{-1}[\text{CH}_3\text{NC}^*][\text{CH}_3\text{NC}] \quad 1$$

$$\cdot s_2 = k_2[\text{CH}_3\text{NC}^*] \quad 1$$

· notion that  $[\text{CH}_3\text{NC}^*]$  does not change in time 1

$$\cdot \frac{d[\text{CH}_3\text{NC}^*]}{dt} = k_1[\text{CH}_3\text{NC}]^2 - k_{-1}[\text{CH}_3\text{NC}^*][\text{CH}_3\text{NC}] - k_2[\text{CH}_3\text{NC}^*] = 0 \quad 1$$

$$\cdot [\text{CH}_3\text{NC}^*] = \frac{k_1[\text{CH}_3\text{NC}]^2}{k_{-1}[\text{CH}_3\text{NC}] + k_2} \quad 1$$

$$\cdot \frac{d[\text{CH}_3\text{CN}]}{dt} = k_2[\text{CH}_3\text{NC}^*] = \frac{k_1 k_2 [\text{CH}_3\text{NC}]^2}{k_{-1}[\text{CH}_3\text{NC}] + k_2} \quad 1$$

□15 Maximum score 2

For the overall reaction it applies that  $\frac{d[\text{CH}_3\text{CN}]}{dt} = k_{\text{exp}}[\text{CH}_3\text{NC}]$ , if we combine this with the

given rate equation, we get  $k_{\text{exp}} = \frac{k_1 k_2 [\text{CH}_3\text{NC}]}{k_{-1}[\text{CH}_3\text{NC}] + k_2}$ .

$$\cdot \text{notion that for the overall reaction applies } \frac{d[\text{CH}_3\text{CN}]}{dt} = k_{\text{exp}}[\text{CH}_3\text{NC}] \quad 1$$

· correct expression for  $k_{\text{exp}}$  1



□16 Maximum score 2

An example of a correct answer is:

For the return reaction in equilibrium (1) two molecules have to collide, while in reaction (2) only one molecule reacts. So the return reaction in equilibrium (1) is more favored when the pressure is increased. So  $s_{-1}$  becomes higher than  $s_2$  at high pressure and lower than  $s_2$  at low pressure.

· mentioning that  $s_{-1}$  is dependent of two species and  $s_2$  of one

1

· rest of the explanation

1

□17 Maximum score 4

An example of a correct answer is::

When at high pressure  $s_{-1} \gg s_2$ , then  $k_{-1}[\text{CH}_3\text{NC}] \gg k_2$ . In that case  $k_2$  can be neglected to  $k_{-1}[\text{CH}_3\text{NC}]$ . For the rate equation applies then

$$\frac{d[\text{CH}_3\text{CN}]}{dt} = \frac{k_1 k_2 [\text{CH}_3\text{NC}]^2}{k_{-1} [\text{CH}_3\text{NC}] + k_2} \approx \frac{k_1 k_2 [\text{CH}_3\text{NC}]^2}{k_{-1} [\text{CH}_3\text{NC}]} = \frac{k_1 k_2 [\text{CH}_3\text{NC}]}{k_{-1}}$$
 and that is first order in  $[\text{CH}_3\text{NC}]$ .

When at low pressure  $s_{-1} \ll s_2$ , then  $k_{-1}[\text{CH}_3\text{NC}] \ll k_2$ . In that case  $k_{-1}[\text{CH}_3\text{NC}]$  can be neglected to  $k_2$ . For the rate equation applies then

$$\frac{d[\text{CH}_3\text{CN}]}{dt} = \frac{k_1 k_2 [\text{CH}_3\text{NC}]^2}{k_{-1} [\text{CH}_3\text{NC}] + k_2} \approx \frac{k_1 k_2 [\text{CH}_3\text{NC}]^2}{k_2}$$
 and that is second order in  $[\text{CH}_3\text{NC}]$ .

· notion that at high pressure  $k_{-1}[\text{CH}_3\text{NC}] \gg k_2$

1

· rest of the explanation for high pressure

1

· notion that at low pressure  $k_{-1}[\text{CH}_3\text{NC}] \ll k_2$

1

· rest of the explanation for low pressure

1

## Problem 5 Electrochemical cell

15 points

□18 Maximum score 3

To half cell I applies  $V_I = 0,80 + \frac{0,059}{1} \log[\text{Ag}^+] = 0,80 + \frac{0,059}{1} \log 0,150 = 0,75 \text{ V}$ .

To half cell II applies  $V_{II} = 0,34 + \frac{0,059}{2} \log[\text{Cu}^{2+}] = 0,34 + \frac{0,059}{2} \log 0,300 = 0,32 \text{ V}$ .

So  $\text{EMF} = V_I - V_{II} = 0,75 - 0,32 = 0,43 \text{ V}$ .

- calculation of  $V_I$  1
- calculation of  $V_{II}$  1
- calculation of  $V_{\text{bron}}$  1

If the answer  $\Delta V = 0,80 - 0,34 - \frac{0,059}{2} \log \frac{0,30}{0,15} = 0,45 \text{ V}$  is given 2

□19 Maximum score 6

Let it take  $t$  seconds, that is  $0,200 \times t \text{ C}$  and this corresponds to  $\frac{0,200 \times t}{96485}$  moles of electrons.

On the silver electrode  $\frac{0,200 \times t}{96485}$  moles of Ag are formed, that is  $\frac{0,200 \times t}{96485} \times 107,9 \text{ g}$ .

So, the mass of the silver electrode becomes  $15,00 + \frac{0,200 \times t}{96485} \times 107,9 \text{ g}$ .

From the copper electrode  $\frac{1}{2} \times \frac{0,200 \times t}{96485}$  moles of Cu are dissolved, that is

$\frac{1}{2} \times \frac{0,200 \times t}{96485} \times 63,55 \text{ g}$ .

So, the mass of the copper electrode is  $30,00 - \frac{1}{2} \times \frac{0,200 \times t}{96485} \times 63,55 \text{ g}$ .

From  $15,00 + \frac{0,200 \times t}{96485} \times 107,9 = 30,00 - \frac{1}{2} \times \frac{0,200 \times t}{96485} \times 63,55$  it follows that  $t = 5,18 \cdot 10^4 \text{ s}$ .

- calculation of the number of C 1
- calculation of the number of moles of electrons 1
- calculation of the number of moles of Ag that are formed and of the number of moles of Cu that are dissolved 1
- calculation of the number of grams of Ag that are formed and of the number of grams of Cu that are dissolved 1
- calculation of the masses of both electrodes 1
- calculation of  $t$  1

□20 Maximum score 6

A correct answer can be formulated as follows:

When a solution of sodium carbonate is added tot half cell I, a precipitate of silver carbonate is formed. In halfcel I  $[Ag^+]$  becomes lower and so does  $V_I$  and (because  $V_{II}$  does not change) the EMF becomes smaller.

When a solution of sodium carbonate is added tot half cell II, a precipitate of copper carbonate is formed. In halfcel II  $[Cu^{2+}]$  becomes lower and so does  $V_{II}$  and (because  $V_I$  does not change) the EMF becomes higher.

When a solution of sodium chloride is added tot half cell II (no reaction takes place, but) the solution is diluted, so  $[Cu^{2+}]$  becomes lower and so does  $V_{II}$  and (because  $V_I$  does not change) the EMF becomes higher.

- correct explanation that  $V_I$  becomes lower on adding a solution of sodium carbonate to half cell I 1
- correct conclusion regarding the effect on the EMF on adding a solution of sodium carbonate to half cell I 1
- correct explanation that  $V_{II}$  becomes lower on adding a solution of sodium carbonate to half cell II 1
- correct conclusion regarding the effect on the EMF on adding a solution of sodium carbonate to half cell II 1
- correct explanation that  $V_{II}$  becomes lower on adding a solution of sodium chloride to half cell II 1
- correct conclusion regarding the effect on the EMF on adding a solution of sodium chloride to half cell II 1

## Problem 6 Barbituric acid

13 points

□21 Maximum score 3

A correct answer can be formulated as follows:

In point A / at 221 nm applies that the absorbance of 1 M HZ solution is equal to the absorbance of 1 M  $Z^-$  solution. Because  $[HZ] + [Z^-]$  equals  $1,00 \text{ mol L}^{-1}$  the graph corresponding to pH 3,60 also passes through A.

- (in point A / at 221 nm applies that) the absorbance of 1 M HZ solution is equal to the absorbance of 1 M  $Z^-$  solution 1
- $[HZ] + [Z^-]$  equals  $1,00 \text{ mol L}^{-1}$  1
- correct conclusion 1

or

Because  $[HZ] = [Z^-]$  ( $= 1,00 \text{ mol L}^{-1}$ ) and  $E_{HZ} = E_{Z^-}$ , in punt A / at 221 nm the molar absorptivity of HZ equals the molar absorptivity of  $Z^-$ . So the graph corresponding to pH 3,60 also passes through A.

- $\varepsilon_{HZ} = \varepsilon_{Z^-}$  (in point A / at 221 nm) 1
- Correct explanation why  $\varepsilon_{HZ} = \varepsilon_{Z^-}$  (in point A / at 221 nm) 1
- correct conclusion 1

If an answer is given like: „ $[HZ] + [Z^-]$  at pH=3,60 equals  $[HZ]$  at pH = 2,00, so the graph corresponding to pH 3,60 also passes through A.” 1

If one of the following answers is given:

„At 221 nm and at pH=3,60  $[HZ]$  equals  $[Z^-]$ , so the graph corresponding to pH 3,60 also passes through A.

o

„HZ and  $Z^-$  induce both, apart from each other, an absorbance, so the absorbance at 221 nm in the graph corresponding to pH = 3,60 double the absorbance of point A” 0

If only a conclusion is given 0

□22 Maximum score 2

At pH = 2,00:  $A = 1,0 \cdot 10^3$

At pH = 3,60:  $A = 8,0 \cdot 10^3$

At pH = 7,20:  $A = 23,0 \cdot 10^3$

If only two readings are correct 1

If only one reading is correct 0

Remarks

- The readings may deviate maximum  $0,1 \cdot 10^3$  from the above mentioned readings.
- When instead of  $1,0 \cdot 10^3$ ,  $8,0 \cdot 10^3$  en  $23,0 \cdot 10^3$  the readings  $1 \cdot 10^3$ ,  $8 \cdot 10^3$  and  $23 \cdot 10^3$  are given, give full marks.

□23 Maximum score 5

An example of a correct calculation is:

Let  $[Z^-] = a$  (mol L<sup>-1</sup>), then  $[HZ] = (1 - a)$  (mol L<sup>-1</sup>)

Then applies:  $a \times 23 \cdot 10^3 + (1 - a) \times 1,0 \cdot 10^3 = 8,0 \cdot 10^3$

Solving this equation yields:  $a = 0,32$  mol L<sup>-1</sup> =  $[Z^-]$ .

So  $[Z^-] : [HZ] = 0,32 : 0,68$ .

- taking  $[Z^-] = a$  (mol L<sup>-1</sup>) and  $[HZ] = (1 - a)$  (mol L<sup>-1</sup>) 1
- notion that  $A_{Z^-} = a \times 23 \cdot 10^3$  and  $A_{HZ} = (1 - a) \times 1,0 \cdot 10^3$  1
- formulating the equation  $a \times 23 \cdot 10^3 + (1 - a) \times 1,0 \cdot 10^3 = 8,0 \cdot 10^3$  1
- solving of  $a$  from the equation 1
- calculation of the ratio  $[Z^-] : [HZ] = a : (1 - a)$  1

*When an incorrect answer to question 23 is consequently due to an incorrect answer to question 22, accept this answer to question 23 as correct.*

□24 Maximum score 3

An example of a correct calculation is:

$$K_Z = \frac{[H^+][Z^-]}{[HZ]}, \text{ so } K_Z = \frac{10^{-3.60} \times 0.32}{0.68} = 1.2 \cdot 10^{-4}$$

- $K_Z = \frac{[H^+][Z^-]}{[HZ]}$ , eventually already filled in partially 1
- calculation of  $[H^+] = 10^{-3.60}$  from pH = 3.60 1
- calculation of  $K_Z$  from the calculated  $[H^+]$  and the calculated ratio  $[Z^-] : [HZ]$  1

If the calculation  $K_Z = \frac{10^{-3.60} \times 10^{-3.60}}{\frac{0.68}{0.32} \times 10^{-3.60}} = 1.2 \cdot 10^{-4}$  is given 2

*Remark*

*When an incorrect answer to question 24 is a direct consequence of an incorrect answer to question 23, do not penalize this.*

## Problem 7 Melphalan

25 points

□25 Maximum score 4

An example of a correct answer is:

Number 2 (is the steric centre).

The priority order is:

1:  $\text{NH}_2$ ; 2:  $\text{COOH}$ ; 3:  $\text{CH}_2$ ; 4: H.

(With H facing backwards) 1-2-3 turns counterclockwise, so the S-configuration.

- (steric centre is C) number 2 1
- correct priority 1
- explanation how to look at the surroundings of the steric centre 1
- correct conclusion 1

□26 Maximum score 4

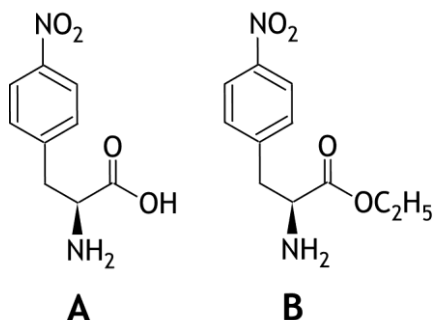
chemical shift (ppm)	multiplicity	integral	number(s) of the C atom(s)
2.8	doublet	2 H	3
3.5	triplet	4 H	10, 12
3.6	triplet	1 H	2
3.9	triplet	4 H	11, 13
6.7	doublet	2 H	6, 8
6.8	doublet	2 H	5, 9

- only number 3 at 2.8 ppm are filled in correctly 1
- only number 2 at 3.6 ppm are filled in correctly 1
- only the numbers 10 and 12 at 3.5 ppm are filled in correctly and only the numbers 11 and 13 at 3.9 ppm are filled in correctly 1
- only the numbers 6 and 8 at 6.7 ppm are filled in correctly and only the numbers 5 and 9 at 6.8 ppm are filled in correctly 1

*Remarks*

- The numbers 10 and 12 may be interchanged with the numbers 11 and 13.
- The numbers 6 and 8 may be interchanged with the numbers 5 and 9.

□27 Maximum score 2



- A correct 1
- B correct 1

□28 Maximum score 2

A correct answer can be formulated as follows:

(Nitration of an aromatic ring is an electrophilic substitution.) The group that is present already at the aromatic ring, apparently is a *para*-director. Such a group cannot be a *meta*-director at the same time (but it can be a *ortho*-director).

- the group that is present already at the aromatic ring, apparently is a *para*-director 1
- *para*-directing effect and *meta*-directing effect cannot happen together 1

If only an answer has been given as: „The group that is present already at the aromatic ring, is a *ortho-para*-director.” 1

□29 Maximum score 2

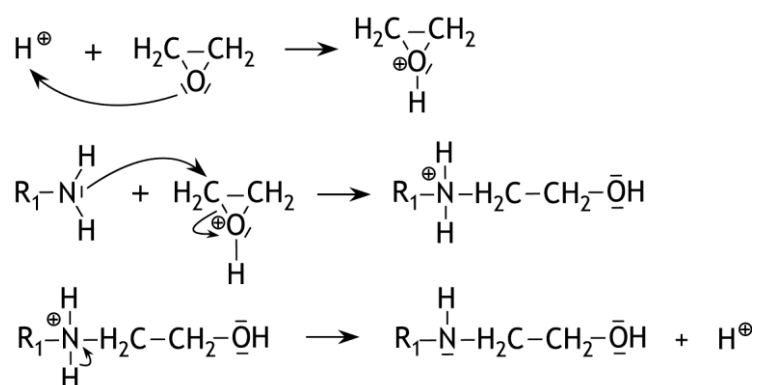
A correct answer can be formulated as follows:

(The substitution at the *para*-position can take place unhindered.) The substitution at the *ortho*-positions is steric hindered by the bulky group at the aromatic ring.

- there already is a bulky group at the aromatic ring 1
- substitution at the *ortho*-positions is steric hindered by that group 1

□30 Maximum score 5

A correct answer can be given as follows:



- the structures of the intermediates correctly drawn 1
- the structure of the product correctly drawn 1
- the non-bonding electron pairs correctly drawn 1
- the curved arrows correctly drawn 1
- the formal charges correctly placed 1

□31 Maximum score 2

A correct answer can be formulated as follows:

In step 4 (only) the nitro group is hydrogenated. The C = O group(s) is (are) not hydrogenated.

- the nitro group is hydrogenated 1
- the C = O group(s) is (are) not hydrogenated 1

*Remark*

When an answer has been given as: „In step 4 (only) the nitro group is hydrogenated. The aromatic ring(s) is (are) not hydrogenated.”, give full marks.

□32 Maximum score 4

A correct answer can be formulated as follows:

In step 2 a protection is introduced, that is removed in step 7.

The reason for this protection is to prevent the COOH group reacting in step 3 / in step 4 / in step 5 / in step 6 (too).

In step 3 a protection is introduced, that is removed in step 7.

The reason for this protection is to prevent the NH<sub>2</sub> group reacting in step 5 (too).

- introduction and removal of the first protection correctly indicated 1
- correct reason for the first protection 1
- introduction and removal of the second protection correctly indicated 1
- correct reason for the second protection 1