46th National Chemistry Olympiad

Symeres, Nijmegen

THEORY TEST

Marking scheme

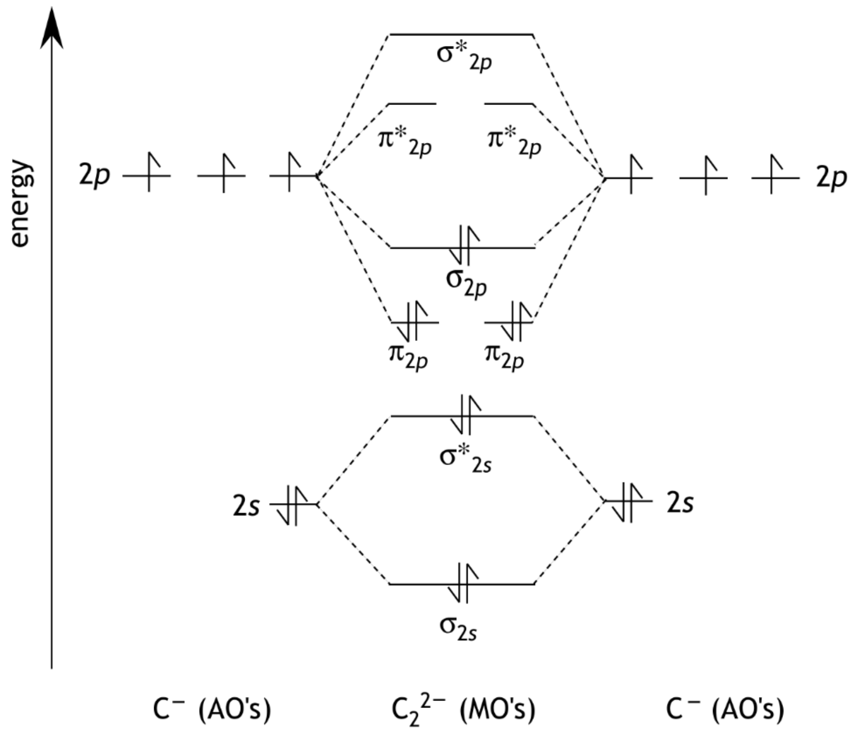
Wednesday June 4 2025

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

Problem 1 Carbide shooting — 13 points

□1 maximum score 6

A correct answer could look like this:



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

□2 maximum score 2

An example of a correct answer is:

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

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

Notes

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

▫3 maximum score 5

An example of a correct answer is:

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

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

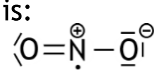
The mole ratio of ethyne : oxygen is therefore 0.33 : 0.28, and that is equal to the volume ratio, which is indeed approximately equal to the ideal volume ratio.

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

Problem 2 The NO_2 - N_2O_4 equilibrium 30 points

□4 maximum score 5

An example of a correct answer is:

The Lewis structure of NO_2 is: 

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

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

□5 maximum score 6

An example of a correct calculation is:

The reaction equation is:

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

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

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

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

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

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

Note

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

□6 maximum score 4

An example of a correct answer is:

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

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

Note

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

□7 maximum score 5

An example of a correct calculation is:

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

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

So at a temperature T_1, the following applies:

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

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

This gives T_1 = 281 K.

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

□8 maximum score 7

An example of a correct calculation is:

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

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

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

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

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

This gives $x = 0.14$.

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

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

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

□9 maximum score 3

Examples of correct answers are:

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

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

and

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

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

Problem 3 Paracetamol from lignin — 25 points

▫10 maximum score 2

This is a condensation reaction.

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

▫11 maximum score 1

A correct answer could look like this:

H_3C—OH or ——OH

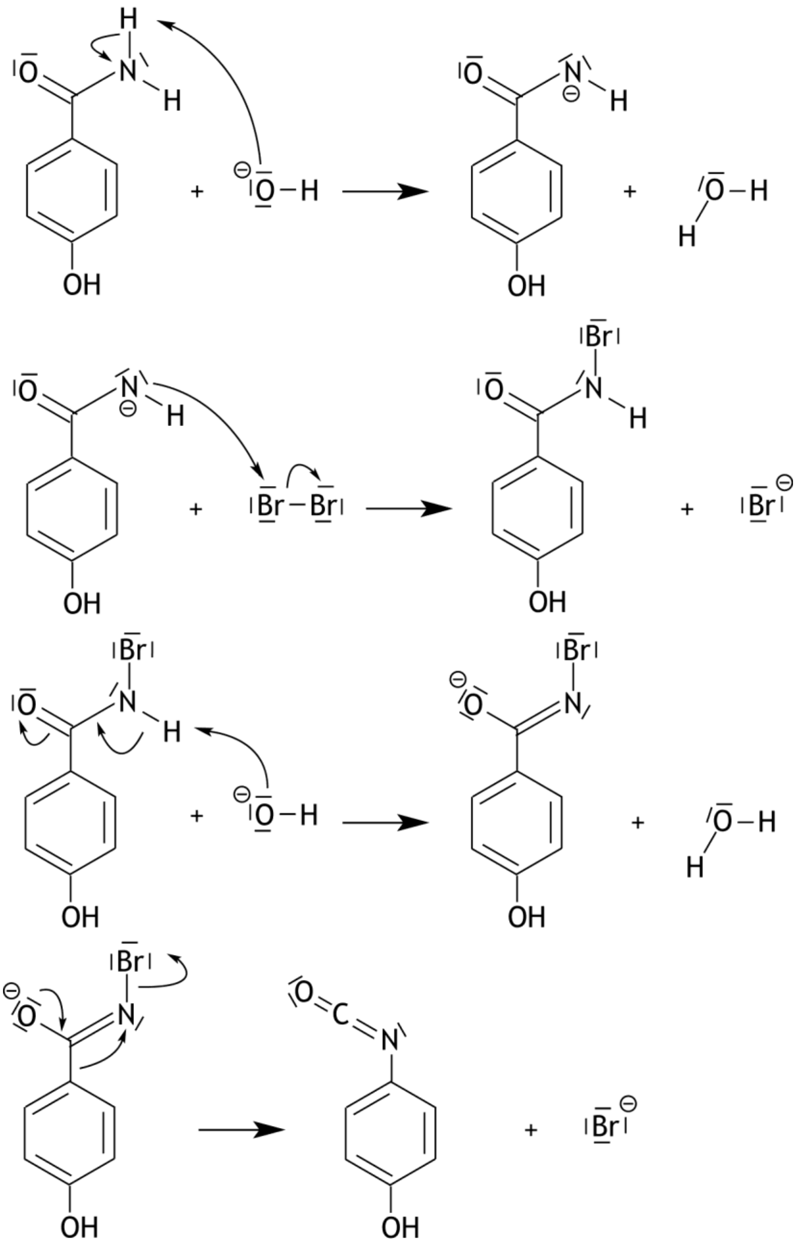
▫12 maximum score 2

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

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

▫13 maximum score 6

A correct answer could look like this:



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

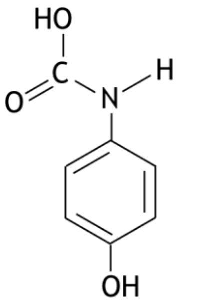
If in an otherwise correct answer one curly arrow is missing and/or incorrectly drawn 5

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

□14 maximum score 3

A correct answer could look like this:

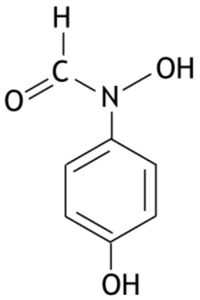
The structural formula of the addition product is:



And substance **X** is CO_2.

- correct structual formula of the addition product 2
- substance **X** is CO_2 1

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



2

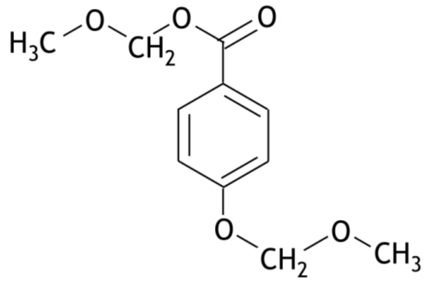
□15 maximum score 4

A correct answer could look like this:

- in the first structure, two lone pairs on the O atom 1
- in the first structure, the formal charge on the C atom 1
- in the second structure, one lone pair on the O atom and a double bond between O and C 1
- in the second structure, the formal charge on the O atom 1

□16 maximum score 1

A correct answer could look like this:



□17 maximum score 6

An example of a correct calculation is:

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

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

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

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

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

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

Problem 4 Tankyrase inhibitors 8 points

□18 maximum score 2

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

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

□19 maximum score 3

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

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

□20 maximum score 3

An example of a correct calculation is:

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

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

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

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

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

Problem 5 Shono oxidation 11 points

□21 maximum score 2

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

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

□22 maximum score 2

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

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

□23 maximum score 2

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

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

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

□24 maximum score 5

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

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

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

▌Problem 6 Cobalt complexes 22 points

□25 maximum score 4

An example of a correct calculation is:

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

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

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

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

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

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

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

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

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

□26 maximum score 4

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

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

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

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

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

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

This gives $x = -0.19$ V.

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

□27 maximum score 3

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

A at 475 nm is 0.112.

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

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

Note

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

▫28 maximum score 8

An example of a correct calculation is:

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

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

and that is 0.109×267.5 = 29.1 mg.

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

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

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

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

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

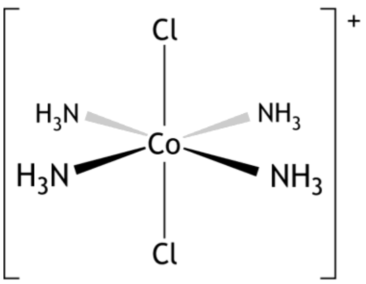
Note:
When an incorrect answer to question 28 is the logical consequence of an incorrect answer to question 27, accept this answer to question 28 as correct.

▫29 maximum score 1

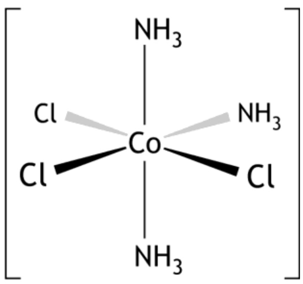
$n = 3 - x$

▫30 maximum score 2

A correct answer could look like this:



isomer of complex II



isomer of complex III

per correctly drawn isomer 1

Problem 7 Permanganometry 11 points

31 maximum score 4

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

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

32 maximum score 7

An example of a correct calculation is:

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

Therefore the tested sample contained

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

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

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

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

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