46th National Chemistry Olympiad

Symeres, Nijmegen

THEORY TEST

Question booklet

Wednesday June 4 2025

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

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Problem 1 Carbide shooting 13 points

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

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

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

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

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

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

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

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

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

Problem 2 The NO_2 – N_2O_4 equilibrium 30 points

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

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

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

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

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

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

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

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

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

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

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

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

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

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

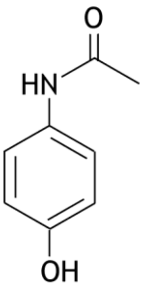
□8 Calculate the total pressure (in Pa) in the test tube once equilibrium has been established. 7

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

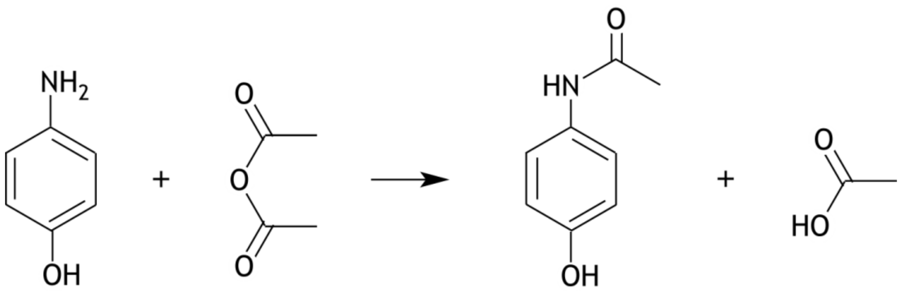
□9 In which of the two test tubes will the gas mixture appear lighter in colour? Explain your answer. 3

Problem 3 Paracetamol from lignin 25 points

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

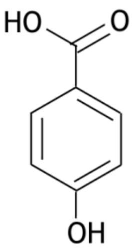


Paracetamol is produced by reacting *para*-aminophenol with acetic anhydride:



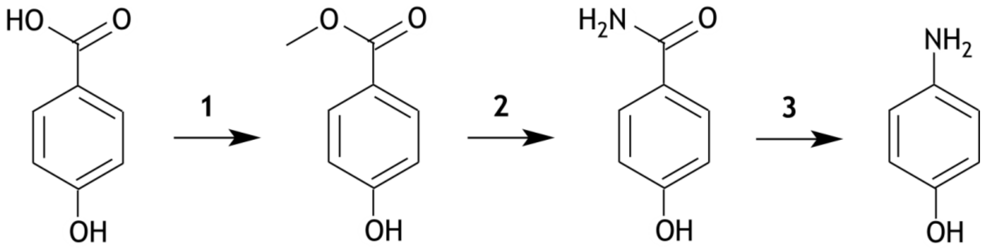
▫10 What type of reaction is this? 2

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



I

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



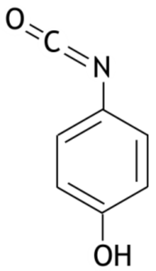
I **II** **III** **IV**

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

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

□12 Which side reaction might take place? 2

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



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

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

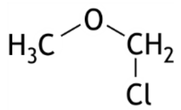
□13 Represent this mechanism using chemical equations with structural formulas.

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

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

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

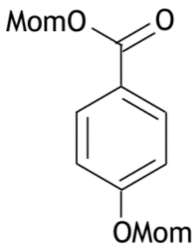
One disadvantage of this synthetic route to *para*-aminophenol is that the yield of the Hofmann rearrangement is rather low, resulting in an overall yield of less than 20%. This can be improved by replacing conversion step **1** with a reaction in which

para-hydroxybenzoic acid is reacted with chloromethoxymethane, 

,

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

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

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

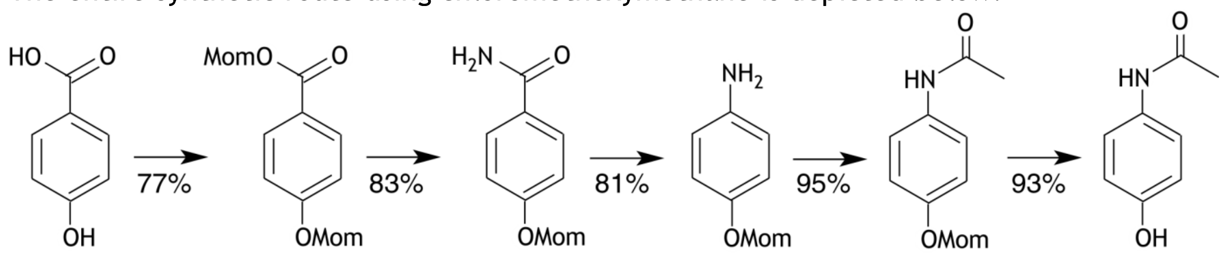
V

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

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

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

The entire synthetic route using chloromethoxymethane is depicted below:



I V VI VII VIII paracetamol

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

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

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

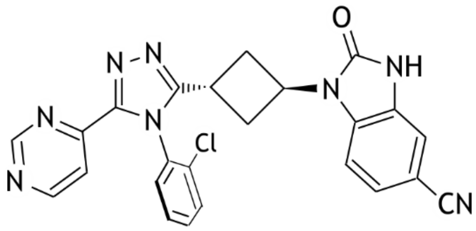
□17 Calculate the value of *F*. In addition to the given conversion percentages, use the following data:

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

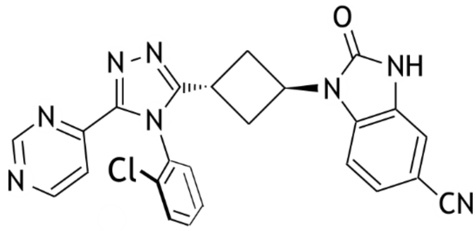
Problem 4 Tankyrase inhibitors   8 points

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

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



I



II

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

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

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

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

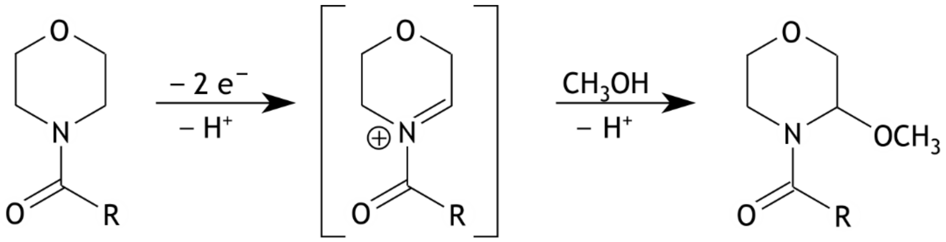
At elevated temperatures, the stereoisomers **I** and **II** gradually convert into one another due to the fact that rotation around the relevant C – N bonds becomes possible. This isomerisation follows first-order kinetics. Starting from compound **I**, after 72 hours at a temperature of 70 °C, 10 percent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

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

Problem 5 Shono oxidation — 11 points

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

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



I — intermediate — II

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

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

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

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

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

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

Problem 6 Cobalt Complexes 22 points

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

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

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

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

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

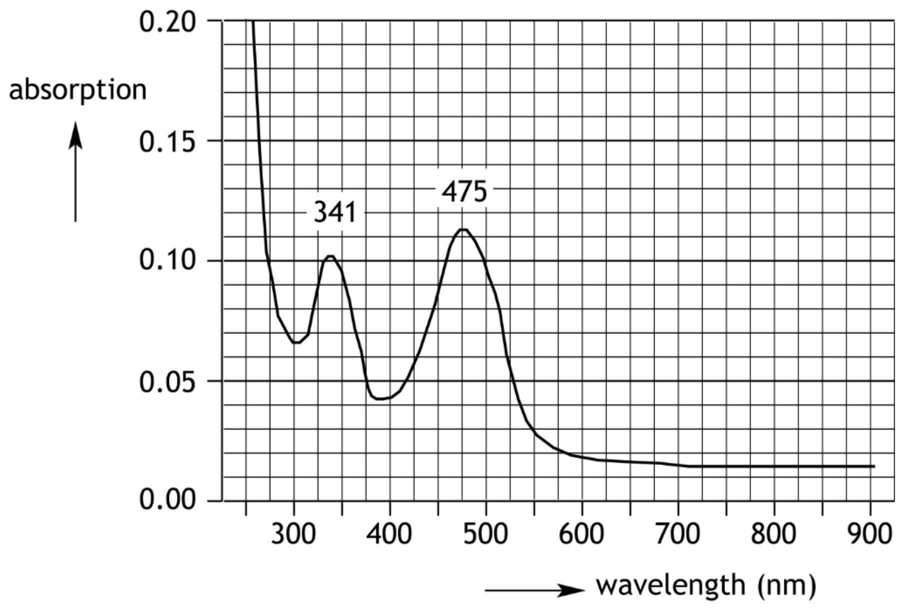
□25 Calculate, based on data from the overview above, the value of the standard electrode potential for the half-reaction $Co^{3+} + e^- \rightarrow Co^{2+}$. 4

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

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

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

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



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

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

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

$CoCl_2.6H_2O + NH_4Cl \rightarrow Co(H_2O)_6^{2+} + NH_4^+ + 3\ Cl^-$
$Co(H_2O)_6^{2+} + 6\ NH_3 \rightarrow Co(NH_3)_6^{2+} + 6\ H_2O$
$Co(NH_3)_6^{2+} + ½\ H_2O_2 \rightarrow Co(NH_3)_6^{3+} + OH^-$
$Co(NH_3)_6^{3+} + 3\ Cl^- \rightarrow Co(NH_3)_6Cl_3$

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

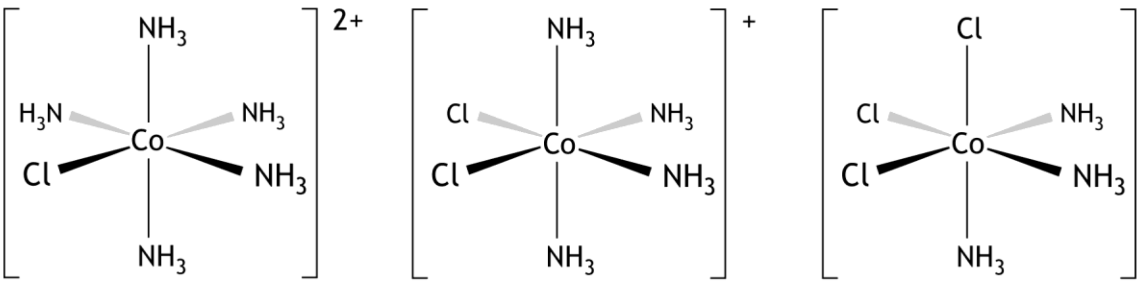
During an experiment, $Co(NH_3)_6Cl_3$ is synthesised via the above reactions, starting with 6.0065 g of cobalt(II) chloride hexahydrate. Ultimately, 5.4543 g of impure product is obtained. From this impure product, 30.0 mg is dissolved in a 100.0 mL volumetric flask. The absorbance of this solution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

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

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

29 What is the relationship between n and x? 1

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



complex I complex II complex III

An isomer exists for complex II and complex III.

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

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

Problem 7 Permanganometry 11 points

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

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

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

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

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

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

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