



Oxford Cambridge and RSA

Wednesday 19 June 2019 – Morning

A Level Chemistry B (Salters)

H433/03 Practical skills in chemistry

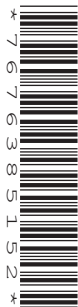
Time allowed: 1 hour 30 minutes

You must have:

- the Insert (inserted)
- the Data Sheet for Chemistry B (Salters)
(sent with general stationery)

You may use:

- a scientific or graphical calculator



Please write clearly in black ink. **Do not write in the barcodes.**

Centre number

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Candidate number

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First name(s)

Last name

StemUp Model Solution

INSTRUCTIONS

- Use black ink. You may use an HB pencil for graphs and diagrams.
- The practical insert is needed with this paper.
- Answer **all** the questions.
- Where appropriate, your answers should be supported with working. Marks may be given for a correct method even if the answer is incorrect.
- Write your answer to each question in the space provided. If additional space is required, use the lined page(s) at the end of this booklet. The question number(s) must be clearly shown.

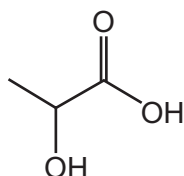
INFORMATION

- The total mark for this paper is **60**.
- The marks for each question are shown in brackets [].
- Quality of extended responses will be assessed in questions marked with an asterisk (*).
- This document consists of **20** pages.

Answer **all** the questions.

- 1 A student taking A level chemistry and biology was researching the use of polymers in medicine. These are sometimes called biopolymers.

The student found that one of the most frequently used biopolymers is polylactic acid, PLA. PLA is made from lactic acid.



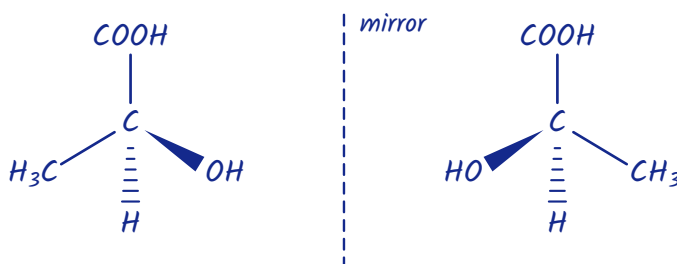
Lactic acid

- (a) Lactic acid is a chiral molecule.

Explain the term **chiral** in this context and use 3-D structures to help your explanation.

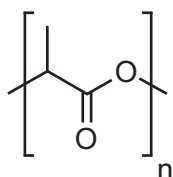
Explanation *A chiral molecule has a mirror image that is non-superimposable; lactic acid exists as two optical isomers (enantiomers).*

Structures



[3]

- (b) The structure of PLA is shown below.



PLA

PLA has a wide variety of uses. One use is in biodegradable medical devices (e.g. screws and plates that are expected to biodegrade within 6–12 months).

- (i) Name the functional group in PLA and suggest the **type** of reaction that occurs when PLA biodegrades.

Functional group: ester

Type of reaction: hydrolysis [2]

- (ii) State the strongest type of intermolecular bonding that occurs between PLA polymer chains.

Explain, in terms of electronegativity, how this intermolecular bonding arises.

Permanent dipole-permanent dipole bonds.
O is more electronegative than C, so the C=O (and C-O) bonds in the
ester groups are polar, C^{δ+} and O^{δ-}; the δ+ C of one chain attracts
the δ- O of a neighbouring chain. [2]

- (c) The industrial manufacture of PLA uses heterogeneous catalysts.

A simple model of heterogeneous catalysis has four steps.

Describe the four steps involved.

- 1 *Reactant molecules are adsorbed onto the surface of the catalyst (form bonds with the active sites).*
- 2 *Bonds within the reactant molecules break.*
- 3 *New bonds form to make the product molecules.*
- 4 *The product molecules are desorbed (released) from the catalyst surface and diffuse away.*

[2]

- 2 A pair of chemistry students are asked to prepare a sample of paracetamol. They use the reaction shown in **Fig. 2.1**.

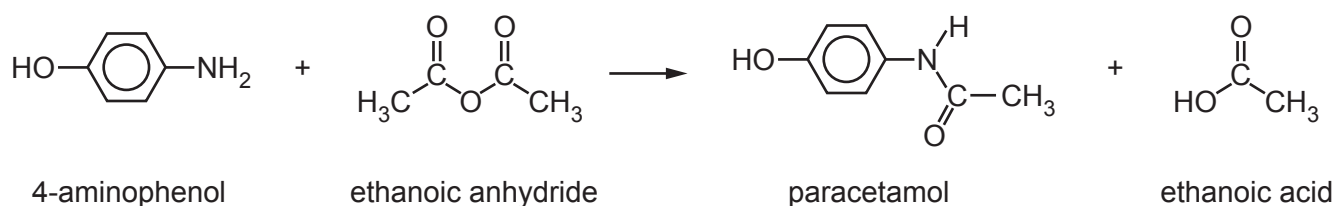
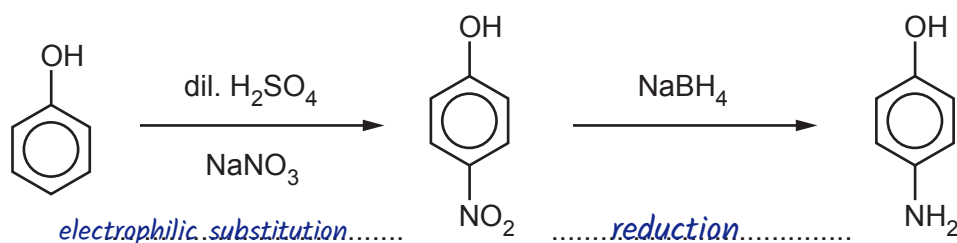


Fig. 2.1

- (a) Identify the **two** functional groups in paracetamol, apart from the benzene ring.

1 ...*phenol*.....
 2 ...*(secondary) amide*..... [2]

- (b) The reactant 4-aminophenol can be made from phenol in the two-step synthesis shown below.



Name the **type** of reaction for each step.

Write your answers on the dotted lines.

[2]

(c) Fig. 2.2 shows some information found on a bottle of ethanoic anhydride.

The students use the information in Fig. 2.2 to write a risk assessment for ethanoic anhydride.

Ethanoic anhydride	Hazards
  	Flammable Harmful by inhalation and if swallowed Corrosive – causes burns

Fig. 2.2

Suggest **three** precautions that the students should take when using ethanoic anhydride.

- 1 *Keep away from naked flames (no lit Bunsen burners), as it is flammable.*
- 2 *Use it in a fume cupboard, as it is harmful by inhalation.*
- 3 *Wear protective gloves, as it is corrosive and causes burns.*

[3]

(d) The mechanism for the reaction for the formation of paracetamol is shown in Fig. 2.3.

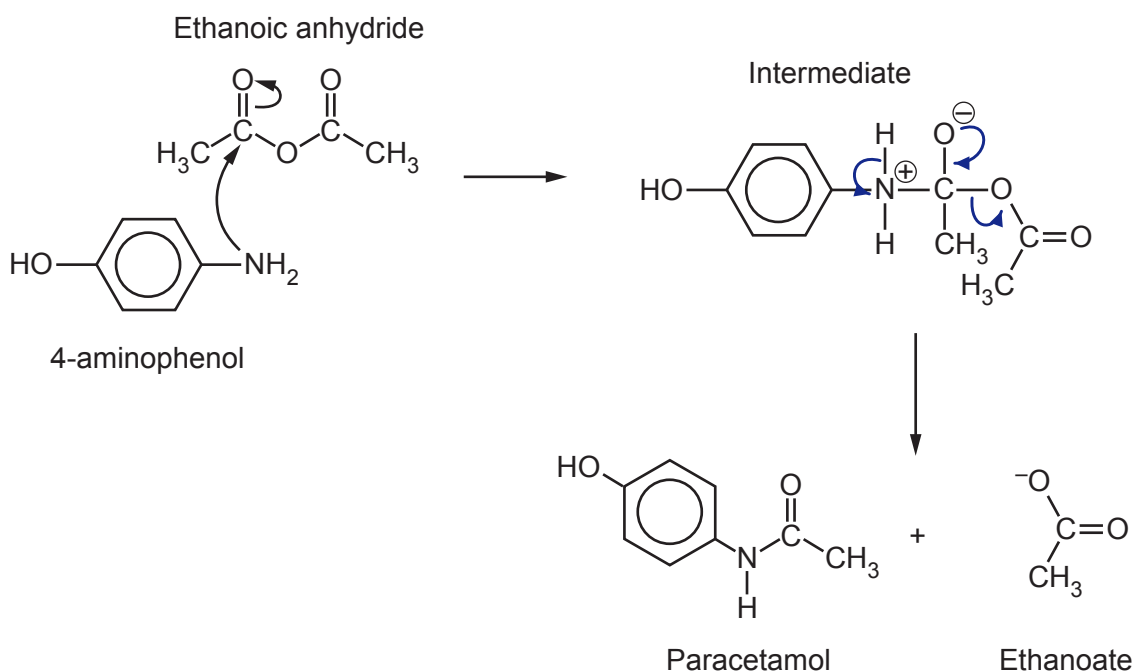


Fig. 2.3

Mark curly arrows to show the electron movements that occur in the **intermediate** to allow formation of the products in Fig. 2.3.

[1]

- (e) The students carry out the preparation using water as solvent. Paracetamol is insoluble in water.

The students use the apparatus in **Fig. 2.4** to separate the paracetamol from the reaction mixture.

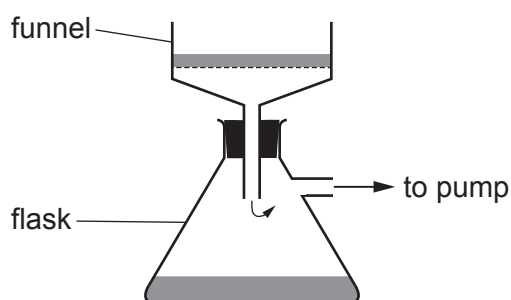


Fig. 2.4

- (i) Name the technique in **Fig. 2.4** and explain how this apparatus is used to get a sample of impure solid paracetamol.

Vacuum (suction) filtration, using a Büchner funnel and flask connected to a pump.
Moisten the filter paper with water, pour in the mixture; the reduced pressure sucks the water through into the flask.
The impure solid paracetamol is left on the filter paper; wash it with a little cold water and suck it dry. [3]

- (ii) Suggest a reason for using the technique in **Fig. 2.4** rather than simple filtration.

It is much quicker (faster) than simple filtration. [1]

Fig. 2.1 is repeated below.

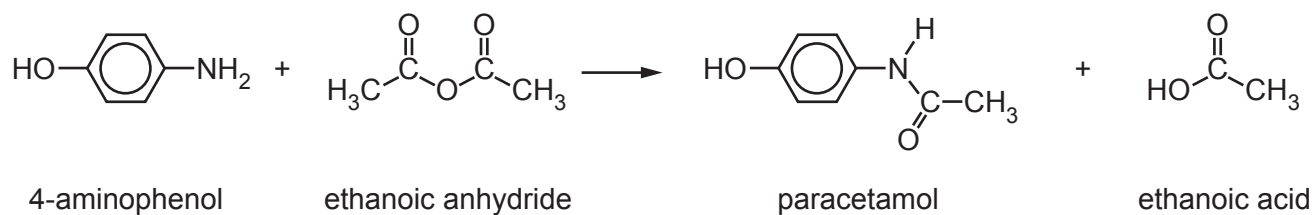


Fig. 2.1

- (f) The students then recrystallised their paracetamol sample.

The students started with a mass of 2.1 g of 4-aminophenol and used excess ethanoic anhydride.

The mass of the dried recrystallised paracetamol produced was 1.5 g.

Calculate the percentage yield for the students' reaction.

Give your answer to an **appropriate** number of significant figures.

$$M_r(4\text{-aminophenol}, C_6H_7NO) = 109.0; \quad M_r(\text{paracetamol}, C_8H_9NO_2) = 151.0$$

1 mol 4-aminophenol gives 1 mol paracetamol

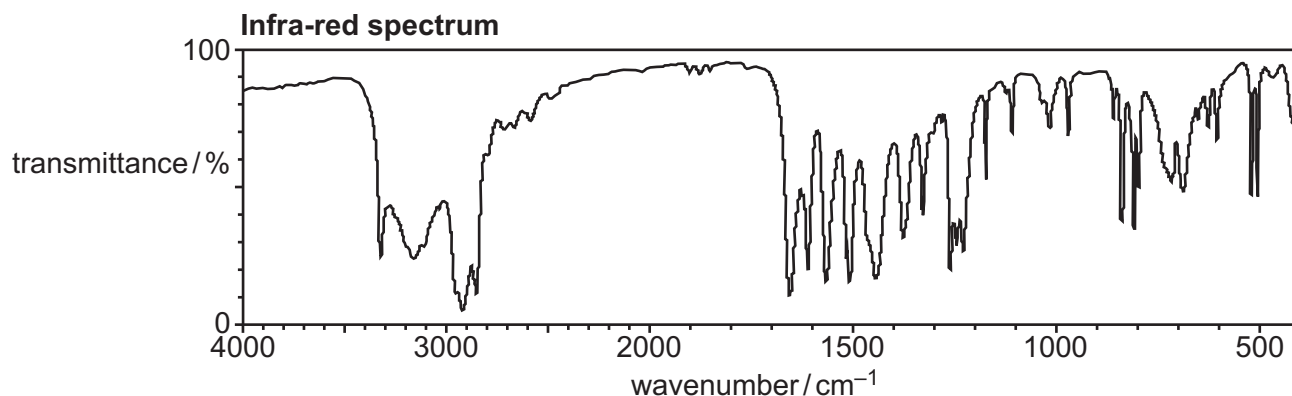
$$\text{maximum mass} = 2.1 \times 151 / 109 = 2.9 \text{ g}$$

$$\% \text{ yield} = 1.5 / 2.9 \times 100 = 51.7 = 52\% \text{ (2 s.f.)}$$

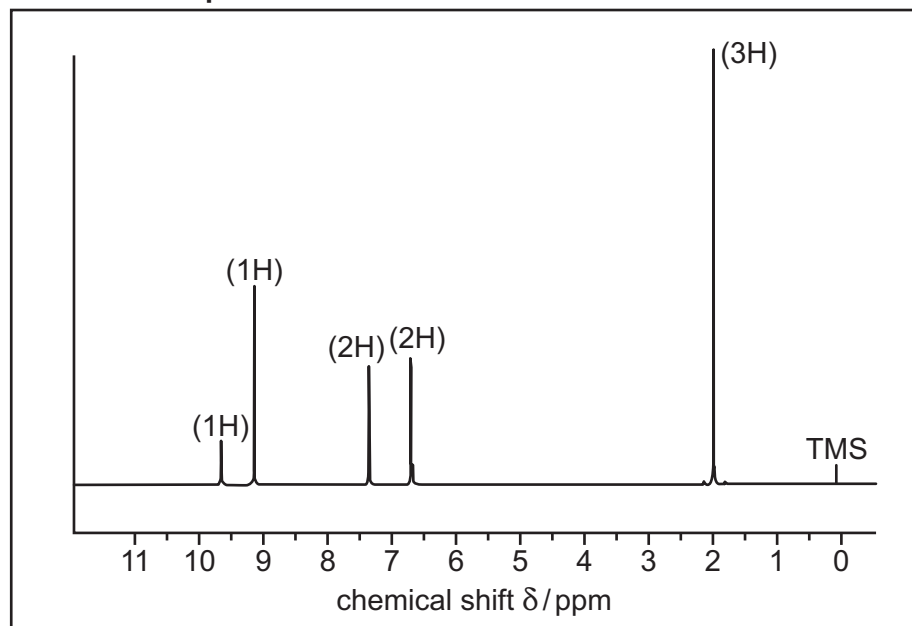
percentage yield = ...52..... % [3]

- (g) The students sent pure samples of their reagents and products to a university lab. Spectra of all the compounds were produced.

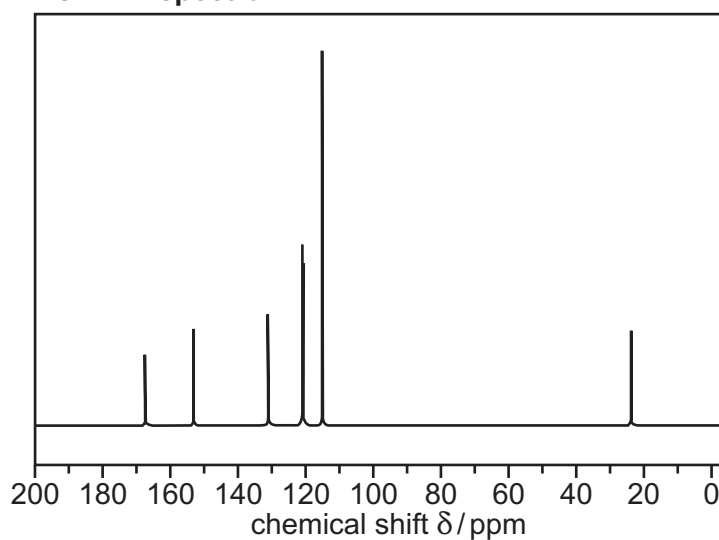
The spectra from **one** of the compounds are shown below.



Proton NMR spectrum



^{13}C NMR spectrum



You may do working on this page but it will not be marked

Use pieces of evidence from **all** the spectra to identify the compound.

[6]

IR: a strong absorption at about 1650 cm^{-1} shows a $\text{C}=\text{O}$ group, so it cannot be 4-aminophenol. A broad absorption at about 3100 to 3350 cm^{-1} shows O-H (phenol) and N-H bonds, so it cannot be ethanoic anhydride or ethanoic acid.

Proton NMR: there are 5 peaks, so 5 proton environments, in the ratio 3:2:2:1:1. This rules out 4-aminophenol (4 environments), ethanoic acid (2) and ethanoic anhydride (1). The 3H peak at $\delta\ 2.0$ is the CH_3 next to $\text{C}=\text{O}$, the two 2H peaks at about $\delta\ 7$ are the two pairs of H atoms on the para-substituted benzene ring, and the 1H peaks at about $\delta\ 9.2$ and 9.6 are the single OH and NH protons.

^{13}C NMR: 6 peaks, so 6 carbon environments: $\text{C}=\text{O}$ at about $\delta\ 168$, four aromatic carbons at $\delta\ 115$ to 155 (the ring is symmetrical) and CH_3 at about $\delta\ 24$. The reactants and ethanoic acid have fewer carbon environments (too few carbons).

So the compound is paracetamol, $\text{HOC}_6\text{H}_4\text{NHCOCH}_3$.

Additional answer space if required

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(h) The mass spectrum of ethanoic acid is shown below.

Mass Spectrum

© National Institute of Standards and Technology, webbook11@nist.gov. Item removed due to third party copyright restrictions. Link to material: <https://webbook.nist.gov/cgi/cbook.cgi?Spec=C64197&Index=0&Type=Mass&Large=on>

(i) Give the structures that produce the peaks at:

60 CH_3COOH^+

43 CH_3CO^+ [2]

(ii) Suggest why there is a small peak at 61.

It is the M+1 peak, caused by molecules containing one ^{13}C atom instead of ^{12}C [1]

PLEASE DO NOT WRITE ON THIS PAGE

- 3 A group of students are investigating the properties of weak acids and buffer solutions.

They take measurements of the pH of some solutions before and after adding an equal volume of 0.01 mol dm^{-3} sodium hydroxide solution.

Some of the students' results are shown in the table below.

Experiment	Original solution	pH before addition	pH after addition
A	0.01 mol dm^{-3} ethanoic acid	3.4	8.2
B	0.1 mol dm^{-3} ethanoic acid plus an equal volume of 0.1 mol dm^{-3} sodium ethanoate	4.8	4.9
C	0.1 mol dm^{-3} sodium ethanoate	8.9	11.7
D	Distilled water	7.0	

- (a) The solution in experiment B is behaving as a buffer solution.

Explain the meaning of the term **buffer solution**.

A solution that resists (minimises) changes in pH when small amounts of acid or alkali are added.

[2]

- (b) K_a for ethanoic acid is $1.7 \times 10^{-5} \text{ mol dm}^{-3}$.

Show by calculation that the initial pH in experiment B is 4.8.

$$K_a = [H^+][A^-] / [HA], \text{ so } [H^+] = K_a \times [HA] / [A^-]$$

equal volumes of 0.1 mol dm^{-3} acid and salt, so $[HA] = [A^-]$ (0.05 mol dm^{-3})

$$[H^+] = K_a = 1.7 \times 10^{-5} \text{ mol dm}^{-3}$$

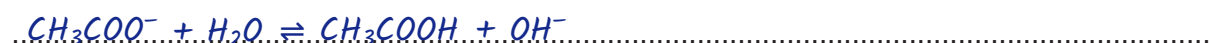
$$\text{pH} = -\log(1.7 \times 10^{-5}) = 4.77 = 4.8 \quad (\text{pH} = \text{p}K_a)$$

[2]

- (c) Explain why the pH of sodium ethanoate in experiment C is alkaline.

Include an equation in your answer.

Ethanoate ions are the conjugate base of a weak acid, so they react with water:



This makes OH^- ions, so $[\text{OH}^-] > [\text{H}^+]$ and the solution is alkaline.

[2]

- (d) Calculate the pH of the solution formed after the addition of sodium hydroxide solution in experiment D.

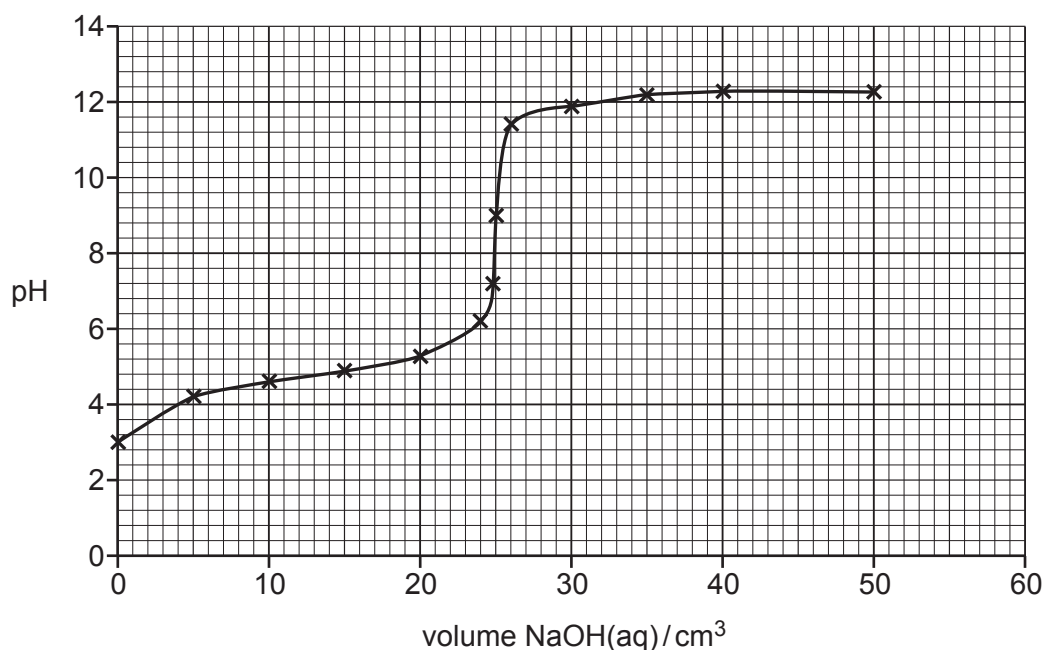
equal volumes mixed, so $[OH^-] = 0.01 / 2 = 0.005 \text{ mol dm}^{-3}$

$[H^+] = K_w / [OH^-] = 1.00 \times 10^{-14} / 0.005 = 2.00 \times 10^{-12} \text{ mol dm}^{-3}$

$pH = -\log(2.00 \times 10^{-12}) = 11.7$

pH = ...11.7..... [3]

- (e) In a follow-up experiment, 25.0 cm^3 of the ethanoic acid solution is titrated with a solution of sodium hydroxide of unknown concentration and the following graph is obtained.



Suggest a suitable practical procedure that would enable this graph to be obtained.

Pipette 25.0 cm^3 of the ethanoic acid into a conical flask (beaker); put the NaOH(aq) in a burette.
Measure the pH with a (calibrated) pH meter.
Add NaOH in 5 cm^3 portions, swirling, and record the pH after each addition; where the pH changes rapidly add 1 cm^3 portions. [3]

4 This question refers to the **Practical Insert** that is provided as an insert to this paper.

(a) Suggest why the titre values in **Table 2** increase from sample 1 to sample 4.

*The longer the spinach stands in the acid, the more iron compounds
dissolve; it takes time for the iron to get into solution.* [1]

(b) The students use a titre value of 8.00 cm^3 to calculate the mass of iron in the spinach in sample 4.

(i) Show how the students calculated the value of 8.00 cm^3 as their titre for the calculation.

$(7.95 + 8.05) / 2 = 8.00 \text{ cm}^3$; mean of the concordant titres [1]

(ii) Foods 'high' in iron usually contain more than 4 mg of iron per 100 g of foodstuff. A student states that the data in **Tables 1** and **2** show that spinach is 'high in iron'.

Comment on the student's statement.

Show calculations to support your comments, using the data for **sample 4**.

$$n(\text{MnO}_4^-) = 5.0 \times 10^{-6} \times 8.00 / 1000 = 4.0 \times 10^{-8} \text{ mol}$$

$$n(\text{Fe}^{2+}) \text{ in } 25 \text{ cm}^3 = 5 \times 4.0 \times 10^{-8} = 2.0 \times 10^{-7} \text{ mol}$$

$$n(\text{Fe}^{2+}) \text{ in } 250 \text{ cm}^3 = 10 \times 2.0 \times 10^{-7} = 2.0 \times 10^{-6} \text{ mol}$$

$$\text{mass of Fe} = 2.0 \times 10^{-6} \times 55.8 = 1.12 \times 10^{-4} \text{ g} = 0.112 \text{ mg}$$

$$\text{mass of Fe in 100 g spinach} = 0.112 \times 100 / 5.10 = 2.2 \text{ mg}$$

*Sample 4 contains only about 2.2 mg of iron per 100 g of spinach,
which is less than 4 mg per 100 g, so the data show spinach is not
'high in iron': the student's statement is wrong.*

[4]

(c) A student suggests that the titre values in the experiment are too small and give an unacceptable error for the final answer.

(i) Calculate the percentage uncertainty in titre 1 for **sample 4**.

$$\text{uncertainty in titre} = 2 \times 0.05 = 0.10 \text{ cm}^3$$

$$\% \text{ uncertainty} = 0.10 / 8.05 \times 100 = 1.24\%$$

percentage uncertainty = *1.24* % [1]

- (ii) The students want to reduce the percentage uncertainty in the titre values, while using the same equipment.

Suggest **two** ways in which they can do this.

- 1 *Use a greater mass of spinach, so more iron is present and the titre is larger.*
- 2 *Use a lower concentration of potassium manganate(VII) solution, so a larger titre is needed.* [2]

- (d)* There are several d block metal ions, including complex ions, mentioned in the insert. These ions are different colours.

Explain the term **complex ion** and why different complexes of d block elements have different colours.

Give examples from the Insert.

[6]

A complex ion is a central metal ion surrounded by ligands: molecules or ions with a lone pair that form co-ordinate (dative) bonds to the metal ion. In the Insert, $\text{Fe}^{2+}(\text{aq})$ and $\text{Mn}^{2+}(\text{aq})$ are $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ with six water ligands, and MnO_4^- has four oxide ligands around Mn.

Colour: when ligands bond to the metal ion, the d orbitals split into two groups with different energies. The gap ΔE is the right size to absorb visible light: an electron absorbs a photon and is promoted from a lower d orbital to a higher (excited) d orbital, with $\Delta E = h\nu$. The colour we see is the complementary colour, made of the frequencies that are not absorbed.

Different colours: the size of the d orbital splitting depends on the metal, its oxidation state and the ligands. A different ΔE means a different frequency is absorbed, so a different complementary colour is seen: MnO_4^- (Mn +7) is purple, $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ (Mn +2) is almost colourless, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ is pale green and $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is yellow-orange.

Additional answer space if required

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END OF QUESTION PAPER

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