Candidate Name:			
		Shift	
	millennia institute	Laboratory	
2024 Preliminary Examination			

Pre-University 3

H2 CHEMISTRY

Paper 4 Practical

9729/04

27 Sep 2024 2 hours 30 minutes

Class

Adm No

Candidates answer on the Question paper.

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write your name, class and admission number on all the work you hand in. Give details of the practical shift and laboratory where appropriate, in the boxes provided. Write in dark blue or black pen. You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate. You may lose marks if you do not show your working or if you do not use appropriate units. Qualitative Analysis Notes are printed at the back of the Question Paper.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.



1 Determination of enthalpy change of reaction

FA1 is solid sodium hydrogencarbonate, NaHCO₃

FA 2 is 1.50 mol dm⁻³ sulfuric acid, H_2SO_4 (also required in both question 2 and 3)

Sodium hydrogencarbonate is commonly known as baking soda and is used as a reagent in various reactions. It is soluble in water according to equation 1.

equation 1 NaHCO₃(s) + aq \rightarrow Na⁺(aq) + HCO₃⁻(aq) ΔH_1

It can also react with acids in both solid and aqueous state.

equation 2	$2NaHCO_{3}(s) + H_{2}SO_{4}(aq) \rightarrow Na_{2}SO_{4}(aq) + 2H_{2}O(I) + 2CO_{2}(g)$	ΔH_2
equation 3	$2NaHCO_3(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(I) + 2CO_2(g)$	ΔH_3

In this question, you will carry out experiments to determine ΔH_1 and ΔH_2 , then use Hess's Law to determine ΔH_3 .

(a) In this experiment, you will determine the maximum temperature change when a known mass of solid sodium hydrogencarbonate, **FA 1**, reacts with sulfuric acid, **FA 2**. Then, you will determine ΔH_2 .

In an appropriate format in the space provided below, record

- all weighings to an appropriate level of precision,
- all values of temperature to an appropriate level of precision.

Procedure

- 1. Weigh the capped bottle containing **FA 1**.
- 2. Place one polystyrene cup inside a second polystyrene cup. Place these in a glass beaker to prevent them from tipping over.
- Use a measuring cylinder to transfer 25 cm³ of FA 2 into the first polystyrene cup. Cover the cup with the lid provided.
- 4. Stir **FA 2** in the cup gently with the thermometer. Read and record its temperature.
- 5. Transfer all the **FA1** to the polystyrene cup. Stir the mixture.
- 6. Continue to stir the mixture. Observe the temperature and record the value that shows the maximum change from the initial temperature.
- 7. Reweigh the empty bottle and its cap.
- 8. Record the maximum temperature change and the mass of **FA 1** used.

For
Examiners'
Use

(i) Results

Mass of capped bottle with FA1/g	9.05
Mass of capped bottle with residual FA 1 / g	5.07
Mass of FA 1 used / g	3.98

Initial temperature of FA 2 / °C	30.8
Final temperature of mixture / °C	22.6
Maximum temperature change / °C	8.2

[5]

[1] correct headers and units

[1] mass readings to 2 d.p. and temperature readings to 1 d.p.

[1] correctly determined maximum temperature change and mass of FA 1 used

[2] $\Delta T/m$ accuracy

Examiners' Comments:

- Common mistakes include omitting the word "capped", or using the phrasing "maximum temperature" instead of "final temperature of mixture".
- It was immediately obvious that some students faked their values when their reaction mixture increased in temperature, and it is reasonable to expect to be penalised for it. Additionally, depending on the nature of the question, having the wrong sign could potentially have implications on subsequent questions.
- (ii) Calculate the heat change, q, using the values you obtained in (a)(i).

You should assume that the specific heat capacity of the solution is 4.18 J g^{-1} K⁻¹, and that the density of the solution is 1.00 g cm⁻³.

q = mc∆T = 25.0 × 4.18 × 8.2 = 856.9 ≈ 857 J (3sf)

heat change = $\frac{857 \text{ J}}{1}$

- Students performed unexpectedly poorly for this question, showing fundamental misconceptions.
- Common mistakes include using the mass of the solid only, or summing up the mass of the solid with that of the solution. The specific heat capacity, c, value of 4.18 is specifically for water. Since the solid is going to fully react / dissolve, the volume of the solution (which we use to determine the mass of water) does not change much – so we always omit the mass of solid added.
- Some students included a negative sign for their answers, but energy is a scalar quantity (only magnitude). It will also result in fewer mistakes if the sign is only included in ΔH calculations later based on whether the reaction is exo or endo.

(iii) Hence, determine the enthalpy change of reaction, ΔH_2 .

[*A*_r: Na, 23.0; H, 1.0; C, 12.0; O, 16.0]

Amount of FA $1 = 3.98 \div 84.0 = 0.04738$ mol Amount of FA $2 = 0.025 \times 1.50 = 0.0375$ mol FA 1 is limiting reagent [1] calculation of both amounts required

 $\Delta H_2 = \frac{q}{amt \ of \ LR} \times \text{CLR} = \frac{+856.9}{0.04738} \times 2 = +36170 \text{ J mol}^{-1} = +36.2 \text{ kJ mol}^{-1} \text{ (3sf) [1] sign}$ required

Examiners' Comments:

 $\Delta H_2 = +36.2 \text{ kJ mol}^{-1} [2]$

- Students performed poorly for this question, with many not being familiar with the equation for enthalpy change of reaction, as well as lacking conceptual understanding of the coefficient of LR (CLR).
- A significant number of students also did not show calculation to determine the LR, which is required before the calculation of the enthalpy change of reaction.
- (iv) Calculate the percentage error of the temperature change when using the thermometer.

Percentage error = $\frac{2(0.1)}{\Delta T} \times 100\% = \frac{0.2}{8.2} \times 100\% = 2.44\%$ (3sf)

percentage error = 2.44 % [1]

Examiners' Comments:

- Students performed poorly for this question.
- All students had to do was to relate this question to the usual one for titre value. The thermometer given had a smallest interval of 0.2 °C, thus the uncertainty of a single reading is ±0.1 °C. Two readings had to be taken to determine for ΔT.
- (v) Suggest the effect on the value for △T when 50 cm³ of FA 2 is used instead of 25 cm³ in the experiment.

FA 1 is the limiting reagent and thus <u>q will not change</u>. Since <u>mass of the solution is</u> <u>doubled</u>, ΔT will be halved.

- Students performed poorly for this question.
- For stronger students who understood what the question was testing for, many did not recognise that the specific volumes given required "halved" as part of the answer requirement.
- (b) A second experiment was conducted to find out ΔH_1 and the results of the experiment are presented in Table 1.1.

mass of FA1 used / g	4.00
volume of water used / cm ³	50.0
initial temperature of water / °C	29.4
minimum temperature reached / °C	21.0

Table 1.1

(i) Use the information in Table 1.1 to determine a value of ΔH_1 .

 $q = mc\Delta T = 50 \times 4.18 \times (29.4 - 21.0) = 1756 J [1] no double penalty based on (a)(ii)$

amount of FA 1 = 4 / 84.0 = 0.04762 mol ΔH_1 = +1756 / 0.04762 = +36.9 kJ mol⁻¹ [1] sign required

 $\Delta H_1 = +36.9 \text{ kJ mol}^{-1} [2]$

Examiners' Comments: - Refer to comments in (a)(iii).

(ii) Use Hess's Law and your answers from (a)(iii) and (b)(i) to determine a value for ΔH_3 for the reaction shown in equation 3.

 $\Delta H_3 = \Delta H_2 - 2\Delta H_1$ [1] correct application of Hess' Law

 $= (+36.2) - 2(+36.9) = -37.6 \text{ kJ mol}^{-1}$ [1]

 $\Delta H_3 = -37.6 \text{ kJ mol}^{-1}$ [2]

Examiners' Comments:

- Although an energy cycle was not required for this question, it proved to be the most helpful to utilise Hess' Law.
- Most common mistake was neglecting to multiply by 2 for the stoichiometry of ΔH_{1} .

[Total: 14]

2 Investigation of the kinetics of the Mn²⁺ catalysed reaction between MnO₄⁻ and C₂O₄²⁻

- **FA 3** is 0.0200 mol dm⁻³ potassium manganate(VII), KMnO₄
- FA 4 is 0.200 mol dm⁻³ sodium ethanedioate, $Na_2C_2O_4$
- FA 5 is 0.0100 mol dm⁻³ sodium thiosulfate, $Na_2S_2O_3$
- FA 6 is 0.100 mol dm⁻³ potassium iodide, KI
- FA7 is aqueous Mn²⁺

Starch indicator

FA 3, FA 4 and FA 7 are also required in question 3.

Ethanedioate ions, $C_2O_4^{2-}$, can be oxidised by manganate(VII) ions, MnO_4^{-} ions in acidic medium based on the equation below.

 $2MnO_4^{-}(aq) + 5C_2O_4^{2-}(aq) + 16H^{+}(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(I)$

However, in the absence of a catalyst, the reaction proceeds slowly. The reaction can be catalysed through autocatalysis when Mn²⁺ is formed, or when Mn²⁺ is added at the start of the reaction.

In this experiment, you will prepare investigate the kinetics of a reaction mixture containing **FA 3** and **FA 4**. At timed intervals, you will draw 10 cm³ aliquots from the reaction mixture. The concentration of MnO_4^- ions in each aliquot will then be determined through titration against $S_2O_3^{2-}$ after adding each aliquot to an excess of **FA 6**.

Acidified potassium manganate(VII) ions oxidises I⁻ ions according to the following reaction:

 $2MnO_4(aq) + 10I(aq) + 16H(aq) \rightarrow 2Mn^{2+}(aq) + 5I_2(aq) + 8H_2O(I)$

The reaction between iodine from the reaction mixture and $S_2O_3^{2-}$ solution is given below.

 $2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$

(a) Preparation and titration of the reaction mixture

Notes: You will perform each titration **once** only. Great care must be taken that you do not overshoot the end point.

Once you have started the stopwatch, it must continue running for the duration of the experiment. You must **not** stop it until you have finished this experiment.

In an appropriate format in the space provided in page 7, prepare a table to which to record for each aliquot

- the time of transfer, *t*, in minutes and seconds,
- the decimal time, t_d , in minutes, to 0.1 min, for example if t = 4min 33s then $t_d = 4$ min + 33/60 min = 4.6min,
- the burette readings and the volume of **FA 5** added.
- 1. Fill a burette with **FA 5**.

2. Label each of the boiling tubes **1** to **5**. Using a measuring cylinder, add approximately 10 cm³ of **FA 6** to each of these boiling tubes.

3. Using appropriate measuring cylinders, transfer 50.0 cm³ of **FA 4**, 5.0 cm³ of **FA 2**, 5.0 cm³ of **FA 7** and 40.0 cm³ of deionised water into a conical flask. Label the conical flask reaction mixture.

4. Using an appropriate measuring cylinder, transfer 25.0 cm³ of **FA 3** to the conical flask labelled **reaction mixture**. Start the stopwatch and swirl the mixture thoroughly to mix its contents.

5. At approximately t = 1 min, use a 10 cm³ pipette to remove a 10.0 cm³ aliquot of the reaction mixture. **Immediately** transfer this aliquot into the boiling tube labelled **1** and swirl the mixture. Note and record the transfer time (in minutes and seconds, to the nearest second) when half of the reaction mixture has emptied from the pipette.

6. Pour the contents of the boiling tube labelled **1** into a clean 250 cm³ conical flask. Transfer all washings from the boiling tube into the conical flask.

7. Titrate the iodine in this solution with **FA 5** until the solution turns pale yellow. Then add about 1 cm³ of starch indicator. Continue the titration. The end-point is reached when the blue-black colour is discharged. Record your result.

8. Repeat steps 5 to 7 with around three-minute interval until a total of **five** aliquots have been titrated and their results recorded.

Boiling tube	1	2	3	4	5
t	1min 8s	4min 7s	7min 8s	10mins 8s	13mins 8s
t _d / min	1.1	4.1	7.1	10.1	13.1
Initial burette reading / cm ³	0.00	15.00	22.70	26.90	29.20
Final burette reading / cm ³	15.00	22.70	26.90	29.25	30.55
Volume of FA 5 used / cm ³	15.00	7.70	4.20	2.35	1.35

Results

[3]

Table with correct headers and units [1] 1dp for t_d [1] Correctly calculated t_d [1]

Penalty if: time intervals not 3min; Vol of FA5 used increases

- Students were observed to not physically perform this experiment well. Due to the nature of the experiment, students are advised to ensure that they are well prepared before starting the reaction. For example, the table should already be drawn nicely with headers filled in; titration setup should be ready; pipette and filler prepared.
- Students also have to pay close attention to the question requirements, especially for what has to be in the table, as well as the sf/dp to leave certain values to.
- Do note that "mins" and "sec" are not acceptable units, and Cambridge has made mention of students committing this mistake before. The correct SI units are "min" and "s".
- Students are also reminded again that they should not be using pencil for their headers, values, and answers in general. Cambridge has also made mention of students being penalised due to this.
- Once again, it was apparent that some students faked their values, and it is reasonable to expect some form of penalty. Additionally, depending on the nature of the question, having incorrect values could potentially have implications on subsequent questions. In this question, the impact was severe as failure to get a curve meant that there would be no way to calculate for half-life or draw a tangent. Students are also reminded to always link back their data to theoretically correct principles for example, the graph cannot be a horizontal line as that is not a possible shape for a conc-time graph.

(b) (i) On the grid in Fig. 2.1, plot a graph of volume of sodium thiosulfate, FA 5, on the *y*-axis, against decimal time, t_d , on the *x*-axis. You should draw the most suitable line that takes into account all of your plotted points.



Best fit curve / straight line [1]

Examiners' Comments:

- Students did not do well for this question.
- Students should recognise that a poor choice of scale (even if not odd) results in immense difficulty in plotting the points, which also leads to more mistakes (e.g. 1.0 per large box is better than 1.5 per large box). As long as the graph ends up larger than 50% on each axis, students should opt for the friendlier scale.
- Students also presented the working for $t_{1/2}$, tangent coordinates, and $t_d = 10$ min value poorly. Values required by the question should always be indicated clearly in the graph (specifics elaborated on later).
- (ii) State and explain the relationship between [FA 3] and volume of FA 5 used in each titration.

The volume of **FA 5** used is directly proportional to the number of moles of I_2 liberated by the unreacted MnO₄⁼ from the reaction. Hence, the volume of **FA 5** is directly proportional to [MnO₄⁻].

Examiners' Comments:

- Students did not do well for this question.
- The most common mistake was students thinking that FA3 and FA5 react with each other, demonstrating a lack of understanding of the reactions involved.
- (iii) Hence, use your graph in (b)(i) and answer in (b)(ii) to determine the order of reaction with respect to [MnO₄⁻].

Since $t_{1/2}(1) = 3.3$ min is <u>approximately the same</u> as $t_{1/2}(2) = 3.6$ min, <u>half-life is constant</u>. $t_{1/2}$ "brackets" required [1]

The order of reaction with respect to $[MnO_4^-]$ is <u>1</u>. [1] Do not award mark if no working is given

- Students did not perform as well as expected for this question.
- Some students did not present their t_{1/2} working on the graph clearly, which is usually done by showing construction lines and indicating clearly the value of each t_{1/2} calculated (a min of 2 values is required for comparison). Some students did an extrapolation backwards from their first plotted point, not recognising that extrapolation was neither required for t_{1/2} determination nor requested for in the question. Extrapolating for a curve tends to be highly inaccurate.
- Merely using the shape of the curve is insufficient, as it could be 1st or 2nd order.

(c) (i) Using your graph in (b)(i), calculate the concentration of MnO_4^- ions in the reaction mixture at $t_d = 10$ min.

Volume of $S_2O_3^{2^-}$ ions at t = 10 min = 2.50 cm³ Amount of $S_2O_3^{2^-}$ ions = $\frac{2.50}{1000} \times 0.0100 = 2.5 \times 10^{-5}$ mol [1] Amount of MnO₄⁻ ions = $2.5 \times 10^{-5} \div 5 = 5 \times 10^{-6}$ mol Concentration of MnO₄⁻ ions = $\frac{5 \times 10^{-6}}{10/1000} = 5 \times 10^{-4}$ mol dm⁻³ [1]

concentration of MnO_4^- ions = $5 \times 10^{-4} \text{ mol dm}^{-3}$ [2]

Examiners' Comments:

- Most students were able to obtain at least 1m for this question.
- The most common mistake was mixing up the mole ratios, with some students even incorrectly finding the I⁻ product and using it as the I⁻ reactant. The volume of analyte used was also 10.0 cm³ and not 25.0 cm³.
- (ii) Draw a tangent to your graph line in Fig 2.1 at time $t_d = 10.0$ min.

Determine the gradient of this line, showing clearly how you did this, and hence determine the rate of change of the amount of $S_2O_3^{2-}$ ions required in mol min⁻¹.

Drawing of tangent [1]

from tangent, gradient = $\frac{7.00-0.0}{0.0-15.30}$ = -0.4575 cm³ min⁻¹

Correct calculation of gradient [1] coordinates required (can be on graph or shown in calculations); triangle bigger than 3 big boxes on x-axis

rate of change of the amount of $S_2O_3^{2-}$ ions = $\frac{-0.4575}{1000} \times 0.0100 = -4.58 \times 10^{-6}$ mol min⁻¹ Do not mark for sign

rate of change of the amount of $S_2O_3^{2-}$ ions = -4.58×10^{-6} mol min⁻¹ [3]

- Most students were able to draw the tangent correctly. However, calculation of the gradient proved problematic, with some not choosing coordinates that are sufficiently far apart, and some removing the negative sign of the gradient although the question did not ask for magnitude.
- Students should recognise that writing out units dutifully helps them in solving the question. In this case, realising that the units of gradient was in volume per unit time should help in the conversion of volume to amount.

(iii) Using your answer in (c)(ii), calculate the rate of change of the amount of MnO₄⁻ in mol min⁻¹.

Mole ratio of $MnO_4^{-1}:S_2O_3^{2-} = 1:5$

rate of change of the amount of MnO₄⁻ions $=\frac{-4.58 \times 10^{-6}}{5} = -9.15 \times 10^{-7}$ mol min⁻¹

rate of change of the amount of MnO_4^{-1} ions = -9.15×10^{-7} mol min⁻¹ [1]

Examiners' Comments:

- The most common mistake was mixing up the mole ratios.
- (iv) Hence, calculate the rate of disappearance of $[MnO_4^-]$ in the reaction mixture, at time t = 10 min.

rate of disappearance of $[MnO_4^-] = \frac{9.15 \times 10^{-7}}{10/1000} = 9.15 \times 10^{-5} \text{ mol dm}^{-3} \text{ min}^{-1}$

rate of disappearance of $[MnO_4^-] = 9.15 \times 10^{-5} \text{ mol dm}^{-3} \text{ min}^{-1} [3]$

Shows working in all calculations for **Expt 2**. All calculations must be present although they may not be complete or correct. Any calculation not attempted loses this mark. [1]

Shows appropriate significant figures (3 or 4 sf) and units in all final answers for **Expt 2**. Any calculation not attempted loses this mark. [1]

Examiners' Comments:

- As many students left (iii) and (iv) blank, they lost the 2 bonus marks here. Never ever leave any blanks, or omit showing working.

[Total: 18]

3 Qualitative analysis

(a) In question 2, you used a solution of Mn²⁺, FA 7, containing an unknown anion. The anion in FA 7 is not a nitrate, nitrite or carbonate ion.

You will devise and perform a series of simple tests to identify the anion present in FA7.

Use the Qualitative Analysis Notes on pages 19 and 20 to deduce the possible anions in **FA7** and describe **two different** tests, that will allow you to distinguish between the possible anions. You can only use the bench reagents provided.

Perform the tests described and record your observations in the space below. Hence, deduce the identity of the anion in **FA 7.** [3]

Test	Observations
To a test-tube containing 1cm depth FA 7 , add AgNO ₃ (aq), followed by excess	No ppt formed.
NH ₃ (aq).	Penalty for "no observable change" / "colourless solution seen".
To a test-tube containing 1cm depth FA 7 , add Ba(NO ₃) ₂ (aq), followed by excess HNO ₃ (aq). Penalty for "BaNO ₃ "; using H ₂ SO ₄ (aq) If effervescence is observed upon addition of HNO ₃ (aq), bubble gas through 1cm depth KMnO ₄ (aq) solution.	White ppt formed, which is insoluble in excess HNO ₃ (aq).

Test + Observation [1] x 2

Anion is SO₄^{2–}. [1]

Examiners' Comments:

- The question is only 3m, so only the test itself and the actual observations are required. Since this is sort of a planning question as well, students should minimally describe the test properly, with all the relevant reagents required.
- For the test of halides, some students still added NaOH(aq), demonstrating a lack of understanding that NaOH is only required to break the C–X bond in alkyl halides in order to obtain the free halide ion for reaction with Ag⁺. The halide ion (if any) in this question is already free. Some students also added dilute acid first, but CO₃^{2–} is not possible and there is no use for it.
- Students should also note that the follow-up test using NH₃(aq) is required. Students who added the NH₃(aq) first before the unknown confused the reaction with the preparation of Tollen's reagent.
- For the test using Ba(NO₃)₂(aq), the most common mistake was omitting the dilute strong acid solubility test (required to distinguish from SO₃^{2–}), or using H₂SO₄(aq) as the dilute strong acid (adding SO₄^{2–} to a test for SO₄^{2–}).

For Examiners[®] Use (b) **FA 8** is a solid sample of a metal oxide.

You will need access to the FA 2, FA 3 and FA 4 from question 1 and 2.

Perform the tests described in Table 3.1 and record your observations in the table. Test and identify any gases evolved.

The observation in (b)(iii) has been completed for you. There is no need to carry out this test.

tests		observations
(i)	Add 2 cm depth of FA 2 and 2 cm depth of FA 4 to a test-tube.	
	Add half a spatula of FA 8 to the mixture with swirling until no further change. Test for any gas evolved.	Effervescence. Gas gave white ppt with limewater / Ca(OH) ₂ .
	Keep the reaction mixture for (ii).	
(ii)	Filter the mixture from (b)(i) into a fresh test-tube. Divide the filtrate into two	<u>Colourless (or grey) filtrate</u> and <u>black</u> <u>residue</u> grey is technically wrong and is a result of some unfiltered solid
	portions. To one portion, add aqueous sodium hydroxide until no further change.	Off-white ppt, insoluble in excess NaOH(aq). Ppt rapidly turns brown upon contact with air.
	To the other portion, add aqueous ammonia until no further change.	<u>Off-white ppt, insoluble in excess NH₃(aq).</u> <u>Ppt rapidly turns brown upon contact with air</u> .
(iii)	Aqueous hydrogen peroxide is added to an equal volume of $H_2SO_4(aq)$ in a test-tube, followed by addition of one spatula of FA 8 . The mixture is filtered into another test-tube.	Vigorous effervescence observed. Gas rekindled glowing splint. Gas is O ₂ . A black residue and a colourless filtrate obtained.
	Leave the filtrate to stand.	The filtrate remains colourless.

[5]

- A large majority of students said that the gas evolved was either H₂ or O₂, despite there not being any reagents used that could possibly give those gases (e.g. if a metal such as Mg or Zn is used, H₂ is likely; if H₂O₂ is used, O₂ is a possibility). Students were unfamiliar with ethanedioate C₂O₄²⁻, which is covered in the topic of Redox to oxidise to CO₂. Ethanedioate is the deprotonated version of ethanedioic acid, HOOCCOOH, which is covered in OC to be oxidised to CO₂ when KMnO₄ is present. For this experiment, students had to be patient and bubble the gas for longer through the Ca(OH)₂ solution.
- For the 2nd test, most students neglected to provide observations for the residue and filtrate. Many students also did not correctly identify the precipitate due to unfamiliarity with Mn²⁺ perhaps.

(iv) Deduce the metal in **FA 8** using your results in (b)(ii).

Mn accept Mn²⁺ (technically not a metal)

(v) The filtrate obtained in (b)(i) turned pale yellow on standing.

Compare the role of **FA 8** in **(b)(i)** and **(b)(iii)**. Explain your answer with reference to your observations in both tests. [2]

[1]

In (b)(i), **FA 8** is an <u>oxidising agent</u> because $C_2O_4^{2-}$ was oxidised to CO_2 that gives white precipitate in limewater while MnO₂ solid is reduced to colourless Mn²⁺ ions.

In (b)(iii), **FA 8** is a <u>catalyst</u> as <u>evolution of oxygen gas</u> was vigorous **OR** MnO₂ remained <u>chemically unchanged</u> as the <u>filtrate remains colourless on standing</u> black residue not accepted since in excess (also present in (b)(i))

- Most students lost the 1st mark due to the misidentification of gas in (b)(i).
- The 2nd mark was lost as students did not pay close attention to the context provided in the question stem (pale yellow). H₂O₂ also gives O₂ when it disproportionates, which is what is happening in this question.

(c) FA 9 can either be a carbonyl compound with molecular formula C₃H₆O or an alcohol with molecular formula C₃H₈O. Perform the tests described in Table 3.2 and record your observations in the table. If there is no observable change, write no observable change.

Table	3.2
IUNIC	

	tests	observations
(i)	Add about 1 cm depth of FA 9 in a test-tube.	
	To this test-tube, add 6 drops of sodium hydroxide solution, followed by adding iodine solution, dropwise, until a permanent orange colour is present.	
	Half fill a 250 cm ³ beaker with hot water. Immerse the test-tube into the water bath for two minutes.	(pale) yellow precipitate formed white not accepted
(ii)	Add about 1 cm depth of FA 9 in a test-tube.	
	To this test-tube, add 2 drops of FA 3 followed by 1 cm depth of FA 2 .	
	Half fill a 250 cm ³ beaker with hot water. Immerse the test-tube into the water bath for two minutes.	Purple FA 3 decolourised

[2]

- Students are reminded to always anticipate the desired observations based on the tests. Unless it is a novel reaction, students should aim to give the theoretical observations as far as possible. Actual reaction observations, unlike theory, always have slight variations. Even if a white ppt is observed for the triiodomethane test, students should immediately take the formation of a ppt as a sign that the test is positive.
- For the 2nd test, students who only saw a brown ppt / solution (is actually ppt) did not leave it to heat for long enough / added more than 2 drops of KMnO₄. These students should recognise that the brown ppt is MnO₂(s), which is the product formed under alkaline conditions (or in this case, when there is insufficient H⁺ / too much KMnO₄). This is an indicator that the unknown has indeed undergone oxidation.

(iii) Using the information in Table 3.2, draw the structure of FA 9. [1] FA3 is decolourised + positive triiodomethane test: alcohol with CH₃CH(OH)- group $CH_3 - C-CH_3$ H no ecf

4 Planning

Calcium is an essential element that is vital to human life. Cow's milk is a good source of calcium, and the concentration of calcium can be determined using complexometric titration. A farmer wants to determine the concentration of calcium ions in the milk produced by his cows for marketing purposes. An experiment involving complexometric titration can be performed to find out the concentration.

Calcium ions can form a complex with disodium ethylenediaminetetraacetic acid, disodium EDTA, in a 1:1 ratio. Murexide is a violet indicator in basic conditions, which turns pink when bonded to Ca²⁺ ions. The murexide-Ca²⁺ complex, is however, less stable than the EDTA-Ca²⁺ complex. Hence, when a mixture containing murexide-Ca²⁺ is titrated against disodium EDTA solution, murexide will be displaced by disodium EDTA. The endpoint of the titration is hence determined when the colour of the reaction mixture changes from pink to violet.

EDTA is hazardous to the environment and can cause serious eye damage.

You may assume you are provided with:

- Cow's milk, FB 1
- 0.250 mol dm⁻³ disodium EDTA solution, **FB 2**
- 2.00 mol dm⁻³ sodium hydroxide solution
- Murexide indicator
- Waste bottle
- the equipment normally found in a school or college laboratory.
- (a) Define the term complex.

A complex contains a <u>central metal atom or ion</u> bonded to one or more surrounding <u>molecules or ions (called ligands)</u> by <u>dative covalent bonds</u>.

Examiners' Comments:

- Almost all students could not get this question correct, missing keywords.

(b) Based on a previous investigation, the estimated calcium concentration in the milk is 100 mg per 100 cm³ serving. Determine a suitable concentration of disodium EDTA such that 25 cm³ of milk will react completely with 25 cm³ of disodium EDTA solution. Justify your answer with calculations.

[*A*_r: Ca, 40.1]

[2]

[1]

Amount of $Ca^{2+} = 100 \times 10^{-3} \text{ g} / 40.1 = 2.493 \times 10^{-3} \text{ mol}$ Concentration of Ca^{2+} in 100 cm³ = 0.02493 mol dm⁻³ Amount in 25 cm³ = 6.234 × 10⁻⁴ mol [1]

Amount of EDTA needed = 6.234×10^{-4} mol Hence concentration of EDTA = 6.234×10^{-4} mol / 0.025 dm³ = 0.02493 mol dm⁻³ = 0.0249 mol dm⁻³ (3sf) [1]

Examiners' Comments:

- There was a mistake in the question as the *A*_r of Ca was not provided. Students were awarded the marks leniently here.
- However, many students could not see that mole ratio ≠ mass ratio. The weakest students also had trouble with unit conversion from mg to g.

[Turn over

(c) Plan an experiment to determine the concentration of calcium ions in a sample of cow's milk using complexometric titration. Your plan should include the preparation of a standard solution of the EDTA solution at the concentration in part (b). In your titration, you will also need to ensure that the reaction mixture is basic by adding 10.0 cm³ of the provided NaOH solution.

In your plan you should include details of

- the apparatus you would use,
- the procedure you would follow and
- the measurements you would make.

[4]

Dilution Procedure [1]

- Using a <u>25.0 cm³ pipette</u>, add <u>25.0 cm³ of EDTA solution</u> to a <u>250 cm³ volumetric</u> <u>flask</u>.
- 2. <u>Make up to the mark with distilled water</u>.
- 3. Stopper, invert and shake. Label this solution as **FB 3**.

Titration Procedure [1]

- 4. Pipette 25.0 cm³ of FB 1 into a 250 cm³ conical flask.
- 5. Use a <u>10.0 cm³ measuring cylinder</u> to add <u>10.0 cm³ of NaOH</u> into the same conical flask.
- 6. Add <u>3 drops of murexide indicator</u> to the same conical flask.
- 7. Fill a burette with FB 3.
- 8. <u>Titrate **FB 1** against **FB 3** until the solution turns from pink to violet.</u>
- 9. Repeat the titration to obtain two consistent readings of ±0.10cm³.
- [1] Suitable choice of apparatus (with capacity)
- [1] Suitable quantities of reagents used

Examiners' Comments:

- This question was performed poorly.
- The worst performing students did not do a dilution as instructed in the question, losing nearly all the marks. In the event where you could not obtain an answer for **(b)**, you should at least state a concentration so that you can continue with this question.
- Common mistakes in procedure include omitting the shaking step for dilution, the indicator colour change for the titration, and to repeat titration to obtain consistent readings of ±0.10cm³.
- For the choice of apparatus, a significant number of students chose to use measuring cylinders for the preparation of standard solution and/or transferring of analyte. These are procedures where accuracy is important, so we only use more precise apparatus such as the pipette or burette.

(d) Suggest a safety precaution that should be taken throughout the experiment.

[1]

Wear eye protection / safety goggles

- Most students were able to extract the relevant part of the question stem pertaining to this question.
- Weaker students gave generic answers which did not take into account the information given.

(e) EDTA can be represented as H₄EDTA because it is a weak acid. The EDTA^{4–} anion can be formed from four successive deprotonation of H₄EDTA.

 $H_4EDTA(aq) \Rightarrow EDTA^{4-}(aq) + 4H^{+}(aq)$ equation (1)

At high pH, Mg²⁺ readily forms a complex with EDTA⁴⁻.

 $[Mg(H_2O)_6]^{2+} + EDTA^{4-} \rightleftharpoons [Mg(EDTA)]^{2-} + 6H_2O \qquad equation (2)$

In cow's milk, there is a small amount of Mg^{2+} ions present. Suggest how the presence of Mg^{2+} ions will affect the titration results in part (c). [1]

As <u>some disodium EDTA added will complex with Mg^{2+} </u>, a <u>larger titrant volume</u> will be obtained to complex with the same amount of Ca^{2+} .

Examiners' Comments:

- Most students talked about LCP and POE shifting, but that was actually not needed for this question, as simply more EDTA titrant would be needed.

[Total: 9]