Class | Adm No

Candidate Name: ____________________

Shift
Laboratory

H

millennia institute

2025 Preliminary Examination
Pre-University 3

H2 CHEMISTRY **9729/04**

Paper 4 Practical

28^{th} Aug 2025

2 h 30 min

Suggested answers

1 Identification of anions

FA 1 is an aqueous solution containing two anions.

You will perform tests to identify the two anions in **FA 1**.
You are **not** expected to identify the cations.

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured.

Test and identify any gases evolved.

(a) Carry out the following tests. Carefully record your observations in Table 1.1.

Table 1.1

	tests	observations
1	Test **FA 1** solution using Universal Indicator paper.	Universal Indicator paper turns blue/dark blue/dark violet (pH 14)
2	To a 1 cm depth of **FA 1** in a clean test-tube, add 1 cm depth of aqueous silver nitrate. Add excess aqueous ammonia.	Brown ppt forms Ppt dissolves in excess aqueous ammonia to give a colourless solution
3	To a 1 cm depth of **FA 1** in a clean boiling tube, add a small piece of aluminium foil into the boiling tube, then heat gently over a Bunsen flame.	Gas evolved upon warming turns damp red litmus blue. Gas is NH_3.
4	To a 1 cm depth of **FA 1** in a clean test-tube, add 2 cm depth of dilute hydrochloric acid.	No effervescence observed

[4]

(b) Identify the two anions in **FA 1** and state the evidence for each anion by completing Table 1.2. The evidence given must be sufficiently conclusive in identifying the anions.

Table 1.2

anion	evidence
OH^-	Test 1: Solution is alkaline, indicating presence of OH^- ions **and** Test 2: Solution contains OH^- which forms brown ppt (Ag_2O) when $AgNO_3$ is added **OR** Test 3: NH_3 gas is evolved when heated with Al, hence OH^- ions are must be present
NO_3^-	Test 3: NH_3 gas evolved indicates presence of NO_3^- or NO_2^- **and** Test 4: brown NO_2 gas not evolved, indicating absence of NO_2^-

[4]

[Total: 8]

2 Investigation on a solution of oxalic acid

Oxalic acid is a common organic acid containing the carboxylic acid functional group.

You will perform two separate experiments to investigate its properties.

(a) Determination of concentration and enthalpy change of neutralisation by thermometric titration

Oxalic acid is an organic acid that occurs naturally in many foods, such as quinoa and rhubarb leaves. It is known to be a dibasic acid, potentially donating two H^+ ions per molecule of oxalic acid.

FA 2 is aqueous oxalic acid of unknown concentration.
FA 3 is 2.2 mol dm^{-3} sodium hydroxide, NaOH.

Prepare a table in the space provided on the next page and record, to the appropriate level of precision:

- all volumes of **FA 3** added, *V*
- the maximum temperature, *T*, after each addition of **FA 3**

It is important that the volume of **FA 3** recorded is the total volume you have added up to the point when the temperature reading was made.

Procedure

1. Place a polystyrene cup inside a second polystyrene cup and place both cups in a glass beaker.
2. Use a pipette to transfer 10.0 cm^3 of **FA 2** into the polystyrene cup.
3. Fill the burette with **FA 3**.
4. Stir the **FA 2** in the cup gently with the thermometer. Read and record its temperature, tilting the cup to ensure that the bulb of thermometer is fully submerged in the solution.
5. Use the burette to add 2.00 cm^3 of **FA 3** to the cup and stir the mixture gently with the thermometer. Read and record both the maximum temperature and the actual total volume of **FA 3** added.
6. Repeat step 5 until a total of 30.00 cm^3 of **FA 3** has been added. For each addition of **FA 3**, read and record both the maximum temperature, *T*, and the actual total volume of **FA 3** added up to that point, *V*.

Note: If you overshoot on an addition, record the actual total volume of **FA 3** added up to that point.

Results

V / cm^3	T / °C
0.00	31.2
2.00	34.2
4.00	37.2
6.00	42.0
8.00	43.6
10.00	43.8
12.00	43.2
14.00	42.8
16.00	41.8
18.00	40.8
20.00	40.0
22.00	39.2
24.00	38.2
26.00	37.8
28.00	37.2
30.00	37.0

[3]

(i) Plot a graph of temperature, *T*, on the *y*-axis, against total volume of **FA 3**, *V*, on the *x*-axis on the grid in Fig. 2.1. Your scale on the *y*-axis should allow for extrapolation above the highest temperature recorded.

Draw two lines of best fit, taking into account the points when the temperature of the mixture was rising and the points when the temperature was falling. Each line should have a shape best suited to its plotted points.

Extrapolate both lines until they intersect.

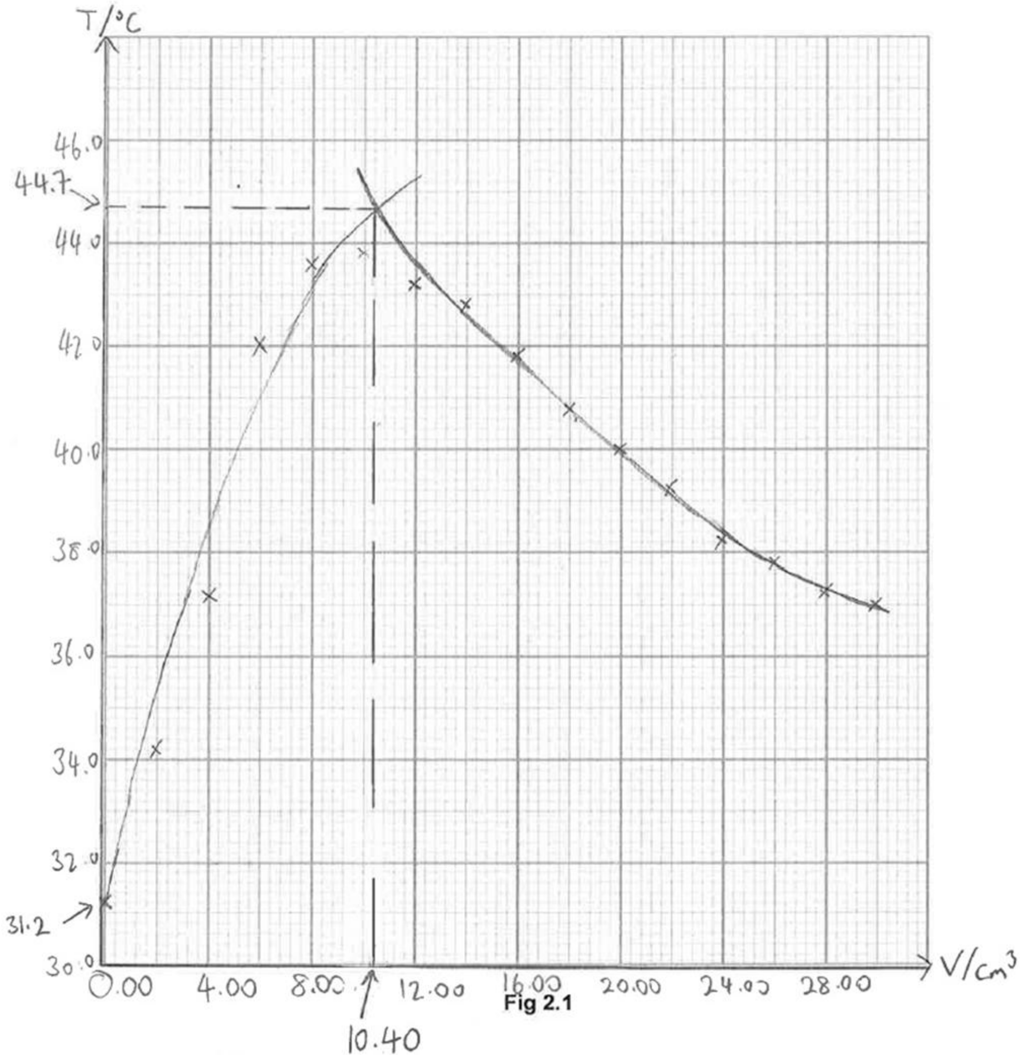


Fig 2.1

[3]

(ii) Explain the shape of your line of best-fit drawn in **(a)(i)**, when the temperature is falling.

The temperature starts to fall after the reaction is complete. As the temperature of **FA 3** is less than temperature of reaction mixture, the temperature falls when extra **FA 3** is added.

The temperature falls at a decreasing rate because the temperature difference between **FA 3** and mixture decreases, hence the cooling effect of each **FA 3** addition decreases.

[2]

(iii) Hence, from your graph, identify the total volume of **FA 3** added at the point of neutralisation, V_{neut}.

V_{neut} = 10.40 cm^3

Using the initial temperature of **FA 2**, $T_{initial}$, and the maximum temperature of the mixture from the graph, T_{max}, calculate the change in temperature, ΔT.

$\Delta T = 44.7 - 31.2 = 13.5$ °C

$T_{initial}$ = 31.2 °C

T_{max} = 44.7 °C

ΔT = 13.5 °C

[4]

(iv) Determine the concentration of oxalic acid in **FA 2**.

$H_2A + 2NaOH \rightarrow Na_2A + 2H_2O$

Amount of NaOH used = $2.2 \times \frac{10.40}{1000}$ = 0.02288 mol

Amount of oxalic acid in 10.0 cm^3 = $\frac{0.02288}{2}$ = 0.01144 mol

[oxalic acid] = $\frac{0.01144}{10.0/1000}$ = 1.14 mol dm^{-3}

Concentration of oxalic acid in **FA 2** = …………………………….. [2]

(v) Calculate the heat change, *q*, at the point of neutralisation in your experiment.

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 1.0 g cm^{-3}.

q = mcΔT = (10.0+10.40)(4.18)(13.5) = 1151.17 J = 1150 J (3sf)

q = ... [1]

(vi) Calculate the enthalpy change of neutralisation, ΔH_{neut}, for the reaction between oxalic acid and sodium hydroxide.

Amount of H_2O produced = Amount of NaOH used = 0.02365 mol

$\Delta H_{neut} = -\frac{1151.17/1000\ kJ}{0.02288\ mol}$ = –50.3 kJ mol^{-1} (3sf)

ΔH_{neut} = ... [3]

(vii) The enthalpy change of neutralisation for hydrochloric acid reacting with sodium hydroxide is -57.3 kJ mol^{-1}.

Comment on your value of ΔH_{neut} obtained in **(a)(vi)**. [2]

The value obtained is less exothermic.

This is because oxalic acid is a weak acid and some energy released from the neutralisation reaction is used to complete its dissociation.

•

(b) Determination of concentration by acid-base titration

The concentration of oxalic acid can also be determined via a simple acid-base titration.

Procedure

1. Fill the burette with **FA 3**.
2. Use a pipette to transfer 10.0 cm^3 of **FA 2** into a 250 cm^3 conical flask.
3. Add 2-3 drops of thymol blue indicator.
4. Titrate **FA 2** against **FA 3**. The end-point is reached when the mixture first turns blue.
5. Record your titration results, to an appropriate level of precision, in the space provided below.
6. Repeat steps 2 to 5 until consistent results are obtained.

Results

	1	2
initial burette reading / cm^3	0.00	0.10
final burette reading / cm^3	11.00	11.10
volume of **FA 3** used / cm^3	11.00	11.00
	✓	✓

[4]

(i) From your titrations, obtain a suitable volume of **FA 3** to be used in your calculations. Show clearly how you obtained this volume.

Average volume of **FA 3** = $\frac{11.00+11.00}{2}$ = 11.00 cm^3

Volume of **FA 3** = ……………………………. cm^3 [1]

(ii) Calculate the concentration of oxalic acid in **FA 2**.

$H_2A + 2NaOH \rightarrow Na_2A + 2H_2O$

Amount of NaOH used = 2.2 × $\frac{11.00}{1000}$ = 0.0242 mol

Amount of oxalic acid in 10.0 cm^3 = $\frac{0.0242}{2}$ = 0.0121 mol

[oxalic acid] = $\frac{0.0121}{10.0/1000}$ = 1.21 mol dm^{-3} (3sf)

Concentration of oxalic acid in **FA 2** = ……………………………. mol dm^{-3} [2]

(iii) Consider the two different methods used to determine the concentration of oxalic acid in **FA 2**, **(a)** thermometric titration, and **(b)** acid-base titration.

Suggest, with explanation, which method is likely to give a more accurate result. [1]

(a) thermometric titration
- indicator pH working range / endpoint may not have coincided with the equivalence point accurately

(b) acid-base titration
- indicator colour change more distinct / accurate compared to extrapolation from graph
- titrant is added dropwise to obtain colour change, more accurate compared to fixed additions in (a)
- initial volume used for thermometric titration was too little, making temperature reading inaccurate

[Total: 28]

3 Qualitative analysis of salicylic acid

Salicylic acid is a common ingredient used in acne treatments due to its ability to exfoliate the skin, unclog pores, and reduce inflammation. Like oxalic acid, it is also an organic acid containing the carboxylic acid functional group.

FA 4 is aqueous salicylic acid.

You will perform tests to deduce the structure of salicylic acid.

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured. **Discard all waste into the container labelled "waste".**

If there is no observable change, write **no observable change**.

(a) Carry out the following tests using the **FA 4** provided. Carefully record your observations and corresponding deductions of functional groups in Table 3.1.

Table 3.1

	Tests	observations and deductions of functional groups
1	To a 1 cm depth of **FA 4** in a test-tube, add 8 drops of aqueous sodium hydroxide followed by aqueous iodine dropwise, until a permanent yellow/orange colour is present. Warm the mixture in a beaker of hot water for 5 minutes. Add aqueous sodium hydroxide until no further change is seen.	no yellow ppt forms absence of CH_3CO- / $CH_3CH(OH)$-
2	To a test-tube containing 1 cm depth of **FA 4**, add 2 cm depth $Br_2(aq)$.	orange $Br_2(aq)$ decolourises / white ppt forms presence of C=C, phenol or phenylamine
3	To a test-tube containing 1 cm depth of **FA 4**, add 1 cm depth neutral $FeCl_3$.	yellow $FeCl_3$ turns violet presence of phenol
4	To a test-tube, mix 5 drops of Fehling's solution A and 5 drops of Fehling's solution B. Add 1 cm depth of **FA 4** and warm the solution in a beaker of hot water for 5 minutes.	deep blue solution forms no brick red ppt forms absence of aldehyde

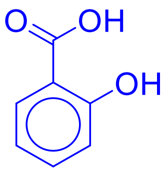
[8]

(b) Salicylic acid is known to have an M_r between 130.0 to 140.0.

It also exhibits a lower than expected melting point.

Using your deductions from **(a)** as well as all other information provided, deduce the structure of salicylic acid.

[A_r: C, 12.0; H, 1.0; O, 16.0; N, 14.0] [2]

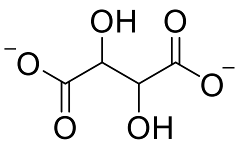


$C_7H_6O_3$ (138.0)

(c) In test 4, Fehling's reagent is prepared by mixing Fehling's solution A and B. The identities of the solutions are as follows.

Fehling's solution A: aqueous copper(II) sulfate

Fehling's solution B: sodium hydroxide and tartrate ions



tartrate ion

By considering the reaction between copper(II) and hydroxide ions, as well as relevant observations of test 4, suggest the role of tartrate ions. [1]

Tartrate ions complex to Cu^{2+}, preventing them from precipitating as $Cu(OH)_2(s)$. This allows the Cu^{2+} ions to be available to act as the oxidising agent.

For Examiners' Use

4 Planning

Oxalic acid is oxidised readily by MnO_4^- in the presence of excess H^+.

The rate equation for this redox reaction can be expressed as

$$\text{rate} = k\,[\text{oxalic acid}]^{\mathbf{a}}\,[MnO_4^-]$$

where **a** represents the order of reaction with respect to oxalic acid.

Oxalic acid can be found in sufficiently high concentrations in the stalks of the rhubarb plant. It can be extracted by heating thin slices of rhubarb stalk gently in water for 5 minutes.

The rate of reaction between oxalic acid and MnO_4^- can then be studied by measuring the time taken for a fixed concentration of MnO_4^- to decolourise into Mn^{2+}.

You are to plan experiment(s) to:

1) prepare a standard solution of oxalic acid from rhubarb stalks, then use it to
2) determine the order of reaction with respect to oxalic acid, **a**.

You may assume that you are provided with

- whole rhubarb stalks,
- a kitchen knife,
- 0.1 mol dm^{-3} $KMnO_4$ solution,
- 1 mol dm^{-3} sulfuric acid,
- 250 cm^3 volumetric flask,
- filter funnel and filter paper,
- stopwatch,
- the equipment normally found in a school or college laboratory.

In your plan you should include brief details of

- the reactants and conditions that you would use,
- the apparatus that you would use,
- the procedure that you would follow,
- the measurements that you would take,
- how you would determine the order of reaction with respect to oxalic acid, **a**.

[8]

Experiment 1 – Preparation of oxalic acid standard solution

1. Using the kitchen knife, thinly slice the whole rhubarb stalks and transfer them into a 250 cm^3 beaker.
2. Cover the rhubarb slices with about 100 cm^3 of distilled water and heat it gently over a bunsen flame for 5 mins.
3. Filter the resultant mixture and transfer the filtrate into a 250 cm^3 volumetric flask.
4. Top up to the mark with distilled water, then stopper, invert and shake to obtain a homogeneous solution.
5. Ensure that the solution is cooled down to room temperature before usage in Experiment 2.

Experiment 2 – Determination of OOR wrt to oxalic acid

1. Using measuring cylinders of appropriate capacity, prepare the solutions as follows:

Run	Vol of rhubarb solution / cm^3	Vol of $KMnO_4$ solution / cm^3	Vol of H_2SO_4 solution / cm^3	Vol of distilled water / cm^3	time / s	$\frac{1}{\text{time}}$ / s^{-1}
1	50	25	25	0		
2	40	25	25	10		
3	30	25	25	20		
4	20	25	25	30		
5	10	25	25	40		

2. For each run, transfer the solutions into a 250 cm^3 beaker placed on top of a white tile, ensuring that the $KMnO_4$ solution is added last. Start the stopwatch upon addition of $KMnO_4$.
3. Stop the stopwatch when the purple $KMnO_4$ completely decolourises and record the time taken. Calculate $\frac{1}{\text{time}}$ as a measure of rate.
4. Plot a graph of $\frac{1}{\text{time}}$ against volume of rhubarb solution used. If the graph obtained is a horizontal straight line, the OOR wrt oxalic acid is 0. If the graph obtained is a straight line of positive gradient passing through the origin, the OOR wrt oxalic acid is 1. If the graph obtained is a quadratic curve of increasing gradient passing through the origin, the OOR wrt oxalic acid is 2.