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**9729/04**

**26 August 2025**

**2 hours 30 minutes**

Additional Materials: As listed in the Confidential Instructions

Write your Centre number, index number, class and name on all the work that you hand in.  
Write 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.  
**DO NOT WRITE IN ANY BARCODES.**

You may lose marks if you do not show your working or if you do not use appropriate units.

Qualitative Analysis Notes are printed on pages 19 and 20.

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

<b>Shift</b>
<b>Laboratory</b>

<b>For Examiner's Use</b>	
	<b>55</b>

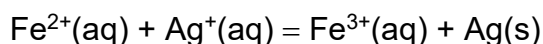
This document consists of **20** printed pages.



## 1 Determination of the equilibrium constant

Aqueous iron(II) ions,  $\text{Fe}^{2+}(\text{aq})$ , are usually kept in acidic conditions to prevent them from readily oxidising to aqueous iron(III) ions,  $\text{Fe}^{3+}(\text{aq})$ .

$\text{Fe}^{2+}(\text{aq})$  ions react with  $\text{Ag}^{+}(\text{aq})$  ions in a redox reaction. The following equilibrium is established.



The concentration of  $\text{Ag}^{+}(\text{aq})$  at equilibrium can be found by a titration with a standard solution of aqueous potassium thiocyanate,  $\text{KSCN}(\text{aq})$ . The equilibrium constant for the reaction can be found using the following equation.

$$K_c = \frac{[\text{Fe}^{3+}(\text{aq})]_{\text{eqm}}}{[\text{Fe}^{2+}(\text{aq})]_{\text{eqm}} \times [\text{Ag}^{+}(\text{aq})]_{\text{eqm}}}$$

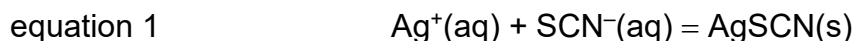
**FA 1** is the equilibrium mixture.

**FA 2** is  $0.0100 \text{ mol dm}^{-3}$  potassium thiocyanate,  $\text{KSCN}$ .

The equilibrium mixture has been prepared for you using the following instructions. You do not need to perform the preparation.

- Step 1 Add  $100.0 \text{ cm}^3$  of  $0.100 \text{ mol dm}^{-3} \text{ Ag}^{+}(\text{aq})$  to  $100.0 \text{ cm}^3$  of acidified  $0.100 \text{ mol dm}^{-3} \text{ Fe}^{2+}(\text{aq})$  in a  $500 \text{ cm}^3$  conical flask and stopper the flask.
- Step 2 Ag precipitate forms. Leave the resultant solution for 4 hours. This is the equilibrium mixture, **FA 1**.

When the equilibrium mixture is titrated against a standard solution of potassium thiocyanate, white ppt of silver thiocyanate is formed as shown in equation 1.



The end point is indicated by formation of complex ion between thiocyanate and iron(III) ion when one excess drop of aqueous potassium thiocyanate is added.

In this experiment, you will determine the equilibrium constant,  $K_c$ , for the reaction between silver(I) and iron(II) ions. You will titrate **FA 1** against **FA 2**.

**You are to rinse all glassware with deionised water thoroughly before starting any practical work.**



(a) (i) **Titration of FA 1 against FA 2.**

1. Fill the burette with **FA 2**.
2. Use a pipette to transfer  $10.0\text{ cm}^3$  of **FA 1** into a  $250\text{ cm}^3$  conical flask.

**Do not disturb the silver ppt.**

3. Run **FA 2** from the burette into this flask. A white ppt forms.
4. Continue adding **FA 2** slowly. The end-point is reached when the solution turns from colourless to permanent pale orange. The white ppt remains and the mixture appears off-white.
5. Record your titration results, to an appropriate level of precision, in the space provided.

**Results**

[5]

- (ii) From your titrations, obtain a suitable volume of **FA2**,  $V_{\text{FA2}}$ , to be used in your calculations. Show clearly how you obtained this volume.

volume of **FA 2** used = ..... $\text{cm}^3$  [1]



(iii) Calculate the concentration of  $\text{Ag}^+(\text{aq})$  in the equilibrium mixture.

concentration of  $\text{Ag}^+(\text{aq}) = \dots\dots\dots$  [1]

(iv) Hence, determine the concentration of  $\text{Fe}^{3+}(\text{aq})$  in the equilibrium mixture.

concentration of  $\text{Fe}^{3+}(\text{aq}) = \dots\dots\dots$  [2]

(v) Determine the value of  $K_c$ . Include units in your answer

$K_c = \dots\dots\dots$  [2]

- Apart from considering the effect of temperature on  $K_c$ , explain whether you agree with student **A**.

.....

.....

..... [1]

- .....

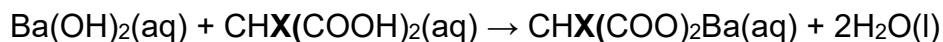
..... [1]

[Total: 13]

## 2 Investigation of the enthalpy change of neutralisation

You will investigate the enthalpy change of neutralisation,  $\Delta H_{\text{neut}}$ , between aqueous barium hydroxide of known concentration and a dilute organic acid. You will use your results to suggest the identity of the organic acid.

The acid is a halogenodicarboxylic acid containing one halogen atom, **X**, per molecule.



**FA 3** is  $0.950 \text{ mol dm}^{-3}$  barium hydroxide,  $\text{Ba(OH)}_2$ .

**FA 4** is a solution containing  $141.3 \text{ g dm}^{-3}$  of the organic diacid,  $\text{CHX(COOH)}_2$ .

### (a) Method

Prepare a table in the space provided on page 6, to appropriate degree of precision:

- All volumes of **FA 4** added,  $V$
- The maximum temperature,  $T$ , reached after each addition of acid, **FA 4**.

It is important that the volume of **FA 4** recorded is the total volume you have added up to the point when the temperature reading was made.

Note: If you overshoot on an addition, record the actual total volume of **FA 4** added up to that point.

### Procedure

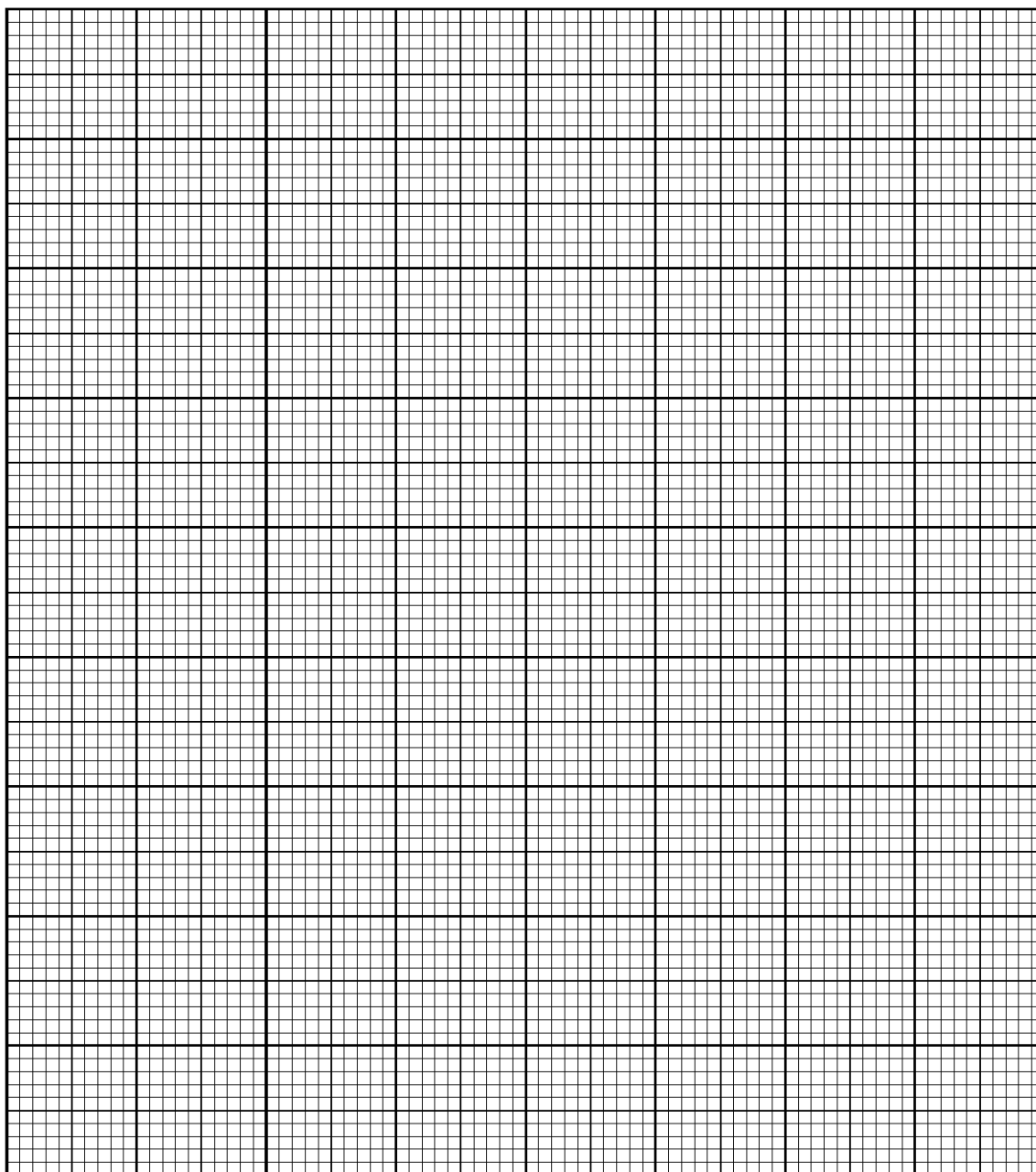
1. Support the cup in the  $250 \text{ cm}^3$  beaker.
2. Pipette  $25.0 \text{ cm}^3$  of **FA 3** into the cup.
3. Place the thermometer into **FA 3**. Read and record its temperature.
4. This is the temperature when the volume of **FA 4** is  $0.00 \text{ cm}^3$ .
5. Fill the burette with **FA 4**.
6. Run  $5.00 \text{ cm}^3$  of **FA 4** into the cup containing **FA 3**.
7. Stir the mixture. Record the highest temperature observed.
8. Run further  $5.00 \text{ cm}^3$  portions of **FA 4** into the same cup.
9. On each addition of **FA 4** stir the contents of the cup. Record the highest temperature after each addition.
10. Repeat 8 and 9 until a total of  $40.0 \text{ cm}^3$  of **FA 4** has been added.

[2]



- (b) (i) Plot a graph of temperature (y-axis) against volume of **FA 4** added (x-axis) on the grid. Select a scale on the y-axis to include a temperature of 2 °C above your maximum thermometer reading.

Draw two lines of best fit, the first for the increase in temperature and the second for after the maximum temperature has been reached. Extrapolate the two lines so they intersect. This intersection corresponds to the volume of **FA 4** required to form a neutral solution.



[3]



- (ii) Use your graph to determine the volume of **FA 4**,  $V_{\text{neut}}$ , required to neutralise  $25.0 \text{ cm}^3$  of **FA 3**. Show your working on the graph clearly.

$$V_{\text{neut}} = \dots\dots\dots \text{cm}^3 \quad [1]$$

- (iii) Calculate the energy change, in J, when the volume of **FA 4** recorded in (b)(ii) neutralises  $25.0 \text{ cm}^3$  of **FA 3**.

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

$$\text{energy change} = \dots\dots\dots [1]$$

- (iv) Calculate the amount of barium hydroxide, **FA 3**, pipetted into the cup.

$$\text{amount of Ba(OH)}_2 = \dots\dots\dots [1]$$

- (v) Calculate the enthalpy change of neutralisation,  $\Delta H_{\text{neut}}$ , in  $\text{kJ mol}^{-1}$ .

$$\Delta H_{\text{neut}} = \dots\dots\dots [2]$$





- (vi) Use your answers to (b)(ii) and (b)(iv), and the information given on page 6 to calculate the relative formula mass of the organic acid  $\text{CHX}(\text{COOH})_2$ . Show your working.

relative formula mass = ..... [1]

- (vii) The acid is known to be one of the following:  $\text{CHF}(\text{COOH})_2$ ,  $\text{CHCl}(\text{COOH})_2$ ,  $\text{CHBr}(\text{COOH})_2$  and  $\text{CHI}(\text{COOH})_2$ .

Use your answer to (b)(vi) to identify the acid used to make solution **FA 4**.

[Ar: F, 19.0; Cl, 35.5; Br, 79.9, I, 126.9]

.....

.....

..... [1]

- (viii) Calculate the percentage error in the relative formula mass, you calculated in (b)(vi).

percentage error = ..... [3]

- (c) Your value of  $V_{\text{neut}}$  could be used to calculate the relative formula mass of halogenodicarboxylic acid. Explain why a conventional titration using a suitable indicator gives a more accurate volume of neutralisation for this calculation.

.....

..... [1]

[Total: 16]





(iv)	To a 1 cm depth of <b>FA 6</b> in a test-tube add a 1 cm depth of sulfuric acid and then add a few drops <b>FA 7</b> .	
(v)	To a 1 cm depth of aqueous potassium iodide in a test-tube add a few drops of <b>FA 7</b>	
	then add a few drops of aqueous starch.	

[5]

(b) Complete Table 3.2 with identities of metal ions in **FA 5**, **FA 6** and **FA 7**.

Table 3.2

	<b>FA 5</b>	<b>FA 6</b>	<b>FA 7</b>
Metal ions			

[3]



(c) **FA 6** contains one of the anions  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{SO}_4^{2-}$  or  $\text{SO}_3^{2-}$ .

- (i) Devise and perform a series of simple tests to identify the anion present. Your tests should be based on the Qualitative Analysis Notes and should use only the bench reagents provided. Record your tests and observations in the space below.

**Any test requiring heating must be performed in a boiling tube.**

[2]

- (ii) Identify the anion in **FA 6**. Give evidence from the observations above to support your conclusions.

Anion	Evidence

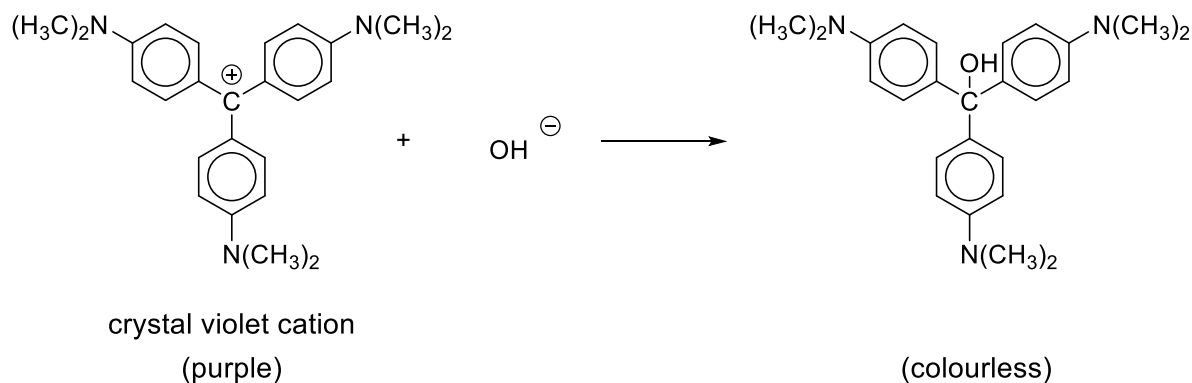
[1]

[Total: 11]

#### 4 Planning: Determining the rate constant of the reaction between crystal violet and sodium hydroxide

Crystal violet,  $\text{C}_{25}\text{H}_{30}\text{N}_3^+\text{Cl}^-$  (aq), is a purple dye. The predominant form of crystal violet in aqueous solution is the monovalent cation,  $\text{C}_{25}\text{H}_{30}\text{N}_3^+$ , which can be represented as  $\text{CV}^+$ .

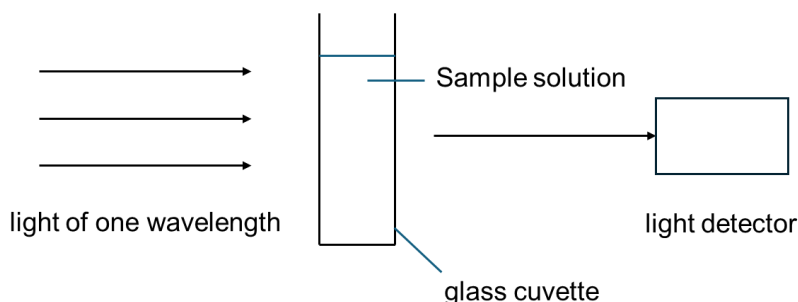
The cation,  $\text{CV}^+$ , reacts with hydroxide ions,  $\text{OH}^-$ , to form a colourless product.



The rate of the reaction may be followed by analysing the colour intensity or the absorbance of the solution against time using a spectrophotometer. Absorbance is the proportion of light absorbed at a particular wavelength.

Some light is absorbed when it passes through  $\text{CV}^+(\text{aq})$  at 565 nm. Absorbance,  $A$ , is directly proportional to the concentration of complex ion in the solution. The greater intensity of colour, the higher the absorbance, which corresponds with a higher concentration of  $\text{CV}^+$ .

A simplified diagram of a spectrophotometer is shown in Fig. 4.1. A glass cuvette is a rectangular vessel.



**Fig. 4.1**

- (a) Light passes through both sides of the cuvette. These two sides must be wiped with cloth to ensure they are clean.

Explain why this procedure makes the readings more accurate.

..... [1]

The rate equation for this reaction is shown.

$$\text{rate} = k [\text{CV}^+] [\text{OH}^-]^n$$

If the concentration of the hydroxide ions is kept constant throughout the experiment, the rate equation becomes

$$\text{rate} = k' [\text{CV}^+]$$

where  $k' = k[\text{OH}^-]^n$ .

Since the reaction is first order with respect to  $[\text{CV}^+]$ , the value of  $k'$  can be determined graphically using the following equation:

$$\text{equation I: } \ln [\text{CV}^+] = -k' t + \ln [\text{CV}^+]_0$$

where  $[\text{CV}^+]_0$  represents the initial concentration of  $\text{CV}^+$  and  $t$  represents time.

- (b) Absorbance,  $A$ , is directly proportional to the concentration of complex ion in the solution.

Rewriting equation I, for a first order reaction,

$$\text{equation II: } \ln A = -k' t + \ln A_0$$

In Fig. 4.2, write the y-axis label, in terms of absorbance,  $A$ , that will provide a linear relationship for the first order reaction. Indicate how  $k'$  can be obtained from the graph.

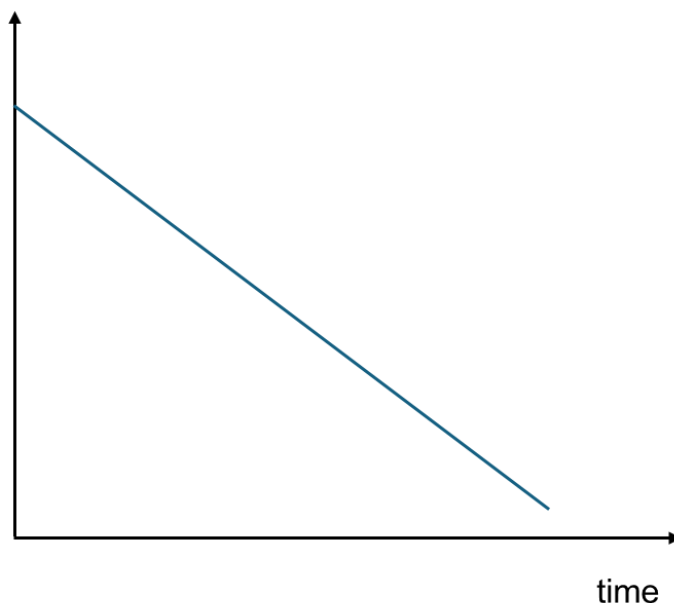


Fig. 4.2

[2]



To determine  $k'$  and the order of reaction with respect to  $[\text{OH}^-]$ ,  $n$ , a chemist came up with the technique as follows.

$10 \text{ cm}^3$  of  $1.80 \times 10^{-5} \text{ mol dm}^{-3}$  crystal violet was added to  $10 \text{ cm}^3$  of  $0.200 \text{ mol dm}^{-3}$  sodium hydroxide. The mixture was mixed well. 20 seconds after mixing, a portion of this mixture was transferred to a dry cuvette using a plastic teat pipette and analysed in the spectrophotometer. The absorbance readings were taken at timed intervals.

- (c) The chemist needed a solution of  $1.80 \times 10^{-5} \text{ mol dm}^{-3}$  of crystal violet but this was not prepared directly. Instead, it was prepared by diluting a solution of  $1.80 \times 10^{-3} \text{ mol dm}^{-3}$  for use in the experiments.

- (i) Calculate the mass of solid crystal violet needed to prepare  $250 \text{ cm}^3$  of  $1.80 \times 10^{-3} \text{ mol dm}^{-3}$  of crystal violet measured using a mass balance that records to three decimal places.

$[M_r: \text{crystal violet}, 407.5]$

.....  
.....  
.....  
..... [1]

- (ii) Explain why the chemist did not prepare a solution of  $1.80 \times 10^{-5} \text{ mol dm}^{-3}$  of crystal violet directly by dissolving the required mass of crystal violet in  $250 \text{ cm}^3$  of water.

.....  
..... [1]



**(d) (i)** Plan a procedure to determine the rate constant of this reaction.

The procedure shown by the chemist should be followed and modified to collect sufficient data from a series of experiments to:

- determine the observed rate constant,  $k'$ , of this reaction using a graphical method from one experiment
- determine the order of reaction,  $n$ , with respect to  $[\text{OH}^-]$  in **(d)(ii)**

You may assume that you are provided with:

- $0.200 \text{ mol dm}^{-3}$  aqueous sodium hydroxide
- $1.80 \times 10^{-5} \text{ mol dm}^{-3}$  of crystal violet cation,  $\text{CV}^+$  in aqueous solution
- $10 \text{ cm}^3$  volumetric flask
- access to a spectrophotometer and instructions for its use
- common apparatus found in the school laboratory

In your plan, you should include brief details of

- the preparation of a suitable range of diluted sodium hydroxide solutions of accurate concentrations,
- the procedure you would follow and the measurements that you would take to obtain accurate reading,
- how you would use your absorbance results to obtain the observed rate constant,  $k'$

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[illegible][illegible]

[6]





RVHS Chemistry

