Suggested Solutions



H2 CHEMISTRY

9729/04

Paper 4 Practical

24 August 2023 2 hours 30 minutes

Candidates answer on the Question Paper.

READ THESE INSTRUCTIONS FIRST

Write your centre number, index number, name and class at the top of this page.

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 on pages 23 and 24.

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.

Shift
Laboratory

For Examiner's Use		
1		
•	16	
2		
	13	
3		
	15	
4		
,	11	
Total		
I Otal	55	

Answer **all** questions in the spaces provided.

1 Determination of change in oxidation number in XO₃-oxidant.

FA 1 is 0.0265 mol dm⁻³ potassium manganate(VII), KMnO₄(aq)

FA 2 is 0.0750 mol dm⁻³ XO_3 oxidant solution.

X is the symbol of an element whose identity is not needed in this question.

FA 3 is a solution containing 0.150 mol dm⁻³ iron(II) ions, Fe²⁺.

FA 3 solution is prepared by dissolving an iron(II) salt in sulfuric acid.

In the presence of acid, XO_3^- oxidises iron(II) to iron(III) while itself is reduced to X^{b_+} . In order to determine b, a sample of XO_3^- is added to a known amount of iron(II) in excess. The amount of remaining iron(II) ions can then be determined by titration against manganate(VII) ions as shown in equation 1.

equation 1
$$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(I)$$

(a) Procedure

- 1. Pipette 25.0 cm³ of **FA 3** into a conical flask.
- 2. Using another pipette, add exactly 10.0 cm³ of **FA 2** to **FA 3** in the conical flask.
- 3. Fill the burette with **FA 1**.
- 4. Titrate the mixture in the conical flask with **FA 1** until the appearance of the first permanent pale orange or pale pink colour.
- 5. Repeat the titration as many times as you think necessary to obtain accurate results.
- 6. Record your results of titration in a suitable tabulated form below.

Results

	1	2
Final burette reading / cm ³	17.00	34.00
Initial burette reading / cm ³	0.00	17.00
Volume of FA 1 (KMnO ₄) / cm ³	17.00	17.00
	/	,

[2]

(b) From your titrations, obtain a suitable volume of **FA 1**, $V_{\text{FA 1}}$, to be used in your calculations. Show clearly how you have obtained this volume.

(c) (i) Calculate the amount of Fe²⁺ ions pipetted into the conical flask.

Moles/amount of
$$Fe^{2+} = \frac{25.0}{1000} \times 0.150$$

= 0.00375 mol

(ii) Calculate the amount of XO_3^- ions present in the conical flask.

Moles/amount of
$$XO_3^- = \frac{10.0}{1000} \times 0.075$$

= 0.000750 mol

amount of
$$XO_3^-$$
 ions = ...0.000750 mol [1]

(iii) Using your answer to (b), calculate the amount of Fe^{2+} ions that remain after reaction with XO_3^- .

Number of moles of KMnO₄ =
$$\frac{17.00}{1000}x$$
 0.0265
= 4.505 x 10⁻⁴ mol
Since MnO₄⁻ \equiv 5Fe²⁺,
Number of moles of Fe²⁺ = 5 x 4.505 x 10⁻⁴
= 2.2525 x 10⁻³ mol

amount of Fe²⁺ ions remaining =
$$\dots 2.25 \times 10^{-3} \text{ mol } \dots$$
 [1]

(iv) Calculate the amount of Fe^{2+} ions that reacted with XO_3^- ions in the conical flask and hence, the amount of Fe^{2+} that reacted with one mole of XO_3^- ions.

Number of moles of Fe²⁺ that reacted with
$$XO_3^- = 0.00375 - 0.0022525$$

= 1.4975 x 10⁻³

Number of moles of Fe²⁺ that reacted with one mole of
$$XO_3^-$$
 ions = $\frac{0.0014975}{0.00075}$ = 2.00

amount of Fe²⁺ that reacted with one mole of
$$XO_3^-$$
 ions = ...2.00 mol... [2]

(v) Hence, calculate the final oxidation number of the element X when Fe²⁺ reacts with XO_3^- .

Initial oxidation number of
$$X$$
 in $XO_3^- = +5$
 $Fe^{2+} \rightarrow Fe^{3+} + e^-$
Since $2Fe^{2+} \equiv XO_3^-$,
total mol of electrons gained per mol of $XO_3^- = 2$
final oxidation number of X in $XO_3^- = 5 - 2$
 $= +3$

final oxidation number of the element X = ...+3 [2]

(d) A student carries out the same experiment in (a). However unknowingly, he uses a sample of FA 2 with concentration 0.100 mol dm⁻³ instead.

Suggest what effect this will have on the volume of FA 1 obtained. Explain your answer.

The amount of FA 2 increases and hence **the amount of FA 3** after reacting with **FA 2 decreases**.

Less amount of FA 1 is required to react with the remaining FA 3 and the <u>volume of</u> FA 1 will be smaller.

[1]

(e) (i) A student followed the procedure described in (a) using a different oxidant instead of FA 2. The student obtained a mean titre value of 22.20 cm³. The actual volume of FA 1 required should have been 22.40 cm³.

Calculate the difference between the actual value and the student's value as a percentage. This is the experimental error.

(ii) Using his mean titre value, the student calculates that the maximum total percentage error of the apparatus used is 0.77%.

Use the following data to verify the student's calculation.

apparatus	uncertainty
25 cm ³ pipette	±0.03 cm ³
10 cm ³ pipette	±0.02 cm ³

Hence, determine if the student performed the experiment well. Explain your answer.

maximum total percentage error =
$$\left(\frac{0.03}{25} + \frac{0.02}{10} + \frac{0.10}{22.20}\right) \times 100\% = 0.770\%$$

Since the experimental error (0.893%) is **bigger** than the maximum total percentage error of the apparatus used (0.770%), the student **did not** perform the experiment well.

OR

Since the <u>difference</u> between the experimental error (0.893%) and the maximum total percentage error of the apparatus used (0.770%) is <u>very small</u> (0.123%), the student <u>did</u> perform the experiment well.

[2]

[Total: 16]

2 Determination of the kinetics of the reaction between Fe³⁺ ions and iodide ions, I⁻.

You are provided with the following reagents.

FA 4 contains 0.0250 mol dm⁻³ acidified iron(III) chloride, FeCl₃

FA 5 is 0.0800 mol dm⁻³ aqueous potassium iodide, KI

FA 6 is 0.00500 mol dm⁻³ sodium thiosulfate, Na₂S₂O₃ starch solution

 Fe^{3+} ions oxidise iodide ions, I^- , to iodine, I_2 , as shown in equation 2. In this experiment, you will investigate how the rate of this reaction is affected by the concentration of Fe^{3+} ions.

equation 2
$$2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$$

A fixed and small amount of thiosulfate ions, $S_2O_3^{2-}$, and starch indicator will be added to a mixture of Fe³⁺(aq) and I⁻(aq). The iodine, I₂, produced reacts immediately with thiosulfate ions, $S_2O_3^{2-}$, as shown in equation 3.

equation 3
$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$$

When all the thiosulfate has been used, the iodine produced will turn starch indicator blue-black. The rate of the reaction can therefore be measured by finding the time it takes for the reaction mixture to turn blue-black.

You will perform a series of **four** experiments. In the series of experiments, the rate equation for the reaction can be simplified to rate = $k[Fe^{3+}]^n$, where \mathbf{n} is the order of reaction with respect to $[Fe^{3+}]$ and k' is $k[I^-]^2$. You will graphically analyse your results to determine \mathbf{n} .

For each experiment, you will note the volume of **FA 4** added, $V_{\text{FA 4}}$, and the time taken, t, to the nearest second, for the reaction mixture to become blue-black. In each experiment, you will need to ensure that the same total volume of reaction mixture is used by adding deionised water as required.

- (a) Prepare a table in the space provided on page 8 in which to record, to an appropriate level of precision:
 - volumes of **FA 4**, $V_{\text{FA 4}}$, and deionised water,
 - all values of t,
 - all calculated values of $\frac{1}{t}$, $\lg\left(\frac{1}{t}\right)$ and $\lg(V_{\mathsf{FA}\,4})$.

(i) Experiment 1

- 1. Fill a burette with **FA 4**.
- 2. Transfer 20.00 cm³ of **FA 4** into a 100 cm³ conical flask.
- 3. Use appropriate measuring cylinders, place the following in a 100 cm³ beaker.
 - 10.0 cm³ of **FA 5**
 - 15.0 cm³ of **FA 6**
 - 10.0 cm³ of starch solution
- 4. Add the contents of the beaker rapidly to the conical flask and start the stopwatch.
- 5. Swirl the mixture and place the conical flask on the white tile.
- 6. The mixture turns purple and then yellow before turning a blue-black colour. Stop timing when this **blue-black colour** appears.
- 7. Record the time taken, *t*, to the nearest second in your table.
- 8. Discard the reaction mixture **immediately** down the sink. Wash out the conical flask and stand it upside down on a paper towel to drain.

(ii) Experiment 2

- 1. Run 6.00 cm³ of **FA 4** into a 100 cm³ conical flask.
- 2. Using another burette, add 14.00 cm³ of deionised water into the conical flask containing **FA 4**.
- Use the measuring cylinders from experiment 1 to place the following in a 100 cm³ beaker.
 - 10.0 cm³ of **FA 5**
 - 15.0 cm³ of **FA 6**
 - 10.0 cm³ of starch solution
- 4. Add the contents of the beaker rapidly to the conical flask and start the stopwatch.
- 5. Swirl the mixture and place the conical flask on the white tile.
- The mixture turns purple and then yellow before turning a blue-black colour.
 Stop timing when this blue-black colour of similar intensity as experiment 1 appears.
- 7. Record the time taken, *t*, to nearest second in your table.
- 8. Discard the reaction mixture **immediately** down the sink. Wash out the conical flask and stand it upside down on a paper towel to drain.

In **experiment 1** you will have obtained the time taken for a 'fast' reaction and in **experiment 2** the time taken for a 'slow' reaction.

Carry out **two** further experiments to investigate the effect of changing the concentration of Fe³⁺(aq), **FA 4**, used. In each case, you will need to ensure that the **same total volume** of reaction mixture is used by adding deionised water as required.

You should alternate the use of the two 100 cm³ conical flasks.

Record all required volumes, time taken and calculated values in your table.

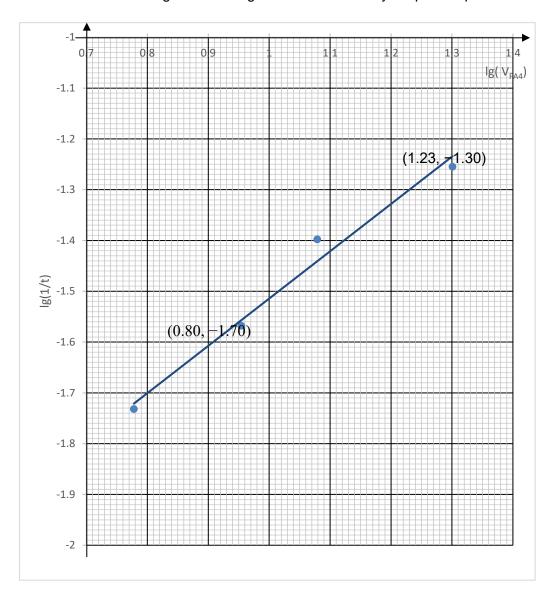
(iii) Results

Expt	V _{FA 4} / cm ³	Volume of deionised H ₂ O / cm ³	t /s	$\frac{1}{t}$ / s ⁻¹	Ig (V _{FA 4})	$\lg\left(\frac{1}{t}\right)$
1	20.00	0.00	18	0.0556	1.30	-1.26
2	6.00	14.00	55	0.0185	0.778	-1.73
3	9.00	11.00	37	0.0270	0.954	-1.57
4	12.00	8.00	25	0.0400	1.08	-1.40

[4]

(b) (i) Plot a graph of $Ig(\frac{1}{t})$ on the y-axis against $Ig(V_{FA \cdot 4})$ on the x-axis.

Draw the best-fit straight line taking into account all of your plotted points.



(ii) Calculate the gradient of the line to three significant figures, showing clearly how you did this. Hence deduce n, the order of the reaction with respect to $[Fe^{3+}]$ in rate = k[Fe^{3+}] n .

[3]

Gradient =
$$\frac{-1.30 - (-1.70)}{1.23 - 0.80}$$
 = **0.930** (3 s.f.)
rate = k' [Fe³⁺]ⁿ
since rate α (1/t) and initial [Fe³⁺] α **V**_{FA 4}
(1/t) = k **V**_{FA 4}ⁿ
lg (1/t) = lg k + n lg **V**_{FA 4}

Hence, the gradient of the graph of $\lg\left(\frac{1}{t}\right)$ vs $\lg(V_{FA 4})$ is the order of the reaction w.r.t. $[Fe^{3+}]$.

n, order of reaction with respect to [Fe³⁺] is 1.

[3]

(c) (i) A student wants to investigate the effect of concentration of iodide ions on the rate of this reaction. He plans to carry out another one experiment, **Experiment 5.**

Suggest appropriate volumes of chemicals to be used in the procedure by completing Table 2.1 so that his results in **Experiment 5**, together with that from **Experiment 1**, could be used to determine the order of reaction with respect to $[I^-]$.

Table 2.1

Expt	Volume of FA 4 / cm ³	Volume of FA 5 / cm ³	Volume of FA 6 / cm ³	Volume of deionised water / cm ³	time taken for blue-black to appear / s
1	20.00	10.0	15.0	0.0	t ₁
5	20.00	5.0	15.0	5.0	t ₂

[1]

(ii) Taking the time for the blue-black colour to appear in **Experiments 1 and 5** to be t₁ and t₂ respectively, explain how the results of the two experiments can be used to confirm that this reaction is second order with respect to [I⁻].

[1

Halving the concentration (or volume) of I^- caused the rate to decrease by 4 times, rate for experiment 5 is one-quarter that of experiment 1, hence, the time taken for experiment 5 is quadruple (four times) that of experiment 1. That is, $\underline{t_2} = 4 \underline{t_1}$

(iii) Suggest an improvement to the experimental procedure so that the order of reaction with respect to $[I^-]$ can be more **reliably** determined.

Conduct more experiments by varying the volume of FA 5 while keeping the total volume constant. Then plot the rate (1/time) against the volume of FA 5 to observe how the rate (1/time) is dependent on the volume or $[I^-]$.

OR

Repeat each experiment and take average of the timings for the blue-black colouration to appear.

[1]

[Total: 13]

3 Qualitative Analysis

(a) FA 7 contains two cations.

FA 5 is $0.0800 \text{ mol dm}^{-3}$ aqueous potassium iodide, KI, provided in **Question 2**.

FA 8 is a solution of a dilute acid.

Perform the tests described in Table 3.1 and record your observations in the spaces provided.

Your answers should include:

- details of colour changes and precipitates formed.
- the names of gases evolved and details of the test used to identify each gas.

Table 3.1

	test	observations
(i)	To 1 cm depth of FA 7 in a test—tube, add an equal depth of aqueous ammonia.	blue ppt soluble in excess giving dark blue solution
(ii)	To 1 cm depth of FA 7 in a test—tube, add one spatula of zinc powder. Stir well.	Blue solution turns pale blue/colourless.
	Leave to stand for a few minutes.	Pink/reddish brown solid formed.
(iii)	To 1 cm depth of FA 7 in a test–tube, add about 2 cm depth of FA 5 and shake the mixture thoroughly.	Blue solution turns yellow / yellow-brown / brown. White / cream / off-white ppt formed
	Then add a few drops of starch.	Blue-black colouration seen
(iv)	To 1 cm depth of FA 7 in a boiling tube, add aqueous sodium hydroxide.	pale <u>blue ppt insoluble</u> in excess
	Warm the mixture	blue <u>ppt</u> turns <u>black</u> <u>Moist red litmus paper turns blue</u> Gas is <u>NH</u> ₃
		[5

(b) Identify the cations present in **FA 7**. Use evidence from your observations in (a) to support your deduction.

Cation Evidence

[2]

Cu ²⁺	blue ppt which remained insoluble when NaOH is added in (a)(iv) OR blue ppt which dissolves to give dark blue solution when NH ₃ is added in (a)(i).
NH ₄ ⁺	Gas evolved turned moist red litmus blue when warmed with NaOH in (a)(iv) .

(c) With the aid of chemical equations, explain your observations for the test in (a)(i).

[3]

When a few drops of NH₃ is added, blue ppt Cu(OH)₂ is formed.

$$Cu(H_2O)_6^{2+} + 2OH^- \rightleftharpoons Cu(OH)_2 + 6H_2O$$
 (1) or

 $Cu^{2+}(aq) + 2OH^{-}(aq) \rightleftharpoons Cu(OH)_2(s)$

When NH₃(aq) is added in excess, a **ligand exchange reaction** occurs.

The stronger NH₃ ligands replace weaker H₂O ligands in the $[Cu(H_2O)_6]^{2+}$ ions to form a <u>dark blue $[Cu(NH_3)_4]^{2+}$ </u> complex.

 $Cu(H_2O)_6^{2+} + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{2+} + 6H_2O$

 $[Cu(H_2O)_6^{2+}]$ decreases. Hence <u>position of equilibrium (1) shifts to the left to increase $[Cu(H_2O)_6^{2+}]$ and blue ppt dissolves.</u>

(d) Using your observations in test (a)(iii), state and explain the role of FA 7.

[1]

Colourless I⁻ is oxidised to brown I_{2.} (also accept blue-black colouration with starch as confirmation of iodine formation) Hence FA 7 acts as an oxidising agent.

- (e) The identity of **FA 8** could be hydrochloric acid, nitric acid or sulfuric acid.
 - (i) Devise a series of tests that will identify FA 8. For each of the possible acids, you should indicate the expected observations for a positive test in Table 3.2. Your tests should be based on the Qualitative Analysis Notes on pages 19–20 and should use only the bench reagents provided.

[3]

Table 3.2

	test	expected observations for a positive test
1	To 1 cm depth of dilute HC l in a test-tube, add aqueous silver nitrate dropwise.	White ppt formed

2	2	To 1 cm depth of dilute nitric acid in a boiling tube, add 2 cm depth of aqueous sodium hydroxide and a piece of aluminium foil. Heat the resulting mixture.	Gas evolved turns moist red litmus paper blue.
3	3	To 1 cm depth of dilute sulfuric acid in a test- tube, add aqueous barium nitrate dropwise.	White ppt formed

(ii) Perform your tests on FA 8 to confirm its identity.

Any test requiring heating MUST be performed in a boiling tube.

	[1]
FA 8	
H ₂ SO ₄	
	[Total: 15]

4 Planning: Determining the equilibrium constant, K_c , for a reaction

The hydrolysis of an ester is catalysed by either an acid or alkali. In the presence of an acid catalyst, the reaction is reversible and reaches equilibrium in three days.

Ethyl ethanoate hydrolyses to give ethanoic acid and ethanol as shown in equation 4.

equation 4
$$CH_3CO_2CH_2CH_3(I) + H_2O(I) \implies CH_3CO_2H(I) + CH_3CH_2OH(I)$$

To determine the equilibrium constant, K_c , it is necessary to determine the amounts of ethyl ethanoate, water, ethanoic acid and ethanol present in the equilibrium mixture. One way of doing this is described below.

Known amounts of ethyl ethanoate and an acid catalyst are mixed. After sufficient time, about 50 cm³ of deionised water is added to the equilibrium mixture. The whole mixture is then titrated against a standard solution of sodium hydroxide. This allows the total amount of acid in the mixture to be found. The total amount of acid is made up of the acid catalyst and the ethanoic acid present in the equilibrium mixture.

Since the amount of acid catalyst does not change, it is possible to deduce the amount of ethanoic acid in the equilibrium mixture. If the initial amounts of ethyl ethanoate and water are known, the amounts of all species present in the equilibrium mixture can be determined.

These data could then be used in the following expression to determine K_c .

$$K_c = \frac{[ethanoic\ acid][ethanol]}{[ethyl\ ethanoate][water]}$$

(a) Using the information given above, write a plan to determine the equilibrium constant, K_c , for the hydrolysis of ethyl ethanoate at 35 °C.

In your plan, you should make an initial reaction mixture containing

- 5.00 cm³ of ethyl ethanoate,
- 5.00 cm³ of 3.00 mol dm⁻³ hydrochloric acid.

You are also provided with:

- 1.00 mol dm⁻³ sodium hydroxide,
- thymolphthalein indicator (colourless in acidic medium, blue in alkaline)
- the equipment and materials normally found in a school or college laboratory.

You should include brief details of:

- the apparatus you would use.
- the procedure you would use to prepare the equilibrium mixture,
- the procedure you would use to determine the total amount of acid in the equilibrium mixture.
- the measurements you would make.

In your plan, you will titrate the **whole** equilibrium mixture so only **one** titration can be carried out. You do not need to describe any calculations.

Procedure:

Preparation of the reaction mixture

- 1) Using a **burette**, add 5.00 cm³ of ethyl ethanoate into a 250 cm³ conical flask.
- 2) Using another **burette**, add 5.00 cm³ of 3.00 mol cm⁻³ hydrochloric acid into the same conical flask.
- 3) **Stopper** and **shake** the flask to mix the contents **well**.
- 4) Leave the conical flask in a thermostatically controlled water bath at 35 °C for three days.

Titration of the reaction mixture

- 5) Fill the **burette** with 1.00 mol dm⁻³ sodium hydroxide.
- 6) Using a measuring cylinder, add **50 cm³ of deionised water** into the conical flask containing the equilibrium mixture.
- 7) Add **a few drops** (3) drops of thymolphthalein indicator.
- 8) Titrate the equilibrium mixture (quickly) **against NaOH** with swirling until the indicator changes from **colourless to blue**.
- 9) Record the burette reading.
- **(b)** Table 4.1 gives information about the densities of the reactants.

Table 4.1

Name	<i>M</i> _r	density / g cm ⁻³
water	18.0	1.00
ethyl ethanoate	88.0	0.90

Assume that 40.00 cm³ of 1.00 mol dm⁻³ sodium hydroxide was needed to neutralise the acids present in the equilibrium mixture, calculate the amounts (in moles) of

- ester and water present in your initial reaction mixture,
- ethanoic acid present in this mixture at equilibrium,
- all the other components in this mixture at equilibrium.

You may assume that 1.00 cm³ of hydrochloric acid contains 1.00 cm³ of water.

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[6]

Hence, determine the value of equilibrium constant, K_c , for equation 4.

[4]

Mass of ethyl ethanoate used = $5.00 \times 0.90 = 4.50 \text{ g}$ Initial moles of ethyl ethanoate used = 4.50/88.0 = 0.0511 mol

Mass of water used = $5.00 \times 1.00 = 5.00 \text{ g}$ Initial moles of water used = 5.00/18.0 = 0.278 mol

Initial moles of BOTH ester and water

Use of titration result.

Moles of NaOH required =(40.00/1000) x 1.00 = 0.0400 mol moles of hydrochloric acid used + ethanoic acid present at equilibrium = 0.0400 mol

moles of hydrochloric acid used = $(5.00/1000) \times 3.00 = 0.015 \text{ mol}$ moles of ethanoic acid present at equilibrium = 0.0400 - 0.015 = 0.0250 mol

$$CH_{3}CO_{2}CH_{2}CH_{3}(I) + H_{2}O(I) \Longrightarrow CH_{3}CO_{2}H(I) + CH_{3}CH_{2}OH(I)$$
 Initial 0.0511 0.278 0 0 0 moles Change in - 0.0250 - 0.0250 + 0.0250 + 0.0250 moles Eqm 0.0261 0.253 0.0250 0.0250
$$\mathcal{K}_{c} = \frac{[ethanoic\ acid][ethanol]}{[ethyl\ ethanoate][water]} = \frac{\binom{0.0250}{V}\binom{0.0250}{V}}{\binom{0.0250}{V}\binom{0.0253}{V}} = 0.0946$$

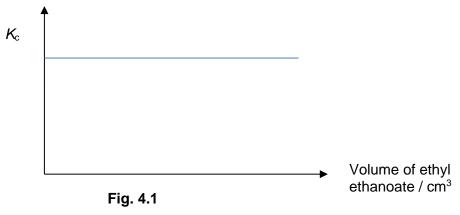
(c) Two other experiments were carried out using different volumes of ethyl ethanoate as shown in Table 4.2.

Table 4.2

Experiment	Volume of ethyl	Volume of	Volume of
	ethanoate /cm³	hydrochloric acid /cm ³	water /cm ³
1	5.00	5.00	0.00
2	4.00	5.00	1.00
3	3.00	5.00	2.00

Sketch a graph in Fig. 4.1 to show how the value of K_c obtained for experiments 2 and 3 would compare with experiment 1.





[Total: 11]