Name	Index Number	Form Class	Tutorial Class	Subject Tutor

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY
Higher 2

9729/04

Paper 4 Practical

3 August 2021

2 hours 30 minutes

Candidates answer on the Question Paper.

READ THESE INSTRUCTIONS CAREFULLY

Write your name, class and index 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 on pages 19 and 20.

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.

For Examiner's Use	
Question No.	**Marks**
1 (15 m)	
2 (23 m)	
3 (17 m)	
Presentation of answers	
TOTAL (55 m)	

Shift
Laboratory

This document consists of **19** printed pages and **1** blank page.

1 Determination of the total concentration of ethanedioate ions with sodium hydroxide and potassium manganate(VII)

(a) Procedure

FA 1 is an aqueous mixture of ethanedioic acid, $H_2C_2O_4$, and sodium ethanedioate, $Na_2C_2O_4$

FA 2 is 0.100 mol dm^{-3} sodium hydroxide, NaOH

FA 3 is 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$

You are advised to read parts **(a)(i)** and **(a)(ii)** before starting practical work and to carry out a **ROUGH** titration until the relevant colour change is seen in each part of the titration.

(i) Determine by titration, with sodium hydroxide, the concentration, in mol dm^{-3}, of the ethanedioic acid in FA 1.

- Fill the burette with **FA 2**.
- Pipette 25.0 cm^3 of **FA 1** into a conical flask and add to the flask a few drops of thymol blue indicator.
- Run **FA 2** from the burette into the conical flask until the solution turns green (just before it turns blue).
- Repeat the titration as many times as necessary to provide reliable results.
- Tabulate your titration results in the space provided.

(ii) Determine by titration, with potassium manganate(VII), the total concentration, in mol dm^{-3}, of ethanedioate ions in FA 1.

- Fill the second burette with **FA 3**.
- Pipette 25.0 cm^3 of **FA 1** into a conical flask. Use the measuring cylinder provided to add to the flask 25 cm^3 of 1 mol dm^{-3} sulfuric acid, 10 cm^3 of 0.01 mol dm^{-3} manganese(II) sulfate and 40 cm^3 of distilled water.
- Put the thermometer in the conical flask and heat the solution until the temperature is just over 65 °C.
- Carefully remove the thermometer and place the hot flask under the burette.
- If the neck of the flask is too hot to hold safely, use a folded paper towel to hold the flask. Run in 1 cm^3 of **FA 3** and swirl the flask until the colour of the potassium manganate(VII) has disappeared then continue the titration as normal until a permanent pale pink colour is obtained. This is the end-point.
  - ***If a brown colour appears during titration**, reheat the flask to 65°C. The brown colour should disappear and the titration can be completed as above.*
  - ***If the brown colour does not disappear on reheating**, discard the solution and start the titration again.*
- Repeat the titration as many times as necessary to provide reliable results.
- Tabulate your titration results in the space provided.

(b) Results

(i) Tabulate your titration results from **(a)(i)**.
Make certain your recorded results show the precision of your practical work.

(ii) From your titration results in **(b)(i)**, obtain a suitable volume of **FA 2**, $V_{FA\,2}$, to be used in your calculations. Show clearly how you obtained this volume.

$V_{FA\,2}$ = ...

(iii) Tabulate your titration results from **(a)(ii)**.
Make certain your recorded results show the precision of your practical work.

(iv) From your titration results in **(b)(iii)**, obtain a suitable volume of **FA 3**, $V_{FA\,3}$, to be used in your calculations. Show clearly how you obtained this volume.

$V_{FA\,3}$ = ...

[5]

(c) Calculations

(i) Calculate the amount of NaOH used in **(a)(i)**.

amount of NaOH = ... [1]

(ii) Use the titration data from **(a)(i)** to calculate the concentration, in mol dm^{-3}, of $H_2C_2O_4$ in **FA 1**.

$$H_2C_2O_4 + 2NaOH \rightarrow Na_2C_2O_4 + 2H_2O$$

$[H_2C_2O_4]$ in **FA1** = ... [1]

(iii) Calculate the amount of $KMnO_4$ added from the burette in **(a)(ii)**.

amount of $KMnO_4$ = ... [1]

(iv) Use titration data from **(a)(ii)** to calculate the total concentration, in mol dm^{-3}, of $C_2O_4^{2-}$ ions in **FA 1**.

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$
$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$$

$[C_2O_4^{2-}]$ in **FA1** = ... [1]

(v) Use your answers to **(c)(ii)** and **(c)(iv)** to calculate the concentration, in g dm^{-3}, for each of the following:
[M_r of $H_2C_2O_4$ = 90.0 ; M_r of $Na_2C_2O_4$ = 134.0]

- $H_2C_2O_4$

[$H_2C_2O_4$] in **FA1** = ... [1]

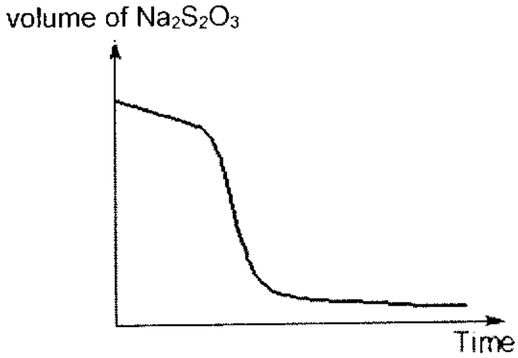
- $Na_2C_2O_4$

[$Na_2C_2O_4$] in **FA1** = ... [1]

(d) In a kinetics experiment, 50 cm^3 of ethanedioic acid with 10 cm^3 of sulfuric acid and 40 cm^3 of deionised water were added in a 250 cm^3 conical flask. 25 cm^3 of potassium manganate(VII) solution was added to the conical flask and the start time recorded.

Small aliquots from the mixture were drawn and added to a conical flask containing potassium iodide at regular time intervals. The conical flask was then titrated with aqueous sodium thiosulfate from a burette.

The diagram shows the sketch for the graph of volume of sodium thiosulfate against time for the experiment.



Describe and explain any unusual features in the graph.

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.... [4]

[Total: 15]

2 Determination of the concentration of an acid and the enthalpy change of neutralisation, ΔH_{neu}

FA 4 is a solution of sulfuric acid, H_2SO_4, of unknown concentration
FA 5 is 1.50 mol dm^{-3} sodium hydroxide, NaOH

The enthalpy change of neutralisation is the heat evolved when one mole of water is formed during a neutralisation reaction as shown in the equation below.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

You will perform a series of experiments using different volumes of **FA 4** and **FA 5** to determine the temperature change for each reaction. The maximum amount of heat is evolved when all the acid present is exactly neutralised by all the alkali present.

You will then analyse the results graphically to determine the equivalence point of the reaction and hence calculate the concentration of **FA 4** and the value of the enthalpy change of neutralisation, ΔH_{neu}.

In an appropriate format in the space provided on the next page, prepare a table in which to record the data for each experiment to an appropriate level of precision:
- all measurements of volumes used,
- all values of temperatures measured and the change in temperature.

For each experiment, you will calculate and record the weighted average initial temperature, T_{avg}, before the reaction occurs when the two solutions are mixed, corrected to 1 decimal place. The formula for T_{avg} is given below.

$$T_{avg} = \frac{(\text{volume } \mathbf{FA4} \times \text{initial temperature of } \mathbf{FA4}) + (\text{volume } \mathbf{FA5} \times \text{initial temperature } \mathbf{FA5})}{\text{total volume of reaction mixture}}$$

The change in temperature, ΔT, is thus obtained by subtracting the maximum temperature reached, T_{max}, with T_{avg}.

State clearly the units of each parameter on the header of the column.

Procedure

1. Place a clean and dry polystyrene cup inside a second polystyrene cup, which is supported in a 250 cm^3 glass beaker to prevent the cups from tipping over.

2. Fill the burette with **FA 4** and transfer 10.00 cm^3 of **FA 4** into the polystyrene cup.

3. Measure the initial temperature of **FA 4** in the polystyrene cup using the thermometer. Tilt the cup if necessary to ensure that the bulb of the thermometer is fully immersed. Record this temperature as T_{FA4}.

4. Wash and dry the thermometer.

5. Measure 40.0 cm^3 of **FA 5** using a measuring cylinder.

6. Measure the initial temperature of **FA 5** in the measuring cylinder using the thermometer. Record this temperature as T_{FA5}.

7. Transfer the **FA 5** in the measuring cylinder into the polystyrene cup.

8. Stir the reaction mixture in the polystyrene cup using the thermometer. Measure and record the maximum temperature reached, T_{max}.

9. Rinse and dry the polystyrene cup and the thermometer.

10. Repeat steps 1 to 9 using 15.00 cm^3, 20.00 cm^3, 25.00 cm^3, 30.00 cm^3 and 35.00 cm^3 of **FA 4** and appropriate volumes of **FA 5** each time, ensuring that the total volume of the reaction mixture is 50 cm^3.

(a) (i) Results

[3]

(ii) Using the data obtained in **(a)(i)**, plot a graph of ΔT against volumes of **FA 4** added.

Draw **two** straight lines of best-fit for the ascending and descending points respectively. Extrapolate both lines until they intersect to determine the:

- equivalence point of the reaction, V_{eq},
- temperature change at equivalence point, ΔT_{eq}.

V_{eq} = ...

ΔT_{eq} = ... [5]

(b) **(i)** Calculate the amount of sulfuric acid in **FA 4** that reacted with sodium hydroxide in **FA 5** at the equivalence point.

amount of H_2SO_4 reacted = ... [2]

(ii) Hence, calculate the concentration of sulfuric acid in **FA 4**.

$[H_2SO_4]$ in **FA 4** = ... [1]

(c) Calculate the enthalpy change of neutralisation, ΔH_{neu}.

Assume that the specific heat capacity of the reaction mixture is 4.18 J g^{-1} K^{-1} and its density is 1.00 g cm^{-3}.

ΔH_{neu} = ... [2]

(d) A student proposed to start the experiment using 5.00 cm^3 instead of 10.00 cm^3 of **FA 4** in the polystyrene cup.

Suggest a reason why this is not recommended.

....

....

.... [1]

(e) Explain whether replacing **FA 4** with ethanedioic acid, a weak dibasic acid, of equal concentration would have any effect on the:

- equivalence point of the reaction, V_{eq},
- temperature change at equivalence point, ΔT_{eq}.

effect on V_{eq} ....

explanation

....

....

....

effect on ΔT_{eq} ....

explanation

....

....

.... [2]

(f) **Planning**

FA 4 is a solution of sulfuric acid, H_2SO_4, of unknown concentration
FA 5 is 1.50 mol dm^{-3} sodium hydroxide, NaOH

Another experiment that can be performed to determine the concentration of **FA 4** and the enthalpy change of neutralisation is thermometric titration, which makes use of temperature change instead of colour change conferred by an indicator.

The reaction is followed by measuring the temperature of the reaction mixture as portions of **FA 4** are progressively added to a fixed volume of **FA 5**. The equivalence point and the maximum temperature change can then be determined graphically.

(i) Write a plan for the thermometric titration of 25 cm^3 of **FA 5** with **FA 4**.

You are provided with:

- 50 cm^3 of **FA 4**,
- 50 cm^3 of **FA 5**,
- polystyrene cups,
- any other equipment normally found in a school or college laboratory.

In your plan, you should include details of:

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

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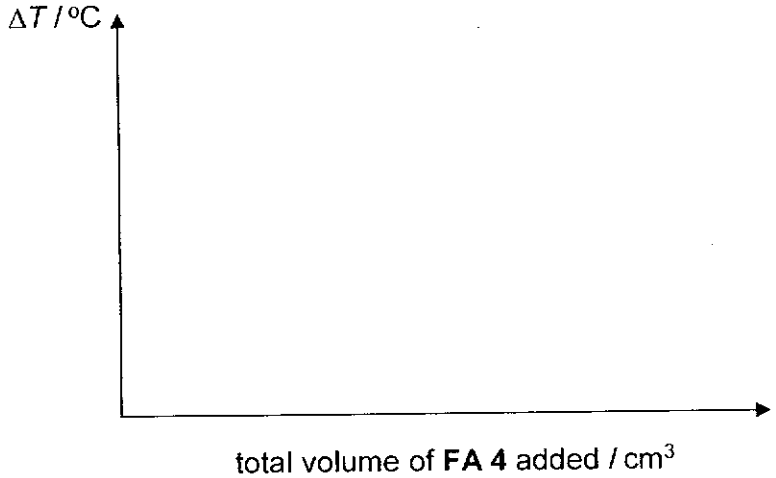
....[5]

(ii) A graph of temperature change against total volume of **FA 4** added can possibly be plotted. In this case, two best-fit curves can be drawn to determine the equivalence point and the maximum temperature change.

On the axes below, sketch the graph you would expect to obtain from the experimental data. Explain the shape of your graph.



explanation ....

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....

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.... [2]

[Total: 23]

3 Inorganic Analysis

In this question you will deduce the identities of three cations and one anion.

FA 6 is a mixture containing four cations and one anion. One of the cations is dioxovanadium(V), VO_2^+. It is the **only species responsible for colour** in **FA 6** and can be **assumed to remain soluble** during the various tests in this question.

In addition to having access to the usual bench reagents, you are also provided with the following:

- magnesium turnings,
- barium chloride solution.

(a) Perform the tests described in Table 3.1, and record your observations in the table. Test and identify any gases evolved. If there is no observable change, write **no observable change**.

Unless otherwise stated, use a fresh sample of FA 6 in each test.

Table 3.1

	tests	observations
1.	Add about 1 cm depth of **FA 6** to a test-tube. Add, using the tip of a spatula, a small portion of magnesium turnings to this test-tube. Observe the mixture until no further changes are seen.	
While you are waiting, continue with test 2.		
2.	Add about 2 cm depth of **FA 6** to a boiling tube. Add aqueous sodium hydroxide slowly, with shaking, until no further change is seen. Gently heat the boiling tube, taking care to avoid sputtering, until no further changes are seen. Leave the solution to cool and add aqueous barium chloride.	
3.	Add about 1 cm depth of **FA 6** to a test-tube. Add aqueous ammonia slowly, with shaking, until no further change is seen.	

[6]

(b) Complete Table 3.2 with the identities of the other three cations deduced in **FA 6**.

Give evidence from the observations in Table 3.1 to support your conclusions.

Table 3.2

identity	evidence

[3]

(c) The final observation in test 2 in Table 3.1 would have helped you conclude the identity of the anion in **FA 6**.

(i) Use the Qualitative Analysis Notes on pages 19–20 to deduce the anion in **FA 6**.

.... [1]

(ii) Explain your reasoning in **(c)(i)**.

....

....

....

.... [1]

(d) Vanadium is a transition metal exhibiting various oxidation states of +2, +3, +4 and +5. Each of these states have species giving different colours in the aqueous medium. Table 3.3 gives the species and their associated colours.

Table 3.3

species	V^{2+}	V^{3+}	VO^{2+}	VO_2^+/VO_3^-	VO_4^{3-}
colour	violet	green	blue	yellow	colourless

Table 3.4 gives some standard electrode potential values involving magnesium, vanadium and their ions.

Table 3.4

electrode reaction	$E^\ominus$ / V
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	–2.38
$V^{2+}(aq) + 2e^- \rightleftharpoons V(s)$	–1.20
$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$	–0.26
$VO^{2+}(aq) + 2H^+(aq) + e^- \rightleftharpoons V^{3+}(aq) + H_2O(l)$	+0.34
$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$	+1.00
$VO_3^-(aq) + 4H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + 2H_2O(l)$	+1.00

Consider your observations when magnesium turnings were added to **FA 6** in test 1 in Table 3.1 and the information in Tables 3.3 and 3.4.

(i) Write an overall equation for the reaction that occurred between magnesium and vanadium species when you added magnesium turnings to **FA 6** in test 1 in Table 3.1.

.... [1]

(ii) Based on the standard electrode potential values given in Table 3.4, predict the expected final colour of the solution in test 1 in Table 3.1 and state if your observations agree or do not agree with the prediction.

Provide a reason for your observations.

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.... [2]

Consider your observations when the boiling tube was heated in test 2 in Table 3.1 and the information in Table 3.3.

(iii) State the observation that is related to information given in Table 3.3 and write an equation for the reaction that occurred.

Explain the need for heat to bring about the change observed.

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....

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....

....

....[3]

[Total: 17]

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Qualitative Analysis Notes
[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	*reaction with*	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. rapidly turning brown on contact with air insoluble in excess	off-white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^- (aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^- (aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^- (aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^- (aq)	NH_3 liberated on heating with OH^-(aq) and Al foil
nitrite, NO_2^- (aq)	NH_3 liberated on heating with OH^-(aq) and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-} (aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-} (aq)	SO_2 liberated on warming with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

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2 (23 m)	
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TOTAL (55 m)	

Shift
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1 **Determination of the total concentration of ethanedioate ions with sodium hydroxide and potassium manganate(VII)**

(a) **Procedure**

FA 1 is an aqueous mixture of ethanedioic acid, $H_2C_2O_4$, and sodium ethanedioate, $Na_2C_2O_4$
FA 2 is 0.100 mol dm^{-3} sodium hydroxide, NaOH
FA 3 is 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$

You are advised to read parts **(a)(i)** and **(a)(ii)** before starting practical work and to carry out a **ROUGH** titration until the relevant colour change is seen in each part of the titration.

(i) **Determine by titration, with sodium hydroxide, the concentration, in mol dm^{-3}, of the ethanedioic acid in FA 1.**

- Fill the burette with **FA 2**.
- Pipette 25.0 cm^3 of **FA 1** into a conical flask and add to the flask a few drops of thymol blue indicator.
- Run **FA 2** from the burette into the conical flask until the solution turns green (just before it turns blue).
- Repeat the titration as many times as necessary to provide reliable results.
- Tabulate your titration results in the space provided.

(ii) **Determine by titration, with potassium manganate(VII), the total concentration, in mol dm^{-3}, of ethanedioate ions in FA 1.**

- Fill the second burette with **FA 3**.
- Pipette 25.0 cm^3 of **FA 1** into a conical flask. Use the measuring cylinder provided to add to the flask 25 cm^3 of 1 mol dm^{-3} sulfuric acid, 10 cm^3 of 0.01 mol dm^{-3} manganese(II) sulfate and 40 cm^3 of distilled water.
- Put the thermometer in the conical flask and heat the solution until the temperature is just over 65 °C.
- Carefully remove the thermometer and place the hot flask under the burette.
- If the neck of the flask is too hot to hold safely, use a folded paper towel to hold the flask. Run in 1 cm^3 of **FA 3** and swirl the flask until the colour of the potassium manganate(VII) has disappeared then continue the titration as normal until a permanent pale pink colour is obtained. This is the end-point.
  - ***If a brown colour appears during titration****, reheat the flask to 65°C. The brown colour should disappear and the titration can be completed as above.*
  - ***If the brown colour does not disappear on reheating****, discard the solution and start the titration again.*
- Repeat the titration as many times as necessary to provide reliable results.
- Tabulate your titration results in the space provided.

(b) Results

(i) Tabulate your titration results from **(a)(i)**.
Make certain your recorded results show the precision of your practical work.

Final burette reading / cm^3	19.10	38.10
Initial burette reading / cm^3	0.00	19.10
Volume of **FA 2** used / cm^3	19.10	19.00

(ii) From your titration results in **(b)(i)**, obtain a suitable volume of **FA 2**, $V_{FA\,2}$, to be used in your calculations. Show clearly how you obtained this volume.

Average titre = (19.10 + 19.00) / 2 = 19.05 cm^3

$V_{FA\,2}$ = ...

(iii) Tabulate your titration results from **(a)(ii)**.
Make certain your recorded results show the precision of your practical work.

Final burette reading / cm^3	28.00	28.00
Initial burette reading / cm^3	0.00	0.00
Volume of **FA 3** used / cm^3	28.00	28.00

(iv) From your titration results in **(b)(iii)**, obtain a suitable volume of **FA 3**, $V_{FA\,3}$, to be used in your calculations. Show clearly how you obtained this volume.

Average titre = (28.00 + 28.00) / 2 = 28.00 cm^3

$V_{FA\,3}$ = ...

[5]

(c) Calculations

(i) Calculate the amount of NaOH used in **(a)(i)**.

Amount of NaOH = 0.100 x 19.05 x 10^{-3} = 1.91 x 10^{-3} mol

amount of NaOH = ... [1]

(ii) Use the titration data from **(a)(i)** to calculate the concentration, in mol dm^{-3}, of $H_2C_2O_4$ in **FA 1**.

$$H_2C_2O_4 + 2NaOH \rightarrow Na_2C_2O_4 + 2H_2O$$

Amount of $C_2O_4^{2-}$ = 1.91 x 10^{-3} / 2 = 9.55 x10^{-4} mol

[$H_2C_2O_4$] = 9.55 x 10^{-4} / 25 x 10^{-3} = 0.0382 mol dm^{-3}

[$H_2C_2O_4$] in **FA1** = ... [1]

(iii) Calculate the amount of $KMnO_4$ added from the burette in **(a)(ii)**.

Amount of $KMnO_4$ = 28.00 x 10^{-3} x 0.0200 = 5.60 x 10^{-4} mol

amount of $KMnO_4$ = ... [1]

(iv) Use titration data from **(a)(ii)** to calculate the total concentration, in mol dm^{-3}, of $C_2O_4^{2-}$ ions in **FA 1**.

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$
$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$$

$2MnO_4^- \equiv 5\ C_2O_4^{2-}$

Amount of $C_2O_4^{2-}$ = (5.60 x 10^{-4} / 2) x 5 = 1.40 x 10^{-3} mol

[$C_2O_4^{2-}$] = 1.40 x10^{-3} / 25 x10^{-3} = 0.0560 mol dm^{-3}

[$C_2O_4^{2-}$] in **FA1** = ... [1]

(v) Use your answers to **(c)(ii)** and **(c)(iv)** to calculate the concentration, in g dm^{-3}, for each of the following:
[M_r of $H_2C_2O_4$ = 90.0 ; M_r of $Na_2C_2O_4$ = 134.0]

- $H_2C_2O_4$

[$H_2C_2O_4$] = 0.0382 x 90.0 = 3.44 g dm^{-3}

[$H_2C_2O_4$] in **FA1** = ... [1]

- $Na_2C_2O_4$

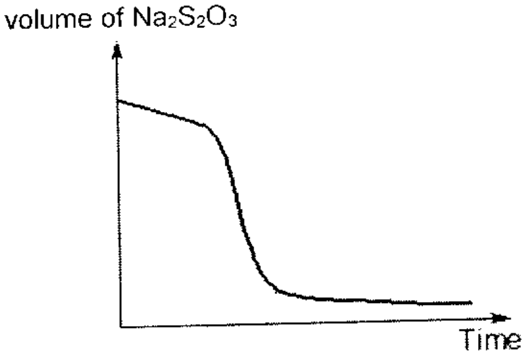
Amount of $C_2O_4^{2-}$ from $Na_2C_2O_4$ in 1 dm^3 solution = 0.0560 – 0.0382 = 0.0178 mol
[$Na_2C_2O_4$] = (0.0178 x 134.0) = 2.39 g dm^{-3}

[$Na_2C_2O_4$] in **FA1** = ... [1]

(d) In a kinetics experiment, 50 cm^3 of ethanedioic acid with 10 cm^3 of sulfuric acid and 40 cm^3 of deionised water were added in a 250 cm^3 conical flask. 25 cm^3 of potassium manganate(VII) solution was added to the conical flask and the start time recorded.

Small aliquots from the mixture were drawn and added to a conical flask containing potassium iodide at regular time intervals. The conical flask was then titrated with aqueous sodium thiosulfate from a burette.

The diagram shows the sketch for the graph of volume of sodium thiosulfate against time for the experiment.



Describe and explain any unusual features in the graph.

The initial gradient of the graph was a gentle negative slope, but it became a steeper negative gradient and ended with a gentle negative slope.

The reaction was slow at the start of the reaction due to high activation energy, but sped up when Mn^{2+} autocatalyst ions were produced in the reaction. The rate of reaction decreased eventually as the concentration of the reactants were decreasing.

[4]

[Total: 15]

2 Determination of the concentration of an acid and the enthalpy change of neutralisation, ΔH_{neu}

FA 4 is a solution of sulfuric acid, H_2SO_4, of unknown concentration
FA 5 is 1.50 mol dm^{-3} sodium hydroxide, NaOH

The enthalpy change of neutralisation is the heat evolved when one mole of water is formed during a neutralisation reaction as shown in the equation below.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

You will perform a series of experiments using different volumes of **FA 4** and **FA 5** to determine the temperature change for each reaction. The maximum amount of heat is evolved when all the acid present is exactly neutralised by all the alkali present.

You will then analyse the results graphically to determine the equivalence point of the reaction and hence calculate the concentration of **FA 4** and the value of the enthalpy change of neutralisation, ΔH_{neu}.

In an appropriate format in the space provided on the next page, prepare a table in which to record the data for each experiment to an appropriate level of precision:
- all measurements of volumes used,
- all values of temperatures measured and the change in temperature.

For each experiment, you will calculate and record the weighted average initial temperature, T_{avg}, before the reaction occurs when the two solutions are mixed, corrected to 1 decimal place. The formula for T_{avg} is given below.

$$T_{avg} = \frac{(\text{volume } \mathbf{FA4} \times \text{initial temperature of } \mathbf{FA4}) + (\text{volume } \mathbf{FA5} \times \text{initial temperature } \mathbf{FA5})}{\text{total volume of reaction mixture}}$$

The change in temperature, ΔT, is thus obtained by subtracting the maximum temperature reached, T_{max}, with T_{avg}.

State clearly the units of each parameter on the header of the column.

Procedure

1. Place a clean and dry polystyrene cup inside a second polystyrene cup, which is supported in a 250 cm^3 glass beaker to prevent the cups from tipping over.

2. Fill the burette with **FA 4** and transfer 10.00 cm^3 of **FA 4** into the polystyrene cup.

3. Measure the initial temperature of **FA 4** in the polystyrene cup using the thermometer. Tilt the cup if necessary to ensure that the bulb of the thermometer is fully immersed. Record this temperature as T_{FA4}.

4. Wash and dry the thermometer.

5. Measure 40.0 cm^3 of **FA 5** using a measuring cylinder.

6. Measure the initial temperature of **FA 5** in the measuring cylinder using the thermometer. Record this temperature as T_{FA5}.

7. Transfer the **FA 5** in the measuring cylinder into the polystyrene cup.

8. Stir the reaction mixture in the polystyrene cup using the thermometer. Measure and record the maximum temperature reached, T_{max}.

9. Rinse and dry the polystyrene cup and the thermometer.

10. Repeat steps 1 to 9 using 15.00 cm^3, 20.00 cm^3, 25.00 cm^3, 30.00 cm^3 and 35.00 cm^3 of **FA 4** and appropriate volumes of **FA 5** each time, ensuring that the total volume of the reaction mixture is 50 cm^3.

(a) **(i)** **Results**

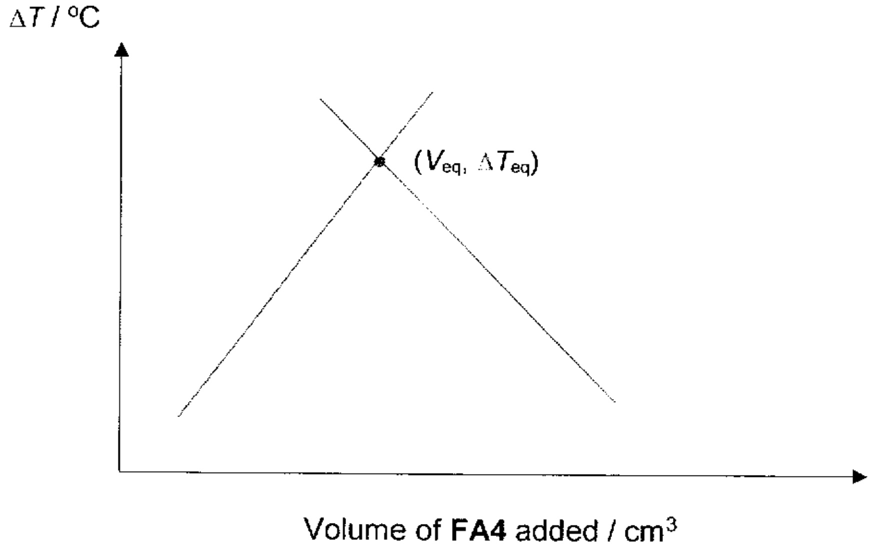
V_{FA4} / cm^3	V_{FA5} / cm^3	T_{FA4} / °C	T_{FA5} / °C	T_{avg} / °C	T_{max} / °C	ΔT / °C
10.00	**40.0**					
15.00	**35.0**					
20.00	**30.0**					
25.00	**25.0**					
30.00	**20.0**					
35.00	**15.0**					

[3]

(ii) Using the data obtained in **(a)(i)**, plot a graph of ΔT against volumes of **FA 4** added.

Draw **two** straight lines of best-fit for the ascending and descending points respectively. Extrapolate both lines until they intersect to determine the:

- equivalence point of the reaction, V_{eq},
- temperature change at equivalence point, ΔT_{eq}.



V_{eq} = ...

ΔT_{eq} = ... [5]

(b) **(i)** Calculate the amount of sulfuric acid in **FA 4** that reacted with sodium hydroxide in **FA 5** at the equivalence point.

n(NaOH) = (50.00 – V_{eq})/1000 x 1.50

n(H_2SO_4) = ½ n(NaOH)

amount of H_2SO_4 reacted = ... [2]

(ii) Hence, calculate the concentration of sulfuric acid in **FA 4**.

[H_2SO_4] = n(H_2SO_4) / V_{eq}/1000

[H_2SO_4] in **FA 4** = ... [1]

(c) Calculate the enthalpy change of neutralisation, ΔH_{neu}.

Assume that the specific heat capacity of the reaction mixture is 4.18 J g^{-1} K^{-1} and its density is 1.00 g cm^{-3}.

q = mcΔT = 50 x 4.18 x ΔT_{eq}

n(H_2O) = n(NaOH)
ΔH_{neu} = –q / n(H_2O)

ΔH_{neu} = ... [2]

(d) A student proposed to start the experiment using 5.00 cm^3 instead of 10.00 cm^3 of **FA 4** in the polystyrene cup.

Suggest a reason why this is not recommended.

Possible answers:

- **A larger percentage error may be incurred when measuring a smaller volume of FA 4.**
- **The temperature increase may be too small, resulting in a larger percentage error of the temperature measured.** .... [1]
- **The bulb of the thermometer cannot be fully immersed, therefore the initial temperature recorded is not accurate.**

(e) Explain whether replacing **FA 4** with ethanedioic acid, a weak dibasic acid, of equal concentration would have any effect on the:

- equivalence point of the reaction, V_{eq},
- temperature change at equivalence point, ΔT_{eq}.

effect on V_{eq} ..**does not change**..........

explanation

Regardless of the acid strength, there are exactly equal amounts of the acid neutralised by the alkali at the equivalence point as the concentrations of the acid and the alkali are the same.

effect on ΔT_{eq} .**decrease**....................

explanation

Some of the heat evolved from the neutralisation reaction would be absorbed to allow for complete dissociation of ethanedioic acid to reach the equivalence point. [2]

(f) **Planning**

FA 4 is a solution of sulfuric acid, H_2SO_4, of unknown concentration
FA 5 is 1.50 mol dm^{-3} sodium hydroxide, NaOH

Another experiment that can be performed to determine the concentration of **FA 4** and the enthalpy change of neutralisation is thermometric titration, which makes use of temperature change instead of colour change conferred by an indicator.

The reaction is followed by measuring the temperature of the reaction mixture as portions of **FA 4** are progressively added to a fixed volume of **FA 5**. The equivalence point and the maximum temperature change can then be determined graphically.

(i) Write a plan for the thermometric titration of 25 cm^3 of **FA 5** with **FA 4**.

You are provided with:

- 50 cm^3 of **FA 4**,
- 50 cm^3 of **FA 5**,
- polystyrene cups,
- any other equipment normally found in a school or college laboratory.

In your plan, you should include details of:

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

Procedure:

1. Fill the 50.00 cm^3 burette to the 0.00 cm^3 mark with FA 4.
2. Place a clean and dry polystyrene cup inside a second polystyrene cup, which is supported in a 250 cm^3 glass beaker to prevent the cups from tipping over.
3. Use a 25.0 cm^3 pipette to transfer 25.0 cm^3 of FA 5 into the cup.
4. Measure the initial temperature of FA 5 using the thermometer. Record this temperature as T_{init}.
5. Run 3.00 cm^3 of FA 4 from the burette into the cup, stir the solution using the thermometer and record the maximum temperature, T_{final}.
6. Immediately run a further 3.00 cm^3 of FA 4 from the burette into the cup, stir and record the maximum temperature as before.
7. Continue the addition of FA 4 in 3.00 cm^3 and record the maximum temperature reached after each addition. Do this until a total of 45.00 cm^3 of solution have been run from the burette.

....

....

....

....

....

....

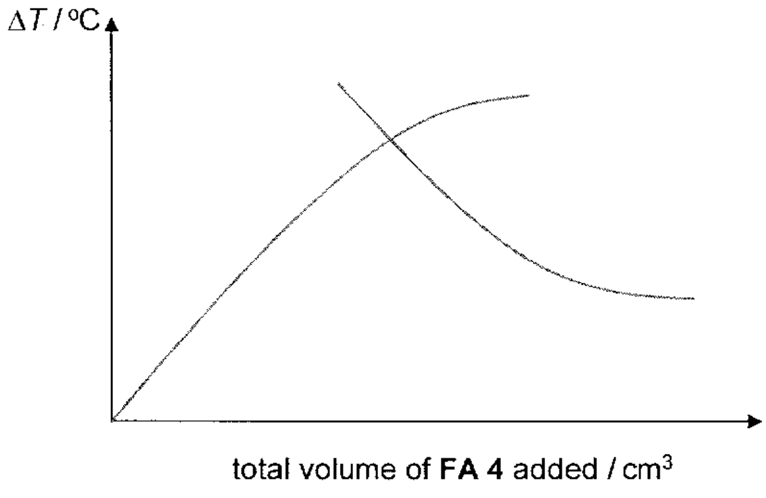
....

....

....[5]

(ii) A graph of temperature change against total volume of **FA 4** added can possibly be plotted. In this case, two best-fit curves can be drawn to determine the equivalence point and the maximum temperature change.

On the axes below, sketch the graph you would expect to obtain from the experimental data. Explain the shape of your graph.



explanation ....

As the total volume of the reaction mixture increases throughout the experiment (unlike the experiment done where the total volume was kept constant at 50 cm³), ΔT will vary less linearly with the total volume of FA 4 added because the heat is distributed over a larger volume.

....

.... [2]

[Total: 23]

3 Inorganic Analysis

In this question you will deduce the identities of three cations and one anion.

FA 6 is a mixture containing four cations and one anion. One of the cations is dioxovanadium(V), VO_2^+. It is the **only species responsible for colour** in **FA 6** and can be **assumed to remain soluble** during the various tests in this question.

In addition to having access to the usual bench reagents, you are also provided with the following:

- magnesium turnings,
- barium chloride solution.

(a) Perform the tests described in Table 3.1, and record your observations in the table. Test and identify any gases evolved. If there is no observable change, write **no observable change**.

Unless otherwise stated, use a fresh sample of FA 6 in each test.

Table 3.1

	tests	observations
1.	Add about 1 cm depth of **FA 6** to a test-tube. Add, using the tip of a spatula, a small portion of magnesium turnings to this test-tube. Observe the mixture until no further changes are seen.	Effervescence observed. Colourless odourless gas evolved extinguishes lighted splint with a 'pop' sound. H_2 gas evolved. Yellow solution turns blue/ green/ violet/ colourless. (dependent on time)
While you are waiting, continue with test 2.		
2.	Add about 2 cm depth of **FA 6** to a boiling tube. Add aqueous sodium hydroxide slowly, with shaking, until no further change is seen. Gently heat the boiling tube, taking care to avoid sputtering, until no further changes are seen. Leave the solution to cool and add aqueous barium chloride.	White ppt. formed in yellow solution. Soluble in excess leaving yellow solution. Yellow solution turned colourless. Colourless pungent gas evolved turns damp red litmus paper blue. NH_3 gas evolved. White ppt. formed
3.	Add about 1 cm depth of **FA 6** to a test-tube. Add aqueous ammonia slowly, with shaking, until no further change is seen.	White ppt. formed in yellow solution. soluble in excess leaving yellow solution.

[6]

(b) Complete Table 3.2 with the identities of the other three cations deduced in **FA 6**.

Give evidence from the observations in Table 3.1 to support your conclusions.

Table 3.2

identity	evidence
H^+	Colourless odourless gas evolved extinguishes lighted splint with a 'pop' sound or H_2 gas evolved.
NH_4^+	Colourless pungent gas evolved turns damps red litmus paper blue when heated in aqueous sodium hydroxide or NH_3 gas evolved.
Zn^{2+}	White ppt. formed when aqueous sodium hydroxide and ammonia were added. White ppt. soluble in excess aq NaOH and NH_3.

2[√] = [1] [3]

(c) The final observation in test 2 in Table 3.1 would have helped you conclude the identity of the anion in **FA 6**.

(i) Use the Qualitative Analysis Notes on pages 19–20 to deduce the anion in **FA 6**.

SO_4^{2-} .... [1]

(ii) Explain your reasoning in **(c)(i)**.

$Ba^{2+}(aq)$ tests for the presence of SO_3^{2-} or SO_4^{2-} when a white ppt. is formed.

Since **FA 6** contains H^+, SO_2 would have been liberated from SO_3^{2-} and thus

the only possible anion is SO_4^{2-}.

.... [1]

(d) Vanadium is a transition metal exhibiting various oxidation states of +2, +3, +4 and +5. Each of these states have species giving different colours in the aqueous medium. Table 3.3 gives the species and their associated colours.

Table 3.3

species	V^{2+}	V^{3+}	VO^{2+}	VO_2^+/VO_3^-	VO_4^{3-}
colour	violet	green	blue	yellow	colourless

Table 3.4 gives some standard electrode potential values involving magnesium, vanadium and their ions.

Table 3.4

electrode reaction	$E^\ominus$ / V
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	–2.38
$V^{2+}(aq) + 2e^- \rightleftharpoons V(s)$	–1.20
$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$	–0.26
$VO^{2+}(aq) + 2H^+(aq) + e^- \rightleftharpoons V^{3+}(aq) + H_2O(l)$	+0.34
$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$	+1.00
$VO_3^-(aq) + 4H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + 2H_2O(l)$	+1.00

Consider your observations when magnesium turnings were added to **FA 6** in test 1 in Table 3.1 and the information in Tables 3.3 and 3.4.

(i) Write an overall equation for the reaction that occurred between magnesium and vanadium species when you added magnesium turnings to **FA 6 in** test 1 in Table 3.1.

$2VO_2^+ + Mg + 4H^+ \longrightarrow 2VO^{2+} + Mg^{2+} + 2H_2O$ (blue) OR .... [1]
$VO_2^+ + Mg + 4H^+ \longrightarrow V^{3+} + Mg^{2+} + 2H_2O$ (green) OR
$2VO_2^+ + 3Mg + 8H^+ \longrightarrow 2V^{2+} + 3Mg^{2+} + 4H_2O$ (violet) OR
$2VO_2^+ + 5Mg + 8H^+ \longrightarrow 2V + 5Mg^{2+} + 4H_2O$ (colourless)

(ii) Based on the standard electrode potential values given in Table 3.4, predict the expected final colour of the solution in test 1 in Table 3.1 and state if your observations agree or do not agree with the prediction.

Provide a reason for your observations.

Colourless. Yes/No (depending on observation in test 1 in Table 3.1.)

Agree because excess Mg was able to reduce VO_2^+ to V. OR

Disagree because the reaction is kinetically slow and takes time to be

reduced to V.

.... [2]

Consider your observations when the boiling tube was heated in test 2 in Table 3.1 and the information in Table 3.3.

(iii) State the observation that is related to information given in Table 3.3 and write an equation for the reaction that occurred.

Explain the need for heat to bring about the change observed.

Yellow VO_2^+ reacted with OH^- to produce colourless VO_4^{3-}.

$VO_2^+ + 4OH^- \rightleftharpoons VO_4^{3-} + 2H_2O$

Heating the solution increased the rate of reaction and the change in colour occurred faster.

.....[3]

[Total: 17]

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Qualitative Analysis Notes
[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	*reaction with*	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. rapidly turning brown on contact with air insoluble in excess	off-white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^- (aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^- (aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^- (aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^- (aq)	NH_3 liberated on heating with OH^-(aq) and Al foil
nitrite, NO_2^- (aq)	NH_3 liberated on heating with OH^-(aq) and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-} (aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-} (aq)	SO_2 liberated on warming with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple