CANDIDATE NAME	( )	CLASS	23S0		

RAFFLES INSTITUTION
2023 YEAR 6 PRELIMINARY EXAMINATION

Higher 2

CHEMISTRY

9729/04

Paper 4 Practical

23 August 2023

2 hours 30 minutes

Do NOT turn over the Question Booklet until you are told to do so.

READ THESE INSTRUCTIONS FIRST.

Write your name and class on the space provided when instructed to do so.
Give details of the practical shift and laboratory where appropriate, in the space provided.
Write in dark blue or black pen.
You may use a 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 number of marks is given in brackets [ ] at the end of each question or part question.

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.

Shift	
Laboratory	
Bench Number	

For Examiner's Use	
Question	**Marks**
1	**/ 14**
2	**/ 13**
3	**/ 17**
4	**/ 11**
Total	**/ 55**

This document consists of **21** printed pages and **3** blank pages.

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

1 Determination of the kinetics of the reaction between iron(III) and iodide ions

Iron(III) ions, Fe^{3+}, oxidise iodide ions, I^-, to iodine, I_2.

equation 1 $2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(aq)$

The rate of this reaction can be measured by adding thiosulfate ions, $S_2O_3^{2-}$, and some starch indicator to the mixture. As the iodine is produced, it reacts immediately with the thiosulfate ions and is reduced back to iodide ions.

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

When all the thiosulfate ions have reacted, the iodine which continues to be produced in equation 1 then turns the starch indicator blue-black. The rate of reaction may be determined by measuring the time taken for the reaction mixture to turn blue-black.

FA 1 is aqueous iron(III) chloride, $FeCl_3$.
FA 2 is 0.0500 mol dm^{-3} aqueous potassium iodide, KI.
FA 3 is 0.00500 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$.

You will perform a series of four experiments. You will add a fixed amount of sodium thiosulfate, **FA 3**, to each of your experiments. 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) Experiment 1

1. Using appropriate measuring cylinders, add the following into a 250 cm^3 conical flask.
   - 20 cm^3 of **FA 2**
   - 20 cm^3 of **FA 3**
2. Using a measuring cylinder, add 25.0 cm^3 of deionised water into the same conical flask.
3. Add 10 drops of starch indicator into the same conical flask.
4. Measure 5.0 cm^3 of **FA 1** using a measuring cylinder.
5. Transfer the **FA 1** to the 250 cm^3 conical flask and start the stopwatch at the same time.
6. Swirl the conical flask once to mix the contents thoroughly before placing it on a white tile.
7. Stop the stopwatch when a blue-black colour first appears. You may ignore any initial colour changes that appear before the intense blue-black colouration.
8. Record the time taken, *t*, to the nearest 0.1 second for the first appearance of the intense blue-black colour.
9. Discard the reaction mixture. Wash out the conical flask and stand it upside down on a paper towel to drain.

Experiments 2, 3 and 4

Repeat Experiment 1 using three other volumes of **FA 1**, keeping the volumes of **FA 2**, **FA 3** and starch indicator the same.

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 use suitable volumes of **FA 1** that are more than 5.0 cm^3 to a maximum of 15.0 cm^3.

You should alternate the use of two 250 cm^3 conical flasks.

Prepare a table in the space provided below, in which to record:

- all volumes, to an appropriate level of precision, except those of **FA 2**, **FA 3** and the starch indicator,
- all values of *t* to the nearest 0.1 second,
- all values of rate, to 3 significant figures, which you will calculate in part **(c)**.

Results

[4]

(b) Calculate the amount of iodine produced in each experiment just before the blue-black colour first appeared. Hence, calculate the concentration of this iodine in the reaction mixture (you may ignore the volume of starch indicator used in each experiment).

amount of iodine produced = ……………….................... mol

concentration of iodine = ……………….................... mol dm^{-3}

[2]

(c) The rate of the reaction can be represented by the following formula.

$$\text{rate} = \frac{\text{concentration of iodine from } \textbf{(b)}}{\text{time taken, } t}$$

Use your experimental results in **(a)** to calculate the rate for Experiments 1 to 4. Then, in your table of results in **(a)**, include the value of rate, to 3 significant figures, for each experiment in a separate column.

If you were unable to answer **(b),** you may assume the concentration of iodine is 0.00130 mol dm^{-3} (this is not the correct value).

[1]

(d) **(i)** Plot a graph of rate, on the y-axis, against the volume of **FA 1**, on the x-axis on the grid in Fig 1.1.

Draw a line of best-fit, taking into account all of your plotted points.

[3]

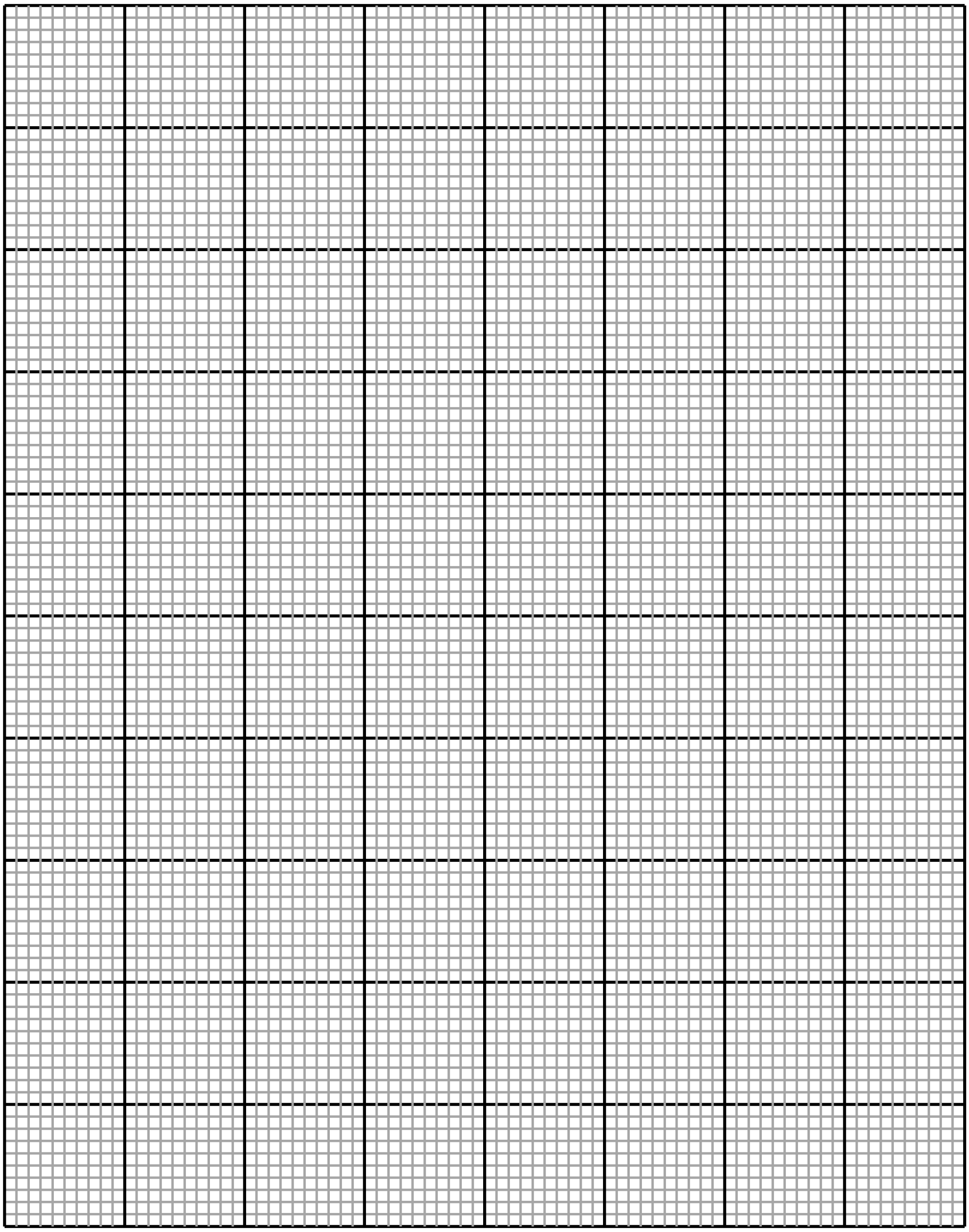

Fig. 1.1

(ii) With reference to your graph in Fig 1.1, show that the reaction is first order with respect to Fe^{3+}.

……

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……………………………………………………………………………………………………[1]

(e) A student suggested that the percentage error in the time taken for the intense blue black colour to appear could be reduced if a higher concentration of sodium thiosulfate was used in place of **FA 3**.

Do you agree with this student? Explain your answer.

……

……

…………………………………………………………………………………………………… [1]

(f) For the reaction between Fe^{3+} and I^- in equation 1, the order of reaction was experimentally determined to be second order with respect to I^-.

(i) Write the rate equation for the reaction between Fe^{3+} and I^-.

……………………………………………………………………………………………………[1]

A student proposed the following mechanism for this reaction.

Step 1: $Fe^{3+}(aq) + I^-(aq) \longrightarrow [FeI]^{2+}(aq)$ (fast)
Step 2: $[FeI]^{2+}(aq) + I^-(aq) \longrightarrow Fe^{2+}(aq) + I_2^-(aq)$ (slow)
Step 3: $2I_2^-(aq) \longrightarrow I_3^-(aq) + I^-(aq)$ (fast)

(ii) Suggest, with reasoning, if the proposed mechanism is consistent with the observed kinetics data.

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……………………………………………………………………………………………………[1]

[Total: 14]

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2 Investigation of an inorganic compound and an organic compound

FA 4 contains one cation and one anion.

FA 5 is an aqueous solution of an organic compound, $\mathbf{H_2L}$.

FA 1 contains an aqueous solution of $FeCl_3$.

You will perform tests to identify:

- the ions present in **FA 4**
- one of the functional groups in $\mathbf{H_2L}$ and hence deduce its possible structure.

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

Test and identify any gases evolved. If there is no observable change, write **no observable change**.

(a) **(i)** Carry out the following tests. Carefully record your observations in Table 2.1.

Table 2.1

	test	observations
1	Test solution **FA 4** with Universal Indicator paper.	
2	To 1 cm depth of **FA 4** in a clean test-tube, add 1 cm depth of aqueous sodium carbonate.	
3	Add 1 cm depth of **FA 4** into a clean test-tube. Add aqueous sodium hydroxide, slowly with shaking, until no further change is seen.	

[3]

(ii) Identify the cation in **FA 4**. Use evidence from your observations in Table 2.1 to support your deduction.

cation ……………………………………………………………………………………..……..

evidence …………………………………………………………………………………………

……………………………………………………………………………..……….........

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

(iii) Devise and perform a series of simple tests to identify the anion in **FA 4**. Your test should be based on the Qualitative Analysis Notes on pages 23 – 24 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.

The anion is not a nitrite, sulfite or sulfate ion.

test	observations

[2]

(iv) Use your observations in **(a)(iii)** to deduce the identity of the anion in **FA 4**.

anion ……..……………………………………………………………………………[1]

(b) **(i)** Carry out the following tests. Carefully record your observations in Table 2.2.

Table 2.2

	test	observations
	To 1 cm depth of **FA 1**, aqueous iron(III) chloride, in a clean test-tube, add 1 drop of aqueous sodium hydroxide. A precipitate will form immediately. Then, add **FA 1**, dropwise, with shaking, until the precipitate just dissolves. You may use a clean glass rod to stir the mixture and dissolve the precipitate. This solution is neutral iron(III) chloride. The complex ion $[Fe(H_2O)_6]^{3+}$ is responsible for the orange colour of neutral iron(III) chloride. Proceed to test 1 using this solution.	
1	To 1 cm depth of neutral iron(III) chloride in a clean test-tube, add 10 drops of **FA 5** and shake the test-tube. This solution is **FA 6**. Proceed to test 2 using this solution.	
2	To the solution of **FA 6,** add aqueous sodium hydroxide dropwise, with shaking, until no further change is seen.	
3	**Do not perform the following test.** Add about 1 cm depth of **FA 5** in a clean test-tube. To this test-tube, add 2 cm depth of dilute sulfuric acid followed by 3 drops of potassium manganate(VII) solution and shake well. Heat the test-tube in a hot water bath.	No decolourisation of purple $KMnO_4$.

[2]

(ii) With reference to the colour of **FA 6** in Table 2.2, suggest one of the functional groups present in **H_2L**.

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

(iii) The molecular formula of **H_2L** is $C_7H_6O_3$. Draw one possible structure for **H_2L**. Use the observations from Table 2.2.

[1]

(iv) The anion form of **H_2L** is a bidentate ligand. Using **L^{2-}** to represent the ligand, write a chemical equation for the reaction that occurred when you added **FA 5** to neutral iron(III) chloride in test 1 in Table 2.2.

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

(v) Suggest an explanation for the observations in test 2 in Table 2.2.

…………………………………………………………………………………...……..........

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

[Total: 13]

3 Determination of the percentage by mass of magnetite in iron ore

Iron ore consists mainly of magnetite, Fe_3O_4. Magnetite contains **equal amounts** of FeO and Fe_2O_3.

Sample **A** is a 15.0 g sample of iron ore.

When sample **A** is added to excess dilute sulfuric acid, the following reaction takes place.

equation 3 $FeO(s) + H_2SO_4(aq) \longrightarrow FeSO_4(aq) + H_2O(l)$

The resulting mixture is filtered and transferred quantitatively to a 250 cm^3 volumetric flask. Deionised water was added to the 250 cm^3 mark. This solution is **FA 7**.

FA 8 is 0.00500 mol dm^{-3} potassium manganate(VII), $KMnO_4$.
FA 9 is 1.00 mol dm^{-3} sulfuric acid, H_2SO_4.

You will perform a dilution of **FA 7** before titration with potassium manganate(VII).

(a) (i) Dilution of FA 7

1. Using the burette (labelled **FA 7**), measure between 30.00 cm^3 and 30.70 cm^3 of **FA 7** into the 250 cm^3 volumetric flask.
2. Make up the contents of the flask to the 250 cm^3 mark with deionised water.
3. Stopper the flask and mix the contents thoroughly. Label this diluted solution **FA 10**.
4. Record your volume of **FA 7** used, to an appropriate level of precision, in the space provided on page 13.

Titration of FA 10 against FA 8

5. Fill the other burette provided with **FA 8**.
6. Pipette 25.0 cm^3 of **FA 10** into the conical flask.
7. Using a measuring cylinder, transfer 10.0 cm^3 of **FA 9** to the same conical flask.
8. Run **FA 8** from the burette into this flask until the first permanent pale pink (or orange) colour is obtained.
9. Record your titration results, to an appropriate level of precision, in the space provided on page 13.
10. Repeat steps 6 to 9 until consistent results are obtained.

Dilution of FA 7

Titration results

[3]

(ii) From your titration results, obtain a suitable volume of **FA 8** to be used in your calculations. Show clearly how you obtained this volume.

volume of **FA 8** = ……………….................... [3]

(b) **(i)** Calculate the amount of MnO_4^- ions present in the volume calculated in **(a)(ii)**.

amount of MnO_4^- ions = ……………….................... [1]

(ii) equation 4 $MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

Using equation 4, calculate the amount of Fe^{2+} ions in 250 cm^3 of **FA 10**.

amount of Fe^{2+} ions in 250 cm^3 of **FA 10** = ……………................................ [1]

(iii) Calculate the amount of Fe^{2+} ions in 250 cm^3 of **FA 7**.

amount of Fe^{2+} ions in 250 cm^3 of **FA 7** = …………………................................ [1]

(iv) Calculate the percentage by mass of magnetite in sample **A**.
[A_r: Fe, 55.8; O, 16.0]

percentage by mass of magnetite in sample **A** = ……………….................... [4]

(c) Instead of titrating against potassium manganate(VII) solution, a student wanted to use potassium dichromate(VI) solution.

(i) By considering the reduction potentials, $E^\ominus$, of the following half-equations, show that this redox reaction is spontaneous.

electrode reaction	$E^\ominus$ / V
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77

[1]

(ii) Other than toxicity concerns, suggest a reason why using potassium dichromate(VI) solution for the titrimetric determination of Fe^{2+} ions is not suitable, in spite of the redox reaction being spontaneous.

……………………………………………………………………………………..…….......

……………………………………………………………………………………..…….......

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

(d) **(i)** A student follows the whole procedure described on page 12 using a 8.00 g sample of iron ore from another region. The student calculates the value of the mass of magnetite to be 5.95 g. The actual value of the mass of magnetite is 6.03 g.

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

percentage error = ……………….................... % [1]

(ii) The student calculates that the maximum total percentage error of the whole procedure is 1.73%.

Did the student perform the experiment well? Explain your answer.

……………………………………………………………………………………..……......

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

[Total: 17]

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4 Planning

The precipitation of Elpasolite, NaK_2AlF_6, is an exothermic reaction which can be used to determine the concentration of Na^+ in food samples.

$$Na^+(aq) + 2K^+(aq) + Al^{3+}(aq) + 6F^-(aq) \longrightarrow \underset{\text{Elpasolite}}{NaK_2AlF_6(s)} \quad \Delta H_{reaction} < 0$$

Solution **B** contains 0.120 mol dm^{-3} $Al^{3+}(aq)$ and excess amounts of $K^+(aq)$ and $F^-(aq)$.
Solution **Z** contains approximately 0.075 mol dm^{-3} of $NaCl$, prepared by dissolving a packet of instant noodle seasoning.

A series of experiments is conducted to measure the increase in temperature when different volumes of solution **B** and solution **Z** are mixed. The total volume of the mixture is kept at 60.0 cm^3 for all the experiments.

A graph of temperature increase, ΔT, against volume of **B** is then plotted. The equivalence volume is obtained when stoichiometric amounts of Al^{3+} in solution **B**, and Na^+ in solution **Z**, have reacted. Two best-fit graph lines are drawn. One line is drawn using data before the equivalence volume and the second line using the remaining data. These lines are then extrapolated (extended) until they cross.

Using the data obtained graphically, the concentration of Na^+ in solution **Z** and the molar enthalpy change of reaction, $\Delta H_{reaction}$, for the precipitation of Elpasolite may be determined.

(a) Keeping the total volume of the reaction mixture at 60.0 cm^3, calculate the approximate equivalence volume of solution **B**.

[1]

(b) Plan a procedure that would provide sufficient data to allow you to experimentally determine the equivalence volume of the reaction between solutions **B** and **Z**, and the corresponding ΔT.

You may assume that you are provided with:

- solutions **B** and **Z**,
- Styrofoam cup,
- the equipment normally found in a school or college laboratory.

In your plan you should include brief details of:

- the apparatus you would use,
- the quantities you would use, so that the total volume of solution is 60.0 cm^3,
- the procedure you would follow,
- the measurements you would make to allow a suitable graph to be drawn and the tabulation of data.

[6]

(c) Sketch the graph you would expect to obtain on the axes in Fig 4.1. On your graph, label

- V_{eq} for the equivalence volume of solution **B** added,
- ΔT_{eq} for the ΔT at the equivalence volume.

Fig 4.1

[2]

(d) Describe how the V_{eq} and ΔT_{eq} data obtained from the graph in **(c)** may be used to determine

- the concentration of Na^+ in solution **Z**, in mol dm^{-3},
- molar enthalpy change of reaction, $\Delta H_{reaction}$, for the precipitation of Elpasolite, in kJ mol^{-1}.

You may assume the following:

- specific heat capacity of all solutions is 4.18 J g^{-1} °C^{-1},
- density of all solutions is 1.00 g cm^{-3}.

[2]

[Total: 11]

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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 A*l* foil
nitrite, NO_2^-(aq)	NH_3 liberated on heating with OH^-(aq) and A*l* 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 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 CO_2)
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