NAME ______________________ CLASS **18S**

JURONG PIONEER JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2019

CHEMISTRY

9729/04

Higher 2

Paper 4 Practical

26 August 2019
2 hours 30 minutes

Candidates answer on the Question paper.

Additional Materials: As listed in the Confidential Instructions

READ THESE INSTRUCTIONS FIRST

Write your name, class and exam 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 a HB pencil for any diagrams, 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	
2	
3	
4	
Total	

This document consists of **23** printed pages and **1** blank page.

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

1 Determination of the identity of the halogen, X, in CH_2XCO_2H

Compound **W** is a halogenoethanoic acid, $CH_2\mathbf{X}CO_2H$, where **X** is a halogen.

A halogenoethanoic acid reacts with aqueous sodium hydroxide in two reactions.

The alkali neutralises the carboxylic acid.

reaction 1 $NaOH + CH_2\mathbf{X}CO_2H \rightarrow CH_2\mathbf{X}CO_2Na + H_2O$

The halogenoalkyl group then undergoes a substitution reaction.

reaction 2 $NaOH + CH_2\mathbf{X}CO_2Na \rightarrow CH_2(OH)CO_2Na + Na\mathbf{X}$

4 g of **W** were heated for one minute with 250 cm^3 of 0.40 mol dm^{-3} aqueous sodium hydroxide in a beaker. Some of the sodium hydroxide reacted with compound **W** as shown by equations 1 and 2. The solution that remained contains unreacted sodium hydroxide. This solution is **FA 1**.

In **1(a)**, you will perform a dilution and by titrating **FA 1** with the diluted sulfuric acid, you will determine the identity of **X** in $CH_2\mathbf{X}CO_2H$.

FA 1 is aqueous sodium hydroxide after reaction with **W**.

FA 2 is 2.00 mol dm^{-3} sulfuric acid, H_2SO_4.

methyl orange indicator

(a) (i) Dilution of FA 2

1. Use a pipette to transfer 10.0 cm^3 of **FA 2** into a 250 cm^3 volumetric flask.
2. Make up the contents of the flask to the 250 cm^3 mark with deionised water.
3. Place the stopper in the flask and mix the contents thoroughly by slowly inverting the flask a number of times.
4. Label this diluted solution of sulfuric acid as **FA 3**.

(ii) Titration of FA 1 against FA 3

1. Fill the burette labelled **FA 3**, with **FA 3**.
2. Use a pipette to transfer 25.0 cm^3 of **FA 1** into the conical flask.
3. Add a few drops of methyl orange indicator.
4. Run **FA 3** from the burette into the conical flask. The end-point is reached when the yellow solution becomes orange.
5. Record your titration results, to an appropriate level of precision, in the space provided on Page 3.
6. Repeat points 2 to 5 as necessary until consistent results are obtained.

Titration results

[3]

(iii) From your titrations, obtain a suitable volume of **FA 3,** V_{FA3}**,** to be used in your calculations. Show clearly how you obtained this volume.

V_{FA3} = ... [3]

(b) **(i)** Calculate the concentration of sulfuric acid in **FA 3** that you have prepared.

[H_2SO_4] in **FA 3** = ... [1]

(ii) Calculate the amount of sodium hydroxide present in 25.0 cm^3 of **FA 1**.

amount of NaOH in 25.0 cm^3 of **FA 1** = ... [1]

(iii) Calculate the amount of sodium hydroxide in 250 cm^3 of **FA 1** and hence, calculate the amount of sodium hydroxide that reacted with **W**.

amount of NaOH that reacted with **W** = ... [2]

(iv) Use your answer to **(b)(iii)** to calculate the M_r of **W**, $CH_2\mathbf{X}CO_2H$.

Hence, deduce the identity of **X** in $CH_2\mathbf{X}CO_2H$.
[A_r: C,12.0; O,16.0; H, 1.0; F, 19.0; C*l*, 35.5; Br, 79.9; I, 126.9]

X is .... [2]

(c) **(i)** The maximum error in any single burette reading is ±0.05 cm^3.

Calculate the maximum percentage error in the volume of **FA 3** used in **1(a)(iii)**.

maximum percentage error in the volume of **FA 3** used = ... [1]

(ii) Apart from the inaccuracies in reading the volumes of solutions, suggest a significant source of error in this experiment.

Explain how you could minimise this error.

....

.... [1]

[Total: 14]

2 An experiment to investigate the behaviour of acids and bases in aqueous solutions

FA 4 is 1.00 mol dm^{-3} sodium hydrogencarbonate, $NaHCO_3$.

FA 5 is aqueous sodium hydroxide.

You will need access to the **FA 2** solution you used earlier.

According to Arrhenius theory of acids and bases, an acid produces H^+ ions and a base produces OH^- ions, in aqueous solution. An acid–base reaction involves reacting together these two ions to produce water molecules as shown in the following equation.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \qquad \Delta H_{neutralisation} = -57.0 \text{ kJ mol}^{-1}$$

This experiment involves two different acid-base reactions.

The first reaction is between sodium hydrogencarbonate, **FA 4**, and sodium hydroxide, **FA 5**.

reaction 3 $\quad NaHCO_3(aq) + NaOH(aq) \rightarrow Na_2CO_3(aq) + H_2O(l) \qquad \Delta H_3$

The molar enthalpy change for reaction 3, ΔH_3, is the enthalpy change when 1.00 mol of $NaHCO_3$ reacts completely with NaOH.

Instead of using an indicator to determine the end–point, you will perform a thermometric titration to determine the equivalence point of the reaction. You will add portions of **FA 5** progressively to a known volume of **FA 4**. You will continue adding **FA 5** until the equivalence point is reached and passed. Throughout the experiment you will note and record the temperature of the mixture after each addition.

You will then analyse your results graphically to determine the

- titration volume at the equivalence point, $V_{equivalence}$,
- maximum temperature change, ΔT_{max},
- molar enthalpy change, ΔH_3, for reaction 3.

(a) Determination of the enthalpy change of reaction between FA 4 and FA 5

In this experiment you will need to record the maximum temperature of the reaction mixture when specified volumes of **FA 5** have been added. It is important that the volume of **FA 5** recorded is the total volume you have added up to that point when the temperature reading was made.

Note: If you overshoot on an addition, record the **actual** total volume of **FA 5** added up to that point.

In an appropriate format in the space provided below, record all values of temperature, *T*, and each total volume of **FA 5** added.

1. Fill a burette with **FA 5**.
2. Place a Styrofoam cup inside a second Styrofoam cup which is held in a glass beaker to prevent it tipping over.
3. Using a pipette, transfer 25.0 cm^3 of **FA 4** into the first Styrofoam cup.
4. Stir the **FA 4** solution in the cup with the thermometer. Read and record its temperature. Tilt the cup if necessary to ensure the thermometer bulb is fully immersed.
5. From the burette, add 2.00 cm^3 of **FA 5** to the cup and stir the mixture thoroughly.
6. Read and record the maximum temperature of the mixture, *T*, and the volume of **FA 5** added.
7. Repeat points **5** and **6** until a total of 30.00 cm^3 of **FA 5** has been added. After each addition of **FA 5**, record the maximum temperature of the mixture and the total volume of **FA 5** added up to that point.

Results

[2]

(b) **(i)** On the grid below, plot a graph of temperature, T on the y–axis against volume of **FA 5** added on the x–axis.

[3]

(ii) Draw **two** smooth lines of best fit.

- The first best–fit curve or straight line should be drawn using the plotted points where the temperature is **rising.**
- The second best–fit curve or straight line should be drawn using the plotted points where the temperature is **falling**.
- Extrapolate these lines until they cross.

(iii) Determine from your graph

- the maximum temperature reacted, T_{max},
- the maximum temperature change, ΔT_{max}, and
- the volume, $V_{\text{equivalence}}$, of **FA 5** needed to completely react with 25.0 cm^3 of **FA 4**.

Show on your graph how you obtained these values.
Record these values in the spaces provided below.

Maximum temperature reached, $\boldsymbol{T}_{\text{max}}$ = ...

Maximum temperature change, $\Delta\boldsymbol{T}_{\text{max}}$ = ...

Volume of **FA 5** required, $\boldsymbol{V}_{\text{equivalence}}$ = ... [3]

(iv) Calculate the concentration of sodium hydroxide, [NaOH], in **FA 5**.

[NaOH], in **FA 5** = ... [1]

(v) Calculate the heat change, *q*, for your experiment in **(a)** and hence determine a value for the molar enthalpy change for reaction 3, ΔH_3.

You should assume that the:

- Specific heat capacity of the mixture is 4.18 J g^{-1} K^{-1};
- Density of the mixture is 1.00 g cm^{-3}.

ΔH_3 = ... [2]

Question 2 continues on the next page.

(c) **The reaction between FA 4 and FA 2**

The second acid–base reaction is between sodium hydrogencarbonate, **FA 4**, and sulfuric acid, **FA 2**.

reaction 4 $NaHCO_3(aq) + \frac{1}{2}H_2SO_4(aq) \rightarrow \frac{1}{2}Na_2CO_3(aq) + H_2O(l) + CO_2(g)$ ΔH_4

The molar enthalpy change for reaction 4, ΔH_4, is the enthalpy change when 1.00 mol of $NaHCO_3$ reacts completely with H_2SO_4.

A student carried out an experiment to determine the molar enthalpy change for reaction 4, ΔH_4, using a known volume of **FA 4** that reacts with excess **FA 2**.

The student carried out the experiment according to the following instructions.

1. Using a measuring cylinder, transfer 40.0 cm^3 of **FA 4** into a Styrofoam cup, which is placed in a 250 cm^3 glass beaker.
2. Stir and measure the temperature of this **FA 4**, $T_{\textbf{FA 4}}$.
3. Using another measuring cylinder, measure 15.0 cm^3 of **FA 2**.
4. Stir and measure the temperature of this **FA 2**, $T_{\textbf{FA 2}}$.
5. Carefully add the **FA 2** from the measuring cylinder to the **FA 4** in the Styrofoam cup in small portions to avoid too much frothing.
6. Using the thermometer, stir the mixture continuously. Measure and record the lowest temperature, T_{min}, of the mixture.

The results are shown in the table in Table 2.1.

$T_{FA\ 4}$ / °C	28.6
$T_{FA\ 2}$ / °C	28.9
T_{min} / °C	28.2

Table 2.1

(d) Calculate the molar enthalpy change for reaction 4, ΔH_4. For this experiment, the weighted average initial temperature, T_{average}, of **FA 4** and **FA 2** may be calculated using the formula below.

$$T_{average} = \frac{(V_{FA2} \times T_{FA2}) + (V_{FA4} \times T_{FA4})}{(V_{FA2} + V_{FA4})}$$

You should assume that the:

- Specific heat capacity of the mixture is 4.18 J g^{-1} K^{-1};
- Density of the mixture is 1.00 g cm^{-3}

ΔH_4 = ... [2]

(e) Ionic equations for neutralisation, reaction 3 and reaction 4 are shown below.

$H^+ + OH^- \rightarrow H_2O$ $\Delta H_{\text{neutralisation}} = -57.0$ kJ mol^{-1}

reaction 3 $HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$ ΔH_3

reaction 4 $HCO_3^- + H^+ \rightarrow H_2O + CO_2$ ΔH_4

Carbon dioxide may be removed from stale air by bubbling the air through aqueous alkali. An equation for this reaction is given below.

reaction 5 $2OH^-(aq) + CO_2(g) \rightarrow CO_3^{2-}(aq) + H_2O(l)$ ΔH_5

Use your answers to **2(b)(v)** and **2(d)**, together with the molar enthalpy change of neutralisation, $\Delta H_{\text{neutralisation}}$, to determine a value for the molar enthalpy change for this reaction, ΔH_5.

ΔH_5 = ... [4]

(g) An alternative definition of acid-base behavior was proposed by Brønsted and Lowry.

In terms of the Brønsted–Lowry theory of acids and bases, suggest the role of hydrogencarbonate ions, HCO_3^-, in reaction 3 and in reaction 4. Explain your answer.

reaction 3

role of HCO_3^- ions ....

explanation ....

reaction 4

role of HCO_3^- ions ....

explanation .... [2]

[Total: 19]

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3 **Investigation of some reactions involving transition element ions.**

Manganese containing compounds are often used in redox reactions in the laboratory.

In aqueous solution, $MnO_4^-(aq)$ ions are stable. However, $MnO_4^{2-}(aq)$ ions, which has a characteristic green colour, are unstable as they spontaneously undergo a redox reaction.

Both MnO_4^- and MnO_4^{2-} solid compounds are stable.

FA 6 is solid potassium manganate(VII), $KMnO_4$.

FA 8 is a hydrocarbon compound.

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**.

Table 3.1

		tests	observations
(a)	**(i)**	Add one spatula of **FA 6** to a hard–glass test–tube. Heat gently for about 10s and then strongly for about 20s. Leave the test–tube and residue to cool completely. Keep the residue for use in **3(a)(ii)**. **While waiting, you can start on 3(d).**	
	(ii)	Add deionised water to a small beaker until it is about half full. Place the beaker on a white tile. Pour the cooled residue from **3(a)(i)** **slowly** into the deionised water in the beaker. **Observe the solution closely.** Swirl the solution and filter a small portion of this solution into a clean test–tube. The filtrate is **FA 7**.	
	(iii)	Add 1 cm depth of **FA 7** to a test–tube. Add $Fe^{2+}(aq)$, slowly with shaking, until no further change is seen.	

[3]

(b) Table 3.2 gives some standard electrode potential values involving manganese containing ions.

Table 3.2

electrode reaction	*E* / V
$MnO_4^- + 8H^+ + 5e^- \ll Mn^{2+} + 4H_2O$	+1.52
$MnO_4^- + e^- \ll MnO_4^{2-}$	+0.56
$MnO_4^{2-} + 4H^+ + 2e^- \ll MnO_2 + 2H_2O$	+2.26

Consider your observations when deionised water was added to the residue in **3(a)(ii)**, together with those you made in **3(a)(iii)** and the information in Table 3.2.

(i) Use data from Table 3.2 to explain what happens to manganese during this reaction.

....

....

.... [1]

(ii) State the type of reaction that has occurred in **3(a)(ii)**.

.... [1]

(c) The decomposition reaction in **3(a)(i)** also produces MnO_2 as one of the products.

Write a balanced equation for the decomposition reaction occurring in **3(a)(i)** using your observations in Table 3.1.

.... [1]

Question 3 continues on the next page.

(d) **Before starting this question, ensure your Bunsen burner is turned off.**

Hot water is provided for the hot water bath required in this question.

Perform the tests described in Table 3.3, and record your observations in the table. Test and identify any gases evolved. If there is no observable change, write **no observable change**.

Table 3.3

		tests	observations
	(i)	Add 2 cm depth of aqueous sodium hydroxide in a test–tube. Add 5 drops of **FA 8** to this test-tube. Add a few drops of aqueous potassium manganate(VII).	
	(ii)	Add 2 cm depth of aqueous sulfuric acid in a test–tube. Add 5 drop of **FA 8** to this test–tube. Add a few drops of aqueous potassium manganate(VII). Place the mixture in the hot water bath for a few minutes.	
	(iii)	Add 5 cm depth of deionised water in a test–tube. Add 1 drop of **FA 8** to this test–tube. Add aqueous bromine slowly, with shaking, until no further change is seen.	Yellow aqueous bromine decolourises

[1]

(e) When **FA 8** reacts with aqueous potassium managanate(VII) under alkaline conditions in **3(d)(i)**, compound **Z** is the main organic product formed.

The molecular formula of **Z** is $C_6H_{12}O_2$.

(i) Deduce the molecular formula of **FA 8**.

Explain your deduction. Your explanation should be supported by evidence from your observations in **3(d)(i)**.

molecular formula of **FA 8** .... [2]

explanation ....

....

(ii) Draw possible structures of **FA 8** and compound **Z**.

FA 8	compound **Z**

[1]

[Total: 10]

4 Planning

In acidic solution, potassium manganate(VII) undergoes a redox reaction with ethanedioate ions, $C_2O_4^{2-}$ as shown in reaction 6.

reaction 6 $2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$

As the initial reaction between potassium manganate(VII) and ethanedioate ions is slow, a small amount of Mn^{2+} is added to the reaction mixture to speed up the reaction. The order of the reaction with respect to the concentration of potassium manganate(VII) may be determined by performing a number of experiments and measuring the time taken, *t*, for a fixed volume of CO_2 to be produced in each of these experiments.

A teacher demonstrated one of the experiments as follows.

> She prepared a mixture containing 50 cm^3 of potassium manganate(VII), 50 cm^3 of sulfuric acid and 1 cm^3 of aqueous manganese(II) sulfate.
>
> 50 cm^3 of sodium ethandioate was added to the mixture and, 40 cm^3 of gas was collected after 12 seconds.

The order of reaction can be graphically determined by plotting the common logarithm of 1/*t*, lg(1/*t*) against the common logarithm of the volume of $KMnO_4$ used, $\lg(V_{KMnO_4})$.

(a) Write a plan for such a series of experiments.

You may assume that you are provided with:

- 0.02 mol dm^{-3} potassium manganate(VII), $KMnO_4$,
- 0.2 mol dm^{-3} sodium ethandioate, $Na_2C_2O_4$,
- 1.0 mol dm^{-3} dilute sulfuric acid, H_2SO_4,
- aqueous manganese(II) sulfate solution,
- deionised water,
- the apparatus normally found in a school or college laboratory.

Your plan should include details of:

- a clearly labelled diagram of the experimental set–up used for gas collection,
- the quantities of reactants and the apparatus to be used,
- the procedure that you would follow,
- the measurements you would make to allow a suitable graph to be drawn.

Diagram of the experimental set–up:

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(b) Sketch, on Fig. 4.1, the graph you would expect to obtain.

Explain your answer.

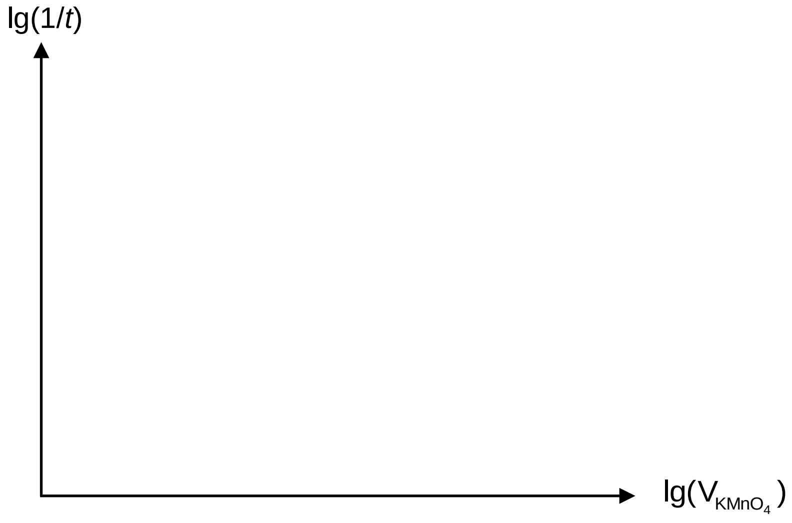

Fig 4.1

explanation ....

....

....

....

.... [3]

(c) Describe how you would use your graph to determine the order of reaction with respect to the concentration of potassium manganate(VII).

.... [1]

(d) **(i)** Suggest why the initial reaction between manganate(VII) ions and ethanedioate ions is slow.

....

.... [1]

(ii) A small amount of Mn^{2+} is added to catalyse the reaction.

State the type of catalyst involved in the reaction. Explain your answer.

.... [1]

(iii) Using the information given in **4(d)(ii)** and reaction 6, sketch, on Fig. 4.2, the graph you would expect to obtain if the experiment was conducted without the addition of $Mn^{2+}(aq)$ solution.

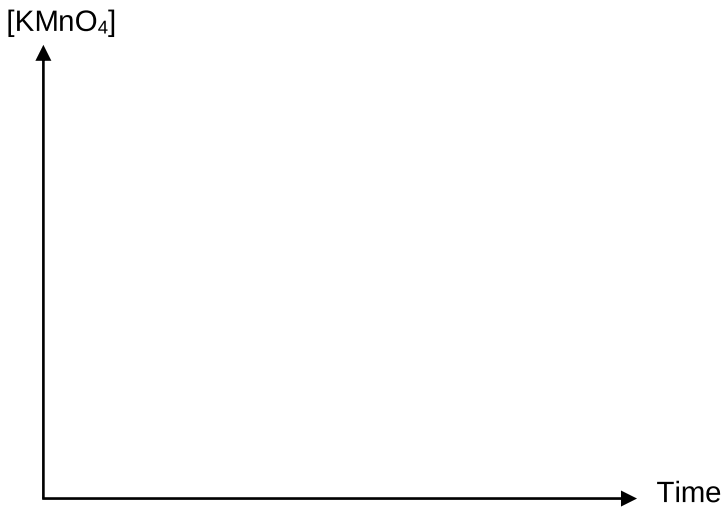

Fig 4.2

[1]

[Total: 12]

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 Aqueous Anions

Anion	***Reaction***
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
choride, 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 on warming with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in excess dilute strong acids)

(c) Tests for Gases

gas	***Test and test results***
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 acidified aqueous 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