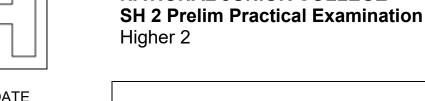
NATIONAL JUNIOR COLLEGE



CANDIDATE NAME

SUBJECT CLASS

REGISTRATION NUMBER

# **CHEMISTRY**

Paper 4 Practical

Tuesday 15 August 2023

9729/04

2 hours 30 minutes

Candidates answer on the Question paper.

# **READ THESE INSTRUCTIONS FIRST**

or if you do not use appropriate units.

question or part question.

Write your identification number and name.

Give details of the practical shift and laboratory where appropriate, in the boxes provided. Write in blue or black pen.

You may use an HB pencil for any diagrams or graphs.

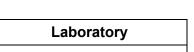
Do not use staples, paper clips, glue or correction fluid.

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

The number of marks is given in brackets [] at the end of each

Qualitative Analysis Notes are printed on pages 19 and 20.



Shift

For Examiner's use		
1	/ 13	
2	/ 17	
3	/ 13	
4	/ 12	
Total	/ 55	

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

#### Determine the reacting mole ratio of reagent X with Fe<sup>2+</sup> 1

A common oxidising agent for  $Fe^{2+}$  ions is manganate(VII) ions in an acidic medium.

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

Another oxidising agent that is also able to oxidise  $Fe^{2+}$  to  $Fe^{3++}$  is reagent **X**.

In this experiment, a limited amount of **X** is added to a solution of  $Fe^{2+}$ . The resultant mixture containing unreacted Fe(II) ions will be titrated with acidified MnO<sub>4</sub><sup>-</sup>.

FA 1 is a solution containing 0.075 mol dm<sup>-3</sup> iron(II) sulfate, FeSO<sub>4</sub>.

**FA 2** is 0.010 mol dm<sup>-3</sup> potassium manganate(VII), KMnO<sub>4</sub>.

**FA 3** is 0.025 mol dm<sup>-3</sup> of a reagent **X**.

**FA 4** is 1.0 mol dm<sup>-3</sup> sulfuric acid, H<sub>2</sub>SO<sub>4</sub>.

#### (a) Procedure

- 1. Fill a burette with FA 3 and another burette with FA 2.
- 2. Pipette 25.0 cm<sup>3</sup> of FA 1 into a conical flask and add 10 cm<sup>3</sup> of FA 4 using a 10.0 cm<sup>3</sup> measuring cylinder into the same conical flask.
- 3. Run 12.00 cm<sup>3</sup> of **FA 3** from the burette into the conical flask.
- 4. Titrate the mixture against FA 2 until the first permanent pink colour remains in the solution.

You only need to do the titration ONCE. Record your titration result in the space below.

(b) (i) Calculate the amount of  $Fe^{2+}$  ions in **FA 1** that reacted with  $MnO_4^-$  in **FA 2**.

amount of  $Fe^{2+}$  ions in **FA 1** reacted with  $MnO_4^-$  in **FA 2** = ...... mol [1]

(ii) Calculate the total amount of Fe<sup>2+</sup> ions in **FA 1** that was pipetted into the conical flask initially.

Hence, calculate the amount of  $Fe^{2+}$  ions in **FA 1** that reacted with **X** in **FA 3** added.

Total amount of  $Fe^{2+}$  ions in **FA 1** =..... mol

amount of  $Fe^{2+}$  ions in **FA 1** reacted with **X** in **FA 3** =..... mol [2]

(iii) Calculate the amount of **X** in the 12.00 cm<sup>3</sup> of **FA 3** added.

Hence, calculate the number of moles of  $Fe^{2+}$  ions that react with 1 mol of **X**.

amount of **X** =..... mol

number of moles of  $Fe^{2+}$  ions that react with 1 mol of **X** =.....[2]

(iv) The redox half equations for the possible identity of X are given below.

 $VO^{2+} + 2H^{+} + e^{-} \rightleftharpoons V^{3+} + H_2O$   $H_2O_2 + 2H^{+} + 2e^{-} \rightleftharpoons 2H_2O$   $NO_3^{-} + 4H^{+} + 3e^{-} \rightleftharpoons NO + 2H_2O$   $IO_3^{-} + 5H^{+} + 4e^{-} \rightleftharpoons HIO + 2H_2O$   $NO_3^{-} + 10H^{+} + 8e^{-} \rightleftharpoons NH_4^{+} + 3H_2O$ 

Using your answer from (b)(iii), deduce with reasoning, a possible identity for X. [You may use number of moles of  $Fe^{2+}$  ions that react with 1 mol of X = 8.12 for this question if you did not get an answer for (b)(iii). Note that this value is **not** the correct answer for (b)(iii).]

(v) Use the information below to calculate the percentage error for each volume measurement in Table 1.1.

A 25 cm<sup>3</sup> measuring cylinder is graduated to 1 cm<sup>3</sup>.

The maximum error for a 25 cm<sup>3</sup> pipette is ±0.06 cm<sup>3</sup>.

Table	1.1	
-------	-----	--

Solution	Apparatus used	Volume measured /cm <sup>3</sup>	% Error
FA 1	Pipette	25.0	
FA 2	Burette	23.50	
FA 4	25 cm <sup>3</sup> Measuring cylinder	10.0	

[2]

[Total: 13]

#### 2 Determine the order of reaction with respect to iodide

In acidic solutions, iron(III) ions are reduced by iodide ions to form iron(II) ions. The iodide ions are oxidised to iodine.

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

The iodine,  $I_2$ , produced can be reacted immediately with thiosulfate ions,  $S_2O_3^{2-}$ .

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

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 for the blue-black colour to appear.

**FA 5** is 0.0500 mol dm<sup>-3</sup> potassium iodide, KI.

FA 6 is 0.0500 mol dm<sup>-3</sup> acidified iron(III) chloride, FeCl<sub>3</sub>.

**FA 7** is 0.0100 mol dm<sup>-3</sup> sodium thiosulfate, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.

FA 8 is starch.

#### (a) Procedure

#### **Experiment 1**

- 1. Using a 25.0 cm<sup>3</sup> measuring cylinder, transfer into a 100 cm<sup>3</sup> beaker
  - 20.0 cm<sup>3</sup> of **FA 5**
  - 10.0 cm<sup>3</sup> of **FA 7**
  - 10.0 cm<sup>3</sup> of **FA 8**
- 2. Swirl the beaker to mix the solutions thoroughly. Place the beaker on a white tile.
- 3. Using a 10.0 cm<sup>3</sup> measuring cylinder, transfer 10.0 cm<sup>3</sup> of **FA 6** into the same 100 cm<sup>3</sup> beaker and start timing immediately.
- 4. Swirl the beaker once and place the beaker on the white tile.
- 5. Stop timing as soon as the solution turns blue-black.
- 6. Record this reaction time, *t*, to the nearest second, in Table 2.1.
- 7. Wash out the beaker and dry it with a paper towel.

# Experiment 2

- 1. Using a 25.0 cm<sup>3</sup> measuring cylinder, transfer into a 100 cm<sup>3</sup> beaker
  - 10.0 cm<sup>3</sup> of **FA 5**
  - 10.0 cm<sup>3</sup> of deionised water
  - 10.0 cm<sup>3</sup> of **FA 7**
  - 10.0 cm<sup>3</sup> of **FA 8**
- 2. Swirl the beaker to mix the solutions thoroughly. Place the beaker on a white tile.
- 3. Using a 10.0 cm<sup>3</sup> measuring cylinder, transfer 10.0 cm<sup>3</sup> of **FA 6** into the same 100 cm<sup>3</sup> beaker and start timing immediately.
- 4. Swirl the beaker once and place the beaker on the white tile.
- 5. Stop timing as soon as the solution turns blue-black.
- 6. Record this reaction time, *t*, to the nearest second, in Table 2.1.
- 7. Wash out the beaker and dry it with a paper towel.

#### Experiments 3–5

- 1. Carry out three further experiments to investigate how the reaction time changes with different volumes of potassium iodide, **FA 5**.
- 2. The combined volume of **FA 5** and distilled water must always be 20.0 cm<sup>3</sup>.
- 3. Do not use a volume of **FA 5** that is less than  $5.0 \text{ cm}^3$ .
- 4. Record all your values of *t* and volume of **FA 5**, **FA 6**, **FA 7**, **FA 8** and deionised water used in Table 2.1.

#### (b) Results

The rate of reaction can be calculated as rate =  $\frac{1000}{\text{reaction time}}$ 

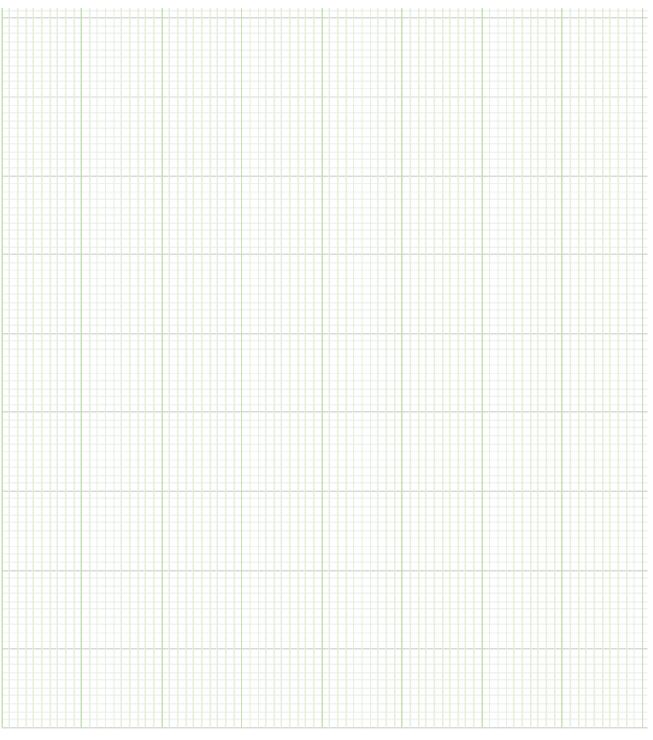
experiment	vol. of <b>FA 6</b> / cm <sup>3</sup>	vol. of <b>FA7</b> / cm <sup>3</sup>	vol. of <b>FA 8</b> / cm <sup>3</sup>	vol. of <b>FA 5</b> / cm <sup>3</sup>	vol. of deionised water / cm <sup>3</sup>	total volume / cm <sup>3</sup>	time, <i>t</i> /s	rate / s⁻¹
1	10.0	10.0	10.0	20.0	0.0	50.0		
2	10.0	10.0	10.0	10.0	10.0	50.0		
3								
4								
5								

#### Table 2.1

[3]

7

(i) On the grid below, plot a graph of rate of reaction against volume of FA 5.Include the origin, (0,0), in your scales and draw a line of best fit.



[2]

(ii) Use your graph to calculate the time that the reaction would have taken if 4.00 cm<sup>3</sup> of FA 5 had been used. Show on the graph how you obtained your answer.

(iii) Suggest why rate is inversely proportional to time as shown in the relationship.

rate =  $\frac{1000}{\text{reaction time}}$ 

 	 [1]

(c) (i) Calculate the concentration of KI in the reaction mixture for **Experiments 1** and **2**. Hence, state the relationship between volume of KI used and its concentration in the reaction mixture.

[2]

(ii) Explain, by referring to your graph, how the rate of reaction is affected by an increase in the concentration of aqueous potassium iodide, **FA 5**.

.....[2]

(d) (i) A student carries out another experiment, **Experiment 6**, to investigate the effect of iron(III) concentration on the rate of this reaction.

The rate is compared to that of **Experiment 2**. Suggest the volumes that the student could use for **Experiment 6** in Table 2.2 provided below.

			Table 2.	.2		
	vol. of	total				
experiment	FA 6	FA7	FA 8	FA 5	deionised	volume
	/ cm <sup>3</sup>	/ cm <sup>3</sup>	/ cm <sup>3</sup>	/ cm <sup>3</sup>	water / cm <sup>3</sup>	/ cm <sup>3</sup>
2	10.0	10.0	10.0	10.0	10.0	50.0
6						

[1]

# (ii) This student records a time of 215 s for **Experiment 2**.

The rate of the reaction is directly proportional to the concentration of iron(III) ions.

Suggest how long it would take the reaction mixture proposed for **Experiment 6** in (d)(i) to turn blue-black. Assume that **Experiment 6** is carried out at the same temperature as **Experiment 2**.

### Do not carry out Experiment 6.

time = ..... s [1]

- (e) Thiosulfate ions can also react with acid to form sulfur, sulfur dioxide and water.
  - (i) Write an equation for the reaction between thiosulfate ions and hydrogen ions in aqueous solution.

.....[1]

(ii) A student carries out the same investigation as **Experiment 2** in (d)(ii) but the solutions are mixed in a different order.

The student places **FA 5** and distilled water in one beaker and all the other reactants in a second beaker. The student then transfers the mixture **after 5 minutes** from the second beaker to the first and starts timing.

Suggest if the time taken for this experiment would be greater than, less than or no change from 215 s.

[Total: 17]

# 3. Identification of ions in inorganic compounds

FA 9 and FA 10 are aqueous solutions each containing a cation and chloride.

**FA 11** is an aqueous solution containing a cation and an anion.

FA 12 is a solution of potassium iodide, KI.

- **FA 13** is a solution of sodium thiosulfate,  $Na_2S_2O_3$ .
- (a) Carry out the following tests. Carefully record your observations in Table 3.1.

Unless stated otherwise, 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**.

(i)

Table	3.1

	tests	observations	
		FA 9	FA 10
1	To a 1 cm depth of the respective <b>FA</b> in a test tube, add an equal volume <b>FA 12</b> .		
	To the resultant mixture, add excess <b>FA 13</b> .		
2	To a 1 cm depth of the respective <b>FA</b> in a test tube, add aqueous ammonia, slowly with shaking, until no further change is observed.		
	1		[3]

(ii) Identify the cation in **FA 9** and **FA 10** and state the evidence for each cation by completing Table 3.2.

		Table 3.2
	cation	evidence
FA 9		
FA 10		

# [2]

(iii) When a spatula of magnesium powder is added to a 1 cm depth of **FA 10** in a test tube, effervescence was observed.

Write equations to explain the observation.

.....[1]

- (b) **FA 11** is an aqueous solution containing one anion and one cation. Only one of these ions contains nitrogen. **FA 11** does not contain sulfite,  $SO_3^{2^-}$  ion.
  - (i) Carry out the following tests to identify the **cation** in **FA 11** and record the observations in Table 3.3.

Table 3	3.3
---------	-----

	tests	observations
1	To 1 cm depth of <b>FA 11</b> in a boiling tube, add aqueous sodium hydroxide slowly with shaking, until no further change is observed. Warm the resultant solution.	
2	To 1 cm depth of <b>FA 11</b> in a test tube, add aqueous ammonia slowly with shaking, until no further change is observed.	

### 

(ii) Carry out further tests to identify the anion in **FA 11**, using only any bench reagent provided, and hence write the formula of **FA 11**.

Record, in a table in the space below, the reagents, conditions and observations for the tests.

You **must** use a boiling tube if any liquid is heated.

#### 4. Planning

A more reactive metal will displace a less reactive metal from a solution of its salt. This reaction is exothermic. If the same reaction is set up in an electrochemical cell, instead of an enthalpy change, electrical energy is produced, and a cell voltage can be measured. This relationship can be shown in the equation below.

$$\Delta H - T\Delta S = -nFE_{cell}$$

You are to plan an investigation of the reaction of three different metals (zinc, magnesium and iron) with aqueous copper(II) sulfate. You will plan to investigate whether there is a relationship between their cell potential values, and their enthalpy changes of reaction,  $\Delta H_{\rm r}$ .

$$Zn(s) + Cu2+ (aq) \longrightarrow Zn2+ (aq) + Cu(s)$$
$$Mg(s) + Cu2+ (aq) \longrightarrow Mg2+ (aq) + Cu(s)$$
$$Fe(s) + Cu2+ (aq) \longrightarrow Fe2+ (aq) + Cu(s)$$

(a) The first part of the investigation is to determine the enthalpy change,  $\Delta H_r$ , for the reaction of zinc with 1.00 mol dm<sup>-3</sup> copper(II) sulfate.

You are provided with a sample of powdered zinc and aqueous copper(II) sulfate.

$$Zn(s) + CuSO_4 (aq) \longrightarrow ZnSO_4 (aq) + Cu(s)$$
  $\Delta H_r$ 

The maximum temperature change occurring during this reaction can be determined graphically. The maximum temperature change,  $\Delta T_{max}$ , obtained from the graph can be used to calculate the enthalpy change of reaction,  $\Delta H_{r.}$ 

In this question, you are to plan a procedure that would provide sufficient data to allow you to determine a reliable value for the enthalpy change of reaction,  $\Delta H_r$ .

(i) Calculate the minimum mass of zinc that needs to be added to 100 cm<sup>3</sup> of 1.00 mol dm<sup>-1</sup> copper(II) sulfate to ensure that zinc is in excess.

[A<sub>r</sub> : Zn, 65.4 ; Cu, 63.5 ; S, 32.1 ; O, 16.0]

[1]

(ii) Plan an investigation to determine the maximum temperature change,  $\Delta T_{max}$ , graphically for the reaction between aqueous copper(II) sulfate and zinc powder.

Measurements should be taken

- before reaction starts
- during the reaction
- for some time after the reaction is complete

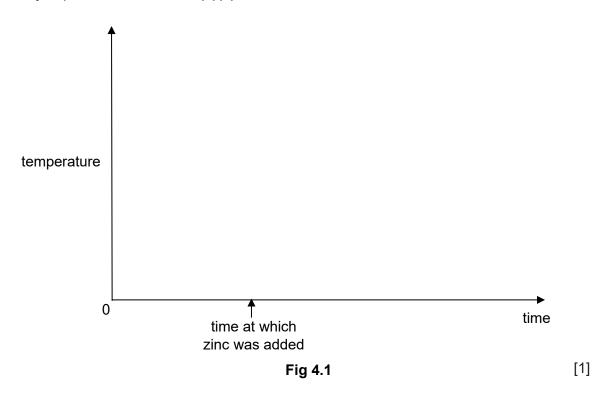
You may assume that you are provided with

- 100 cm<sup>3</sup> of 1.00 moldm<sup>-3</sup> copper(II) sulfate
- 10 g powdered zinc
- 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
- the procedures you would follow
- the measurements you would make to allow a suitable temperature-time graph to be drawn
- how you would ensure that an **accurate** value for  $\Delta T_{max}$  is obtained.

..... .....[5] (iii) Sketch, on Fig. 4.1, the graph you would expect to obtain using the measurements you planned to make in **4(a)(ii)**.



(b) In one experiment, the increase in temperature when the excess zinc powder is added to 50.0 cm<sup>3</sup> of 0.500 mol dm<sup>-3</sup> aqueous copper(II) sulfate is 25.9 °C.

Calculate the enthalpy change for this reaction,  $\Delta H_r$ , in kJ mol<sup>-1</sup>. Include a sign in your answer.

$$Zn(s) + Cu^{2+} (aq) \longrightarrow Zn^{2+} (aq) + Cu(s)$$

Assume the specific heat capacity, *c*, of the reaction mixture is  $4.18 \text{ J g}^{-1} \text{K}^{-1}$ . Assume 1.0 cm<sup>3</sup> of 0.500 mol dm<sup>-3</sup> aqueous copper(II) sulfate has a mass of 1.0 g.

(c) Predict how  $\Delta H_r$  may change as  $E_{cell}$  increases. Give a reason for your prediction.

.....[1]

(d) Explain why the enthalpy change determination and cell potential determination should not be carried out at different temperature from each other.

.....[1]

(e)  $E_{\text{cell}}$  values are shown for the cell reactions.

Use your answer to (b), prediction in (c) and data from the table below to predict  $\Delta H_r$  values for reactions 2 and 3.

Complete the table with these values.

	cell reaction	$E_{ m cell}$ / V	$\Delta H_{\rm r}$ / kJ mol <sup>-1</sup>
1	$Zn(s)$ + $Cu^{2+}$ (aq) $\rightarrow Zn^{2+}$ (aq) + $Cu(s)$	+1.10	
2	$Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s)$	+2.72	
3	$Fe(s) + Cu^{2+} (aq) \rightarrow Fe^{2+} (aq) + Cu(s)$	+0.78	
			[4]

[1]

[Total: 12]

# **Qualitative Analysis Notes**

# [ppt. = precipitate]

# (a) Reactions of aqueous cations

cation	reaction with			
cation	NaOH(aq)	NH₃(aq)		
aluminium, A <i>l</i> <sup>3+</sup> (aq)	white ppt. soluble in excess	white ppt. insoluble in excess		
ammonium, NH₄ <sup>+</sup> (aq)	ammonia produced on heating	_		
barium, Ba <sup>2+</sup> (aq)	no ppt. (if reagents are pure)	no ppt.		
calcium, Ca <sup>2+</sup> (aq)	white ppt. with high [Ca <sup>2+</sup> (aq)]	no ppt.		
chromium(III), Cr <sup>3+</sup> (aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess		
copper(II), Cu <sup>2+</sup> (aq),	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution		
iron(II), Fe <sup>2+</sup> (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 <sup>3+</sup> (aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess		
magnesium, Mg <sup>2+</sup> (aq)	white ppt. insoluble in excess	white ppt. insoluble in excess		
manganese(II), Mn <sup>2+</sup> (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 <sup>2+</sup> (aq)	white ppt. soluble in excess	white ppt. soluble in excess		

# (b) Reactions of anions

anion	reaction	
carbonate, CO <sub>3</sub> <sup>2-</sup>	CO <sub>2</sub> liberated by dilute acids	
chloride, C/⁻(aq)	gives white ppt. with Ag⁺(aq) (soluble in NH₃(aq))	
bromide, Br⁻(aq)	gives pale cream ppt. with Ag⁺(aq) (partially soluble in NH₃(aq))	
iodide, I <sup>–</sup> (aq)	gives yellow ppt. with Ag⁺(aq) (insoluble in NH₃(aq))	
nitrate, NO <sub>3</sub> <sup>-</sup> (aq)	NH₃ liberated on heating with OH <sup>−</sup> (aq) and A <i>l</i> foil	
nitrite, NO <sub>2</sub> <sup>-</sup> (aq)	NH <sub>3</sub> liberated on heating with OH <sup>-</sup> (aq) and A <i>l</i> foil; NO liberated by dilute acids (colourless NO $\rightarrow$ (pale) brown NO <sub>2</sub> in air)	
sulfate, SO4 <sup>2-</sup> (aq)	gives white ppt. with Ba <sup>2+</sup> (aq) (insoluble in excess dilute strong acids)	
sulfite, SO <sub>3</sub> <sup>2–</sup> (aq)	SO <sub>2</sub> liberated with dilute acids; gives white ppt. with Ba <sup>2+</sup> (aq) (soluble in dilute strong acids)	

# (C) Tests for gases

gas	test and test result	
ammonia, NH₃	turns damp red litmus paper blue	
carbon dioxide, CO <sub>2</sub>	gives a white ppt. with limewater (ppt. dissolves with excess CO <sub>2</sub> )	
chlorine, Cl <sub>2</sub>	bleaches damp litmus paper	
hydrogen, H <sub>2</sub>	"pops" with a lighted splint	
oxygen, O2	relights a glowing splint	
sulfur dioxide, SO2	turns aqueous acidified potassium manganate(VII) from purple to colourless	

# (d) Colour of halogens

halogen	colour of element	colour in aq. solution	colour in hexane
chlorine, Cl <sub>2</sub>	greenish yellow gas	pale yellow	pale yellow
bromine, Br2	reddish brown gas / liquid	orange	orange-red
iodine, I2	black solid / purple gas	brown	purple