

TEMASEK JUNIOR COLLEGE
2022 JC2 PRELIMINARY EXAMINATION
Higher 2



CANDIDATE
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Chemistry

9729/02

Paper 2 Structured Questions

25 August 2022

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number and name in the spaces at the top of this page.

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** the questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.

The number of marks is given in brackets [] at the end of each question or part question.

For Examiner's Use		
Paper 1		/30
Paper 2	Q1	/9
	Q2	/14
	Q3	/10
	Q4	/8
	Q5	/20
	Q6	/14
	Total	/75
Paper 3		/80
TOTAL (%)		/100

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

Answer all the questions in the space provided.

- 1 (a) Element **W** is from Period 5 of the Periodic Table. The first eight ionisation energies of element **W**, in kJ mol^{-1} , are

869 1800 2690 3610 5720 6670 12000 13800

- (i) Identify element **W** and explain your answer.

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..... [2]

- (ii) Explain the difference between the first ionisation energy of element **W** compared to the element to its left on the Periodic Table.

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- 2 Boron trifluoride, BF_3 , and aluminium fluoride, AlF_3 , differ markedly in their physical properties.

compound	melting point / °C
BF_3	-127
AlF_3	1291

- (a) (i) State the type of bonding present in each of these compounds and draw 'dot-and-cross' diagrams in the boxes below to illustrate this bonding.

Type of bonding:	Type of bonding:
BF_3	AlF_3

[2]

- (ii) Outline the principles of the Valence Shell Electron Pair Repulsion theory.

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[2]

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- (iii) Boron trifluoride forms a compound with ammonia.

Use the Valence Shell Electron Pair Repulsion theory to predict and draw the likely shape of the product formed from this reaction.

Shape of product:

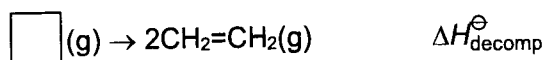
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Cyclobutane is an example of a cyclic alkane. While itself has no commercial or biological significance, more complex derivatives of cyclobutane are important in biology and biotechnology.

Cyclobutane decomposes to ethene as shown by the following equation.



A student planned to determine $\Delta H_{\text{decomp}}^{\ominus}$ by using the standard enthalpy changes of combustion of cyclobutane and ethene, represented by $\Delta H_{\text{c}}^{\ominus}$ (cyclobutane) and $\Delta H_{\text{c}}^{\ominus}$ (ethene) respectively. Both substances are gases at 298 K.

$\Delta H_{\text{c}}^{\ominus}$ (ethene) was previously determined to be $-1411 \text{ kJ mol}^{-1}$ in a flame calorimetric experiment.

To determine $\Delta H_{\text{c}}^{\ominus}$ (cyclobutane), the student decided to conduct another flame calorimetric experiment under the same conditions.

There are two stages to this experiment.

Stage I : Calibration of calorimeter (i.e. copper can, water and other components in the calorimeter)

In the experiment, the calorimeter must first be calibrated by determining its heat capacity, **C**, which is the amount of heat required to raise the temperature of the calorimeter by 1 K.

Stage II : Determination of $\Delta H_{\text{c}}^{\ominus}$ (cyclobutane) using the calibrated calorimeter.

The student carried out the flame calorimetric experiment using the calorimeter. Part of his results is shown below.

Stage I, using ethene as the fuel,

- change in temperature of water = $33.8 \text{ }^{\circ}\text{C}$
- mass of gaseous ethene burnt = 1.00 g

Stage II, using cyclobutane as the fuel,

- change in temperature of water = $32.9 \text{ }^{\circ}\text{C}$
- mass of gaseous cyclobutane burnt = 1.00 g

- (b) (i) Use the above information and experimental results to calculate the heat capacity, **C**, of the calorimeter.

[2]

- (ii) Use your answer to (b)(i) to determine ΔH_c^\ominus (cyclobutane).

[2]

- (iii) Hence, calculate the standard enthalpy change of decomposition of cyclobutane to ethene, $\Delta H_{\text{decomp}}^\ominus$.

[1]

- (c) (i) Use data from the *Data Booklet* and the $\Delta H_{\text{decomp}}^\ominus$ obtained in (b)(iii) to calculate the actual C–C bond energy in cyclobutane.

[You may assume that the difference between the C–H bond energy in cyclobutane and in ethene, and the difference between the C=C bond energy from the *Data Booklet* and in ethene are insignificant.]

[2]

- (ii) Suggest an explanation for the difference between the average C–C bond energy from the *Data Booklet* and the actual value calculated in (c)(i).

.....

 [1]

[Total: 14]

- 3 (a) SO₂ gas is found in air near volcanoes. 213 cm³ of SO₂ collected at r.t.p. near a volcano required 25.0 cm³ of 0.120 mol dm⁻³ acidified potassium dichromate(VI) solution for complete reaction.

Calculate the final oxidation state of sulfur in the product mixture.

[2]

- (b) The Contact process is an important industrial method of manufacturing sulfuric acid. The key stage of the Contact process is the reaction between sulfur dioxide and oxygen:

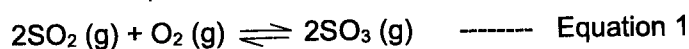


Table 3.1 shows how the percentage of sulfur trioxide in the equilibrium mixtures varies with temperature as well as the volume of the reaction vessels.

Table 3.1

Temperature /°C	Percentage of sulfur trioxide in the equilibrium mixture for vessel		
	A	B	C
800	1.68	0.009	0.88
700	2.98	0.016	1.54
600	5.70	0.032	3.02
500	11.9	0.077	6.71

Using the data in Table 3.1,

- (i) explain whether the forward reaction is exothermic or endothermic.

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- (ii) explain and rank the three vessels in order of decreasing volume.

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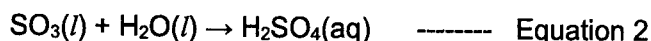
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A mixture containing 2 moles of SO₂ and 1 mole of O₂ was heated in a closed 3.60 dm³ flask at 500 °C and allowed to reach equilibrium. The flask was then rapidly cooled to liquefy SO₃. After removing gaseous SO₂ and O₂, excess water was carefully added to the liquid SO₃, causing the following reaction to occur:



The resulting solution was made up to 250 cm³ in a standard volumetric flask. 25.0 cm³ of this solution was titrated with 5.00 mol dm⁻³ NaOH and required 38.50 cm³ for complete neutralisation.

- (iii) Calculate the equilibrium amount of SO₃ at 500 °C.

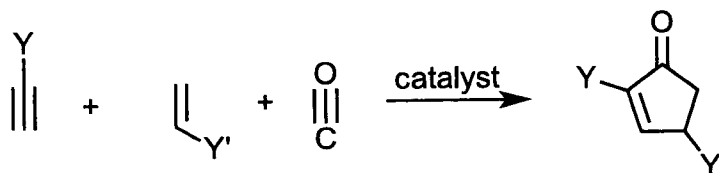
[2]

- (iv) Hence, calculate a value for the equilibrium constant, K_c , of equation 1.

[2]

[Total: 10]

- 4 (a) The Pauson-Khand reaction is a gas phase reaction between an alkyne, an alkene and carbon monoxide to form a cyclic carbonyl compound, as shown in Fig. 4.1.



where Y and Y' can be Cl or H.

Fig. 4.1

An organic compound **A** was produced from the Pauson-Khand reaction. The compound has the following composition by mass; 51.5 % C, 13.7% O, 30.5% Cl and 4.3% H. The relative molecular mass of **A** is 116.5.

Upon heating with ethanolic AgNO_3 , **A** gave a white precipitate.

- (i) Determine the molecular formula of **A** and draw its structural formula.

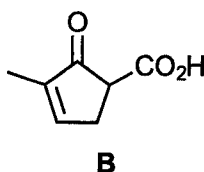
[2]

- (ii) Draw a diagram to show the orbitals of the carbonyl carbon in compound **A**. State the type of hybridisation involved.

Type of hybridisation:

[1]

- (b) Another possible product of the Pauson-Khand reaction is shown below:



Draw the organic product formed when **B** reacts with each of the following.

- (i) cold $\text{KMnO}_4(\text{aq})$ in $\text{KOH}(\text{aq})$

- (ii) LiAlH_4

[2]

12

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- (c) A flask with a volume of 100 cm^3 was first weighed with air filling the flask, and then with another gas **Z**, filling the flask. The results, measured at $26 \text{ }^\circ\text{C}$ and $1.00 \times 10^5 \text{ Pa}$ are shown.

Mass of flask containing air	= 47.930 g
Mass of flask containing Z	= 47.989 g
Density of air	= $0.00118 \text{ g cm}^{-3}$

Calculate the relative molecular mass of **Z**.

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[3]
[Total:8]

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- (iii) Using your answer in (a)(ii), calculate the value of x .

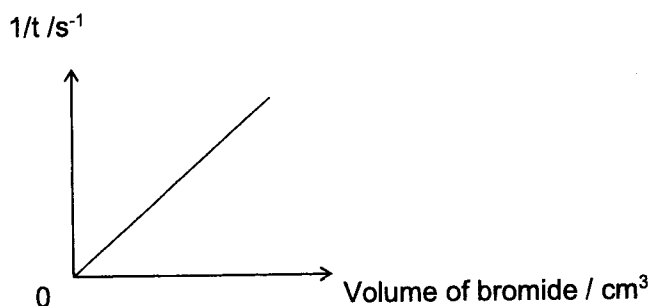
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- (iv) Another series of experiments were conducted with varying volumes of bromide ions and large excess of BrO_3^- and H^+ . The total volume of the mixture was kept constant. The results obtained were used to plot a graph of $1/t$ against the volume of bromide.



Deduce the order with respect to $[\text{Br}^-]$, explain your reasoning.

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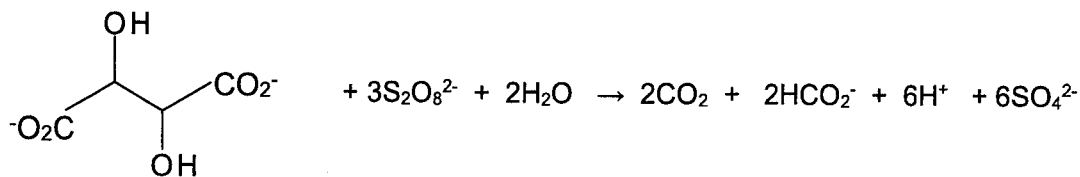
- (v) Given that the unit of the rate constant is $\text{mol}^{-3} \text{dm}^9 \text{s}^{-1}$, deduce the order with respect to $[\text{H}^+]$.

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.....[1]

- (b) The reaction between $S_2O_8^{2-}$ and tartrate ions is catalysed by iron(III) ions and the overall equation is as shown.



Tartrate ions

Write equations to illustrate how iron(III) ions catalyses the reaction.

[2]

- (c) Methyl red is a pH indicator. It is red when the pH is less than 4.4 and yellow when the pH is above 6.2.

In microbiology, methyl red is used to identify bacteria that produces acids from the metabolism of glucose. The type of acid produced depends on the specific enzymatic pathways present in the bacteria.

All the bacteria initially metabolise glucose to pyruvic acid, $\text{CH}_3\text{COCO}_2\text{H}$. After which, some bacteria use the mixed acid pathway to metabolise pyruvic acid while other bacteria use the butanediol fermentation pathway. The products formed and the colour of methyl red are shown in Table 5.2.

Table 5.2

Metabolism pathway	Products formed per mole of glucose	Colour of methyl red
Mixed acid pathway	4 mol of acids (mainly lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}$, and ethanoic acid), 1 mol of ethanol, 1 mol of CO_2 1 mol of H_2	Red
Butanediol fermentation pathway	1 mol of acid	Yellow

- (i) Explain the colours of methyl red shown in Table 5.2.

.....

 [1]

- (d) Table 5.3 shows the pK_a values of some compounds, including phenol.

Table 5.3

Compound	pK_a
Phenol	10.0
Phenylmethanol, $C_6H_5CH_2OH$	15.4
Phenylmethanethiol, $C_6H_5CH_2SH$	9.93

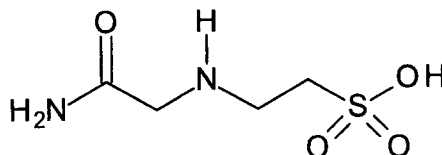
- (i) Suggest how the acidities of phenol and phenylmethanol compare with each other.

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- (ii) Suggest a reason why the pK_a for $C_6H_5CH_2SH$ is much lower than that for $C_6H_5CH_2OH$.

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- (e) ACES, $C_4H_{10}N_2O_4S$, is another compound containing sulfur.



ACES

ACES has a pK_a value of 6.88.

- (i) Draw the structure of the product formed when dilute hydrochloric acid is added to ACES at room temperature.

[1]

- (ii) Draw the structure of the conjugate base of ACES.

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[1]

- (iii) The pH of a solution of ACES is 2.2.
Calculate the ratio of [conjugate base of ACES] to [ACES].

[1]

- (iv) 0.0200 mol of the conjugate base of ACES is dissolved in 100 cm³ of deionised water. 50 cm³ of 0.300 mol dm⁻³ of hydrochloric acid was added to the solution.

Given that the conjugate base reacts with hydrochloric acid in a 1:1 stoichiometry, calculate the pH of the solution.

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[2]

[Total: 20]

- 6 The Gabriel synthesis is a 3-step approach to synthesis amines. Phthalimide is used as the main reactant, which has a nitrogen atom flanked by two carbonyl groups.

Propylamine is obtained from the Gabriel synthesis method as shown in Fig. 6.1.

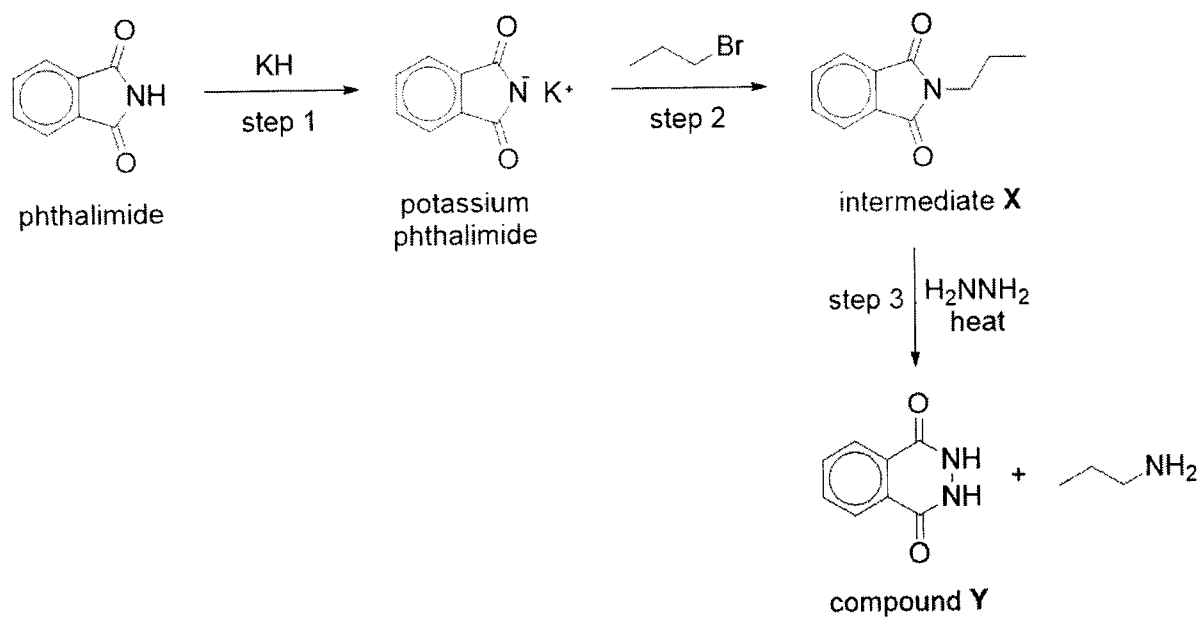


Fig. 6.1

- (a) (i) State the role of phthalimide in the above reaction in step 1.

.....[1]

- (ii) With reference to the product formed in step 1, explain why phthalimide is able to function as the role identified in (a)(i).

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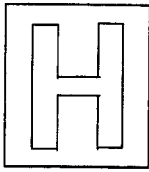
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Chemistry

9729/03

Paper 3 Free Response

14 September 2022

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do **NOT** open this booklet until you are told to do so.

Write your name, civics class, centre number and index number on all the work you hand in.
 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.

Section A

Answer **all** questions.

Section B

Answer **one** question.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

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

For Examiner's Use		
Paper 3	Q1	/18
	Q2	/20
	Q3	/22
	Q4	/20
	Q5	/20
	Total	/80

This document consists of **28** printed pages.

Section A

Answer **all** the questions in this section.

- 1 (a) Iodolactonisation reaction was first reported by M. J. Bougalt in 1904 and has since become one of the most effective ways to synthesise lactones.

An example of the iodolactonisation is the reaction of 4-pentenoic acid as shown in Fig 1.1.

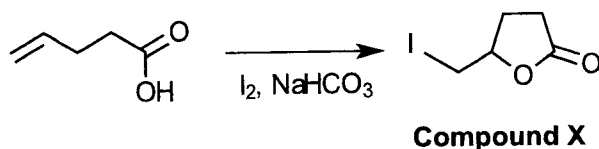


Fig 1.1

Two simplified steps in the iodolactonisation mechanism are given in Fig 1.2.

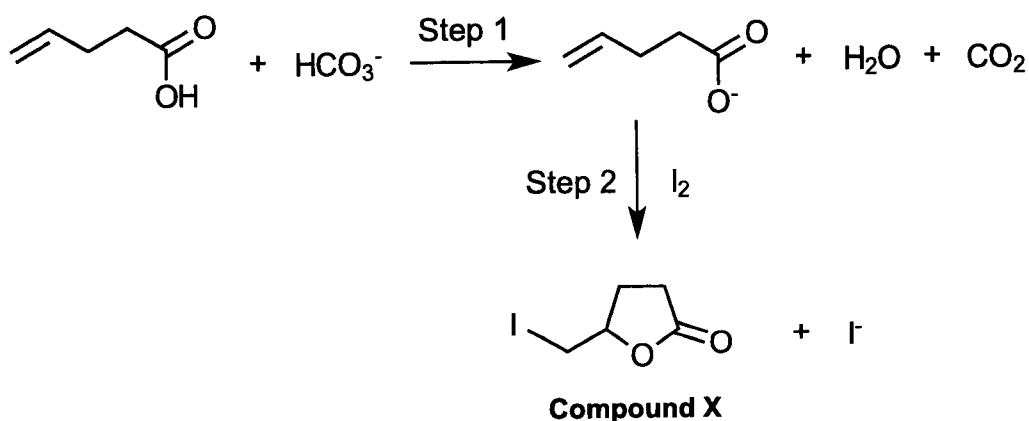


Fig 1.2

- (i) Suggest the role of HCO_3^- in **step 1**. [1]
- (ii) Suggest the mechanism for reaction taking place in **step 2**. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [3]
- (iii) Sketch a well-labelled reaction pathway diagram for the reaction in **step 2**, given that the reaction is exothermic. [2]
- (iv) Suggest the structural formulae of the final organic product formed when $\text{CH}_2=\text{CHCH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{COOH}$ undergoes iodolactonisation in a similar process in Fig 1.1. [1]
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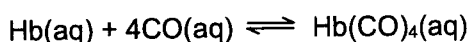
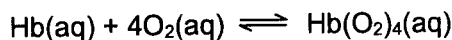
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- (b) Carbon monoxide is one of the most widespread and dangerous industrial hazards. The formation of carboxyhaemoglobin, $\text{Hb}(\text{CO})_4$, takes place much more readily than the formation of oxyhaemoglobin, $\text{Hb}(\text{O}_2)_4$.



A treatment method for carbon monoxide poisoning is to provide the patient with pure oxygen gas over a period of time.

With reference to the equations given above, explain why this is a suitable treatment method. [2]

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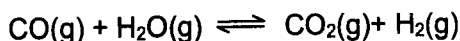
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- (c) The water-gas shift reaction is used to produce hydrogen gas industrially by reacting carbon monoxide with water vapour.



An evacuated tank was initially filled with 0.0197 atm of CO and 0.0394 atm of H_2O at 600 K. It was sealed and left to stand. At equilibrium, the partial pressure of CO_2 was found to be 0.0191 atm.

- (i) Calculate the value of K_p at 600 K. [2]

Table 1.1 shows how the value of K_p varies with temperature.

Table 1.1

T / K	300	900	1500
value of K_p	1.170×10^5	1.978	0.2195

- (ii) The Gibbs free energy, ΔG^\ominus (in J mol^{-1}), and the equilibrium constant, K_p , of a reaction are related by the following equation:

$$\Delta G^\ominus = -RT \ln K_p,$$

where R is the molar gas constant and T is the temperature in Kelvins.

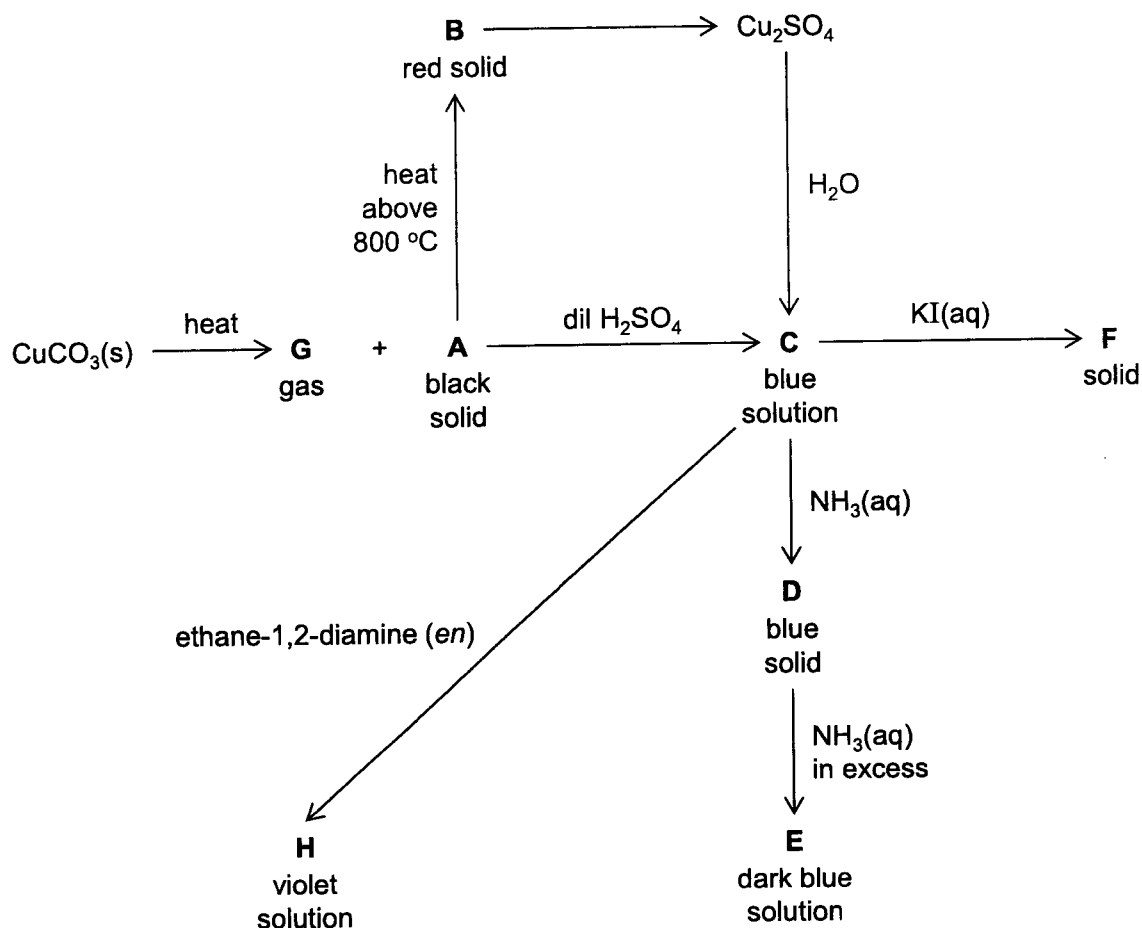
Using the given values of K_p , calculate the values of ΔG^\ominus at 300 K and 900 K. Hence, determine the value of ΔS^\ominus for the water-gas shift reaction.

(Assume that both ΔH^\ominus and ΔS^\ominus are independent of temperature.) [3]

- (iii) Comment on the magnitude of the calculated value of ΔS^\ominus . [1]
- (iv) With the aid of a sketch of the Boltzmann distribution, explain how an increase in temperature affects the rate of water-gas shift reaction. [3]

- 2 Copper is a typical transition element with more than one oxidation state. Many of its compounds have colours in the blue-green-yellow part of the visible spectrum.

The following reaction scheme shows the chemistry of some copper-containing species.



- (a) (i) **A** and **B** are both compounds of copper and oxygen only.
 Cu_2SO_4 can be made from **B** under certain anhydrous conditions. The oxidation number of copper in **B** is the same as in Cu_2SO_4 .
 Identify gas **G**, and write the formula of the copper-containing species in **A** to **C**. [2]
- (ii) Suggest, with reason, the colour of solid **F**. [2]

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(b) Explain the transformations from **C** to **E** in terms of the competing equilibria and the type of reaction that has occurred. Include equations and the formulae of all copper-containing species. [4]

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- (d) Selective precipitation is a technique of separating ions in an aqueous solution by using a reagent that precipitates one or more of the ions, while leaving other ions in solution. In the case of Cu^{2+} ions, the separation is achieved by adjusting the pH so that only Cu^{2+} ions are precipitated.

In an experiment, a student adds sodium hydroxide gradually to a solution containing $0.100 \text{ mol dm}^{-3} \text{ Cu}^{2+}$ ions and $0.100 \text{ mol dm}^{-3} \text{ Fe}^{2+}$ ions.

Relevant K_{sp} values are given in Table 2.1.

Table 2.1

metal hydroxide	$K_{\text{sp}} / \text{mol}^3 \text{ dm}^{-9}$
$\text{Cu}(\text{OH})_2$	2.2×10^{-20}
$\text{Fe}(\text{OH})_2$	8.0×10^{-16}

Determine the pH at which maximum separation of the two cations is achieved. [2]

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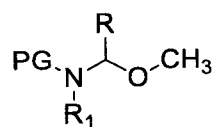
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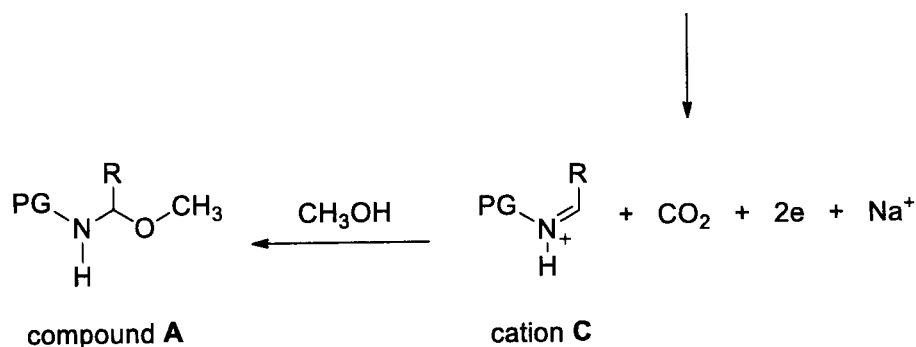
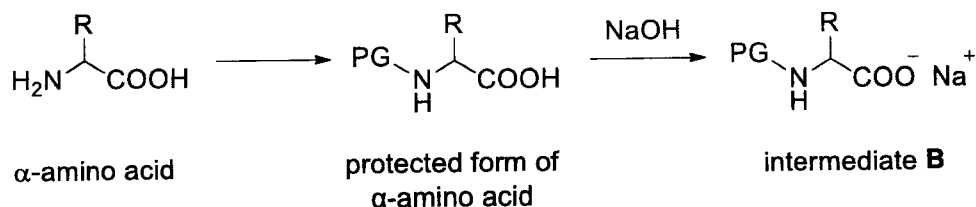
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Compound **A** is formed from the electrolysis from α -amino acids in methanol solvent,

compound **A**

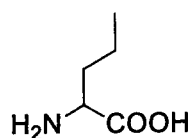
where R is alkyl, R₁ is alkyl or hydrogen and PG is the protecting group, $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-$.

The α -amino acids are first converted to its protected form, followed by reaction with sodium hydroxide to form an intermediate, **B**.



At the anode, the anion in intermediate **B** undergoes decarboxylation to form cation **C**. No other reactions occur at the anode.

Norvaline is an α -amino acid which is used in dietary supplement for bodybuilding. It undergoes the electrolysis reaction above.

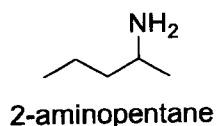


norvaline

- (c) State the reagent and condition to convert norvaline to its protected form. [1]

- (d) Compound **A** undergoes hydrolysis to form amine **X**.

- (i) Draw the structure of amine **X**, when norvaline undergoes the electrolysis reaction above, followed by hydrolysis. [1]
- (ii) Explain the difference in basicity of amine **X** and 2-aminopentane. [2]



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- (e) Cation **C** subsequently reacts with methanol, which acts as a nucleophile, to give **A** in 2 steps.

Step 1: methanol attacks the electron deficient carbon in cation **C**, to form another cation intermediate.

Step 2: the intermediate undergoes deprotonation to give **A**.

Starting with the appropriate structure of **C** which is produced from norvaline, use appropriate curly arrows to show how the **A** is formed at the anode. Show clearly the charges and lone pair of electrons as well as structure of intermediate formed. [2]

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- (f) (i) The standard reduction potential of $\text{CO}_2/\text{CH}_3\text{OH}$ is +0.45 V, measured against the standard hydrogen electrode.

Write the ion-electron half reaction for the complete oxidation of methanol. [1]

- (ii) With reference to the reaction occurring at the anode for the electrolysis, suggest a suitable standard reduction potential value for (cation **C**)/(intermediate **B**) and explain your answer. [2]

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- (g) The efficiency of the electrolysis reaction of compound **A** is around 95%.

A current of 0.1 A was applied to the electrolytic cell consisting of *N*-protected norvaline for 1 hour.

Calculate the mass of compound **A** produced at the anode when norvaline undergoes the electrolysis reaction. [M_r of **A**: 145.0] [2]

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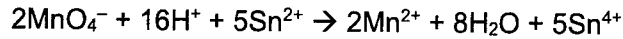
Handwriting practice area consisting of 25 horizontal dotted lines.

- (b) An oxide of tin, **G**, contains the metal in both oxidation states II and IV. **G** was dissolved in excess $\text{H}_2\text{SO}_4(\text{aq})$ to produce solution **H**, which contains a mixture of tin(II) sulfate and tin(IV) sulfate. Solution **H** was divided into two portions.

A 25.0 cm^3 of one portion required 17.40 cm^3 of $0.0150 \text{ mol dm}^{-3} \text{ KMnO}_4$ to reach the end-point.

An excess of powdered zinc was added to another portion of **H**. The mixture was stirred until the reaction was complete, and then filtered. 25.0 cm^3 of the filtrate required 26.10 cm^3 of $0.0150 \text{ mol dm}^{-3} \text{ KMnO}_4$ to reach the end-point.

The equation for the titration reaction is as follows.



- (i) Deduce the $\text{Sn}^{2+}/\text{Sn}^{4+}$ ratio in the oxide **G**, and hence suggest the formula of **G**. [3]
 (ii) Tin(IV) oxide, SnO_2 , reacts separately with both acids and alkalis.

Write separate equations for the reaction of tin(IV) oxide with

- hydrochloric acid
- sodium hydroxide

[2]

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- 5 (a) In 1944, T. Ellingham published plots of Gibbs free energy change, ΔG , against temperature, T , for several reactions. Today, such plots are called Ellingham diagrams.

At present, titanium is more commonly produced by reducing titanium tetrachloride with magnesium. Titanium tetrachloride is a colourless liquid that boils at 400 K. To optimise this reduction process, it is necessary to know how ΔG of the reaction changes with T .

Fig. 5.1 shows the variation in ΔG with T for the following reactions:

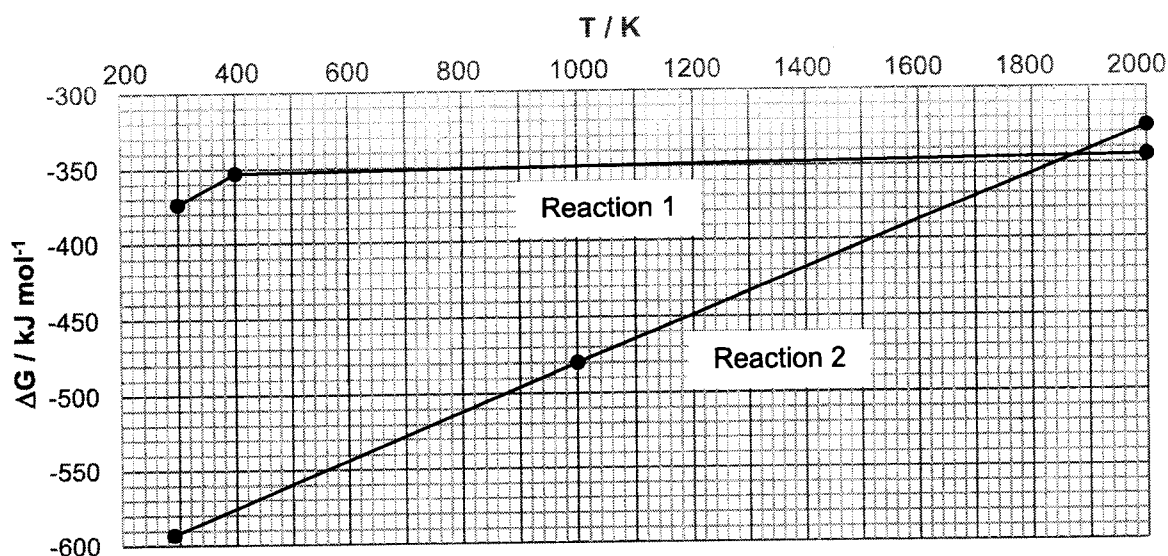
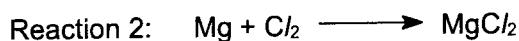
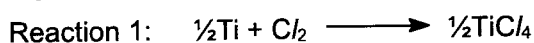


Fig. 5.1

- (i) With reference to the gradient of the graph for Reaction 2, deduce the sign of ΔS .
Hence, explain why the graph for Reaction 2 becomes more positive with increasing temperature. [2]

Industrially, the reduction of titanium tetrachloride by magnesium is carried out at 1100 K in an atmosphere of argon:



- (ii) Suggest a reason for the reduction to be carried out in an atmosphere of argon. [1]

Similar to enthalpy change of reaction, the Gibbs free energy, ΔG , of a reaction can be calculated using the following expression.

$$\Delta G = \sum \Delta G (\text{products}) - \sum \Delta G (\text{reactants})$$

With reference to Fig. 5.1,

- (iii) evaluate ΔG for the reduction of TiCl_4 by Mg at 1100 K. [1]
(iv) state the temperature above which it is **not** feasible to reduce TiCl_4 with Mg . [1]

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Cobalt(II) chloride has been extensively used as a catalyst for various organic transformations.

- (b) Using the data in Table 5.1 and relevant data from the *Data Booklet*, construct a Born-Haber cycle to determine the standard enthalpy change of formation of cobalt(II) chloride.

Table 5.1

Enthalpy term	$\Delta H / \text{kJ mol}^{-1}$
Lattice energy of CoCl_2	-2624
Standard enthalpy change of atomisation of cobalt	+427
First electron affinity for chlorine	-364

[3]

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- (c) Cobalt(II) chloride is known to be a useful catalyst for the synthesis of α -aminonitriles by a one-pot 3-component condensation as shown:

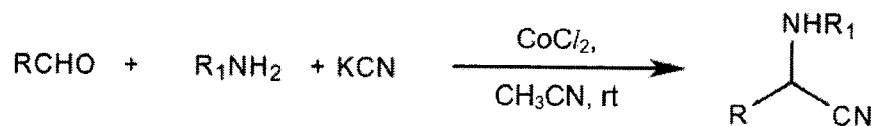
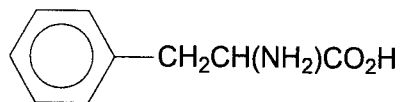


Fig. 5.2

Using the information in Fig. 5.2, propose a pathway to synthesize the following α -amino acid:



phenylalanine

Suggest the structures of the aldehyde that can be used as starting material and the intermediate. State the reagents and conditions for each step clearly. [3]

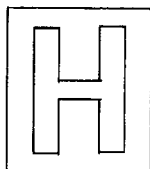
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TEMASEK JUNIOR COLLEGE
2022 JC2 PRELIMINARY EXAMINATION
Higher 2



CANDIDATE
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Chemistry

9729/04

Paper 4 Practical

29 August 2022

2 hours 30 minutes

Candidates answer on the Question Paper.

READ THESE INSTRUCTIONS FIRST

Write your Civics Group and name 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 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	/ 12
2	/ 19
3	/ 14
4	/ 10
Total	/ 55

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

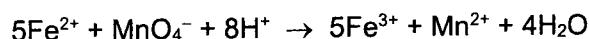
Answer **all** the questions in the spaces provided.

1 Determination of the percentage by mass of water of crystallisation in $\text{FeSO}_4 \cdot n\text{H}_2\text{O}$

Read through the whole method before starting any practical work. Where appropriate, prepare a table for your results in the space provided.

Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

The amount of Fe^{2+} ions can be determined quantitatively by a titration against a standard solution of potassium manganate(VII), KMnO_4 . The reaction is shown below.



In this experiment, you will determine the percentage by mass of water of crystallisation in $\text{FeSO}_4 \cdot n\text{H}_2\text{O}$. You will titrate a solution of **FA 1** against **FA 3**.

You are provided with

FA 1, contains 26.07 g dm^{-3} of hydrated iron(II) sulfate, $\text{FeSO}_4 \cdot n\text{H}_2\text{O}$, where n is an integer.

FA 2, 1.0 mol dm^{-3} dilute sulfuric acid, H_2SO_4

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

You are to keep **FA 2** and **FA 3** for questions 2 and 3.

(a) (i) Titration of FA 1 against FA 3

1. Fill a burette, labelled **FA 3**, with **FA 3**.
2. Use a pipette to transfer 10.0 cm^3 of **FA 1** into a 250 cm^3 conical flask.
3. Use a measuring cylinder to add about 10 cm^3 of **FA 2** to this flask.
4. Titrate **FA 1** with **FA 3** from the burette until the appearance of the first permanent pale-pink colour.
5. Record your titration results, to an appropriate level of precision, in the space on **Page 3**.
6. Repeat steps 1 to 4 until consistent results are obtained.

Titration Results

[2]

- (ii) From your titrations, obtain a suitable volume of **FA 3** to be used in your calculations. Show clearly how you obtained this volume.

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volume of **FA 3** =[3]

- (b) (i) Calculate the amount of Fe^{2+} in 10.0 cm^3 of **FA 1**.

amount of Fe^{2+} in 10.0 cm^3 of **FA 1** = [1]

- (ii) Calculate the amount of Fe^{2+} in 1 dm^3 of **FA 1**.

amount of Fe^{2+} in 1 dm^3 of **FA 1** = [1]

- (iii) Calculate the M_r of the hydrated iron(II) sulfate, $\text{FeSO}_4 \cdot n\text{H}_2\text{O}$, in **FA 1**.

M_r of the hydrated iron(II) sulfate =

Hence, deduce the value of n , the water of crystallisation in the hydrated iron(II) sulfate.

[A_r: Fe, 55.8; S, 32.1; O, 16.0; H, 1.0]

$n = \dots\dots\dots$

[2]

(iv) Hence, determine the percentage by mass of water of crystallisation in $\text{FeSO}_4 \cdot n\text{H}_2\text{O}$.

Show your working.

Percentage by mass of water of crystallisation =

[1]

(v) Iron(II) sulfate in solution is readily oxidised by air to form iron(III) sulfate.

State the effect, on the value of n calculated in (b)(iii), if some of your sample of FA 1 had oxidised before you carried out the titration. Explain your answer.

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[2]

[Total: 12]

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2 To investigate the reaction between manganate(VII) ions and $C_2O_4^{2-}$ ions

In this experiment, you will investigate the kinetics of the reaction between MnO_4^- and $C_2O_4^{2-}$.

FA 4 is $0.0100 \text{ mol dm}^{-3}$ sodium thiosulfate, $Na_2S_2O_3$

FA 5 is $0.200 \text{ mol dm}^{-3}$ sodium ethanedioate, $Na_2C_2O_4$

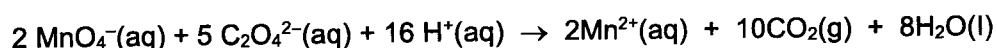
FA 6 is $0.100 \text{ mol dm}^{-3}$ potassium iodide, KI

FA 2 and **FA 3** are solutions from question 1.

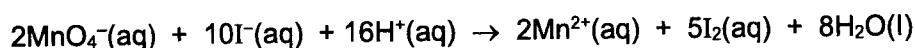
You are to keep **FA 5** for question 3.

You are also provided with a starch indicator.

Acidified potassium manganate(VII) ions oxidises $C_2O_4^{2-}$ ions to produce Mn^{2+} ions which act as an autocatalyst for the reaction.

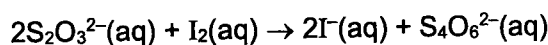


Acidified potassium manganate(VII) ions also oxidises I^- ions according to the following reaction:



You will add a solution of acidified potassium manganate(VII) to a mixture containing **FA 2** and **FA 5**. At timed intervals, you will draw 10 cm^3 aliquots of the reaction mixture. The concentration of MnO_4^- ions in each aliquot will be determined after adding the aliquot to an excess of I^- solution and titrating the iodine produced against $S_2O_3^{2-}$ solution.

The reaction between iodine from the reaction mixture and $S_2O_3^{2-}$ solution is given below.



Note: $C_2O_4^{2-}$ does not react with I^- in the reaction mixture.

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Question 2 continues on the next page.

Note: Read all instructions in the procedure before you start performing the experiment.

Recording your results

In an appropriate format in the space provided on **page 9**, draw a table to record your

- transfer time (in minutes and seconds, to the nearest second) when half of the reaction mixture has emptied from the pipette,
- the decimal time, t_d , in minutes, to 0.1 min, for example, if $t = 3 \text{ min } 20 \text{ s}$ then $t_d = 3 \text{ min} + 20/60 = 3.3 \text{ min}$,
- titration results for each of your aliquots. Make certain that your recorded results show the precision of your working.

Procedure

1. Label each of the large test-tubes **1** to **6**. Using a measuring cylinder, add approximately 10 cm^3 of **FA 6** to each of these test-tubes.
2. Using appropriate measuring cylinders, transfer 50.0 cm^3 of **FA 5**, 5.0 cm^3 of **FA 2** and 45.0 cm^3 of deionised water into a conical flask labelled **reaction mixture**.
3. Using an appropriate measuring cylinder, transfer 25.0 cm^3 of **FA 3** to the conical flask labelled **reaction mixture**. Start the stopwatch and swirl the mixture thoroughly to mix its contents.
4. At approximately 1 minute, use a 10 cm^3 pipette to remove a 10.0 cm^3 aliquot of the reaction mixture. **Immediately** transfer this aliquot into the test-tube labelled **1** and swirl the mixture. Note and record the transfer time (in minutes and seconds, to the nearest second) when half of the reaction mixture has emptied from the pipette.
5. At approximately 2 minutes, repeat step 4. Transfer this aliquot into the large test-tube labelled **2**.
6. Repeat step 4 four more times at about three minute intervals, transferring the aliquots into test-tubes labelled **3** to **6**.

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Titration

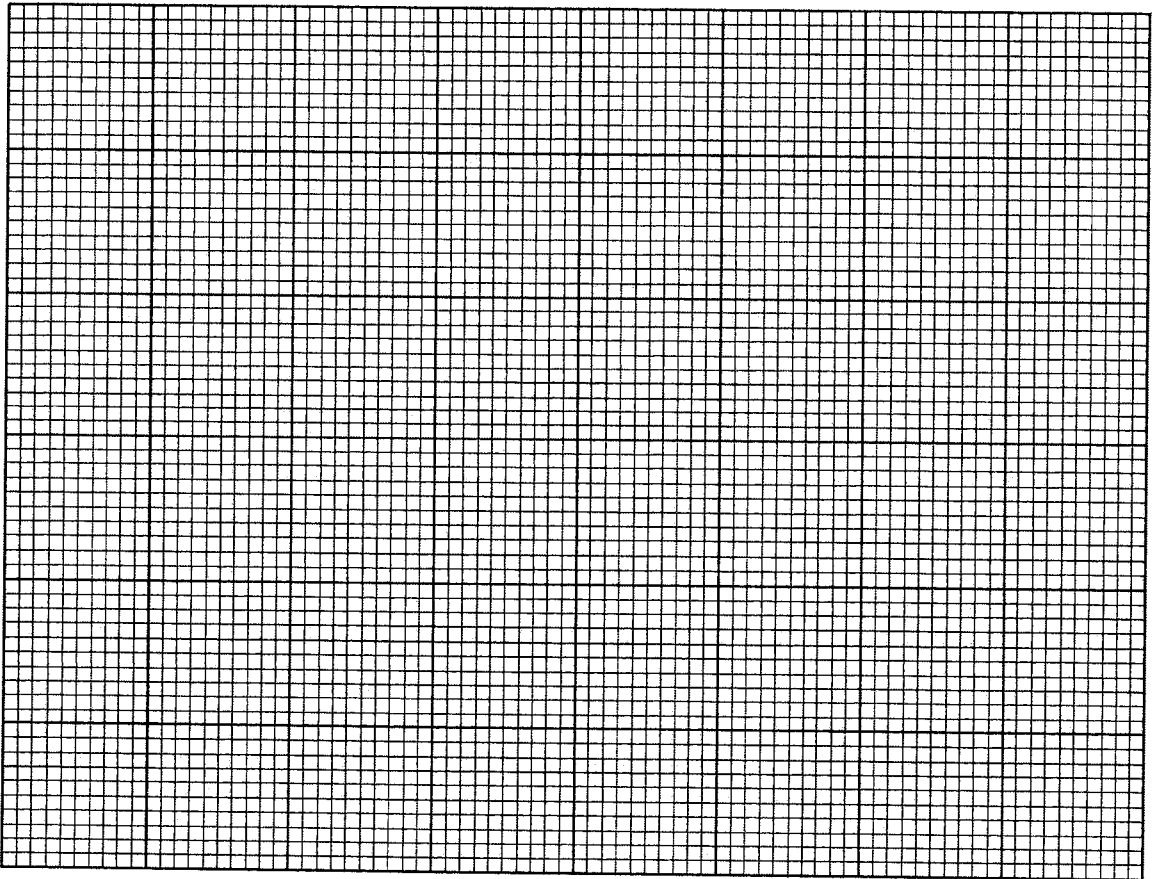
Note: You will only be able to perform each titration **once**. Be careful not to overshoot the end-point. Performing all of the titrations only after all the aliquots have been collected may affect time management.

7. Pour the contents of test-tube labelled **1** into a clean 250 cm^3 conical flask. Rinse the test-tube and add the washings to the conical flask.
8. Titrate the iodine in this solution with **FA 4**. When the colour of the solution turns pale yellow, add about 1 cm^3 of starch indicator. The solution will turn dark blue/black. The end-point is reached when the dark blue/black colour just disappears. Record your results.
9. Repeat steps **8** to **9** for each of the remaining test-tubes labelled **2** to **6**.

(a) Experimental results

[3]

- (b) (i)** On the grid in **Fig. 2.1**, plot a graph of **volume of sodium thiosulfate, FA 4**, on the y-axis, against time, t_d , on the x-axis. You should draw the most suitable line that takes into account all of your plotted points.

Fig. 2.1

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[3]

10

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- (ii) Consider the **shape** of the graph in **Fig. 2.1**.
Describe the shape and explain how it relates to the rate of reaction between MnO_4^- and $\text{C}_2\text{O}_4^{2-}$.

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[1]

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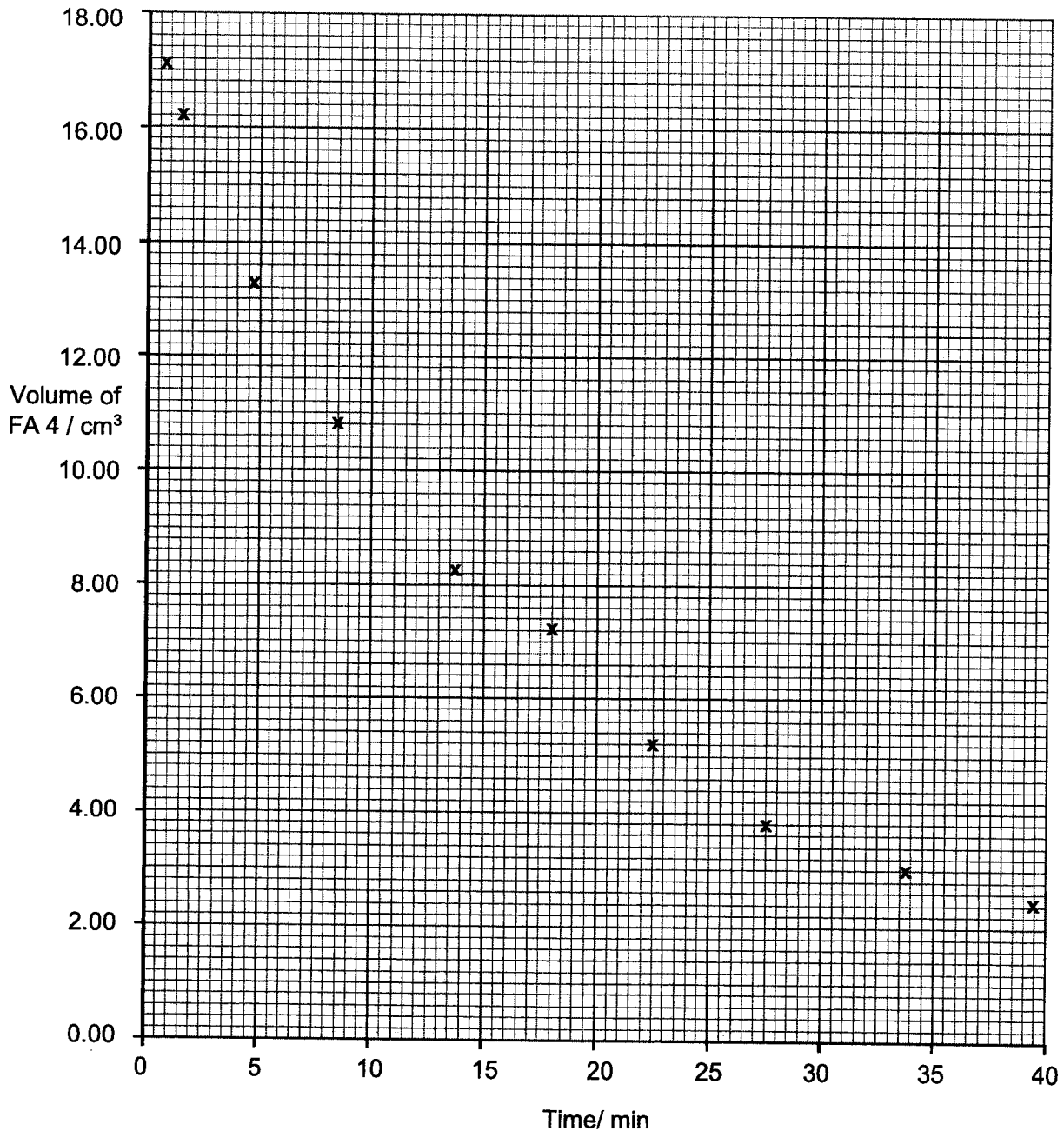
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- (c) A student performed a similar experiment under a different temperature. In step 2 of the procedure on page 8, she used the same volumes of FA 2 and FA 5 that you used but she also added 5.0 cm³ of 1.00 mol dm⁻³ manganese(II) sulfate. To keep the total volume of the same as your experiment, she added 40.0 cm³ of deionised water.

The data from the student's experiment has been plotted in Fig. 2.2.

- (i) Draw the most appropriate line taking into account all of the plotted points.

Fig. 2.2



[1]

- (ii) Using the graph in (c)(i), calculate the $[\text{MnO}_4^-]$ in the reaction mixture at $t = 15$ min.

[2]

- (iii) Draw a tangent to your graph line in (c)(i) at $t = 15$ min. Calculate the gradient of this line, and hence determine the rate of change of the amount of $\text{S}_2\text{O}_3^{2-}$ ions required in mol min^{-1} .

[3]

- (iv) Using your answer in (c)(iii), calculate the rate of change of MnO_4^- in mol min^{-1} .

[1]

- (v) Hence, calculate the rate of disappearance of $[\text{MnO}_4^-]$ in the reaction mixture, at time $t = 15$ min.

[3]

- (d) Using the graph in (c)(i), show that the reaction between MnO_4^- and $\text{C}_2\text{O}_4^{2-}$ is first order with respect to $[\text{MnO}_4^-]$.

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[2]

[Total: 19]

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3 To explore the chemistry of some compounds of unknown transition elements X and a hydrocarbon

FA 7 is a solid sample of a common dioxide of the unknown transition element **X**

FA 8 is a pure solution of compound **Y**, which is the product formed in **3(a)**

FA 9 is a hydrocarbon

You will need **FA 2**, **FA 3** and **FA 5** from question 1 and 2.

Perform the tests described in Table 3.1 and record your observations in the table. Test and identify any gases evolved. The observation in **(c)(iii)** has been completed for you, there is no need to carry out this test.

Table 3.1

tests		observations
(a)	<p>Add 2 cm depth of FA 2 and 2 cm depth of FA 5 to a test-tube.</p> <p>Using a spatula, add FA 7 to the mixture in small portion with swirling until no further change.</p> <p>Filter the mixture into a test-tube. The filtrate contains compound Y.</p> <p>Divide the filtrate into two portions. To one portion, add aqueous sodium hydroxide until no further change.</p> <p>To the other portion, add aqueous ammonia until no further change.</p>	
(b)(i)	Place 1 cm depth of FA 8 in a test-tube, add aqueous sodium hydroxide.	
(b)(ii)	Place 1 cm depth of FA 8 in a test-tube, add aqueous ammonia solution.	

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(c)(i)	Place 5 cm depth of aqueous sodium hydroxide in a test-tube. Add 5 drops of FA 9 to this test-tube. Add FA 3 , dropwise with shaking, until no further change is seen. Allow to stand for 5 minutes, with occasional shaking. Continue with the remaining parts of Question 3.	
(c)(ii)	Place 5 cm depth of FA 2 in a test-tube. Add 5 drops of FA 9 to this test-tube. Add FA 3 , dropwise with shaking, until no further change is seen. Allow to stand for 5 minutes, with occasional shaking. Continue with the remaining parts of Question 3.	
(c)(iii)	Place 5 cm depth of water in a test-tube. Add 1 drop of FA 9 to this test-tube. Add bromine water, dropwise with shaking.	Bromine water decolourised.

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[6]

- (d)** Consider your observations in **(a)** and **(b)**, identify the transition ion formed in **(a)**. Justify your choice by referring to the observations in **(b)**.

Ion present is

Justification.....

.....

[1]

- (e) The anion in **FA 8** is not a nitrate, nitrite or carbonate ion.

You will devise and perform a series of simple tests to identify the anion present in **FA 8**.

Use the Qualitative Analysis Notes on pages 23-24 to deduce the possible anions in **FA 8** and describe **two different** tests, that will allow you to distinguish between the possible anions. You can only use the bench reagents provided.

Perform the tests described and record your observations in the space below. Hence, deduce the identity of the anion in **FA 8**.

Possible anions:

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Identity of anion:

[3]

(f) Compound **Z** is the main organic product in (c)(i) when **FA 9** reacts with **FA 3** under alkaline conditions. The molecular formula of **Z** is $C_6H_{12}O_2$.

(i) Deduce the molecular formula of **FA 9**.

Explain your deduction. Your explanation should be supported by evidence from your observations in (c).

Molecular formula of **FA 9** is

Explanation:.....

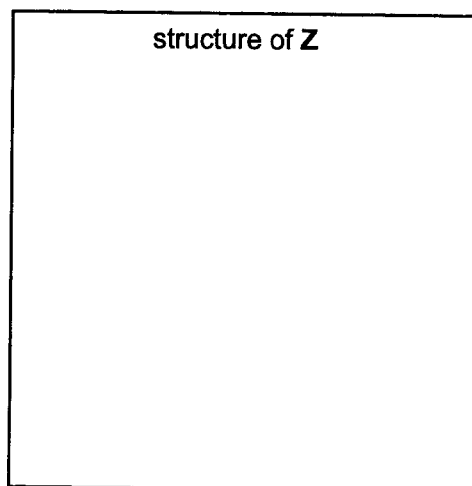
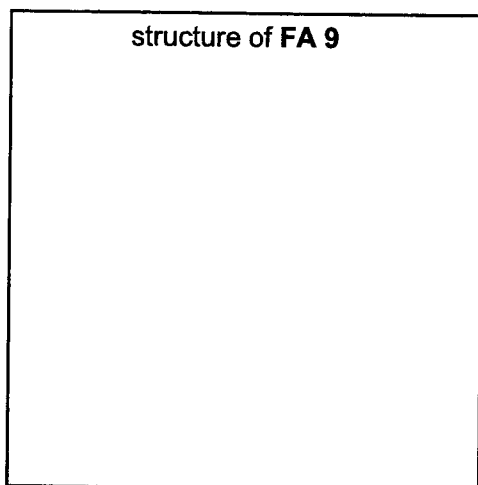
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[2]

(ii) Draw the structural formulae for **FA 9** and compound **Z**.



[2]

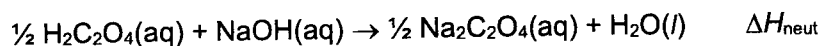
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4 Planning

You are to plan an experiment to determine the concentration of a solution of $\text{H}_2\text{C}_2\text{O}_4$ and the ΔH_{neut} between ethanedioic acid and sodium hydroxide.



You are provided with 2.00 mol dm^{-3} NaOH and a solution of $\text{H}_2\text{C}_2\text{O}_4$ of approximately the same concentration. A series of experiments can be carried out using different volumes of the two solutions. In each experiment, the total volume of the two solutions is to be kept at 50 cm^3 and the increase in temperature, ΔT , is determined.

A graph of ΔT against *volume of $\text{H}_2\text{C}_2\text{O}_4$* can then be used to determine the exact concentration of the $\text{H}_2\text{C}_2\text{O}_4$ solution and ΔH_{neut} .

- (a) Determine the volume of $\text{H}_2\text{C}_2\text{O}_4$ and of NaOH to be used such that both solutions will react completely. Show your working clearly and give your answers to the **nearest whole number**.

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[1]

- (c) Using your answer in (a), sketch, on Fig. 4.1, the graph you would expect to obtain from the results.

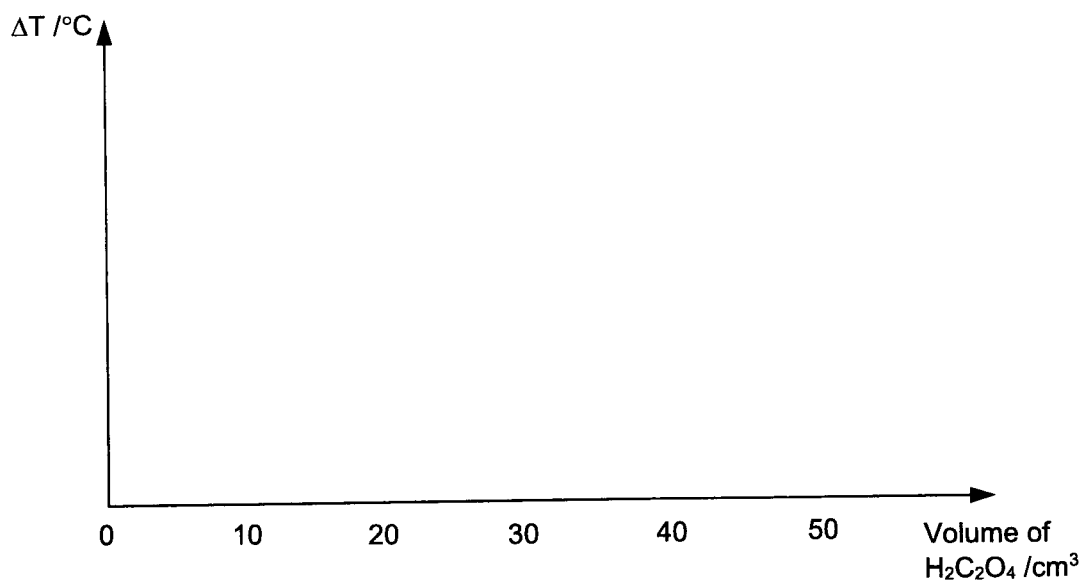


Fig. 4.1

[2]

- (d) Suggest a method to minimise heat lost to the surroundings to ensure the results obtained are accurate.

.....

.....

[1]

- (e) Another student conducted a similar experiment but used 1.00 mol dm^{-3} of NaOH instead. He obtained the following results:
- Volume of ethanedioic acid needed for complete neutralisation = 15 cm^3
 - Maximum temperature change = 9.0°C

Calculate the concentration of the $\text{H}_2\text{C}_2\text{O}_4$ solution, in mol dm^{-3} and the ΔH_{neut} in kJ mol^{-1} .

You may assume the following:

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

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[2]

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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

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(b) Reactions of aqueous anions

anion	reaction
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $\text{Cl}^-(\text{aq})$	gives white ppt. with $\text{Ag}^+(\text{aq})$ (soluble in $\text{NH}_3(\text{aq})$)
bromide, $\text{Br}^-(\text{aq})$	gives pale cream ppt. with $\text{Ag}^+(\text{aq})$ (partially soluble in $\text{NH}_3(\text{aq})$)
iodide, $\text{I}^-(\text{aq})$	gives yellow ppt. with $\text{Ag}^+(\text{aq})$ (insoluble in $\text{NH}_3(\text{aq})$)
nitrate, $\text{NO}_3^-(\text{aq})$	NH_3 liberated on heating with $\text{OH}^-(\text{aq})$ and Al foil
nitrite, $\text{NO}_2^-(\text{aq})$	NH_3 liberated on heating with $\text{OH}^-(\text{aq})$ and Al foil; NO liberated by dilute acids (colourless NO \rightarrow (pale) brown NO_2 in air)
sulfate, $\text{SO}_4^{2-}(\text{aq})$	gives white ppt. with $\text{Ba}^{2+}(\text{aq})$ (insoluble in excess dilute strong acids)
sulfite, $\text{SO}_3^{2-}(\text{aq})$	SO_2 liberated with dilute acids; gives white ppt. with $\text{Ba}^{2+}(\text{aq})$ (soluble in dilute strong acids)

(c) Test 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