Paper Reference(s) **9CH0 / 03**

Pearson Edexcel Level 3 GCE

Chemistry

Advanced

Paper 3: General and Practical Principles in Chemistry

Tuesday 27 June 2017 – Morning

Time: 2 hours 30 minutes plus your additional time allowance

INSTRUCTIONS TO CANDIDATES

Write your centre number, candidate number, surname, other names and your signature in the boxes below. Check that you have the correct question paper.

Centre No.							
Candidate No.							
Surname							
Other names							
Signature							
Paper Reference	9	C	H	0	/	0	3

- Use BLACK ink or BLACK ball-point pen.
- Answer ALL questions.
- Answer the questions in the spaces provided – there may be more space than you need.

MATERIALS REQUIRED FOR EXAMINATION

Data Booklet, scientific calculator, ruler

ITEMS INCLUDED WITH QUESTION PAPERS

Periodic table

INFORMATION FOR CANDIDATES

- The total mark for this paper is 120.
- The marks for EACH question are shown in brackets – use this as a guide as to how much time to spend on each question.
- For the question marked with an ASTERISK (*), marks will be awarded for your ability to structure your answer logically showing the points that you make are related or follow on from each other where appropriate.
- A Periodic Table is provided.

ADVICE TO CANDIDATES

- Read each question carefully before you start to answer it.
- Try to answer every question.
- Check your answers if you have time at the end.
- Show all your working in calculations and include units where appropriate.

(Turn over)

Answer ALL questions.

Write your answers in the spaces provided.

1 This question is about transition metal chemistry.

(a) The AMPHOTERIC character of solid chromium(III) hydroxide is shown by the fact that it reacts separately with both dilute hydrochloric acid and dilute sodium hydroxide solution.

(i) Write an IONIC equation for the reaction of solid chromium(III) hydroxide with dilute hydrochloric acid, showing the formula of the complex ion formed. Include state symbols in your answer. (2 marks)

(Question continues on next page)

(ii) Describe the changes you would SEE when the reaction in (a)(i) is carried out. (2 marks)

(iii) Write an IONIC equation for the reaction of solid chromium(III) hydroxide with dilute sodium hydroxide solution, showing the formula of the complex ion formed. Include state symbols in your answer. (2 marks)

(Question continues on next page)

(Turn over)

(iv) State the final appearance of the reaction mixture in (a)(iii). (1 mark)

(b) Dilute aqueous ammonia is added, drop by drop, to an aqueous solution of copper(II) sulfate until the aqueous ammonia is in excess.

(i) Describe what you would SEE during this experiment. (2 marks)

(Question continues on next page)

(ii) **The reaction between aqueous copper(II) sulfate and EXCESS aqueous ammonia is an example of a LIGAND SUBSTITUTION reaction.**

Write an equation for the ligand substitution reaction that occurs, showing the formulae of the complex ions involved. State symbols are not required. (2 marks)

(TOTAL FOR QUESTION 1 = 11 MARKS)

(Questions continue on next page)

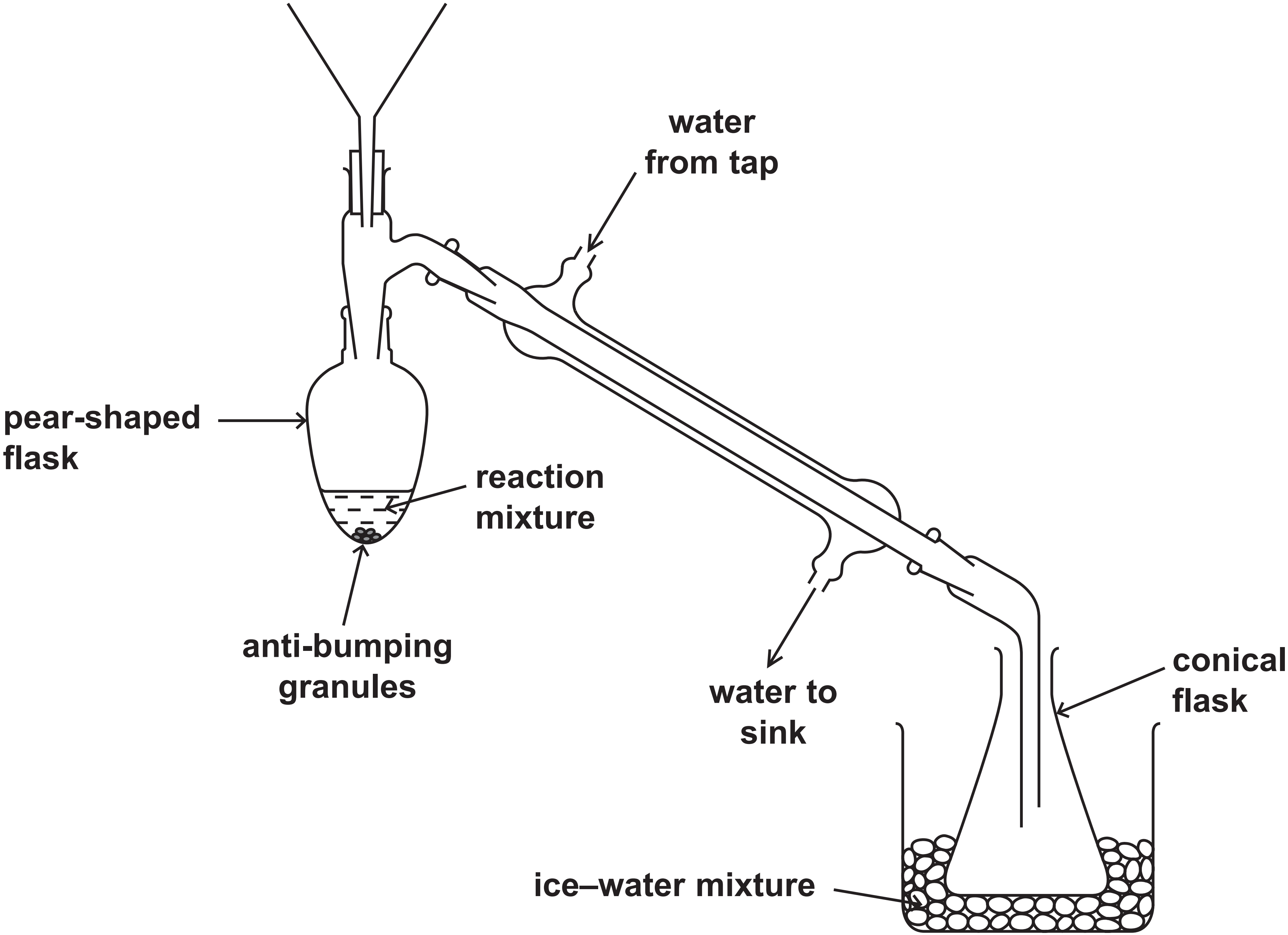
2 This question is about the preparation of a sample of the ketone, 3-methylbutan-2-one.

A student's research suggested that 3-methylbutan-2-one may be prepared by oxidising 3-methylbutan-2-ol with acidified potassium dichromate(VI) solution.

The student sets up the apparatus as shown in the diagram on page 8. You may assume that all the equipment is suitably clamped.

The student adds dilute sulfuric acid to the pear-shaped flask. A mixture of potassium dichromate(VI) and 3-methylbutan-2-ol is then added slowly to the dilute sulfuric acid in the flask.

(Question continues on next page)



(Question continues on next page)

(a) Identify the TWO changes that must be made to the apparatus before heating the pear-shaped flask, giving a reason for each change. (4 marks)

(Question continues on next page)

(Turn over)

(b) Draw the SKELETAL formulae for 3-methylbutan-2-ol and 3-methylbutan-2-one. (2 marks)

3-methylbutan-2-ol

3-methylbutan-2-one

(Question continues on next page)

(Turn over)

(c) Once the essential changes are made to the apparatus, the pear-shaped flask is heated. The distillate formed is collected in the conical flask.

On testing the distillate with pH paper, it is found that its pH is 2.
The student suggests that this pH is due to the formation of 3-methylbutanoic acid.

(i) Give a reason why 3-methylbutanoic acid cannot be formed in the reaction. (1 mark)

(Question continues on next page)

(Turn over)

(ii) Deduce the FORMULA of the compound that could cause the distillate to have a pH value of 2. (1 mark)

(Question continues on next page)

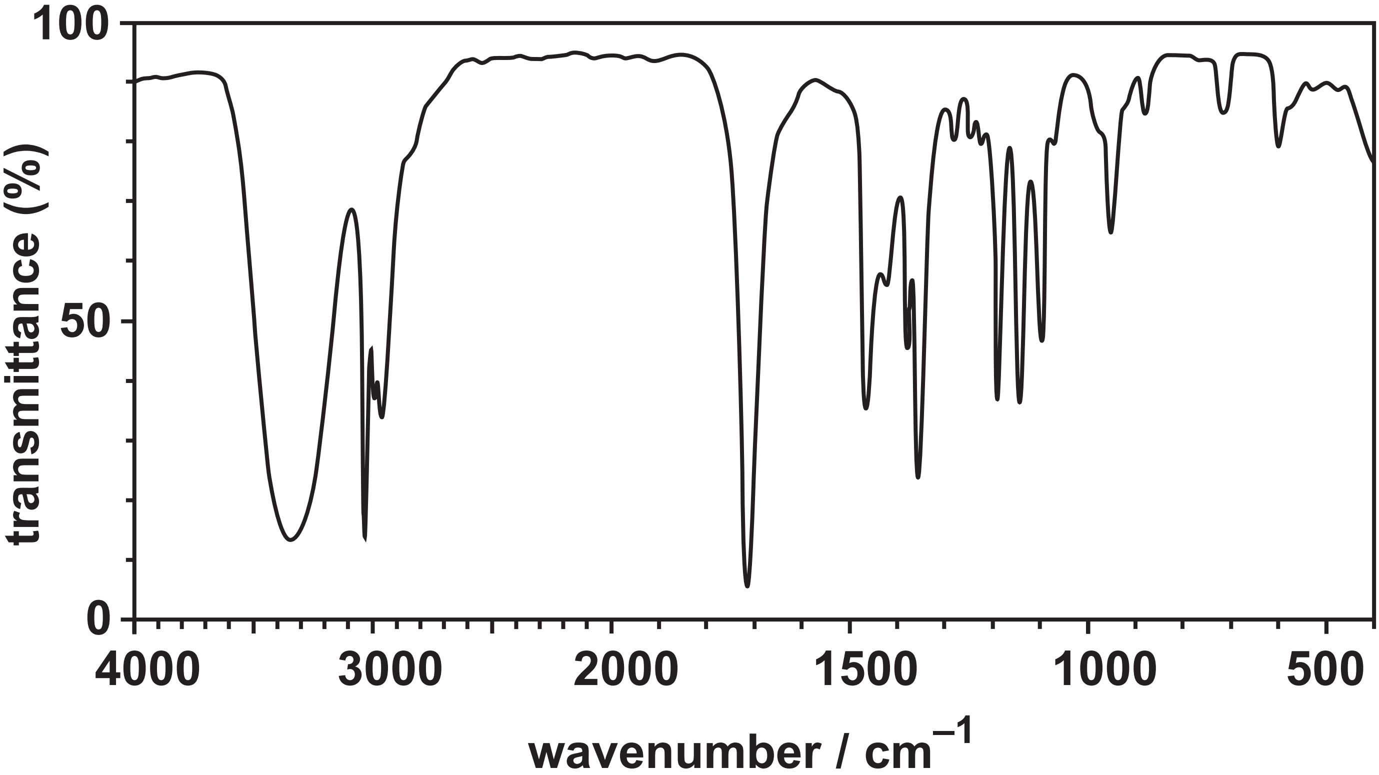
(Turn over)

(iii) **Solid sodium carbonate is added to the distillate. The sodium carbonate disappears and fizzing occurs.**

Write an equation, including state symbols, for the reaction that occurs between sodium carbonate and the compound you have identified in (c)(ii). (2 marks)

(Question continues on next page)

(d) The organic mixture was separated from the aqueous layer and dried. The infrared spectrum of the organic mixture is shown.



(i) By reference to any relevant peak(s), deduce how the infrared spectrum shows that the mixture contains 3-methylbutan-2-one.
(2 marks)

(Continue your answer on next page)

(Turn over)

(ii) From the infrared spectrum, the student concludes that the mixture contains another organic compound.

The mixture is redistilled and the fraction that boils in the range 93–95 °C is collected.

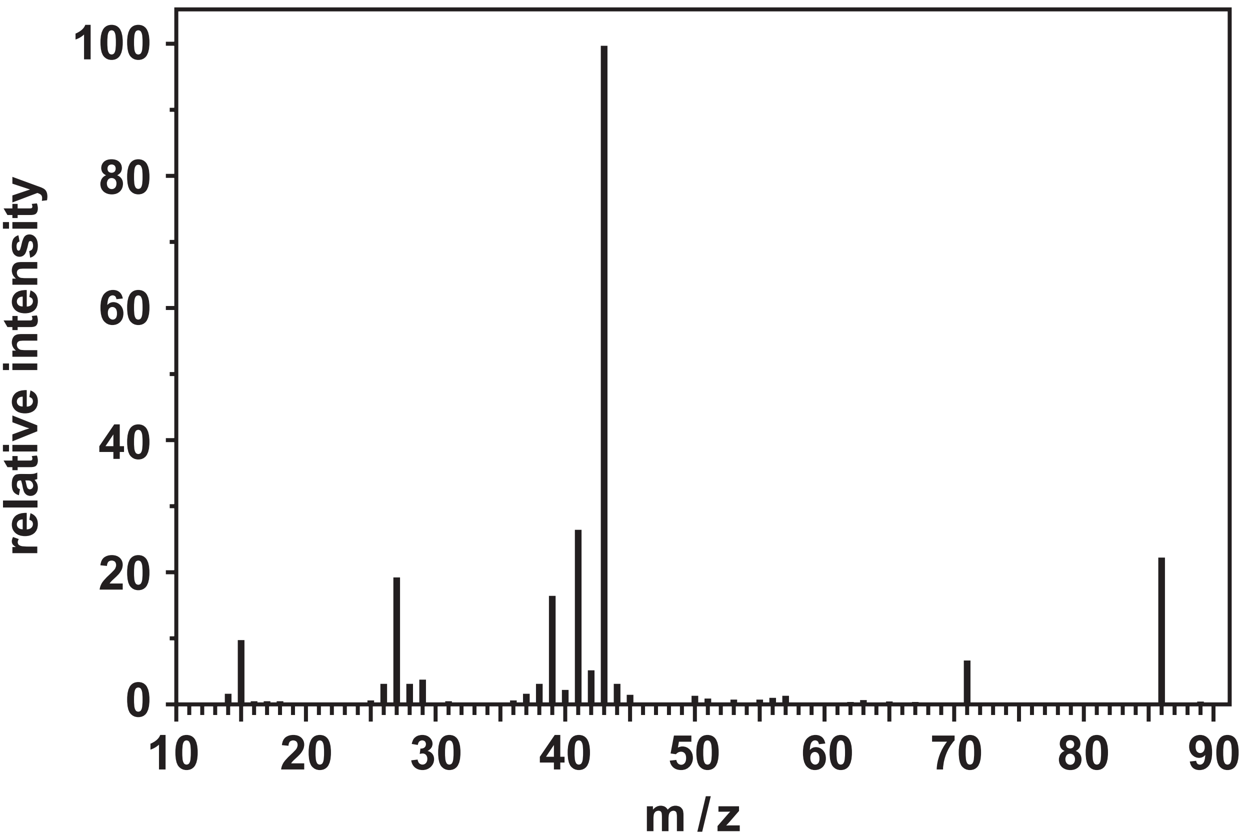
The boiling temperature of 3-methylbutan-2-one is 94 °C.

Predict any change(s) you would see in the infrared spectrum after redistillation, justifying your answer. (2 marks)

(Question continues on next page)

(Turn over)

(e) The mass spectrum of pure 3-methylbutan-2-one is shown.



(i) State how you would find the molar mass of 3-methylbutan-2-one from the mass spectrum. (1 mark)

____

____

____

(Question continues on next page)

(ii) The mass spectrum shows a peak at m/z = 43.

Draw the DISPLAYED formulae of two fragment IONS that might be responsible for this peak. (2 marks)

(Question continues on next page)

(Turn over)

(f) The sample of purified 3-methylbutan-2-one is found to have a mass of 2·15 g.

This mass of 3-methylbutan-2-one represents a yield of 62·5% by mass.

(i) Write an equation, using MOLECULAR formulae, for the oxidation of 3-methylbutan-2-ol to 3-methylbutan-2-one. Use [O] to represent the oxidising agent. (2 marks)

(Question continues on next page)

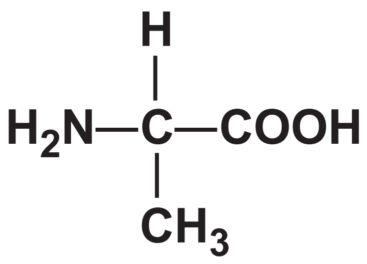
(Turn over)

(ii) Calculate the mass of 3-methylbutan-2-ol that the student uses at the start of the preparation. (2 marks)

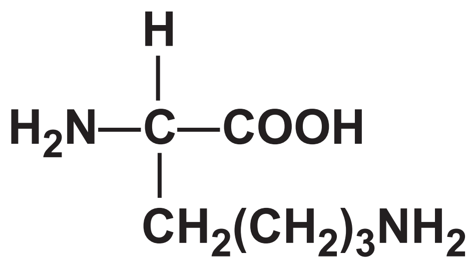
(TOTAL FOR QUESTION 2 = 21 MARKS)

(Questions continue on next page)

3 Alanine and lysine are amino acids.



alanine



lysine

(a) Give the systematic (IUPAC) name for LYSINE. (1 mark)

(b) Draw the STRUCTURE of the organic product formed when LYSINE reacts with the following reagents: (3 marks)

aqueous sodium hydroxide, NaOH(aq)

(Continue your answer on next page)

excess dilute hydrochloric acid, $HCl(aq)$

methanol, with warming, in the presence of a few drops of concentrated sulfuric acid.

(Question continues on next page)

(c) Draw the structure of a dipeptide formed when one molecule of alanine reacts with one molecule of lysine. (1 mark)

(Question continues on next page)

(Turn over)

(d) The dipeptide formed in part (c) is hydrolysed under ACIDIC conditions and the resulting mixture is analysed by column chromatography. The column uses a polar stationary phase.

Explain why lysine leaves the chromatography column after alanine. (2 marks)

(TOTAL FOR QUESTION 3 = 7 MARKS)

(Questions continue on next page)

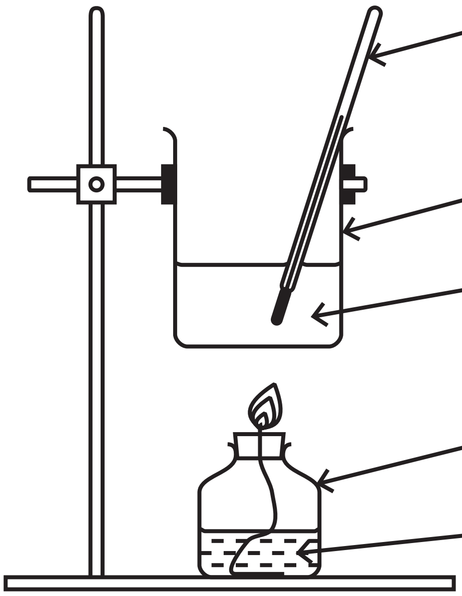
4 **This question is about the enthalpy change of combustion of methanol.**

A teacher asked two students to carry out a practical task to determine the enthalpy change of combustion of methanol.
Both students were provided with the same apparatus and chemicals.
The following procedure was provided for the students.

PROCEDURE

- **Measure out 150 cm^3 of distilled water, using a 250 cm^3 measuring cylinder.**
- **Transfer the water to a copper calorimeter and note the initial temperature of the water (to the nearest 0·5 ^oC) in TABLE 1.**
- **Weigh the spirit burner containing methanol and record its mass in TABLE 1.**
- **Place the spirit burner under the copper calorimeter, as shown in the diagram.**
- **Ignite the spirit burner and burn the methanol, whilst stirring the water with the thermometer.**
- **After heating the water for three minutes, extinguish the flame and immediately record the HIGHEST temperature reached by the water.**
- **As soon as possible, reweigh the spirit burner containing the methanol and record its mass in TABLE 1.**

(Question continues on next page)



The results of Student 1 are recorded in TABLE 1.

Mass of spirit burner plus methanol before burning / g	213·47
Mass of spirit burner plus methanol after burning / g	211·87
Mass of methanol burned / g	
Highest temperature of the water / ^{o}C	64·5
Initial temperature of the water / ^{o}C	22·0
Temperature change of the water / ^{o}C	

TABLE 1

(a) Complete TABLE 1, giving the values to an appropriate number of decimal places. (2 marks)

(Question continues on next page)

(Turn over)

(b) Write the equation that represents the reaction that occurs when the standard enthalpy change of combustion of methanol, $CH_3OH(l)$, is measured. Include state symbols. (2 marks)

(Question continues on next page)

(Turn over)

(c) Use Student 1's result to calculate the enthalpy change of combustion of methanol in kJ mol^{-1}. Give your answer to an appropriate number of significant figures. (4 marks)

Specific heat capacity of water = 4·18 J g^{-1} $^{o}C^{-1}$
Density of water = 1·00 g cm^{-3}

(Question continues on next page)

(Turn over)

(d) Student 1 compared the experimental value for the enthalpy change of combustion of methanol obtained in part (c) with the standard value given on the internet. The student's value was LESS EXOTHERMIC than the standard value.

Student 1 decided to evaluate the uncertainty in the measurements made in this experiment.

(i) Student 1 used a 250 cm^3 measuring cylinder to measure the volume of 150 cm^3 distilled water. The uncertainty in this volume measurement is ±1 cm^3.

Calculate the percentage uncertainty in the volume of distilled water that Student 1 measured in the experiment. (1 mark)

(Question continues on next page)

(ii) **Compare and contrast the use of a 250 cm^3 measuring cylinder to measure out the 150 cm^3 distilled water with the use of a 25 cm^3 measuring cylinder (uncertainty $\pm 0{\cdot}2$ cm^3 for each volume measurement) six times to measure the same volume. (3 marks)**

(Question continues on next page)

(Turn over)

(iii) Student 1 calculated the uncertainties in the remaining measurements. However, Student 1 realised that the measurement uncertainties did NOT explain the difference between the experimental value for the enthalpy change of combustion of methanol calculated in part (c) and the value obtained from the internet.

Other than human error, give THREE reasons for the difference in the values. (3 marks)

(Question continues on next page)

(Turn over)

(e) Student 1 decided to repeat the experiment.

Student 1 used the copper calorimeter and water from the first experiment and recorded the initial temperature as 60·0 ^{o}C.
Student 1 burned EXACTLY the same mass of methanol as in the first experiment.

Explain, with a reason, how the value for the enthalpy change of combustion of methanol from this experiment would differ, if at all, from the value obtained in the first experiment. (2 marks)

(Question continues on next page)

(Turn over)

(f) Student 2 followed the ORIGINAL instructions provided, but extinguished the flame after FOUR minutes rather than after three minutes.

Explain how the value calculated by Student 2 for the enthalpy change of combustion of methanol compared with that obtained in Student 1's first experiment. (2 marks)

(Question continues on next page)

(g) Another student, Student 3, used the results from Student 1's first experiment to find the enthalpy change of combustion of methanol. Student 3 incorrectly used a value of 46·0 g mol^{-1} for the molar mass of methanol.

State and justify how this mistake would affect the calculated value for the enthalpy change of combustion of methanol. (2 marks)

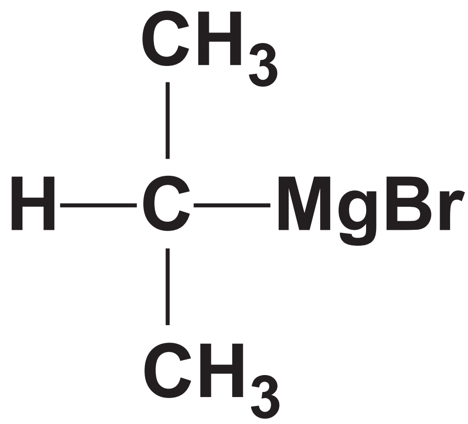
(TOTAL FOR QUESTION 4 = 21 MARKS)

(Questions continue on next page)

(Turn over)

5 Grignard reagents are used in organic synthesis as a way of increasing the length of the carbon chain in a molecule.

(a) The structure of the Grignard reagent formed by the reaction between 2-bromopropane and magnesium is



On the diagram, draw the permanent dipole involving the central carbon atom. (1 mark)

(Question continues on next page)

(b) The Grignard reagent in part (a) reacts with propanal.

(i) Draw the FULLY DISPLAYED formula of the final organic product of this reaction. (1 mark)

(ii) Name the organic product in (b)(i). (1 mark)

(Question continues on next page)

(Turn over)

(c) Identify, by using ticks, TWO boxes in the table to select appropriate terms that describe a Grignard reagent. (2 marks)

acid	
electrophile	
nucleophile	
oxidising agent	
reducing agent	

(Question continues on next page)

(Turn over)

(d) The solvent used for Grignard reagents has to be completely DRY.

By considering the dipole on the O—H bonds in water, predict the identity of the organic product that forms if water is added to the Grignard compound in part (a). (1 mark)

(TOTAL FOR QUESTION 5 = 6 MARKS)

(Questions continue on next page)

6 A student carried out an investigation to determine the value of x in hydrated magnesium nitrate(III), $Mg(NO_2)_2 \bullet xH_2O$, using three different methods.

METHOD 1

- The student prepared an aqueous solution by dissolving 1·15 g of $Mg(NO_2)_2 \bullet xH_2O$ in distilled water, making up the solution to 250·0 cm^3 in a volumetric flask and shaking the mixture.
- The student titrated this solution against 25·0 cm^3 portions of an acidified solution of 0·0200 mol dm^{-3} potassium manganate(VII), $KMnO_4(aq)$.

METHOD 2

- The student mixed a solution of $Mg(NO_2)_2 \bullet xH_2O$ with an excess of aqueous sodium carbonate solution, $Na_2CO_3(aq)$.
- The student obtained a precipitate of magnesium carbonate, $MgCO_3(s)$, and determined the mass of this precipitate.

METHOD 3

- The student heated a known mass of $Mg(NO_2)_2 \bullet xH_2O(s)$.
- The student determined the mass of the anhydrous residue formed.

(Question continues on next page)

METHOD 1 – TITRATION

The student filled the burette with the solution made from $Mg(NO_2)_2 \bullet xH_2O$.

In each titration

- $25{\cdot}0\ cm^3$ of $0{\cdot}0200\ mol\ dm^{-3}$ $KMnO_4(aq)$ was transferred to a conical flask using a pipette.
- An excess of dilute sulfuric acid was added to the conical flask and the mixture heated.
- $Mg(NO_2)_2(aq)$ was added from the burette until the end-point was reached.

The student's titration results are shown in the table (the rough titration results have NOT been included in the table).

Titration number	1	2	3
Final burette reading / cm^3	23·95	48·05	23·85
Initial burette reading / cm^3	0·80	24·50	0·65
Titre / cm^3			
Concordant titres (✓)			
Mean titre / cm^3			

(a) Complete the table. (2 marks)

(Question continues on next page)

(Turn over)

(b) Deduce the colour change that the student would see at the end-point in this titration. (1 mark)

From ________________________ to ________________________

(c) In the titration reaction, 2 mol MnO_4^- react with 5 mol NO_2^-.
Calculate the number of moles of NO_2^-, in the 250 cm^3 of solution prepared by the student and hence the value of x in $Mg(NO_2)_2 \bullet xH_2O$.
Give your answer to the nearest whole number.
(5 marks)

(Question continues on next page)

(Turn over)

(d) The half-equations for the reaction in the titration are

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

$$NO_2^- + H_2O \longrightarrow NO_3^- + 2H^+ + 2e^-$$

Use these half-equations to derive the overall ionic equation for the reaction between manganate(VII) and nitrate(III) ions in acidic conditions.
State symbols are not required. (2 marks)

(Question continues on next page)

(Turn over)

METHOD 2 – PRECIPITATION

The student used the following procedure.

- Dissolve a known mass of $Mg(NO_2)_2 \bullet xH_2O$ in distilled water.
- Add an excess of aqueous sodium carbonate solution, $Na_2CO_3(aq)$, to obtain a precipitate of magnesium carbonate, $MgCO_3(s)$.

$$Mg^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow MgCO_3(s)$$

- Weigh a piece of filter paper.
- Filter the mixture from the above reaction through the pre-weighed filter paper.
- Wash the precipitate of $MgCO_3(s)$ with distilled water.
- Dry the filter paper and precipitate in a desiccator.
- Reweigh the filter paper and the precipitate.
- Calculate the value of x from the results obtained.

The student found that the value of x calculated using METHOD 2 was different from that obtained using METHOD 1. This difference occurred despite having used a pure sample of the hydrated salt and without making any errors in technique during the experiment.

The student found out from a data book that the compound magnesium carbonate is very slightly soluble in water.

(Question continues on next page)

(e) Explain how, if at all, the very slight solubility of magnesium carbonate in water would affect the value calculated for x. (2 marks)

(Question continues on next page)

(f) **The student planned to obtain any dissolved magnesium carbonate by evaporating the filtrate, and then weighing the residue.**

Criticise this student's plan. (2 marks)

(Question continues on next page)

METHOD 3 – THERMAL DECOMPOSITION

NOTE: On heating, $Mg(NO_2)_2 \bullet xH_2O(s)$ loses its water of crystallisation and THEN undergoes further decomposition to give magnesium oxide, MgO.

The student used the following procedure.

- Weigh an empty crucible.
- Add some $Mg(NO_2)_2 \bullet xH_2O(s)$ and then reweigh the crucible plus contents.
- Heat the crucible plus contents and allow to cool.
- Weigh the crucible plus magnesium oxide residue.
- Use these data to calculate a value for x.

The student's results are shown in the table.

Mass of crucible / g	18·02
Mass of crucible + $Mg(NO_2)_2.xH_2O$ / g	18·84
Mass of crucible + MgO residue / g	18·27

(Question continues on next page)

(g) Identify how the student should ensure that the hydrated salt was fully decomposed. (1 mark)

(h) The student carried out an evaluation of the results obtained from METHOD 3

Identify TWO modifications to the method that would enable the student to lower the percentage uncertainty in the measurement of the mass of the solid residue. (2 marks)

(TOTAL FOR QUESTION 6 = 17 MARKS)

(Questions continue on next page)

(Turn over)

7 This question is about the chemistry of elements in the d-block of the Periodic Table.

*(a) Many of the d-block elements are also classified as transition metals.

Explain why two of the d-block elements within Period 4 (scandium to zinc) are NOT classified as transition metals.

You should include FULL electronic configurations where relevant. (6 marks)

(Continue your answer on next page)

(Turn over)

(Continue your answer on next page)

(Turn over)

(Question continues on next page)

(b) Under certain conditions, dichromate(VI) ions, $Cr_2O_7^{2-}$, can oxidise manganese(II) ions, Mn^{2+}.

In this reaction, dichromate(VI) ions are reduced to chromium(III) ions, in acidic conditions, according to the half-equation

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$$

In an experiment it was found that 20·0 cm^3 of 0·100 mol dm^{-3} potassium dichromate(VI) was required to oxidise 30·0 cm^3 of 0·200 mol dm^{-3} manganese(II) sulfate solution.

Use these data to calculate the final oxidation state of the manganese. (5 marks)

(Continue your answer on next page)

(Turn over)

(Question continues on next page)

(c) A student constructed an electrochemical cell as follows:

- a half-cell was made from a strip of chromium metal and a solution of aqueous chromium(III) sulfate
- a second half-cell was made from a piece of metal, X, and a solution of its sulfate, $XSO_4(aq)$
- the two half-cells were connected and a current allowed to pass for some time.

RESULTS

- the chromium electrode increased in mass by 1·456 g
- the electrode made of metal X decreased in mass by 1·021 g.

Use these data to determine the identity of the metal, X. (4 marks)

(Continue your answer on next page)

(TOTAL FOR QUESTION 7 = 15 MARKS)

(Questions continue on next page)

8 The chemistry of organic compounds containing a chlorine atom is affected by the presence of other groups.

Consider the reaction of ammonia, NH_3, with $CH_3CH_2CH_2Cl$ and with CH_3CH_2COCl.

(a) Draw the mechanism for the reaction of $CH_3CH_2CH_2Cl$ with an EXCESS of ammonia to form the primary amine. Include curly arrows and relevant lone pairs. (3 marks)

(Question continues on next page)

(Turn over)

(b) Predict the mechanism for the reaction of CH_3CH_2COCl with ammonia. Include curly arrows and relevant lone pairs. (3 marks)

(TOTAL FOR QUESTION 8 = 6 MARKS)

(Questions continue on next page)

(Turn over)

9 The gas phase reaction between hydrogen and iodine is reversible.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

(a) (i) Write the expression for the equilibrium constant, K_c, for this reaction. (1 mark)

(ii) If the starting concentration of both hydrogen and iodine was a mol dm^{-3} and it was found that 2y mol dm^{-3} of hydrogen iodide had formed once equilibrium had been established, write the K_c expression in terms of a and y. (2 marks)

(Question continues on next page)

(Turn over)

(b) The expression for the equilibrium constant in (a)(ii) can be rearranged as shown.

$$y = \frac{a\sqrt{K_c}}{2 + \sqrt{K_c}}$$

In an experiment, air was removed from a 1 dm^3 flask and amounts of hydrogen and iodine gases were mixed together such that their initial concentrations were both a mol dm^{-3}. This mixture was allowed to reach equilibrium at 760 K. The equilibrium concentration of iodine was then measured.

The experiment was repeated for various initial concentrations, a mol dm^{-3}, and the results recorded in the table.

(Question continues on next page)

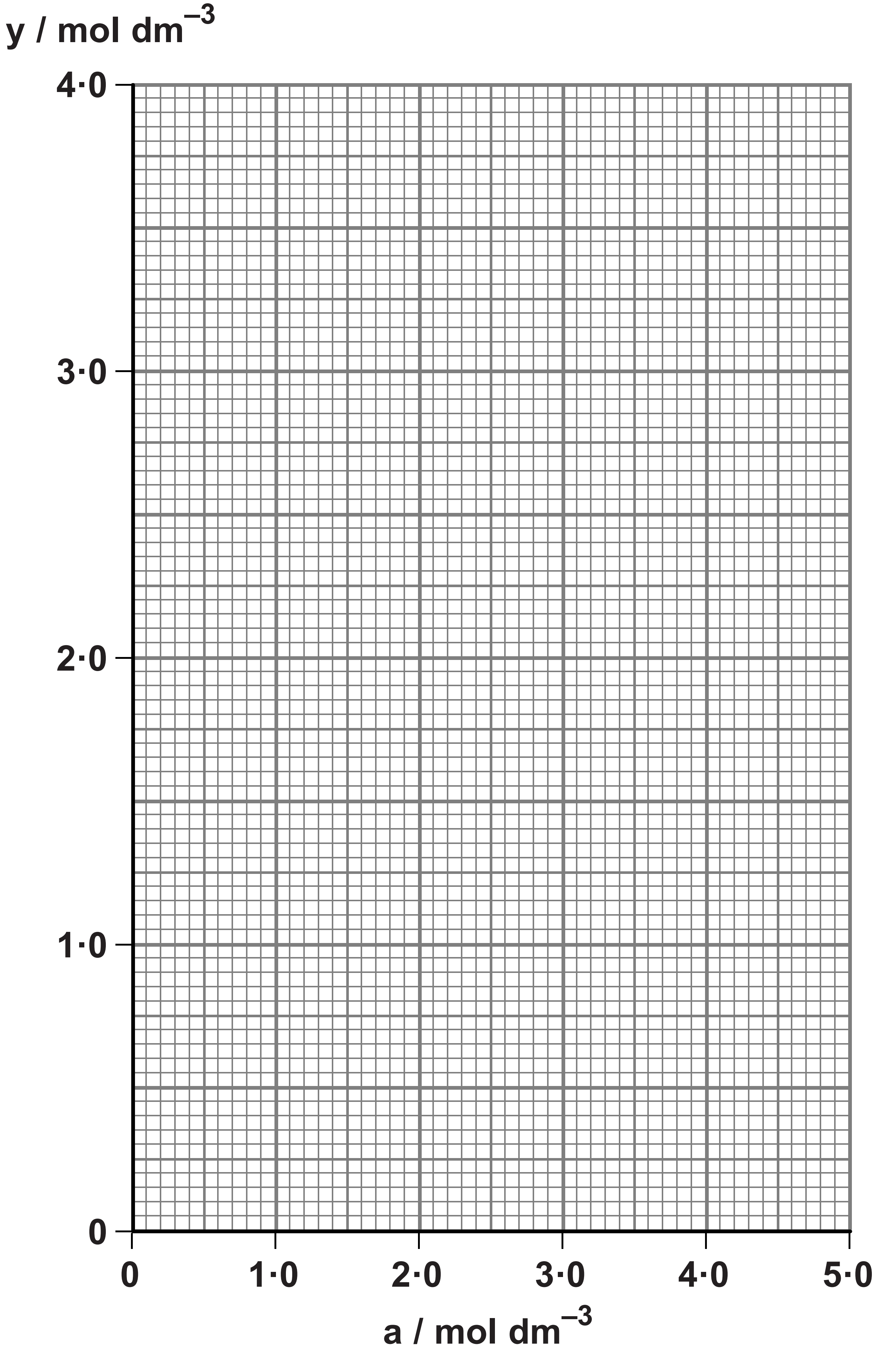
(Turn over)

(i) Complete the table to give the two remaining values of y mol dm^{-3}, to TWO decimal places. (1 mark)

a / mol dm^{-3}	$[I_2]_{eq}$ / mol dm^{-3}	y / mol dm^{-3}
0·20	0·02	0·18
0·80	0·25	0·55
1·50	0.37	
2·10	0·57	1·53
2·80	0·65	2·15
3·80	0·87	
4·90	1·15	3·75

(ii) On page 59 plot a graph to show how y mol dm^{-3} varies with the initial concentrations of hydrogen and iodine, a mol dm^{-3}. (2 marks)

(Question continues on next page)



(Question continues on next page)

(iii) Determine the gradient of your graph.
Show your working on the graph. (2 marks)

(iv) Use your answer to (b)(iii) and the expression

$$y = \frac{a\sqrt{K_c}}{2 + \sqrt{K_c}}$$ **to calculate the value of K_c.**

(2 marks)

(Question continues on next page)

(Turn over)

(c) Identify a safety issue associated with this experiment. (1 mark)

(d) One of the experiments in part (b) was repeated using the same molar quantities of hydrogen and iodine but in a 500 cm^3 flask instead of the 1 dm^3 flask.

Deduce the effect, if any, that this would have on the rate of reaction and on the value of K_c calculated. (2 marks)

(Question continues on next page)

(Turn over)

(e) The equation for the reaction between hydrogen and iodine is

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad \Delta H = -9{\cdot}6 \text{ kJ mol}^{-1}$$

(i) Explain the effect, if any, on the value of K_c when the temperature is increased. (2 marks)

(ii) On your graph in (b)(ii), draw and label the line you would expect if the experiment was carried out at 1000 K instead of 760 K. (1 mark)

(TOTAL FOR QUESTION 9 = 16 MARKS)

TOTAL FOR PAPER = 120 MARKS

END