



Rewarding Learning

ADVANCED
General Certificate of Education
2023

Centre Number

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Candidate Number

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Chemistry

StemUp Model Solution

Assessment Unit A2 3

assessing

Further Practical Chemistry

Practical Booklet B (Theory)



[ACH32]

ACH32

TUESDAY 20 JUNE, MORNING

TIME

1 hour 15 minutes.

INSTRUCTIONS TO CANDIDATES

Write your Centre Number and Candidate Number in the spaces provided at the top of this page.

You must answer the questions in the spaces provided.

Do not write outside the boxed area on each page or on blank pages.

Complete in black ink only. **Do not write with a gel pen or with a pencil.**

Answer **all four** questions.

INFORMATION FOR CANDIDATES

The total mark for this paper is 60.

Figures in brackets printed down the right-hand side of pages indicate the marks awarded to each question or part question.

A Periodic Table of Elements (including some data) is provided.

13624.07R



- 1 (a) Describe, giving experimental details, how the concentration of a solution of hydrogen peroxide may be determined using sodium thiosulfate solution. Include all the colour changes which occur. No details of calculations are required.

Using a pipette, transfer 25.0 cm³ of the hydrogen peroxide solution into a conical flask.

Add excess dilute sulfuric acid and excess potassium iodide solution.

The solution changes from colourless to brown as iodine is liberated:



Fill a burette with standard sodium thiosulfate solution and titrate, swirling, until the brown solution becomes a pale straw (yellow) colour.

Add 3 drops of starch indicator solution: the solution turns blue-black.

Continue adding the thiosulfate dropwise until the indicator changes colour from blue-black to colourless. Record the titre.

Repeat the titration to obtain concordant titres (within 0.10 cm³) and find the mean titre.

[6]



- (b) Sodium thiosulfate solution may also be used in a redox titration to analyse the percentage purity of copper foil. A copper foil electrode from an electrochemical cell has a mass of 1.93 g. All of the copper metal in the electrode was converted into copper(II) ions in 250 cm³ of solution.

Excess potassium iodide was added to 25.0 cm³ samples of this solution and titrated against 0.1 mol dm⁻³ sodium thiosulfate solution. The average titre was 26.4 cm³.

- (i) Write the ionic equation for the reaction between iodine and thiosulfate ions.



- (ii) The ionic equation for the reaction between copper(II) ions and iodide ions is:



Use the ionic equation and your answer to (b)(i) to state the ratio of copper(II) ions to thiosulfate ions.



- (iii) Calculate the percentage purity of the copper foil electrode. Give your answer to the nearest whole number.

$$\text{moles of } S_2O_3^{2-} = 26.4 \times 0.1 \div 1000 = 2.64 \times 10^{-3} \text{ mol}$$

$$\text{moles of } Cu^{2+} \text{ in } 25.0 \text{ cm}^3 = 2.64 \times 10^{-3} \text{ mol}$$

$$\text{moles of } Cu^{2+} \text{ in } 250 \text{ cm}^3 = 2.64 \times 10^{-3} \times 10 = 0.0264 \text{ mol}$$

$$\text{mass of Cu} = 0.0264 \times 64 = 1.6896 \text{ g}$$

$$\% \text{ purity} = 1.6896 \div 1.93 \times 100 = 87.5 = 88 \%$$

Answer 88 % [5]

[Turn over]

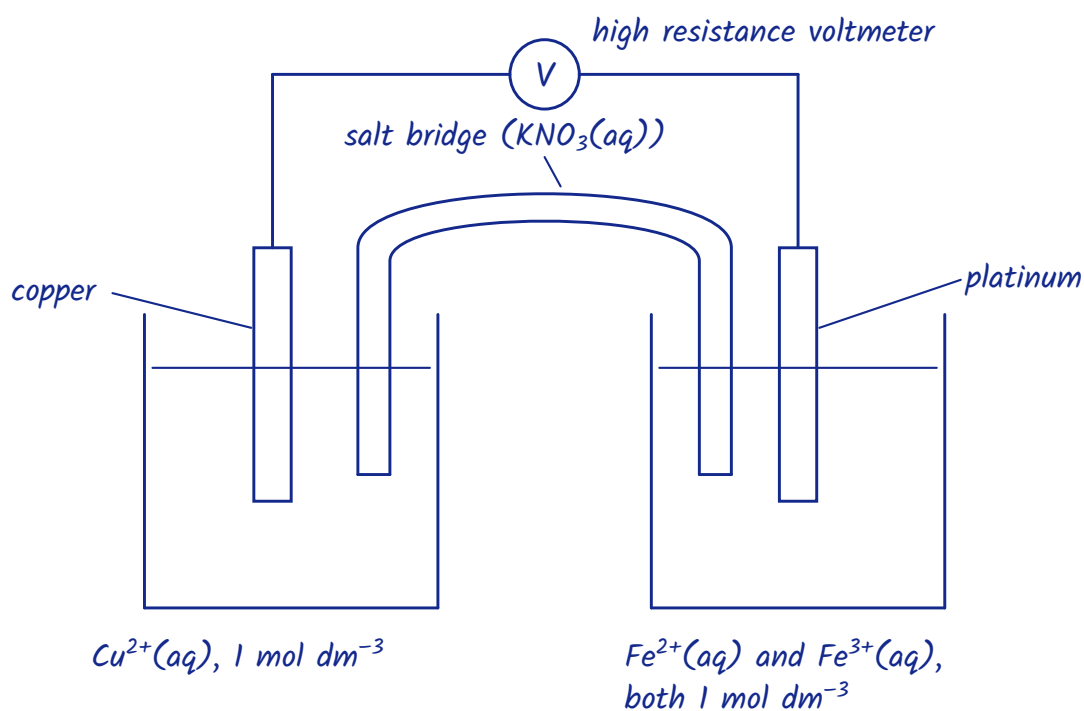
13624.07R



- 2 Electrochemical cells are made up of two half-cells. The table below gives some standard electrode potentials.

Half-equation	$E^\ominus/\text{V}$
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$	-0.76
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$	$+0.34$
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$	$+0.77$

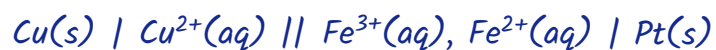
- (a) Draw a labelled diagram of the electrochemical cell which you would use to measure the emf between the $\text{Fe}^{3+}/\text{Fe}^{2+}$ and the Cu^{2+}/Cu half-cells.



[5]



- (b) Write the conventional cell representation of the electrochemical cell you have drawn in (a).



[2]

- (c) Calculate the emf of the electrochemical cell in (a).

$$\text{emf} = E_{\text{right}} - E_{\text{left}} = (+0.77) - (+0.34)$$

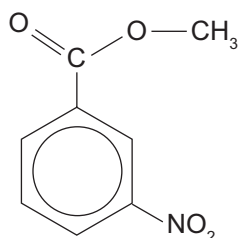
Answer +0.43 V [1]

[Turn over]

13624.07R



- 3 Methyl benzoate may be nitrated by the nitronium ion to form methyl 3-nitrobenzoate. The structure of methyl 3-nitrobenzoate is shown below.

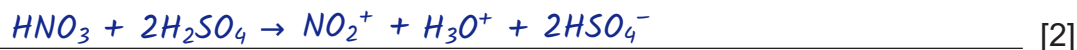


methyl 3-nitrobenzoate

Methyl 3-nitrobenzoate is prepared by the method below.

1. Dissolve methyl benzoate in concentrated sulfuric acid and cool the solution in ice.
2. Prepare the nitrating mixture by carefully adding concentrated sulfuric acid to concentrated nitric acid and then cool this mixture in ice.
3. Add the nitrating mixture drop by drop to the solution of methyl benzoate, stir with a thermometer and keep the temperature below 10 °C.
4. Pour the reaction mixture onto crushed ice and stir until all the ice has melted and solid methyl 3-nitrobenzoate forms.

- (a) (i) Write an equation for the production of the nitronium ion.



- (ii) Explain why the nitrating mixture is added drop by drop and why the temperature is kept below 10 °C.

Nitration is exothermic, so the nitrating mixture is added slowly

(drop by drop) to control the temperature.

The temperature is kept below 10 °C to prevent multiple nitration

(more than one NO₂ group substituting). [2]



(b) The product, methyl 3-nitrobenzoate, is purified by recrystallisation from ethanol.

(i) Describe the appearance of the product.

Cream (crystalline) solid [1]

(ii) Describe how you would determine the melting point of the recrystallised product.

Place a small amount of the dry, powdered crystals in a capillary tube sealed at one end.

Heat the tube slowly in a melting point apparatus, especially near the expected melting point.

Record the temperatures at which the crystals start to melt and finish melting. [3]

(iii) State how the melting point can be used to determine if the product is pure.

A pure sample has a sharp melting point (melts over a narrow range) which matches the data book value.

[1]

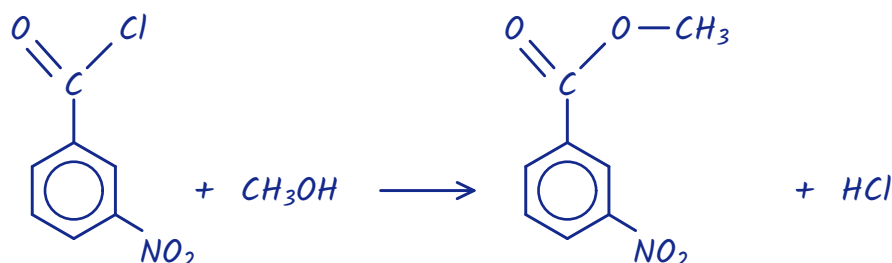
[Turn over]

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(c) Methyl 3-nitrobenzoate may also be prepared from solid 3-nitrobenzoyl chloride and methanol.

(i) Write an equation for this reaction.



[2]

(ii) Calculate the minimum volume of methanol which would be required to react with 14.4 g of 3-nitrobenzoyl chloride. The density of methanol is 0.79 g cm^{-3} . Give your answer to 2 significant figures.

$$M_r \text{ of } \text{O}_2\text{NC}_6\text{H}_4\text{COCl} = 185.5$$

$$\text{moles} = 14.4 \div 185.5 = 0.0776 \text{ mol}$$

$$\text{moles of methanol (1 : 1 ratio)} = 0.0776 \text{ mol}$$

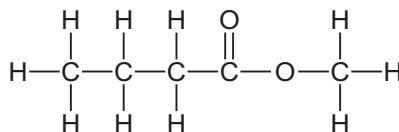
$$\text{mass of methanol} = 0.0776 \times 32 = 2.48 \text{ g}$$

$$\text{volume} = \text{mass} \div \text{density} = 2.48 \div 0.79 = 3.14 = 3.1 \text{ cm}^3$$

Answer 3.1 cm³ [3]

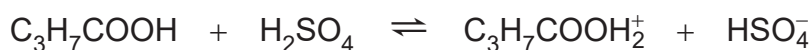


- 4 The liquid ester methyl butanoate, $\text{C}_3\text{H}_7\text{COOCH}_3$, is prepared by the esterification of butanoic acid with methanol in the presence of concentrated sulfuric acid. The crude ester is separated from the reaction mixture by distillation.



methyl butanoate

- (a) The first step in this esterification is shown below.



Write the formula of an acid and its conjugate base from the equation above.

acid H_2SO_4 conjugate base HSO_4^- [2]

- (b) The crude ester is purified in a series of steps using sodium carbonate solution and anhydrous calcium chloride.

- (i) Identify an impurity in the crude ester which could be removed using sodium carbonate solution.

Unreacted butanoic acid (or sulfuric acid)

[1]

[Turn over]



- (ii) Describe, giving practical details, how the crude ester is reacted with sodium carbonate solution and how the layers obtained can be identified practically and separated.

Place the crude ester and sodium carbonate solution together in a separating funnel.

Stopper the funnel and shake (carbon dioxide gas is produced).

Invert the funnel and open the tap periodically to release the gas pressure.

Clamp the funnel, remove the stopper and allow to stand until the two layers settle and separate.

To identify the layers, add some water: the aqueous layer increases in size.

Run off the lower (aqueous) layer through the tap and discard it, keeping the upper ester layer.

[6]

- (iii) Explain the purpose of adding anhydrous calcium chloride to the crude ester and state how it may be removed from the ester.

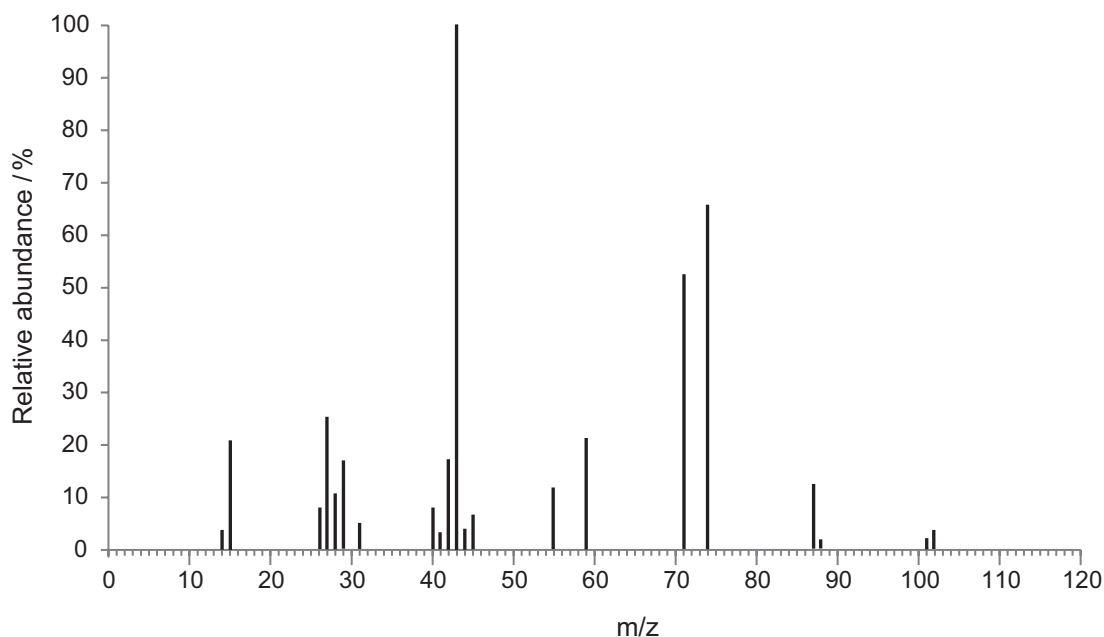
It is a drying agent: it removes water from the ester.

It is removed by filtering (or decanting) off the solid.

[2]



- (c) A sample of pure methyl butanoate was analysed using mass spectrometry. The mass spectrum obtained is shown below.



- (i) Explain what is meant by the term **base peak** and state the m/z value of the base peak in the spectrum above.

The base peak is the peak of greatest abundance (the tallest peak, 100 %) in the mass spectrum.

Base peak: $m/z = 43$

[2]

- (ii) Identify two fragmentation ions, which could be responsible for the peaks at m/z values of 29 and 71.

29 *CH_3CH_2^+ (C_2H_5^+)*

71 *$\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}^+$ ($\text{C}_4\text{H}_7\text{O}^+$)*

[2]

[Turn over]

13624.07R



- (d) Methyl butanoate produces four signals when analysed by nmr spectroscopy as shown in the table below.

Signal	A	B	C	D
Chemical shift /ppm	4.9	3.2	2.6	1.9
Integration	3	2	2	3
Spin-spin splitting pattern	singlet	triplet	multiplet	triplet

- (i) State the name of the compound used as a standard in nmr spectroscopy and state one reason why it is chosen.

Tetramethylsilane, TMS, $\text{Si}(\text{CH}_3)_4$.

All 12 hydrogen atoms are equivalent, so it gives a single signal

(it is also inert and non-toxic).

[2]

- (ii) Explain, with reference to the chemical shift and the structure of methyl butanoate, which hydrogen atoms produce the signal at A.

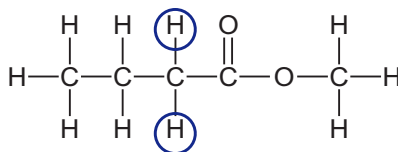
Signal A is due to the 3 H atoms of the CH_3 group adjacent to the O atom ($\text{O}-\text{CH}_3$).

It has the highest chemical shift (4.9 ppm), so these H atoms are the most deshielded, because they are next to the electronegative O atom (singlet: no H on the adjacent atom).

[3]

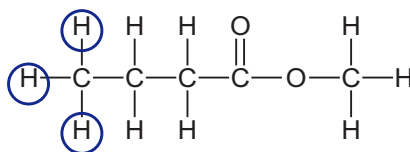


- (iii) On the structure below, circle all the hydrogen atoms which produce the signal at **B**.



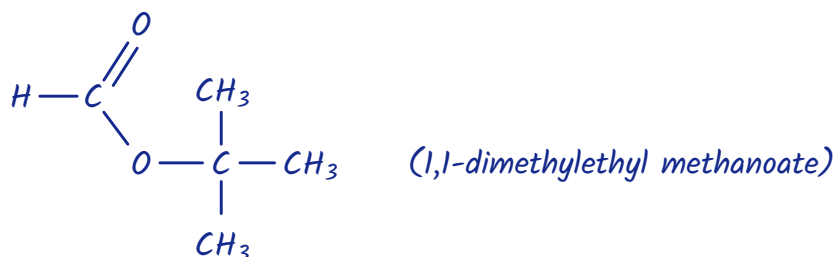
[1]

- (iv) On the structure below, circle all the hydrogen atoms which produce the signal at **D**.



[1]

- (v) Suggest the structure of an ester which is an isomer of methyl butanoate which contains only two peaks, which are both singlets, in its nmr spectrum.



[2]

- (vi) State the integration ratio for the singlet peaks of the isomer drawn in (d)(v).

9 : 1

[1]



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Question Number	Examiner Mark	Remark
1		
2		
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Total Marks		

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General Information

1 tonne = 10^6 g

1 metre = 10^9 nm

One mole of any gas at 293 K and a pressure of 1 atmosphere (10^5 Pa) occupies a volume of 24 dm³

Avogadro Constant = 6.02×10^{23} mol⁻¹

Planck Constant = 6.63×10^{-34} Js

Specific Heat Capacity of water = $4.2 \text{ J g}^{-1} \text{ K}^{-1}$

Speed of Light = $3 \times 10^8 \text{ m s}^{-1}$



Characteristic absorptions in IR spectroscopy

Wavenumber/cm ⁻¹	Bond	Compound
550–850	C–X (X = Cl, Br, I)	Haloalkanes
750–1100	C–C	Alkanes, alkyl groups
1000–1300	C–O	Alcohols, esters, carboxylic acids
1450–1650	C=C	Arenes
1600–1700	C=C	Alkenes
1650–1800	C=O	Carboxylic acids, esters, aldehydes, ketones, amides, acyl chlorides
2200–2300	C≡N	Nitriles
2500–3200	O–H	Carboxylic acids
2750–2850	C–H	Aldehydes
2850–3000	C–H	Alkanes, alkyl groups, alkenes, arenes
3200–3600	O–H	Alcohols
3300–3500	N–H	Amines, amides

Proton Chemical Shifts in Nuclear Magnetic Resonance Spectroscopy (relative to TMS)

Chemical Shift	Structure	
0.5–2.0	–CH	Saturated alkanes
0.5–5.5	–OH	Alcohols
1.0–3.0	–NH	Amines
2.0–3.0	–CO–CH	Ketones
	–N–CH	Amines
	C ₆ H ₅ –CH	Arene (aliphatic on ring)
2.0–4.0	X–CH	X = Cl or Br (3.0–4.0) X = I (2.0–3.0)
4.5–6.0	–C=CH	Alkenes
5.5–8.5	RCONH	Amides
6.0–8.0	–C ₆ H ₅	Arenes (on ring)
9.0–10.0	–CHO	Aldehydes
10.0–12.0	–COOH	Carboxylic acids

These chemical shifts are concentration and temperature dependent and may be outside the ranges indicated above.

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Data Leaflet

Including the Periodic Table of the Elements

For the use of candidates taking
Advanced Subsidiary and
Advanced Level Examinations

Copies must be free from notes or additions of any kind. No other type of data booklet or information sheet is authorised for use in the examinations

gce a/as examinations chemistry

THE PERIODIC TABLE OF ELEMENTS																	
Group																	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H Hydrogen																	4 He Helium
7 Li Lithium	9 Be Beryllium											11 B Boron	12 C Carbon	14 N Nitrogen	16 O Oxygen	19 F Fluorine	20 Ne Neon
23 Na Sodium	24 Mg Magnesium											27 Al Aluminium	28 Si Silicon	31 P Phosphorus	32 S Sulfur	35.5 Cl Chlorine	40 Ar Argon
39 K Potassium	40 Ca Calcium	45 Sc Scandium	48 Ti Titanium	51 V Vanadium	52 Cr Chromium	55 Mn Manganese	56 Fe Iron	59 Co Cobalt	59 Ni Nickel	64 Cu Copper	65 Zn Zinc	70 Ga Gallium	73 Ge Germanium	75 As Arsenic	79 Se Selenium	80 Br Bromine	84 Kr Krypton
85 Rb Rubidium	88 Sr Strontium	89 Y Yttrium	91 Zr Zirconium	93 Nb Niobium	96 Mo Molybdenum	98 Tc Technetium	101 Ru Ruthenium	103 Rh Rhodium	106 Pd Palladium	108 Ag Silver	112 Cd Cadmium	115 In Indium	119 Sn Tin	122 Sb Antimony	128 Te Tellurium	127 I Iodine	131 Xe Xenon
133 Cs Caesium	137 Ba Barium	139 La [*] Lanthanum	178 Hf Hafnium	181 Ta Tantalum	184 W Tungsten	186 Re Rhenium	190 Os Osmium	192 Ir Iridium	195 Pt Platinum	197 Au Gold	201 Hg Mercury	204 Tl Thallium	207 Pb Lead	209 Bi Bismuth	210 Po Polonium	210 At Astatine	222 Rn Radon
223 Fr Francium	226 Ra Radium	227 Ac [†] Actinium	261 Rf Rutherfordium	262 Db Dubnium	266 Sg Seaborgium	264 Bh Bohrium	277 Hs Hassium	268 Mt Meitnerium	271 Ds Darmstadtium	272 Rg Roentgenium	285 Cn Copernicium						
			140 Ce Cerium	141 Pr Praseodymium	144 Nd Neodymium	145 Pm Promethium	150 Sm Samarium	152 Eu Europium	157 Gd Gadolinium	159 Tb Terbium	162 Dy Dysprosium	165 Ho Holmium	167 Er Erbium	169 Tm Thulium	173 Yb Ytterbium	175 Lu Lutetium	
			232 Th Thorium	231 Pa Protactinium	238 U Uranium	237 Np Neptunium	242 Pu Plutonium	243 Am Americium	247 Cm Curium	245 Bk Berkelium	251 Cf Californium	254 Es Einsteinium	253 Fm Fermium	256 Md Mendelevium	254 No Nobelium	257 Lr Lawrencium	
			90	91	92	93	94	95	96	97	98	99	100	101	102	103	
			^aX_b a = relative atomic mass (approx) x = atomic symbol b = atomic number														