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**ADVANCED**  
**General Certificate of Education**  
**2022**

Centre Number

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Candidate Number

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# Chemistry

Assessment Unit A2 3

*assessing*

Further Practical Chemistry

**Practical Booklet B (Theory)**



**[ACH32]**

\*ACH32\*

**TUESDAY 21 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.**

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.

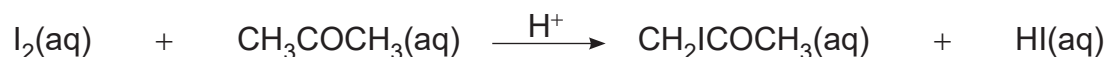
A Periodic Table of Elements (including some data) is provided.

12886.02R



\*16ACH3201\*

- 1 The kinetics of the reaction between iodine and propanone were investigated. The reaction is catalysed by hydrogen ions.



The influence of the iodine concentration on the reaction rate can be studied if large excesses of propanone and sulfuric acid are used. An experiment is carried out as follows:

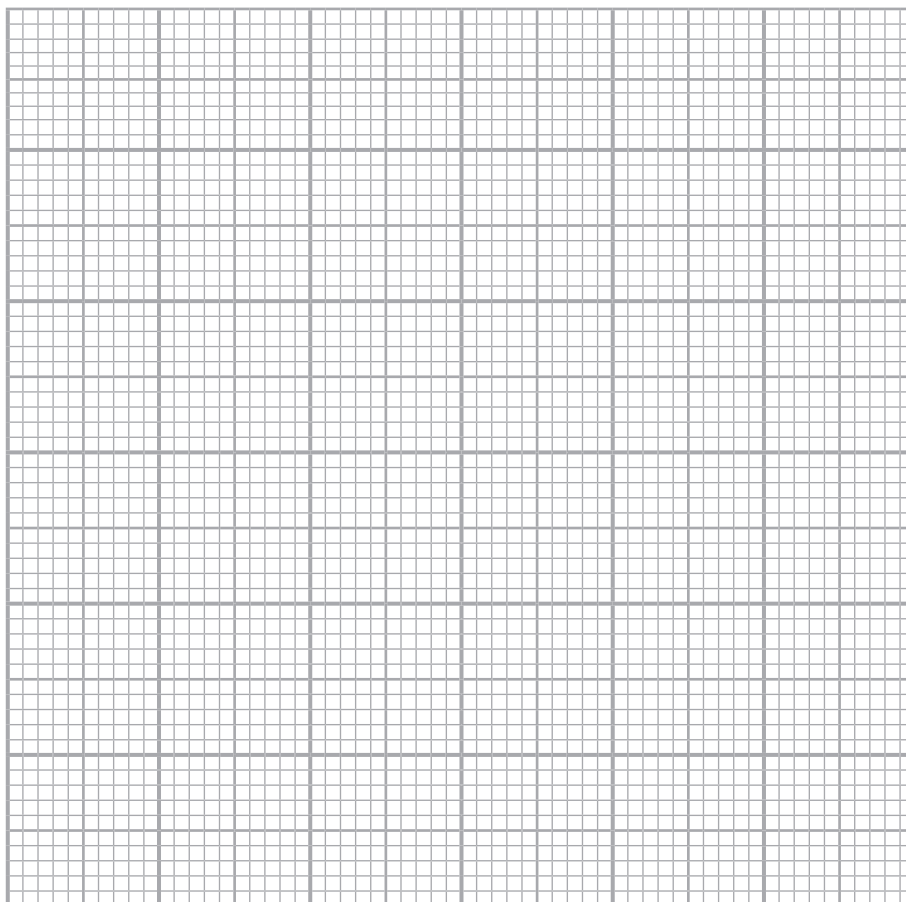
- 1 Mix 25.0 cm<sup>3</sup> of 1.0 mol dm<sup>-3</sup> propanone solution with 25.0 cm<sup>3</sup> of 1.0 mol dm<sup>-3</sup> sulfuric acid in a beaker.
- 2 Add 50.0 cm<sup>3</sup> of 0.02 mol dm<sup>-3</sup> iodine solution, stir the mixture and start a stopwatch.
- 3 Using a pipette, withdraw a 10.0 cm<sup>3</sup> sample of the mixture and transfer it to a conical flask.
- 4 Add sodium hydrogencarbonate, with stirring, until the fizzing ceases. The time at which the sodium hydrogencarbonate is added is recorded.
- 5 Titrate the solution with 0.01 mol dm<sup>-3</sup> sodium thiosulfate solution, using starch indicator.
- 6 Repeat steps 3–5 at five minute intervals.

The following results were obtained from the experiment:

| Time /min | Volume of sodium thiosulfate solution /cm <sup>3</sup> |
|-----------|--|
| 1         | 11.5   |
| 6         | 10.2   |
| 11        | 9.9  |
| 16        | 7.8  |
| 21        | 6.9  |



(a) Plot a graph of volume of sodium thiosulfate solution against time and draw a line of best fit.



[4]

(b) Identify the anomalous result from the graph.

[1]

(c) Suggest why using large excesses of propanone and sulfuric acid allows the order of reaction with respect to iodine to be deduced.

[1]

[Turn over



(d) Explain why sodium hydrogencarbonate is added to each sample.

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[1]

(e) The graph can be used to deduce the order of reaction with respect to iodine.

(i) Explain why a graph of volume of sodium thiosulfate solution against time can be used to deduce the order of reaction with respect to iodine.

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[1]

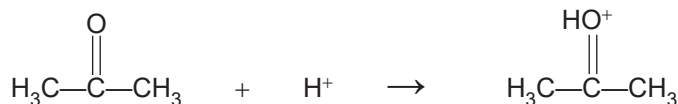
(ii) State and explain the order of reaction with respect to iodine.

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[2]

(iii) The following rate-determining step is proposed for the reaction:



Explain whether it is consistent with your answer to (e)(ii).

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[1]



(f) Starch is added towards the end of each titration.

(i) State the colour changes when starch is added to each flask and at the end point of each titration.

Colour change when starch is added to flask: \_\_\_\_\_

\_\_\_\_\_

Colour change at end point: \_\_\_\_\_

\_\_\_\_\_ [2]

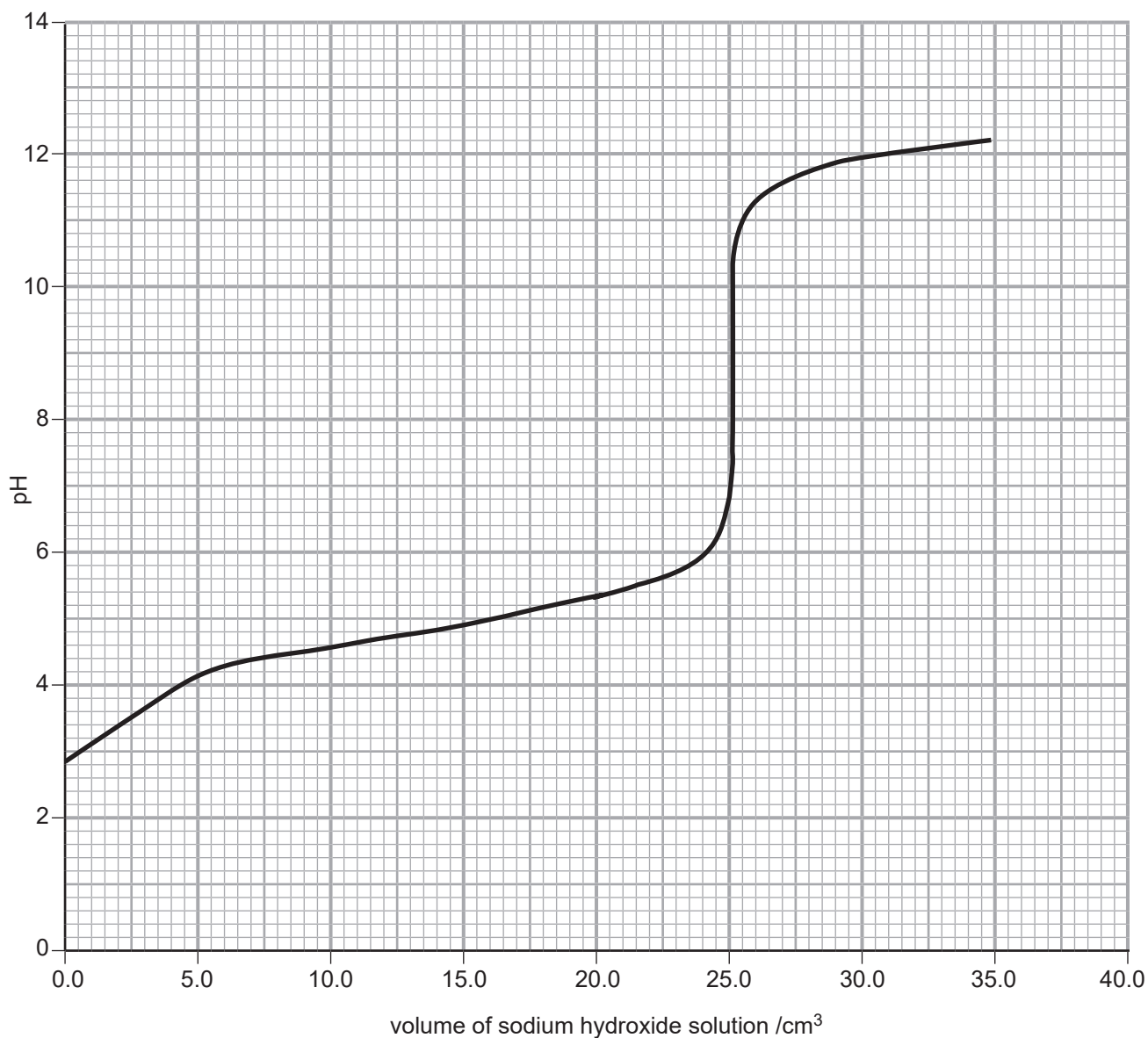
(ii) Suggest why starch is not added at the start of each titration.

\_\_\_\_\_

\_\_\_\_\_ [1]



2 The pH curve shown below was obtained when 25.0 cm<sup>3</sup> of 0.1 mol dm<sup>-3</sup> ethanoic acid were titrated against 0.1 mol dm<sup>-3</sup> sodium hydroxide solution.



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(a) (i) What volume of sodium hydroxide solution is required to neutralise half of the ethanoic acid in the titration?

\_\_\_\_\_ [1]

(ii) Use the pH curve to determine the pH of the mixture when the volume of sodium hydroxide solution in (a)(i) is added.

\_\_\_\_\_ [1]

(iii) At the pH in (a)(ii),  $[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-]$

Use your answer to (a)(ii) to determine the value of  $K_a$  for ethanoic acid. Give your answer to 3 significant figures.

\_\_\_\_\_  
\_\_\_\_\_ [1]

(b) On the axes, sketch the pH curve that would be obtained if  $0.2 \text{ mol dm}^{-3}$  sodium hydroxide solution was used in the titration. [2]

[Turn over

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\*16ACH3207\*

(c) When half of the ethanoic acid is neutralised by the sodium hydroxide solution, the resulting mixture can act as a buffer solution.

(i) Define the term **buffer solution**.

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[1]

(ii) Explain, using an ionic equation, how this solution acts as a buffer when alkali is added.

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[2]

(d) Explain why a solution of sodium ethanoate has a pH above 7.

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[1]

(e) The indicators bromophenol blue and thymol blue both exhibit the same colour change when used in acid-base titrations. Bromophenol blue changes colour in the pH range 3.0–4.5 and thymol blue changes colour in the pH range 8.0–9.6.

State and explain which indicator is suitable when  $0.1 \text{ mol dm}^{-3}$  ethanoic acid is titrated against  $0.1 \text{ mol dm}^{-3}$  sodium hydroxide solution.

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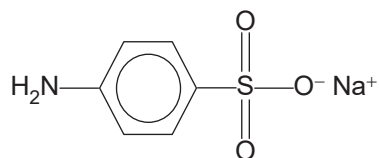
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[2]

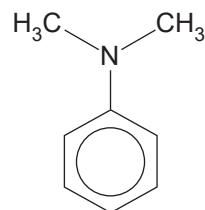




- 3 Methyl orange is an azo dye. It can be synthesised from sodium sulfanilate and N,N-dimethylaniline, which react in equimolar amounts in a coupling reaction.



sodium sulfanilate



N,N-dimethylaniline

The procedure below was used to synthesise methyl orange.

*2.70 g of sodium sulfanilate were dissolved in deionised water and sodium nitrite was added. The solution was poured over crushed ice and concentrated hydrochloric acid was added. N,N-dimethylaniline (1.71 g, density = 0.956 g cm<sup>-3</sup>), in ethanoic acid was added to this diazonium ion and the solid crude product formed. The solid was removed from the solution by suction filtration. It was recrystallised using water as a solvent and 2.32 g of methyl orange were obtained. The melting point of the recrystallised methyl orange was determined. Pure methyl orange melts at 300°C.*

- (a) Sodium sulfanilate is produced by the reaction between sulfanilic acid and sodium hydroxide. Suggest why sodium sulfanilate is used in the preparation of methyl orange rather than sulfanilic acid.

\_\_\_\_\_ [1]



(b) Nitrous acid is formed **in situ** by the reaction of sodium nitrite and hydrochloric acid.

(i) Suggest an explanation of the term **in situ**.

\_\_\_\_\_ [1]

(ii) Write an equation for the reaction between sodium nitrite and hydrochloric acid.

\_\_\_\_\_ [1]

(iii) Suggest why the solution was poured over crushed ice.

\_\_\_\_\_  
\_\_\_\_\_ [1]

(c) (i) Calculate the volume of N,N-dimethylaniline added to ethanoic acid.

\_\_\_\_\_ [1]

(ii) Suggest an equation for the reaction between N,N-dimethylaniline and ethanoic acid.

\_\_\_\_\_ [2]



(d) State a practical use for methyl orange.

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[1]

(e) (i) Draw a labelled diagram to show how suction filtration is carried out.

[3]

(ii) State **two** advantages of suction filtration.

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[2]

[Turn over

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\*16ACH3211\*

- (f) (i) Describe how the melting point of the recrystallised methyl orange was determined.

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[3]

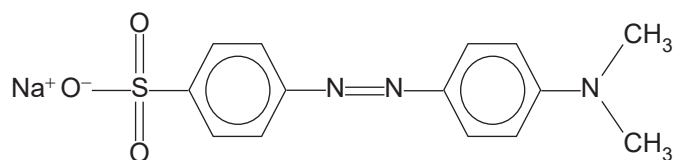
- (ii) Describe how the melting point value obtained in (f)(i) would differ from 300 °C if the sample was impure.

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[2]

- (g) A structure of methyl orange is given below.



- (i) Determine which reactant, sodium sulfanilate (2.70 g) or N,N-dimethylaniline (1.71 g), is the limiting reactant in this synthesis of methyl orange.

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[3]

- (ii) Use your answer to (g)(i) to calculate the percentage yield of methyl orange. Give your answer to 1 decimal place.

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[3]





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**(Questions continue overleaf)**

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**[Turn over**



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4 The structure of a compound with the molecular formula  $C_4H_7ClO$  can be determined using modern spectroscopic techniques. The compound is **not** an acyl chloride.

(a) The mass spectrum of the compound contains peaks at  $m/z = 106$  and  $m/z = 108$ . The base peak occurs at  $m/z = 43$ .

(i) Explain the presence of the peaks at  $m/z = 106$  and  $m/z = 108$  and suggest why the peak at 106 has a higher relative abundance than the peak at 108.

\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_ [2]

(ii) Suggest the formula of the fragment ion which gives rise to the base peak at  $m/z = 43$ .

\_\_\_\_\_ [1]

(b) The high resolution nmr spectrum of the compound was obtained.

(i) State the formula of a suitable solvent used in obtaining the nmr spectrum of the compound.

\_\_\_\_\_ [1]

(ii) Name the compound used as a standard in nmr spectroscopy and give **one** reason why it is used.

\_\_\_\_\_  
\_\_\_\_\_ [2]



- (iii) The high resolution nmr spectrum of the compound shows three peaks. Complete the table below.

|        | Integration value | Splitting pattern | Number of hydrogen atoms bonded to adjacent carbon atoms |
|--------|-------------------|-------------------|--|
| Peak 1 | 3                 | doublet           | 1  |
| Peak 2 | 3                 | singlet           |  |
| Peak 3 | 1                 |                   | 3  |

[2]

- (c) Based on your answers to (a)(ii) and (b)(iii), suggest the structure of the compound.

[1]

- (d) Describe a chemical test which could be used to show that the compound contains a carbonyl group.

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[2]

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| For Examiner's use only |               |        |
|-------------------------|---------------|--------|
| Question Number         | Examiner Mark | Remark |
| 1                       |               |        |
| 2                       |               |        |
| 3                       |               |        |
| 4                       |               |        |
| <b>Total Marks</b>      |               |        |

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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 dm<sup>3</sup>

Avogadro Constant =  $6.02 \times 10^{23}$  mol<sup>-1</sup>

Planck Constant =  $6.63 \times 10^{-34}$  Js

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

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



## Characteristic absorptions in IR spectroscopy

| Wavenumber/cm <sup>-1</sup> | 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 <sub>6</sub> H <sub>5</sub> –CH | Arene (aliphatic on ring)                 |
| 2.0–4.0        | X–CH                              | X = Cl or Br (3.0–4.0)<br>X = I (2.0–3.0) |
| 4.5–6.0        | –C=CH                             | Alkenes                                   |
| 5.5–8.5        | RCONH                             | Amides                                    |
| 6.0–8.0        | –C <sub>6</sub> H <sub>5</sub>    | 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

