

### <u>Paper 4</u>

1 (a) (i) Sample table:

mass of capped container + <b>FA 1</b> / g	8.50
mass of capped container + remaining <b>FA 1</b> / g	5.49
mass of <b>FA 1</b> used / g	3.01

initial temperature of <b>FA 2</b> , $T_i / {}^{\circ}C$	29.1
lowest temperature of mixture, $T_f / °C$	25.4
change in temperature / °C	-3.7

- correct headers + units + mass range (3.00 g ± 0.10 g) [1] need not show 'change in temperature'
- correct precision [1]
  - o masses to 2 d.p.
  - o temperatures to1 d.p.
- (ii)  $\Delta T = T_f T_i = 25.4 29.1 = -3.7 \,^{\circ}C (1 \text{ d.p.})$  [1]  $q = mc\Delta T = 50.0 \times 1.00 \times 4.18 \times 3.7 = 773.3 \text{ J} = 773 \text{ J} (3 \text{ s.f.})$  [1]
- (iii)  $\eta_{citric\ acid}\ used = \frac{3.01}{192} = 0.01568\ mol = 0.0157\ mol\ (3\ s.f.)$   $\eta_{NaHCO3}\ used = \frac{50}{1000} \times 1.00 = 0.0500\ mol\ (3\ s.f.)\ (> 3 \times \eta_{citric\ acid} = 0.0471)$  [1] Citric\ acid\ is\ the\ limiting\ reagent\ (shown)

(iv) 
$$\Delta H_1 = + \frac{773}{0.01568} = +49307 \text{ J mol}^{-1} = +49.3 \text{ kJ mol}^{-1}$$
 [1]

(v)  $q = mc\Delta T$ 

$$\Delta H = \frac{q}{n_{limiting reagen}}$$

As **FA 2** is in excess, doubling its volume does not change the amount of heat absorbed, q, since  $\Delta H \times n$  are both unchanged, but it doubles the mass of solution that the same amount of heat absorbed must cool down. Hence the temperature change will be half that measured in the experiment.

[0.5] same amount of heat absorbed + mass/volume of solution doubled [0.5] temperature change halved

(b) (i) Sample table:

<i>V<sub>FA 2</sub> / cm</i> <sup>3</sup>	V <sub>solution A</sub> / cm <sup>3</sup>
10.00	40.0
15.00	35.0

20.00	30.0
25.00	25.0
30.00	20.0
40.00	10.0

[1]

- 6 sets of V<sub>FA 2</sub> + V<sub>solution A</sub>
- $V_{total} = 50 \ cm^3$
- chosen values of V<sub>FA 2</sub> should be well-spaced

#### Procedure

1. Fill the burette with FA 2.

2. Place two polystyrene cups together and put them in a 250 cm<sup>3</sup> glass beaker. Transfer 40 cm<sup>3</sup> of **FA 2** into the polystyrene cup using the burette.

3. Measure the initial temperature of **FA 2** using the thermometer. Record the initial temperature as  $T_{FA 2}$ .

4. Wash and dry the thermometer.

5. Use a measuring cylinder to measure 10 cm<sup>3</sup> of **solution A**. Measure the initial temperature of **solution A** using the thermometer. Record the initial temperature as  $T_{\text{solution A}}$ .

6. Add **solution A** to **FA 2** in the polystyrene cup. Stir the mixture gently using the thermometer and record the minimum temperature,  $T_{min}$ , reached.

7. Wash and dry the polystyrene cup.

8. Repeat steps 2 to 6 using the volumes of **FA 2** and **solution A** as given in the table above.

9. The weighted initial temperature should be calculated for each experiment according to the formula given and recorded as  $T_{weighted, initial}$ .

10. Calculate the temperature change of each experiment by taking ( $\Delta T = T_{min} - T_{weighted, initial}$ ), and record it as  $\Delta T$  as shown in the table above.

**[0.5]** correct apparatus (burette for **FA 2** & measuring cylinder for **solution A** + polystyrene cups as calorimeter. Also accept use of measuring cylinders for both **FA 2** and **solution A**)

[0.5] wash + dry thermometer & polystyrene cup

[0.5] measures & records T<sub>FA 2</sub> & T<sub>solution A</sub>

[0.5] measures & records T<sub>min</sub> & calculates T<sub>weighted initial</sub>

[0.5] repeats experiments

[0.5] calculates & records  $\Delta T$  for each experiment



- correct axes labels + shape of graph
- marking of ⊿T<sub>min</sub> & V<sub>min</sub>
- graph must pass through origin + x-axis at 50 cm<sup>3</sup> mark

(iii)  $\eta_{NaHCO3}$  (FA 2) used =  $\frac{V_{min}}{1000} \times 1.00 \text{ mol}$   $\eta_{citric\ acid}$  (solution A) present in solution =  $\frac{V_{min}}{1000} \times 1.00 \times \frac{1}{3} \text{ mol}$  [0.5] [citric\ acid] =  $\frac{\frac{V_{min}}{1000} \times 1.00 \times \frac{1}{3}}{\frac{50 - V_{min}}{1000}} \text{ mol} dm^{-3}$  [0.5] (iv)  $q = mc\Delta T = (50 \times 1.00) \times 4.18 \times \Delta T_{min}$  [0.5]  $\Delta H_2 = \frac{q}{\eta_{NaHCO_3}} = \frac{(50 \times 1.00) \times 4.18 \times \Delta T_{min}}{\frac{V_{min}}{1000} \times 1.00} \times 3$  [0.5]

OR

$$\Delta H_2 = \frac{q}{\eta_{citric\,acid}} = \frac{(50 \times 1.00) \times 4.18 \times \Delta T_{min}}{\frac{V_{min}}{1000} \times 1.00 \times \frac{1}{3}} = \frac{(50 \times 1.00) \times 4.18 \times \Delta T_{min}}{\frac{V_{min}}{1000} \times 1.00} \times 3$$

Penalise once for M13 or M14 if student does not multiply by stoichiometric coefficient in 1(b)(iii) and 1(b)(iv))

(c) (molar) enthalpy change of solution of citric acid [1]

$$C_{3}H_{5}O(CO_{2}H)_{3} (s) \xrightarrow{\Delta H_{3}} C_{3}H_{5}O(CO_{2}H)_{3} (aq)$$
+ 3NaHCO<sub>3</sub> (aq)  $\xrightarrow{\Delta H_{1}} \xrightarrow{\Delta H_{2}} + 3NaHCO_{3} (aq)$ 

$$C_{3}H_{5}O(CO_{2}-Na^{+})_{3}(aq) + 3CO_{2} (g) + 3H_{2}O (l)$$

(d) <u>Citric acid is a weak acid</u>, while <u>sodium hydrogencarbonate is a weak base</u>. As there is <u>no</u> rapid pH at the equivalence points for a weak acid – weak base titration, there is <u>no</u> suitable indicator that can be used to signal the end point. Hence the titrimetric method cannot be used to determine the concentration of citric acid in this case.

[0.5] identification of weak acid & weak base [0.5] no rapid pH change + no suitable indicator

t min	S	t <sub>d</sub> / min	final burette reading / cm³	initial burette reading / cm³	V <sub>FA 5</sub> / cm <sup>3</sup>	<i>V<sub>t</sub> / cm</i> <sup>3</sup>
			Cili	CIII		

#### • correct headers <u>and</u> units [1]

- o transfer time (min and s)
- o decimal time  $t_d$  (min)
- o final and initial burette readings,  $V_{FA 5}$  and  $V_t$  (cm<sup>3</sup>)

Accept 'seconds', 'minutes'. Reject 'sec'.

Accept if data is recorded in 2 tables, as long as it is clear which titre is linked to which transfer time.

Penalise this mark if raw transfer time is not recorded or final and initial burette readings are inverted.

#### • correct precision [1]

- o transfer times in min and s (to nearest s)
- o  $t_d$  to 0.1 min
- o burette readings and volumes to 0.05 cm<sup>3</sup>

For transfer times, e.g. for 2 min 30 s, reject 2' 30" or 2.30 min Ignore first point if transfer time in min and s are not recorded.

### [1]:

• calculates t<sub>d</sub> correctly

1 – 2 s = 0.0 min	21 – 26 s = 0.4 min	45 – 50 s = 0.8 min
3 – 8 s = 0.1 min	27 – 32 s = 0.5 min	51 – 56 s = 0.9 min
9 – 14 s = 0.2 min	33 – 38 s = 0.6 min	57 – 59 s = 1.0 min
15 – 20 s = 0.3 min	39 – 44 s = 0.7 min	

and

calculates V<sub>FA 5</sub> and V<sub>t</sub> correctly

[1]:

- records five sets of data within 16 minutes (accept max 16.4 min)
- *first data taken within 0 to 2.4 min*

No penalty if time intervals are not well-spaced

(b) (i) [1]:

• plots  $V_t$  (y-axis) vs  $t_d$  (x-axis) with correct axes labels and units

and

• sensible linear scale chosen so that plotted points occupy at least ½ of graph grid in both x and y directions.

[1]:

• plots all points correctly within ½ small square

includes V<sub>max</sub> = 20.00 cm<sup>3</sup> point in graph

## [1]:

• draws **best-fit** smooth curve

Do not allow this mark if anomalous points are included in the curve.

Do not allow mark if shape of graph is wrong.

Award mark based on what the student has plotted (do not re-plot for wrongly plotted points).

[1]:

• At least 4 out of 5 points are no more than 1 small square away from the best-fit curve in both x and y directions.

Do not allow this mark if more than 1 point is plotted wrongly.

Do not allow mark if shape of graph is wrong.

Award mark based on what the student has plotted (do not re-plot for wrongly plotted points).

- (ii) Total  $\eta(I_2)$  formed =  $\eta(S_2O_8^{2^-})$  used =  $0.010 \times \frac{30}{1000} = 3.00 \times 10^{-4}$  mol  $\eta(I_2)$  in 10 cm<sup>3</sup> =  $3.0 \times 10^{-4} \times \frac{10}{100} = 3.00 \times 10^{-5}$  mol [1]  $\eta(S_2O_3^{2^-})$  needed =  $2 \times \eta(I_2) = 2 \times 3.00 \times 10^{-5} = 6.00 \times 10^{-5}$  mol Volume of **FA 3** =  $\frac{6.00 \times 10^{-5}}{0.0030} \times 1000 = \frac{20.0 \text{ cm}^3}{2000000}$  [1] Ignore missing working at this point
- (iii) quotes at least two  $t_{\frac{1}{2}}$  values or label on graph (accept non-consecutive  $t_{\frac{1}{2}}$ )
  - gives conclusion based on whether t<sub>½</sub> is (approximately) constant or not e.g. first order with respect to [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>] as t<sub>½</sub> is approximately constant [0.5] at e.g. <u>1/2(5.3 + 5.7) ≈ 5.5 min</u> [0.5] average t<sub>½</sub> can be shown in (b)(iv)
     rate = k' [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>]
- (iv) value of  $k' = \frac{\ln 2}{t^{\frac{1}{2}}} = \frac{\ln 2}{5.5} = 0.1260 = \underline{0.126} (3 \text{ s.f.})$  (units = min<sup>-1</sup>) [0.5] using correct eqn [0.5] using average  $t_{\frac{1}{2}}$ Ignore missing working and s.f. errors at this point
- (v)  $[I^{-}] = (\frac{70}{1000} \times 0.400) \div (\frac{100}{1000}) = 0.280 \text{ mol } dm^{-3} (3 \text{ s.f.})$  [1] value of  $k = \frac{k'}{[I^{-}]} = \frac{0.126}{0.280} = 0.450$  (3 s.f.) ecf from (iv) [1] (units = mol^{-1} dm^{3} min^{-1}) Ignore missing working, incorrect/missing units or s.f. errors at this point.

[1]: Shows working in all calculations in 1(a)(ii)-(iv); 2(b)(ii) and 2(b)(iv)-(v). All calculations must be relevant although they may not be complete or correct. Any calculation not attempted loses this mark.

[1]: Shows appropriate significant figures (3 or 4 s.f.) or decimal places in all <u>final</u> <u>answers</u> in 1(a)(ii),(iv) and 2(b)(iv)-(v).

Final answers refer to those written on the line provided. If this is absent, consider final answer in working.

Any calculation not attempted loses this mark.

[1]: Shows appropriate units in all answers in 1(a)(ii) (°C or K; J or kJ), 1(a)(iv) (J mol<sup>-1</sup> or kJ mol<sup>-1</sup>) and 2(b)(v) [ $\Gamma$ ] only (mol dm<sup>-3</sup>) Any calculation not attempted loses this mark.

(c)  $t_{\frac{1}{2}} = \ln 2 / k' = \ln 2 / (k[i])$  OR rate is halved OR rate  $\propto \frac{1}{t_{\frac{1}{2}}}$  [0.5]

When [ $\Gamma$ ] is halved,  $t_{y_2}$  doubles. **[0.5]** no mark for ' $t_{y_2}$  increases'

(d) [1]: Iron is able to exhibit <u>variable (accept 'multiple', 'a few', 'many') oxidation states</u>.
 [1]: Step 1: S<sub>2</sub>O<sub>8</sub><sup>2-</sup> + 2Fe<sup>2+</sup> → 2SO<sub>4</sub><sup>2-</sup> + 2Fe<sup>3+</sup>
 [1]: Step 2: 2I<sup>-</sup> + 2Fe<sup>3+</sup> → I<sub>2</sub> + 2Fe<sup>2+</sup>

			Table 3.1	Table 3.1		
ſ		tests	observations	obs		
_	1	<ul> <li>Place about 1 cm depth of dilute sulfuric acid into a test-tube. Add a spatula of FA 6 to this test tube, followed by another 2 cm depth of FA 3.</li> <li>Filter the mixture into a clean test-tube and retain the filtrate.</li> <li>To the filtrate, add aqueous sodium thiosulfate dropwise, with shaking, until the solution first becomes colourless. Retain this solution for use in test 2.</li> </ul>	<ul> <li><u>Black</u> residue.</li> <li><u>Yellowish-brown/yellow-orange</u> filtrate.</li> </ul>	1 <b>[0.5]</b> 2 <b>[0.5]</b>		
	2	To the solution from test 1, add aqueous sodium hydroxide dropwise until no further change is seen.	<ul> <li><u>Off-white/beige</u> ppt formed.</li> <li>Ppt <u>insoluble</u> in excess NaOH.</li> <li>The ppt turned <u>brown</u> on standing.</li> </ul>	3 [0.5] 4 [0.5] 5 [0.5]		
	3	Place 1 cm depth of hydrogen peroxide into a test-tube. Add, using the tip of a spatula, a small	<ul> <li><u>Effervescence</u> observed.</li> <li>Gas <u>relit glowing splint</u>.</li> <li>Gas is <u>O<sub>2</sub></u>.</li> </ul>	6 <b>[0.5]</b> 7 <b>[0.5]</b> 8 <b>[0.5]</b>		

# 3 (a)

portion of <b>FA 6</b> to this test-tube.		
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Note: [0.5] for each observation  $\Rightarrow$  total [4].

(i) **FA 6**,  $MnO_2$ , <u>oxidises</u>  $I^-$  to  $I_2$ , itself <u>reduced</u> to  $Mn^{2+}$ . [1] It is a redox reaction.

Evidence 1: Upon addition of **FA6** to **FA 3**, a <u>yellowish-brown solution of  $I_2(aq)</u>$  was formed that decolourises  $S_2O_3^{2^2}$ ,  $I^-$  was oxidised to  $I_2$  by  $MnO_2$ . **[0.5]** Evidence 2:  $MnO_2$  was reduced to  $Mn^{2^+}$ , as seen by the <u>off-white ppt</u>  $Mn(OH)_2$  formed with NaOH(aq) and NH<sub>3</sub>(aq) which turned brown on standing to form  $Mn(OH)_3$ . **[0.5]**</u>

- (ii) Heterogeneous <u>catalyst</u> [1] Evidence: Since there was <u>vigorous effervescence</u>, it indicates that the <u>rate of</u> <u>decomposition of H<sub>2</sub>O<sub>2</sub> was increased</u> by the addition of MnO<sub>2</sub>. [1]
- (b) (i) FA 7: <u>Effervescence</u> of a colourless, odourless gas that forms <u>white precipitate with</u> <u>limewater</u>. Gas is <u>CO<sub>2</sub>(g)</u>. [0.5]
   FA 8 and FA 9: No observable change [0.5]

(ii) [1]: FA 7 + compound: HC