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

1 Redox reactions of vanadium compounds

(a) **FA 1** is a solution containing the VO_2^+ ion in acidic solution. Vanadium forms ions of different oxidation states and colours.

In addition to having access to the usual bench reagents, you are also provided with the following:
FA 2, aqueous sodium thiosulfate
FA 3, zinc powder
FA 4, zinc powder
FA 5, aqueous copper(II) sulfate.

Perform the tests described in Table 1.1 and record your observations in the table.
The volumes given are approximate and should be estimated rather than measured.
You do **not** need to test and identify any gases evolved.

Table 1.1

	test	observations
1	Add 1 cm depth of **FA 1** to a test-tube. Add 1 cm depth of aqueous potassium iodide. Allow to stand for 1 minute. Then add **FA 2** drop by drop until no further change is seen.	Upon adding KI (aq), yellow solution turns orange Upon standing, orange solution turns brown. On adding FA2, brown solution turns yellow, then green and eventually blue.
2	Add 3 cm depth of **FA 1** to a test-tube. Add **FA 3** in three separate portions using a spatula, shaking after each separate addition. Then add all of **FA 4**. Shake and continue to observe the test-tube until there are no further colour changes. Keep this mixture for use in Test 3.	When FA3 is added, yellow solutions turns green, then blue, then darker blue. Effervescence is observed. (Not required to test for gas) On adding all of FA4, blue solution turns violet/purple. Effervescence is observed. (Not required to test for gas)
3	Carefully transfer about 1 cm depth of the solution from the final mixture in Test 2 into a test-tube using a dropping pipette. Ensure you do not transfer solids into this test-tube.	
	Add 1 cm depth of **FA 5** to this solution.	Red-brown solid is formed. Upon standing, purple solution turns blue.

[6]

(b) Table 1.2 gives standard electrode potential values for some vanadium compounds and some of the substances you have used in **(a)**.

Table 1.2

electrode reaction	$E^{\ominus}$ /V
$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$	+1.00
$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$VO^{2+}(aq) + 2H^+(aq) + e^- \rightleftharpoons V^{3+}(aq) + H_2O(l)$	+0.34
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$	–0.26
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	–0.76
$V^{2+}(aq) + 2e^- \rightleftharpoons V(s)$	–1.20

(i) Write an ionic equation for the reaction occurring between acidified $VO_2^+(aq)$ and iodide ions in Test 1.

$2VO_2^+ + 4H^+ + 2I^- \longrightarrow 2VO^{2+} + 2H_2O + I_2$

..... [1]

(ii) State the vanadium species present at the end of Test 2. Explain your answer, referring to the data in Table 1.2.

In presence of excess zinc, VO_2^+ is reduced to V^{2+}.

VO_2^+ is reduced by Zn to VO^{2+} (E_{cell} = +1.76 V), VO^{2+} is reduced by Zn to V^{3+} (E_{cell} = +1.10 V), V^{3+} is reduced by Zn to V^{2+} (E_{cell} = +0.50 V).

V^{2+} cannot be reduced by Zn to V (E_{cell} = –0.44 V)

..... [3]

(iii) Use your observations in Table 1.1 and the information in Table 1.2 to complete Table 1.3.

Table 1.3

oxidation number of vanadium ion	colour of vanadium ion
+2	Violet
+5	Yellow

[1]

[Total: 11]

2 Determination of the kinetics of an acid-carbonate reaction

In this experiment you will follow the reaction between calcium carbonate (in the form of calcium carbonate tablets) and hydrochloric acid of two different concentrations. The apparatus used to follow this reaction is shown in Fig. 2.1. The equation for the reaction is shown.

$$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

You will measure the level of water in the burette at timed intervals and determine the initial rate of reaction for each concentration of acid.

FA 6 is 0.0800 mol dm^{-3} hydrochloric acid.
FA 7 is two calcium carbonate tablets.

Prepare a table in the space provided on page 6 in which to record:

- your burette readings recorded to 1 decimal place for each concentration of acid
- the time at which each reading is taken (you will take a reading every 1.0 minute for 6 minutes)
- the total volume of carbon dioxide collected up to that time for each concentration of hydrochloric acid, recorded to one decimal place.

Experiment 1

1. Set up the apparatus as shown in Fig. 2.1 as follows:

   - Use a beaker to add tap water to a burette until it is full.
   - Place your thumb over the top of the burette and invert it in the large container half-filled with tap water. Remove your thumb.
   - Clamp the burette in the vertical position.
   - Insert the plastic or rubber tubing into the burette to a sufficient depth so that it will not fall out.
   - Adjust the water level in the burette until it is between 48.0 cm^3 and 50.0 cm^3 by opening the burette tap very carefully. You may find it helpful to use an empty dropping pipette to introduce small amounts of air from the bottom of the burette.

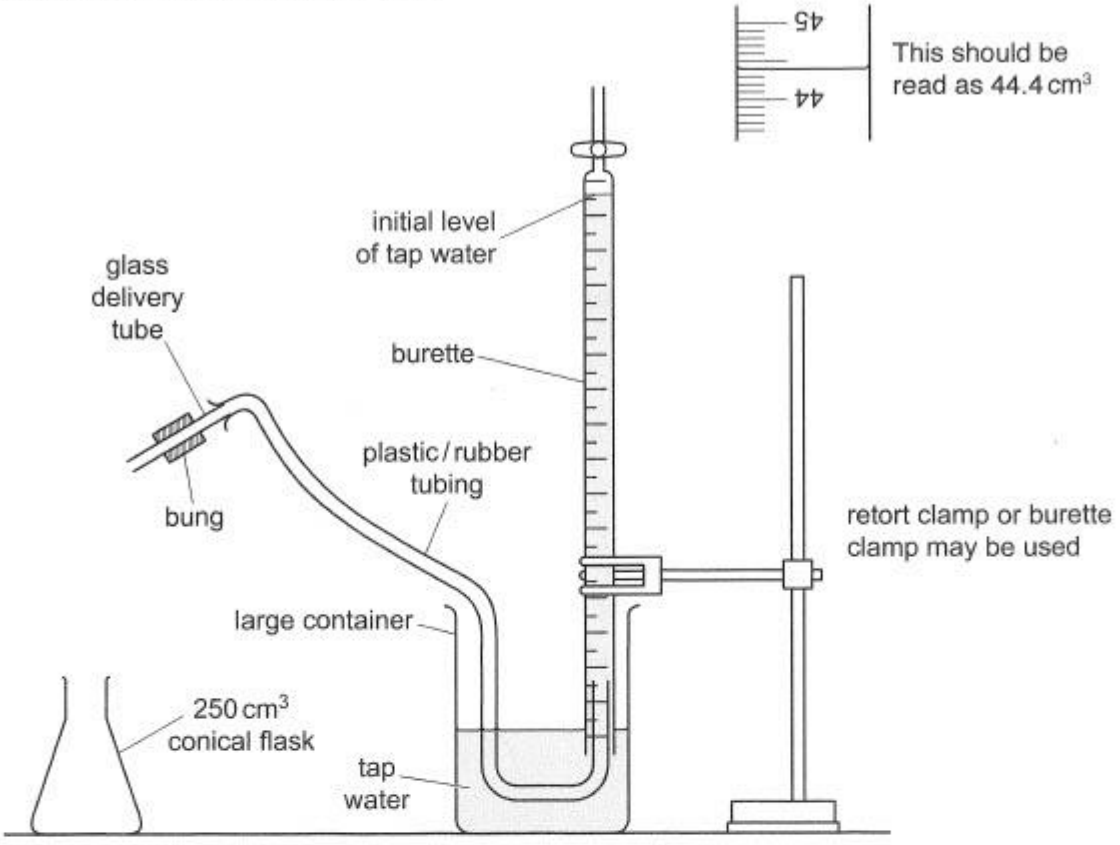


Fig. 2.1

2. Using a measuring cylinder, add 50.0 cm^3 of **FA 6** to a dry conical flask.

3. Transfer one of the calcium carbonate tablets, **FA 7**, into the conical flask. Insert the bung into the conical flask as quickly as possible.

4. Immediately start the stopwatch. Read and record the initial water level in the burette.

   Note: Once you have started the stopwatch, allow it to continue running for the duration of the experiment. You **must not stop** the stopwatch during the experiment.

5. Check that the plastic/rubber tubing is securely positioned in the burette.

6 Hold the flask by its neck and swirl it continuously throughout the experiment. Try to keep as much as possible of the plastic/rubber tubing that is not positioned in the burette out of the water while swirling.

7. At t = 1.0 min, read and record the water level in the burette, to 1 decimal place, and the time, t, in your table.

8. Continue to swirl the flask. Read and record the water level in the burette every 1.0 min, for a total of 6 min.

9. Dispose of the flask contents into the container labelled Waste. Rinse the flask.

Experiment 2

1. Repeat step 1 from experiment 1.
2. Using a measuring cylinder, add 30.0 cm^3 of **FA 6** and 20.0 cm^3 of deionised water to a dry conical flask.
3. Repeat steps 3–9 from experiment 1.

Keep FA 6 for use in Question 3

(a) (i) Results

Experiment 1

Time / min (1.d.p.)	Burette reading / cm^3 (1.d.p.)	Volume of gas collected / cm^3 (1.d.p.)
0.0	49.8	0.0
1.0	39.4	10.4
2.0	28.4	21.4
3.0	16.6	33.2
4.0	8.9	40.9
5.0	7.3	42.5
6.0	7.2	42.6

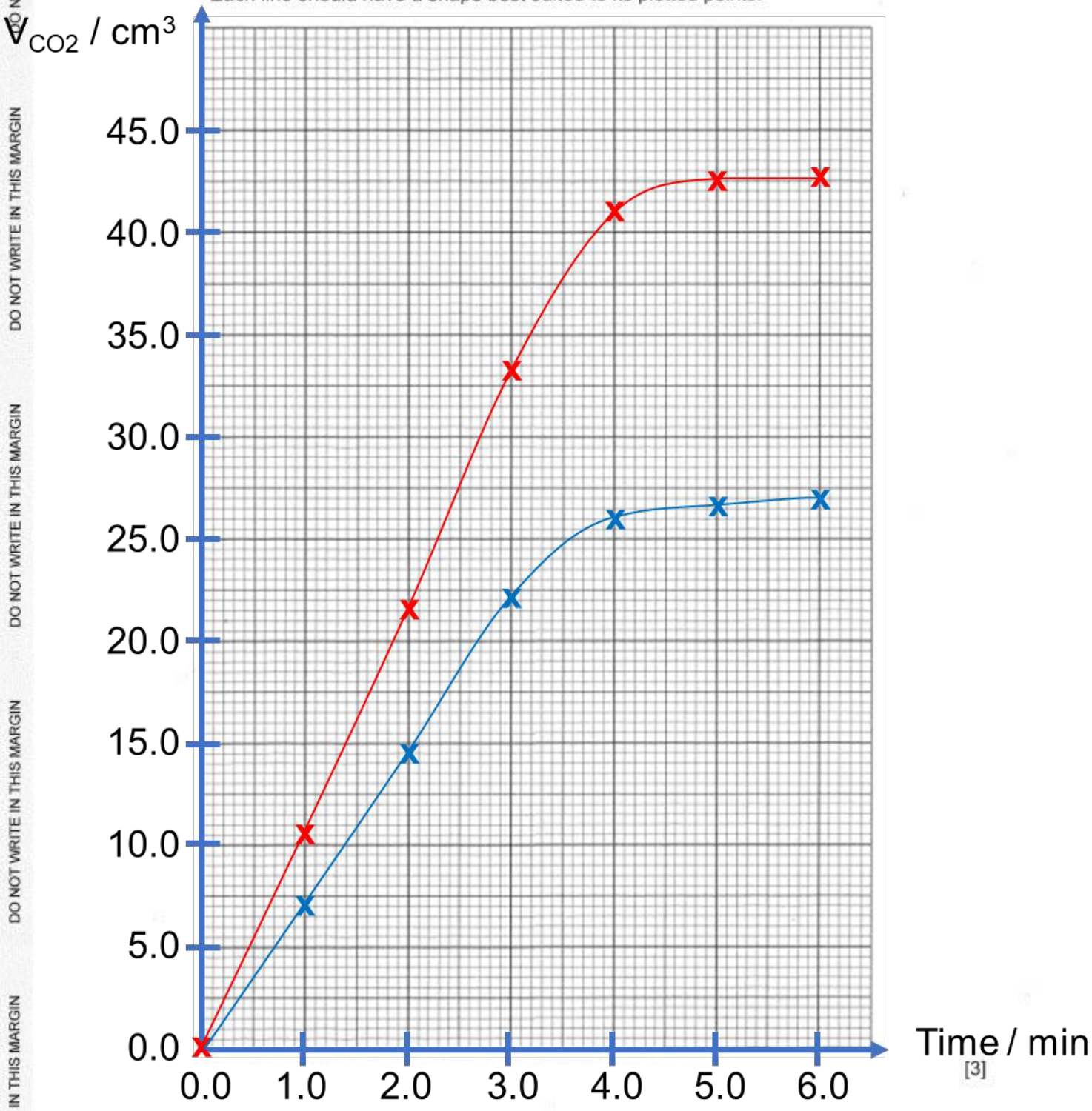
Experiment 2

Time / min (1.d.p.)	Burette reading / cm^3 (1.d.p.)	Volume of gas collected / cm^3 (1.d.p.)
0.0	50.0	0.0
1.0	43.0	7.0
2.0	35.4	14.6
3.0	27.8	22.2
4.0	24.0	26.0
5.0	23.6	26.4
6.0	23.2	26.8

[3]

(ii) On the grid below, plot a graph of the total volume of CO_2 on the *y*-axis, against time, *t*, on the *x*-axis. You should plot two sets of points, one for experiment 1 and one for experiment 2.

Draw a best-fit line for each experiment and label these experiment 1 and experiment 2. Each line should have a shape best suited to its plotted points.



[3]

(iii) Determine, for each experiment, the initial rate of reaction, showing clearly how you obtained your values.

Experiment 1

Gradient of tangent (at t = 0) = $\frac{33.0 - 0}{3.0 - 0}$ = **11.0 cm^3 min^{-1}**

initial rate = ... $cm^3 min^{-1}$

Experiment 2

Gradient of tangent (at t = 0) = $\frac{22.0 - 0}{3.0 - 0}$ = **7.33 cm^3 min^{-1}**

initial rate = ... $cm^3 min^{-1}$

[4]

(b) Deduce the order of the reaction with respect to concentration of HC*l*. Explain your deduction in terms of your experimental results.

For expt 1, [HC*l*]= 0.0800 mol dm^{-3}, for expt 2, [HC*l*] = 0.08 × $\frac{30}{50}$ = 0.480 mol dm^{-3}

When [HC*l*] × 0.6, rate of reaction × 0.67, hence it is first order w.r.t [HC*l*].

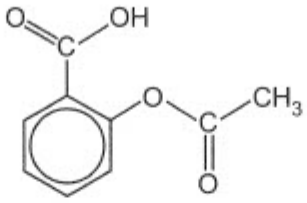
.....

..... [2]

[Total: 12]

3 Analysis of aspirin tablets

Aspirin is used in medicine for reducing pain and fever. It has the structure shown.



With a strong alkali, the carboxylic acid group reacts quickly and the ester group hydrolyses slowly. The equation for the overall reaction is shown.

$$HOOCC_6H_4OCOCH_3 + 2NaOH \rightarrow NaOOCC_6H_4OH + CH_3COONa + H_2O$$

No further reaction with the strong alkali occurs after the hydrolysis.

Aspirin cannot be titrated directly with a strong alkali because of the slow hydrolysis reaction. Instead, it is reacted with excess alkali. The unreacted alkali is then titrated with an acid.

FA 8 was prepared as follows:

- Five aspirin tablets were crushed and transferred to a conical flask.
- 25.0 cm^3 of 1.00 mol dm^{-3} sodium hydroxide, NaOH, was added by pipette.
- The solution was heated for 20 minutes to ensure complete reaction.
- The solution was then cooled and filtered into a 250 cm^3 volumetric flask to remove insoluble components of the tablet.
- The conical flask and filter paper were washed with deionised water, with the washings being added to the volumetric flask.
- The solution was then made up to the mark with deionised water and shaken to mix.

FA 6 is 0.0800 mol dm^{-3} hydrochloric acid, HC*l*.
Solution I is thymol blue indicator.

You are to titrate **FA 8** with **FA 6** using **Solution I**, thymol blue, as the indicator.

(a) (i) Procedure

1. Fill the burette with **FA 6**.
2. Pipette 25.0 cm^3 of **FA 8** into a 250 cm^3 conical flask.
3. Add 4 to 5 drops of **Solution I**.
4. Titrate the solution in the conical flask with **FA 6**. The end-point is reached when the solution turns from blue to yellow.
5. Record your titration results to an appropriate level of precision in the space on page 11.
6. Repeat steps 2 to 5 until consistent results are obtained.

Titration results

Titration	1	2
Final burette reading / cm^3	15.10	15.10
Initial burette reading / cm^3	0.00	0.10
Volume of FA6 used /cm^3	15.10	15.00

[3]

(ii) From your titrations, obtain a suitable volume of **FA 6** to be used in your calculations. Show clearly how you obtained this volume.

Volume of FA6 = $\frac{15.10 + 15.00}{2}$ = **15.05 cm^3**

volume of **FA 6** = ... [4]

(b) (i) Calculate the amount in moles of sodium hydroxide added to the aspirin tablets during the preparation of **FA 8**.

Amount of NaOH added = $1.00 \times \frac{25.0}{1000}$ = **0.0250 mol**

amount of sodium hydroxide added to tablets = ... [1]

(ii) Use your titration results to calculate the amount of sodium hydroxide in the volumetric flask after reaction with the aspirin during the preparation of **FA 8**. Hence calculate the amount of sodium hydroxide that reacted with the aspirin.

Amount of HCl used = $0.0800 \times \frac{15.05}{1000}$ = 0.001204 mol

Amount of NaOH in 25 cm^3 (withdrawn sample) = 0.001204 mol

Amount of NaOH in 250 cm^3 (volumetric flask) = $0.001204 \times \frac{250}{25}$ = **0.01204 mol**

amount of sodium hydroxide in volumetric flask = ...

Amount of NaOH reacted with aspirin = Total NaOH added – NaOH remaining

= 0.0250 – 0.01204

= **0.01296 mol**

amount of sodium hydroxide that reacted with aspirin = ...

[3]

(iii) Calculate the mass of aspirin (M_r = 180) in one tablet.

Total amount of aspirin reacted with NaOH

= ½ × 0.01296

= 0.00648 mol (5 tablets)

Amount of aspirin in 1 tablet = $0.00648 \times \frac{1}{5} = 0.001296$ mol

Mass of aspirin in 1 tablet = 0.001296 × 180 = **0.233 g**

mass of aspirin per tablet = ... [6]

(c) The manufacturer of the aspirin states that each tablet contains 300 mg of aspirin.

Calculate the difference between your value and the manufacturer's value as a percentage of the manufacturer's value. This is the percentage error.

0.233 g = 233 mg

Percentage error

$= \frac{233 - 300}{300} \times 100\%$

= **–22.3 %**

percentage error = ... % [1]

[Total: 18]

4 Planning – preparation of aspirin

Aspirin, $HOOCC_6H_4OCOCH_3$, is a white, crystalline solid at room temperature. It is made by the reaction of 2-hydroxybenzoic acid, $HOOCC_6H_4OH$, (a white solid) with ethanoic anhydride, $(CH_3CO)_2O$, (a colourless liquid). The equation for this reaction is shown.

$$HOOCC_6H_4OH + (CH_3CO)_2O \rightarrow HOOCC_6H_4OCOCH_3 + CH_3COOH$$

The reaction is catalysed by a strong acid.

Ethanoic anhydride is used as a safer alternative to ethanoyl chloride in reactions with phenols.

A teacher demonstrated the preparation of aspirin as follows.

5 cm^3 (an excess) of ethanoic anhydride was added to 2.0 g of 2-hydroxybenzoic acid. A few drops of concentrated sulfuric acid were added and the mixture was swirled thoroughly. The mixture was then warmed under reflux for 20 minutes, with the temperature not being allowed to rise above 60 °C.

The mixture was allowed to cool for a few minutes and then poured into 25 cm^3 of cold water, stirring well to precipitate the impure solid aspirin. The impure aspirin was separated by filtration and then purified.

Table 4.1 gives information about some of the chemicals involved.

Table 4.1

chemical	M_r	melting point / °C	other properties
2-hydroxybenzoic acid	138	159	eye irritant
ethanoic anhydride	102	–73	corrosive, flammable
aspirin	180	135	harmful

You are required to plan a procedure to prepare a sample of 6.0 g of aspirin using the method used by the teacher.

(a) Calculate the minimum mass of 2-hydroxybenzoic acid required to produce a sample of 6.0 g of aspirin, assuming the percentage yield in the whole process is 65%.

Amount of 6.0 g of aspirin = $\frac{6.0}{180}$ = 0.03333 mol (65%)

Amount of aspirin (100% yield) = $0.03333 \times \frac{100}{65}$ = 0.05128 mol

Amount of 2-hydroxybenzoic acid required = 0.05128 mol

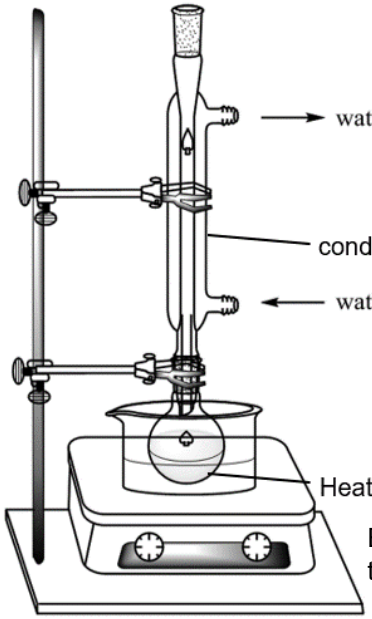
Mass of 2-hydroxybenzoic acid required = 0.05128×138 = **7.08 g**

mass of 2-hydroxybenzoic acid = ... g [2]

(b) Plan a procedure for the preparation of 6.0 g of pure and dry aspirin using 2-hydroxybenzoic acid and ethanoic anhydride.

In your plan you should include details of:

- an estimate of the volume of ethanoic anhydride to be used
- the apparatus you would use
- a diagram of the apparatus you would use to warm the mixture under reflux
- the procedure you would follow to obtain pure and dry aspirin.



Note on sketching of reflux set-up:

1. *Water must enter and leave the condenser in a correct manner*
2. *Condenser must be opened. The opening of the condenser cannot be closed with a bung or a thermometer as heating in a closed container is dangerous due to pressure built up*
3. *Beaker or conical flask should not be used. Only round bottom flask is allowed for refluxing of chemicals.*
4. *Cannot heat with a direct flame.*

Note: From the example, 2.0 g of 2-hydroxybenzoic acid reacts with 5 cm^3 of ethanoic anhydride. 7.08 g of 2-hydroxybenzoic acid would require 17.7 cm^3 of ethanoic anhydride.

We can use 20 cm^3 since ethanoic anhydride is in excess as stated in question.

Sample Procedure

1. Using an electronic weighing balance, measure 7.08 g of 2-hydroxybenzoic acid in a weighing bottle and transfer it into a 250 ml round bottom flask.
2. Using a 50 cm^3 measuring cylinder, transfer **20 cm^3 of** ethanoic anhydride into the round bottom flask.
3. In a **fume hood**, add a few drops of concentrated sulfuric acid into the reaction mixture, swirl thoroughly.
4. Set up reflux as shown in the diagram above and heat under reflux at 55 °C for twenty minutes. **Use a thermometer to monitor the temperature of the water bath, if temperature goes above 60°C, add water to lower the water bath temperature.**

5. Reaction mixture is allowed to cool and the mixture is poured into 25 cm^3 of cold water, stirring well to precipitate impure solid aspirin.
6. Using a filter funnel and filter paper, filter the mixture to obtain the impure solid aspirin.
7. Dissolve impure aspirin in small amount of water in a 100 cm^3 beaker, warm the solution until all solid just dissolves. After which, allow the solution to cool by putting the beaker in an ice water bath. Pure aspirin will crystallize as temperature drops.
8. Filter the mixture to obtain pure aspirin crystals as residue. Wash the crystals with a little ice cold water to remove soluble impurities (ethanoic acid and ethanoic anhydride).
9. Leave the crystals on a watch glass to dry overnight or dry in a desiccator.

[9]

(c) Describe briefly how you would show that your sample of aspirin is pure.

Purity of the aspirin can be checked by its melting point. Melting point of pure aspirin should be within ±2 °C from 135 °C. [1]

(d) Complete Table 4.2 to give two **different** safety precautions you would take, relating to the properties of the reactants.

Table 4.2

	substance	hazard	precaution
1	Ethanoic anhydride	corrosive	handle with rubber glove In fumehood
2	2-hydroxybenzoic acid	eye irritant	wear safety goggles

[2]

[Total: 14]