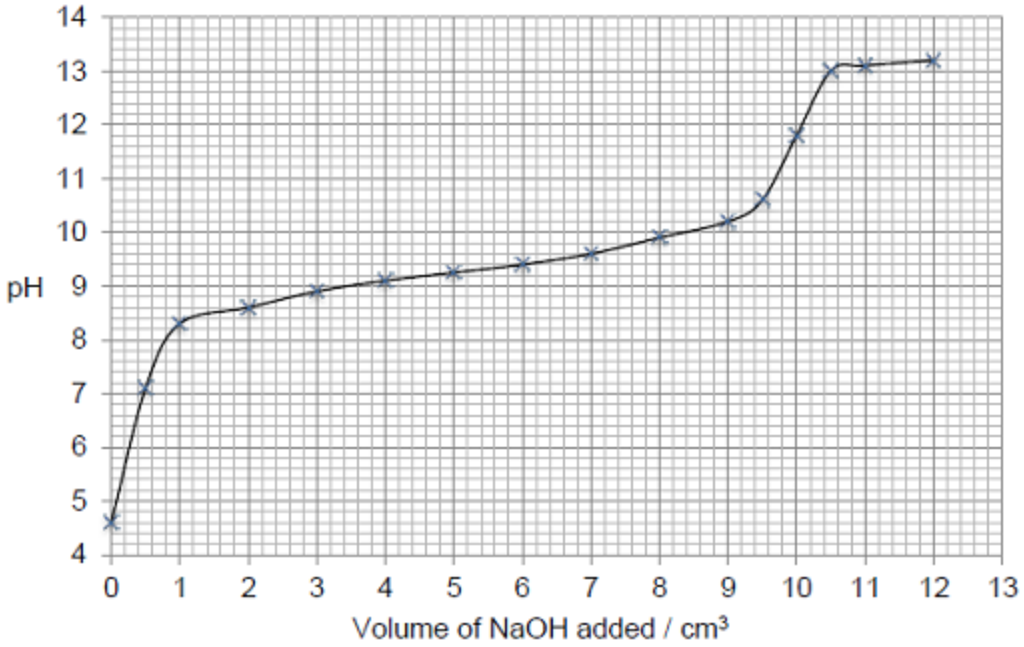
1 Ammonium chloride, when dissolved in water, can act as a weak acid as shown by the following equation.

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$$

The following figure shows a graph of data obtained by a student when a solution of sodium hydroxide was added to a solution of ammonium chloride. The pH of the reaction mixture was measured initially and after each addition of the sodium hydroxide solution.



(a) Suggest a suitable piece of apparatus that could be used to measure out the sodium hydroxide solution.
Explain why this apparatus is more suitable than a pipette for this purpose.

Apparatus .....

Explanation .....

.....

.....

(2)

(b) Use information from the curve in the figure above to explain why the end point of this reaction would be difficult to judge accurately using an indicator.

.....

.....

.....

.....

.....

(2)

(c) The pH at the end point of this reaction is 11.8.

Use this pH value and the ionic product of water, $K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6}, to calculate the concentration of hydroxide ions at the end point of the reaction.

Concentration = ... mol dm^{-3}

(3)

(d) The expression for the acid dissociation constant for aqueous ammonium ions is

$$k_a = \frac{[NH_3][H^+]}{[NH_4^+]}$$

The initial concentration of the ammonium chloride solution was 2.00 mol dm^{-3}.

Use the pH of this solution, before any sodium hydroxide had been added, to calculate a value for K_a

K_a = ... mol dm^{-3}

(3)

(e) A solution contains equal concentrations of ammonia and ammonium ions.

Use your value of K_a from part **(d)** to calculate the pH of this solution. Explain your working.

(If you were unable to calculate a value for K_a you may assume that it has the value 4.75×10^{-9} mol dm^{-3}. This is **not** the correct value.)

pH= .....

(2)

(Total 12 marks)

2 Describe briefly how you would ensure that a reading from a pH meter is accurate.

.....

.....

.....

(Total 2 marks)

3 In a titration experiment, a good technique is essential for an accurate result to be obtained.

(a) Suggest a reason for removing the funnel after it has been used for filling the burette.

.....

.....

(1)

(b) Suggest **one** other source of error in using the burette to carry out a titration.

.....

.....

(1)

(c) During the titration, the inside of the conical flask is rinsed with distilled water.

Suggest why rinsing improves the accuracy of the titre.

.....

.....

(1)

(d) Explain why adding this extra water does **not** change the volume of EDTA solution that is required in the titration.

.....

.....

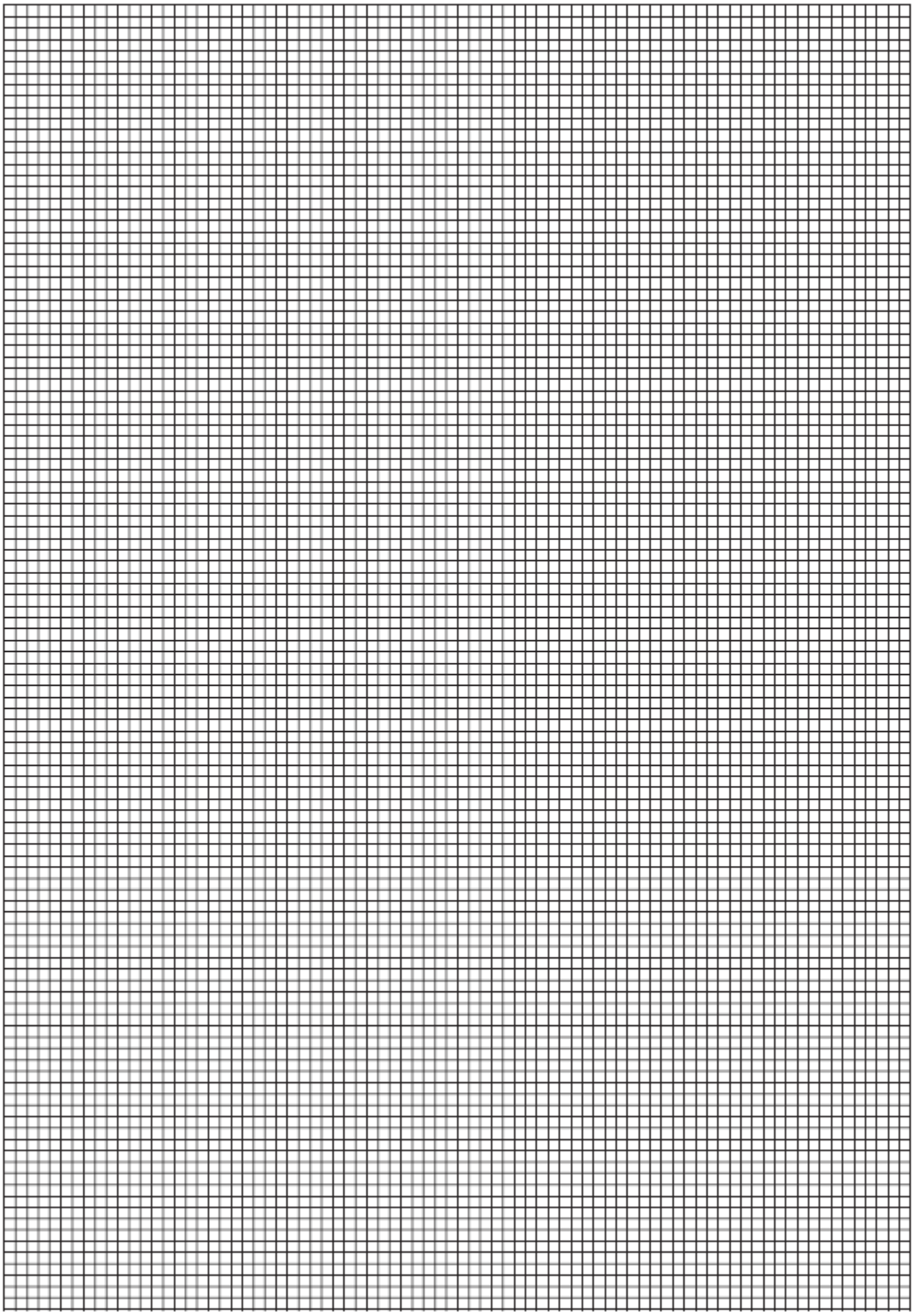
(1)
(Total 4 marks)

4 In an experiment to determine the acid dissociation constant (K_a) of a weak acid, 25.0 cm^3 of an approximately 0.1 mol dm^{-3} solution of this acid were titrated with a 0.10 mol dm^{-3} solution of sodium hydroxide.
The pH was measured at intervals and recorded. The table below shows the results.

Volume of NaOH / cm^3	0.0	1.0	2.0	3.0	4.0	5.0	10.0	15.0
pH	5.1	7.8	8.1	8.7	8.4	8.5	8.9	9.3

Volume of NaOH / cm^3	20.0	22.0	23.0	24.0	25.0	26.0	27.0	28.0
pH	9.7	10.0	10.2	11.0	11.3	11.4	11.5	11.6

(a) On the grid below, plot the values from the table above on a graph of pH (y-axis) against volume of NaOH.
You should start your y-axis at pH 4.0.
Draw a curve that represents the curve of best fit through these points. Ignore any anomalous points.



(4)

(b) Deduce the volume of the sodium hydroxide solution that would have been added at the half-neutralisation point of this experiment. This is the point where half the amount of the weak acid has been neutralised.

.....

(1)

(c) When half of the weak acid has been neutralised, the pH of the mixture at this point is equal to the pK_a of the weak acid.

Use your answer to part (b) and your graph to determine the pK_a of the weak acid and, hence, its K_a value.

pK_a .....

K_a .....

(2)

(d) State the pH value for the anomalous point on your graph.
Suggest **one** reason for this anomaly. Assume that the reading on the pH meter is correct.

pH .....

Reason for anomaly .....

.....

.....

(1)

(e) Suggest how the experimental procedure could be slightly modified in order to give a more reliable value for the end-point.

.....

.....

.....

(1)
(Total 9 marks)

5 Describe briefly how you could measure the melting point of aspirin.

.....

.....

.....

.....

(Total 2 marks)

6 A student prepared a sample of aspirin (melting point 135 °C) in the laboratory and attempted to purify it by recrystallisation. To check the purity of the aspirin the student determined its melting point.

(a) State **two** observations, during this melting point determination, that would indicate that the sample is **not** pure.

Observation 1 .....

.....

Observation 2 .....

.....

(2)

(b) Suggest why a pure sample of aspirin may sometimes appear to melt at a temperature different from 135 °C.

.....

.....

(1)
(Total 3 marks)

7 Salicylic acid can be used to make aspirin. Before using a sample of salicylic acid to make aspirin, a student purified the acid by recrystallisation. The method for recrystallisation is outlined below.

Step 1: The sample is dissolved in a minimum volume of hot water.
Step 2: The solution is filtered hot.
Step 3: The filtrate is cooled in ice to form crystals.
Step 4: The crystals are collected by filtration, washed with cold water and left to dry.

Explain the purpose of each underlined point.

Minimum volume .....

.....

Hot water .....

.....

Filtered hot .....

.....

Cooled in ice .....

.....

Washed with cold water .....

.....

(Total 5 marks)

8 (a) During the preparation of aspirin, it is necessary to filter the crude product under reduced pressure.

Draw a diagram to show the apparatus you would use to filter the crude product under reduced pressure. (Do **not** include the vacuum pump.)

(2)

(b) You are provided with a small sample of pure aspirin in a melting point tube. Describe briefly how you would determine an accurate value for the melting point of aspirin.

.....

.....

.....

.....

(2)
(Total 4 marks)

9 N-phenylethanamide is used as an inhibitor in hydrogen peroxide decomposition and also in the production of dyes.

N-phenylethanamide can be produced in a laboratory by the reaction between phenylammonium sulfate and an excess of ethanoic anhydride:

(a) A student carried out this preparation using 1.15 g of phenylammonium sulfate (M_r = 284.1) and excess ethanoic anhydride.

$$(C_6H_5NH_3)_2SO_4 + 2(CH_3CO)_2O \rightarrow 2C_6H_5NHCOCH_3 + 2CH_3COOH + H_2SO_4$$

(i) Calculate the maximum theoretical yield of N−phenylethanamide that could be produced in the reaction. Record your answer to an appropriate precision.

Show your working.

.....

.....

.....

.....

.....

.....

.....

(3)

(ii) In the preparation, the student produced 0.89 g of N−phenylethanamide.

Calculate the percentage yield for the reaction.

.....

.....

.....

.....

(1)

(b) The student purified the crude solid product, N−phenylethanamide, by recrystallisation.

(i) Outline the method that the student should use for this recrystallisation.

.....

.....

.....

.....

.....

.....

.....

.....

.....

(4)

(ii) Outline how you would carry out a simple laboratory process to show that the recrystallised product is a pure sample of N−phenylethanamide.

.....

.....

.....

.....

.....

.....

.....

.....

(3)

(iii) Assume that the reaction goes to completion.

Suggest **two** practical reasons why the percentage yield for this reaction may **not** be 100%.

1 .....

.....

2 .....

.....

(2)

(c) The reaction to form N−phenylethanamide would happen much more quickly if the student used ethanoyl chloride instead of ethanoic anhydride.

Explain why the student might prefer to use ethanoic anhydride, even though it has a slower rate of reaction.

.....

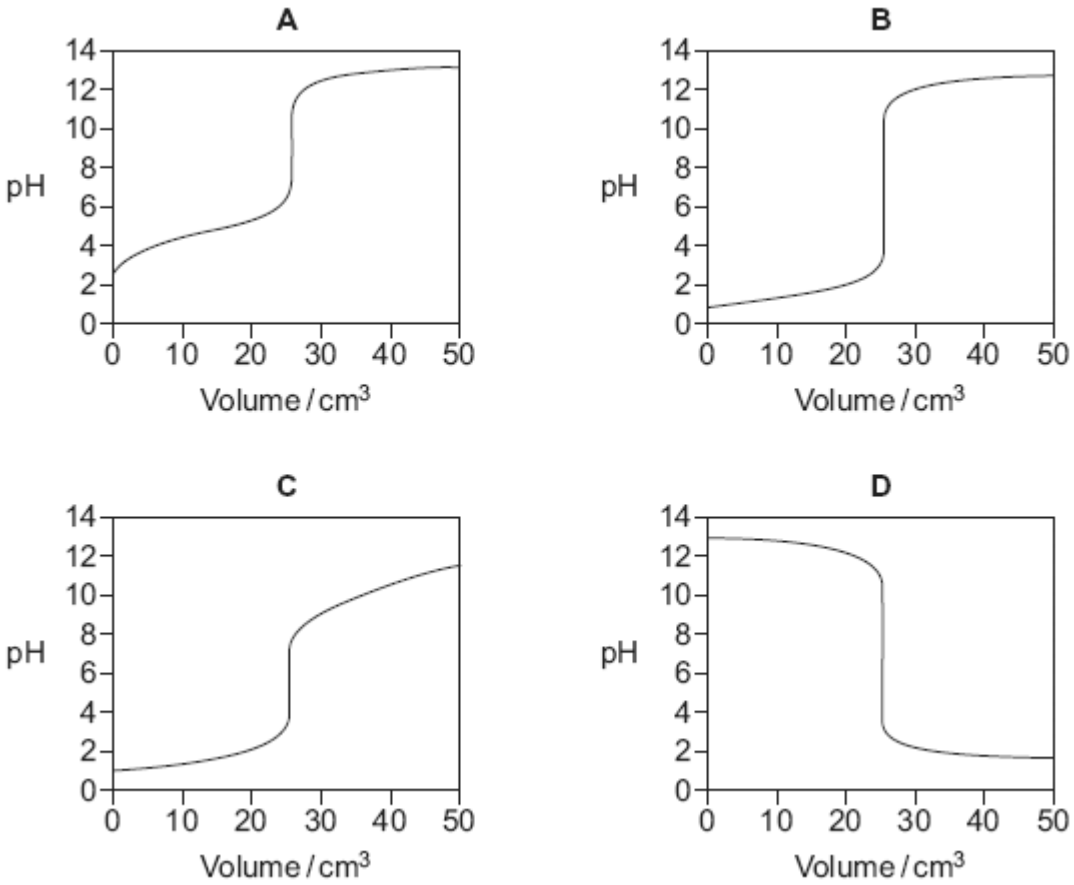
.....

.....

(2)
(Total 15 marks)

10 Titration curves labelled **A**, **B**, **C** and **D** for combinations of different aqueous solutions of acids and bases are shown below.

All solutions have a concentration of 0.1 mol dm^{-3}.



(a) In this part of the question write the appropriate letter in each box.

From the curves **A**, **B**, **C** and **D**, choose the curve produced by the addition of

ammonia to 25 cm^3 of hydrochloric acid ☐

sodium hydroxide to 25 cm^3 of ethanoic acid ☐

nitric acid to 25 cm^3 of potassium hydroxide ☐

(3)

(b) A table of acid.base indicators is shown below.
The pH ranges over which the indicators change colour and their colours in acid and alkali are also shown.

Indicator	**pH range**	**Colour in acid**	**Colour in alkali**
Trapaeolin	1.3 – 3.0	red	yellow
Bromocresol green	3.8 – 5.4	yellow	blue
Cresol purple	7.6 – 9.2	yellow	purple
Alizarin yellow	10.1 – 12.0	yellow	orange

(i) Select from the table an indicator that could be used in the titration that produces curve **B** but **not** in the titration that produces curve **A**.

.....

(1)

(ii) Give the colour change at the end point of the titration that produces curve **D** when cresol purple is used as the indicator.

.....

(1)
(Total 5 marks)

Mark schemes

1

(a) Burette

1

Because it can deliver variable volumes

1

(b) The change in pH is gradual / not rapid at the end point

1

An indicator would change colour over a range of volumes of sodium hydroxide

Allow indicator would not change colour rapidly / with a few drops of NaOH

1

(c) $[H^+] = 10^{-pH} = 1.58 \times 10^{-12}$

1

$K_w = [H^+]\,[OH^-]$ therefore $[OH^-] = K_w / [H^+]$

1

Therefore, $[OH^-] = 1 \times 10^{-14} / 1.58 \times 10^{-12} = 6.33 \times 10^{-3}$ (mol dm^{-3})

Allow 6.31–6.33 × 10^{-3} (mol dm^{-3})

1

(d) At this point, $[NH_3] = [H^+]$

Therefore $K_a = \dfrac{[H^+]^2}{[NH_4^+]}$

1

$[H^+] = 10^{-4.6} = 2.51 \times 10^{-5}$

1

$K_a = (2.51 \times 10^{-5})^2 / 2 = 3.15 \times 10^{-10}$ (mol dm^{-3})

Allow 3.15 – 3.16 × 10^{-10} (mol dm^{-3})

1

(e) When $[NH_3] = [NH_4^+]$, $K_a = [H^+]$ therefore $-\log K_a = -\log [H^+]$

Answer using alternative value

1

Therefore $pH = -\log_{10}(3.15 \times 10^{-10}) = 9.50$

M2 $pH = -\log_{10}(4.75 \times 10^{-9}) = 8.32$

Allow consequential marking based on answer from part (d)

1

[12]

2

(Calibrate) meter with solution(s) of known pH/buffer(s)

Do not accept 'repeat reading'

1

Adjust meter/plot calibration curve

1

[2]

3

(a) As a droplet from the funnel could enter the burette / affect volume / readings / titre

1

(b) Air bubble in jet or wtte

Do not allow misreading burette or overshooting end point.

1

(c) Ensures **all** reagents are able to react / mix / come into contact

Accept no reagent is left unreacted on sides of flask

Do not allow any reference to 'removal' of the solution unless it is clear that it is added to the flask.

1

(d) The added water does not affect the mols / amount of reagents / reactants / solution Z

Do not allow mols of solution or mols in the flask.

Allow water does not react with the reagents / water is not one of the reactants

Do not allow 'water is not involved'

1

[4]

4

(a) Correct orientation of graph (pH on *y*-axis)

1

Scale – plotted points cover at least half the grid and *y*-axis should start at pH 4

1

All points plotted correctly

+ / – one small square.

1

Curve of best fit drawn correctly

Allow some leniency here with a complex graph – it is important that the section between pH 8.5 and 9.7 is close to linear.

Lose this mark if the line is pulled towards the anomaly at 3.0 cm^3.

Lose this mark if first point at pH 5.1 is treated as an anomaly.

Do not accept doubled lines but allow some slight discontinuity where the curve changes direction.

1

(b) 11.6-11.9 (cm^3) only

Do not mark consequentially to student's graph.

1

(c) pK_a = value of pH related to part (b) **M1**

Mark consequentially on student's graph – ideally 9.0-9.1

Do not penalise precision of answer.

1

$K_a = 10^{-pKa}$ **M2**

Ideally 1.0×10^{-9} to 7.9×10^{-10}

*Ignore precision of answer but lose **M2** for 1 significant figure here.*

1

(d) pH 8.7

Ineffective stirring / swirling of the mixture

Both points needed for this mark.

Do not allow pH 5.1

Do not allow 'overshooting (at 3 cm^3 addition)'.

1

(e) Take more pH readings around the end-point / add smaller volumes of NaOH near the end-point

Do not allow 'use a more accurate / reliable pH meter / probe'.

Do not allow the use of a thermostatted mixture.

1

[9]

5 Sample in capillary / melting point tube

Accept alternative as long as small container used

1

Heat in melting point apparatus / heat <u>gently / slowly</u> near melting point

1

[2]

6 (a) Melting range would be
wide (>3 deg C) / not sharp

Allow melts over a range of temperatures.

1

below / before the true m.p.

Do not allow 'above or below'.

1

(b) Temperature on <u>thermometer</u> not the same as the sample

Allow sample heats up at a different / higher / lower rate than <u>thermometer</u>.

1

[3]

7 Minimum volume and hot water:

Note that this question is worth a total of 5 marks.

Any **two** from:

to obtain saturated solution

to increase yield / reduce amount left in solution

enable crystallisation (on cooling)

Do not allow 'because acid doesn't dissolve well in cold water'.

Max 2

Filtered hot: to remove insoluble impurities / to prevent crystals forming during filtration

1

Cooled in ice: to increase amount of crystals that are formed

Do not allow 'to cool quickly'.

1

Washed with cold water: to remove soluble impurities

Allow 'washing with hot water would dissolve some of the crystals'.

1

[5]

8 (a) Side-arm flask / side-arm test tube

Do not allow sealed side-arm flask.

1

Flat-bottomed filter funnel with filter paper clearly shown

Either Buchner or Hirsch versions are suitable.

Allow Hirsch funnel and horizontal filter paper.

Allow three-dimensional filter funnels.

Do not allow standard Y-shaped funnel.

Do not allow sealed funnel.

If it is not clearly air-tight between the funnel and the flask, maximum 1 mark.

1

(b) Heat melting point tube in an oil bath

Accept 'melting point apparatus' or Thiele tube.

Do not accept water bath.

1

slowly near the melting point

Ignore any additional correct details.

Apply list principle for additional incorrect details.

1

[4]

9 (a) (i) M_r N−phenylethanamide = 135.0

1

Theoretical yield = 135.0 × 2 (1.15 / 284.1) = 1.09 g

1

Answer recorded to 3 significant figures.

1

(ii) $\frac{0.89}{\text{Ans to (a)}} \times 100$

= 81.4 %

Mark consequentially to (a)
Allow 81 to 82

1

(b) (i) Dissolve the product in the **minimum** volume of water / solvent (in a boiling tube / beaker)

If dissolving is not mentioned, CE = 0 / 4

1

Hot water / solvent

Steps must be in a logical order to score all 4 marks

1

Allow the solution to cool and allow crystals to form.

1

Filter off the pure product under reduced pressure / using a Buchner funnel and side arm flask

Ignore source of vacuum for filtration (electric pump, water pump, etc.)

1

(ii) Measure the melting point

1

Use of melting point apparatus or oil bath

1

Sharp melting point / melting point matches data source value

1

(iii) Any **two** from:
Product left in the beaker or glassware
Sample was still wet
Sample lost during recrystallisation.

Do not allow "sample lost" without clarification.

2 Max

(c) An identified hazard of ethanoyl chloride

E.g. "Violent reaction", "harmful", "reacts violently with water"
Do not allow "toxic", "irritant" (unless linked with HCl gas).

1

HCl gas / fumes released / HCl not released when ethanoic anhydride used

1

[15]

10 (a) C

1

A

1

D

1

(b) (i) Bromocresol green

Allow wrong spellings

1

(ii) Purple to yellow

Must have both colours:
Purple start – yellow finish

1

[5]