

CANDIDATE
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CHEMISTRY

9701/52

Paper 5 Planning, Analysis and Evaluation

October/November 2019

1 hour 15 minutes

Candidates answer on the Question Paper.

No Additional Materials are required.

READ THESE INSTRUCTIONS FIRST

Write your centre number, candidate number and name on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

DO **NOT** WRITE IN ANY BARCODES.

Answer **all** questions.

Electronic calculators may be used.

You may lose marks if you do not show your working or if you do not use appropriate units.

Use of a Data Booklet is unnecessary.

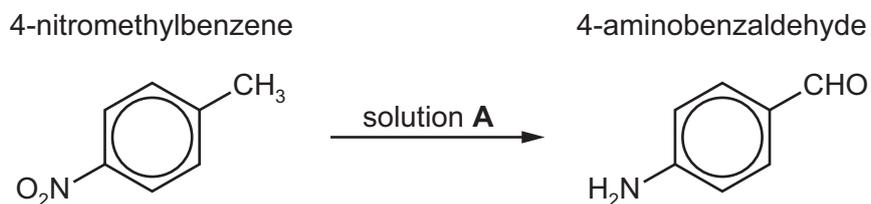
At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.

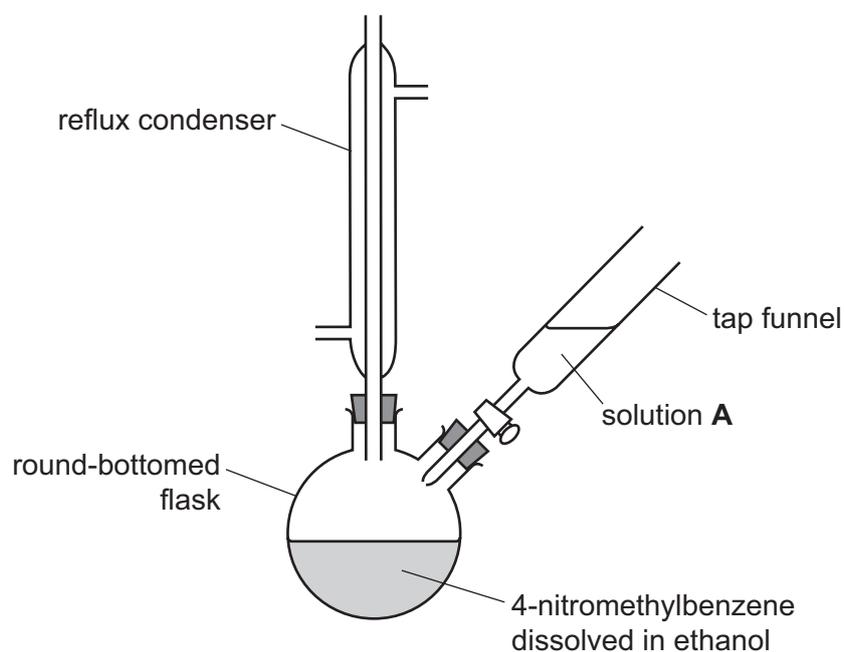
This document consists of **12** printed pages.

1 Many organic reactions performed in the laboratory require heating under reflux.

4-nitromethylbenzene can be converted directly to 4-aminobenzaldehyde by heating it under reflux with an excess of solution **A**. Solution **A** is an aqueous alkaline mixture of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ and S_8 . Ethanol is used as a solvent for the reaction.



The apparatus for this reaction is shown in the diagram.



(a) (i) Show, using a labelled arrow, where the cooling water enters the reflux condenser. [1]

- (ii) After the complete addition of solution **A** to the solution in the round-bottomed flask, a vigorous exothermic reaction takes place.

What should be done to control the vigorous exothermic reaction during the addition of solution **A**?

.....
..... [1]

- (iii) The mixture is heated to increase the rate of reaction. This is carried out under reflux.

Other than to increase the rate of reaction, explain why a reflux process is used for heating the mixture.

.....
..... [1]

- (iv) A student suggests that placing a bung in the top of the condenser would improve the experiment.

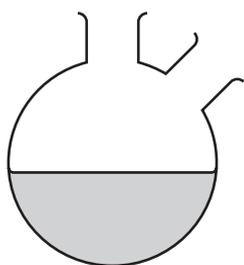
Comment on whether the student is correct. Explain your answer.

.....
.....
..... [1]

- (b) Once the reaction is complete, the round-bottomed flask is removed from the set-up on page 2 and included in a new set-up for distillation.

The distillation process separates the substances in the mixture in the flask.

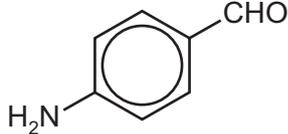
- (i) Complete and label the diagram to show how the apparatus could be set up for distillation.



[2]

- (ii) The mixture in the round-bottomed flask is heated until all of the first substance distils off. The heating is then stopped. After distillation a hot solution remains in the round-bottomed flask.

The table shows some data relevant to the experiment.

| substance | melting point/ $^{\circ}\text{C}$ | boiling point/ $^{\circ}\text{C}$ |
|---|-----------------------------------|-----------------------------------|
|  | 72 | 138 |
| H_2O | 0 | 100 |
| $\text{CH}_3\text{CH}_2\text{OH}$ | -114 | 78 |

Use the data to identify the liquid that is first distilled off.
Explain your answer.

.....
..... [1]

- (iii) 4-aminobenzaldehyde is soluble in hot water, but not in cold water.

Starting with the hot solution in the round-bottomed flask, suggest how pure crystals of 4-aminobenzaldehyde can be obtained.

.....
.....
..... [2]

- (c) Under acidic conditions, 4-aminobenzaldehyde (C_7H_7NO) forms a solid compound with molecular formula $C_{14}H_{12}N_2O$.



A student carries out two experiments according to the method on page 2 to make C_7H_7NO .

In Experiment 1, the student obtains 6.00 g of solid.

In Experiment 2, the student uses the same method as in Experiment 1 but adds acid to neutralise the alkali in the mixture in the flask after heating under reflux.

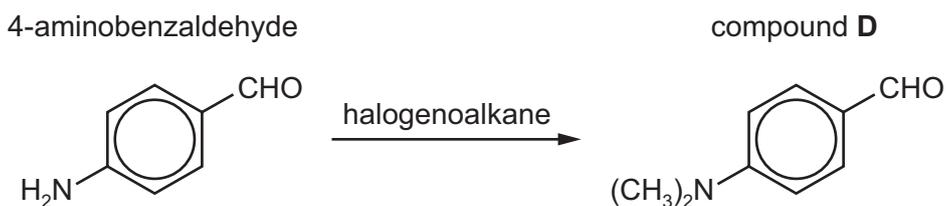
The same quantities of reagents are used in Experiment 1 and Experiment 2.

Suggest how the mass of solid obtained in Experiment 2 compares to that of Experiment 1.

Explain your answer.

.....
.....
..... [2]

(d) 4-aminobenzaldehyde can be reacted with a halogenoalkane to form 4-(dimethylamino)benzaldehyde, compound **D**.



Some data is given that is relevant to this reaction.

| halogenoalkane | boiling point /°C | carbon-halogen bond energy /kJ mol ⁻¹ |
|--------------------|-------------------|--|
| CH ₃ Cl | -97 | 340 |
| CH ₃ Br | 4 | 280 |
| CH ₃ I | 43 | 240 |

Give **two** reasons why CH₃I is the preferred halogenoalkane in the conversion of 4-aminobenzaldehyde to compound **D**.

1

.....

2

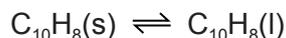
.....

[2]

[Total: 13]

- 2 Naphthalene, $C_{10}H_8$, is an aromatic organic compound that is a solid at room temperature and pressure.

The enthalpy change of fusion, ΔH_{fusion} , of naphthalene is the enthalpy change that occurs when naphthalene melts. It cannot be directly measured.



The melting point of naphthalene depends on its purity. When other compounds dissolve in liquid naphthalene its melting point is lowered.

Diphenylamine, $(C_6H_5)_2NH$, dissolves in liquid naphthalene. By varying the amount of diphenylamine and measuring the melting points of the different mixtures, the enthalpy change of fusion of naphthalene can be calculated.

- (a) The equation that links the melting point of a naphthalene-diphenylamine mixture with its enthalpy change of fusion, ΔH_{fusion} , is shown.

$$\log Y = A - \frac{\Delta H_{\text{fusion}}}{2.30 \times RT_m}$$

Y = mole fraction of naphthalene

R = molar gas constant, $8.31 \text{ JK}^{-1} \text{ mol}^{-1}$

T_m = melting point of naphthalene in K

A is a constant

- (i) A series of experiments is performed using the same amount, 0.100 mol, of naphthalene each time.

Calculate the mass of naphthalene, $C_{10}H_8$, that should be used for each of these experiments.

[A_r : C, 12.0; H, 1.0]

mass of naphthalene = g [1]

- (ii) The melting point and freezing point of a substance are the same. The melting point, T_m , of a substance can be found by recording the temperature at which the substance freezes, measured when crystals first start to appear on cooling.

The results of a series of experiments using 0.100 mol of naphthalene and different masses of diphenylamine are shown.

Process the results to complete the table.

Record all your data to **three** significant figures.

The mole fraction of naphthalene, Y , is calculated as shown.

$$Y = \frac{n_N}{n_N + n_D}$$

n_N = amount in moles of naphthalene, $C_{10}H_8$, = 0.100

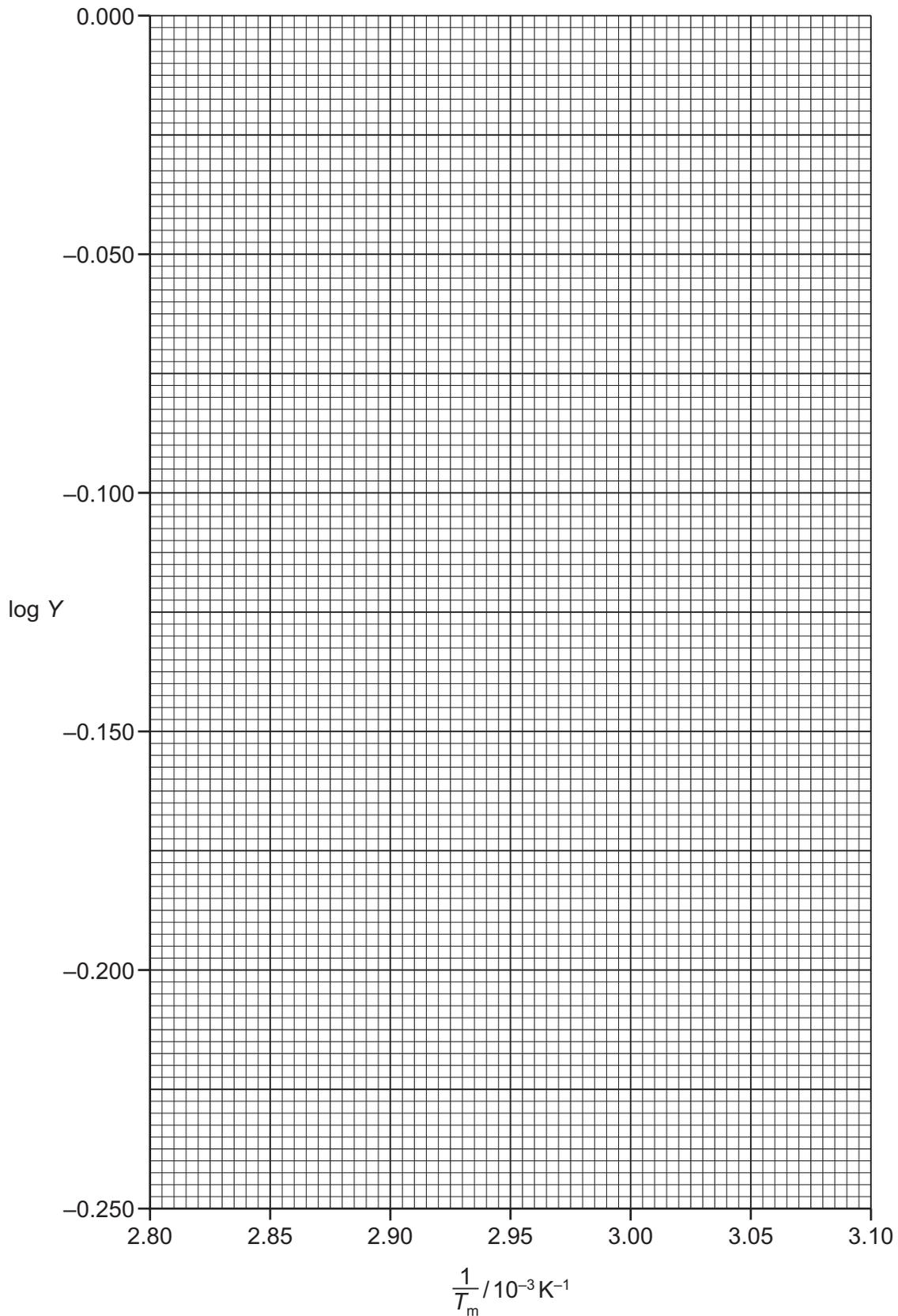
n_D = amount in moles of diphenylamine, $(C_6H_5)_2NH$

| amount of $(C_6H_5)_2NH$, n_D / mol | mole fraction of $C_{10}H_8$, Y | temperature at which crystals appear, T_m / K | $\frac{1}{T_m}$ / $10^{-3} K^{-1}$ | log Y |
|--|------------------------------------|---|------------------------------------|---------|
| 0.00 | 1.00 | 353 | 2.83 | 0.00 |
| 0.00888 | | 349 | | |
| 0.0178 | | 345 | | |
| 0.0266 | | 341 | | |
| 0.0355 | | 338 | | |
| 0.0444 | | 334 | | |
| 0.0533 | | 331 | | |
| 0.0621 | | 329 | | |
| 0.0769 | | 325 | | |

[3]

(b) Plot a graph on the grid to show the relationship between $\frac{1}{T_m}$ and $\log Y$.

Use a cross (×) to plot each data point. Draw the straight line of best fit.



[2]

- (c) (i) Use the graph to determine the gradient of the line of best fit. State the co-ordinates of both points you used in your calculation.

co-ordinates 1 co-ordinates 2

gradient = K
[2]

- (ii) Use your answer to (c)(i) to determine the value of the enthalpy change of fusion of naphthalene, ΔH_{fusion} , in kJ mol^{-1} .

$\Delta H_{\text{fusion}} = \dots\dots\dots \text{kJ mol}^{-1}$ [1]

- (d) (i) Do you consider the results obtained to be reliable? Explain your answer.

.....
.....
..... [1]

- (ii) Different literature values for the enthalpy change of fusion of naphthalene suggest that 10.00 g of naphthalene require between 1.45 kJ and 1.47 kJ to melt.

Use this information to calculate the range of ΔH_{fusion} values of naphthalene, C_{10}H_8 , given in literature.

Use your values to comment on the accuracy of the experimental procedure.

[A_r : C, 12.0; H, 1.0]

If you were not able to calculate ΔH_{fusion} in (c)(ii), you may use 18.4 kJ mol^{-1} , but this may not be the correct answer.

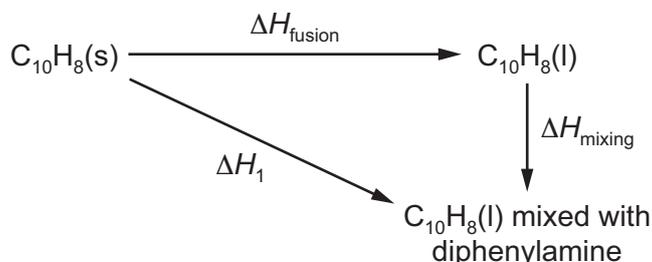
range kJ mol^{-1}

comment

.....

[2]

- (e) The enthalpy change calculated in this reaction is actually ΔH_1 , shown in the Hess' cycle.



It is assumed that the enthalpy change when $\text{C}_{10}\text{H}_8(\text{l})$ and diphenylamine are mixed, ΔH_{mixing} , is zero, and therefore $\Delta H_1 = \Delta H_{\text{fusion}}$.

State how the value of ΔH_1 compares to the value of ΔH_{fusion} if the mixing of naphthalene and diphenylamine is endothermic.

Explain your answer.

.....

.....

.....

..... [2]

- (f) A student incorrectly uses a value for the M_r of diphenylamine that is too low. This produces incorrect values for the mole fraction, Y .
- (i) Predict the effect this will have on the calculated values of Y .

Explain your answer.

$$Y = \frac{n_N}{n_N + n_D}$$

n_N = amount in moles of naphthalene
 n_D = amount in moles of diphenylamine

.....

 [1]

- (ii) The student uses the incorrectly calculated value of Y from (f)(i) in the determination of ΔH_{fusion} .

$$\log Y = A - \frac{\Delta H_{\text{fusion}}}{2.30 \times RT_m}$$

Predict how the student's calculated value of ΔH_{fusion} is different from the actual value.

Explain your answer.

.....

 [2]

[Total: 17]

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