Cambridge Assessment International Education

Cambridge International AS & A Level

CANDIDATE NAME

CENTRE NUMBER

CANDIDATE NUMBER

2488285374

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **October/November 2020**

2 hours

You must answer on the question paper.

You will need: Data booklet

INSTRUCTIONS

- Answer **all** questions.
- Use a black or dark blue pen. You may use an HB pencil for any diagrams or graphs.
- Write your name, centre number and candidate number in the boxes at the top of the page.
- Write your answer to each question in the space provided.
- Do **not** use an erasable pen or correction fluid.
- Do **not** write on any bar codes.
- You may use a calculator.
- You should show all your working, use appropriate units and use an appropriate number of significant figures.

INFORMATION

- The total mark for this paper is 100.
- The number of marks for each question or part question is shown in brackets [ ].

This document has **20** pages. Blank pages are indicated.

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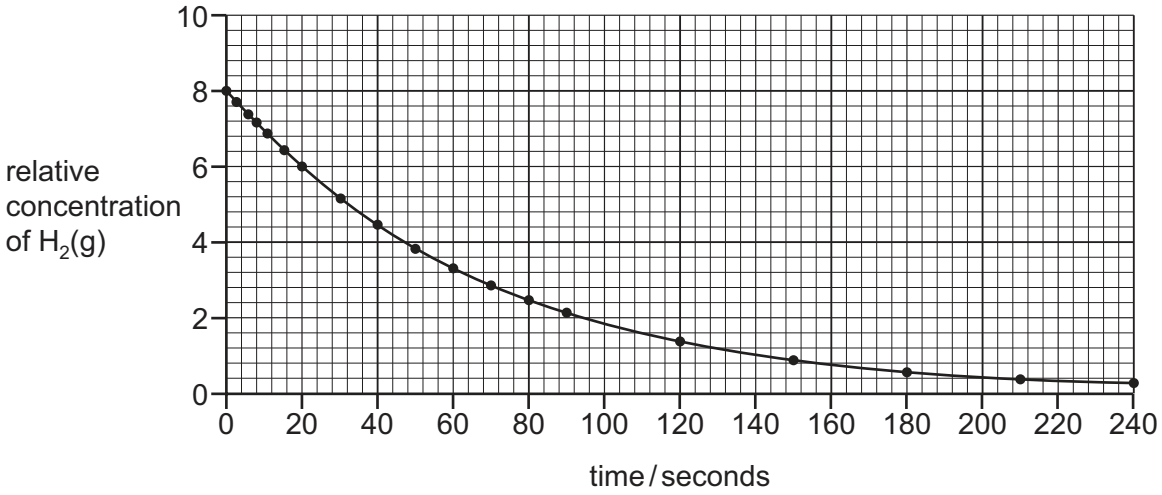
Answer **all** the questions in the spaces provided.

1 The rate of the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is studied.

(a) A small amount of $H_2(g)$ is mixed with a large excess of $I_2(g)$ at a temperature of 400 K and the reaction is monitored. The graph obtained is shown.



(i) Suggest why a large excess of $I_2(g)$ is used in this experiment.

..... [1]

(ii) The reaction is first order with respect to $H_2(g)$.

Use data from the graph to confirm this statement.

.....

.....

.....

..... [2]

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(b) Three separate experiments were carried out at 400 K with different starting concentrations of $H_2(g)$ and $I_2(g)$. The results are shown in the table.

experiment	$[H_2(g)]$ / mol dm^{-3}	$[I_2(g)]$ / mol dm^{-3}	rate of reaction / mol dm^{-3} s^{-1}
1	1.0×10^{-2}	1.0×10^{-2}	2.0×10^{-17}
2	1.0×10^{-1}	1.0×10^{-1}	2.0×10^{-15}
3	5.0×10^{-1}	5.0×10^{-1}	5.0×10^{-14}

(i) Use the data, and the order of reaction with respect to $H_2(g)$ given in **(a)(ii)**, to deduce the order of reaction with respect to $I_2(g)$.

Explain your answer, giving data in support of your explanation.

.....

.....

.....

..... [3]

(ii) Use information from **(a)(ii)** and your answer to **(b)(i)** to write the rate equation for the forward reaction.

rate = ... [1]

(iii) Use your rate equation and data from experiment 1 to calculate the value of the rate constant, *k*, for the forward reaction at 400 K. Include units for *k*.

k = ... units = ...
[2]

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(c) At 400 K the rate constant for the forward reaction is approximately 1000 times greater than the rate constant for the backward reaction. The overall orders of the forward and backward reactions are the same.

forward reaction	$H_2(g) + I_2(g) \rightarrow 2HI(g)$
backward reaction	$2HI(g) \rightarrow H_2(g) + I_2(g)$

(i) Use this information to explain what will happen if equal concentrations of HI(g), $H_2(g)$ and $I_2(g)$ are mixed at 400 K.

You should comment on:
- the relative initial rates of the forward and backward reactions
- the position of the equilibrium reached.

.....

.....

..... [1]

(ii) At 700 K the rate constant for the forward reaction is approximately 50 times greater than the rate constant for the backward reaction.

Use this information and the information in **(c)(i)** to deduce the signs of the ΔH values of the forward and backward reactions. Explain your answer.

.....

.....

.....

..... [2]

[Total: 12]

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2 **(a)** Write an expression for the K_a of the weak acid HA in terms of the concentrations of the species involved.

K_a =

[1]

(b) The hydroxylammonium ion, $HONH_3^+$, is a weak acid. A 1.00×10^{-3} mol dm^{-3} solution of hydroxylammonium ions has a pH of 4.41.

(i) Calculate the K_a of $HONH_3^+$.

K_a = ... [2]

(ii) Calculate the pK_a of $HONH_3^+$.

pK_a = ... [1]

(c) The solubility product of manganese(II) hydroxide, $Mn(OH)_2$, in water is 1.1×10^{-11} mol^3 dm^{-9} at 298 K.

Calculate the solubility of $Mn(OH)_2$ in water at 298 K.

solubility = ... mol dm^{-3} [2]

[Total: 6]

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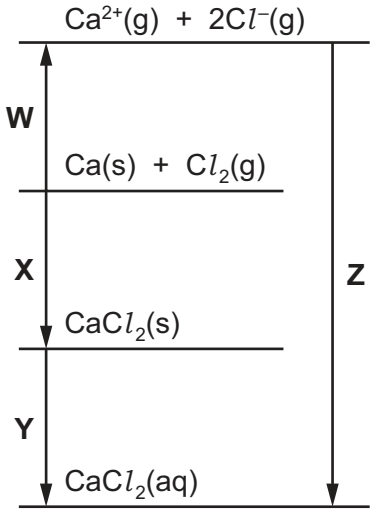
3 **(a)** The energy cycle shown can be used, along with suitable data, to calculate the enthalpy change of hydration of $Ca^{2+}(g)$.
Each arrow indicates a transformation, **W**, **X**, **Y** and **Z**. Each transformation consists of one or more steps.



The following data and data from the *Data Booklet* should be used.

electron affinity of $Cl(g)$	$= -349\,kJ\,mol^{-1}$
enthalpy change of atomisation of Ca(s)	$= +193\,kJ\,mol^{-1}$
enthalpy change of formation of $CaCl_2(s)$	$= -795\,kJ\,mol^{-1}$
enthalpy change of solution of $CaCl_2(s)$	$= -83\,kJ\,mol^{-1}$
enthalpy change of hydration of $Cl^-(g)$	$= -364\,kJ\,mol^{-1}$

(i) Calculate the value of the enthalpy change corresponding to transformation **W**.
Show your working.

enthalpy change **W** = ... $kJ\,mol^{-1}$ [2]

(ii) Use your answer to **(a)(i)** and other data to calculate the value of the enthalpy change corresponding to transformation **Z**.

enthalpy change **Z** = ... $kJ\,mol^{-1}$ [2]

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(iii) Use your answer to **(a)(ii)** to calculate the enthalpy change of hydration of $Ca^{2+}(g)$.

enthalpy change of hydration of $Ca^{2+}(g)$ = ... $kJ\,mol^{-1}$ [2]

(iv) Write an expression, in terms of **W**, **X**, **Y** and/or **Z**, to show how the enthalpy changes of **two** of the transformations can be used to calculate the lattice energy of $CaCl_2(s)$.

lattice energy of $CaCl_2(s)$ = ... [1]

(v) State whether the lattice energy of $CaCl_2(s)$ is more or less exothermic than the lattice energy of $MgF_2(s)$.

Explain your answer.

.....

.....

..... [1]

(b) The sulfates of the Group 2 elements vary in solubility down Group 2.

(i) Give the names of **two** solutions that could be mixed to form barium sulfate.

..... [1]

(ii) State and explain how the solubilities of the sulfates of the Group 2 elements vary down Group 2.

.....

.....

.....

.....

.....

.....

..... [4]

[Total: 13]

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4 **(a)** Identify the substances liberated at the anode and at the cathode during the electrolysis of saturated KC*l*(aq).

at the anode .....

at the cathode .....

[1]

(b) When dilute sulfuric acid is electrolysed, oxygen is liberated at the anode.

Dilute sulfuric acid is electrolysed for 15.0 minutes using a current of 0.750 A.

Calculate the volume of oxygen that is liberated under room conditions.

volume of oxygen = ... cm^3 [3]

(c) The halogens chlorine, bromine and iodine differ in their strengths as oxidising agents. These strengths are indicated by the $E^{\ominus}$ values for these halogens.

(i) Give the $E^{\ominus}$ values for chlorine, bromine and iodine acting as oxidising agents.

..... [1]

(ii) Deduce which of chlorine, bromine and iodine will react with a solution of $Sn^{2+}(aq)$ under standard conditions.

Explain your answer. Include a relevant equation in your explanation.

.....

.....

..... [3]

(iii) An excess of chlorine is added to a solution of acidified $Mn^{2+}(aq)$ under standard conditions.

Give the formula of the product of this reaction that contains manganese.

..... [1]

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(d) An electrochemical cell can be made by connecting an Fe^{3+}/Fe^{2+} half-cell to an $S_2O_8^{2-}/SO_4^{2-}$ half-cell under standard conditions.

(i) Calculate the standard cell potential of this electrochemical cell.

$E^{\ominus}_{cell}$ = ... V [1]

(ii) State the material that should be used as the electrode in each half-cell.

in the Fe^{3+}/Fe^{2+} half-cell .....

in the $S_2O_8^{2-}/SO_4^{2-}$ half-cell .....
[1]

(iii) Describe **one** change to each half-cell that would **increase** the value of the cell potential. The temperature should remain at 298 K.

Fe^{3+}/Fe^{2+} half-cell .....

.....

$S_2O_8^{2-}/SO_4^{2-}$ half-cell .....

.....
[1]

[Total: 12]

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5 **(a)** Define the term *transition element*.

.....

..... [1]

(b) **(i)** Complete the electronic configuration of an isolated gaseous Fe^{3+} ion.

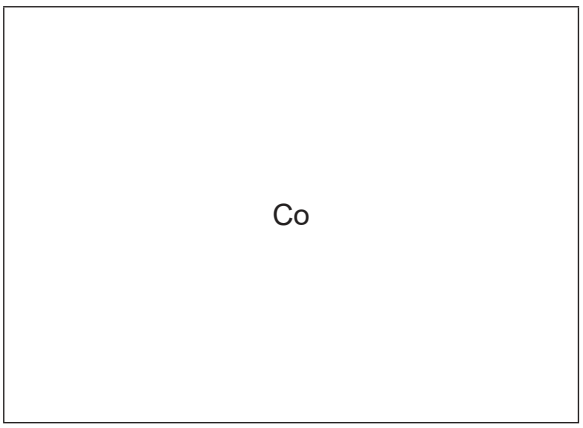
$1s^2$ ..... [1]

(ii) Name **two** transition elements whose isolated gaseous **atoms** have the same number of electrons in the 3d subshell as an isolated gaseous Fe^{3+} ion.

..... [1]

(c) Cobalt(II) sulfate is added to water to form a pink solution containing complex ion **P**. An excess of concentrated hydrochloric acid is added to this solution to form a blue solution containing complex ion **Q**.

(i) Complete the diagram to show the three-dimensional structure of **Q**.
State the charge on this complex ion.



charge .....

[2]

(ii) Name the type of reaction in which **P** forms **Q**.

..... [1]

(iii) Explain why solutions that contain transition element ions are often coloured.

.....

.....

.....

.....

.....

..... [4]

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(iv) Explain why the colours of **P** and **Q** are different.

.....

.....

..... [2]

(d) A solution of the bidentate ligand 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$, is added to an aqueous solution of cobalt(II) sulfate. Oxygen is then bubbled into the mixture forming a complex ion with the formula $[Co(H_2NCH_2CH_2NH_2)_3]^{3+}$.

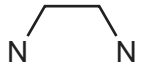
This complex ion exists as a mixture of two isomers. The geometry of both of these isomeric complexes is octahedral.

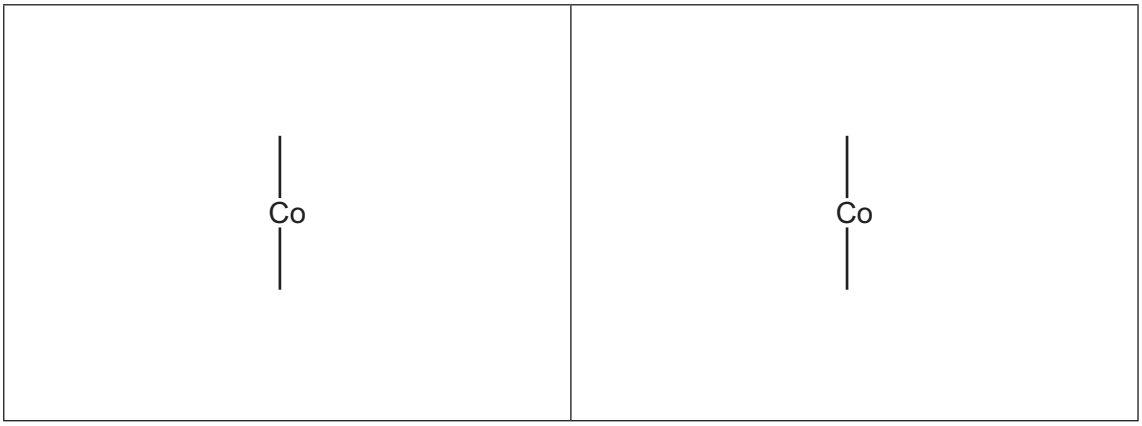
(i) In this reaction, cobalt undergoes **two** types of reaction. One type of reaction is the same as that described in **(c)(ii)**.

Name the **other** type of reaction that cobalt undergoes.

..... [1]

(ii) Draw the three-dimensional structures of the two isomeric complexes in the boxes.

You may use  to represent a molecule of $H_2NCH_2CH_2NH_2$.



[2]

(iii) Name the type of stereoisomerism shown by these two isomeric complexes.

..... [1]

(iv) State the co-ordination number of cobalt in these two isomeric complexes.

..... [1]

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(e) The stability constants, K_{stab}, of three complexes of mercury(II) are given in the table.

complex	K_{stab}
$[Hg(CN)_4]^{2-}$	2.5×10^{41}
$[HgCl_4]^{2-}$	1.7×10^{16}
$[HgI_4]^{2-}$	2.0×10^{30}

(i) Write an expression for the K_{stab} of $[Hg(CN)_4]^{2-}$.

K_{stab} =

[1]

(ii) An aqueous solution containing Hg^{2+} is added to a solution containing equal concentrations of CN^-(aq), Cl^-(aq) and I^-(aq). The mixture is left to reach equilibrium.

Predict which of the complexes $[Hg(CN)_4]^{2-}$, $[HgCl_4]^{2-}$ and $[HgI_4]^{2-}$ is present in the resulting mixture in the highest concentration and which is present in the lowest concentration. Explain your answer.

.....

.....

.....

..... [2]

[Total: 20]

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6 **(a)** Ethanoic acid, CH_3CO_2H and trichloroethanoic acid, CCl_3CO_2H, are both carboxylic acids. Ethanoic acid can be used to make ethanamide, CH_3CONH_2.

Place these three compounds in order of acidity, starting with the **least** acidic.
Explain your answer.

..... < ..... < .....

least acidic most acidic

.....

.....

.....

.....

.....

[3]

(b) Methanoic acid, HCO_2H, and ethanedioic acid, HO_2CCO_2H, are two other carboxylic acids.

(i) State which, if any, of ethanoic acid, methanoic acid and ethanedioic acid will react with Fehling's reagent.

..... [1]

(ii) State which, if any, of ethanoic acid, methanoic acid and ethanedioic acid will react with warm acidified manganate(VII) ions.

..... [1]

(c) Ethanamide can be made from ethanoic acid in a two-step synthesis.

$$\text{ethanoic acid} \xrightarrow{\text{step 1}} \mathbf{A} \xrightarrow{\text{step 2}} \text{ethanamide}$$

(i) Compound **A** contains chlorine.

Give the structural formula and name of **A**.

structural formula .....

name .....

[2]

(ii) Suggest suitable reagents for steps 1 and 2.

step 1 .....

step 2 .....

[2]

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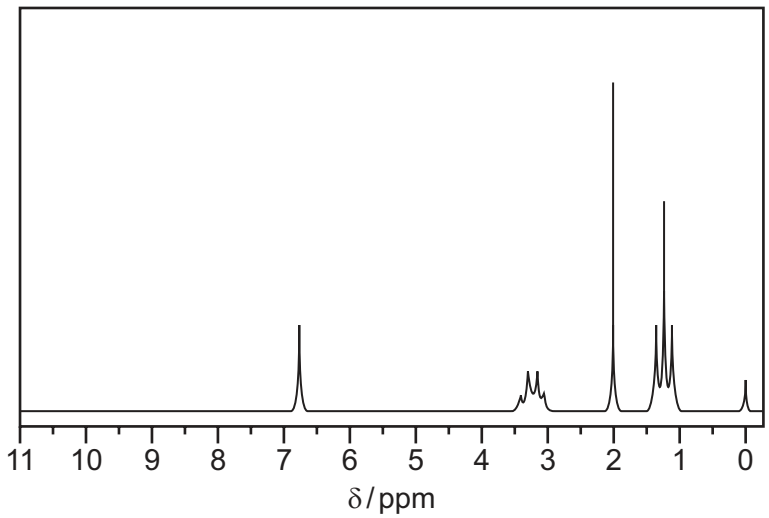
(d) Compound **A** can also be used to make the amide $CH_3CONHC_2H_5$.

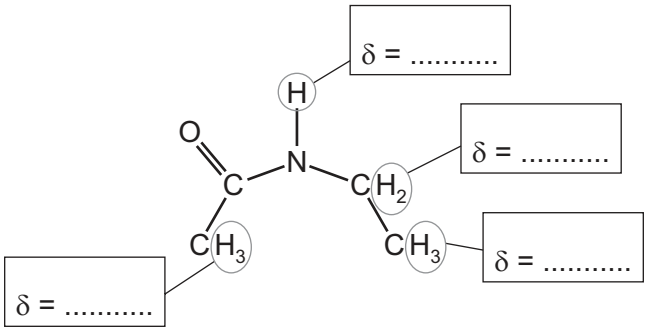
The proton NMR spectrum of the amide $CH_3CONHC_2H_5$ in the solvent $CDCl_3$ is shown.



(i) Explain why $CDCl_3$ is used as a solvent instead of $CHCl_3$.

..... [1]

(ii) Complete the diagram with the chemical shifts, δ, of the protons labelled in the $CH_3CONHC_2H_5$ molecule.



[2]

(iii) State and explain how the proton NMR spectrum of the amide $CH_3CONHC_2H_5$ differs when dissolved in D_2O rather than $CDCl_3$.

.....

.....

..... [2]

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(e) The mass spectrum of the amide $CH_3CONHC_2H_5$ includes a fragment ion with *m*/*e* value of 58.

Give the molecular formula of this fragment ion.

fragment ion with *m*/*e* value of 58 is ..... [1]

(f) The amide undergoes the following reaction to produce diethylamine.

$$CH_3CONHC_2H_5 \xrightarrow{\text{reagent } \mathbf{B}} \underset{\text{diethylamine}}{C_2H_5NHC_2H_5}$$

(i) Identify reagent **B**.

..... [1]

(ii) State the number of different absorptions in the carbon-13 NMR spectrum of diethylamine.

..... [1]

[Total: 17]

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7 **(a)** Describe the structure of a benzene molecule, C_6H_6.

Your answer should include:
- the shape of the molecule
- the relative lengths of the C–C bonds
- bond angles
- the hybridisation of the carbon atoms
- the overlap between orbitals that produces each type of bond present.

.....

.....

.....

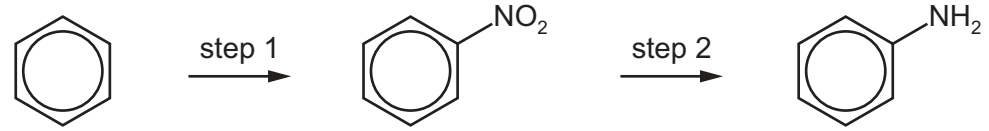
.....

.....

.....

..... [4]

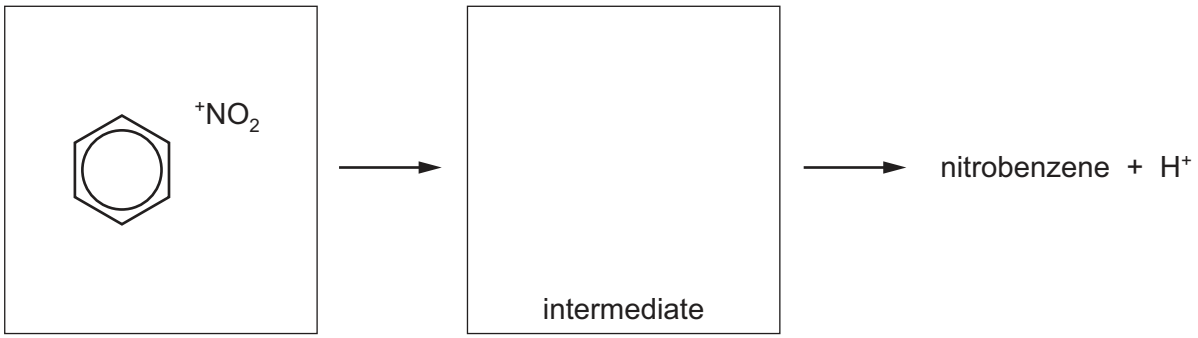
(b) Benzene can be used as a starting material to produce phenylamine by a two-step synthesis.



benzene nitrobenzene phenylamine

(i) Step 1 is the reaction of benzene with NO_2^+ ions.

Complete the mechanism and draw the intermediate of step 1.
Include all relevant charges and curly arrows to show the movement of electron pairs.



[2]

(ii) State the name of the mechanism in **(b)(i)**.

..... [1]

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(iii) Identify the reagents needed to produce NO_2^+ ions.

Write an equation to explain how these reagents produce NO_2^+ ions.

.....

.....

..... [2]

(iv) Give reagents and conditions for the production of phenylamine from nitrobenzene in step 2.

.....

..... [2]

(c) Phenylamine reacts with $Br_2(aq)$.

(i) Write an equation for this reaction. You may use structural or displayed formulae.

..... [1]

(ii) Name the organic product of this reaction.

..... [1]

(iii) Describe **two** observations that can be **seen** when phenylamine reacts with $Br_2(aq)$.

observation 1 .....

observation 2 .....
[1]

(d) Describe the relative basicities of ammonia, ethylamine and phenylamine, starting with the **least** basic.
Explain your answer in terms of their structures.

..... < ..... < .....
least basic most basic

.....

.....

.....

.....
[3]

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(e) 1,3-diaminopropane, $H_2NCH_2CH_2CH_2NH_2$, can be used to make polyamides.

(i) Identify **one** compound that would react with 1,3-diaminopropane to form a polyamide.

..... [1]

(ii) Draw a section of the polymer chain formed from 1,3-diaminopropane and the compound you chose in **(e)(i)**.

Your answer should:
- include four monomer residues (two of each type of monomer)
- show the amide link fully displayed
- clearly identify **one** repeat unit of this polymer.

[2]

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