

CANDIDATE
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CHEMISTRY

9701/41

Paper 4 A Level Structured Questions

October/November 2019

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

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.

A Data Booklet is provided.

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 **20** printed pages.

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

1 An electrochemical cell is constructed using two half-cells.

- an $\text{Sn}^{4+}/\text{Sn}^{2+}$ half-cell
- an Al^{3+}/Al half-cell

(a) State the material used for the electrode in each half-cell.

- $\text{Sn}^{4+}/\text{Sn}^{2+}$ half-cell
- Al^{3+}/Al half-cell

[1]

(b) The cell is operated at 298 K.

The Al^{3+}/Al half-cell has standard concentrations.

The $\text{Sn}^{4+}/\text{Sn}^{2+}$ half-cell has $[\text{Sn}^{4+}] = 0.300 \text{ mol dm}^{-3}$ and $[\text{Sn}^{2+}] = 0.150 \text{ mol dm}^{-3}$.

(i) Use the Nernst equation to calculate the electrode potential, E , of the $\text{Sn}^{4+}/\text{Sn}^{2+}$ half-cell under these conditions.

$E = \dots\dots\dots \text{ V [2]}$

(ii) Calculate the E_{cell} under these conditions.

$E_{\text{cell}} = \dots\dots\dots \text{ V [1]}$

(iii) Write an equation for the overall cell reaction that occurs.

..... [2]

- (c) Aluminium is produced industrially by electrolysis of a melt containing large amounts of Al^{3+} ions.

Calculate the mass of aluminium that is obtained when a current of 300 000 A is passed for 24 hours. Give your answer to **three** significant figures.

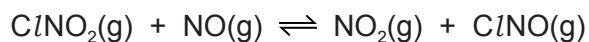
mass = ... units = ... [4]

- (d) Explain why chromium metal cannot be obtained by the electrolysis of dilute aqueous chromium(II) sulfate. Your answer should include data from the *Data Booklet*.

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

[Total: 12]

- 2 When ClNO_2 reacts with NO an equilibrium is established.



In each ClNO_2 molecule the nitrogen atom is bonded to the chlorine atom and bonded to each of the oxygen atoms separately.

- (a) Draw a 'dot-and-cross' diagram for the ClNO_2 molecule.

[2]

- (b) The reaction between ClNO_2 and NO is first order with respect to each reactant.

- (i) Write the rate equation for this reaction.

rate = ... [1]

- (ii) Deduce the units of the rate constant, k , when the concentrations of both gases are measured in mol dm^{-3} and the rate is measured in $\text{mol dm}^{-3} \text{s}^{-1}$.

..... [1]

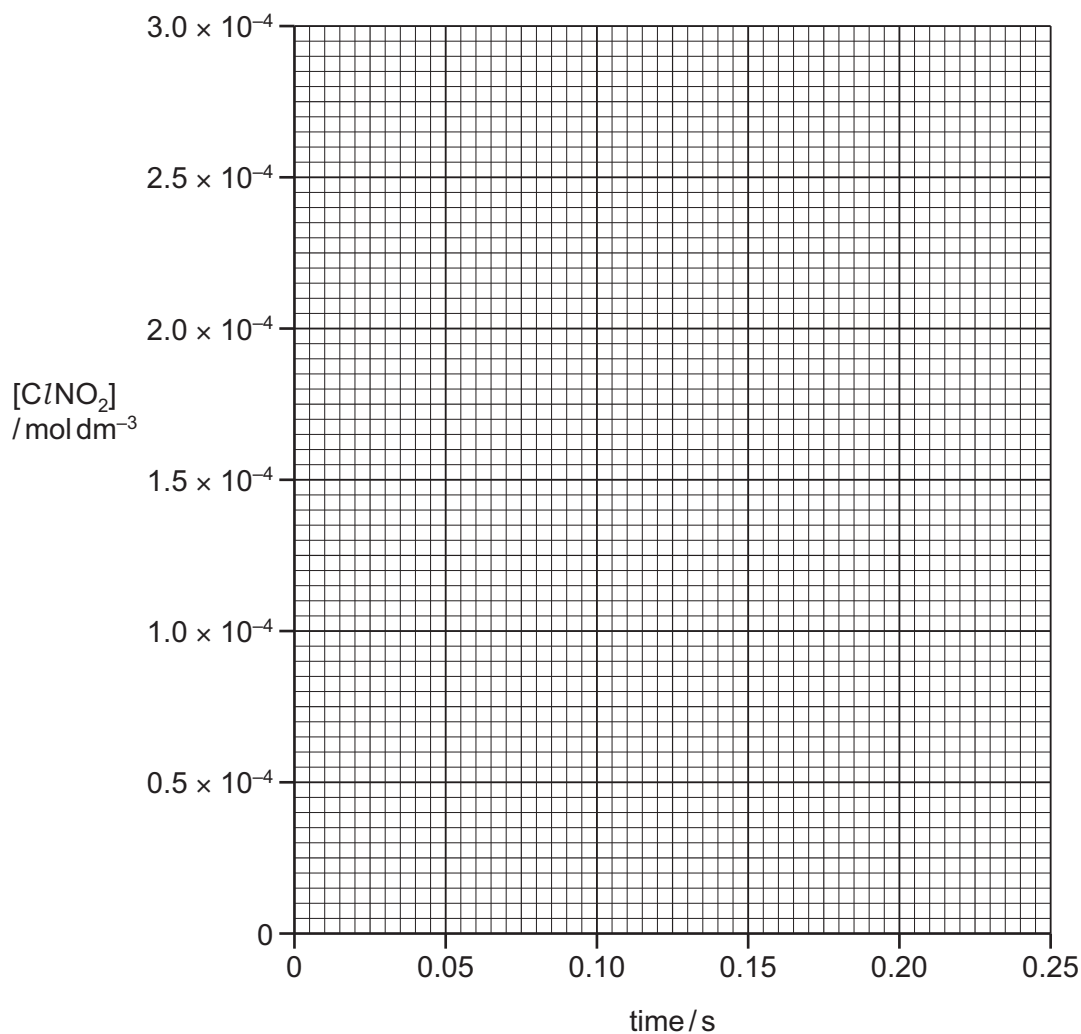
- (iii) State and explain whether or not the reaction **could** take place in a single step.

.....

 [1]

(c) An experiment is carried out in which the initial $[C\ell NO_2]$ is $2.0 \times 10^{-4} \text{ mol dm}^{-3}$. A large excess of NO is used. The initial rate of reaction is $1.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$. The rate of the reaction is assumed to be constant for the first 0.20 seconds.

(i) Draw a graph on the grid to show how the concentration of $C\ell NO_2$ varies for the first 0.20 seconds.



[2]

(ii) Deduce the concentration of the NO_2 product at 0.20 seconds.

..... [1]

(iii) After 20 seconds the concentration of $C\ell NO_2$ remains constant.

Explain this observation.

..... [1]

[Total: 9]

- 3 (a) Explain what is meant by the term *entropy of a system*.

.....
 [1]

- (b) State and explain whether the entropy change of each of the following processes is positive or negative. Do not consider the entropy change of the surroundings.

- liquid water at 80 °C is cooled to 60 °C

The entropy change is because

.....

- solid calcium chloride is added to water and the mixture is stirred

The entropy change is because

.....

- the change corresponding to the lattice energy of calcium chloride, $\Delta H_{\text{latt}} \text{CaCl}_2(\text{s})$, takes place

The entropy change is because

.....

[3]

- (c) The reaction $\text{ZnCO}_3(\text{s}) \rightarrow \text{ZnO}(\text{s}) + \text{CO}_2(\text{g})$ is not spontaneous at room temperature.

- (i) Give the full name for the term ΔG° .

..... [1]

- (ii) Describe how the temperature at which the reaction becomes spontaneous can be calculated. Include an equation in your answer.

equation

.....

.....

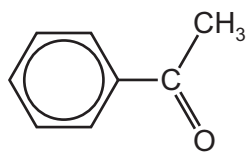
.....

[2]

[Total: 7]

4 Phenylethanone is an important chemical with many uses.

phenylethanone



(a) Phenylethanone can be synthesised using benzene as one of the starting materials.

Identify the other reagents used and describe any essential reaction conditions.

.....
 [2]

(b) Phenylethanone is treated separately with three reagents.

Complete the table, for each reagent, to give the structural formula of one organic product formed and the name of the mechanism involved. If there is no reaction you should write 'no reaction'.

reagent	organic product	name of mechanism
chlorine gas at 10 °C in the presence of ultra-violet light		
a mixture of concentrated nitric and sulfuric acids at 50 °C		
bromine water		

[5]

(c) Phenylethanone reacts with HCN in the presence of a small amount of NaCN.

(i) Name the mechanism of this reaction.

..... [1]

(ii) Draw the mechanism of this reaction below. Include all relevant charges, dipoles, lone pairs and curly arrows. Your mechanism should show the catalytic role of CN^- ions.

phenylethanone

intermediate

product



[4]

(d) Phenylethanone can be used as a starting material to make phenylethene in a two-step synthesis.



(i) Draw the structure of compound **D** in the box.

[1]

(ii) Identify a suitable reagent for step 1.

..... [1]

(iii) Identify a suitable reagent for step 2.

..... [1]

(iv) State the number of peaks in the C-13 NMR spectrum of **phenylethene**.

..... [1]

(v) Suggest C-13 chemical shift ranges expected for the different types of carbon environment in **phenylethanone**.

.....

.....

..... [2]

[Total: 18]

5 Silver sulfide, Ag_2S , is very insoluble in water.

(a) (i) Write an expression for the solubility product, K_{sp} , of $\text{Ag}_2\text{S}(\text{s})$.

$$K_{\text{sp}} =$$

[1]

(ii) The solubility of $\text{Ag}_2\text{S}(\text{s})$ in water at 298 K is $1.16 \times 10^{-17} \text{ mol dm}^{-3}$.

Calculate the numerical value of the solubility product, K_{sp} , of $\text{Ag}_2\text{S}(\text{s})$ at 298 K.

$$K_{\text{sp}} = \dots\dots\dots [2]$$

(iii) Calculate the minimum volume of water needed to dissolve 1.00 g of $\text{Ag}_2\text{S}(\text{s})$ under standard conditions.

$$\text{volume} = \dots\dots\dots \text{ dm}^3 [2]$$

(b) Bromic(I) acid, HOBr(aq) , is a weak acid. Its K_a is $2.0 \times 10^{-9} \text{ mol dm}^{-3}$.

(i) Calculate the pH of $0.20 \text{ mol dm}^{-3} \text{ HOBr(aq)}$.

pH = ... [2]

(ii) 5.0 cm^3 of 0.20 mol dm^{-3} potassium hydroxide, KOH , are added to 20.0 cm^3 of $0.20 \text{ mol dm}^{-3} \text{ HOBr(aq)}$.

Calculate the pH of the buffer solution produced.

pH = ... [2]

[Total: 9]

6 The elements in Group 2 include magnesium, calcium, strontium and barium.

- (a) (i)** Write an equation for the change representing the first ionisation energy of magnesium. Include state symbols.

..... [1]

- (ii)** Write an equation for the reaction of strontium with cold water. Include state symbols.

..... [1]

- (iii)** Describe and explain the trend in reactivity observed in the reactions of these Group 2 metals with cold water.

.....

.....

..... [1]

- (b)** The Group 2 metal nitrates decompose when heated.

- (i)** Describe fully what is seen when anhydrous calcium nitrate is heated in a test-tube and decomposition occurs.

.....

..... [1]

- (ii)** Write an equation for the decomposition of calcium nitrate.

..... [1]

- (iii)** Describe and explain the variation in thermal stability of the Group 2 metal nitrates down the group.

.....

.....

..... [3]

- (c) Describe and explain the variation in the solubility of the Group 2 metal sulfates down the group.

.....

.....

.....

.....

.....

.....

..... [4]

[Total: 12]

7 Manganese, chromium and ruthenium are all transition elements.

(a) Explain what is meant by a *transition element*.

.....

 [1]

(b) MnO_4^- (aq) and $\text{Cr}_2\text{O}_7^{2-}$ (aq) act as oxidising agents in acidic solution. Both these oxidising agents will oxidise a solution of Sn^{2+} to give a solution of Sn^{4+} . Solutions containing Sn^{2+} and solutions containing Sn^{4+} are colourless.

(i) Describe the colour change seen when an excess of Sn^{2+} (aq) is added separately to

- dilute acidified MnO_4^- (aq)

from to

- dilute acidified $\text{Cr}_2\text{O}_7^{2-}$ (aq).

from to [1]

(ii) Write an equation for the reaction between Sn^{2+} (aq) and acidified $\text{Cr}_2\text{O}_7^{2-}$ (aq).

..... [1]

(c) Ruthenium, Ru, forms complex ions. In one such complex ion, **X**, the ruthenium ion has a co-ordination number of six. Each complex ion **X** contains one Ru^{2+} ion, one Cl^- ion, one SO_2 molecule and the remaining ligands are NH_3 molecules.

The SO_2 molecule acts as a monodentate ligand and is attached to the Ru^{2+} ion via the sulfur atom. **X** exists in two isomeric forms.

(i) State what is meant by a *co-ordination number of six*.

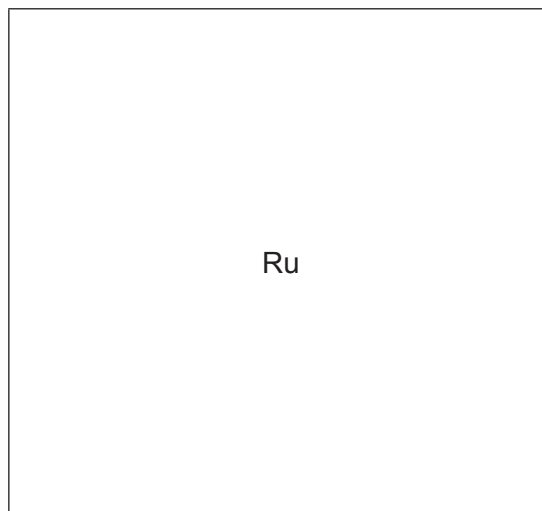
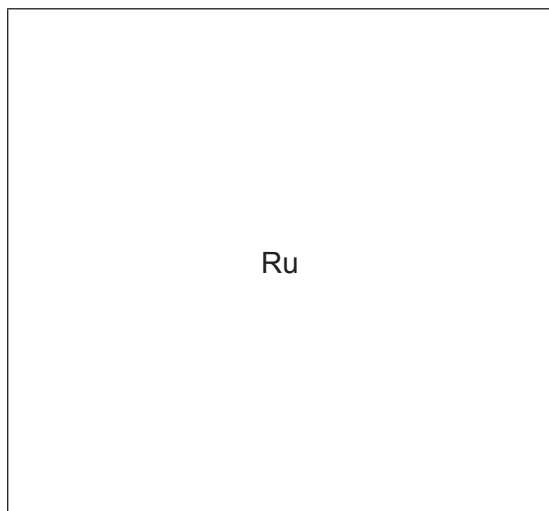
..... [1]

(ii) State the formula of **X**. Include its charge.

..... [1]

(iii) Draw the two isomeric forms of **X** in the boxes below. Your diagrams should show

- the three-dimensional shapes of the two isomers
- how each ligand is attached to the central ruthenium ion.



[3]

(iv) Suggest the type of isomerism shown by **X**.

..... [1]

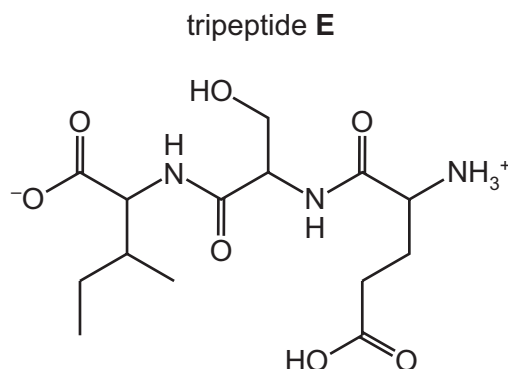
(v) Explain the origin of colour in a transition element complex such as **X**.

.....

 [3]

[Total: 12]

- 8 Proteins are natural polymers. When one particular protein is partially hydrolysed the product mixture includes tripeptide **E**.



- (a) (i) Describe the conditions that could be used to hydrolyse **E** to produce a mixture of three amino acids.

..... [1]

- (ii) Draw the structures of the three amino acids produced by this hydrolysis reaction.

The three amino acids should be shown in the correct form for the conditions you have chosen in (a)(i).

--	--	--

[2]

- (b) If a pure sample of **E** is obtained in aqueous solution, several different types of intermolecular forces are possible between pairs of **E** molecules.

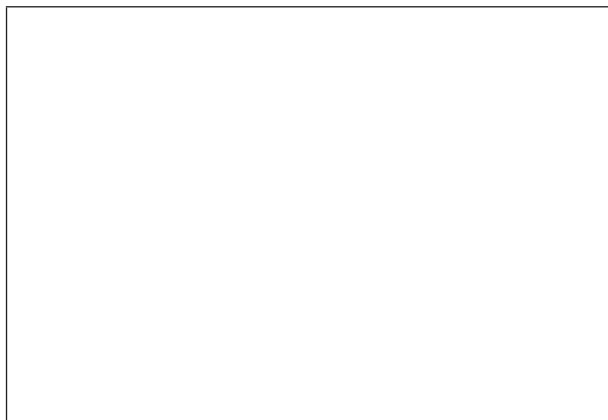
Name three different types of intermolecular force that exist between pairs of **E** molecules, stating the groups on the molecules where the forces are acting.

type of force/bond	pair of groups responsible

[3]

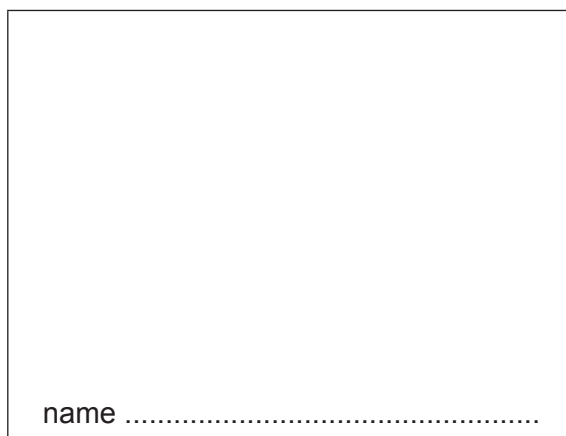
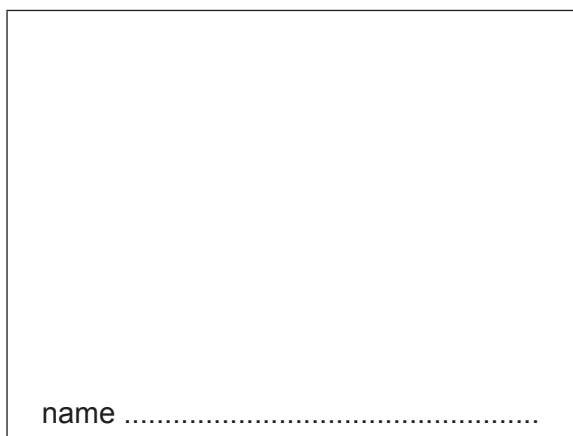
(c) Polyesters and polyamides are two important types of condensation polymer.

- (i) Draw the structure of a compound that can polymerise to produce a polyamide, without the need for a second monomer.



[1]

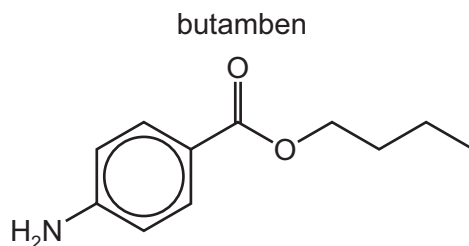
- (ii) Draw the structures of two different compounds that can polymerise together to produce a polyester with **four** carbon atoms per repeat unit. Name the two compounds.



[4]

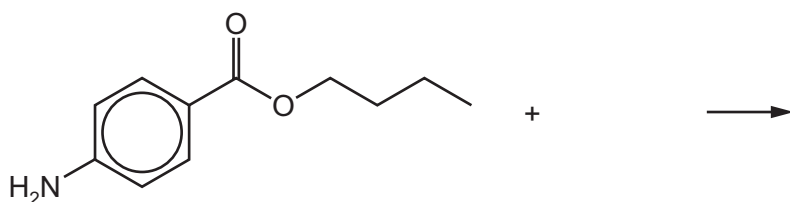
[Total: 11]

9 The structure of butamben is shown.



(a) Butamben can act as a base.

(i) Complete the equation for a reaction in which butamben acts as a base.



[1]

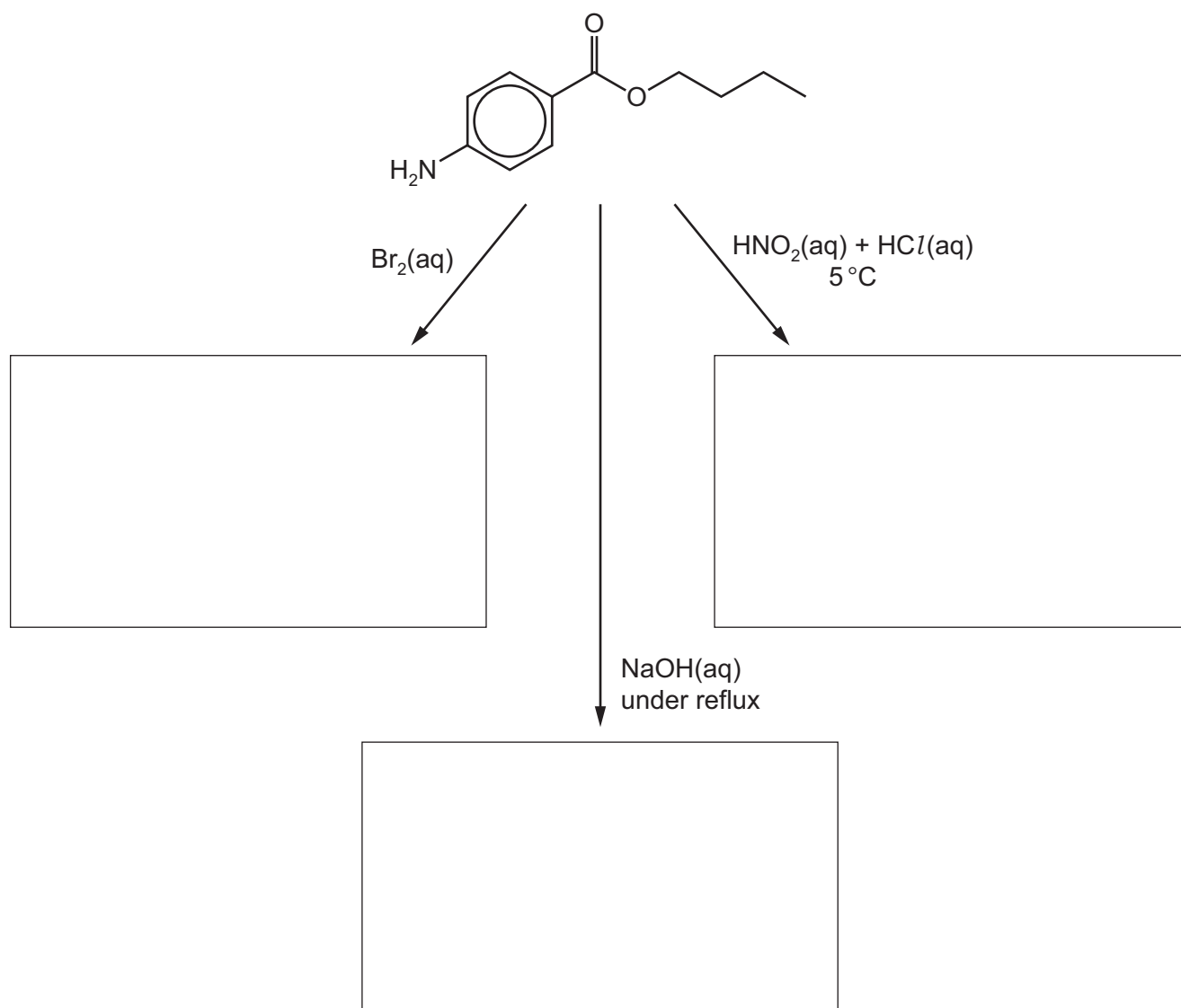
(ii) Predict whether butamben is a stronger or weaker base than ammonia. Give a reason for your answer.

.....

.....

..... [1]

- (b) Complete the reaction scheme below to show the structural formulae of the products formed when butamben is treated separately with the stated reagent.



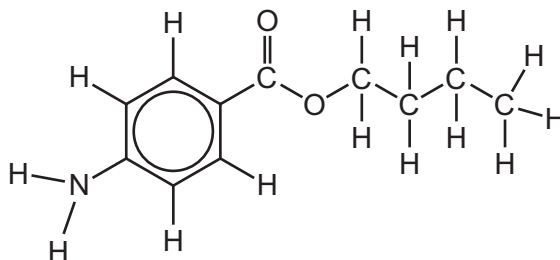
[3]

- (c) The proton NMR spectrum of butamben in CDCl_3 contains one or more peaks that show a triplet splitting pattern.

(i) State the number of peaks in the spectrum that show a triplet splitting pattern.

..... [1]

(ii) On the diagram of butamben below, circle the protons responsible for the peak or peaks you identified in (c)(i).



[1]

(iii) Describe and explain how the proton NMR spectrum of butamben in D_2O would differ from the proton NMR spectrum of butamben in CDCl_3 .

.....

..... [2]

- (d) The mass spectrum of butamben includes peaks at m/e 92 and 57.

Identify the fragments responsible for these peaks.

m/e 92 = ...

m/e 57 = ...

[1]

[Total: 10]

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9701/42

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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 **19** printed pages and **1** blank page.

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

1 An electrochemical cell is constructed using two half-cells.

- a Br_2/Br^- half-cell
- an $\text{Mn}^{3+}/\text{Mn}^{2+}$ half-cell

(a) State the material used for the electrode in each half-cell.

Br_2/Br^- half-cell

$\text{Mn}^{3+}/\text{Mn}^{2+}$ half-cell

[1]

(b) The cell is operated at 298 K.

The Br_2/Br^- half-cell has standard concentrations.

The $\text{Mn}^{3+}/\text{Mn}^{2+}$ half-cell has $[\text{Mn}^{3+}] = 0.500 \text{ mol dm}^{-3}$ and $[\text{Mn}^{2+}] = 0.100 \text{ mol dm}^{-3}$.

(i) Use the Nernst equation to calculate the electrode potential, E , of the $\text{Mn}^{3+}/\text{Mn}^{2+}$ half-cell under these conditions.

$E = \dots\dots\dots \text{ V [2]}$

(ii) Calculate the E_{cell} under these conditions.

$E_{\text{cell}} = \dots\dots\dots \text{ V [1]}$

(iii) Write an equation for the overall cell reaction that occurs.

..... [2]

- (c) An aqueous solution of copper(II) sulfate is electrolysed using copper electrodes. A current of 1.50 A is passed for 3.00 hours. 5.09 g of copper is deposited on the cathode.

The charge on one electron is $-1.60 \times 10^{-19} \text{ C}$.

The relative atomic mass of copper is 63.5.

Use these data to calculate an experimentally determined value for the Avogadro constant, L .
Give your answer to **three** significant figures.

$L = \dots\dots\dots \text{ mol}^{-1}$ [5]

- (d) Explain why magnesium metal cannot be obtained by the electrolysis of dilute aqueous magnesium sulfate. Your answer should include data from the *Data Booklet*.

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

[Total: 13]

2 (a) Explain what is meant by the following terms.

half-life of a reaction

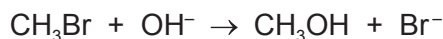
.....

rate-determining step

.....

[2]

(b) The reaction between hydroxide ions and bromomethane is first order with respect to $[\text{OH}^-]$ and first order with respect to $[\text{CH}_3\text{Br}]$.



Suggest a practical method that would confirm that the reaction is first order with respect to $[\text{OH}^-]$.

- Your method should include details of measurements that would be taken in order to calculate the rate of the reaction.
- You should include a method of presenting the results to show that the reaction is first order with respect to $[\text{OH}^-]$.

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

..... [4]

- (c) The hydrolysis of methyl ethanoate, $\text{CH}_3\text{CO}_2\text{CH}_3$, by hydroxide ions, OH^- , is first order with respect to $[\text{CH}_3\text{CO}_2\text{CH}_3]$ and also first order with respect to $[\text{OH}^-]$.

In a particular experiment,

- $[\text{CH}_3\text{CO}_2\text{CH}_3] = 0.100 \text{ mol dm}^{-3}$
- $[\text{OH}^-] = 0.100 \text{ mol dm}^{-3}$
- rate of reaction = $2.06 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$.

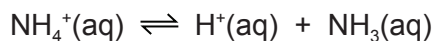
Write a rate equation for this reaction and calculate the value of the rate constant, k , under these conditions. State the units of k .

rate = ...

$k = \dots\dots\dots$ units = ...
[3]

[Total: 9]

- 3 Ammonium chloride, $\text{NH}_4\text{Cl}(\text{s})$, dissolves in water to form an acidic solution. This is due to the dissociation of the ammonium ions.



- (a) The ammonium ion is a weak acid. The pH of a $0.300 \text{ mol dm}^{-3}$ solution of ammonium chloride is 4.89 under standard conditions.

- (i) Calculate the $[\text{H}^+]$ in a $0.300 \text{ mol dm}^{-3}$ solution of ammonium chloride.

$$[\text{H}^+] = \dots\dots\dots \text{mol dm}^{-3} \quad [1]$$

- (ii) Calculate the value of $\text{p}K_{\text{a}}$ of the ammonium ion.

$$\text{p}K_{\text{a}} = \dots\dots\dots [2]$$

- (b) A buffer solution can be made by mixing ammonium chloride with ammonia solution.

- (i) Explain, with the aid of an equation, how this solution can behave as a buffer when a small amount of a strong acid is added.

.....
 [1]

- (ii) Explain, with the aid of an equation, how this solution can behave as a buffer when a small amount of a strong base is added.

.....
 [1]

- (c) (i) Use the value of K_w to calculate $[H^+]$ in pure water under standard conditions.

Show your working.

$$[H^+] = \dots\dots\dots \text{mol dm}^{-3} \quad [1]$$

- (ii) The pH of pure water at 50 °C is 6.64.

Calculate the numerical value of K_w at 50 °C.

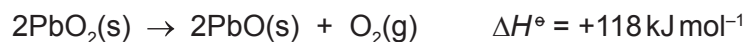
$$K_w = \dots\dots\dots [2]$$

[Total: 8]

4 The table shows some standard entropy data.

substance	standard entropy, S° / JK ⁻¹ mol ⁻¹
PbO ₂ (s)	77
PbO(s)	69
O ₂ (g)	205

Lead(IV) oxide, PbO₂, decomposes to lead(II) oxide, PbO, and oxygen when heated.



(a) Use the data to calculate the value of ΔS° for this reaction.

$$\Delta S^\circ = \dots\dots\dots \text{ JK}^{-1} \text{ mol}^{-1} \quad [2]$$

(b) Use the value of ΔH° and your answer to (a) to calculate the temperature at which this reaction becomes feasible.

$$T = \dots\dots\dots \text{ K} \quad [3]$$

(c) Solid lead(II) oxide can be made by heating lead metal in air.

Predict the **sign** of the standard entropy change of this reaction. Explain your answer.

.....
 [1]

[Total: 6]

- 5 (a) Describe fully what would be seen when magnesium and strontium are heated separately in oxygen.

magnesium

strontium

[2]

- (b) (i) Write an equation for each of the following processes. Include state symbols.

calcium is burned in air

.....

calcium carbonate is heated strongly

.....

[2]

- (ii) Calcium hydroxide is formed when water is added to calcium oxide. Calcium hydroxide and calcium carbonate are both used in agriculture.

Describe the main benefit of adding calcium hydroxide or calcium carbonate to soil.

.....

..... [1]

- (iii) Explain why the Group 2 hydroxides become more soluble down the group.

.....

.....

.....

..... [3]

- (c) Describe the observations, if any, that you would make when:

- a few drops of NaOH(aq) are added to $\text{BaCl}_2\text{(aq)}$

.....

- a few drops of $\text{H}_2\text{SO}_4\text{(aq)}$ are added to $\text{BaCl}_2\text{(aq)}$.

.....

[2]

- (d) Describe and explain how the thermal stability of the Group 2 carbonates varies down the group.

.....

.....

.....

.....

..... [3]

[Total: 13]

- 6 Many copper compounds, such as CuSO_4 and $\text{Cu}(\text{NO}_3)_2$ contain Cu^{2+} ions. Aqueous solutions of this ion contain the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex ion, in which water behaves as a monodentate ligand.

(a) Explain what is meant by the term *monodentate ligand*.

.....
 [1]

(b) Copper(II) sulfate solution, $\text{CuSO}_4(\text{aq})$, undergoes visible changes with certain reagents.

Complete the table below.

reagent added to a solution of $\text{CuSO}_4(\text{aq})$	observations	formula of the copper(II) compound or complex ion that is formed
a few drops of $\text{NH}_3(\text{aq})$		
an excess of $\text{NH}_3(\text{aq})$		
an excess of $\text{NaOH}(\text{aq})$		
an excess of concentrated $\text{HCl}(\text{aq})$		

[4]

(c) When water is added to concentrated aqueous cobalt(II) chloride the colour of the solution changes from blue to pink. Explain this observation.

No equation is needed, but you should include reference to electron movement between orbitals in your answer.

.....

 [3]

- (d) When chlorine gas is bubbled into $\text{FeSO}_4(\text{aq})$ the colour of the solution changes from pale green to yellow.

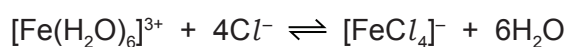
Use data from the *Data Booklet* to explain this observation. Include an equation in your answer.

Reference to electron movement between orbitals is not needed.

.....

 [2]

- (e) If a solution of chloride ions is added to a solution containing $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ an equilibrium is established.



- (i) Write an expression for the stability constant of $[\text{FeCl}_4]^-$, K_{stab} .

$$K_{\text{stab}} =$$

[1]

- (ii) For the above equilibrium the numerical value of $K_{\text{stab}} = 0.080$.

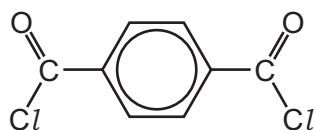
Calculate the concentration of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ in a solution in which the concentration of Cl^- is 2.0 mol dm^{-3} and the concentration of $[\text{FeCl}_4]^-$ is 0.10 mol dm^{-3} .

concentration of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+} = \dots\dots\dots \text{mol dm}^{-3}$ [1]

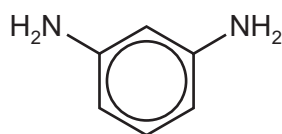
[Total: 12]

- 7 (a) A polymer, **P**, can be made from the monomers benzene-1,4-dioyl chloride and benzene-1,3-diamine.

benzene-1,4-dioyl chloride



benzene-1,3-diamine



- (i) Draw a section of the polymer chain of **P**. Your structure should include two repeat units.

P

[2]

- (ii) Place **one** tick in the table to describe polymer **P** and its method of polymerisation.

type of polymer	type of polymerisation	
	addition	condensation
polyalkene		
polyamide		
polyester		

[1]

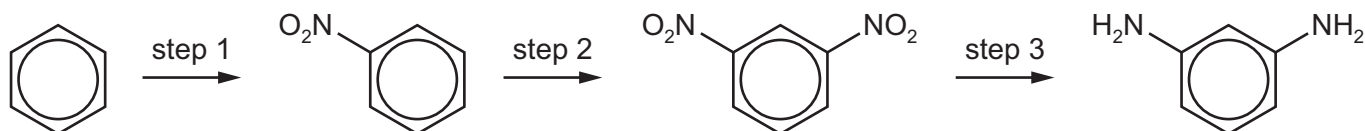
- (iii) State whether or not polymer **P** is biodegradable. Give a reason for your answer.

.....
 [1]

- (iv) State a suitable reagent to produce benzene-1,4-dioyl chloride from benzene-1,4-dicarboxylic acid.

..... [1]

(v) Benzene-1,3-diamine can be made from benzene using the reaction sequence shown.



State the reagents used for steps 1 and 3.

step 1

step 3

[2]

(b) Proteins are natural polymers. A protein is said to have a primary, secondary and tertiary structure.

(i) Describe what is meant by each of these terms.

primary structure

.....

secondary structure

.....

tertiary structure

.....

[3]

(ii) Name the forces or bonds responsible for holding together the primary structure of a protein molecule.

..... [1]

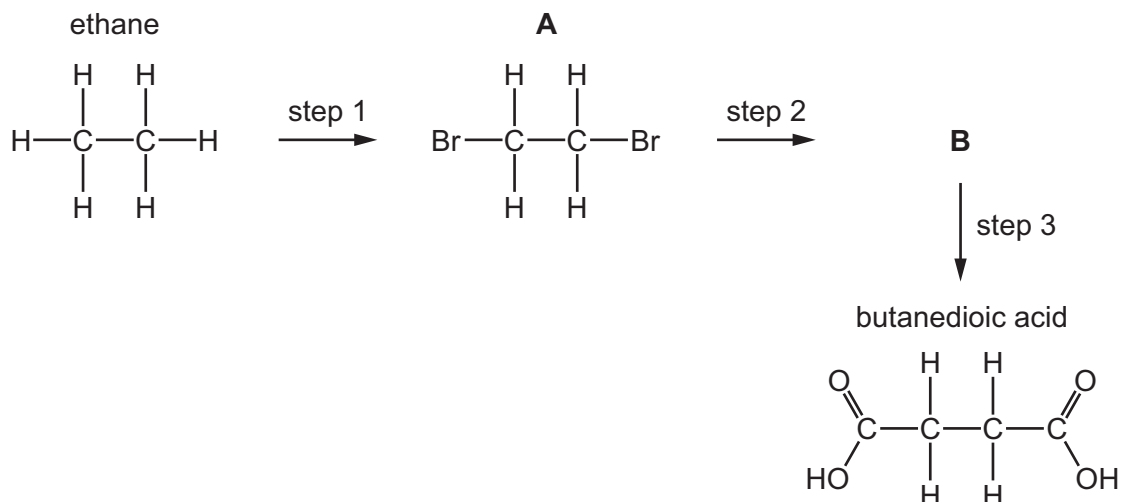
(iii) Name the forces or bonds responsible for the stabilisation of the secondary structure of a protein molecule, and identify the groups of atoms within the protein molecule that are held together by these forces or bonds.

.....

..... [2]

[Total: 13]

- 8 Butanedioic acid can be made in a three-step synthesis using ethane as the starting material.



- (a) Describe the reagents and conditions needed for step 1.

..... [1]

- (b) Name the other product also formed in step 1 which is an isomer of **A**.

..... [1]

- (c) Give the structural formula of **B**.

[1]

- (d) State the reagents and conditions needed for step 2.

..... [2]

- (e) Butanedioic acid cannot be oxidised by a warm, aqueous solution of any commonly used oxidising agents but ethanedioic acid can.

- (i) Identify the oxidising agent that could be used to oxidise ethanedioic acid.

..... [1]

- (ii) State the product(s) of the reaction in (e)(i).

..... [1]

- (f) Compare and explain the relative acidities of hexanoic acid, hexan-1-ol and phenol.

.....

.....

.....

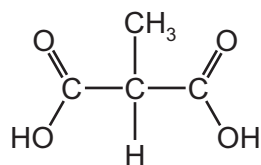
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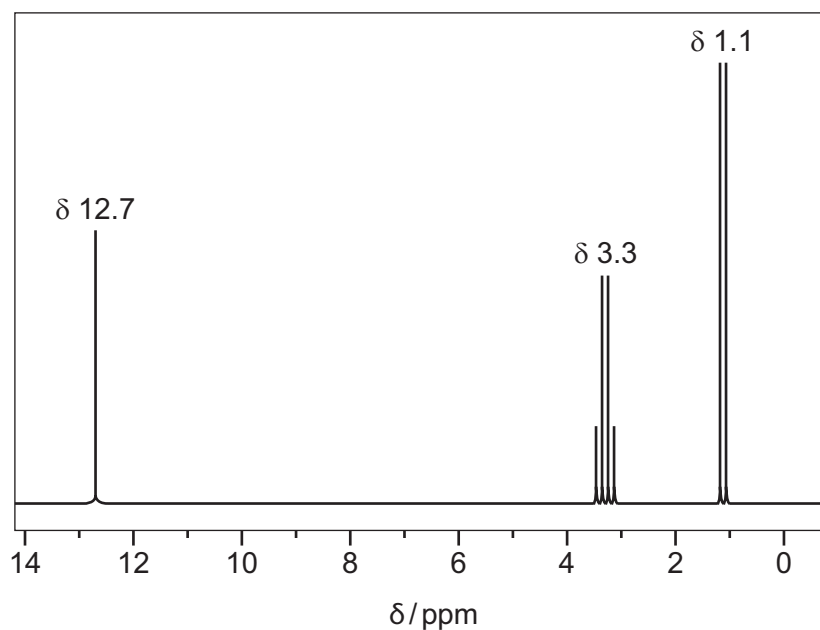
..... [3]

- (g) Methylpropanedioic acid is an isomer of butanededioic acid.

methylpropanedioic acid



The proton NMR spectrum of methylpropanedioic acid in CCl_4 is shown.



- (i) Identify the protons in the methylpropanedioic acid molecule that are responsible for each area of the proton NMR spectrum.

δ 12.7

δ 3.3

δ 1.1

[2]

(ii) Name the splitting pattern shown at δ 3.3 and explain how it arises.

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

The carbon-13 NMR spectra of butanedioic acid, $\text{HO}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{H}$, and methylpropanedioic acid, $\text{HO}_2\text{CCH}(\text{CH}_3)\text{CO}_2\text{H}$ are different.

(iii) State the number of peaks

- in the carbon-13 NMR spectrum of butanedioic acid

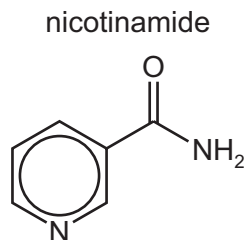
.....

- in the carbon-13 NMR spectrum of methylpropanedioic acid.

..... [1]

[Total: 14]

9 The structure of nicotinamide is shown.



(a) The nitrogen atom in the six-membered ring has one electron in an unhybridised p-orbital. This electron becomes delocalised, becoming part of a single delocalised system of electrons. This delocalised system also includes:

- electrons from the carbon atoms in the six-membered ring
- the two electrons in the π bond of the C=O group
- the two electrons in the lone pair on the nitrogen atom of the amide group.

(i) State the number of delocalised electrons in one nicotinamide molecule.

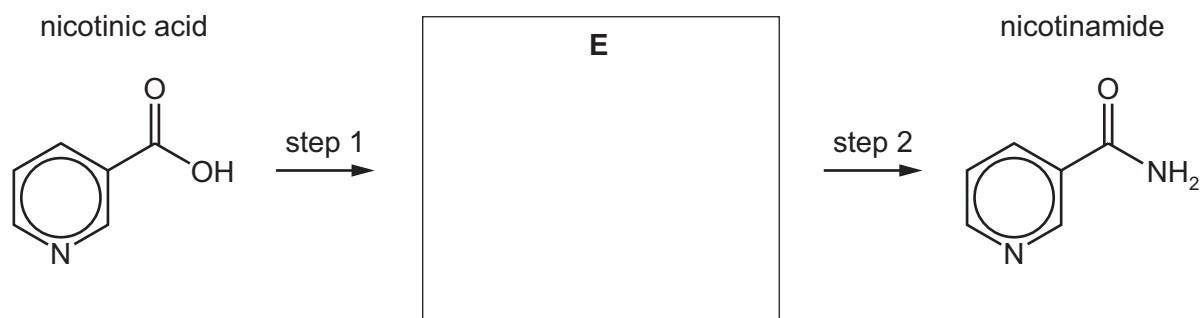
..... [1]

(ii) Predict the H–N–H bond angle in the NH_2 group in nicotinamide.

..... [1]

(b) Nicotinamide can be synthesised from nicotinic acid.

The synthesis involves two steps.



(i) Draw the structural formula of **E** in the box.

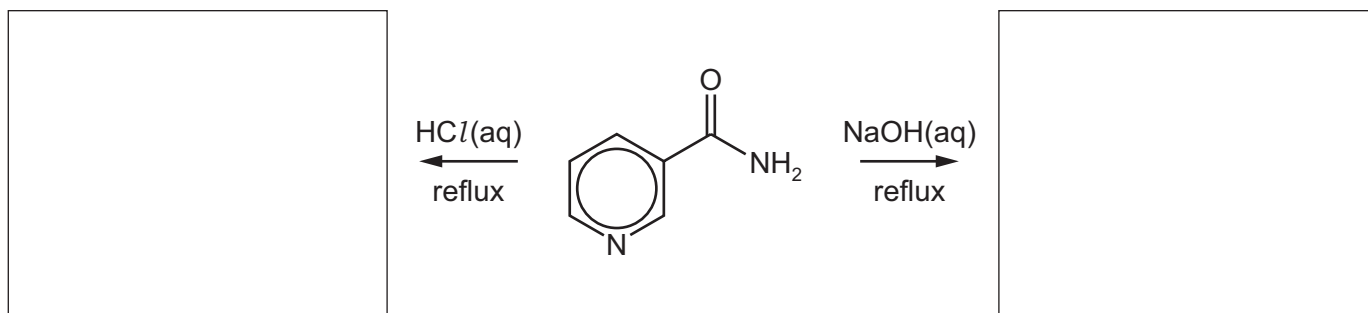
[1]

(ii) Give the name or formula of a suitable reagent for step 2.

..... [1]

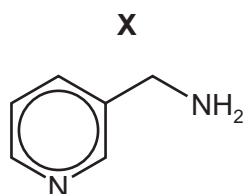
- (c) Nicotinamide reacts separately with aqueous acid and aqueous alkali. The six-membered ring remains unchanged in these reactions.

Complete the reaction scheme below to give the structural formula of the organic product of each reaction.



[2]

- (d) Nicotinamide can be reduced to compound **X**.



- (i) Identify a suitable reducing agent for this reaction.

..... [1]

- (ii) Predict and explain the relative basicities of the NH_2 groups in phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$, nicotinamide and compound **X**.

.....

 [3]

- (e) The height of the M peak in a mass spectrum of nicotinamide is 80.

Calculate the expected height of the M+1 peak.

[2]

[Total: 12]

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CHEMISTRY

9701/43

Paper 4 A Level Structured Questions

October/November 2019

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

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.

A Data Booklet is provided.

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 **20** printed pages.

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

1 An electrochemical cell is constructed using two half-cells.

- an $\text{Sn}^{4+}/\text{Sn}^{2+}$ half-cell
- an Al^{3+}/Al half-cell

(a) State the material used for the electrode in each half-cell.

- $\text{Sn}^{4+}/\text{Sn}^{2+}$ half-cell
- Al^{3+}/Al half-cell

[1]

(b) The cell is operated at 298 K.

The Al^{3+}/Al half-cell has standard concentrations.

The $\text{Sn}^{4+}/\text{Sn}^{2+}$ half-cell has $[\text{Sn}^{4+}] = 0.300 \text{ mol dm}^{-3}$ and $[\text{Sn}^{2+}] = 0.150 \text{ mol dm}^{-3}$.

(i) Use the Nernst equation to calculate the electrode potential, E , of the $\text{Sn}^{4+}/\text{Sn}^{2+}$ half-cell under these conditions.

$E = \dots\dots\dots \text{ V [2]}$

(ii) Calculate the E_{cell} under these conditions.

$E_{\text{cell}} = \dots\dots\dots \text{ V [1]}$

(iii) Write an equation for the overall cell reaction that occurs.

..... [2]

- (c) Aluminium is produced industrially by electrolysis of a melt containing large amounts of Al^{3+} ions.

Calculate the mass of aluminium that is obtained when a current of 300 000 A is passed for 24 hours. Give your answer to **three** significant figures.

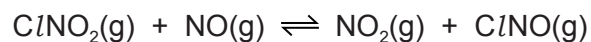
mass = ... units = ... [4]

- (d) Explain why chromium metal cannot be obtained by the electrolysis of dilute aqueous chromium(II) sulfate. Your answer should include data from the *Data Booklet*.

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

[Total: 12]

- 2 When ClNO_2 reacts with NO an equilibrium is established.



In each ClNO_2 molecule the nitrogen atom is bonded to the chlorine atom and bonded to each of the oxygen atoms separately.

- (a) Draw a 'dot-and-cross' diagram for the ClNO_2 molecule.

[2]

- (b) The reaction between ClNO_2 and NO is first order with respect to each reactant.

- (i) Write the rate equation for this reaction.

rate = ... [1]

- (ii) Deduce the units of the rate constant, k , when the concentrations of both gases are measured in mol dm^{-3} and the rate is measured in $\text{mol dm}^{-3} \text{s}^{-1}$.

..... [1]

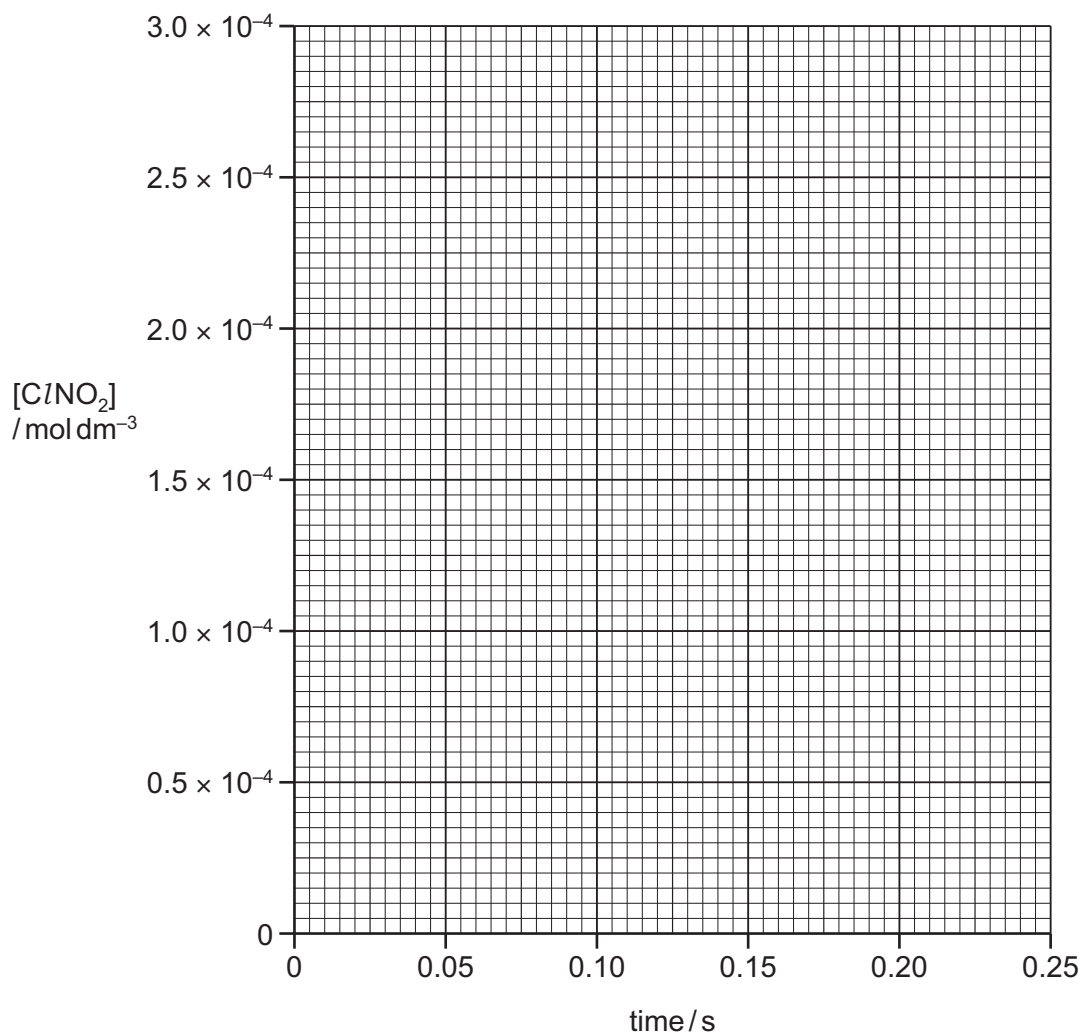
- (iii) State and explain whether or not the reaction **could** take place in a single step.

.....

 [1]

(c) An experiment is carried out in which the initial $[C\ell NO_2]$ is $2.0 \times 10^{-4} \text{ mol dm}^{-3}$. A large excess of NO is used. The initial rate of reaction is $1.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$. The rate of the reaction is assumed to be constant for the first 0.20 seconds.

(i) Draw a graph on the grid to show how the concentration of $C\ell NO_2$ varies for the first 0.20 seconds.



[2]

(ii) Deduce the concentration of the NO_2 product at 0.20 seconds.

..... [1]

(iii) After 20 seconds the concentration of $C\ell NO_2$ remains constant.

Explain this observation.

..... [1]

[Total: 9]

3 (a) Explain what is meant by the term *entropy of a system*.

.....
 [1]

(b) State and explain whether the entropy change of each of the following processes is positive or negative. Do not consider the entropy change of the surroundings.

- liquid water at 80 °C is cooled to 60 °C

The entropy change is because

.....

- solid calcium chloride is added to water and the mixture is stirred

The entropy change is because

.....

- the change corresponding to the lattice energy of calcium chloride, $\Delta H_{\text{latt}} \text{CaCl}_2(\text{s})$, takes place

The entropy change is because

.....

[3]

(c) The reaction $\text{ZnCO}_3(\text{s}) \rightarrow \text{ZnO}(\text{s}) + \text{CO}_2(\text{g})$ is not spontaneous at room temperature.

(i) Give the full name for the term ΔG° .

..... [1]

(ii) Describe how the temperature at which the reaction becomes spontaneous can be calculated. Include an equation in your answer.

equation

.....

.....

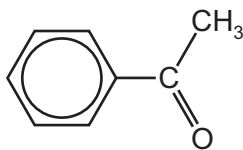
.....

[2]

[Total: 7]

4 Phenylethanone is an important chemical with many uses.

phenylethanone



(a) Phenylethanone can be synthesised using benzene as one of the starting materials.

Identify the other reagents used and describe any essential reaction conditions.

.....
 [2]

(b) Phenylethanone is treated separately with three reagents.

Complete the table, for each reagent, to give the structural formula of one organic product formed and the name of the mechanism involved. If there is no reaction you should write 'no reaction'.

reagent	organic product	name of mechanism
chlorine gas at 10 °C in the presence of ultra-violet light		
a mixture of concentrated nitric and sulfuric acids at 50 °C		
bromine water		

[5]

(c) Phenylethanone reacts with HCN in the presence of a small amount of NaCN.

(i) Name the mechanism of this reaction.

..... [1]

(ii) Draw the mechanism of this reaction below. Include all relevant charges, dipoles, lone pairs and curly arrows. Your mechanism should show the catalytic role of CN^- ions.

phenylethanone

intermediate

product



[4]

(d) Phenylethanone can be used as a starting material to make phenylethene in a two-step synthesis.



(i) Draw the structure of compound **D** in the box.

[1]

(ii) Identify a suitable reagent for step 1.

..... [1]

(iii) Identify a suitable reagent for step 2.

..... [1]

(iv) State the number of peaks in the C-13 NMR spectrum of **phenylethene**.

..... [1]

(v) Suggest C-13 chemical shift ranges expected for the different types of carbon environment in **phenylethanone**.

.....

.....

..... [2]

[Total: 18]

5 Silver sulfide, Ag_2S , is very insoluble in water.

(a) (i) Write an expression for the solubility product, K_{sp} , of $\text{Ag}_2\text{S}(\text{s})$.

$$K_{\text{sp}} =$$

[1]

(ii) The solubility of $\text{Ag}_2\text{S}(\text{s})$ in water at 298 K is $1.16 \times 10^{-17} \text{ mol dm}^{-3}$.

Calculate the numerical value of the solubility product, K_{sp} , of $\text{Ag}_2\text{S}(\text{s})$ at 298 K.

$$K_{\text{sp}} = \dots\dots\dots [2]$$

(iii) Calculate the minimum volume of water needed to dissolve 1.00 g of $\text{Ag}_2\text{S}(\text{s})$ under standard conditions.

$$\text{volume} = \dots\dots\dots \text{ dm}^3 [2]$$

(b) Bromic(I) acid, HOBr(aq) , is a weak acid. Its K_a is $2.0 \times 10^{-9} \text{ mol dm}^{-3}$.

(i) Calculate the pH of $0.20 \text{ mol dm}^{-3} \text{ HOBr(aq)}$.

pH = ... [2]

(ii) 5.0 cm^3 of 0.20 mol dm^{-3} potassium hydroxide, KOH , are added to 20.0 cm^3 of $0.20 \text{ mol dm}^{-3} \text{ HOBr(aq)}$.

Calculate the pH of the buffer solution produced.

pH = ... [2]

[Total: 9]

6 The elements in Group 2 include magnesium, calcium, strontium and barium.

- (a) (i)** Write an equation for the change representing the first ionisation energy of magnesium. Include state symbols.

..... [1]

- (ii)** Write an equation for the reaction of strontium with cold water. Include state symbols.

..... [1]

- (iii)** Describe and explain the trend in reactivity observed in the reactions of these Group 2 metals with cold water.

.....

.....

..... [1]

- (b)** The Group 2 metal nitrates decompose when heated.

- (i)** Describe fully what is seen when anhydrous calcium nitrate is heated in a test-tube and decomposition occurs.

.....

..... [1]

- (ii)** Write an equation for the decomposition of calcium nitrate.

..... [1]

- (iii)** Describe and explain the variation in thermal stability of the Group 2 metal nitrates down the group.

.....

.....

..... [3]

- (c) Describe and explain the variation in the solubility of the Group 2 metal sulfates down the group.

.....

.....

.....

.....

.....

.....

..... [4]

[Total: 12]

7 Manganese, chromium and ruthenium are all transition elements.

(a) Explain what is meant by a *transition element*.

.....

 [1]

(b) MnO_4^- (aq) and $\text{Cr}_2\text{O}_7^{2-}$ (aq) act as oxidising agents in acidic solution. Both these oxidising agents will oxidise a solution of Sn^{2+} to give a solution of Sn^{4+} . Solutions containing Sn^{2+} and solutions containing Sn^{4+} are colourless.

(i) Describe the colour change seen when an excess of Sn^{2+} (aq) is added separately to

- dilute acidified MnO_4^- (aq)

from to

- dilute acidified $\text{Cr}_2\text{O}_7^{2-}$ (aq).

from to [1]

(ii) Write an equation for the reaction between Sn^{2+} (aq) and acidified $\text{Cr}_2\text{O}_7^{2-}$ (aq).

..... [1]

(c) Ruthenium, Ru, forms complex ions. In one such complex ion, **X**, the ruthenium ion has a co-ordination number of six. Each complex ion **X** contains one Ru^{2+} ion, one Cl^- ion, one SO_2 molecule and the remaining ligands are NH_3 molecules.

The SO_2 molecule acts as a monodentate ligand and is attached to the Ru^{2+} ion via the sulfur atom. **X** exists in two isomeric forms.

(i) State what is meant by a *co-ordination number of six*.

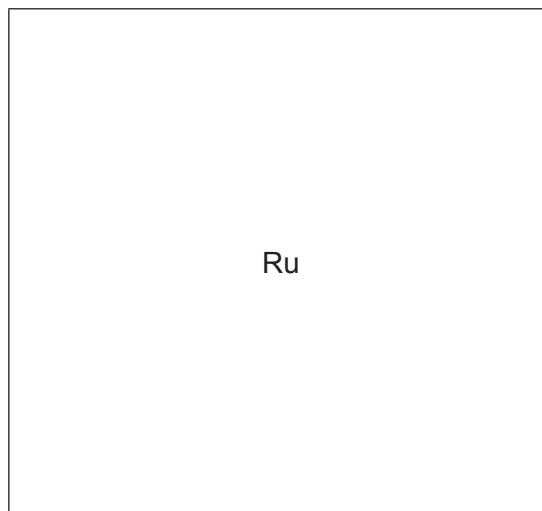
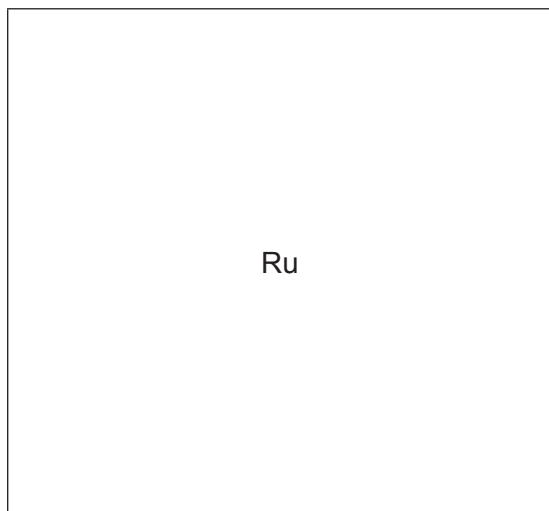
..... [1]

(ii) State the formula of **X**. Include its charge.

..... [1]

(iii) Draw the two isomeric forms of **X** in the boxes below. Your diagrams should show

- the three-dimensional shapes of the two isomers
- how each ligand is attached to the central ruthenium ion.



[3]

(iv) Suggest the type of isomerism shown by **X**.

..... [1]

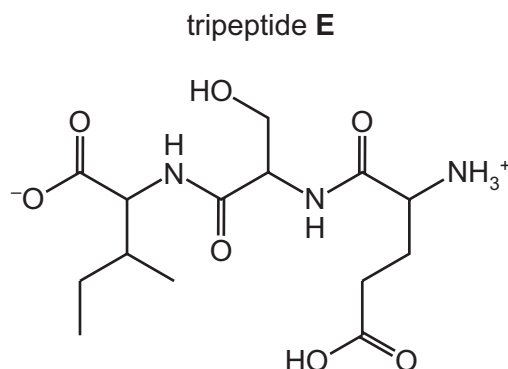
(v) Explain the origin of colour in a transition element complex such as **X**.

.....

 [3]

[Total: 12]

- 8 Proteins are natural polymers. When one particular protein is partially hydrolysed the product mixture includes tripeptide **E**.



- (a) (i) Describe the conditions that could be used to hydrolyse **E** to produce a mixture of three amino acids.

..... [1]

- (ii) Draw the structures of the three amino acids produced by this hydrolysis reaction.

The three amino acids should be shown in the correct form for the conditions you have chosen in (a)(i).

--	--	--

[2]

- (b) If a pure sample of **E** is obtained in aqueous solution, several different types of intermolecular forces are possible between pairs of **E** molecules.

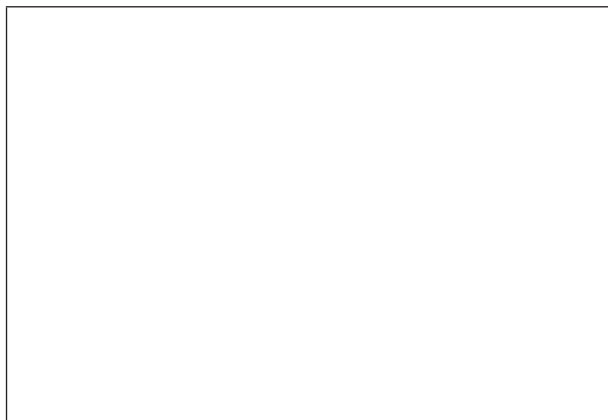
Name three different types of intermolecular force that exist between pairs of **E** molecules, stating the groups on the molecules where the forces are acting.

type of force/bond	pair of groups responsible

[3]

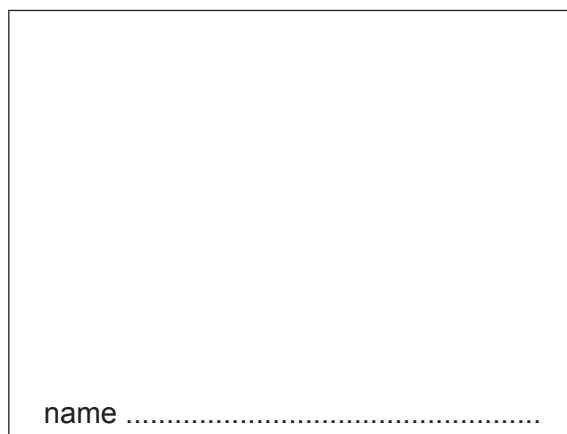
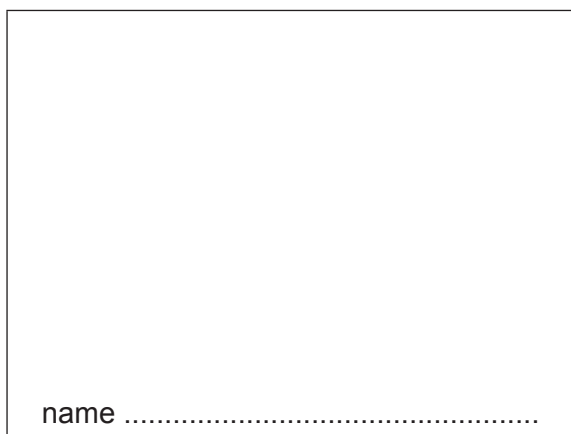
(c) Polyesters and polyamides are two important types of condensation polymer.

- (i) Draw the structure of a compound that can polymerise to produce a polyamide, without the need for a second monomer.



[1]

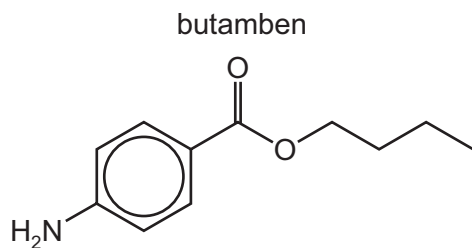
- (ii) Draw the structures of two different compounds that can polymerise together to produce a polyester with **four** carbon atoms per repeat unit. Name the two compounds.



[4]

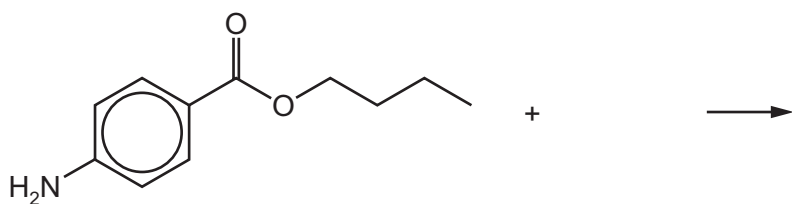
[Total: 11]

9 The structure of butamben is shown.



(a) Butamben can act as a base.

(i) Complete the equation for a reaction in which butamben acts as a base.



[1]

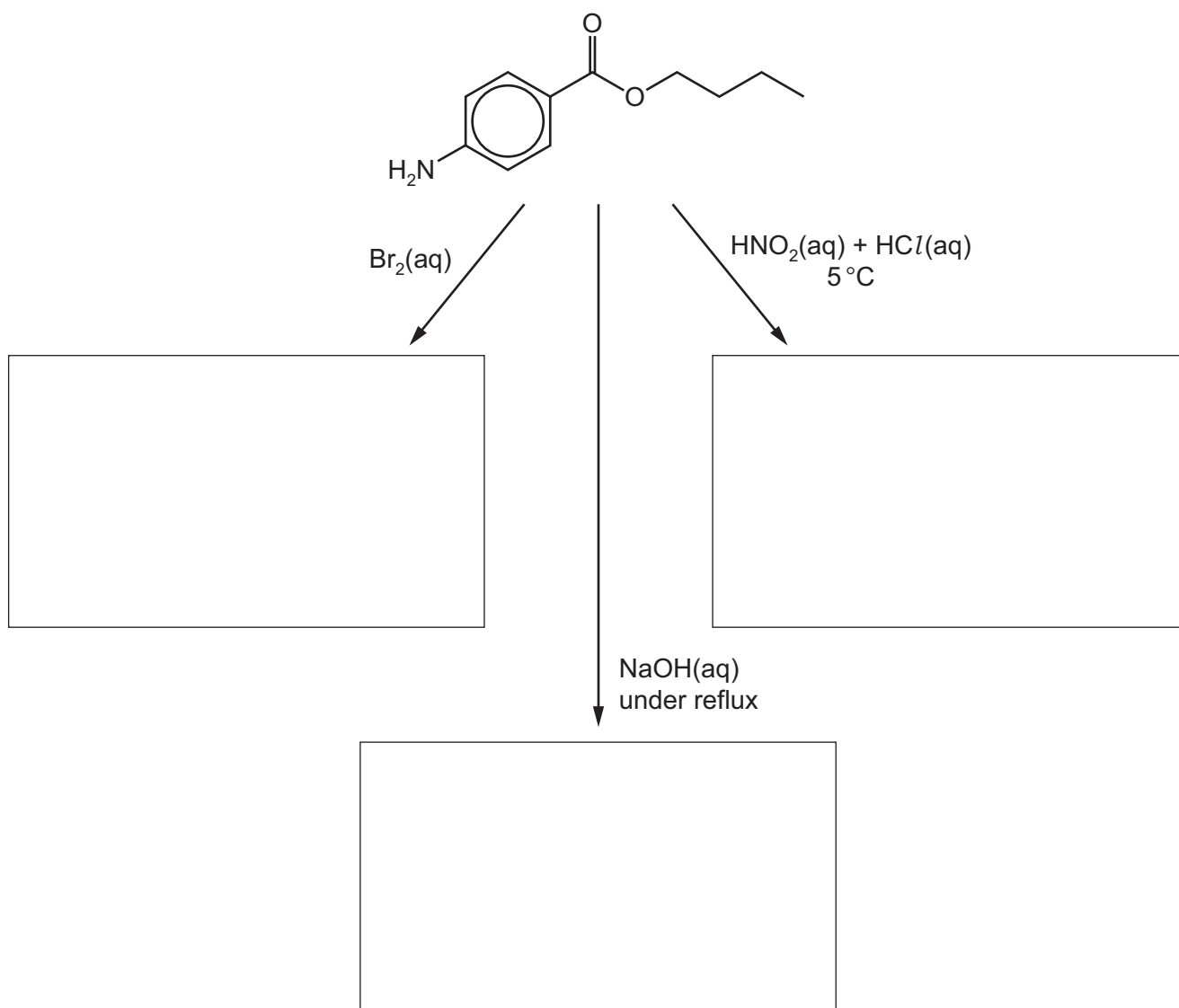
(ii) Predict whether butamben is a stronger or weaker base than ammonia. Give a reason for your answer.

.....

.....

..... [1]

- (b) Complete the reaction scheme below to show the structural formulae of the products formed when butamben is treated separately with the stated reagent.



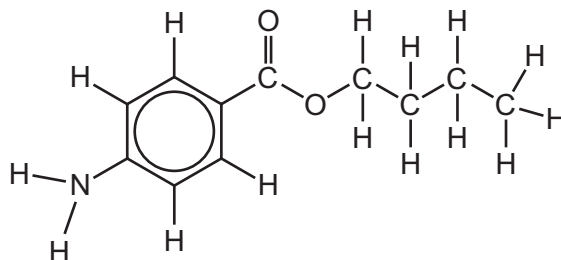
[3]

- (c) The proton NMR spectrum of butamben in CDCl_3 contains one or more peaks that show a triplet splitting pattern.

(i) State the number of peaks in the spectrum that show a triplet splitting pattern.

..... [1]

(ii) On the diagram of butamben below, circle the protons responsible for the peak or peaks you identified in (c)(i).



[1]

(iii) Describe and explain how the proton NMR spectrum of butamben in D_2O would differ from the proton NMR spectrum of butamben in CDCl_3 .

.....

..... [2]

- (d) The mass spectrum of butamben includes peaks at m/e 92 and 57.

Identify the fragments responsible for these peaks.

m/e 92 = ...

m/e 57 = ...

[1]

[Total: 10]

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