

CANDIDATE
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CHEMISTRY

9701/41

Paper 4 A Level Structured Questions

May/June 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 (a) Aqueous solutions of copper(II) salts contain the blue-coloured $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex ion. Separate portions of this blue solution react with aqueous sodium hydroxide and with concentrated hydrochloric acid.

Give the following information for each of these reactions.

- reaction with aqueous sodium hydroxide

ionic equation

type of reaction

colour and state of the copper-containing product

- reaction with concentrated hydrochloric acid

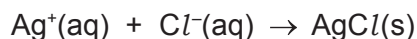
ionic equation

type of reaction

colour and state of the copper-containing product

[6]

- (b) Chloride ions can be identified using aqueous silver nitrate, $\text{AgNO}_3(\text{aq})$.



0.303 g of a chloride of sulfur is completely hydrolysed with water. All the chlorine atoms present in the chloride of sulfur are converted into chloride ions. The solution is diluted to 100.0 cm^3 . A 25.00 cm^3 sample of this solution is titrated with $0.0500 \text{ mol dm}^{-3} \text{ AgNO}_3(\text{aq})$. The titration requires 22.40 cm^3 of $0.0500 \text{ mol dm}^{-3} \text{ AgNO}_3(\text{aq})$.

Calculate the empirical formula of the chloride of sulfur. Show all your working.

empirical formula of chloride of sulfur = ... [3]

[Total: 9]

- 2 (a) Group 2 nitrates decompose when heated.

Write an equation for the decomposition of strontium nitrate.

..... [1]

- (b) Describe and explain how the thermal stability of Group 2 nitrates changes with increasing atomic number.

.....

 [3]

- (c) The variation in the thermal stability of Group 2 amides is similar to that of Group 2 nitrates.

- (i) Suggest whether calcium amide, $\text{Ca}(\text{NH}_2)_2$, will decompose more or less readily than barium amide, $\text{Ba}(\text{NH}_2)_2$. Explain your answer.

.....
 [1]

- (ii) $\text{Ba}(\text{NH}_2)_2$ decomposes when heated to form barium nitride, Ba_3N_2 , and ammonia as the only products.

Write an equation for this reaction.

..... [1]

- (d) $\text{Ba}(\text{NH}_2)_2$ contains the NH_2^- ion.

Predict the bond angle of NH_2^- . Explain your answer using the qualitative model of electron-pair repulsion.

bond angle

explanation

 [3]

[Total: 9]

3 Chlorate(V) ions are powerful oxidising agents.

- (a)** The reduction of chlorate(V) ions, ClO_3^- , with SO_2 forms chlorine dioxide, ClO_2 , and sulfate ions, SO_4^{2-} , as the only products.

Construct an equation for this reaction.

..... [1]

- (b) (i)** Chlorine dioxide, ClO_2 , disproportionates with hydroxide ions, $\text{OH}^-(\text{aq})$, to form a mixture of ClO_2^- and ClO_3^- ions.



Explain, using this reaction as an example, what is meant by *disproportionation*.

..... [1]

- (ii)** Deduce the ionic half-equations for the reaction in **(b)(i)**.

..... [2]

- (c)** A lithium-iodine electrochemical cell can be used to generate electricity for a heart pacemaker. The cell consists of a lithium electrode and an inert electrode immersed in body fluids. When current flows lithium is oxidised and iodine is reduced.

- (i)** Use the *Data Booklet* to write half-equations for the reactions taking place at the two electrodes. Hence write the overall equation for when a current flows.

-
-

overall equation [2]

- (ii)** Use the *Data Booklet* to calculate the $E_{\text{cell}}^\ominus$ for this cell.

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

- (iii) A current of $2.5 \times 10^{-5} \text{ A}$ is drawn from this cell.

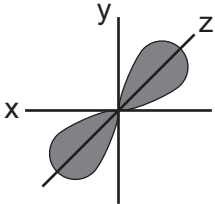
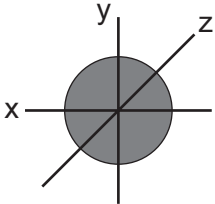
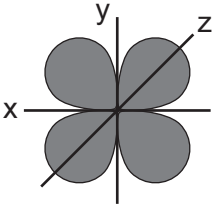
Calculate the time taken for 0.10 g of lithium electrode to be used up. Assume the current remains constant throughout this period.

time = ... s [3]

[Total: 10]

- 4 (a) Sketches of the shapes of some atomic orbitals are shown.

Identify the type of orbital, s, p, or d.

shape of orbital			
type of orbital			

[1]

- (b) Cadmium forms the two ions, Cd_2^{2+} and Cd^{2+} . The electronic configuration of cadmium in these ions is shown.

- $[\text{Kr}] 4d^{10}5s^1$
- $[\text{Kr}] 4d^{10}$

Use this information to explain why cadmium is **not** a transition element.

.....
 [1]

- (c) Methylamine, CH_3NH_2 , is a monodentate ligand.

- (i) State what is meant by the term *monodentate* in this context.

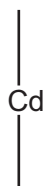
.....
 [1]

In the presence of aqueous methylamine, $[\text{Cd}(\text{H}_2\text{O})_6]^{2+}$ reacts to form a mixture of two isomeric octahedral complexes.



(ii) Complete the three-dimensional diagrams to show the isomers of $[\text{Cd}(\text{CH}_3\text{NH}_2)_4(\text{H}_2\text{O})_2]^{2+}$.

Use L to represent CH_3NH_2 in your diagrams.



[2]

(d) (i) State what is meant by the term *stability constant*.

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

(ii) Complete the table by placing **one** tick (✓) in each row to suggest how increasing temperature will affect K_{stab} and the equilibrium concentration of the cadmium complex, $[\text{Cd}(\text{CH}_3\text{NH}_2)_4(\text{H}_2\text{O})_2]^{2+}$, for equilibrium 1. Explain your answer.

	decreases	no change	increases
K_{stab}			
$[\text{Cd}(\text{CH}_3\text{NH}_2)_4(\text{H}_2\text{O})_2]^{2+}$			

explanation
..... [2]

EDTA⁴⁻ is a polydentate ligand. When a solution of EDTA⁴⁻ is added to [Cd(H₂O)₆]²⁺ a new complex [CdEDTA]²⁻ is formed.

The values for the stability constants for two Cd²⁺ complexes are shown.

	K_{stab}
$[\text{Cd}(\text{CH}_3\text{NH}_2)_4(\text{H}_2\text{O})_2]^{2+}$	4.0×10^6
$[\text{CdEDTA}]^{2-}$	4.0×10^{16}

- (iii) A solution containing equal numbers of moles of CH₃NH₂ and EDTA is added to [Cd(H₂O)₆]²⁺.

Predict which complex is formed in the larger amount. Explain your answer.

.....
 [1]

- (e) Methylamine is a Brønsted-Lowry base.

Write an equation showing how methylamine dissolves in water to give an alkaline solution.

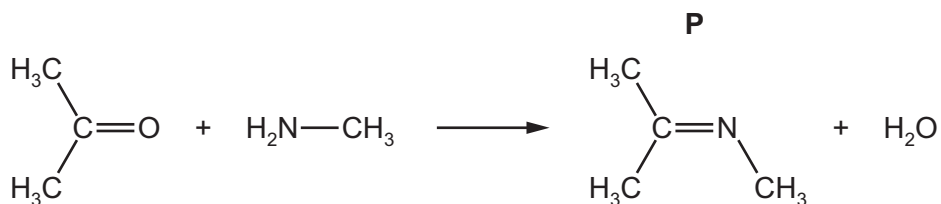
..... [1]

- (f) Methylamine is a useful reagent in organic chemistry.

- (i) Write an equation for the reaction of ethanoyl chloride with methylamine.

..... [2]

- (ii) Methylamine also reacts with propanone to form compound **P** as shown.



Deduce the *type of reaction* shown here.

..... [1]

[Total: 13]

- 5 (a) Chlorate(I) ions undergo the following reaction under aqueous conditions.



A series of experiments was carried out at different concentrations of ClO^- and NH_3 .

The table shows the results obtained.

experiment	$[\text{ClO}^-]$ / mol dm^{-3}	$[\text{NH}_3]$ / mol dm^{-3}	initial rate / $\text{mol dm}^{-3} \text{s}^{-1}$
1	0.200	0.100	0.256
2	0.400	0.200	2.05
3	0.400	0.400	8.20

- (i) Use the data in the table to determine the order with respect to each reactant, ClO^- and NH_3 .

Show your reasoning.

.....

.....

.....

.....

.....

..... [2]

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

rate = ... [1]

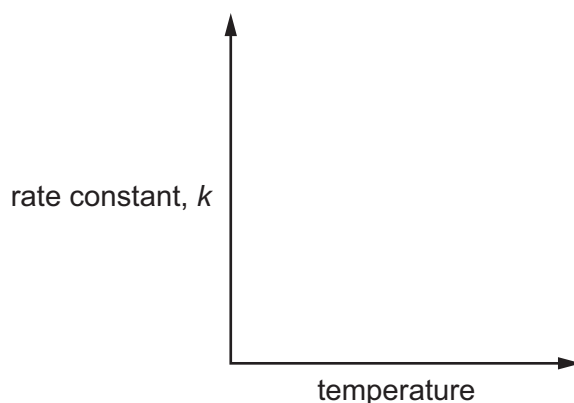
- (iii) Use the results of experiment 1 to calculate the rate constant, k , for this reaction. Include the units of k .

k = ...

units = ...

[2]

- (iv) On the axes sketch a graph to show how the value of k changes as temperature is increased.



[1]

- (b) In another experiment, the reaction between chlorate(I) ions and iodide ions in aqueous alkali was investigated.

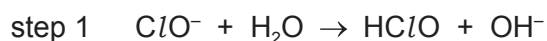
A solution of iodide ions in aqueous alkali was added to a large excess of chlorate(I) ions and $[I^-]$ was measured at regular intervals.

- (i) Describe how the results of this experiment can be used to confirm that the reaction is first-order with respect to $[I^-]$.

.....

 [2]

A three-step mechanism for this reaction is shown.



- (ii) Use this mechanism to deduce the overall equation for this reaction.

..... [1]

- (iii) Identify a step that involves a redox reaction. Explain your answer.

.....
 [1]

[Total: 10]

- 6 (a) Complete the table by placing **one** tick (✓) in each row to indicate the sign of each type of energy change under standard conditions.

energy change	always positive	always negative	either negative or positive
bond energy			
enthalpy change of formation			

[1]

- (b) Explain what is meant by the term *enthalpy change of atomisation*.

.....
 [1]

- (c) The overall reaction for the atomisation of liquid bromine molecules, Br₂(l), is shown.



This happens via a two-step process.

- Construct a **labelled** energy cycle to represent this atomisation process, including state symbols.
- Use your cycle and relevant data from the *Data Booklet* to calculate the enthalpy change of vaporisation of Br₂(l), $\Delta H_{\text{vap}}^\ominus$.
 The enthalpy change of atomisation of bromine, $\Delta H_{\text{at}}^\ominus = +112 \text{ kJ mol}^{-1}$.

$$\Delta H_{\text{vap}}^\ominus = \dots\dots\dots \text{kJ mol}^{-1} \quad [3]$$

- (d) Suggest how the $\Delta H_{\text{vap}}^\ominus$ of iodine, I₂(l), would compare to that of bromine, Br₂(l). Explain your answer.

.....
 [1]

- (e) (i) Explain what is meant by the term *enthalpy change of hydration*.

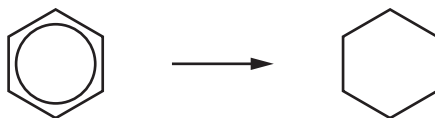
.....
..... [1]

- (ii) Suggest why the enthalpy change of hydration of $\text{Br}^-(\text{g})$ is **more** exothermic than that of $\text{I}^-(\text{g})$.

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

[Total: 9]

- 7 (a) Benzene can be converted into cyclohexane.



- (i) For this reaction name the type of reaction and identify the reagent and conditions needed.

type of reaction

reagent and conditions

[2]

- (ii) State the bond angles in benzene and cyclohexane.

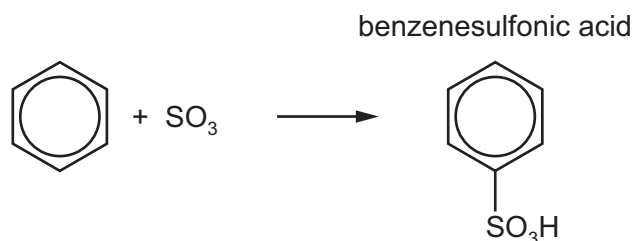
bond angle in benzene bond angle in cyclohexane

Explain your answers.

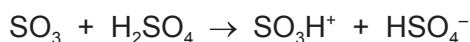
.....

[2]

- (b) When benzene reacts with SO_3 , benzenesulfonic acid is produced.



The mechanism of this reaction is similar to that of the nitration of benzene. Concentrated H_2SO_4 is used in an initial step to generate the SO_3H^+ electrophile as shown.



- (i) Draw a mechanism for the reaction of benzene with SO_3H^+ ions. Include all necessary curly arrows and charges.

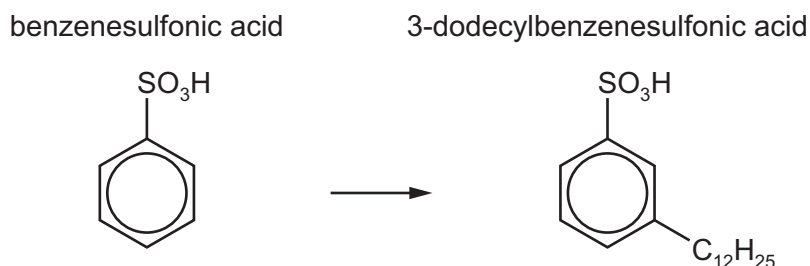


[3]

- (ii) Write an equation to show how the H_2SO_4 catalyst is reformed.

..... [1]

- (c) 3-dodecylbenzenesulfonic acid can be prepared from benzenesulfonic acid.



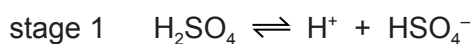
Suggest the reagents and conditions and name the mechanism for this reaction.

reagents and conditions

mechanism

[2]

- (d) When concentrated sulfuric acid is added to water, dissociation takes place in two stages.



K_{a2} is the acid dissociation constant for stage 2.

- (i) Write the expression for the acid dissociation constant K_{a2} .

$$K_{a2} =$$

[1]

- (ii) H_2SO_4 is considered a strong acid whereas HSO_4^- is considered a weak acid.

Suggest how the magnitude of the acid dissociation constant for stage 1 compares to K_{a2} .

..... [1]

- (e) Benzoic acid, $\text{C}_6\text{H}_5\text{CO}_2\text{H}$, is a weak acid. A solution of $0.0250 \text{ mol dm}^{-3}$ benzoic acid has a pH of 2.90.

Calculate the K_a of benzoic acid.

$$K_a = \dots\dots\dots \text{mol dm}^{-3}$$

[2]

[Total: 14]

- 8 (a) The mass spectrum of compound **X**, $\text{C}_5\text{H}_{10}\text{O}_2$, is recorded.

The peak heights of the M and M+1 peaks are 22.65 and 1.25 respectively.

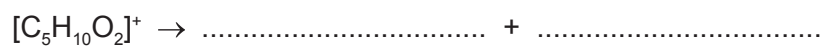
- (i) Use these data to show that there are five carbon atoms present in one molecule of **X**.

Show your working.

[1]

- (ii) The mass spectrum has a peak at $m/e = 57$.

Complete the equation to show the fragmentation of **X** to produce this peak.



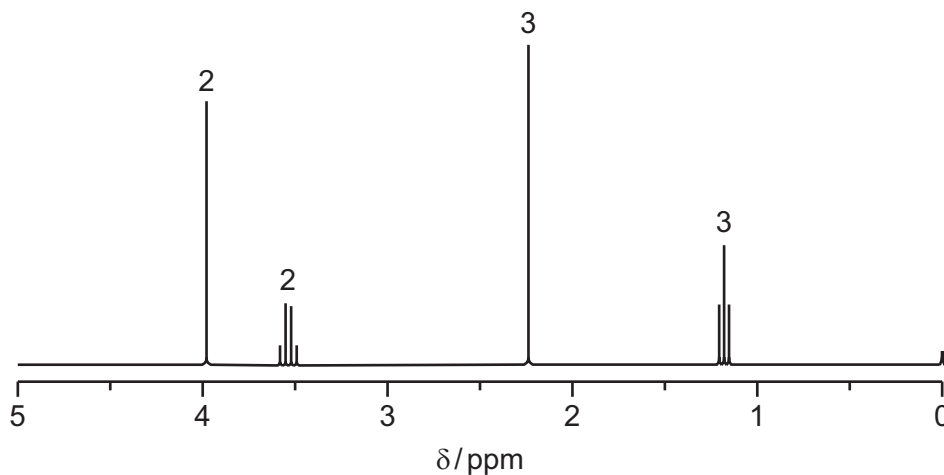
[2]

- (b) State the use of TMS and CDCl_3 in NMR spectroscopy.

- TMS
- CDCl_3

[1]

(c) The proton NMR spectrum of compound **X**, $\text{C}_5\text{H}_{10}\text{O}_2$, is shown.



(i) By considering both the relative peak areas and their δ values, use the *Data Booklet* to

- deduce the part of the molecule that produces the peak at $\delta 2.2$,
.....
- deduce the part of the molecule that produces the peaks at $\delta 1.2$ and $\delta 3.5$,
.....
- deduce the part of the molecule that produces the peak at $\delta 4.0$.
.....

[3]

(ii) When reacted with aqueous alkaline iodine, **X** produces a yellow precipitate.

Use this information and your answers to (c)(i) to suggest a structure for **X**.

[1]

(d) Compound **W** is an ester with the molecular formula $C_5H_{10}O_2$.

The proton NMR spectrum of **W** contains only **two** peaks.

The relative areas of these two peaks are in the ratio 9 : 1.

Suggest a structure for this ester, **W**.

[1]

(e) Compound **V** is a carboxylic acid which contains a chiral centre. It also has the molecular formula $C_5H_{10}O_2$.

(i) Explain what is meant by the term *chiral centre*.

.....

..... [1]

(ii) Suggest a structure for **V**.

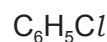
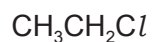
[1]

[Total: 11]

- 9 (a) Organochlorine compounds can undergo hydrolysis.



State and explain the relative rates of hydrolysis of the following compounds.

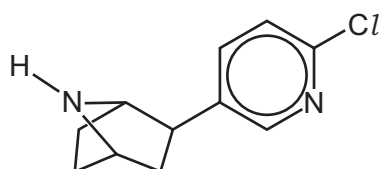


.....

 [3]

- (b) Epibatidine is a naturally occurring organochlorine compound.

epibatidine



- (i) Epibatidine is a weak base.

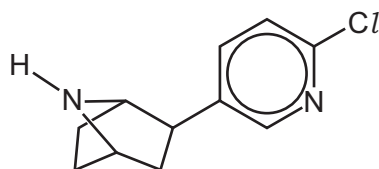
State what is meant by the term *weak base*.

.....
 [1]

A molecule of epibatidine contains two nitrogen atoms, both of which can act as a base.

- (ii) Epibatidine reacts with HCl(aq) .

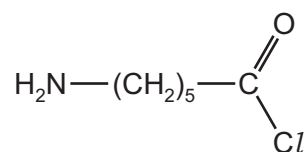
Complete the structure to suggest the product formed in this reaction.



[1]

- (c) Polyamides, such as nylon-6, can be prepared from a monomer that contains both an amine and an acyl chloride functional group.

nylon-6 monomer



- (i) When the nylon-6 monomer is hydrolysed, bonds are broken and formed.

By considering the two steps in the mechanism of the reaction, complete the table by placing **one** tick (✓) in each row to indicate the types of bonds broken and formed during the mechanism.

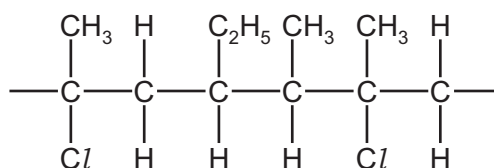
	σ bonds only	π bonds only	both σ and π bonds
bonds broken			
bonds formed			

[1]

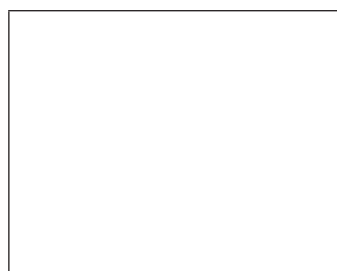
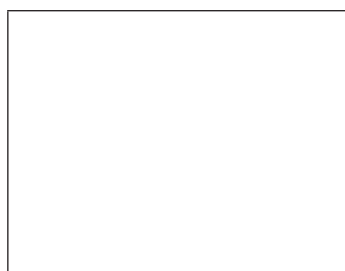
- (ii) Draw **two** repeat units of nylon-6. The amide bond should be shown fully displayed.

[2]

- (d) An addition polymer made from two different alkene monomers is called a co-polymer. A section of a polyalkene co-polymer is shown.



Draw the structure of the **two** alkene monomers which produce this co-polymer.

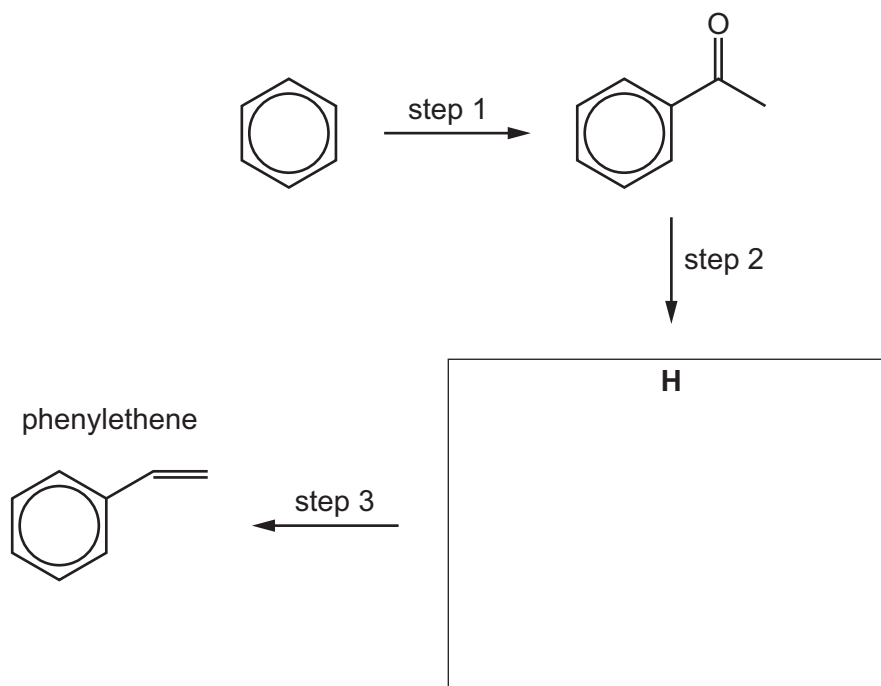


[2]

- (e) Explain why polyamides normally biodegrade more readily than polyalkenes.

.....
 [1]

- (f) The alkene phenylethene can be prepared from benzene in three steps.



- (i) Deduce the identity of compound **H** and draw its structure in the box. [1]
- (ii) Suggest reagents and conditions for each of the steps 1–3.

step 1
 step 2
 step 3 [3]

[Total: 15]

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CHEMISTRY

9701/42

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This document consists of **23** printed pages and **1** blank page.

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

- 1 (a) (i) Complete the electronic configuration of the copper(II) ion.

$1s^2 2s^2 2p^6$ [1]

- (ii) State the colour of the solutions containing the following ions.

- $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$
- $[\text{CuCl}_4]^{2-}(\text{aq})$ [1]

- (iii) Octahedral complexes of Cu^{2+} with different ligands can have different colours.

Explain why.

.....

 [2]

- (b) Copper(I) and silver(I) salts are colourless.

Suggest why.

.....

 [2]

(c) Consider the following two equilibria and associated data values at 298 K.



The equilibrium constant for equilibrium 1 is the solubility product, K_{sp} , of AgBr(s). The equilibrium constant for equilibrium 2 is the stability constant, K_{stab} , for the formation of $[\text{Ag}(\text{NH}_3)_2]^+(\text{aq})$.

(i) Calculate the solubility of AgBr at 298 K in mol dm^{-3} .

solubility of AgBr = ... mol dm^{-3} [1]

(ii) Use Le Chatelier's principle as applied to equilibria 1 and 2 to suggest why AgBr(s) dissolves in concentrated $\text{NH}_3(\text{aq})$.

.....

 [2]

(iii) Use equilibria 1 and 2 to construct an equation for the reaction of AgBr(s) with concentrated $\text{NH}_3(\text{aq})$. This is equilibrium 3.

..... equilibrium 3 [1]

(iv) Write an expression for the equilibrium constant of equilibrium 3, K_{eq3} , in terms of K_{sp} for equilibrium 1 and K_{stab} for equilibrium 2.

$$K_{\text{eq3}} =$$

[1]

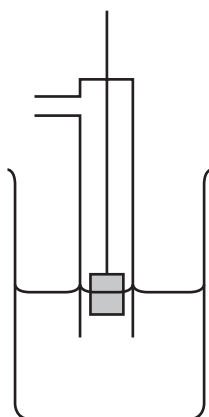
(d) Define the term *standard electrode potential*, $E^\ominus$.

.....

.....

..... [1]

(e) (i) Complete and **label** the diagram to show how the standard electrode potential, $E^\ominus$, of $\text{Ag}^+(\text{aq})/\text{Ag}(\text{s})$ could be measured under **standard conditions**.



[4]

(ii) Use the *Data Booklet* to label the diagram in (e)(i) to show

- which is the positive electrode,
- the direction of electron flow in the external circuit when a current flows.

[1]

[Total: 17]

- 2 (a) Group 2 carbonates decompose when heated.

Write an equation for the decomposition of the carbonate ion.

..... [1]

- (b) Describe and explain how the thermal stability of the Group 2 carbonates changes with increasing atomic number.

.....

 [3]

- (c) Lead(II) carbonate, PbCO_3 , and zinc carbonate, ZnCO_3 , decompose on heating in a similar way to calcium carbonate, CaCO_3 .

State relevant data from the *Data Booklet* and use it to predict the order of thermal stability of these three carbonates.

data

(most stable) > > (least stable)
 [2]

- (d) Dolomite contains the double carbonate of calcium and magnesium, $\text{CaMg}(\text{CO}_3)_2$, and some impurities. When 0.642 g of a sample of dolomite reacts with an excess of hydrochloric acid, 125.0 cm^3 of CO_2 is formed under room conditions.

Calculate the percentage of $\text{CaMg}(\text{CO}_3)_2$ in the sample of dolomite. Show all your working.

Assume that none of the impurities react with HCl .

% of $\text{CaMg}(\text{CO}_3)_2$ in dolomite = ... %
 [3]

[Total: 9]

3 (a) Sketch the shape of a d orbital.

[1]

(b) (i) Explain what is meant by the term *transition element*.

.....
 [1]

Transition elements can form complex ions which contain ligands.

(ii) Name the *type of bonding* that occurs between a ligand and a transition element.

..... [1]

(c) Give the formulae of two oxides of iron. State the oxidation number of iron in each compound.

.....
 [1]

(d) CO and CN⁻ are monodentate ligands.

Complete the table for the following two complexes.

metal ion	ligand	co-ordination number	formula of complex ion	charge of complex ion
Ni ²⁺	CO	4		
Fe ³⁺	CN ⁻			3-

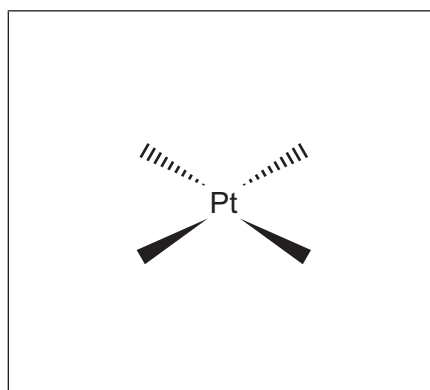
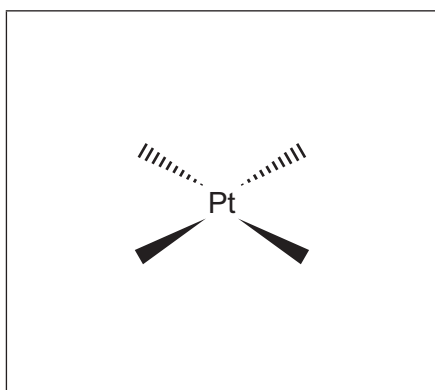
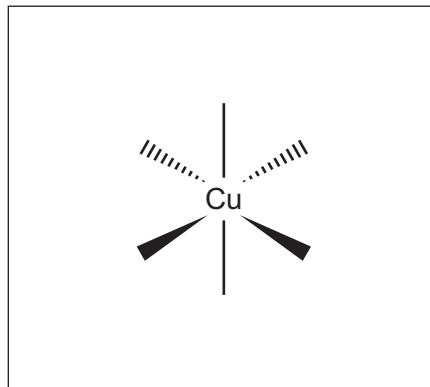
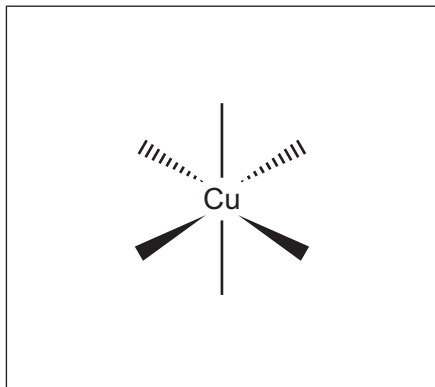
[2]

- (e) Transition element complexes can exhibit stereoisomerism. $[\text{Cu}(\text{H}_2\text{O})_4(\text{NH}_3)_2]^{2+}$ and $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ show the **same** type of isomerism.

(i) Name this type of isomerism.

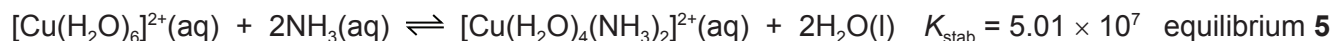
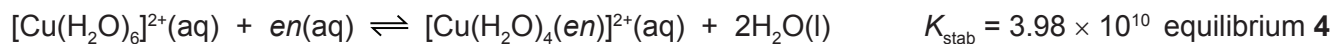
..... [1]

- (ii) Complete the three-dimensional diagrams of the two isomers for $[\text{Cu}(\text{H}_2\text{O})_4(\text{NH}_3)_2]^{2+}$ and $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$.



[2]

(f) Copper can form complexes with the ligands ammonia and *en*, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, as shown.



(i) Write an expression for the stability constant, K_{stab} , for equilibrium 5. State its units.

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

units = ...
[2]

(ii) The standard entropy change, ΔS° , for equilibrium 4 is $+23 \text{ J K}^{-1} \text{ mol}^{-1}$ and for equilibrium 5 is $-8.4 \text{ J K}^{-1} \text{ mol}^{-1}$.

Suggest an explanation for this difference by reference to both equilibria.

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

(iii) Of the three copper complexes in equilibria 4 and 5, state the formula of the copper complex that is the most stable and explain your choice.

copper complex

explanation

..... [1]

[Total: 13]

Question 4 starts on the next page.

- 4 The initial rate of reaction for propanone and iodine in acid solution is measured in a series of experiments at a constant temperature.



The rate equation was determined experimentally to be as shown.

$$\text{rate} = k[\text{CH}_3\text{COCH}_3][\text{H}^+]$$

- (a) State the order of reaction with respect to

- CH_3COCH_3
- I_2
- H^+

and state the overall order of this reaction. [2]

- (b) The rate of this reaction is $5.40 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$ when

- the concentration of CH_3COCH_3 is $1.50 \times 10^{-2} \text{ mol dm}^{-3}$
- the concentration of I_2 is $1.25 \times 10^{-2} \text{ mol dm}^{-3}$
- the concentration of H^+ is $7.75 \times 10^{-1} \text{ mol dm}^{-3}$.

- (i) Calculate the rate constant, k , for this reaction. State the units of k .

$k =$

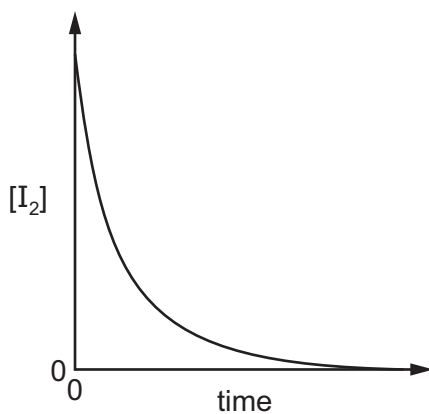
units = ... [2]

- (ii) Complete the table by placing **one** tick (✓) in each row to describe the effect of **decreasing** the temperature on the rate constant and on the rate of reaction.

	decreases	no change	increases
rate constant			
rate of reaction			

[1]

- (c) From the results, a graph is produced which shows how the concentration of I_2 changes during the reaction.

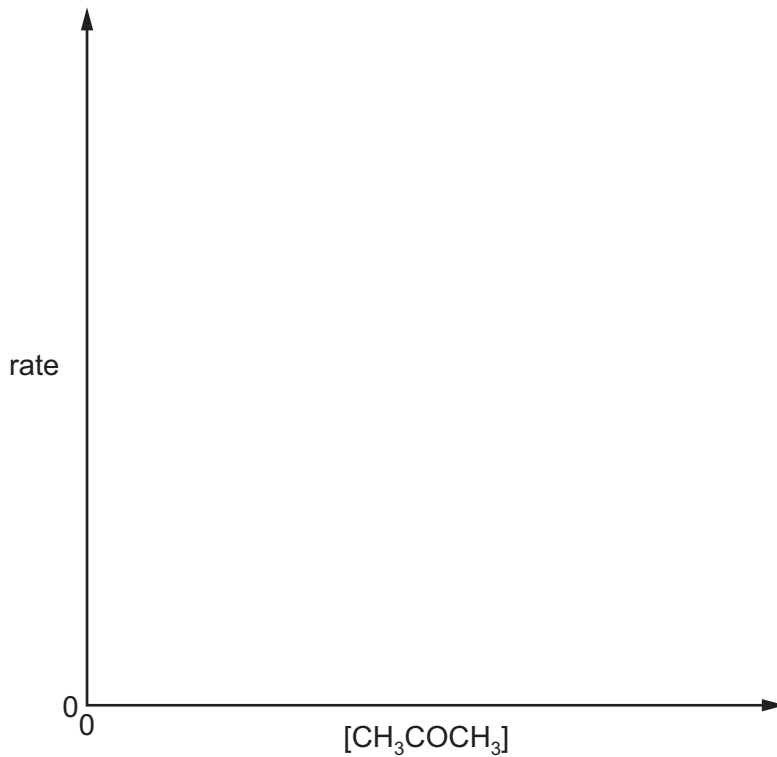


Describe how this graph could be used to determine the initial rate of the reaction.

.....

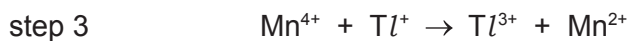
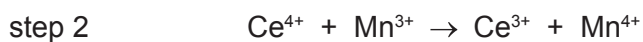
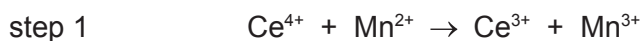
 [2]

- (d) On the axes below, sketch a graph to show how the initial rate changes with different initial concentrations of CH_3COCH_3 in this reaction.



[1]

- (e) The rate of a reaction between metal ions was studied. The following three-step mechanism has been suggested for this reaction. Step 1 is the rate-determining step.



- (i) Explain the meaning of the term *rate-determining step*.

.....
 [1]

- (ii) Use this mechanism to

- determine the overall equation for this reaction

.....

- suggest the role of Mn^{2+} ions in this mechanism. Explain your answer.

.....

.....

.....

[2]

[Total: 11]

- 5 (a) Complete the table by placing **one** tick (✓) in each row to indicate the sign of each type of energy change under standard conditions.

energy change	always positive	always negative	either negative or positive
lattice energy			
enthalpy change of neutralisation			

[1]

- (b) Define, in words, the term *enthalpy change of solution*.

.....
 [1]

- (c) The following enthalpy changes are given.

enthalpy change	value / kJ mol ⁻¹
standard enthalpy change of formation, $\Delta H_f^\ominus$, for $K_3PO_4(s)$	-2035
standard enthalpy change, $\Delta H^\ominus$, for $P(s) + 2O_2(g) + 3e^- \rightarrow PO_4^{3-}(aq)$	-1284
standard enthalpy change, $\Delta H^\ominus$, for $K(s) \rightarrow K^+(aq) + e^-$	-251

Determine the standard enthalpy change of solution of potassium phosphate, $K_3PO_4(s)$. It may be helpful to draw a labelled energy cycle.

$$\Delta H_{\text{sol}}^\ominus = \dots\dots\dots \text{kJ mol}^{-1} \quad [3]$$

(d) Some lattice energy values are shown in the table.

compound	lattice energy value / kJ mol^{-1}
$\text{CaBr}_2(\text{s})$	-2176
$\text{KBr}(\text{s})$	-679

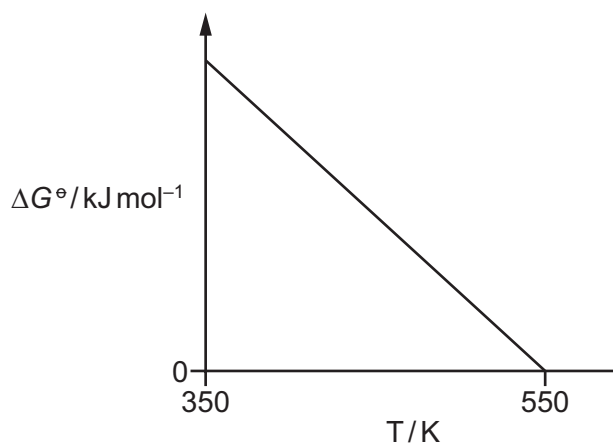
Suggest an explanation for why $\Delta H_{\text{latt}}^\circ$ CaBr_2 is **more** exothermic than $\Delta H_{\text{latt}}^\circ$ KBr .

.....

 [2]

(e) For a particular gas phase reaction the variation in standard Gibbs free energy change, ΔG° , with temperature is shown.

Assume standard enthalpy change, ΔH° , and standard entropy change, ΔS° , remain constant with temperature.



(i) Write the equation that relates ΔG° to ΔH° and ΔS° .

..... [1]

(ii) Use this equation to explain why ΔG° becomes **less** positive as temperature increases in this reaction.

.....
 [1]

[Total: 9]

Question 6 starts on the next page.

- 6 (a) By reference to the formation of σ and π bonds, describe and explain the shape of a benzene molecule, C_6H_6 .

.....

.....

.....

.....

.....

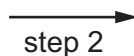
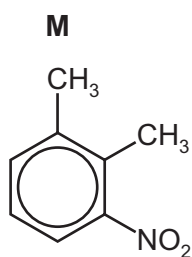
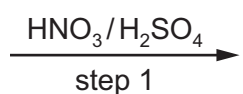
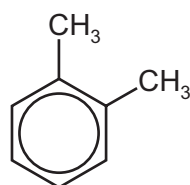
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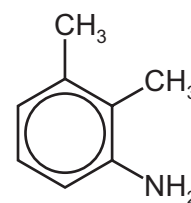
..... [3]

- (b) 2,3-dimethylphenylamine can be prepared from 1,2-dimethylbenzene in two steps as shown.

1,2-dimethylbenzene



2,3-dimethylphenylamine

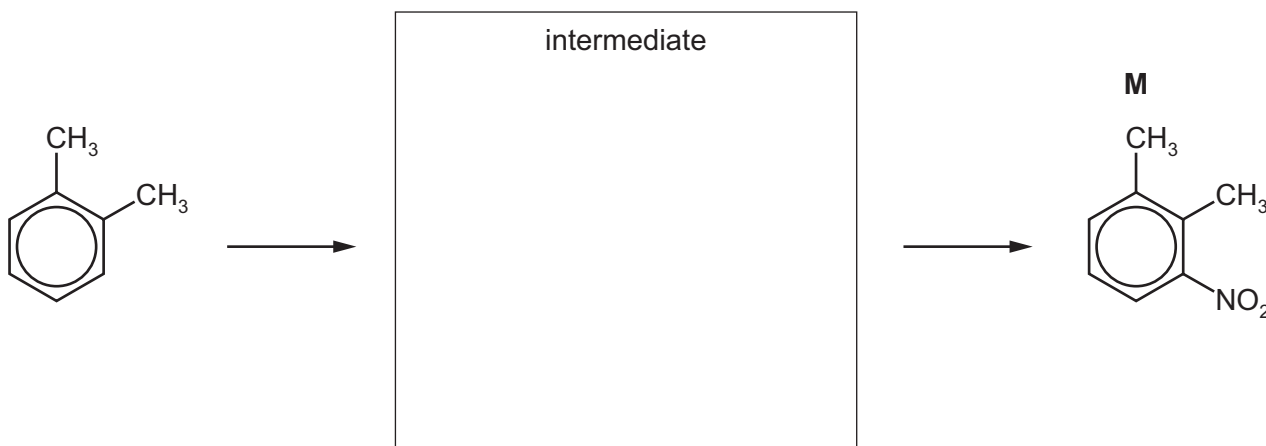


Step 1 is catalysed by H_2SO_4 .

- (i) Write an equation to show how H_2SO_4 generates the electrophile during step 1.

..... [1]

- (ii) Draw the mechanism of the reaction between this electrophile and 1,2-dimethylbenzene to form **M**. Include all relevant curly arrows and charges.



[3]

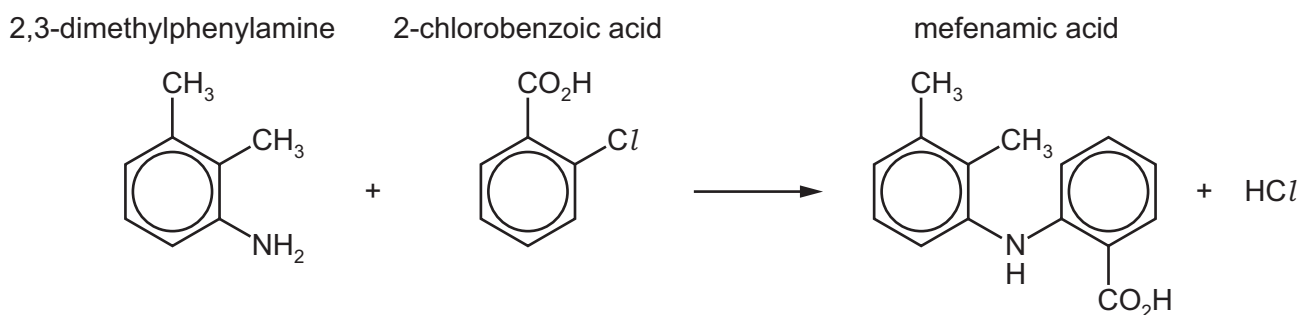
(iii) Write an equation to show how the H_2SO_4 catalyst is reformed.

..... [1]

(iv) For step 2, suggest the reagents and conditions and name the *type of reaction*.

- reagents and conditions
 - type of reaction
- [2]

(c) The drug mefenamic acid can be made using 2,3-dimethylphenylamine in an excess of 2-chlorobenzoic acid.



(i) Deduce the molecular formula of mefenamic acid.

..... [1]

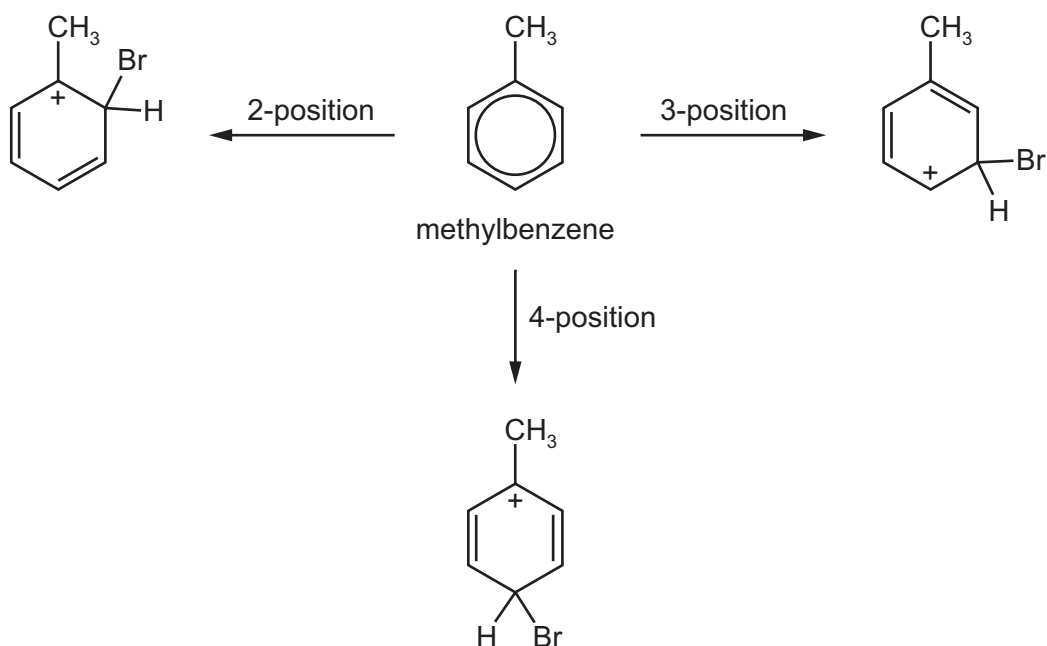
(ii) Name the functional groups, apart from the benzene ring, in mefenamic acid.

..... [1]

(iii) Calculate the maximum mass of mefenamic acid that could be formed from 5.00 g of 2,3-dimethylphenylamine in this reaction. Give your answer to **three** significant figures.

mass of mefenamic acid = ... g [2]

- (d) The position of substitution in the electrophilic substitution of arenes can be explained based on the stability of the intermediate cations formed in the first step. The example given involves the bromination of methylbenzene.



Use this information and your knowledge about the stability of cations to suggest why the CH_3 group directs incoming electrophiles to the 2- and 4-positions in preference to the 3-position.

.....

.....

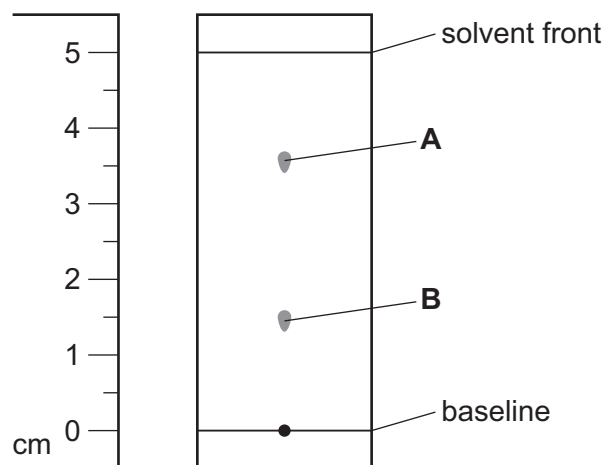
.....

..... [2]

[Total: 16]

- 7 (a) Amino acids can be separated by thin-layer chromatography. A mixture of amino acids is analysed using this technique.

The chromatogram obtained is shown, drawn to scale. The table shows some R_f values for different amino acids in the solvent used.



amino acid	R_f value
alanine	0.40
glutamic acid	0.29
leucine	0.71
valine	0.61

- (i) Use the chromatogram and the R_f values to deduce the amino acid responsible for spot **A** and spot **B**.

amino acid responsible for spot **A**

amino acid responsible for spot **B**

[1]

- (ii) A second chromatogram of the same mixture is taken using a **more polar** solvent.

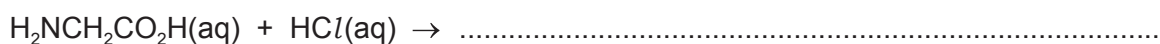
Predict the effect on the R_f values of the amino acids. Explain your reasoning.

.....

 [1]

- (b) Glycine, $\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$, is the simplest amino acid.

- (i) Complete the equations to show the acid-base properties of glycine.



[2]

- (ii) In aqueous solution, amino acids exist as zwitterions.

Draw the zwitterionic structure of glycine. Explain how the zwitterion for glycine is formed.

.....

.....

.....

[2]

- (c) Apart from glycine, all naturally occurring amino acids have a chiral centre and exhibit stereoisomerism.

Draw the two stereoisomers of alanine, $\text{CH}_3\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$.



[1]

- (d) The amino acid alanine can be synthesised from 2-chloropropanoic acid, $\text{CH}_3\text{CHClCO}_2\text{H}$.

- (i) State the reagents and conditions and name the mechanism for this reaction.

reagents and conditions

name of mechanism

[2]

- (ii) State and explain the relative acidities of trichloroethanoic acid, chloroethanoic acid and ethanoic acid.

.....

.....

.....

.....

.....

[3]

- (e) Serine, $\text{HOCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$, can react with alanine, $\text{CH}_3\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$, to form three different **structural** isomers, each with the molecular formula $\text{C}_6\text{H}_{12}\text{N}_2\text{O}_4$.

Draw the structures of these three structural isomers.

isomer 1 ($\text{C}_6\text{H}_{12}\text{N}_2\text{O}_4$)

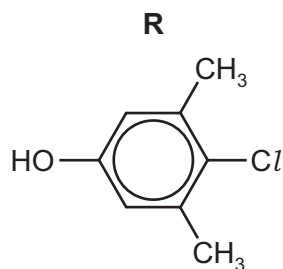
isomer 2 ($\text{C}_6\text{H}_{12}\text{N}_2\text{O}_4$)

isomer 3 ($\text{C}_6\text{H}_{12}\text{N}_2\text{O}_4$)

[3]

[Total: 15]

8 Compound **R** is shown.



(a) State the systematic name of compound **R**.

..... [1]

(b) (i) **R** is dissolved in CDCl_3 and analysed using carbon-13 and proton NMR spectroscopy.

- Predict the number of peaks that are seen in the carbon-13 NMR spectrum of **R**.

.....

- Predict the number of peaks that are seen in the proton NMR spectrum of **R**.

.....

[2]

(ii) A separate sample of **R** is dissolved in D_2O . The proton NMR spectrum of this solution shows **one less** peak than is obtained in CDCl_3 .

Explain why.

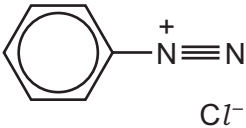
.....

..... [1]

(c) Compound **R** reacts separately with the four reagents shown in the table.

Complete the table by

- drawing the structures of the organic products formed,
- stating the type of reaction.

reagent	organic product structure	type of reaction
Na		
CH_3COCl		
$\text{Br}_2(\text{aq})$		
		

[6]

[Total: 10]

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CHEMISTRY

9701/43

Paper 4 A Level Structured Questions

May/June 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 (a) Aqueous solutions of copper(II) salts contain the blue-coloured $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex ion. Separate portions of this blue solution react with aqueous sodium hydroxide and with concentrated hydrochloric acid.

Give the following information for each of these reactions.

- reaction with aqueous sodium hydroxide

ionic equation

type of reaction

colour and state of the copper-containing product

- reaction with concentrated hydrochloric acid

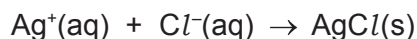
ionic equation

type of reaction

colour and state of the copper-containing product

[6]

- (b) Chloride ions can be identified using aqueous silver nitrate, $\text{AgNO}_3(\text{aq})$.



0.303 g of a chloride of sulfur is completely hydrolysed with water. All the chlorine atoms present in the chloride of sulfur are converted into chloride ions. The solution is diluted to 100.0 cm^3 . A 25.00 cm^3 sample of this solution is titrated with $0.0500 \text{ mol dm}^{-3} \text{ AgNO}_3(\text{aq})$. The titration requires 22.40 cm^3 of $0.0500 \text{ mol dm}^{-3} \text{ AgNO}_3(\text{aq})$.

Calculate the empirical formula of the chloride of sulfur. Show all your working.

empirical formula of chloride of sulfur = ... [3]

[Total: 9]

- 2 (a) Group 2 nitrates decompose when heated.

Write an equation for the decomposition of strontium nitrate.

..... [1]

- (b) Describe and explain how the thermal stability of Group 2 nitrates changes with increasing atomic number.

.....

 [3]

- (c) The variation in the thermal stability of Group 2 amides is similar to that of Group 2 nitrates.

- (i) Suggest whether calcium amide, $\text{Ca}(\text{NH}_2)_2$, will decompose more or less readily than barium amide, $\text{Ba}(\text{NH}_2)_2$. Explain your answer.

.....
 [1]

- (ii) $\text{Ba}(\text{NH}_2)_2$ decomposes when heated to form barium nitride, Ba_3N_2 , and ammonia as the only products.

Write an equation for this reaction.

..... [1]

- (d) $\text{Ba}(\text{NH}_2)_2$ contains the NH_2^- ion.

Predict the bond angle of NH_2^- . Explain your answer using the qualitative model of electron-pair repulsion.

bond angle

explanation

 [3]

[Total: 9]

3 Chlorate(V) ions are powerful oxidising agents.

- (a)** The reduction of chlorate(V) ions, ClO_3^- , with SO_2 forms chlorine dioxide, ClO_2 , and sulfate ions, SO_4^{2-} , as the only products.

Construct an equation for this reaction.

..... [1]

- (b) (i)** Chlorine dioxide, ClO_2 , disproportionates with hydroxide ions, $\text{OH}^-(\text{aq})$, to form a mixture of ClO_2^- and ClO_3^- ions.



Explain, using this reaction as an example, what is meant by *disproportionation*.

.....
 [1]

- (ii)** Deduce the ionic half-equations for the reaction in **(b)(i)**.

.....
 [2]

- (c)** A lithium-iodine electrochemical cell can be used to generate electricity for a heart pacemaker. The cell consists of a lithium electrode and an inert electrode immersed in body fluids. When current flows lithium is oxidised and iodine is reduced.

- (i)** Use the *Data Booklet* to write half-equations for the reactions taking place at the two electrodes. Hence write the overall equation for when a current flows.

-
-

overall equation [2]

- (ii)** Use the *Data Booklet* to calculate the $E_{\text{cell}}^\ominus$ for this cell.

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

- (iii) A current of $2.5 \times 10^{-5} \text{ A}$ is drawn from this cell.

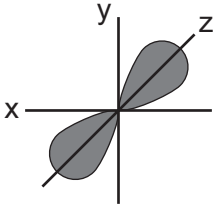
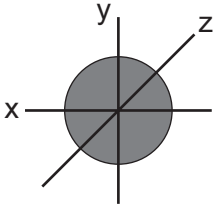
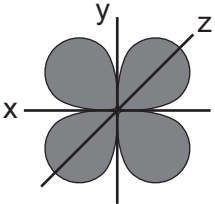
Calculate the time taken for 0.10 g of lithium electrode to be used up. Assume the current remains constant throughout this period.

time = ... s [3]

[Total: 10]

- 4 (a) Sketches of the shapes of some atomic orbitals are shown.

Identify the type of orbital, s, p, or d.

shape of orbital			
type of orbital			

[1]

- (b) Cadmium forms the two ions, Cd_2^{2+} and Cd^{2+} . The electronic configuration of cadmium in these ions is shown.

- $[\text{Kr}] 4d^{10}5s^1$
- $[\text{Kr}] 4d^{10}$

Use this information to explain why cadmium is **not** a transition element.

.....
 [1]

- (c) Methylamine, CH_3NH_2 , is a monodentate ligand.

- (i) State what is meant by the term *monodentate* in this context.

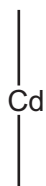
.....
 [1]

In the presence of aqueous methylamine, $[\text{Cd}(\text{H}_2\text{O})_6]^{2+}$ reacts to form a mixture of two isomeric octahedral complexes.



(ii) Complete the three-dimensional diagrams to show the isomers of $[\text{Cd}(\text{CH}_3\text{NH}_2)_4(\text{H}_2\text{O})_2]^{2+}$.

Use L to represent CH_3NH_2 in your diagrams.



[2]

(d) (i) State what is meant by the term *stability constant*.

.....
 [1]

(ii) Complete the table by placing **one** tick (✓) in each row to suggest how increasing temperature will affect K_{stab} and the equilibrium concentration of the cadmium complex, $[\text{Cd}(\text{CH}_3\text{NH}_2)_4(\text{H}_2\text{O})_2]^{2+}$, for equilibrium 1. Explain your answer.

	decreases	no change	increases
K_{stab}			
$[\text{Cd}(\text{CH}_3\text{NH}_2)_4(\text{H}_2\text{O})_2]^{2+}$			

explanation
 [2]

EDTA⁴⁻ is a polydentate ligand. When a solution of EDTA⁴⁻ is added to [Cd(H₂O)₆]²⁺ a new complex [CdEDTA]²⁻ is formed.

The values for the stability constants for two Cd²⁺ complexes are shown.

	K_{stab}
$[\text{Cd}(\text{CH}_3\text{NH}_2)_4(\text{H}_2\text{O})_2]^{2+}$	4.0×10^6
$[\text{CdEDTA}]^{2-}$	4.0×10^{16}

(iii) A solution containing equal numbers of moles of CH₃NH₂ and EDTA is added to [Cd(H₂O)₆]²⁺.

Predict which complex is formed in the larger amount. Explain your answer.

.....
 [1]

(e) Methylamine is a Brønsted-Lowry base.

Write an equation showing how methylamine dissolves in water to give an alkaline solution.

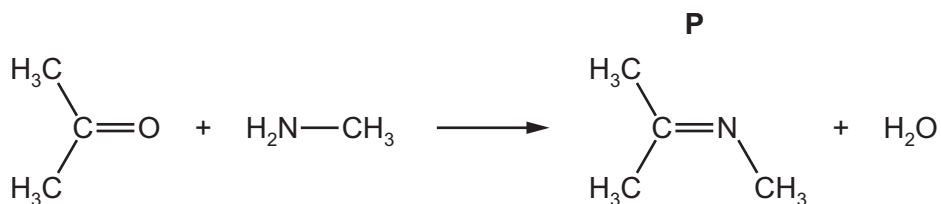
..... [1]

(f) Methylamine is a useful reagent in organic chemistry.

(i) Write an equation for the reaction of ethanoyl chloride with methylamine.

..... [2]

(ii) Methylamine also reacts with propanone to form compound **P** as shown.



Deduce the *type of reaction* shown here.

..... [1]

[Total: 13]

- 5 (a) Chlorate(I) ions undergo the following reaction under aqueous conditions.



A series of experiments was carried out at different concentrations of ClO^- and NH_3 .

The table shows the results obtained.

experiment	$[\text{ClO}^-]$ / mol dm^{-3}	$[\text{NH}_3]$ / mol dm^{-3}	initial rate / $\text{mol dm}^{-3} \text{s}^{-1}$
1	0.200	0.100	0.256
2	0.400	0.200	2.05
3	0.400	0.400	8.20

- (i) Use the data in the table to determine the order with respect to each reactant, ClO^- and NH_3 .

Show your reasoning.

.....

.....

.....

.....

.....

..... [2]

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

rate = ... [1]

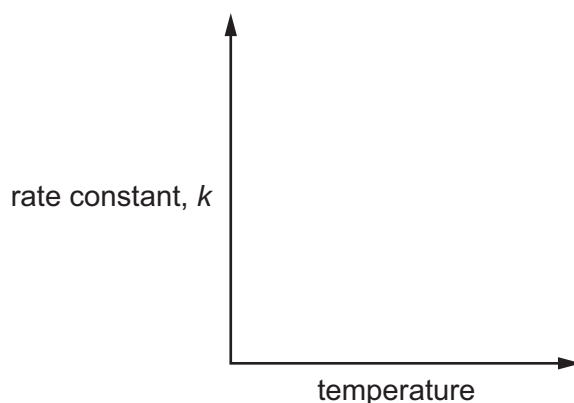
- (iii) Use the results of experiment 1 to calculate the rate constant, k , for this reaction. Include the units of k .

k = ...

units = ...

[2]

- (iv) On the axes sketch a graph to show how the value of k changes as temperature is increased.



[1]

- (b) In another experiment, the reaction between chlorate(I) ions and iodide ions in aqueous alkali was investigated.

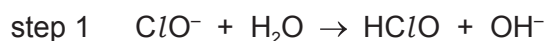
A solution of iodide ions in aqueous alkali was added to a large excess of chlorate(I) ions and $[I^-]$ was measured at regular intervals.

- (i) Describe how the results of this experiment can be used to confirm that the reaction is first-order with respect to $[I^-]$.

.....

 [2]

A three-step mechanism for this reaction is shown.



- (ii) Use this mechanism to deduce the overall equation for this reaction.

..... [1]

- (iii) Identify a step that involves a redox reaction. Explain your answer.

.....
 [1]

[Total: 10]

- 6 (a) Complete the table by placing **one** tick (✓) in each row to indicate the sign of each type of energy change under standard conditions.

energy change	always positive	always negative	either negative or positive
bond energy			
enthalpy change of formation			

[1]

- (b) Explain what is meant by the term *enthalpy change of atomisation*.

.....
 [1]

- (c) The overall reaction for the atomisation of liquid bromine molecules, Br₂(l), is shown.



This happens via a two-step process.

- Construct a **labelled** energy cycle to represent this atomisation process, including state symbols.
- Use your cycle and relevant data from the *Data Booklet* to calculate the enthalpy change of vaporisation of Br₂(l), $\Delta H_{\text{vap}}^\ominus$.
 The enthalpy change of atomisation of bromine, $\Delta H_{\text{at}}^\ominus = +112 \text{ kJ mol}^{-1}$.

$$\Delta H_{\text{vap}}^\ominus = \dots\dots\dots \text{kJ mol}^{-1} \quad [3]$$

- (d) Suggest how the $\Delta H_{\text{vap}}^\ominus$ of iodine, I₂(l), would compare to that of bromine, Br₂(l). Explain your answer.

.....
 [1]

- (e) (i) Explain what is meant by the term *enthalpy change of hydration*.

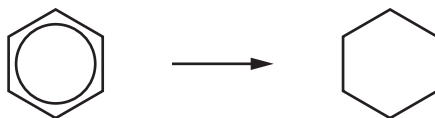
.....
..... [1]

- (ii) Suggest why the enthalpy change of hydration of $\text{Br}^-(\text{g})$ is **more** exothermic than that of $\text{I}^-(\text{g})$.

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

[Total: 9]

- 7 (a) Benzene can be converted into cyclohexane.



- (i) For this reaction name the type of reaction and identify the reagent and conditions needed.

type of reaction

reagent and conditions

[2]

- (ii) State the bond angles in benzene and cyclohexane.

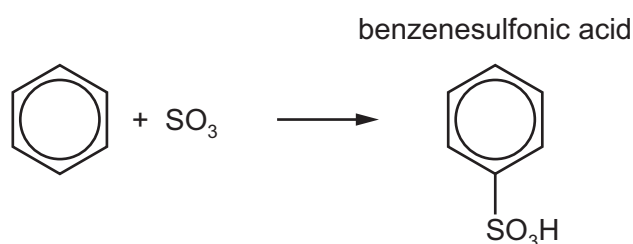
bond angle in benzene bond angle in cyclohexane

Explain your answers.

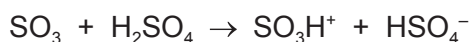
.....

[2]

- (b) When benzene reacts with SO_3 , benzenesulfonic acid is produced.



The mechanism of this reaction is similar to that of the nitration of benzene. Concentrated H_2SO_4 is used in an initial step to generate the SO_3H^+ electrophile as shown.



- (i) Draw a mechanism for the reaction of benzene with SO_3H^+ ions. Include all necessary curly arrows and charges.

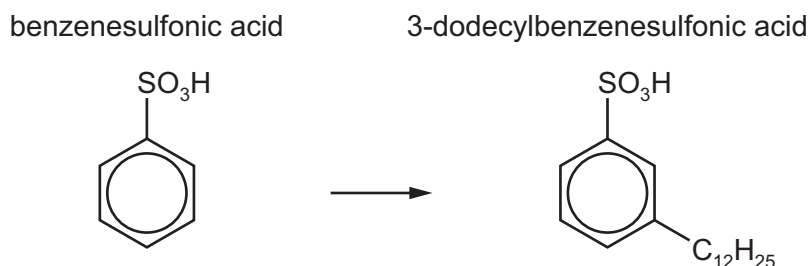


[3]

- (ii) Write an equation to show how the H_2SO_4 catalyst is reformed.

..... [1]

- (c) 3-dodecylbenzenesulfonic acid can be prepared from benzenesulfonic acid.



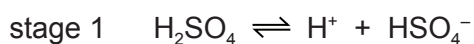
Suggest the reagents and conditions and name the mechanism for this reaction.

reagents and conditions

mechanism

[2]

- (d) When concentrated sulfuric acid is added to water, dissociation takes place in two stages.



K_{a2} is the acid dissociation constant for stage 2.

- (i) Write the expression for the acid dissociation constant K_{a2} .

$$K_{a2} =$$

[1]

- (ii) H_2SO_4 is considered a strong acid whereas HSO_4^- is considered a weak acid.

Suggest how the magnitude of the acid dissociation constant for stage 1 compares to K_{a2} .

..... [1]

- (e) Benzoic acid, $\text{C}_6\text{H}_5\text{CO}_2\text{H}$, is a weak acid. A solution of $0.0250 \text{ mol dm}^{-3}$ benzoic acid has a pH of 2.90.

Calculate the K_a of benzoic acid.

$$K_a = \dots\dots\dots \text{mol dm}^{-3}$$

[2]

[Total: 14]

- 8 (a) The mass spectrum of compound **X**, $\text{C}_5\text{H}_{10}\text{O}_2$, is recorded.

The peak heights of the M and $M+1$ peaks are 22.65 and 1.25 respectively.

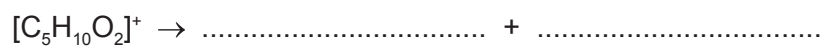
- (i) Use these data to show that there are five carbon atoms present in one molecule of **X**.

Show your working.

[1]

- (ii) The mass spectrum has a peak at $m/e = 57$.

Complete the equation to show the fragmentation of **X** to produce this peak.



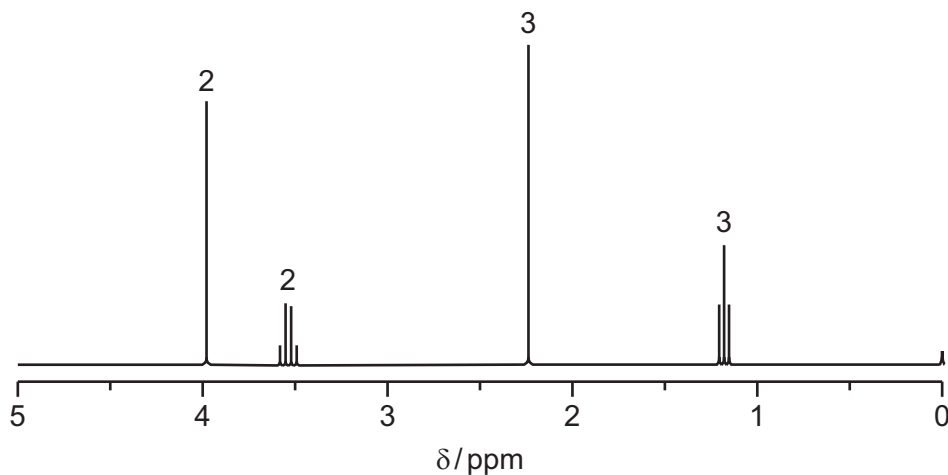
[2]

- (b) State the use of TMS and CDCl_3 in NMR spectroscopy.

- TMS
- CDCl_3

[1]

(c) The proton NMR spectrum of compound **X**, $\text{C}_5\text{H}_{10}\text{O}_2$, is shown.



(i) By considering both the relative peak areas and their δ values, use the *Data Booklet* to

- deduce the part of the molecule that produces the peak at $\delta 2.2$,
.....
- deduce the part of the molecule that produces the peaks at $\delta 1.2$ and $\delta 3.5$,
.....
- deduce the part of the molecule that produces the peak at $\delta 4.0$.
.....

[3]

(ii) When reacted with aqueous alkaline iodine, **X** produces a yellow precipitate.

Use this information and your answers to (c)(i) to suggest a structure for **X**.

[1]

(d) Compound **W** is an ester with the molecular formula $C_5H_{10}O_2$.

The proton NMR spectrum of **W** contains only **two** peaks.

The relative areas of these two peaks are in the ratio 9 : 1.

Suggest a structure for this ester, **W**.

[1]

(e) Compound **V** is a carboxylic acid which contains a chiral centre. It also has the molecular formula $C_5H_{10}O_2$.

(i) Explain what is meant by the term *chiral centre*.

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

(ii) Suggest a structure for **V**.

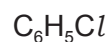
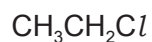
[1]

[Total: 11]

- 9 (a) Organochlorine compounds can undergo hydrolysis.



State and explain the relative rates of hydrolysis of the following compounds.

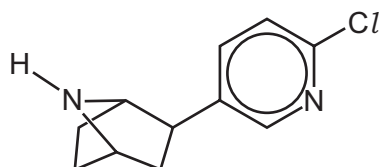


.....

 [3]

- (b) Epibatidine is a naturally occurring organochlorine compound.

epibatidine



- (i) Epibatidine is a weak base.

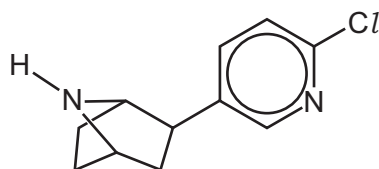
State what is meant by the term *weak base*.

.....
 [1]

A molecule of epibatidine contains two nitrogen atoms, both of which can act as a base.

- (ii) Epibatidine reacts with HCl(aq) .

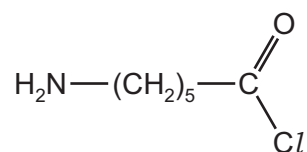
Complete the structure to suggest the product formed in this reaction.



[1]

- (c) Polyamides, such as nylon-6, can be prepared from a monomer that contains both an amine and an acyl chloride functional group.

nylon-6 monomer



- (i) When the nylon-6 monomer is hydrolysed, bonds are broken and formed.

By considering the two steps in the mechanism of the reaction, complete the table by placing **one** tick (✓) in each row to indicate the types of bonds broken and formed during the mechanism.

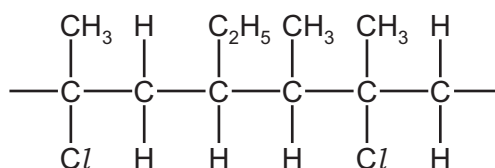
	σ bonds only	π bonds only	both σ and π bonds
bonds broken			
bonds formed			

[1]

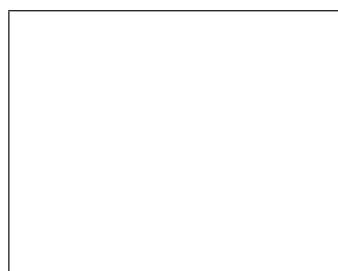
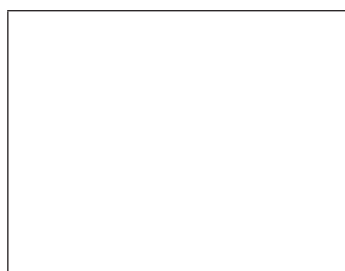
- (ii) Draw **two** repeat units of nylon-6. The amide bond should be shown fully displayed.

[2]

- (d) An addition polymer made from two different alkene monomers is called a co-polymer. A section of a polyalkene co-polymer is shown.



Draw the structure of the **two** alkene monomers which produce this co-polymer.

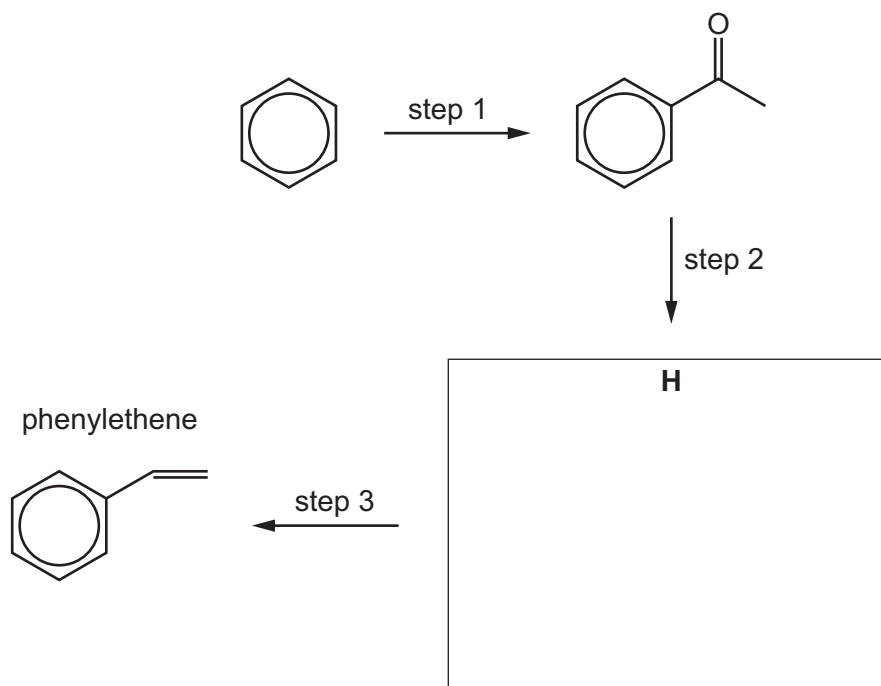


[2]

- (e) Explain why polyamides normally biodegrade more readily than polyalkenes.

.....
 [1]

- (f) The alkene phenylethene can be prepared from benzene in three steps.



- (i) Deduce the identity of compound **H** and draw its structure in the box. [1]
- (ii) Suggest reagents and conditions for each of the steps 1–3.

step 1
 step 2
 step 3 [3]

[Total: 15]

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