#### **SECTION A**

Answer ALL the questions in this section. You should aim to spend no more than 20 minutes on this section. For each question, select one answer from A to D and put a cross in the box ⊠. If you change your mind, put a line through the box ₩ and then mark your new answer with a cross ⋈.

		a cross ⊠.	
1	Fou	ar complex ions have the following formulae:	
	A	Cu(edta) <sup>2-</sup>	
	В	$Zn(H_2O)_6^{2+}$	
	C	Ni(NH <sub>3</sub> ) <sub>6</sub> <sup>2+</sup>	
	D	CrCl <sub>4</sub> <sup>2-</sup>	
	(a)	Which complex ion is most likely to be tetrahedral in shape?	(1)
	X	$\mathbf{A}$	
	X	В	
	X	C	
	X	D	
	(b)	Which complex ion is most likely <b>not</b> to be coloured?	(1)
	X	$\mathbf{A}$	
	X	В	
	X	C	
	X	D	
		Each of these complex ions may be formed by ligand exchange from an aqua complex. For which complex ion is the entropy change of this reaction most positive?	41)
	×	$\mathbf{A}$	(1)
	X	В	
	X	C	
	X	D	
		(Total for Question 1 = 3 ma	ırks)

2		a <b>few drops</b> of aqueous ammonia are added to a solution containing $[Cr(H_2O)_6]^{3+}$ e product formed will be
	$\boxtimes$ A	$[Cr(NH_3)_6]^{3+}$
	$\boxtimes$ B	$Cr(H_2O)_3(OH)_3$
	<b>区</b> C	$[Cr(NH_3)_4]^{3+}$
	$\boxtimes$ <b>D</b>	$[Cr(H_2O)_2(OH)_4]^-$
		(Total for Question 2 = 1 mark)
3	Which not con	of these statements about a standard hydrogen electrode, for which $E^{\oplus} = 0$ V, is rect?
	$\boxtimes$ A	The hydrogen gas is at a pressure of 1 atm.
	$\boxtimes$ B	A solution containing 1 mol dm <sup>-3</sup> of H <sup>+</sup> (aq) ions is used.
		A platinum electrode is used.
	$\boxtimes$ D	The temperature is kept at 20 °C.
		(Total for Question 3 = 1 mark)
	Use th	is space for any rough working. Anything you write in this space will gain no credit.

4 Four polymers labelled **A to D** have the following formulae:

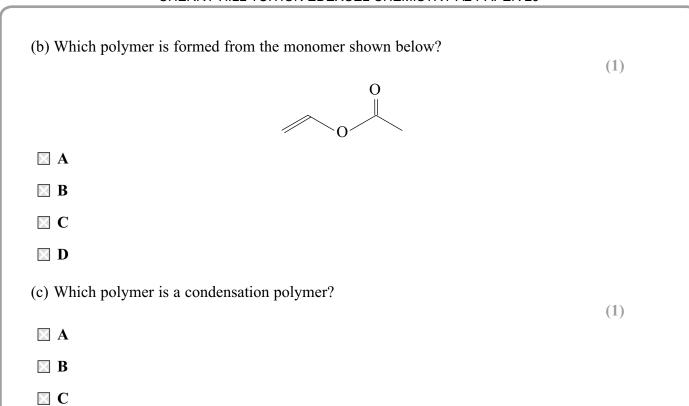
$$\mathbf{A} = \begin{pmatrix} O & O & H \\ \parallel & \parallel & \parallel \\ -C - (CH_2)_4 - C - N - (CH_2)_6 - N \\ \parallel & \parallel & \parallel \\ H & \end{pmatrix}_{n}$$

$$\mathbf{B} \quad \frac{\begin{pmatrix} H & OH & H & OH \\ | & | & | & | \\ C - C - C - C - C - \\ | & | & | & | \\ H & H & H & H \end{pmatrix}_{n}$$

$$\mathbf{D} = \begin{pmatrix} H & CH_3 & H & CH_3 \\ | & | & | & | \\ C & C & C & C \\ | & | & | & | \\ H & H & H & H \end{pmatrix}_n$$

- (a) Which polymer is most soluble in hot water?
- $\mathbf{X}$  A
- $\boxtimes$  B
- $\boxtimes$  C
- $\times$  **D**

(1)

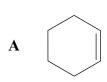


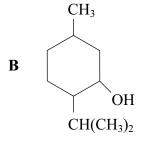
(Total for Question 4 = 3 marks)

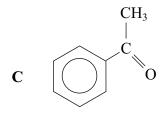
Use this space for any rough working. Anything you write in this space will gain no credit.

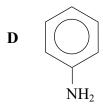
 $\boxtimes$  **D** 

The formulae of some organic compounds labelled **A** to **D** are shown below.









- (a) Which compound reacts with sodium to form hydrogen?
- $\mathbf{X}$  A

(1)

- $\mathbf{B}$
- $\bowtie$  **D**
- (b) Which compound forms a green complex ion with CuSO<sub>4</sub>(aq)?
- $\mathbf{X}$  A

(1)

- $\bowtie$  B
- $\boxtimes$  **D**
- (c) Which compound forms an orange precipitate with 2,4-dinitrophenylhydrazine?

(1)

- $\mathbf{X}$   $\mathbf{A}$
- $\mathbf{B}$
- $\mathbf{K}$  C
- $\times$  **D**

(Total for Question 5 = 3 marks)

6		any peaks would you expect to see in a <b>low resolution</b> proton nmr spectrum of er HCOOCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ?
	$\boxtimes A$	8
	$\boxtimes$ B	7
	<b>区</b> C	4
	$\square$ D	3
		(Total for Question 6 = 1 mark)
7		<b>gh resolution</b> proton nmr spectrum of ethyl ethanoate, CH <sub>3</sub> COOCH <sub>2</sub> CH <sub>3</sub> , the ue to the hydrogen atoms shown <b>in bold</b> would be a
	$\boxtimes \mathbf{A}$	singlet.
	$\boxtimes$ B	doublet.
	<b>区</b> C	triplet.
	<b>⋈</b> D	quartet.
		(Total for Question 7 = 1 mark)
8	Which mixture	of these compounds, whose formulae are shown below, <b>cannot</b> exist as a racemic e?
	$\boxtimes$ A	CH <sub>2</sub> CICHCICOOH
	$\boxtimes$ B	HOOCCHCICOOH
		CH <sub>3</sub> CHClCOOH
	$\boxtimes$ <b>D</b>	CH <sub>3</sub> CH(OH)COOH
		(Total for Question 8 = 1 mark)

9	Phenol of iron	reacts with bromine water whereas benzene reacts with bromine in the presence .	
	(a) The	e mechanism for both these reactions is	(1)
	⊠ A	electrophilic substitution.	(1)
	<b>■</b> B	electrophilic addition.	
	<b>区 C</b>	nucleophilic substitution.	
	<b>■ D</b>	nucleophilic addition.	
	(b) In t	he reaction of benzene with bromine, iron	(1)
	⊠ A	acts as a heterogeneous catalyst.	(1)
	⊠ B	acts as a homogeneous catalyst.	
		reacts with the bromine to make iron(III) bromide, FeBr <sub>3</sub> .	
	<b>■</b> D	allows bromine to attack the hydrogen atoms on benzene more readily.	
		omine reacts more readily with phenol than with benzene because the OH group phenol	(1)
	■ A	is a good leaving group.	(1)
	⊠ B	attracts the bromine particles more readily.	
		is a good nucleophile.	
	<b>■ D</b>	increases the electron density of the ring.	
		(Total for Question 9 = 3 mar	·ks)
10		nia (NH <sub>3</sub> ), butylamine (CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> ) and phenylamine (C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> ) all lkaline solutions in water. The order of <b>increasing</b> pH of equimolar solutions is	
	⊠ A	$C_6H_5NH_2 < CH_3CH_2CH_2CH_2NH_2 < NH_3$	
	$\boxtimes$ B	$NH_3 < CH_3CH_2CH_2CH_2NH_2 < C_6H_5NH_2$	
		$C_6H_5NH_2 < NH_3 < CH_3CH_2CH_2CH_2NH_2$	
	⊠ D	$CH_3CH_2CH_2CH_2NH_2 < NH_3 < C_6H_5NH_2$	
_		(Total for Question 10 = 1 ma	rk)

# CHERRY HILL TUITION EDEXCEL CHEMISTRY A2 PAPER 29

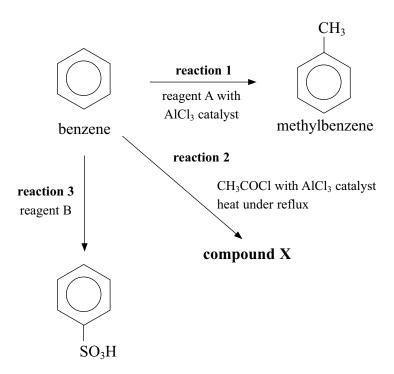
11		stance on a chromatogram moved by an individual amino acid, in a mixture of at amino acids, mainly depends on
	$\boxtimes$ A	the molar mass of the amino acid.
	$\square$ B	the molar mass of the solvent used.
	$\square$ C	the intermolecular forces between the solvent and the stationary phase.
	⊠ D	the intermolecular forces between the amino acid and both the solvent and the stationary phase.
		(Total for Question 11 = 1 mark)
12	Amino	acids are crystalline solids with a high melting temperature because
	$\square$ A	each molecule has a large number of electrons.
	$\square$ B	each molecule forms hydrogen bonds at both ends.
		a proton is transferred from one end of the molecule to the other.
	$\square$ D	their shape allows the molecules to pack close together.
		(Total for Question 12 = 1 mark)

**TOTAL FOR SECTION A = 20 MARKS** 

#### **SECTION B**

# Answer ALL the questions. Write your answers in the spaces provided.

13 Some reactions of benzene are shown below.



(a) (i) Suggest the formula of reagent A in reaction 1.

(1)

(ii) Write the equation to show how the catalyst, AlCl<sub>3</sub>, reacts with reagent A to form the species which attacks the benzene ring.

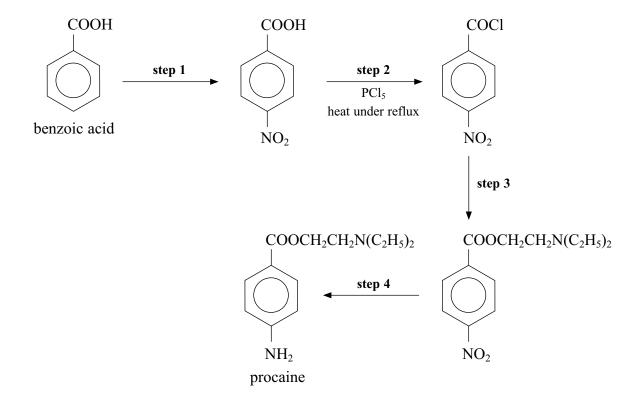
(1)

(iii) Draw the structure of the intermediate ion formed when the species in (ii) attacks the benzene ring.

(1)

	Explain how the presence of a methyl group activates the benzene ring.	(1)
(ii)	Use your answer to (i) to explain why methylbenzene reacts faster.	(1)
) (i)	Draw the structural formula of <b>compound X</b> , formed in <b>reaction 2</b> .	(1)
(ii)	The organic product of <b>reaction 2</b> is also formed when the same reactants, but with an aluminium catalyst, are heated using microwave radiation. Suggest two reasons why this technique may be considered 'greener'.	(2)
) Nar	ne reagent B needed for <b>reaction 3</b> .	

- 14 This question is about synthetically produced painkillers and anaesthetics.
  - (a) The local anaesthetic procaine can be synthesised from benzoic acid. The simplified route is shown below.



(i) Suggest the two reagents needed for **step 1**.

(2)

(ii) Draw the apparatus needed to heat under reflux in step 2.	(3)
(iii) Suggest why the reagents for the reaction in step 2 are heated	(2)
under reflux	
(iv) Give the structural formula for the organic reagent needed in step 3.	(1)
(v) What type of reaction is taking place in <b>step 4</b> ? Suggest the reagents used.	(2)
	12

(b) A student produced a sample of aspirin by the esterification of 9.40 g of 2-hydroxybenzoic acid with excess ethanoic anhydride.

$$\begin{array}{c} O \\ O \\ OH \\ \parallel \\ C \\ OH \\ + (CH_3CO)_2O \end{array} \qquad \begin{array}{c} O \\ H_3C \\ O \\ \parallel \\ C \\ OH \\ + CH_3COOH \end{array}$$

2-hydroxybenzoic acid ethanoic anhydride

aspirin

After purification by recrystallization, 7.77 g of aspirin was obtained.

 $[M_r \text{ of 2-hydroxybenzoic acid} = 138, M_r \text{ of aspirin} = 180]$ 

(i) Calculate the percentage yield obtained.

(3)

\*(ii) Outline how to purify a solid, such as aspirin, by recrystallization, using water as the solvent.

(4)

(-)
13

(iii) Explain what effect recrystallization has on the final yield.	(1)
c) Paracetamol is found in many non-prescription painkillers, often in conjunction with other compounds such as codeine.	
OH	
NHCOCH <sub>3</sub>	
paracetamol	
(i) Suggest, by name or formula, a reagent that could be used to form paracetamol from 4-aminophenol.	(1)
(ii) Suggest why sales of non-prescription painkillers, often containing paracetamol and codeine, are limited to 32 tablets.	(1)
(iii) Explain why paracetamol is only slightly soluble in water although it can form hydrogen bonds with water.	(1)
(Total for Question 14 = 21 mar	

- 15 Although platinum is very unreactive, it is used as a catalyst in catalytic converters in motor cars. Which of the following is true?
  - A It converts nitrogen oxides and carbon monoxide to nitrogen and carbon dioxide by adsorbing the reactants on its surface so weakening their bonds.
  - It converts nitrogen oxides and carbon monoxide to nitrogen and carbon dioxide by being able to change its oxidation state.
  - C It oxidizes unburnt fuel to carbon monoxide.
  - **D** It oxidizes unburnt fuel to carbon dioxide.

(Total for Question = 1 mark)

16 Which of the following gives the electronic configuration for chromium and for the Cr<sup>3+</sup> ion?

		Cr	Cr <sup>3+</sup>
×	A	$[Ar]3d^44s^2$	$[Ar]3d^34s^0$
X	В	[Ar]3d <sup>5</sup> 4s <sup>1</sup>	[Ar]3d <sup>2</sup> 4s <sup>1</sup>
X	C	[Ar]3d <sup>5</sup> 4s <sup>1</sup>	[Ar]3d <sup>3</sup> 4s <sup>0</sup>
X	D	$[Ar]3d^44s^2$	[Ar]3d <sup>1</sup> 4s <sup>2</sup>

(Total for Question = 1 mark)

	ch of the following gives the colours of solutions containing $Cr_2O_7^-$ , $CrO_4^{2-}$ , ted $Cr^{3+}$ and hydrated $Cr^{2+}$ , in this order?
<b>⋈</b> A	Yellow, orange, green, blue
⊠ B	Orange, yellow, green, blue
<b>⋈</b> C	Orange, yellow, blue, green
<b>⋈</b> D	Orange, green, yellow, blue
	(Total for Question = 1 mark)
produ	n dichromate(VI) ions, $Cr_2O_7^{2-}$ , react with iron(II) ions in acidic solution, the cts are chromium(III) ions and iron(III) ions. In what ratio do the dichromate(VI) nd the iron(II) ions react?
⊠ A	1:6
<b>⋈</b> B	1:5
	2:5
<b>■</b> D	1:3
	(Total for Question = 1 mark)
<b>19</b> The c	ompound [Pt(NH <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> ] is
$\boxtimes$ A	tetrahedral with no isomers.
$\boxtimes$ B	square planar with no isomers.
$\boxtimes$ C	tetrahedral with two isomers.
⊠ D	square planar with two isomers.
	(Total for Question = 1 mark)
<b>20</b> The h	exaaquacopper(II) ion, [Cu(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> , is blue because the water ligands
$\boxtimes A$	split the <i>p</i> -orbital energies and <i>p-p</i> electron transitions emit blue light.
$\boxtimes$ B	split the <i>d</i> -orbital energies and <i>d</i> - <i>d</i> electron transitions absorb all but blue light.
<b>区</b> C	split the <i>p</i> -orbital energies and <i>p-p</i> electron transitions absorb all but blue light.
$\square$ D	split the <i>d</i> -orbital energies and <i>d</i> - <i>d</i> electron transitions emit blue light.
	(Total for Question = 1 mark)

	that	ol and benzene are tested separately with bromine water, you would expect to see
		benzene and phenol would both decolorize bromine water.
	$\square$ B	benzene would decolorize bromine water, but phenol would not do so.
		neither benzene nor phenol would decolorize bromine water.
	$\square$ D	benzene would not decolorize bromine water, but phenol would do so.
		(Total for Question = 1 mark)
2	_	anic compound <b>X</b> is much more soluble in dilute hydrochloric acid than in water. bund <b>X</b> forms a coloured complex with aqueous copper(II) ions.
	Compo	ound X could be
	$\mathbf{X}$ A	$C_6H_5COOH$
	<ul><li>☑ A</li><li>☑ B</li></ul>	$C_6H_5COOH$ $C_6H_5NO_2$
	<b>⋈</b> B	$C_6H_5NO_2$
	<ul><li>■ B</li><li>■ C</li></ul>	$C_6H_5NO_2$ $C_6H_5NH_2$
23	<ul><li>□ B</li><li>□ C</li><li>□ D</li></ul> Which	$C_6H_5NO_2$ $C_6H_5NH_2$ $C_6H_5OH$
23	<ul><li>☑ B</li><li>☑ C</li><li>☑ D</li><li>Which benzen</li></ul>	$C_6H_5NO_2$ $C_6H_5NH_2$ $C_6H_5OH$ (Total for Question = 1 mark)  of the following shows the generation of the electrophile in the reaction of
23	<ul><li>□ B</li><li>□ C</li><li>□ D</li><li>Which benzen</li><li>□ A</li></ul>	$C_6H_5NO_2$ $C_6H_5NH_2$ $C_6H_5OH$ (Total for Question = 1 mark)  of the following shows the generation of the electrophile in the reaction of the with ethanoyl chloride in the presence of anhydrous aluminium chloride?
23	<ul><li>☑ B</li><li>☑ C</li><li>☑ D</li><li>Which benzen</li><li>☑ A</li></ul>	$C_6H_5NO_2$ $C_6H_5NH_2$ $C_6H_5OH$ (Total for Question = 1 mark)  of the following shows the generation of the electrophile in the reaction of e with ethanoyl chloride in the presence of anhydrous aluminium chloride? $CH_3COC1 + AlCl_3 \rightarrow [CH_3CO]^+ + AlCl_4^-$
3	<ul><li>□ B</li><li>□ C</li><li>□ D</li><li>Which benzen</li><li>□ A</li><li>□ B</li></ul>	$C_6H_5NO_2$ $C_6H_5NH_2$ $C_6H_5OH$ (Total for Question = 1 mark)  of the following shows the generation of the electrophile in the reaction of the with ethanoyl chloride in the presence of anhydrous aluminium chloride? $CH_3COCl + AlCl_3 \rightarrow [CH_3CO]^+ + AlCl_4^ CH_3COCl + AlCl_3 \rightarrow [CH_3CO]^- + AlCl_4^+$

**24** Which of the following reagents and conditions would enable phenylamine to be converted to the yellow dye 4-hydroxyazobenzene in a good yield?

- A Sodium nitrite, NaNO<sub>2</sub>, in concentrated HCl, between 0°C and 10°C; followed by an alkaline solution of phenol.
- Sodium nitrite, NaNO<sub>2</sub>, in concentrated HCl, between 0°C and 10°C; followed by an acidic solution of phenol.
- Sodium nitrate, NaNO<sub>3</sub>, in concentrated HCl, between 0°C and 10°C; followed by an alkaline solution of phenol.
- **D** Sodium nitrite, NaNO<sub>2</sub>, in concentrated HCl, room temperature; followed by an alkaline solution of phenol.

(Total for Question = 1 mark)

- 25 1-butylamine, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, reacts with ethanoyl chloride to form
  - $\square$  A CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>3</sub>+Cl<sup>-</sup>
  - **■ B** CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHCOCH<sub>3</sub>
  - ☑ C CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>3</sub>
  - **D** CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH(COCH<sub>3</sub>)NH<sub>2</sub>

(Total for Question = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.

- **26** The addition polymer poly(ethenol) is water-soluble. The repeating unit of poly(ethenol) is
  - $\begin{array}{c|c} \square & \mathbf{A} & & & \\ \hline & | & | \\ \hline & C & C \\ \hline & | & | \\ H & OH \end{array}$
  - $\begin{array}{c|c} \mathbf{B} & & \begin{pmatrix} \mathbf{H} & \mathbf{H} \\ | & | \\ -\mathbf{C} \mathbf{C} \\ | & | \\ \mathbf{H} & \mathbf{OH} \end{pmatrix}$
  - $\begin{array}{c|c} \square & C & \begin{pmatrix} H & OH \\ | & | \\ C C \\ | & | \\ H & OH \end{pmatrix}$

(Total for Question = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.

- 27 A white organic compound, X, is optically active and reacts with ninhydrin to give a coloured product. The structural formula of X could be
  - A CH<sub>3</sub>

  - $\begin{array}{c|c} \blacksquare & \mathbf{D} & H \\ & \downarrow \\ & C & NH_2 \\ & HOOC & H \end{array}$

(Total for Question = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.

#### **SECTION C**

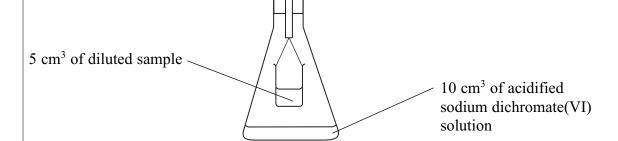
### Answer ALL the questions. Write your answers in the spaces provided.

Alcoholic drinks contain ethanol, CH<sub>3</sub>CH<sub>2</sub>OH, in aqueous solution. The percentage of alcohol in a drink can be determined by a redox titration, whilst the amount of alcohol present on the breath of someone who has consumed such a drink can be estimated using a breathalyser.

28

The earliest breathalysers used the colour change that occurs when dichromate(VI) ions react with ethanol to measure the amount of alcohol. Later models measure the current from a fuel cell. Cheaper versions of these meters are available for drivers to buy for self-testing. Some police forces also use fuel cell breathalysers in conjunction with infrared breath analysers, which can determine the amounts of alcohol from an infrared spectrum.

In an experiment to find out the concentration of ethanol in a drink, a small beaker containing 5.00 cm<sup>3</sup> of a diluted sample of the drink is suspended above 10.0 cm<sup>3</sup> of excess acidified sodium dichromate(VI) solution, of concentration 0.0800 mol dm<sup>-3</sup>, and left for 24 hours in a warm place.



The ethanol vaporizes and reacts with some of the acidified sodium dichromate(VI) ions. Excess potassium iodide is then added to the unreacted acidified sodium dichromate(VI), forming iodine,  $I_2(aq)$ .

The  $I_2(aq)$  is then titrated with a solution of sodium thiosulfate,  $Na_2S_2O_3$ , of concentration 0.0250 mol dm<sup>-3</sup>.

- (a) Ethanol and dichromate(VI) ions in acidic solution react in the mole ratio 3:2.
  - (i) Complete the two half-equations below. State symbols are **not** required.

 $Cr_2O_7^{2-}$   $\rightarrow$   $Cr^{3+}$   $CH_3CH_2OH$   $\rightarrow$   $CH_3COOH$ 

(2)

(ii) Use either the half-equations in (i) or that the mole ratio of CH<sub>3</sub>CH<sub>2</sub>OH:Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> is 3:2 to construct the ionic equation for the reaction between ethanol and acidified dichromate(VI) ions. State symbols are **not** required.

(1)

\*(iii) The iodine formed in the experiment reacted completely with 34.40 cm $^3$  of the 0.0250 mol dm $^{-3}$  sodium thiosulfate solution. Use this information, the fact that the mole ratio of CH $_3$ CH $_2$ OH:Cr $_2$ O $_7^{2-}$  is 3:2 and the equations below, to calculate the concentration of the ethanol in the 5.00 cm $^3$  of the diluted sample of the drink.

**(6)** 

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$
  
 $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$ 

	The solution used in the experiment was made by adding 10.0 cm <sup>3</sup> of the drink to a 100 cm <sup>3</sup> volumetric flask, making up the remainder of the volume using distilled water. Use the information and your final answer to (a)(iii) to calculate the concentration, in mol dm <sup>-3</sup> , of ethanol in the undiluted drink.	(1)
(v)	Suggest why the sample was suspended above the acidified sodium dichromate(VI) solution, rather than simply being mixed with it.	(1)
(vi)	Suggest two reasons why the apparatus was left in a warm place for 24 hours.	
	What would be the effect on the final result if this procedure were not followed?	(3)

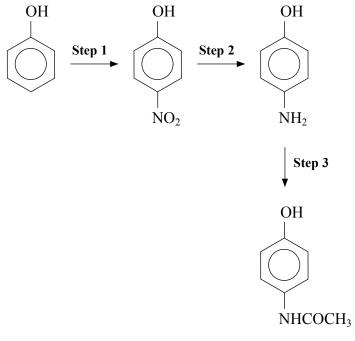
# CHERRY HILL TUITION EDEXCEL CHEMISTRY A2 PAPER 29

*(b) (i)	Explain how each type of breathalyser, mentioned in the passage, shows the amount of ethanol present.	(3)
Earliest ty	pe	
Fuel cell		
Infrared		
(ii)	Suggest why infrared breathalysers do not use the OH absorption to detect the amount of alcohol on the breath.	(1)

# CHERRY HILL TUITION EDEXCEL CHEMISTRY A2 PAPER 29

(iii) Suggest why some police forces use infrared breathalysers together with fuel cell breathalysers.	(1)
(iv) Suggest <b>one</b> advantage and <b>one</b> disadvantage of buying a personal breathalyser.	(2)
(Total for Question = 22 mark	(s)

29 Paracetamol is possibly the most widely used analgesic (painkiller) in the world. It can be made from phenol as shown below.



- Paracetamol
- (a) The nitration of phenol in **step 1** uses dilute nitric acid at room temperature, whereas the nitration of benzene requires a mixture of concentrated nitric and sulfuric acids at about 55 °C.
  - (i) Give the mechanism for the nitration of **benzene**, including the equation for the reaction that produces the electrophile.

**(4)** 

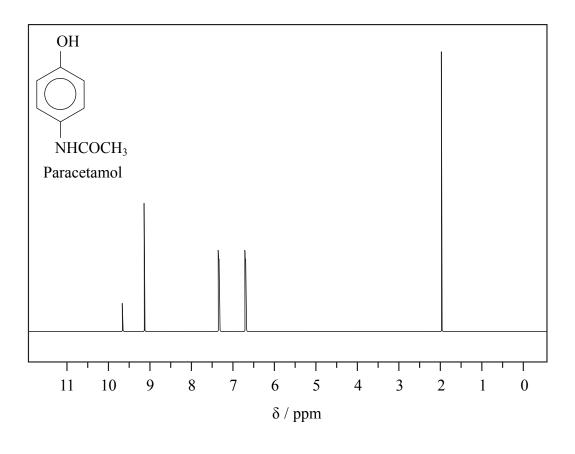
*(ii) Explain why phenol can be nitrated under much milder correquired to nitrate benzene.	onditions than those (2)
(iii) Suggest reagents that could be used for step 2.	(2)
(iv) Suggest the name or formula of a reagent that could be use	ed in <b>step 3</b> . (1)
b) In the nitration of phenol, <b>step 1</b> , two compounds are produce	rd.
$\begin{array}{c c} OH & OH \\ \hline \\ NO_2 & \\ \hline \\ NO_2 & \\ \end{array}$	
2-nitrophenol 4-nitrophenol	
These compounds can be separated by steam distillation, since volatile in steam but 4-nitrophenol is not.	2-nitrophenol is
Describe briefly the technique of steam distillation and give O distillation over normal distillation.	NE advantage of steam
distillation over normal distillation.	(3)

(c) The nmr spectrum of paracetamol is given below. The peaks at 6.7 and 7.4 ppm are due to the protons on the benzene ring and are both doublets.

Explain why these two peaks are doublets but all the other peaks are singlets.

[There is no need to refer to your data booklet]

(2)



(Total for Question = 14 marks)

	nalf of the elements in the Periodic Table are transition elements. Vanadium, is a typical transition element.	
(a) (i)	Give TWO properties shown by vanadium <b>compounds</b> that are characteristic of transition metal chemistry, other than variable oxidation state.	
		(2)
(ii)	Vanadium(III) ions in aqueous solution exist as $[V(H_2O)_6]^{3+}$ .	
	Draw this ion so as to clearly show its shape. Name the type of bond between the ligand and the vanadium ion and state the feature of the ligand that enables this bond to be formed.	
		(3)
		29

(i) Use your data booklet (page 15) to find the standard electrode (reduction) potential for the reduction of vanadium(IV), VO <sup>2+</sup> , to vanadium(III), V <sup>3+</sup> .			
		(1)	
(ii)	Explain the term disproportionation.	(2)	
 (iii)	Use your answer to (b)(i), and the data below, to calculate $E_{\text{cell}}^{\ominus}$ for the formation of vanadium(V) and vanadium(III) from vanadium(IV) in acidic solution. State		
	if the reaction is feasible under standard conditions and justify your answer.		
	$VO_2^+(aq) + 2H^+(aq) + e^- \Longrightarrow VO^{2+}(aq) + H_2O(1)$ $E^{\oplus} = +1.00 \text{ V}$	(2)	
	(Total for Question = 10 marks	s)	

#### **SECTION C**

### Answer ALL the questions. Write your answers in the spaces provided.

31

A major function of the chemical industry is the manufacture of perfumes and flavourings. Perfumes were originally made from natural products, such as spermaceti from whales or civetone from the civet cat. The use of synthetic equivalents is generally cheaper and the supply is more reliable, and does not require the animals to be killed which obtaining spermaceti did. Synthetic perfumes and flavourings are usually nature-identical, although naturally-occurring molecules that have stereoisomers are sometimes produced synthetically as mixtures since the stereospecific synthesis required might be difficult to achieve economically.

Some chiral molecules have a different taste depending on which enantiomer is present. The enantiomer (–)-carvone tastes and smells of spearmint, and its mirror-image, (+)-carvone, of caraway or dill. In some cases only one enantiomer has any taste; this is true for glucose. The mirror image molecule of naturally occurring glucose has no taste and cannot even be absorbed or metabolized. Many drug molecules are chiral, though paracetamol is not. The wrong isomer present in a drug may be positively damaging, which was the case with thalidomide. In order to synthesize optically-pure drug molecules, it is important to understand the mechanism of any reaction used. Using an  $S_{\rm N}1$  reaction which involves the chiral centre would result in the product mixture being racemic. It is advantageous to use stereospecific catalysts wherever possible, and industry on the whole prefers to use heterogeneous rather than homogeneous catalysts.

(a) The skeletal formula of carvone is shown below. Draw a circle around the chiral carbon atom.

(1)

	find the standard electrode (reduction) $lium(IV)$ , $VO^{2+}$ , to vanadium(III), $V^{3+}$ .
1	(1)
(ii) Explain the term <b>disproportionation</b>	on. (2)
(iii) Use your answer to (b)(i), and the of vanadium(V) and vanadium(III)	data below, to calculate $E_{\text{cell}}^{\ominus}$ for the formation from vanadium(IV) in acidic solution. State
if the reaction is feasible under stan	ndard conditions and justify your answer.
	ndard conditions and justify your answer.
if the reaction is feasible under stan	ndard conditions and justify your answer. $E^{+}(aq) + H_2O(l)$ $E^{\oplus} = + 1.00 \text{ V}$
if the reaction is feasible under stan	ndard conditions and justify your answer. $E^{+}(aq) + H_2O(l)$ $E^{\oplus} = + 1.00 \text{ V}$

1	(1)		1 1 1	:		- C
(	a	Carvone can	ne reaucea	ın a	variety	or wavs
١		- C C C	~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~		,,	01

(i) On reduction with hydrogen, in the presence of a platinum catalyst, 4.5 g of carvone reacted with 1.44 dm<sup>3</sup> of hydrogen. Use these data to deduce the skeletal formula of the reduction product.

[Molar mass of carvone is 150 g mol<sup>-1</sup>; molar volume of hydrogen at the temperature and pressure of the experiment is 24 dm³ mol<sup>-1</sup>.]

(3)

# Working

Hence skeletal formula of reduction product.

(ii)	Reduction of carvone, using hydrazine in potassium hydroxide solution, gives limonene.
	How would you show from a comparison of the infra-red spectra of carvone and of limonene that this reduction had occurred? You should quote appropriate data, from the data booklet, to support your answer.  (2)

Draw the skeletal formula of the molecule that would be obtained if carvone were to be reacted with an excess of hydrogen bromide in an inert solvent.	(2)
If the product from (e)(i) were to be heated with ethanolic potassium hydroxide solution, elimination would occur and HBr would be lost. Would the resulting molecule necessarily be carvone? Explain your answer.	(2)
	Were to be reacted with an excess of hydrogen bromide in an inert solvent.  If the product from (e)(i) were to be heated with ethanolic potassium hydroxide solution, elimination would occur and HBr would be lost. Would the resulting

	(Total for Question = 23 ma	
(ii)	Suggest why industrial chemists prefer to use heterogeneous rather than homogeneous catalysts.	(1)
		(5)
	of the starting material. Explain what your mechanism predicts about the stereochemistry of the product.	