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the half-reaction for the reduction is  A MnO <sub>4</sub> <sup>-</sup> + 4H <sup>+</sup> + 3e <sup>-</sup> → MnO <sub>2</sub> + 2H <sub>2</sub> O  B MnO <sub>4</sub> <sup>-</sup> + 4H <sup>+</sup> + 5e <sup>-</sup> → Mn <sup>2+</sup> + 2H <sub>2</sub> O  C MnO <sub>4</sub> <sup>-</sup> + 8H <sup>+</sup> + 3e <sup>-</sup> → Mn <sup>2+</sup> + 4H <sub>2</sub> O  D MnO <sub>4</sub> <sup>-</sup> + 8H <sup>+</sup> + 5e <sup>-</sup> → Mn <sup>2+</sup> + 4H <sub>2</sub> O  In the titration of iodine with standard sodium thiosulfate solution, starch is often used as an indicator. The starch should <b>not</b> be added until nearly all the iodine has reacted because  A it is decomposed by high concentrations of iodine.  B the blue complex formed is bleached by high concentrations of iodine.  C the blue complex formed with high concentrations of iodine is insoluble and does not re-dissolve as more thiosulfate is added.  D the starch reacts with the thiosulfate ions being added.  (Total for Question 2 = 1 mar  The conditions needed for the E <sup>⊕</sup> value of the standard hydrogen electrode to be exactly 0 V are  A 1 mol dm <sup>-3</sup> solution of hydrogen ions, 1 atm pressure of hydrogen, 25°C.  B 1 mol dm <sup>-3</sup> solution of hydrogen ions, 1 atm pressure of hydrogen, room temperature.  C 1 mol dm <sup>-3</sup> solution of hydrogen ions, 1 atm pressure of hydrogen, 25°C.  D 0.1 mol dm <sup>-3</sup> solution of hydrogen ions, 1 atm pressure of hydrogen, 25°C.	the half-reaction for the reduction is  A MnO <sub>4</sub> <sup>-</sup> + 4H <sup>+</sup> + 3e <sup>-</sup> → MnO <sub>2</sub> + 2H <sub>2</sub> O  B MnO <sub>4</sub> <sup>-</sup> + 4H <sup>+</sup> + 5e <sup>-</sup> → Mn <sup>2+</sup> + 2H <sub>2</sub> O  C MnO <sub>4</sub> <sup>-</sup> + 8H <sup>+</sup> + 3e <sup>-</sup> → Mn <sup>2+</sup> + 4H <sub>2</sub> O  D MnO <sub>4</sub> <sup>-</sup> + 8H <sup>+</sup> + 5e <sup>-</sup> → Mn <sup>2+</sup> + 4H <sub>2</sub> O  (Total for Question 1 = 1 mar  2 In the titration of iodine with standard sodium thiosulfate solution, starch is often used as an indicator. The starch should not be added until nearly all the iodine has reacted because  A it is decomposed by high concentrations of iodine.  B the blue complex formed is bleached by high concentrations of iodine.  C the blue complex formed with high concentrations of iodine is insoluble and does not re-dissolve as more thiosulfate is added.  D the starch reacts with the thiosulfate ions being added.  (Total for Question 2 = 1 mar  3 The conditions needed for the E <sup></sup> value of the standard hydrogen electrode to be exactly 0 V are  A 1 mol dm <sup>-3</sup> solution of hydrogen ions, 1 atm pressure of hydrogen, 25 °C.  B 1 mol dm <sup>-3</sup> solution of hydrogen ions, 1 atm pressure of hydrogen, room temperature.  C 1 mol dm <sup>-3</sup> solution of hydrogen ions, laboratory pressure of hydrogen, 25 °C.  D 0.1 mol dm <sup>-3</sup> solution of hydrogen ions, 1 atm pressure of hydrogen, 25 °C.			SECTION A
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<ul> <li>■ B 1 mol dm<sup>-3</sup> solution of hydrogen ions, 1 atm pressure of hydrogen, room temperature.</li> <li>■ C 1 mol dm<sup>-3</sup> solution of hydrogen ions, laboratory pressure of hydrogen, 25 °C.</li> <li>■ D 0.1 mol dm<sup>-3</sup> solution of hydrogen ions, 1 atm pressure of hydrogen, 25 °C.</li> </ul>	<ul> <li>■ B 1 mol dm<sup>-3</sup> solution of hydrogen ions, 1 atm pressure of hydrogen, room temperature.</li> <li>■ C 1 mol dm<sup>-3</sup> solution of hydrogen ions, laboratory pressure of hydrogen, 25 °C.</li> <li>■ D 0.1 mol dm<sup>-3</sup> solution of hydrogen ions, 1 atm pressure of hydrogen, 25 °C.</li> </ul>	3		· · · · · · · · · · · · · · · · · · ·
temperature.  ☑ C 1 mol dm <sup>-3</sup> solution of hydrogen ions, laboratory pressure of hydrogen, 25 °C.  ☑ D 0.1 mol dm <sup>-3</sup> solution of hydrogen ions, 1 atm pressure of hydrogen, 25 °C.	temperature.  ☐ C 1 mol dm <sup>-3</sup> solution of hydrogen ions, laboratory pressure of hydrogen, 25 °C.  ☐ D 0.1 mol dm <sup>-3</sup> solution of hydrogen ions, 1 atm pressure of hydrogen, 25 °C.		$\boxtimes A$	1 mol dm <sup>-3</sup> solution of hydrogen ions, 1 atm pressure of hydrogen, 25 °C.
■ D 0.1 mol dm <sup>-3</sup> solution of hydrogen ions, 1 atm pressure of hydrogen, 25°C.	■ D 0.1 mol dm <sup>-3</sup> solution of hydrogen ions, 1 atm pressure of hydrogen, 25°C.		<b>⊠</b> B	
			$\boxtimes$ C	1 mol dm <sup>-3</sup> solution of hydrogen ions, laboratory pressure of hydrogen, 25 °C.
	(Total for Question 3 = 1 mar		⊠ D	0.1 mol dm <sup>-3</sup> solution of hydrogen ions, 1 atm pressure of hydrogen, 25°C.
(Total for Question 3 = 1 mar				(Total for Question 3 = 1 mar

Turn over ▶

$\square$ <b>A</b> $E_{\text{cell}}^{\ominus}$ i	s propo	rtional t	to ln K.				
		rtional t					
		portiona		<i>K</i> .			
		portiona					
						(1	Total for Question 4 = 1 mark)
Which of the ome from a				ionizatio	on energi	es (valu	es in kJ mol <sup>-1</sup> ) could have
<b>■ A</b> 496	4563	6913	9544	13352	16611	20115	25941
<b>■ B</b> 590	1145	4912	6474	8144	10496	12320	14207
<b>ℂ</b> 717	1509	3249	4940	6985	9200	11508	18956
<b>■ D</b> 2081	3952	6122	9370	12177	15239	19999	23069
						(7)	Total for Question 5 = 1 mark)
Although plat notor cars. W		-			ised as a	catalyst	t in catalytic converters in
		_					nitrogen and carbon dioxide ing their bonds.
oy aa	_						
B It con		_		and cart oxidation		oxide to	nitrogen and carbon dioxide
B It comby be	ing able	e to chai	nge its	oxidatio			nitrogen and carbon dioxide
<ul><li>B It comby be</li><li>C It oxi</li></ul>	ing able	e to char	nge its uel to c	oxidatio	on state. nonoxide		nitrogen and carbon dioxide
<ul><li>B It comby be</li><li>C It oxi</li></ul>	ing able	e to char	nge its uel to c	oxidation carbon n	on state. nonoxide	<b>.</b>	nitrogen and carbon dioxide  Total for Question 6 = 1 mark)
B It comby be  C It oxi  D It oxi	ing able	e to chai	nge its	oxidatic earbon n earbon d	on state.  nonoxide.	<b>(</b> 1	
B It comby be  C It oxi  D It oxi	ing able	e to chai	nge its	oxidatic earbon n earbon d	on state.  nonoxide.	<b>(</b> 1	Total for Question 6 = 1 mark)
B It comby be C It oxi D It oxi	ing able	e to char nburnt fi nburnt fi	nge its fuel to contain the contains the el	oxidatic earbon n earbon d	on state.  nonoxide.  ioxide.  configu	<b>(</b> 1	Total for Question 6 = 1 mark)
B It comby be C It oxi D It oxi Which of the	dizes ur dizes ur followin	e to char nburnt fi nburnt fi ng gives	inge its fuel to constitute to constitute to $\frac{1}{4}$	earbon dearbon	on state.  nonoxide.  ioxide.  configu  Cr <sup>3+</sup>	<b>(</b> 1	Total for Question 6 = 1 mark)
B It comby be C It oxi D It oxi Which of the	dizes ur dizes ur followin	e to char  aburnt fin  ang gives  Cr  [Ar]3d4	inge its fuel to constitute to constitute to constitute to $\frac{1}{4}$	earbon dearbon	on state.  nonoxide.  ioxide.  configu $Cr^{3+}$ $r]3d^34s^0$	<b>(</b> 1	Total for Question 6 = 1 mark)
B It comby be C It oxi D It oxi Which of the	dizes ur dizes ur following	e to char nburnt fin nburnt fin ng gives  Cr  [Ar]3d <sup>4</sup> [Ar]3d <sup>5</sup>	inge its uel to contain the element $4s^2$ $4s^1$ $4s^1$	earbon dearbon	on state.  nonoxide.  configu  Cr <sup>3+</sup> r]3d <sup>3</sup> 4s <sup>0</sup> r]3d <sup>2</sup> 4s <sup>1</sup>	<b>(</b> 1	Total for Question 6 = 1 mark)

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	$\mathbf{X}$ A	Yellow, orange, green, blue
	$\boxtimes$ B	Orange, yellow, green, blue
	<b>区</b> C	Orange, yellow, blue, green
	<b>■</b> D	Orange, green, yellow, blue
		(Total for Question 8 = 1 mark
9	produc	dichromate(VI) ions, $Cr_2O_7^{2-}$ , react with iron(II) ions in acidic solution, the ets are chromium(III) ions and iron(III) ions. In what ratio do the dichromate(VI) and the iron(II) ions react?
	⊠ A	1:6
	<b>⋈</b> B	1:5
	<b>区</b> C	2:5
	<b>■</b> D	1:3
_		(Total for Question 9 = 1 mark
10	The co	ompound $[Pt(NH_3)_2Cl_2]$ is
	$\boxtimes$ A	tetrahedral with no isomers.
	$\boxtimes$ B	square planar with no isomers.
	<b>区</b> C	tetrahedral with two isomers.
	$\boxtimes$ <b>D</b>	square planar with two isomers.
_		(Total for Question 10 = 1 mark
11	The he	exaaquacopper(II) ion, $[Cu(H_2O)_6]^{2+}$ , is blue because the water ligands
	$\mathbf{X}$ A	split the <i>p</i> -orbital energies and <i>p-p</i> electron transitions emit blue light.
	$\square$ B	split the <i>d</i> -orbital energies and <i>d-d</i> electron transitions absorb all but blue light.
	<b>■</b> C	split the <i>p</i> -orbital energies and <i>p-p</i> electron transitions absorb all but blue light.
	<b>■</b> D	split the <i>d</i> -orbital energies and <i>d-d</i> electron transitions emit blue light.
		(Total for Question 11 = 1 mark

Turn over ▶

$\mathbf{X}$ A	benzene and phenol would both decolorize bromine water.
<b>■</b> B	benzene would decolorize bromine water, but phenol would not do so.
⊠ C	neither benzene nor phenol would decolorize bromine water.
$\boxtimes$ D	benzene would not decolorize bromine water, but phenol would do so.
	(Total for Question 12 = 1 mark)
	ganic compound $X$ is much more soluble in dilute hydrochloric acid than in water, bund $X$ forms a coloured complex with aqueous copper(II) ions.
Comp	ound <b>X</b> could be
⊠ A	C <sub>6</sub> H <sub>5</sub> COOH
⊠ B	$C_6H_5NO_2$
<b>■ C</b>	$C_6H_5NH_2$
$\boxtimes$ <b>D</b>	$C_6H_5OH$
	(Total for Question 13 = 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?
$\boxtimes A$	$CH_3COCl + AlCl_3 \rightarrow [CH_3CO]^+ + AlCl_4^-$
	$CH_3COCl + AlCl_3 \rightarrow [CH_3CO]^- + AlCl_4^+$
$\blacksquare$ B	$C113COCI + AIC13 \rightarrow [C113CO] + AIC14$
	$CH_{3}CH_{2}Cl + AlCl_{3} \rightarrow [CH_{3}CH_{2}]^{+} + AlCl_{4}^{-}$ $CH_{3}CH_{2}Cl + AlCl_{3} \rightarrow [CH_{3}CH_{2}]^{+} + AlCl_{4}^{-}$

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15	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, NaNO₂, 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 15 = 1 mark)

- 16 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><sup>+</sup>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>
  - $\square$  **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 16 = 1 mark)

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

5

17 The add is	ition polymer poly(ethenol) is water-soluble. The repeating unit of poly(ethenol)	
<b>△</b> A	OH H	_
<b>⊠</b> B	$ \begin{array}{c c} H & H \\                                $	
☑ C		_
⊠ D	OH OH	_
	(Total for Question 17 = 1 mark)	
	(Total for Question 17 = 1 mark)	
	(Total for Question 17 = 1 mark)	
	(Total for Question 17 = 1 mark)	
	(Total for Question 17 = 1 mark)	
	(Total for Question 17 = 1 mark)	
	(Total for Question 17 = 1 mark)	
	(Total for Question 17 = 1 mark)	

18 A white organic compound, X, is optically active and reacts with ninhydrin to give a coloured product. The structural formula of X could be

- $lacksquare{\mathbb{Z}}$   $lacksquare{\operatorname{CH}_3}$   $lacksquare{\operatorname{CH}_3}$   $lacksquare{\operatorname{CH}_3}$
- $\begin{tabular}{c|c} \end{tabular} \begin{tabular}{c|c} CH_3 \\ \hline & & \\ \hline & &$

(Total for Question 18 = 1 mark)

7

Turn over ▶

	e, H <sub>2</sub> NCH <sub>2</sub> COOH, is a solid that has a melting temperature of about 250°C, and ry soluble in water. This is because of the	
<b>⋈ A</b>	formation of intermolecular hydrogen bonds in the solid and hydrogen bonds with water.	_
⊠ B	formation of H <sub>3</sub> N <sup>+</sup> CH <sub>2</sub> COO <sup>-</sup> ions which interact strongly with each other in the solid and with water.	
<b>☒</b> C	dissociation of the molecule to form $\rm H_2NCH_2COO^-$ and $\rm H^+$ ions in the solid and the solution.	
<b>■ D</b>	protonation of the molecule to form $H_3N^+CH_2COOH$ ions in both the solid and the solution.	
	(Total for Question 19 = 1 mark)	
20 Organic that	c solids are often purified by recrystallization. This technique works on the basis	
$\boxtimes A$	the impurities must be insoluble in the solvent used.	_
$\blacksquare$ B	the impurities must react with the solvent used.	_
	the impurities crystallize first when the hot solution is cooled.	_
<b>■</b> D	the cooled solution is saturated with the desired material but not with the impurities.	
	(Total for Question 20 = 1 mark)	
	TOTAL FOR SECTION A = 20 MARKS	

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# **SECTION B**

21 Brass is an alloy of copper, zinc and, in some cases, other metals too. There are over 30 varieties of brass for different applications.

The amount of copper in a brass can be found as follows:

- A weighed sample of brass is reacted with the minimum amount of concentrated nitric acid.
- The solution is neutralized, a portion of it pipetted into a conical flask, and excess potassium iodide solution is added.
- The iodine produced is titrated with a solution of sodium thiosulfate of known concentration.
- (a) The ionic equation for the reaction between copper metal and concentrated nitric acid is shown below.

$$Cu(s) + 2NO_3^-(aq) + 4H^+(aq) \rightarrow Cu^{2+}(aq) + 2NO_2(g) + 2H_2O(l)$$

(i) Give the oxidation numbers of the copper and nitrogen in both the reactants and products.

(2)

Copper: from	to	
Nitrogen: from	to	

(ii) Write the two half-equations that can be combined to give the ionic equation shown above.

(2)

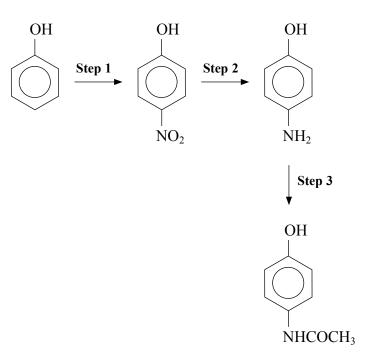
9

(iii)	Explain why the standard electrode potentials for the two ionic half-equations that you have written give an incorrect value for $E_{\rm cell}$ for this reaction as described above.	(2)
	solution produced contains a mixture of zinc ions and copper ions.  State TWO observations that you would <b>see</b> if concentrated ammonia solution were to be added, drop by drop, to the solution until in excess.	(2)
(ii) <b>Equation</b> 1	Copper ions can be separated from the zinc ions in the solution by adding sodium hydroxide solution in excess, followed by filtration of the mixture.  Write equations, including state symbols, for the THREE reactions that occur.	(3)
Equation 2		
Equation 3	3	

*(iii)	Give examples of amphoteric behaviour and ligand exchange, by reference to the reactions of zinc compounds.	(3)
up t 25.0	ample of Admiralty Brass of mass 3.00 g was treated with nitric acid and made of a neutral solution of volume 250 cm <sup>3</sup> . Excess potassium iodide was added to 0 cm <sup>3</sup> portions of this solution, and the liberated iodine was titrated with sodium sulfate solution, concentration 0.100 mol dm <sup>-3</sup> . The mean titre was 33.10 cm <sup>3</sup> .	
(i)	Write the ionic equation for the reaction between thiosulfate ions and iodine.	(1)
*(ii)	The equation for the reaction between copper(II) ions and iodide ions is shown below.	
	$2Cu^{2+} + 4I^{-} \rightarrow 2CuI + I_{2}$	
	Hence calculate the percentage by mass of copper in Admiralty Brass. Give your answer to <b>three</b> significant figures.	
		(6)

(iii) When setting up the burette, a student failed to fill the jet of the burette. Explain the effect that this would have on the value of the first titre.	
If this first titre was included in the calculation of the mean titre, what effect would this have on the value for the percentage of copper in the brass?	(2)
(Total for Question 21 = 23 m	arks)

**22** 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 conditions than those required to nitrate benzene.	(2)
(iii) Suggest reagents that could be used for <b>step 2</b> .	(2)
(iv) Suggest the name or formula of a reagent that could be used in <b>step 3</b> .	(1)
*(b) In the nitration of phenol, step 1, two compounds are produced. $ \begin{array}{c} OH \\ \hline \\ NO_2 \\ \hline \\ NO_2 \\ \end{array} $	
<b>2-nitrophenol</b> These compounds can be separated by steam distillation, since 2-nitrophenol is volatile in steam but 4-nitrophenol is not.	
Describe briefly the technique of steam distillation and give ONE advantage of steadistillation over normal distillation.	am (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) ОН NHCOCH<sub>3</sub> Paracetamol 11 10 3 2  $\delta$  / ppm (Total for Question 22 = 14 marks)

(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)

potential for the reduction of vanadium(IV), VO <sup>2+</sup> , to vanadium(III), V <sup>3+</sup> (iii) Explain the term <b>disproportionation.</b> (iii) Use your answer to (b)(i), and the data below, to calculate $E_{\text{cell}}^{\ominus}$ for the foof vanadium(V) and vanadium(III) from vanadium(IV) in acidic solution if the reaction is feasible under standard conditions and justify your answ VO <sub>2</sub> <sup>+</sup> (aq) + 2H <sup>+</sup> (aq) + e <sup>-</sup> $\rightleftharpoons$ VO <sup>2+</sup> (aq) + H <sub>2</sub> O(l) $E^{\ominus}$ = + 1.00 V	(2) ormation a. State ver.
(iii) Use your answer to (b)(i), and the data below, to calculate $E_{\text{cell}}^{\ominus}$ for the foof vanadium(V) and vanadium(III) from vanadium(IV) in acidic solution if the reaction is feasible under standard conditions and justify your answer.	ormation a. State ver.
of vanadium(V) and vanadium(III) from vanadium(IV) in acidic solution if the reaction is feasible under standard conditions and justify your answer.	a. State ver.
	(2)
	(2)
(Total for Question 23 =	10 marks)
TOTAL FOR SECTION B = 4	7 MARKS

### **SECTION C**

24

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)

18

single enantiomer such as (–)-carvone.	(3)
c) Carvone contains two types of functional group. For each of these, give a suitable chemical test to show its presence, and state what you would see in each case.	
	(4)

(d) Carvone can be reduced in a variety of ways.		
(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 dm <sup>3</sup> mol <sup>-1</sup> .]	(3)	
Working	(3)	
Honor skolatel formula of reduction product		
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)

(e) (i)	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.	
	The second control of the second of the seco	(2)
(::)	If the new death from (a)(i) to be the death of the other in the description becomes its	
(11)	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	
	solution, elimination would occur and HBr would be lost. Would the resulting molecule necessarily be carvone? Explain your answer.	
	solution, elimination would occur and HBr would be lost. Would the resulting	(2)
	solution, elimination would occur and HBr would be lost. Would the resulting	
	solution, elimination would occur and HBr would be lost. Would the resulting	
	solution, elimination would occur and HBr would be lost. Would the resulting	(2)
	solution, elimination would occur and HBr would be lost. Would the resulting molecule necessarily be carvone? Explain your answer.	(2)
	solution, elimination would occur and HBr would be lost. Would the resulting molecule necessarily be carvone? Explain your answer.	(2)
	solution, elimination would occur and HBr would be lost. Would the resulting molecule necessarily be carvone? Explain your answer.	(2)
	solution, elimination would occur and HBr would be lost. Would the resulting molecule necessarily be carvone? Explain your answer.	(2)
	solution, elimination would occur and HBr would be lost. Would the resulting molecule necessarily be carvone? Explain your answer.	(2)
	solution, elimination would occur and HBr would be lost. Would the resulting molecule necessarily be carvone? Explain your answer.	(2)
	solution, elimination would occur and HBr would be lost. Would the resulting molecule necessarily be carvone? Explain your answer.	(2)
	solution, elimination would occur and HBr would be lost. Would the resulting molecule necessarily be carvone? Explain your answer.	(2)
	solution, elimination would occur and HBr would be lost. Would the resulting molecule necessarily be carvone? Explain your answer.	(2)
	solution, elimination would occur and HBr would be lost. Would the resulting molecule necessarily be carvone? Explain your answer.	(2)

, ()	Give the mechanism of one nucleophilic reaction of your choice, which <b>either</b> gives rise to a racemic mixture <b>or</b> results in the inversion of the chirality of the starting material. Explain what your mechanism predicts about the stereochemistry of the product.	
	or me product.	(5)
(ii)	Suggest why industrial chemists prefer to use heterogeneous rather than	
	homogeneous catalysts.	(1)
	(Total for Question 24 = 23 ma	rks)
	TOTAL FOR SECTION C = 23 MAI	RKS

	mock p	papers 2			
	SECTION A				
1	What type of bonding occurs between the metal ion and ligand in the complex ion $[Cu(H_2O)_6]^{2+}$ ?				
	$\boxtimes \mathbf{A}$	Metallic			
	⊠ B	Ionic			
	<b>区</b> C	Hydrogen			
	⊠ D	Dative covalent			
_		(Total for Question 1 = 1 mark)			
	VV/la i a la	of these form and a soid, could not note the alone of alone a classical light?			
2		of these four amino acids could <b>not</b> rotate the plane of plane-polarised light?			
	■ A	H <sub>2</sub> NCH(CH <sub>3</sub> )COOH			
	■ B	H <sub>2</sub> NCH(CH <sub>2</sub> COOH)COOH			
	☑ C	H <sub>2</sub> NCH <sub>2</sub> COOH			
	<b>■</b> D	H <sub>2</sub> NCH(CH <sub>2</sub> SH)COOH			
-		(Total for Question 2 = 1 mark)			
3	In the	solid state, the amino acid serine exists in the form			
	$\boxtimes \mathbf{A}$	$H_3N^+CH(CH_2OH)COOH$			
	⊠ B	$H_3N^+CH(CH_2OH)CO_2^-$			
	⊠ C	H <sub>2</sub> NCH(CH <sub>2</sub> OH)COOH			
	⊠ D	H <sub>2</sub> NCH(CH <sub>2</sub> OH)CO <sub>2</sub> <sup>-</sup>			
_		(Total for Question 3 = 1 mark)			
	The be	est mothed for computing a minimum of amina acida in colution is			
4		est method for separating a mixture of amino acids in solution is			
	■ A	distillation.			
	■ B	solvent extraction.			
	<b>■ C</b>	chromatography.			
	$\times$ <b>D</b>	recrystallization.			

(Total for Question 4 = 1 mark)

5		any different peaks due to hydrogen atoms would you expect to see in a <b>low</b> ion proton nmr spectrum of propanoic acid, CH <sub>3</sub> CH <sub>2</sub> COOH?	
	$\boxtimes A$	Two	
	$\boxtimes$ B	Three	
		Five	
	$\square$ D	Six	
		(Total for Question 5 = 1 mark)	
6	In a <b>high resolution</b> proton nmr spectrum of ethanoic acid, CH <sub>3</sub> COOH, the peak due to the hydrogen atoms in the methyl group would be a		
	$\boxtimes A$	singlet.	
	$\boxtimes$ B	doublet.	
	<b>区</b> C	triplet.	
	$\boxtimes$ <b>D</b>	quartet.	
		(Total for Question 6 = 1 mark)	
7	Which	of these compounds will <b>not</b> form an amide in a reaction with ethanoyl chloride?	
	$\boxtimes A$	$NH_3$	
	$\boxtimes$ B	CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	
	$\mathbf{K}$ C	$CH_3CH_2NH(CH_3)$	
	_	CH <sub>3</sub> CH <sub>2</sub> NH(CH <sub>3</sub> ) CH <sub>3</sub> CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub>	
	_		
_	_ D	$CH_3CH_2N(CH_3)_2$	
	_ D	CH <sub>3</sub> CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub> (Total for Question 7 = 1 mark)	
	_ D	CH <sub>3</sub> CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub> (Total for Question 7 = 1 mark)	
	_ D	CH <sub>3</sub> CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub> (Total for Question 7 = 1 mark)	
	_ D	CH <sub>3</sub> CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub> (Total for Question 7 = 1 mark)	
	_ D	$CH_3CH_2N(CH_3)_2$ (Total for Question 7 = 1 mark)	
	_ D	$CH_3CH_2N(CH_3)_2$ (Total for Question 7 = 1 mark)	

8	This question concerns the following organic compounds.	
	A CH <sub>3</sub> COCl	
	<b>B</b> CH₃COOH	
	C CH <sub>3</sub> COOCH <sub>2</sub> CH <sub>3</sub>	
	$\mathbf{D}$ C <sub>6</sub> H <sub>5</sub> OH	
	Which compound is most likely to	
	(a) form the solution with the lowest pH when mixed with water?	(1)
	lacksquare A	
	$\blacksquare$ <b>B</b>	
	$\square$ D	
	(b) burn with a smoky flame?	(1)
	$oxed{\square}$ A	
	lacksquare B	
	<b>□ C</b>	
	$\square$ D	
	(c) have a fruity smell?	(1)
	lacksquare A	(1)
	<b>■ B</b>	
	<b>□ C</b>	
	lacksquare D	
	(d) have an absorption in its IR spectrum at about 1795 cm <sup>-1</sup> ?	(1)
	lacksquare A	(-)
	$\square$ B	
	ightharpoons D	
	(Total for Question 8 = 4 ma	rks)

9 This question is about the reaction scheme below.

$$\begin{array}{c|c} Cl & Cl & Cl \\ \hline step 1 & Step 2 & Step 3 & NH_2 \\ \hline NO_2 & NH_2 & Step 4 & Cl & NH_2 \\ \hline \end{array}$$

Which step is most likely to need

(a) tin and concentrated hydrochloric acid?

(1)

- A Step 1
- **■ B** Step 2
- C Step 3
- D Step 4
- (b) a catalyst of iron(III) chloride?

(1)

- A Step 1
- **B** Step 2
- C Step 3
- **D** Step 4
- (c) a nickel catalyst?

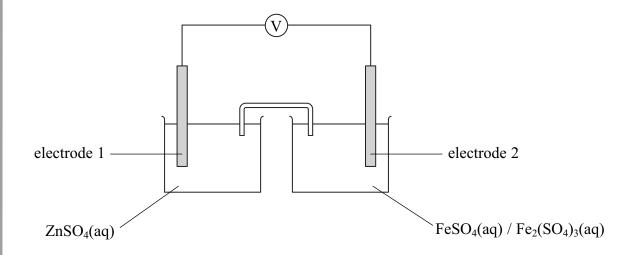
(1)

- A Step 1
- **■ B** Step 2
- C Step 3
- **D** Step 4

(Total for Question 9 = 3 marks)

10 The apparatus below can be used to measure the value of  $E_{\rm cell}$  for the reaction

$$2Fe^{3+}(aq) + Zn(s) \rightarrow 2Fe^{2+}(aq) + Zn^{2+}(aq)$$



The electrodes are:

		electrode 1	electrode 2
X	A	zinc	iron
X	В	iron	zinc
X	C	zinc	platinum
X	D	platinum	platinum

(Total for Question 10 = 1 mark)

11 Copper reacts with silver ions according to the reaction below.

$$Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

 $E_{\text{cell}}^{\ominus}$  for this reaction is

- **■ A** +0.46 V
- $\blacksquare$  **B** +1.14 V
- **≅ C** +1.26 V
- **D** +1.94 V

(Total for Question 11 = 1 mark)

12  $E_{\text{cell}}^{\oplus}$  for four reactions are shown in the table below.

	$E_{ m cell}^{\oplus}$ / $ m V$
Reaction 1	+1.10
Reaction 2	+0.65
Reaction 3	+0.10
Reaction 4	-1.30

Which reaction

(a) is thermodynamically not feasible?

(1)

- **A** Reaction 1
- **B** Reaction 2
- C Reaction 3
- **D** Reaction 4
- (b) has the largest value for  $\ln K$ ?

(1)

- A Reaction 1
- **B** Reaction 2
- C Reaction 3
- **D** Reaction 4

(Total for Question 12 = 2 marks)

13 Consider the reaction scheme below and calculate the mass of aspirin you would expect to form if you started with 47 g of phenol.

OH OCOCH<sub>3</sub>

$$CO_2H$$

$$step 1$$

$$yield 85\%$$

$$Step 2$$

$$yield 80\%$$

$$aspirin, M_r = 180$$

- **△ A** 31.96 g
- **B** 61.20 g
- **☑ C** 74.25 g
- **D** 90.00 g

(Total for Question 13 = 1 mark)

14 Which of the monomers A to D would form the polymer below?

$$\begin{bmatrix} & CH_3 & C_2H_5 \\ & & & \\ & & & \\ & & C & C \\ & & & \\ & & C1 & H \end{bmatrix}_n$$

 $\triangle$  A

Cl B

Cl

Cl Cl

Cl D

(Total for Question 14 = 1 mark)

**TOTAL FOR SECTION A = 20 MARKS** 

#### **SECTION B**

15 In the reaction shown below, the aromatic compound 1,4-dimethylbenzene reacts with 2-bromobutane. The reaction is catalysed by aluminium chloride, AlCl<sub>3</sub>, which dissolves in the reaction mixture.

$$\begin{array}{c|cccc} CH_3 & CH_3 & CH_3 \\ \hline & & & \\ \hline & & \\ \hline & & \\ CH_3CH(Br)CH_2CH_3 \\ \hline & & \\ \hline & & \\ CH_3 & & \\ \hline & \\ \hline & &$$

1,4-dimethylbenzene

(a) (i) Name the type of reaction and the mechanism.

(1)

(ii) Write the equation to show how the attacking species forms and give the mechanism for the reaction.

(4)

# **Equation**

### Mechanism

(b) The same reaction can also be carrunder similar conditions. Assumir suggest one advantage of using the chloride. Justify your answer.	e and yield,
omonus, custily your union on	(2)
(c) A student proposed to synthesise t the manufacture of dyes, following	mine, used in
CH <sub>3</sub>	
	$NH_2$
step 1	
$\overset{ extsf{l}}{ ext{CH}_3}$	
1,4-dimethylbenzene	lamine

(i)	What two	reagents	are	needed	for	step	1
-----	----------	----------	-----	--------	-----	------	---

(2)

(ii) Suggest why 1,4-dimethylbenzene is more reactive than benzene in reactions such as **step 1**.

(2)

(iii) What type of reaction occurs in step 2?	(1)
*(iv) 2,5-dimethylphenylamine can be used to make azo-dyes. State the reagents and conditions needed to make an azo-dye from 2,5-dimethylphenylamine and phenol. Include equations for the organic reactions.	(5)
(Total for Question 15 = 17 ma	rks)

- 16 The leaves of the rhubarb plant contain ethanedioic acid, (COOH)<sub>2</sub>, a toxic white soluble solid. The acid is readily oxidized by potassium manganate(VII) under acidic conditions. A sample of 250 g of rhubarb leaves was finely chopped then soaked in warm water to release any ethanedioic acid present. The mixture was then filtered and made up to a volume of 500 cm<sup>3</sup> using distilled water. 10.0 cm<sup>3</sup> of the solution was then titrated with 0.0100 mol dm<sup>-3</sup> acidified potassium manganate(VII) solution from a burette, requiring 11.30 cm<sup>3</sup> to completely oxidize the sample.
  - (a) (i) Write the half equation for the oxidation of ethanedioic acid to form carbon dioxide, and the half equation for the reduction of manganate(VII) ions, MnO<sub>4</sub><sup>-</sup>, in acidic solution to form manganese(II) ions. State symbols are **not** required.

**(2)** 

(ii) Use your answers to (a)(i) to write the overall equation for the reaction, showing that the ratio of ethanedioic acid to manganate(VII) ions in the full equation is 5:2. State symbols are **not** required.

(1)

\*(iii) Calculate the % by mass of the ethanedioic acid present in the leaves, giving your final answer to **two** decimal places.

(5)

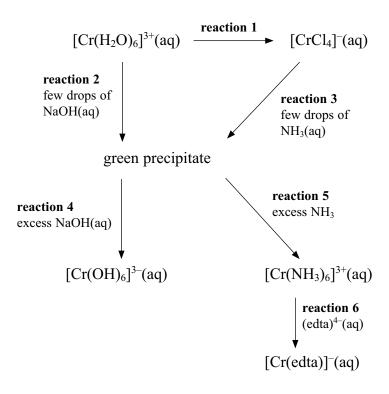
(iv) What is the level of accuracy of a burette in each reading? Use your answer to calculate the percentage error in the titre volume of 11.30 cm<sup>3</sup>.

(2)

	measurements, why the results obtained in this experiment may be considered unreliable.	
		(2)
(vi)	A student risk assessment for this experiment suggested wearing gloves, but a supervisor said that this was unnecessary. Why do you think this precaution was suggested by the student and why was it rejected by the supervisor?	(2)
(vii)	An aqueous solution of MnO <sub>4</sub> <sup>-</sup> ions contained a small amount of chloride ions, Cl <sup>-</sup> , as an impurity. Use this fact, and items 70 and 85 from page 16 of the characteristic state is a later to the characteristic state.	ne
(vii)		ne (2)
(vii)	ions, Cl-, as an impurity. Use this fact, and items 70 and 85 from page 16 of the	
(vii)	ions, Cl-, as an impurity. Use this fact, and items 70 and 85 from page 16 of the	
(vii)	ions, Cl-, as an impurity. Use this fact, and items 70 and 85 from page 16 of the	
(vii)	ions, Cl-, as an impurity. Use this fact, and items 70 and 85 from page 16 of the	
(vii)	ions, Cl-, as an impurity. Use this fact, and items 70 and 85 from page 16 of the	

(i) Complete the electronic conf	
	(1)
(ii) What shape would you expec	ct this complex ion to be?
(ci) (vilat slapt (volta jed cispe)	(1)
	(Total for Question 16 = 18 marks)

17 The reaction scheme below summarises some of the reactions of chromium ions in aqueous solution. Look carefully at the scheme and answer the questions that follow.



(a) (i) Explain why the  $[Cr(H_2O)_6]^{3+}$  ion is coloured.

1	-4	6
ч	0	,
٦,		

(ii) Suggest what reagent is needed for **reaction 1** and identify the type of reaction.

(b) (i)	$[Cr(H_2O)_6]^{3+}$ ions react with water to form an acidic solution. Complete the equation for this reaction.	(2)
	$[Cr(H_2O)_6]^{3+}(aq) + H_2O(1) \rightleftharpoons \dots + \dots + \dots$	
(ii)	The pH of an aqueous solution of $[Cu(H_2O)_6]^{2+}$ is higher than that of an aqueous solution of $[Cr(H_2O)_6]^{3+}$ of the same concentration. Suggest why this is so.	s (2)
(c) Giv	re the formula of the green precipitate formed in reactions 2 and 3.	(1)
` ′	considering the nature of the reactants in <b>reaction 4</b> , explain why the green cipitate reacts as shown in the scheme. Suggest how you could reverse <b>reaction</b>	4. (3)
	ite the equation for <b>reaction 6</b> and use this to explain, in terms of the entropy nge, why the complex $[Cr(edta)]^-$ is relatively more stable than $[Cr(NH_3)_6]^{3+}$ .	(2)
	(Total for Question 17 = 15 ma	rks)
	TOTAL FOR SECTION B = 50 MAR	RKS

## **SECTION C**

Eugenol, a pale yellow oil, and eugenol ethanoate are phenol-derived compounds found in the evergreen clove tree *Eugenia aromaticum*.

Eugenol

Eugenol ethanoate

Eugenol is used in perfumes, the manufacture of food flavourings and as a local anaesthetic. Eugenol ethanoate is mainly used in perfumes and aftershaves. Although used for many years, both compounds are classified as harmful and have been tested to determine their toxicity by ingestion. However, humans would need to consume very large amounts to reach toxic levels.

The compounds are the main constituents of clove oil which can be extracted from the dried buds of *Eugenia aromaticum's* flowers. Traditionally the oil is extracted by steam distillation, though a greater yield of oil can be obtained using a Soxhlet extractor to pass a chlorinated solvent through the dried buds several times to dissolve the clove oil. An alternative technique uses carbon dioxide as a solvent. Above a temperature of 304 K and a high pressure of 73.8 atm, carbon dioxide behaves as a supercritical fluid and when passed through the clove buds, it dissolves the clove oil. Releasing the pressure causes the carbon dioxide to turn back into a gas, leaving the clove oil behind. A summary of the characteristics of the clove oil obtained by the three extraction techniques is shown in the table below.

Extraction method	Mass of oil per 100 g of dried buds/g	% eugenol and eugenol ethanoate in the oil produced	Extraction time / h	Colour and texture	Use of organic solvent
Supercritical carbon dioxide	19.6	78.4	2	pale yellow oil	no
Steam distillation	11.5	53.5	4–6	brown- yellow oil	yes
Soxhlet extraction	41.8	40.1	6	brown paste	yes

Both molecules can also be manufactured synthetically in the laboratory. A reaction scheme for synthesising both molecules is summarised below.

(a) (i) 0.328 g of eugenol produced synthetically was burnt completely in excess oxygen, producing 0.880 g of carbon dioxide and 0.216 g of water. Use these data to show they are consistent with the molecular formula of eugenol.

**(4)** 

	carbon-carbon double bond in the product of <b>step 1</b> . What would you expect to see?	
		(2)
	What technique would you use to heat the reactants in <b>step 3</b> to minimise the loss of any volatile material?	
		(1)
(iv)	Suggest what reagent(s) could be used in <b>step 4</b> .	(1)

(b) (i)	Draw and label the apparatus suitable for extracting clove oil from clove buds by steam distillation in the laboratory.	(3)
(ii)	The distillate formed is a mixture of water and clove oil with a significant amount of oil dissolved in the water. Outline the steps that have to be taken to obtain the dry oil.	(3)

(c) Toxicity data for substances such as eugenol are generally obtained by tests on animals such as rats and guinea pigs. In the case of eugenol, do you think such tests are reasonable? Briefly justify your answer.	
	(1)
uate the three extraction methods for obtaining clove oil using information fable. Give <b>one</b> reason why the synthetic route of obtaining eugenol, shown a 20, is less preferable than extraction from clove buds.	
(Total for Question 18 = 20	marks)
(Total for Question 18 = 20  TOTAL FOR SECTION C = 20 M TOTAL FOR PAPER = 90 M	IARKS

21

	SECTION A	
Four com	plex ions have the following formulae:	
A Cu(e	$dta)^{2-}$	
<b>B</b> Zn(H	$(120)_6^{2+}$	
C Ni(N	$(H_3)_6^{2+}$	
<b>D</b> CrCl	$\overset{2-}{\overset{4}{}}$	
(a) Which	complex ion is most likely to be tetrahedral in shape?	
		(1)
<b>■</b> B		
<b>■ D</b>		
	complex ion is most likely not to be coloured?	
(b) Willen	complex ion is most likely <b>not</b> to be coloured?	(1)
■ A		
$\square$ B		
■ D		
	of these complex ions may be formed by ligand exchange from an aqua ex. For which complex ion is the entropy change of this reaction most re?	
		(1)
<b>■</b> B		
□ C		
□ D		
_ •	(Total for Question $1 = 3$	mard\

		netp.//www.mppc.org.uk
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	$[Cr(NH_3)_6]^{3+}$
	⊠ B	$Cr(H_2O)_3(OH)_3$
	<b>区</b> C	$[Cr(NH_3)_4]^{3+}$
	⊠ D	$[Cr(H_2O)_2(OH)_4]^-$
		(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.
	$\blacksquare$ B	A solution containing 1 mol dm <sup>-3</sup> of H <sup>+</sup> (aq) ions is used.
	<b>区</b> C	A platinum electrode is used.
	<b>■</b> 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:

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

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

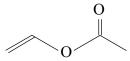
$$\mathbf{D} \quad \frac{\begin{pmatrix} H & CH_3 & H & CH_3 \\ | & | & | & | \\ C & C & C & C \\ | & | & | & | \\ H & H & H & H \end{pmatrix}_n}{\begin{pmatrix} H & CH_3 & H & CH_3 \\ | & | & | & | \\ H & H & H & H \end{pmatrix}_n}$$

(a) Which polymer is most soluble in hot water?

- $\triangle$  A
- $\blacksquare$  B
- $\mathbf{K}$  C
- $\boxtimes$  **D**

(b) Which polymer is formed from the monomer shown below?

(1)



- $\mathbf{X}$  A
- $\square$  B
- $\square$  C
- $\boxtimes$  **D**
- (c) Which polymer is a condensation polymer?

(1)

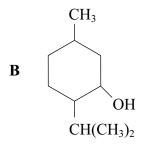
- $\mathbf{X}$  A
- $\square$  B
- $\square$  C
- $\square$  D

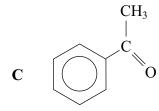
(Total for Question 4 = 3 marks)

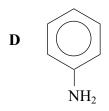
Use this space for any rough working. Anything you write in this space will gain no credit.

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

A (







(a) Which compound reacts with sodium to form hydrogen?

 $\mathbf{X}$  A

(1)

 $\blacksquare$  B

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

(1)

**■** A

 $\boxtimes$  B

 $\mathbf{Z}$  C

 $\times$  D

(c) Which compound forms an orange precipitate with 2,4-dinitrophenylhydrazine?

(1)

 $\mathbf{X}$  A

 $\boxtimes$  B

 $\mathbf{X}$  C

 $\times$  D

(Total for Question 5 = 3 marks)

	nany 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> ?
<b>⋈</b> A	8
⊠ B	7
<b>区</b>	4
⊠ D	3
	(Total for Question 6 = 1 mark)
	<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
⊠ A	singlet.
⊠ B	doublet.
<b>◯</b> C	triplet.
ĭ D	quartet.
	(Total for Question 7 = 1 mark)
Which nixture	of these compounds, whose formulae are shown below, <b>cannot</b> exist as a racemic e?
$\mathbf{X}$ A	CH <sub>2</sub> ClCHClCOOH
<ul><li>■ A</li><li>■ B</li></ul>	CH <sub>2</sub> CICHCICOOH HOOCCHCICOOH
⊠ B	
⊠ B	HOOCCHCICOOH
<ul><li>B</li><li>C</li></ul>	HOOCCHCICOOH CH <sub>3</sub> CHCICOOH
<ul><li>B</li><li>C</li></ul>	HOOCCHCICOOH CH <sub>3</sub> CHCICOOH CH <sub>3</sub> CH(OH)COOH
<ul><li>B</li><li>C</li></ul>	HOOCCHCICOOH CH <sub>3</sub> CHCICOOH CH <sub>3</sub> CH(OH)COOH
<ul><li>B</li><li>C</li></ul>	HOOCCHCICOOH CH <sub>3</sub> CHCICOOH CH <sub>3</sub> CH(OH)COOH
<ul><li>B</li><li>C</li></ul>	HOOCCHCICOOH CH <sub>3</sub> CHCICOOH CH <sub>3</sub> CH(OH)COOH
<ul><li>B</li><li>C</li></ul>	HOOCCHCICOOH CH <sub>3</sub> CHCICOOH CH <sub>3</sub> CH(OH)COOH
<ul><li>B</li><li>C</li></ul>	HOOCCHCICOOH CH <sub>3</sub> CHCICOOH CH <sub>3</sub> CH(OH)COOH
	A B C D n a higheak du A B C D Vhich

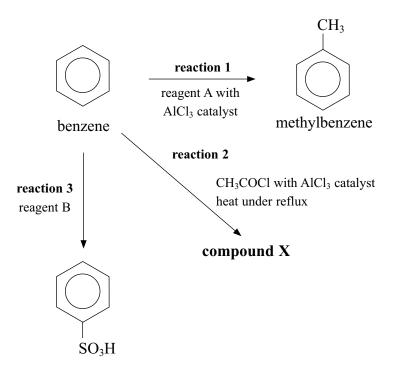
<b>9</b> Phenol reacts with bromine water whereas benzene reacts with bromine in the presence of iron.			
	(a) The	e mechanism for both these reactions is	(4)
		electrophilic substitution.	(1)
	<b>■</b> B	electrophilic addition.	
		nucleophilic substitution.	
	⊠ D	nucleophilic addition.	
	(b) In t	he reaction of benzene with bromine, iron	(4)
	$\square$ 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> .	
	■ 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	
	A	is a good leaving group.	(1)
	<b>■</b> B	attracts the bromine particles more readily.	
	■ C	is a good nucleophile.	
	<b>■</b> D	increases the electron density of the ring.	
		(Total for Question 9 = 3 ma	rks)
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	
	$\boxtimes$ 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	$C_6H_5NH_2 < NH_3 < CH_3CH_2CH_2CH_2NH_2$	
	<b>■ D</b>	$CH_3CH_2CH_2CH_2NH_2 < NH_3 < C_6H_5NH_2$	
		(Total for Question $10 = 1$ magnetical for $10 = 1$	rk)

11		tance on a chromatogram moved by an individual amino acid, in a mixture of at amino acids, mainly depends on
	$\boxtimes \mathbf{A}$	the molar mass of the amino acid.
	$\boxtimes$ B	the molar mass of the solvent used.
		the intermolecular forces between the solvent and the stationary phase.
	<b>■ D</b>	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
	$\boxtimes \mathbf{A}$	each molecule has a large number of electrons.
	⊠ B	each molecule forms hydrogen bonds at both ends.
	⊠ C	a proton is transferred from one end of the molecule to the other.
	<b>⋈</b> D	their shape allows the molecules to pack close together.
		(Total for Question 12 = 1 mark)

**TOTAL FOR SECTION A = 20 MARKS** 

## **SECTION B**

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)

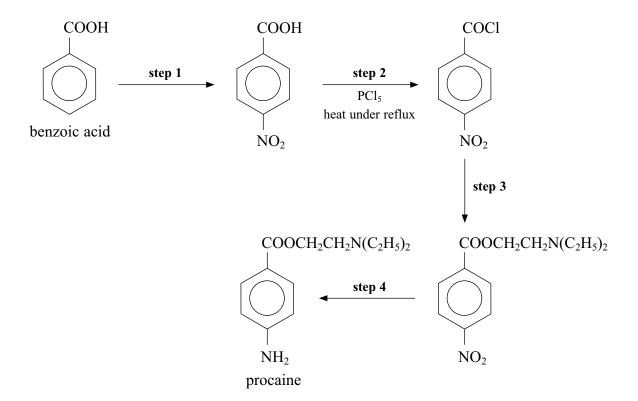
(iii) Draw the structure of the intermediate ion formed when the species in (ii) attacks the benzene ring.

(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)
e) (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)
	with an aluminium catalyst, are heated using microwave radiation. Suggest two	

(2)

- 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**.

(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  under reflux	(2)
<ul><li>(iv) Give the structural formula for the organic reagent needed in step 3.</li><li>(v) What type of reaction is taking place in step 4? Suggest the reagents used</li></ul>	. (2)

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

2-hydroxybenzoic acid ethanoic anhydride

aspirin

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

[ $M_r$  of 2-hydroxybenzoic acid = 138,  $M_r$  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)

(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	·ks)

15	Hydrogen gas can be used as a fuel in car engines by being burnt in a combustion reaction or reacted with oxygen in a fuel cell to produce electricity.	
	(a) Write half-equations for the reaction of hydrogen gas at the anode and oxygen gas a the cathode in the fuel cell.	t
		(2)
Ar	node	
Ca	thode	
	(b) Describe one advantage of using hydrogen in fuel cells rather than burning the hydrogen directly.	
		(1)
	(c) Other fuels, such as ethanol, can also be used in fuel cells. By considering the possible sources of ethanol and hydrogen, explain why some scientists believe the use of such cells could provide a more sustainable source of energy for cars, compared with fossil fuels.	
		(3)
	(Total for Question 15 = 6 ma	rks)

his question is about the transition metal iron and some of its compounds.	
(a) Give the electronic configuration of the Fe <sup>3+</sup> ion and use this to define what is meant by a transition element.	
	(2)
*(b) Iron will act as a surface catalyst in some gaseous reactions. Outline the processes that take place during such catalysis and suggest two reasons to explain why the catalyst speeds up the reaction.	(4)
	(4)

TOTAL FOR SECTION $B = 48$	MARKS
(Total for Question 16 = 1	
Describe how nitrogen atoms in the haemoglobin bond to the iron(II) ions.	(2)
Haemoglobin is a complex containing iron(II) ions.	
step.	(4)

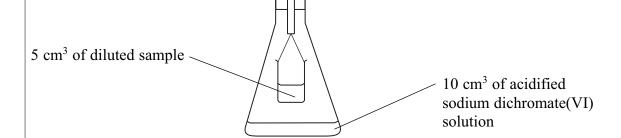
## **SECTION C**

17

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.

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<sub>2</sub>(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.

**(2)** 

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

(ii) Use either the half-equations in (i) or that the mole ratio of  $CH_3CH_2OH:Cr_2O_7^{2-}$  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 cm³ of the 0.0250 mol dm⁻³ sodium thiosulfate solution. Use this information, the fact that the mole ratio of CH<sub>3</sub>CH<sub>2</sub>OH:Cr<sub>2</sub>O<sub>7</sub>²⁻ is 3:2 and the equations below, to calculate the concentration of the ethanol in the 5.00 cm³ of the diluted sample of the drink.

**(6)** 

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

(iv)	The solution used in the experiment was made by adding $10.0 \text{ cm}^3$ of the drink to a $100 \text{ cm}^3$ 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 <b>warm</b> place for <b>24 hours</b> . What would be the effect on the final result if this procedure were not followed?	(3)
(vii)	Do you think that this experiment gives a reliable result? Explain your answer.	(1)

*(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		
(;;)	Suggest why infrared breathalysers do not use the OH absorption to detect the	
(II)	amount of alcohol on the breath.	(1)

(iii) Suggest why some police forces use infrared breachalysers.	
	(1)
iv) Suggest <b>one</b> advantage and <b>one</b> disadvantage of	huving a personal breathalyser
TV) Suggest one advantage and one disadvantage of	(2)
T)	<b>Cotal for Question 17 = 22 marks)</b>
TOTAL	FOR SECTION C = 22 MARKS
TO	TAL FOR PAPER = 90 MARKS

mock papers 4

## **SECTION A**

- An electrochemical cell consists of a standard hydrogen electrode and a Cu<sup>2+</sup>(aq)|Cu(s) electrode which uses copper(II) sulfate solution. Which one of the following does **not** affect the e.m.f. of the cell?
  - ☑ A The volume of the copper(II) sulfate solution.
  - **B** The temperature.
  - C The pressure of the hydrogen.
  - **D** The concentration of the copper(II) sulfate solution.

(Total for Question 1 = 1 mark)

2 Which answer corresponds to the correct value of  $E_{\text{cell}}^{\ominus}$  for the oxidation of hydrogen peroxide by manganate(VII) ions? The half-reactions are

$$2H^+ + O_2 + 2e^- \rightleftharpoons H_2O_2$$
  $E^{\ominus} = + 0.68 \text{ V}$ 

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$$
  $E^{\oplus} = + 1.51 \text{ V}$ 

The overall equation is

$$2MnO_4^- + 6H^+ + 5H_2O_2 \Longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

- $\blacksquare$  **A**  $E_{\text{cell}}^{\ominus} = +2.19 \text{ V}$
- **B**  $E_{\text{cell}}^{\ominus}$  = − 0.83 V
- $\square$  C  $E_{\text{cell}}^{\ominus} = -0.38 \text{ V}$
- $\blacksquare$  **D**  $E_{\text{cell}}^{\ominus} = +0.83 \text{ V}$

(Total for Question 2 = 1 mark)

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

- 3 The transition metal complex  $Pt(NH_3)_2Cl_2$  exists as two geometric isomers. This is because the complex
  - **A** is square-planar.
  - **B** is tetrahedral.
  - C contains a double bond.
  - **D** is octahedral.

(Total for Question 3 = 1 mark)

4 Hydrogen peroxide,  $H_2O_2$ , can be analysed by titration. The hydrogen peroxide solution is treated with acidified potassium iodide solution, and the liberated iodine is titrated with a standard solution of sodium thiosulfate,  $Na_2S_2O_3$ . The products are iodide ions and tetrathionate ions,  $S_4O_6^{2-}$ .

Which of the following applies to this reaction?

		Action of H <sub>2</sub> O <sub>2</sub>	Action of S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>
$\boxtimes$	A	oxidizing agent	oxidizing agent
$\boxtimes$	В	oxidizing agent	reducing agent
$\boxtimes$	C	reducing agent	oxidizing agent
$\boxtimes$	D	reducing agent	reducing agent

(Total for Question 4 = 1 mark)

- 5 A hydrated transition metal ion is colourless. Which of the following could be the electronic configuration of this ion?
  - $\triangle$  A [Ar]  $3d^54s^2$
  - $\square$  **B** [Ar]  $3d^8$
  - $\square$  C [Ar]  $3d^{10}4s^2$
  - $\square$  **D** [Ar]  $3d^{10}$

(Total for Question 5 = 1 mark)

	<b>■</b> D	it has a boiling temperature low enough for it to be easily distilled.  (Total for Question 9 = 1 mark)
	<b>区</b>	it does not readily form complex ions.
	⊠ B	none of its ions has an unpaired electron in the <i>d</i> -subshell.
	<b>⋈</b> A	the oxide of zinc is amphoteric.
)		ement zinc, with electronic configuration $1s^22s^22p^63s^23p^63d^{10}4s^2$ , is <b>not</b> regarded nsition element because
		(Total for Question 8 = 1 mark)
	<b>■</b> D	$\mathrm{NH_4}^+$
	⊠ C	NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>
	⊠ B	$NH_3$
	$\boxtimes$ A	$C_6H_5NH_2$
3		of the following species is <b>not</b> able to act as a ligand in the formation of on metal complexes?
		(Total for Question 7 = 1 mark)
	<b>■</b> D	$[\operatorname{CrCl}_2(\operatorname{H}_2\operatorname{O})_4]^+$
	⊠ C	[CrCl(H2O)5]2+
	$\boxtimes$ B	$[Cr(H_2O)_6]^{3+}$
	$\mathbf{X}$ A	$[Cr(OH)_6]^{3-}$
7	with ex	a solution containing 0.10 mol of chromium(III) chloride, CrCl <sub>3</sub> .6H <sub>2</sub> O, is treated cess silver nitrate solution, 0.20 mol of silver chloride, AgCl, is immediately tated. The formula of the complex ion in the solution is
_		(Total for Question 6 = 1 mark)
	<b>■ D</b>	Sodium hydroxide solution
		Dilute nitric acid
	$\boxtimes$ B	Aqueous ammonia
	$\boxtimes$ A	Dilute hydrochloric acid
		e of iron(III) hydroxide and copper(II) hydroxide?

- 10 The compounds below were heated with aqueous sodium hydroxide solution. Which one of them did **not** give sodium ethanoate, CH<sub>3</sub>COONa, as one of the products?
  - A CH<sub>3</sub>COOCH<sub>3</sub>
  - **■ B** CH<sub>3</sub>COCH<sub>3</sub>

  - $\square$  **D** CH<sub>3</sub>COC1

(Total for Question 10 = 1 mark)

- 11 Which of the following products is formed when phenylamine (aniline) is reacted with **dilute** sulfuric acid?
  - $\square$  A  $\bigcap$   $NO_2$
  - $\square$  B  $\bigcirc$  SO<sub>3</sub>H
  - $\ \, \boxtimes \ \, \mathbf{C} \quad \overline{ \qquad \qquad } \overset{^{+}}{\overset{^{-}}{\mathrm{NH_{3}HSO_{4}}}}$
  - $\square \ \mathbf{D} \qquad \qquad \square$   $SO_3H$

(Total for Question 11 = 1 mark)

12 For the nitration of phenol, which is the most suitable set of conditions and the reason for its use?

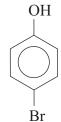
		Conditions	Reactivity of phenol to electrophiles compared with benzene
$\times$	A	dilute nitric acid at room temperature	more reactive
$\times$	В	concentrated nitric and sulfuric acid at room temperature	more reactive
$\times$	С	concentrated nitric and sulfuric acid at 55 °C	the same
×	D	dilute nitric acid and dilute sulfuric acid at room temperature	less reactive

(Total for Question 12 = 1 mark)

13 Phenol reacts with excess bromine water to give as the organic product(s)

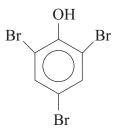


and



⊠ B





 $\square$  D

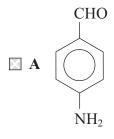


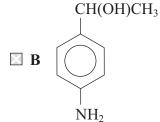
(Total for Question 13 = 1 mark)

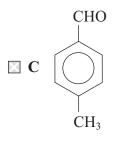
## 14 An organic compound, X, shows the following properties:

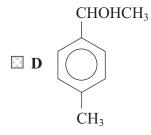
- Oxidation of compound **X** produces a substance that reacts with 2,4-dinitrophenylhydrazine to give a yellow precipitate but does **not** react with Fehling's or Benedict's solution.
- Compound **X** reacts with ice-cold nitrous acid to form a compound that gives a yellow precipitate with an alkaline solution of phenol.

What is the formula of compound X?









(Total for Question 14 = 1 mark)

					nttp.//www.mppe.org.uk
5	Which	sequen	ce shows the bases in orde	er of decreasing strength?	
	⊠ A	1	$NH_2 > CH_3NH_2 > NH_3$		
	⊠ B	NH <sub>3</sub>	$> CH_3NH_2 > C_6H_5NH_2$		
	⊠ C	CH <sub>3</sub> N	$H_2 > NH_3 > C_6H_5NH_2$		
	⊠ D	NH <sub>3</sub>	$> C_6H_5NH_2 > CH_3NH_2$		
				(Total fo	or Question 15 = 1 mark)
The product mixture is shaken with sodium carbonate solution and later with anhydrous sodium sulfate before being re-distilled. Which of the following shows the correct list of impurities removed at each step?  Aqueous sodium  Addition of sodium				•	
			Aqueous sodium carbonate wash	Addition of sodium sulfate	
	×	A	HBr	SO <sub>2</sub> , Br <sub>2</sub> , water	-
		В	$SO_2$ , $Br_2$	HBr, water	
	$\boxtimes$	C	SO <sub>2</sub> , HBr	Br <sub>2</sub> , water	
	$\boxtimes$	D	SO <sub>2</sub> , Br <sub>2</sub> , HBr	water	
				(Total fo	or Question 16 = 1 mark)
 17		of the f		e structure H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> N distinguish between the t	H <sub>2</sub> or H <sub>2</sub> NCH <sub>2</sub> COOH.

 $\boxtimes$  B

 $\mathbf{K}$  C

 $\bowtie$  **D** 

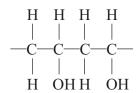
Reaction with nitrous acid.

Reaction with ethanoyl chloride.

Reaction with aqueous sodium hydrogencarbonate.

(Total for Question 17 = 1 mark)

**18** Poly(ethenol) is a water-soluble polymer. A section of the chain has the structure shown below.



The polymer is used for making hospital laundry bags so that laundry can be loaded directly into washing machines without it having to be handled.

Poly(ethenol) is water soluble because the polymer

- $\square$  **A** is broken down by the water into monomers.
- $\square$  **B** is broken down by the washing detergent.
- C breaks into monomers at the temperature of the wash.
- **D** forms many strong hydrogen bonds with the water.

(Total for Question 18 = 1 mark)

- 19 Which of the following substances is capable of damaging the ozone layer?
  - A NaCl
  - $\square$  **B** CO<sub>2</sub>
  - $\square$  **C**  $C_2HF_5$
  - $\square$  **D**  $C_2F_3Cl_3$

(Total for Question 19 = 1 mark)

- **20** Analysis suggests that a particular organic synthesis produces a medicine that contains trace impurities that may be hazardous. What is the best way for this discovery to be reported and evaluated?
  - ☑ A In a scientific journal which subjects its articles to peer review.
  - **B** On the Internet in an article on a website.
  - $\square$  C In a newspaper article in several broadsheet newspapers.
  - **D** In a widely circulated magazine.

(Total for Question 20 = 1 mark)

**TOTAL FOR SECTION A = 20 MARKS** 

## **SECTION B**

21 (a) Chromium is a typical transition metal, although its electronic configuration does **not** fit the general trend found in the first transition series.

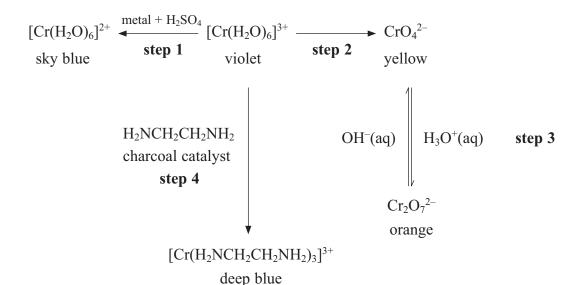
Complete the electronic configurations in *s*,*p*,*d* notation for vanadium and chromium.

(1)

Vanadium: [Ar]

Chromium: [Ar]

(b) Some interconversions found in the chemistry of chromium are shown below. Use this information to answer the questions that follow.



(i) State **two** typical properties of transition metals, other than the formation of coloured ions, which are shown in the diagram above.

1	$^{\prime\prime}$	١.
ı	L	
١.	_	,

<ul> <li>(iii) Explain, using oxidation numbers, whether or not the conversion in step 3 is a redox reaction.</li> <li>(iv) The organic compound H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> that is used in step 4 is 1,2-diaminoethane, often called ethylenediamine. It is a bidentate ligand. Explain the meaning of this term.</li> </ul>	
1,2-diaminoethane, often called ethylenediamine.	(2)
	(1)
(v) Explain, in terms of its structure, how H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> can act as a bidentate ligand whereas H <sub>2</sub> NNH <sub>2</sub> cannot.	(2)

(c) The half-equations relating the interconversion of the species $Cr^{2+}(aq)$ , $Cr^{3+}(aq)$ and $Cr_2O_7^{2-}(aq)$ are given below.		
<b>Half-equation I:</b> $Cr^{3+}(aq) + e^- \rightarrow Cr^{2+}(aq)$		
<b>Half-equation II:</b> $Cr_2O_7^{2-}(aq) + 6e^- + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(1)$		
(i) Use your data booklet to find $E^{\oplus}$ for each of the above half-equations.	(1)	
Half-equation I		Volts
Half-equation II		. Volts
*(ii)Write the overall equation for the disproportionation of $Cr^{3+}$ into $Cr^{2+}$ and $Cr_2O_7^{2-}$ .		
Use the $E^{\oplus}$ values you have obtained in (c)(i) to show whether or not this disproportionation is feasible under standard conditions.	(4)	
(Total for Question 21 = 15 mar	rks)	

22 (a) Tiglic acid is a compound that is used as a defensive agent by some beetles.				
(i) Tiglic acid contains, by mass, 60% carbon, 8% hydrogen, with the remainder being oxygen. Show that these data are consistent with the formula $C_5H_8O_2$ .	(1)			
(ii) Tiglic acid contains a carbon-carbon double bond and a carboxylic acid group.				
Suggest <b>one</b> test for each of these groups in tiglic acid. State what you would do and what you would see as a positive result for the tests.				
do and what you would see as a positive result for the tests.	(4)			
Test for C=C				
Test for —COOH				
Test for C=C	(4)			

(b) It is	CH <sub>3</sub> CH <sub>2</sub> H CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>4</sub> COOH	
(i)	A B State, with a reason, whether B is the E- or Z- isomer.	(2)
(ii)	The mass spectrum of tiglic acid shows two prominent peaks at mass/charge ratios 45 and 55. Write the formulae of the fragments giving rise to each of these peaks.	(2)
	Does this data from the mass spectrum <b>alone</b> enable you to decide which of <b>A</b> or <b>B</b> is the structure of tiglic acid? Explain your answer.	(1)

(c) The position of a C=C double bond in a molecule can be determined by ozonolysis. The compound is reacted with ozone and then dilute acid, two carbonyl compounds being produced as shown below.

Ozonolysis of tiglic acid gives two carbonyl compounds, C and D.

Compound C gives a silver mirror with Tollens' reagent and gives iodoform with iodine in alkali.

Compound **D** does **not** give a silver mirror with Tollens' reagent, but does give iodoform with iodine in alkali.

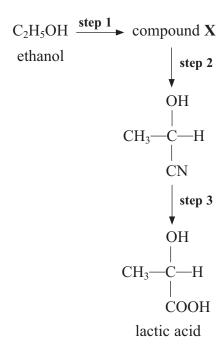
\*(i) From the results of the experiments, deduce the functional groups present in **C** and **D**. By considering the two possible structures for tiglic acid, give the structural formulae of **C** and **D**.

From the structures you have drawn, state which of the structures  ${\bf A}$  or  ${\bf B}$  could represent tiglic acid.

	(6)
(ii) Explain whether or not these tests show definitely that your answer to (c)(i) represents tiglic acid.	
represents tight dord.	(1)

(d) Lactic acid is a chiral molecule that is found in sweat as the (–) isomer only. Its structural formula is

(i) Lactic acid can be made from ethanol in three steps.



Give the structural formula of the intermediate X and the reagents and conditions required for **steps 1** and **2**.

(4)

Step 1	
Step 2	

(ii) Classify the type and mechanism of the reaction that occurs in step 2.	(1)
*(iii) By considering the stereochemistry of the mechanism in <b>step 2</b> , explain why this synthesis would <b>not</b> give a single optical isomer of lactic acid.	(2)
(iv) Suggest why synthetic pathways for the manufacture of pharmaceuticals may require reactions that are highly stereospecific.	(1)
(Total for Question 22 = 25 m	arks)

23 Proteins are polymers of  $\alpha$ -amino acids, the simplest of which is glycine.

$$\begin{array}{c} \text{NH}_2 \\ | \\ \text{C} \\ \text{HOOC} \end{array}$$

(a) (i) Draw the **structural** formula for the zwitterion of glycine in the solid state.

(1)

(ii) Explain, on the basis of your answer to (a)(i), why glycine has a relatively high melting temperature for such a small molecule.

**(2)** 

(iii) Draw the structure of the protein chain that would be formed if glycine alone were to be polymerized. Show part of the chain containing two glycine residues.

(2)

samples of amino acids, to show which amino give detailed experimental instructions.	acids the protein contained. Do not
-	(5)
	(Total for Question 23 = 10 marks)
,	ΓΟΤΑL FOR SECTION B = 50 MARKS

## **SECTION C**

**24** Read the passage below carefully and answer the questions which follow.

## Molecular structure and colour chemistry

The sight of tubes of paint or of coloured pencils in an artists' supply shop is something that most people enjoy; we love colour.

The ability to synthesise brightly-coloured compounds coincides with the rapid growth of the organic chemicals industry. Synthetic organic dyes started to appear in the mid-19th century when William Perkin synthesised Mauve in 1856 at the age of 18. He was trying to synthesise quinine even though he did not know the structure of the molecule.

In the 19th century many chemists did not believe that molecules existed. The work of Butlerov, Couper, and notably Kekulé showed that molecules not only exist but have specific structures. In 1865 Kekulé suggested a ring structure for the aromatic compound benzene which he represented as



Kekulé knew that benzene does not react with bromine water. Later work showed that the enthalpy change of hydrogenation of the compound is  $-205 \text{ kJ mol}^{-1}$ , rather than the value of  $-360 \text{ kJ mol}^{-1}$  that would be expected if the structure was exactly as shown above, given that the enthalpy change of hydrogenation for cyclohexene to cyclohexane

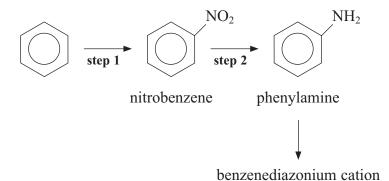
is  $-120 \text{ kJ mol}^{-1}$ .

When Greiss in 1856 discovered diazotisation and the azo dyes, he used a reaction characteristic of aromatic amines. Witt, in 1876, found the functional groups in the dye molecule that make it water-soluble and enable it to attach to the cloth fibres. Graebe, Liebermann and Perkin in 1869 patented the synthesis of alizarin, found in madder root grown in Holland and Von Baeyer synthesised indigo in 1880, until then grown in India. Synthetic dyes were made available in large quantities and were cheaper than the sources from plants.

Now the organic chemical industry produces a vast range of pigments and dyestuffs for use in paints and for fabrics, inks and other materials, making our world the most colourful that it has ever been.

(a) (i)	Explain why Perkin's attempted synthesis of quinine was almost certain to fail.	(1)
(ii)	Suggest the effect that the growth of the organic chemicals industry in the late 19th century had on Holland and India in particular.	(2)
(b) (i)	What observation did Kekulé make to show that benzene does <b>not</b> react with bromine water? Explain the significance of this with reference to his representation of the molecule.	(2)
(ii)	Explain, in terms of the bonding in the benzene ring, why the enthalpy of hydrogenation is less exothermic than would be expected from a molecule with three double bonds.	(3)

(c) The first steps in the preparation of an azo dye from benzene are shown below.



Give the mechanism for the reaction in **step 1**, including the equation for the formation of the electrophile.

**(4)** 

Equation for formation of electrophile

Mechanism

(d) (i)	(i) Phenylamine is converted into the benzenediazonium cation using sodium nitrite and hydrochloric acid at a temperature between 0 °C and 10 °C.	
	Explain why the temperature must <b>not</b> be lower or higher than these limits if a good yield is to be obtained.	
	good yield is to be obtained.	(2)
(ii)	Draw the structural formula of the benzenediazonium cation showing all the bonds and the charge.	(1)
		(1)
<i>(</i> '''`\		
(111)	Suggest how you could convert a sample of the benzenediazonium cation into an azo dye. Give the name of the other compound you would use and the skeletal formula of the azo dye you would obtain.	
		(3)

**TOTAL FOR PAPER = 90 MARKS** 

(e) The structural formula of methyl orange is given below.	
$Na^{+} - O_3S$ $\longrightarrow$ $N = N - (CH_3)_2$	
Suggest the main features of methyl orange which make it water-soluble, giving your	
reasons.	(2)
(Total for Question 24 = 20 marks)	
TOTAL FOR SECTION C = 20 MARKS	