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Tuesday 6 November 2018		
Morning (Time: 1 hour 40 minutes)	Paper Reference WCH05/01	
Chemistry Advanced Unit 5: General Principles of Chemistry II – Transition Metals and Organic Nitrogen Chemistry (including synoptic assessment)		
Candidates must have: Data Booklet Scientific calculator	Total Marks 	

Instructions

- Use **black** ink or **black** ball-point pen.
- **Fill in the boxes** at the top of this page with your name, centre number and candidate number.
- Answer **all** questions.
- Answer the questions in the spaces provided
– *there may be more space than you need.*

Information

- The total mark for this paper is 90.
- The marks for **each** question are shown in brackets
– *use this as a guide as to how much time to spend on each question.*
- Questions labelled with an **asterisk** (*) are ones where the quality of your written communication will be assessed
– *you should take particular care with your spelling, punctuation and grammar, as well as the clarity of expression, on these questions.*
- A Periodic Table is printed on the back cover of this paper.

Advice

- Read each question carefully before you start to answer it.
- Show all your working in calculations and include units where appropriate.
- Check your answers if you have time at the end.

Turn over ►

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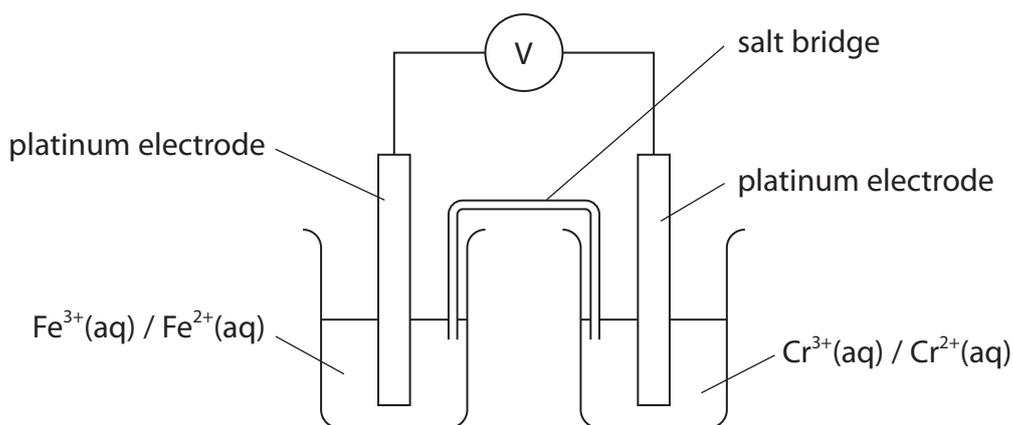
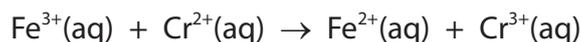



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SECTION A

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 ☒.

- 1 A cell could be set up as shown to measure the electrode potential for the reaction between iron(III) sulfate and chromium(II) sulfate:



- (a) This reaction is classified as a redox reaction because the chromium(II) ions are (1)

- A oxidised and iron(III) acts as an oxidising agent.
 B oxidised and iron(III) acts as a reducing agent.
 C reduced and iron(III) acts as a reducing agent.
 D reduced and iron(III) acts as an oxidising agent.

- (b) This reaction proceeds spontaneously. From this it can be deduced that (1)

- A E_{cell} and ΔS_{total} for this reaction must both be negative.
 B E_{cell} and ΔS_{total} for this reaction must both be positive.
 C E_{cell} for this reaction must be positive and ΔS_{total} negative.
 D E_{cell} for this reaction must be negative and ΔS_{total} positive.

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(c) Which of these saturated solutions should be used in this salt bridge?

(1)

- A Potassium carbonate
- B Potassium hydroxide
- C Potassium iodide
- D Potassium nitrate

(d) What mass of iron(III) sulfate is present in 100 cm^3 of the solution used to measure the **standard** electrode potential of this cell?

[Molar mass of $\text{Fe}_2(\text{SO}_4)_3 = 399.9\text{ g mol}^{-1}$]

(1)

- A 19.995 g
- B 39.990 g
- C 79.980 g
- D 199.950 g

(Total for Question 1 = 4 marks)

2 Which compound does **not** contain a metal with the same oxidation number as manganese in K_2MnO_4 ?

- A BaFeO_4
- B $\text{K}_2\text{Cr}_2\text{O}_7$
- C Na_3FeF_6
- D WO_3

(Total for Question 2 = 1 mark)

3 What happens to hydrogen in the hydrogen-oxygen fuel cell?

- A It is oxidised at the negative electrode.
- B It is oxidised at the positive electrode.
- C It is reduced at the negative electrode.
- D It is reduced at the positive electrode.

(Total for Question 3 = 1 mark)



4 An aqueous solution of zinc nitrate is colourless.

Addition of aqueous sodium hydroxide to zinc nitrate solution results in a white precipitate which dissolves to form a colourless solution when more aqueous sodium hydroxide is added.

(a) The **overall** ionic equation for the conversion of the initial colourless solution to the final colourless solution is

(1)

- A $\text{Zn(OH)}_2 + 2\text{OH}^- \rightarrow [\text{Zn(OH)}_4]^{2-}$
- B $\text{Zn(OH)}_2 + 4\text{OH}^- \rightarrow [\text{Zn(OH)}_6]^{4-}$
- C $[\text{Zn(H}_2\text{O)}_6]^{2+} + 4\text{OH}^- \rightarrow [\text{Zn(OH)}_4]^{2-} + 6\text{H}_2\text{O}$
- D $[\text{Zn(H}_2\text{O)}_6]^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 + 6\text{H}_2\text{O}$

(b) Why is the aqueous solution of zinc nitrate colourless?

(1)

- A There is no splitting of the 3d subshell in zinc complexes.
- B There is no movement of electrons in the 3d subshell as it is empty.
- C There is no movement of electrons in the 3d subshell as it is full.
- D There is movement of electrons in the 3d subshell but the energy absorbed is not in the visible region.

(Total for Question 4 = 2 marks)

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5 Which is the electronic structure of a Ni^{2+} ion?

- | | | 3d | | | | 4s |
|----------------------------|------|----|----|----|----|----|
| <input type="checkbox"/> A | [Ar] | ↑↓ | ↑↓ | ↑↓ | ↑↓ | |
| <input type="checkbox"/> B | [Ar] | ↑↓ | ↑↓ | ↑↓ | ↑ | ↑ |
| <input type="checkbox"/> C | [Ar] | ↑↓ | ↑↓ | ↑↓ | | ↑↓ |
| <input type="checkbox"/> D | [Ar] | ↑↓ | ↑↓ | ↑ | ↑ | ↑ |

(Total for Question 5 = 1 mark)

6 X-ray diffraction of benzene provides evidence that benzene molecules

- A have equal carbon-carbon bond lengths.
- B undergo electrophilic substitution reactions.
- C have higher thermodynamic stability than cyclohexa-1,3,5-triene.
- D have lower thermodynamic stability than cyclohexa-1,3,5-triene.

(Total for Question 6 = 1 mark)

7 Ammonia (NH_3), ethylamine ($\text{CH}_3\text{CH}_2\text{NH}_2$), diethylamine ($(\text{CH}_3\text{CH}_2)_2\text{NH}$) and phenylamine ($\text{C}_6\text{H}_5\text{NH}_2$) all form alkaline solutions in water. The order of **decreasing** pH of equimolar solutions of these compounds is

- A $\text{C}_6\text{H}_5\text{NH}_2 > \text{NH}_3 > \text{CH}_3\text{CH}_2\text{NH}_2 > (\text{CH}_3\text{CH}_2)_2\text{NH}$
- B $(\text{CH}_3\text{CH}_2)_2\text{NH} > \text{CH}_3\text{CH}_2\text{NH}_2 > \text{NH}_3 > \text{C}_6\text{H}_5\text{NH}_2$
- C $(\text{CH}_3\text{CH}_2)_2\text{NH} > \text{CH}_3\text{CH}_2\text{NH}_2 > \text{C}_6\text{H}_5\text{NH}_2 > \text{NH}_3$
- D $\text{CH}_3\text{CH}_2\text{NH}_2 > (\text{CH}_3\text{CH}_2)_2\text{NH} > \text{NH}_3 > \text{C}_6\text{H}_5\text{NH}_2$

(Total for Question 7 = 1 mark)



8 Nitrobenzene, $C_6H_5NO_2$, can be converted into phenylamine, $C_6H_5NH_2$, which is a liquid under normal laboratory conditions.

(a) The reagent normally used for this reaction is

(1)

- A concentrated ammonia in ethanol.
- B lithium tetrahydridoaluminate(III) in dry ether.
- C potassium dichromate(VI) in dilute sulphuric acid.
- D tin in concentrated hydrochloric acid.

(b) Which technique is used to separate phenylamine from the reaction mixture?

(1)

- A Column chromatography
- B Filtration
- C Recrystallisation
- D Steam distillation

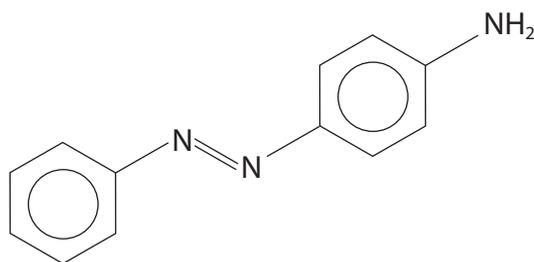
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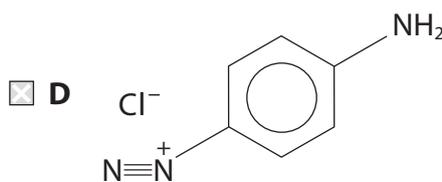
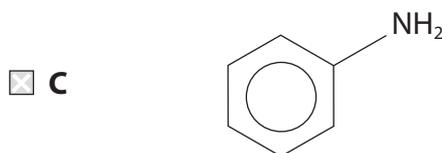
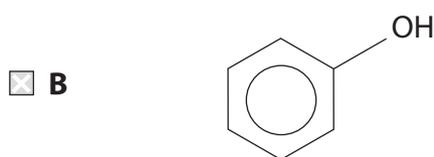
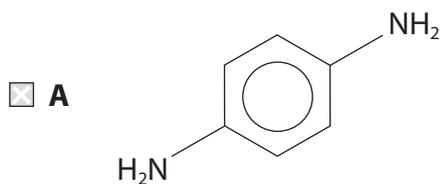


(c) Reaction of phenylamine, first with ice-cold nitrous acid and second with an aromatic organic compound, gave a yellow precipitate with the structure



The aromatic organic compound added in the second step was

(1)

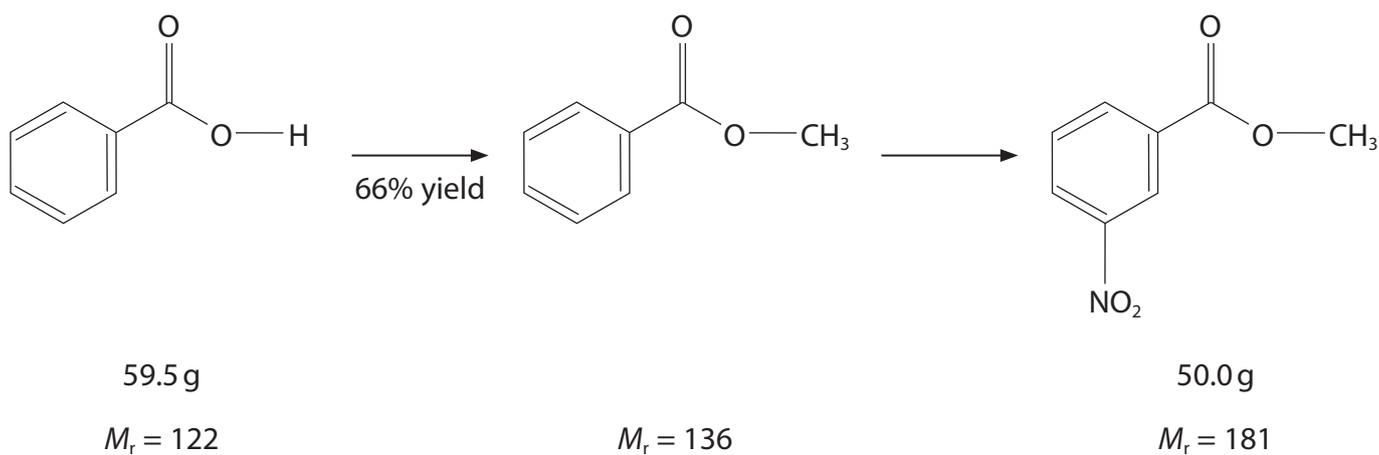


(Total for Question 8 = 3 marks)

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- 9 59.5 g of benzoic acid was converted into 50.0 g of methyl 3-nitrobenzoate in a two-step synthesis as shown.



The percentage yield of the second step, to two significant figures, is

- A 44%
 B 57%
 C 84%
 D 86%

(Total for Question 9 = 1 mark)

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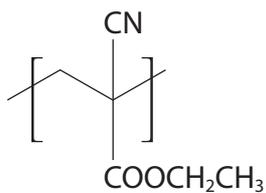
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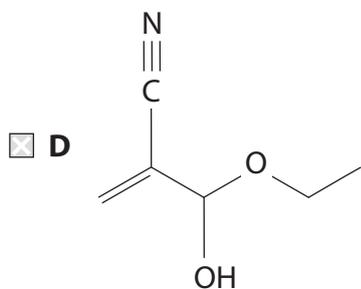
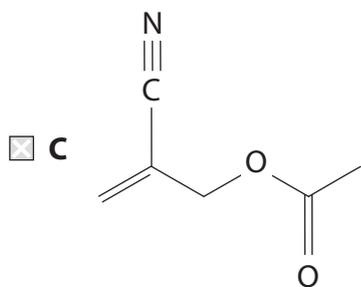
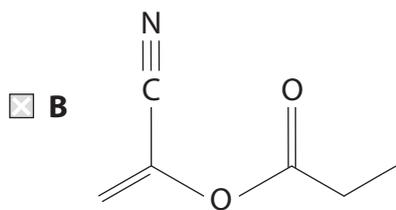
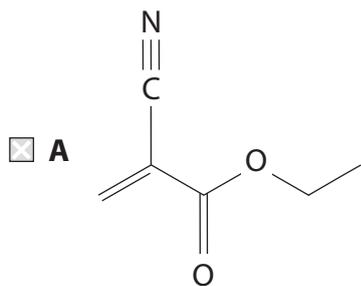
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10 The repeat unit for a polymer found in 'instant glues' is



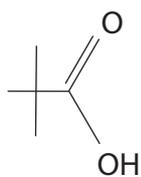
The structure of the monomer from which this polymer is made is



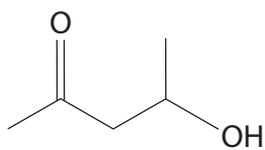
(Total for Question 10 = 1 mark)



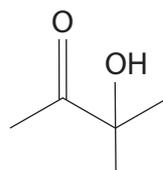
11 This question is about four isomers with the molecular formula $C_5H_{10}O_2$.



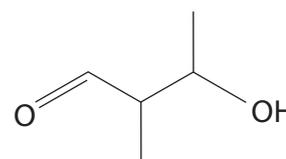
W



X



Y



Z

(a) Which isomer does **not** react with 2,4-dinitrophenylhydrazine?

(1)

- A W
 B X
 C Y
 D Z

(b) Which isomer reacts with Tollens' reagent and also with acidified potassium dichromate(VI)?

(1)

- A W
 B X
 C Y
 D Z

(c) Which isomer(s) will react with an alkaline solution of iodine to give a pale yellow precipitate?

(1)

- A W only
 B X and Y only
 C X and Z only
 D X, Y and Z only

(Total for Question 11 = 3 marks)

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12 Which of these molecules does **not** have a chiral centre?

- A $\text{CH}_3\text{CHClCH}=\text{CHCl}$
- B $\text{CH}_3\text{CH}_2\text{CCl}=\text{CHCl}$
- C $\text{CH}_2\text{ClCHClCH}=\text{CH}_2$
- D $\text{CH}_3\text{CHClCCl}=\text{CH}_2$

(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 ionic half-equations and their standard electrode potentials are given in the table.

Ionic half-equation	E^\ominus / V
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	-0.76
$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$	-0.26
$SO_4^{2-}(aq) + 2H^+(aq) + 2e^- \rightleftharpoons SO_3^{2-}(aq) + H_2O(l)$	+0.17
$VO^{2+}(aq) + 2H^+(aq) + e^- \rightleftharpoons V^{3+}(aq) + H_2O(l)$	+0.34
	+0.77
$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$	+1.00
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23
$Cl_2(aq) + 2e^- \rightleftharpoons 2Cl^-(aq)$	

- (a) Use page 17 of the Data Booklet to complete the table by giving both the ionic half-equation for the system which has a standard electrode potential of +0.77 V **and** the missing electrode potential value. (1)
- (b) From the substances shown in this table select:
- (i) the species which is the most powerful reducing agent. (1)
- (ii) the species which, in acidic solution, will reduce VO^{2+} to V^{3+} , but will not reduce V^{3+} to V^{2+} under standard conditions. (1)

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- (c) An excess of zinc powder was added to an acidic solution containing VO_2^+ ions and warmed gently. When the reaction was complete, a mauve solution had formed.
- (i) Use the data given in the table to determine the vanadium species present in the solution at the end of this reaction. State the oxidation number of vanadium in this species and write the half-equation for its formation from VO_2^+ .

State symbols are not required.

(2)

Oxidation number of vanadium in the final species

Half-equation

- *(ii) Whilst still warm, the mauve solution was filtered into a boiling tube to remove the excess zinc. During filtration, the solution became green. On standing for some time, the solution finally turned blue, showing the presence of VO^{2+} ions.

Explain the changes of colour in the solution and write two equations.
Calculate the relevant E_{cell} values for the reactions occurring.

(4)

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(iii) Suggest why the solution containing blue VO^{2+} ions might be expected to change to yellow VO_2^+ ions, but does not do so.

(2)

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(Total for Question 13 = 11 marks)

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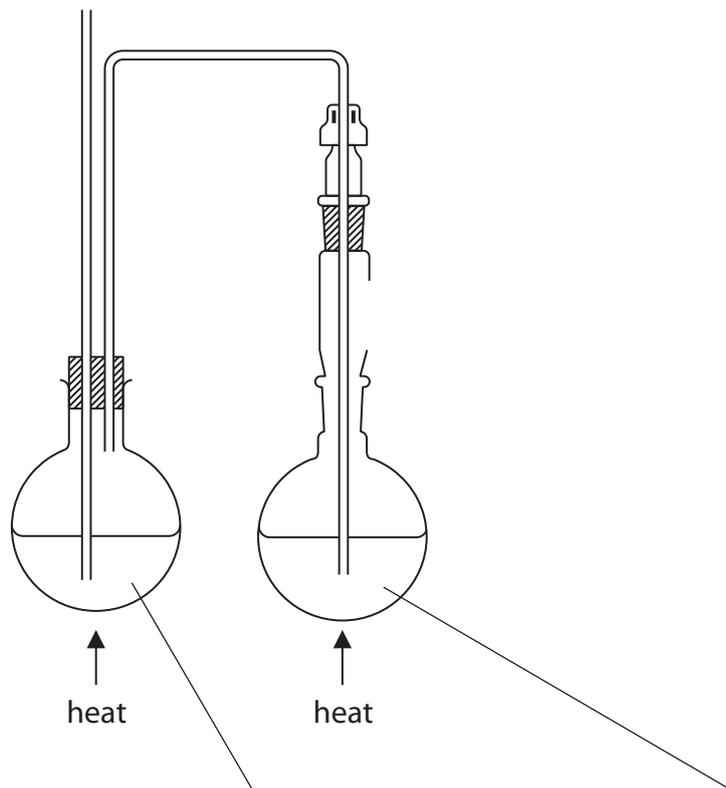
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14 Anethole is used as an aniseed flavouring in food, toothpastes and alcoholic drinks. It is found naturally in the plants fennel, anise and star anise. It has an isomer, estragole, which has a similar flavour and is found in tarragon and basil.

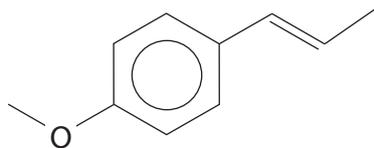
(a) Estragole can be extracted from tarragon leaves by steam distillation.

Complete the diagram to show how this could be done in a school laboratory **and** label the contents of the two flasks.

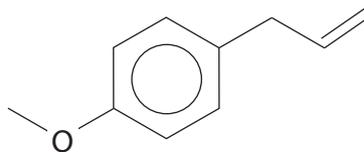
(2)



(b) The skeletal formulae of anethole and estragole are shown.



Anethole



Estragole

(i) Give the molecular formula of these isomers.

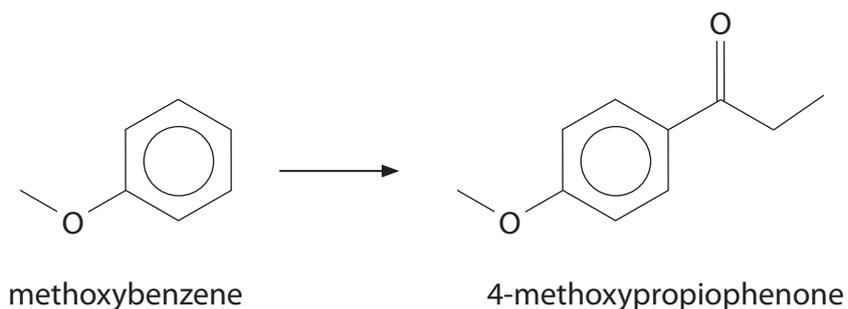
(1)

* (ii) Explain the features of the structure of anethole which means it has a geometric isomer.

(2)



- (c) Anethole can be synthesised from methoxybenzene in four-steps. The first step is the formation of 4-methoxypropiophenone.



This reaction is a Friedel-Crafts acylation reaction, using an electrophilic substitution mechanism similar to the equivalent reaction of benzene, but requiring much milder conditions.

- (i) Using your knowledge of the reactions of benzene, give the **name** of the organic molecule which is required to produce the electrophile to react with methoxybenzene.

(1)

- (ii) Give the mechanism for the reaction. You should include an equation for the formation of the electrophile. You may use RCO^+ to represent the formula of the electrophile.

(4)



(iii) Suggest why the acylation of methoxybenzene requires milder conditions than the equivalent reaction of benzene.

(2)

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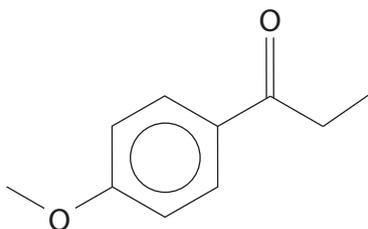
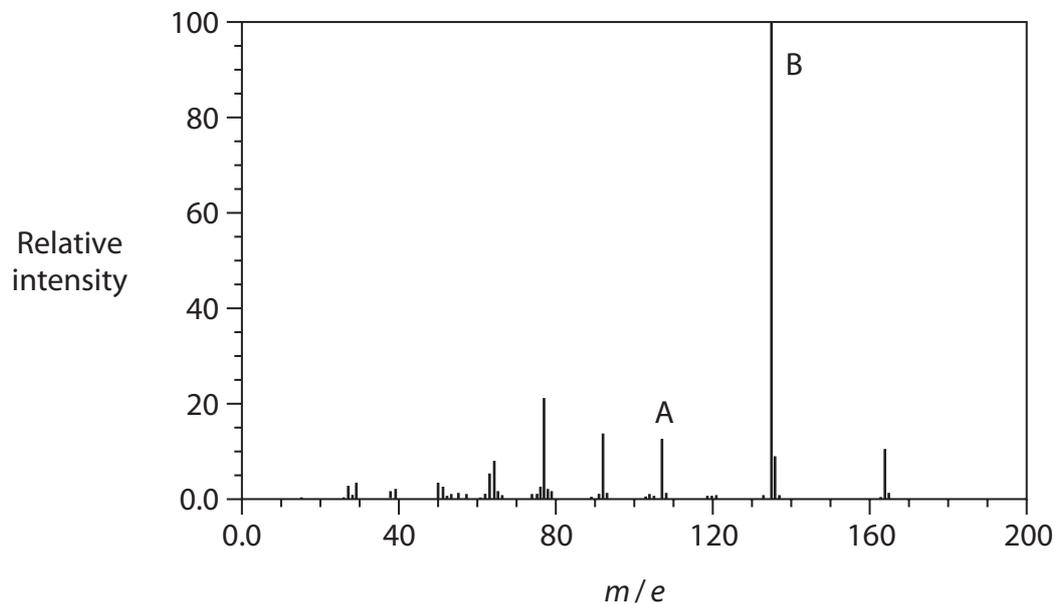
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- (d) Identify the structure of the fragments responsible for the peaks labelled A ($m/e = 107$) and B ($m/e = 135$) in the mass spectrum of 4-methoxypropiofenone. You should give a structural formula for each fragment ion.

(2)



4-methoxypropiofenone

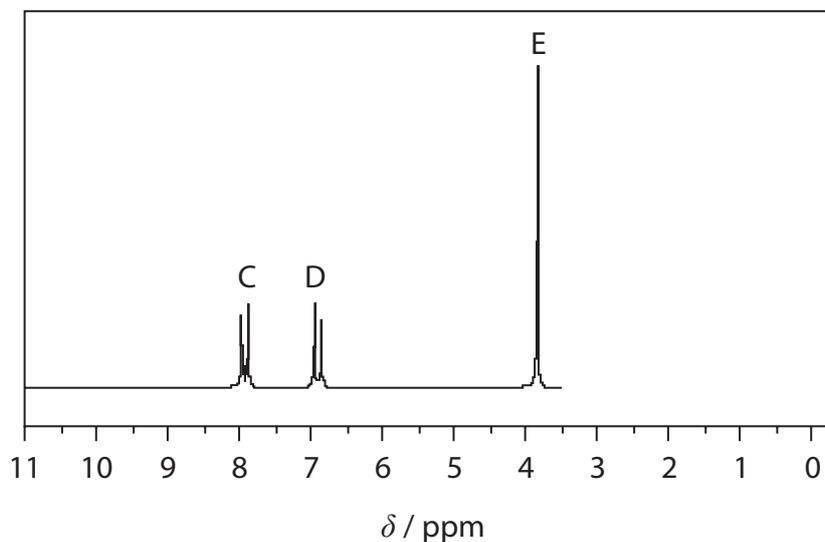
Structural formulae of fragment ions:

A	B



- (e) An incomplete high resolution proton nmr spectrum of 4-methoxypropiophenone is shown.

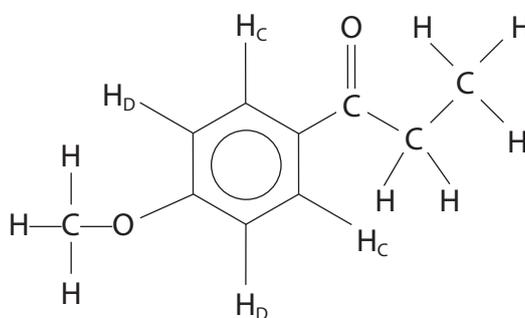
nmr spectrum of 4-methoxypropiophenone



Peaks C and D in the spectrum are caused by the hydrogen atoms on the benzene ring. These hydrogen atoms have been labelled on the structural formula as H_C and H_D .

- (i) On the structural formula below, label as H_E the hydrogen atoms responsible for the singlet peak E.

(1)



- (ii) Using the Data Booklet as a source of data, complete the high resolution nmr spectrum shown in (e) by predicting the peaks found in the region $\delta = 0 - 3.5$.

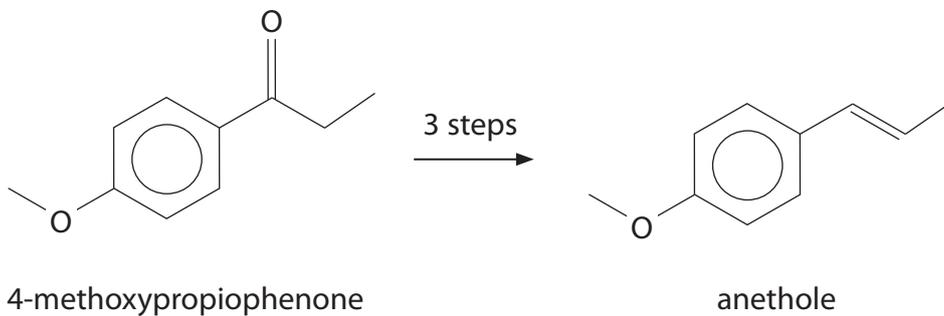
Show any splitting patterns and state the relative peak areas on your completed spectrum.

(3)



- (f) Anethole was synthesised from 4-methoxypropiophenone in a **three** step synthesis. One of the intermediate compounds contained a chlorine atom.

Devise this synthetic route, including reagents and conditions for each step, and the structural formulae of both intermediate compounds.



4-methoxypropiophenone

anethole

(5)

(Total for Question 14 = 23 marks)



15 A double salt has the formula $M_2Cu(SO_4)_2 \cdot nH_2O$, where M is an unknown metal ion which does not react with iodide or thiosulfate ions.

A titration was carried out to determine the mass of copper in the double salt.

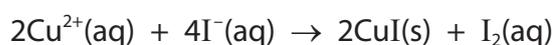
0.500 g of the double salt was dissolved to make 100.0 cm^3 of an aqueous solution.

Excess iodide ions were added to 10.0 cm^3 portions of this solution, forming a white precipitate and a brown solution of iodine.

The iodine was titrated with a solution of sodium thiosulfate of concentration $3.00 \times 10^{-3} \text{ mol dm}^{-3}$.

The mean titre was 21.60 cm^3 .

The equations for the reactions involved are



(a) (i) Calculate the number of moles of copper present in 0.500 g of the double salt, $M_2Cu(SO_4)_2 \cdot nH_2O$.

(2)

(ii) Calculate the mass of copper in 0.500 g of the double salt, giving your answer to **two** significant figures.

(1)

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- (b) An experiment was carried out to determine the mass of water of crystallisation in 0.500 g of the double salt and hence determine the identity of M.

A 0.500 g sample of the double salt was heated to remove the water. The remaining mass when all the water had been driven off was 0.430 g.

Using your answers to (a)(i) and (a)(ii) and these data, identify M and give the formula of the double salt.

(5)

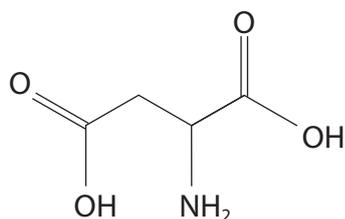
(Total for Question 15 = 8 marks)



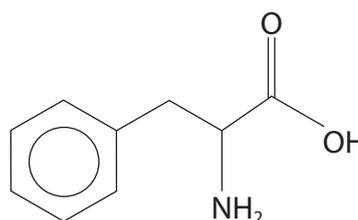
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16 This question is about amino acids and their reactions.

- (a) Aspartic acid and phenylalanine are the non-systematic names of the two amino acids shown.



aspartic acid



phenylalanine

- (i) Give the systematic name of aspartic acid.

(1)

- (ii) Draw the structure of aspartic acid at pH 13.

(1)

- (iii) Draw a diagram of the zwitterion of phenylalanine and use this to explain its relatively high melting temperature.

(2)

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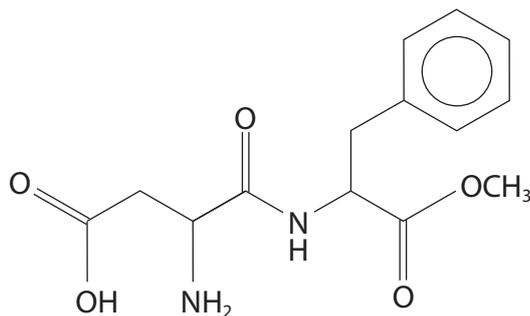
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- (b) Aspartame is an artificial sweetener which is derived from phenylalanine and aspartic acid. The structure of aspartame is shown.



Acid-catalysed hydrolysis of aspartame, followed by chromatography, can be used to confirm the identity of the two amino acids produced. Hydrolysis gives the two amino acids and a third organic product.

- (i) Identify the third organic product of the hydrolysis. (1)

- *(ii) Describe in outline a chromatography experiment that can be used to confirm the identity of the two amino acids. (3)

- (iii) Aspartame is not used as a sweetener in foods which require cooking. Suggest why not. (1)

(Total for Question 16 = 9 marks)

TOTAL FOR SECTION B = 51 MARKS



SECTION C

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

17

Carbon monoxide

Carbon monoxide is a colourless, odourless and tasteless gas that is slightly less dense than air. In concentrations above 43.2 mg m^{-3} , carbon monoxide is toxic to animals which use haemoglobin to transfer oxygen in their blood. This toxicity is due to carbon monoxide acting as a ligand by bonding strongly to the iron ions in haemoglobin.

Carbonylation reactions introduce carbon monoxide into both inorganic and organic compounds. The products of such reactions are termed carbonyl compounds.

In inorganic chemistry, carbonyl compounds contain carbon monoxide acting as a neutral ligand, bonding to the metal through the carbon atom via a dative covalent bond. Several carbonyl complexes of the transition metals, which have only carbonyl groups as ligands, are known, including iron(0) pentacarbonyl, $\text{Fe}(\text{CO})_5$, and compounds of nickel and manganese. Dicobalt(0) octacarbonyl, $\text{Co}_2(\text{CO})_8$, has a cobalt-cobalt covalent bond.

In organic chemistry, a carbonyl group contains a carbon atom double-bonded to an oxygen atom. Carbon monoxide can be used directly to form carbonyl compounds.

Organic chemists make use of the ability of transition metals to form inorganic carbonyl compounds by using them as catalysts for carbonylation reactions. Typical processes include the Cativa™ Process for the production of ethanoic acid, which uses an iridium carbonyl compound as the catalyst, and the synthesis of ibuprofen using palladium metal as a catalyst.

- (a) During a chemical reaction in a school laboratory, 0.35 mol of carbon monoxide was accidentally released. The laboratory has a volume of 200 m^3 . Calculate whether this release is less than the toxicity limit of 43.2 mg m^{-3} .

(2)

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- (b) (i) Predict the shape of iron(0) pentacarbonyl. The shape is not affected by lone pairs on the iron atom. Draw a diagram giving the values of the bond angles.

(2)

Shape

- (ii) Complete the dot-and-cross diagram showing the bonding in a carbon monoxide ligand and its attachment to the iron atom.

Use a dot (•) for the electrons of the carbon and a cross (×) for the electrons of the oxygen.

Only outer shell electrons need to be shown.

Do **not** show the electrons of iron.

(2)

Fe C O



(c) A covalently bonded carbonyl compound of manganese, consisting of only manganese atoms and carbonyl groups, decomposes above 80°C to give manganese metal and carbon monoxide. The carbon monoxide was allowed to return to room temperature and pressure.

- (i) 7.8 g of the compound gave 4.8 dm^3 of carbon monoxide, measured at room temperature and pressure. Find the ratio of manganese atoms to carbon monoxide molecules.

The volume of 1 mol of gas at room temperature and pressure is 24 dm^3 .

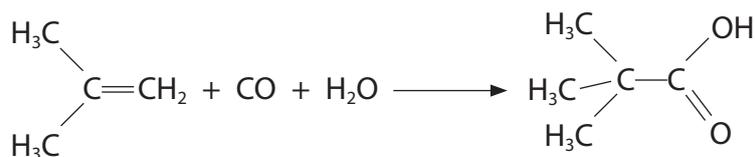
(3)

- (ii) The mass spectrum of the manganese carbonyl compound showed a peak at $m/e = 390$. Using this value and your answer to (c)(i), suggest a possible structure for the carbonyl compound.

(2)



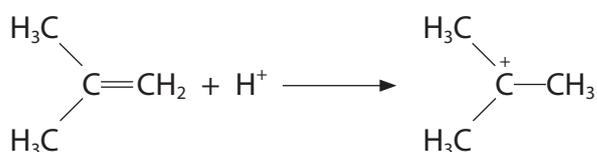
- (d) Carbon monoxide and water can be used to convert 2-methylpropene into 2,2-dimethylpropanoic acid.



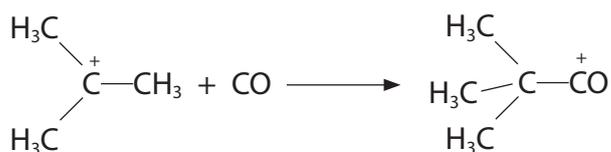
The reaction is carried out at high temperature and pressure and in the presence of a strong acid such as sulfuric acid.

The steps in this process are shown.

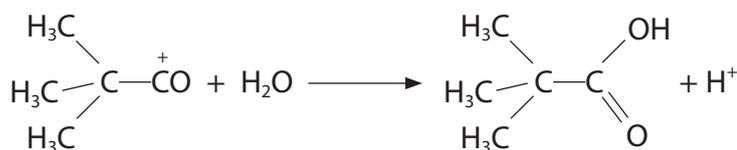
Step 1



Step 2



Step 3



- (i) Explain how these steps demonstrate the role of the sulfuric acid.

(2)

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- (ii) Use your knowledge of reaction mechanisms to draw a diagram to illustrate the role of the carbon monoxide as a nucleophile in the second step of the reaction.

You should include any curly arrows and relevant lone pairs of electrons.

(2)

- (iii) Suggest **one** disadvantage of using concentrated sulfuric acid.

(1)

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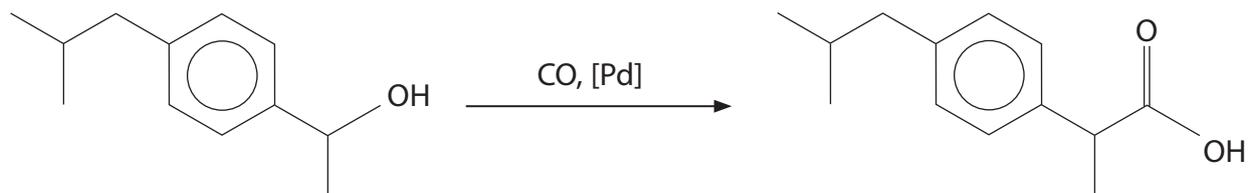
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- (e) In the production of ibuprofen, palladium metal is used as a heterogeneous catalyst to catalyse the carbonylation reaction shown.



Describe fully how a heterogeneous catalyst such as palladium acts as a catalyst in this reaction.

(3)

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(Total for Question 17 = 19 marks)

TOTAL FOR SECTION C = 19 MARKS
TOTAL FOR PAPER = 90 MARKS



