Write your name here

Surname	Other names

Pearson Edexcel
International Advanced Level

Centre Number | | | | | |

Candidate Number | | | | |

Chemistry
Advanced
Unit 5: General Principles of Chemistry II – Transition Metals and Organic Nitrogen Chemistry (including synoptic assessment)

Monday 15 June 2015 – Afternoon
Time: 1 hour 40 minutes

Paper Reference
WCH05/01

You must have: Data Booklet

Candidates may use a calculator.

Total Marks

Instructions

- Use **black** ink or 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.
- Keep an eye on the time.
- Try to answer every question.
- Check your answers if you have time at the end.

Turn over ▶

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5/5/5/4/1/

P 4 5 0 7 4 A 0 1 2 8

PEARSON

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 The oxidation number of oxygen in hydrogen peroxide, H_2O_2, is

☒ **A** +2

☒ **B** 0

☒ **C** –1

☒ **D** –2

(Total for Question 1 = 1 mark)

2 Copper reacts with nitrate ions, NO_3^-, in acid conditions to form copper(II) ions and nitrogen(IV) oxide.

By considering the changes in the oxidation numbers of copper and nitrogen, it can be deduced that the redox reaction involves

☒ **A** 1 mol of copper reacting with 2 mol of nitrate ions.

☒ **B** 2 mol of copper reacting with 1 mol of nitrate ions.

☒ **C** 1 mol of copper reacting with 4 mol of nitrate ions.

☒ **D** 4 mol of copper reacting with 1 mol of nitrate ions.

(Total for Question 2 = 1 mark)

3 The E_{cell} for a reaction is +1.00 V. What can be deduced about this reaction?

☒ **A** At equilibrium there will be mainly reactants.

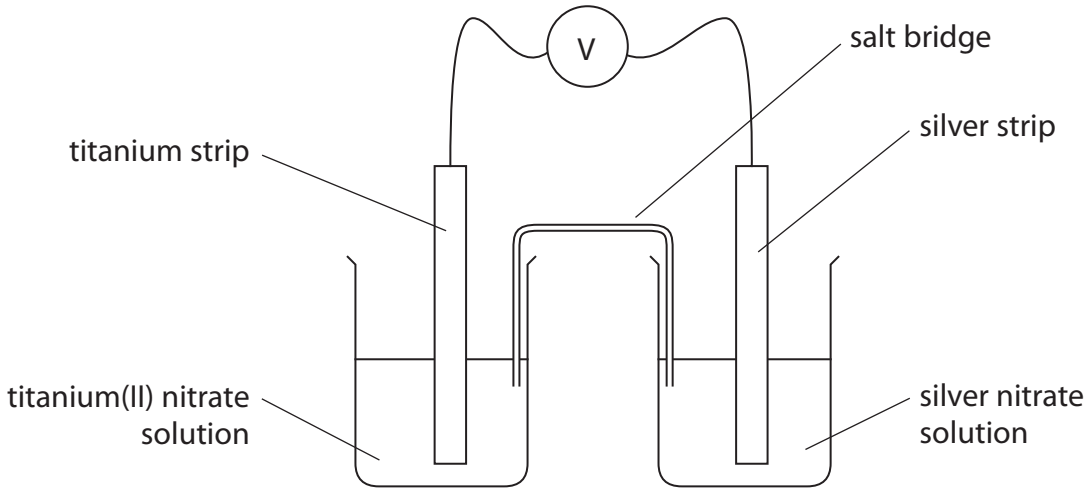
☒ **B** At equilibrium there will be mainly products.

☒ **C** At equilibrium there will be approximately equal amounts of reactants and products.

☒ **D** It is impossible to estimate the relative amounts of reactants and products at equilibrium because the E_{cell} was not measured under standard conditions.

(Total for Question 3 = 1 mark)

4 The cell shown in the diagram below was set up.



The emf of this cell under standard conditions is +2.43 V.
The $E^{\ominus}$ value for the $Ag^{+}(aq)|Ag(s)$ half cell is +0.80 V.

What is the $E^{\ominus}$ value for the $Ti^{2+}(aq)|Ti(s)$ half cell?

☒ **A** +3.23 V

☒ **B** +1.63 V

☒ **C** −1.63 V

☒ **D** −3.23 V

(Total for Question 4 = 1 mark)

5 In the hydrogen-oxygen fuel cell, oxygen is

☒ **A** oxidized at the negative electrode.

☒ **B** oxidized at the positive electrode.

☒ **C** reduced at the negative electrode.

☒ **D** reduced at the positive electrode.

(Total for Question 5 = 1 mark)

6 The electronic configuration of the element vanadium is

		3d					4s
☒ **A**	[Ar]	↑↓	↑↓	↑			
☒ **B**	[Ar]	↑	↑	↑	↑	↑	
☒ **C**	[Ar]	↑	↑	↑	↑		↑
☒ **D**	[Ar]	↑	↑	↑			↑↓

(Total for Question 6 = 1 mark)

7 Transition metals typically form a number of ions which are stable in aqueous solution. The **best** explanation for this property is that

☒ **A** the differences in the successive ionization energies are similar to the differences in hydration enthalpies of the ions.

☒ **B** all the ions are formed by the removal of electrons from the d subshell.

☒ **C** the ionization energies of transition metals are low.

☒ **D** the hydration enthalpies of transition metal ions are always more exothermic than those of ions of s and p block metals.

(Total for Question 7 = 1 mark)

8 Which of the following species **never** combine with ligands to form complexes?

☒ **A** Positively charged ions of d block elements.

☒ **B** Neutral atoms of d block elements.

☒ **C** Negatively charged ions of d block elements.

☒ **D** Positively charged ions of p block elements.

(Total for Question 8 = 1 mark)

9 Transition metal complexes are formed when ethanedioate ions and ethanoate ions are added separately to aqueous solutions of transition metal ions.

The complexes formed by the bidentate ethanedioate ligands are more stable than the complexes formed by the monodentate ethanoate ligands. This is because

- ☒ **A** ethanedioate ligands form stronger bonds with the metal ion of a complex than do ethanoate ligands.
- ☒ **B** the formation of ethanedioate complexes increases the number of particles in the solution.
- ☒ **C** ethanedioic acid is a stronger acid than ethanoic acid.
- ☒ **D** ethanedioic acid is a weaker acid than ethanoic acid.

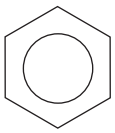
(Total for Question 9 = 1 mark)

10 If the temperature of the nitration of benzene is allowed to rise too high, dinitration and trinitration can occur. This is evidence that the

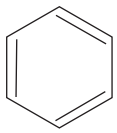
- ☒ **A** nitro group is electron withdrawing.
- ☒ **B** nitro group is electron donating.
- ☒ **C** delocalisation energy of nitrobenzene is greater than that of benzene.
- ☒ **D** delocalisation energy of nitrobenzene is less than that of benzene.

(Total for Question 10 = 1 mark)

11 The benzene molecule may be represented in two ways:



structure I



structure II

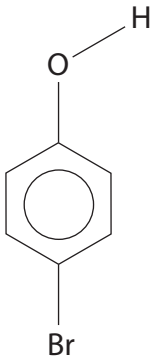
Which of the following does **not** provide evidence that **structure I** is the better representation of benzene?

- ☒ **A** Infrared spectroscopy
- ☒ **B** High performance liquid chromatography
- ☒ **C** Thermochemistry
- ☒ **D** X-ray diffraction

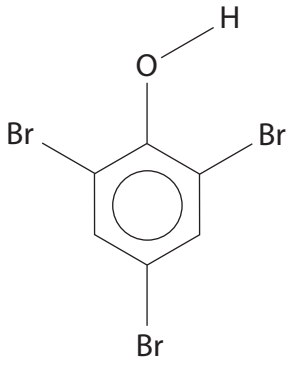
(Total for Question 11 = 1 mark)

12 When phenol, C_6H_5OH, reacts with excess bromine water, the organic product is

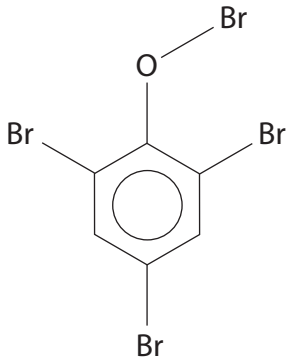
☒ **A**



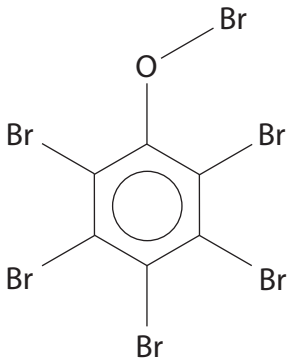
☒ **B**



☒ **C**



☒ **D**



(Total for Question 12 = 1 mark)

13 Ammonia, butylamine and phenylamine are dissolved in separate samples of water to form solutions of the same concentration. The pH of each solution was measured.

The order of **increasing** pH will be

☒ **A** ammonia < butylamine < phenylamine

☒ **B** butylamine < ammonia < phenylamine

☒ **C** phenylamine < ammonia < butylamine

☒ **D** phenylamine < butylamine < ammonia

(Total for Question 13 = 1 mark)

14 Aromatic amines may be converted into benzenediazonium ions. What are the most suitable reagents and conditions for this reaction?

	Reagent 1	Reagent 2	Temperature / °C
☒ **A**	$NaNO_2$	sulfuric acid	+55
☒ **B**	$NaNO_3$	hydrochloric acid	+5
☒ **C**	$NaNO_2$	hydrochloric acid	+5
☒ **D**	$NaNO_3$	sulfuric acid	+55

(Total for Question 14 = 1 mark)

15 The repeat unit of the polymer formed from ethane-1,2-diol and ethanedioic acid is

☒ **A** $-OCH_2CH_2OOCCO-$

☒ **B** $-OCH_2CH_2OCOOCO-$

☒ **C** $-OCH_2OOCCH_2CO-$

☒ **D** $-OCCH_2CH_2OOCO-$

(Total for Question 15 = 1 mark)

16 Poly(ethenol) is an example of

☒ **A** an addition polymer that is soluble in water.

☒ **B** an addition polymer that is insoluble in water.

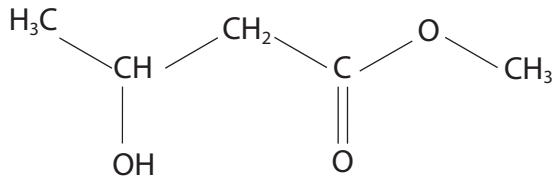
☒ **C** a condensation polymer that is soluble in water.

☒ **D** a condensation polymer that is insoluble in water.

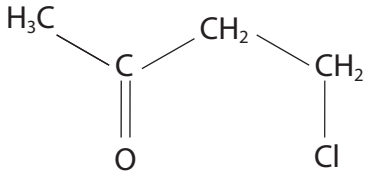
(Total for Question 16 = 1 mark)

17 A compound gives an orange precipitate with 2,4-dinitrophenylhydrazine, Brady's reagent, but does **not** react with ammonia in the cold.
The compound could be

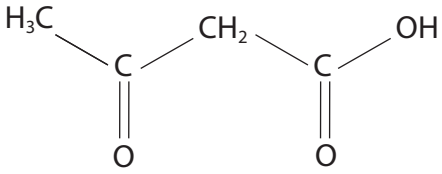
☒ **A**



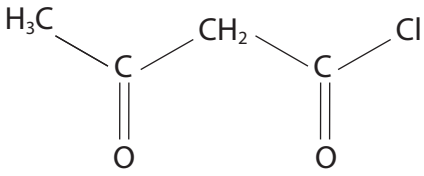
☒ **B**



☒ **C**



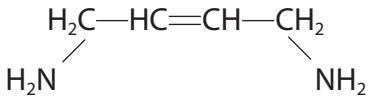
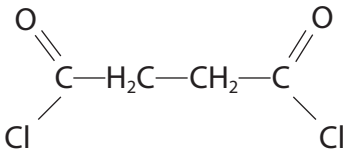
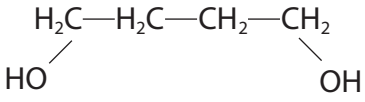
☒ **D**



(Total for Question 17 = 1 mark)

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

18 Three compounds are possible monomers in the formation of a polymer:

I	
II	
III	

Which of the following compounds could **not** react in the stated combination to form a polymer?

☒ **A** I alone

☒ **B** I in combination with II

☒ **C** II in combination with III

☒ **D** I in combination with III

(Total for Question 18 = 1 mark)

19 Pentan-3-one reacts with 2,4-dinitrophenylhydrazine to form a derivative which has a melting temperature of 156 °C.

A student attempted to synthesise pentan-3-one, and converted some of the product into the same derivative. The student's derivative melted gradually from 148 °C to 158 °C.

It is most likely that the student had synthesised

☒ **A** pure pentan-3-one.

☒ **B** impure pentan-3-one.

☒ **C** approximately equal amounts of two carbonyl derivatives, one with a melting temperature of 148 °C and the other with a melting temperature of 158 °C.

☒ **D** a compound that was not a ketone.

(Total for Question 19 = 1 mark)

20 The purification of organic compounds prepared in aqueous mixtures often involves solvent extraction. Desirable properties of the solvent used include that it is

☒ **A** fully miscible in water and has a high boiling temperature.

☒ **B** fully miscible in water and has a low boiling temperature.

☒ **C** immiscible in water and has a high boiling temperature.

☒ **D** immiscible in water and has a low boiling temperature.

(Total for Question 20 = 1 mark)

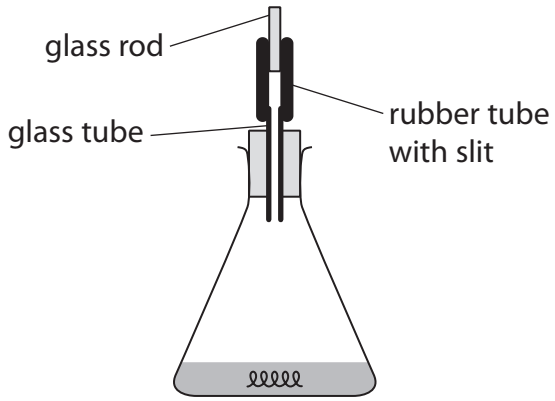
TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

21 Steel is the world's most important structural metal; it is strong and cheap but it corrodes rapidly if unprotected. In its simplest form, steel is an alloy of iron and carbon.

(a) The following method was used to determine the percentage of iron in a sample of wire. Exactly 1.25 g of the wire was placed in a conical flask and about 50 cm^3 of dilute sulfuric acid (an excess) was added. The flask was closed as shown in the diagram below.



When all of the iron in the wire had been converted to iron(II) sulfate, the contents of the flask were used to make 250.0 cm^3 of solution with distilled water.

25.00 cm^3 portions of this final solution were placed in a conical flask, acidified with an equal volume of dilute sulfuric acid and then titrated with a potassium manganate(VII) solution of concentration 0.0195 mol dm^{-3}. The mean titre was 22.15 cm^3.

(i) Write the equation for the reaction between iron and dilute sulfuric acid. Include state symbols in your answer.

(1)

(ii) Suggest why the conical flask was not left open, and how the labelled part of the apparatus shown in the diagram works.

(2)

(iii) State the essential steps of the procedure for making up the reaction mixture to 250.0 cm^3 for use in the titration.

(3)

(iv) Write the **ionic** equation for the titration reaction to show that 5 mol of iron(II) ions react with 1 mol of manganate(VII) ions. State symbols are not required.

(1)

(v) Calculate the percentage by mass of iron in the wire. Give your answer to **three** significant figures.

(4)

(vi) Describe the colour change at the end-point of the titration.

(1)

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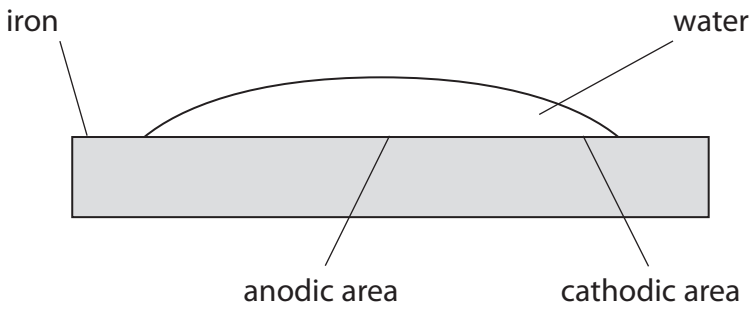
(vii) One student who carried out this experiment forgot to acidify the mixture in the conical flask before the titration.

A brown precipitate formed before the end-point.

Identify the brown precipitate and explain how this error affects the titration value.

(3)

(b) The rusting of iron is an electrochemical process. A piece of iron with a droplet of water on its surface operates as an electrochemical cell. In the first stage of corrosion, iron is oxidized to iron(II) ions in the anodic area and the electrons produced travel to the cathodic area where oxygen from the air is reduced.



(i) From the information about standard electrode potentials on pages 14 and 15 of the Data Booklet, write the ionic half equations for the reactions taking place at the anodic area and at the cathodic area. State symbols are not required.

(2)

Anodic area

Cathodic area

(ii) Calculate $E^{\ominus}_{cell}$ for the overall reaction in (b)(i).

(1)

(iii) By considering the rusting mechanism described in part (b), suggest why the presence of salt in the water droplet speeds up rusting.

(1)

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(iv) The corrosion of oil pipelines made of steel is prevented by connecting the pipeline to magnesium blocks. Suggest how this method works.

(1)

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(Total for Question 21 = 20 marks)

22 Crystals of copper(II) sulfate dissolve in water to form a blue solution, **A**. When dilute aqueous ammonia is added to this solution, a pale blue precipitate, **B**, forms which dissolves in excess aqueous ammonia to form a dark blue solution, **C**.

(a) (i) Give the **formula** of the copper species in **A**, **B** and **C**. You should include all of the ligands present in each species.

(3)

A .....

B .....

C .....

(ii) Explain why solution **A** is coloured.

(4)

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(iii) Explain why solution **A** is a different colour to solution **C**.

(2)

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(b) A more concentrated solution of **C** may be prepared by using concentrated aqueous ammonia in place of dilute aqueous ammonia. The crystalline sulfate of **C** may be obtained by cooling the mixture in an ice bath and adding ethanol. The filtered crystals may be recrystallized using ethanol as the solvent.

The steps of the recrystallization are summarised below. In the spaces provided, explain the purpose of each step, referring particularly to any words in **bold** type.

(5)

Step 1 The solid was dissolved in the **minimum** amount of hot ethanol.

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Step 2 The **hot** solution was **filtered**.

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Step 3 The filtrate was cooled in an **ice bath**.

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Step 4 The mixture was **filtered** using **suction filtration**.

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(Total for Question 22 = 14 marks)

23 This question is about an unknown organic compound, **Q**.

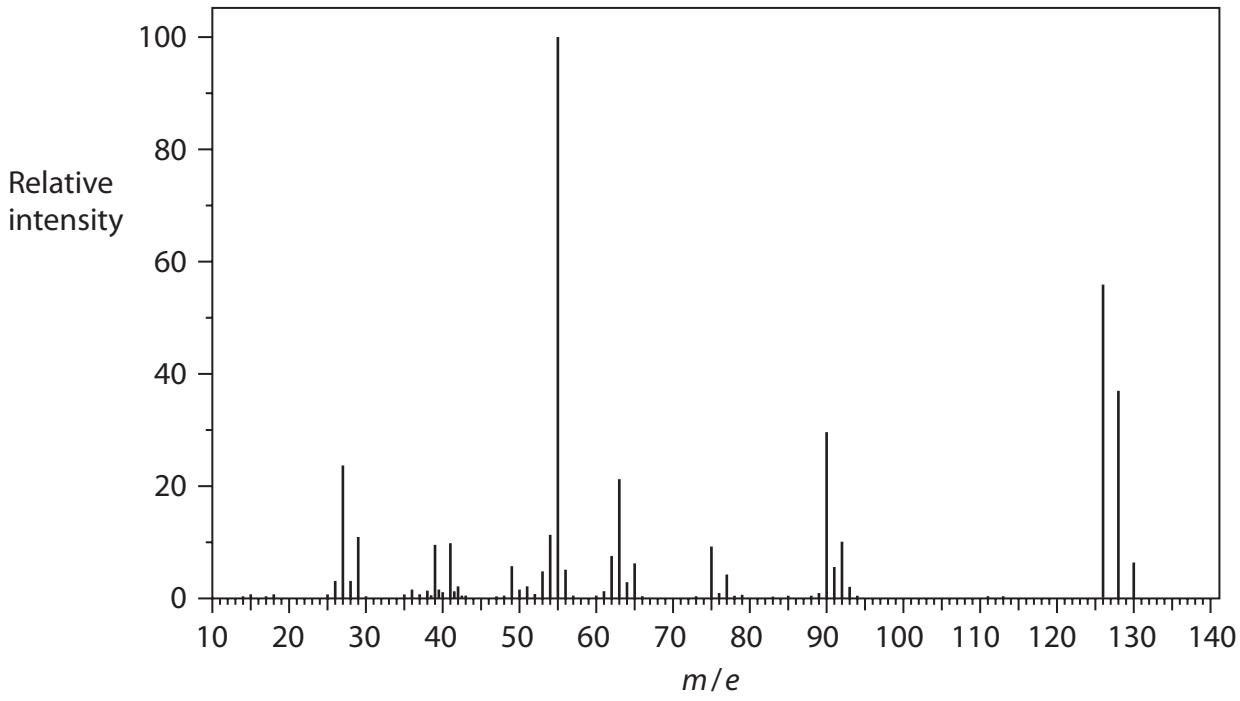
The percentage composition by mass of **Q** is

carbon = 37.8%; hydrogen = 6.30%; chlorine = 55.9%.

(a) Calculate the empirical formula of **Q**.

(2)

(b) The mass spectrum of **Q** is shown below.



(i) Use your answer to part (a) and the mass spectrum to deduce the molecular formula of **Q**.

(1)

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(ii) Explain why there are three peaks in the molecular ion region (*m*/*e* from 126 to 130) of the mass spectrum of **Q**.

(2)

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(iii) State why the peak at *m*/*e* = 126 is the highest of the three peaks in the molecular ion region.

(1)

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*(iv) **Q** reacts with aqueous sodium hydroxide to form an organic compound, **R**.

The functional groups of compound **R** are on different carbon atoms.

Compound **R** reacted slowly with sodium, producing a total of one mole of hydrogen gas per mole of **R**.

When compound **R** was heated under reflux with excess acidified sodium dichromate(VI), an organic compound, **S**, was formed.
Compound **S** reacted rapidly with sodium, producing a total of 0.5 mol of hydrogen gas per mole of **S**.

Draw the **displayed** formulae of the two possible structures for compound **S**.
Explain how your structures are consistent with these data.

(5)

Structure I	Structure II

Explanation .....

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(v) Compound **S** reacted with iodine dissolved in aqueous sodium hydroxide, producing a pale yellow precipitate with an antiseptic smell.

Identify the pale yellow precipitate and hence identify which of the structures that you have given in (b)(iv) is compound **S**. Explain your reasoning.

(2)

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.....

.....

(vi) **Name** compound **R** and give the equation for its reaction with sodium.

(3)

R = ...

Equation

(Total for Question 23 = 16 marks)

TOTAL FOR SECTION B = 50 MARKS

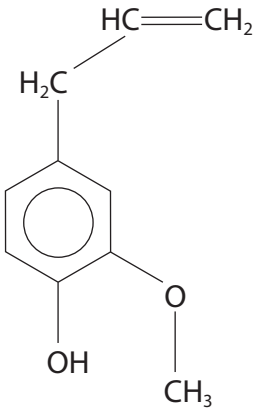
SECTION C

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

24

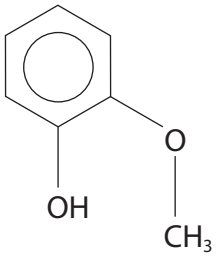
Oil of cloves

Oil of cloves is a traditional remedy for toothache; it is a topical treatment, which means that it is applied externally. The main active ingredient of oil of cloves is eugenol, which also gives cloves their characteristic smell. The structure of eugenol is shown below.



eugenol

(a) A student suggested that eugenol could be prepared by an electrophilic substitution of 2-methoxyphenol, which is produced in the gut of desert locusts. This compound is one of the main components of the pheromones that cause locust swarming. The structure of 2-methoxyphenol is shown below.



2-methoxyphenol

(i) Use your knowledge of electrophilic substitution reactions to suggest the structure of an electrophile that might be used in this reaction.

(1)

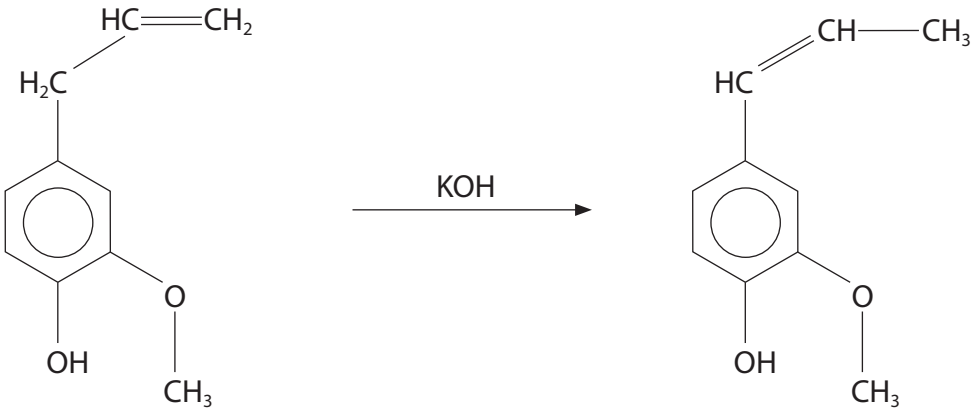
(ii) Suggest an organic compound that could be used to produce the electrophile that you have given in (a)(i).

(1)

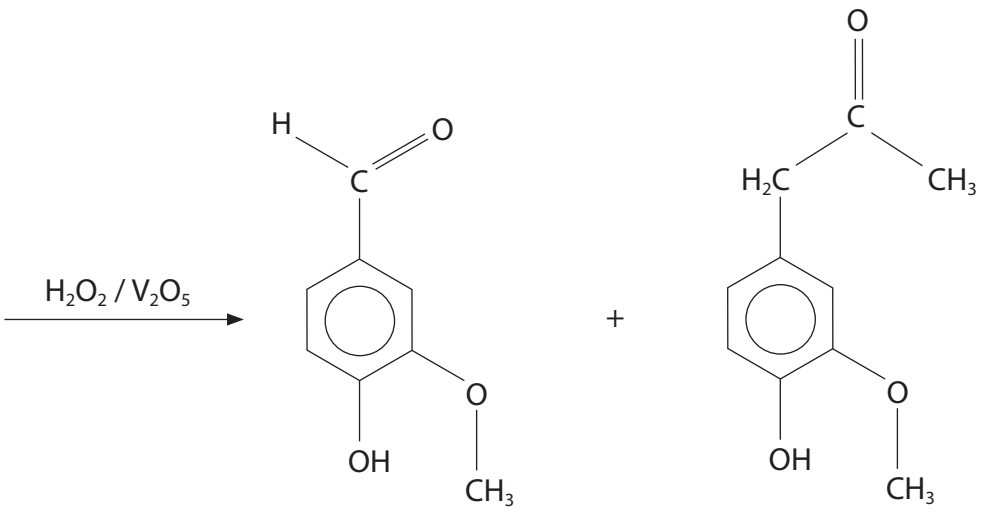
(iii) Write the mechanism for the electrophilic substitution to prepare eugenol from 2-methoxyphenol, using the electrophile that you have given in (a)(i).

(3)

(b) Eugenol has been used in the manufacture of vanillin, the compound responsible for the flavour of vanilla. The process involves the conversion of eugenol to its isomer isoeugenol, which is then oxidized by hydrogen peroxide with a vanadium(V) oxide catalyst.



eugenol isoeugenol



vanillin methyl vanillyl ketone

(i) Isoeugenol exists as two stereoisomers, whereas eugenol has just one structure. State the type of stereoisomerism shown by isoeugenol and explain why it can show this type of stereoisomerism, whereas eugenol does not.

(2)

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.....

.....

.....

*(ii) Discuss whether or not high resolution proton nmr spectroscopy could be used to distinguish between eugenol and a single isomer of isoeugenol.

You should consider the numbers of peaks in the spectra, their splitting patterns and the areas under the peaks. You are **not** expected to suggest chemical shift values.

(4)

(iii) Suggest, in outline, a mechanism by which vanadium(V) oxide acts as a catalyst for the reaction between hydrogen peroxide and isoeugenol to form vanillin. You are **not** expected to give equations for the mechanism.

(2)

(iv) A student suggested that the infrared spectroscopy data on page 5 of the Data Booklet could be used to show whether the purified vanillin contains a trace of methyl vanillyl ketone.

Explain the basis of this idea and suggest why it may not work in practice.

(2)

(c) The Zeisel method for determining the purity of vanillin involves estimating the percentage by mass of methoxy group (CH_3O) in the sample and comparing this with the percentage in pure vanillin.

In a sequence of reactions, each methoxy group produces iodine which is estimated by titration with a sodium thiosulfate solution of known concentration. The Zeisel sequence is

Step 1 $ROCH_3 + HI \rightarrow ROH + CH_3I$

Step 2 $CH_3I + Br_2 \rightarrow CH_3Br + IBr$

Step 3 $IBr + 3H_2O + 2Br_2 \rightarrow HIO_3 + 5HBr$

Step 4 $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$

Step 5 $I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$

(i) Deduce the number of moles of thiosulfate ions that are equivalent to one mole of methoxy group. Explain your answer.

(2)

(ii) A sample of vanillin was found to have 20.09% by mass of methoxy group. Calculate the percentage purity of the vanillin.

(3)

(Total for Question 24 = 20 marks)

TOTAL FOR SECTION C = 20 MARKS
TOTAL FOR PAPER = 90 MARKS

The Periodic Table of Elements

1	2											3	4	5	6	7	0 (8) (18)
							1.0 H hydrogen 1										4.0 He helium 2
(1)	(2)		Key: relative atomic mass / atomic symbol / name / atomic (proton) number									(13)	(14)	(15)	(16)	(17)	
6.9 Li lithium 3	9.0 Be beryllium 4											10.8 B boron 5	12.0 C carbon 6	14.0 N nitrogen 7	16.0 O oxygen 8	19.0 F fluorine 9	20.2 Ne neon 10
23.0 Na sodium 11	24.3 Mg magnesium 12	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	27.0 Al aluminium 13	28.1 Si silicon 14	31.0 P phosphorus 15	32.1 S sulfur 16	35.5 Cl chlorine 17	39.9 Ar argon 18
39.1 K potassium 19	40.1 Ca calcium 20	45.0 Sc scandium 21	47.9 Ti titanium 22	50.9 V vanadium 23	52.0 Cr chromium 24	54.9 Mn manganese 25	55.8 Fe iron 26	58.9 Co cobalt 27	58.7 Ni nickel 28	63.5 Cu copper 29	65.4 Zn zinc 30	69.7 Ga gallium 31	72.6 Ge germanium 32	74.9 As arsenic 33	79.0 Se selenium 34	79.9 Br bromine 35	83.8 Kr krypton 36
85.5 Rb rubidium 37	87.6 Sr strontium 38	88.9 Y yttrium 39	91.2 Zr zirconium 40	92.9 Nb niobium 41	95.9 Mo molybdenum 42	[98] Tc technetium 43	101.1 Ru ruthenium 44	102.9 Rh rhodium 45	106.4 Pd palladium 46	107.9 Ag silver 47	112.4 Cd cadmium 48	114.8 In indium 49	118.7 Sn tin 50	121.8 Sb antimony 51	127.6 Te tellurium 52	126.9 I iodine 53	131.3 Xe xenon 54
132.9 Cs caesium 55	137.3 Ba barium 56	138.9 La* lanthanum 57	178.5 Hf hafnium 72	180.9 Ta tantalum 73	183.8 W tungsten 74	186.2 Re rhenium 75	190.2 Os osmium 76	192.2 Ir iridium 77	195.1 Pt platinum 78	197.0 Au gold 79	200.6 Hg mercury 80	204.4 Tl thallium 81	207.2 Pb lead 82	209.0 Bi bismuth 83	[209] Po polonium 84	[210] At astatine 85	[222] Rn radon 86
[223] Fr francium 87	[226] Ra radium 88	[227] Ac* actinium 89	[261] Rf rutherfordium 104	[262] Db dubnium 105	[266] Sg seaborgium 106	[264] Bh bohrium 107	[277] Hs hassium 108	[268] Mt meitnerium 109	[271] Ds darmstadtium 110	[272] Rg roentgenium 111							

Elements with atomic numbers 112-116 have been reported but not fully authenticated

* Lanthanide series	140 Ce cerium 58	141 Pr praseodymium 59	144 Nd neodymium 60	[147] Pm promethium 61	150 Sm samarium 62	152 Eu europium 63	157 Gd gadolinium 64	159 Tb terbium 65	163 Dy dysprosium 66	165 Ho holmium 67	167 Er erbium 68	169 Tm thulium 69	173 Yb ytterbium 70	175 Lu lutetium 71
* Actinide series	232 Th thorium 90	[231] Pa protactinium 91	238 U uranium 92	[237] Np neptunium 93	[242] Pu plutonium 94	[243] Am americium 95	[247] Cm curium 96	[245] Bk berkelium 97	[251] Cf californium 98	[254] Es einsteinium 99	[253] Fm fermium 100	[256] Md mendelevium 101	[254] No nobelium 102	[257] Lr lawrencium 103

P 4 5 0 7 4 A 0 2 8 2 8

PMT