Pearson Edexcel International Advanced Level

Time 1 hour 45 minutes

Paper reference **WCH15/01**

Chemistry
International Advanced Level
UNIT 5: Transition Metals and Organic Nitrogen Chemistry

You must have:
Scientific calculator, Data Booklet

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*.
- In the question marked with an **asterisk** (*), marks will be awarded for your ability to structure your answer logically, showing how the points that you make are related or follow on from each other where appropriate.
- 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.
- Try to answer every question.
- Check your answers if you have time at the end.

Turn over

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 When copper is added to concentrated nitric acid, a brown gas is given off and the final solution is blue.

In terms of oxidation number and electron transfer, how does the **nitrogen** change in this reaction?

		Oxidation number	Electron transfer
⊠	**A**	decreases	gains electrons
⊠	**B**	decreases	loses electrons
⊠	**C**	increases	gains electrons
⊠	**D**	increases	loses electrons

(Total for Question 1 = 1 mark)

2 What is the pressure of hydrogen gas used in the standard hydrogen electrode?

⊠ **A** 1 Pa

⊠ **B** 100 Pa

⊠ **C** 1 000 Pa

⊠ **D** 100 000 Pa

(Total for Question 2 = 1 mark)

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

3 An electrochemical cell is set up using the electrode systems shown.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$$

$$TiO^{2+} + 2H^+ + e^- \rightleftharpoons Ti^{3+} + H_2O$$
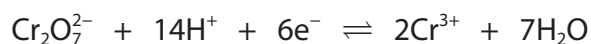
(a) What materials will be used for the electrodes in this cell?

(1)

		$Cr_2O_7^{2-}$, Cr^{3+}	TiO^{2+} , Ti^{3+}
☒	**A**	chromium	titanium
☒	**B**	chromium	platinum
☒	**C**	platinum	titanium
☒	**D**	platinum	platinum

(b) The reaction between $Cr_2O_7^{2-}$ ions and Ti^{3+} ions has $E^{\ominus}_{cell} = +1.14\,V$.
The standard electrode potential for the $Cr_2O_7^{2-}$, Cr^{3+} electrode system is $+1.33\,V$.

What is the standard electrode potential for the TiO^{2+} , Ti^{3+} electrode system?

(1)

☒ **A** −2.47 V

☒ **B** −0.19 V

☒ **C** +0.19 V

☒ **D** +2.47 V

(Total for Question 3 = 2 marks)

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

4 The possibility of a reaction between potassium dichromate(VI) and hydrochloric acid may be assessed using standard electrode potentials but also depends on the activation energy, E_a, of the reaction.

$$Cr_2O_7^{2-} + 14H^+ + 6Cl^- \rightarrow 2Cr^{3+} + 7H_2O + 3Cl_2 \qquad E_{cell}^{\ominus} = -0.03\,V$$
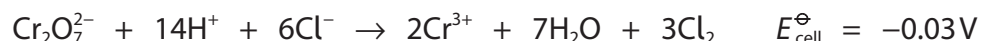
When potassium dichromate(VI) and hydrochloric acid are mixed, very little chlorine is formed under standard conditions but a significant amount of chlorine is produced when concentrated hydrochloric acid is used.

What is the effect on E_{cell} and on E_a of using concentrated hydrochloric acid?

	E_{cell}	E_a
☒ **A**	less positive	decreased
☒ **B**	less positive	unchanged
☒ **C**	more positive	decreased
☒ **D**	more positive	unchanged

(Total for Question 4 = 1 mark)

5 The element zinc is **not** classified as a transition metal. This is because

☒ **A** the 3d subshell of a zinc atom is full

☒ **B** zinc only forms one stable ion

☒ **C** the only stable zinc ion has the electronic configuration [Ar] 3d^{10}

☒ **D** neither zinc nor zinc ions show catalytic properties

(Total for Question 5 = 1 mark)

6 What is the electronic configuration of the Fe^{2+} ion?

☒ **A** [Ar] | ↑ | ↑ | ↑ | ↑ | ↑ | | ↑ |

☒ **B** [Ar] | ↑↓ | ↑ | ↑ | ↑ | ↑ | | |

☒ **C** [Ar] | ↑ | ↑ | ↑ | ↑ | | | ↑↓ |

☒ **D** [Ar] | ↑↓ | ↑↓ | ↑ | ↑ | | | |

3d   4s

(Total for Question 6 = 1 mark)

7 Platinum forms a complex with the formula $Pt(NH_3)_2Cl_2$ which is used in cancer treatment. Three possible structures of this complex are shown.

X	Y	Z
Cl⋯Pt⋯NH₃ / Cl—Pt—NH₃	Cl⋯Pt⋯NH₃ / H₃N—Pt—Cl	Cl—Pt⋯Cl / H₃N—Pt—NH₃
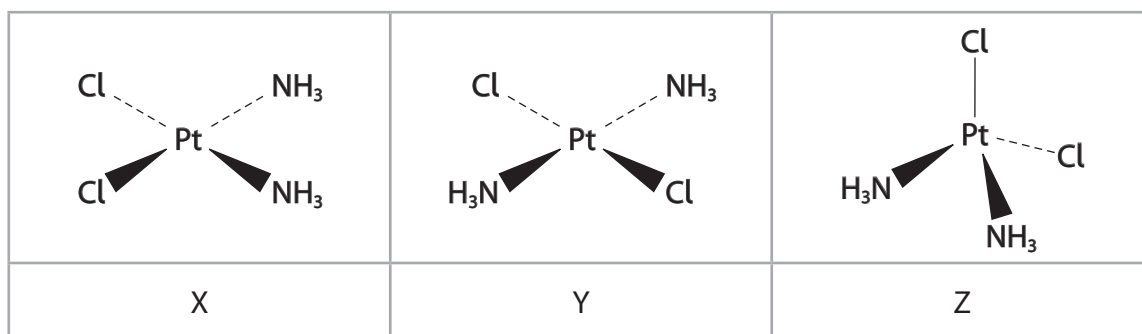
The complex used in cancer treatment contains

☒ **A** structure X only

☒ **B** structure Y only

☒ **C** structure Z only

☒ **D** an equimolar mixture of structures X and Y only

(Total for Question 7 = 1 mark)

8 When oxygen binds to the haem group in haemoglobin, each oxygen molecule

☒ **A** bonds reversibly to an iron(II) ion

☒ **B** bonds irreversibly to an iron(II) ion

☒ **C** replaces an iron(II) ion in a reversible reaction

☒ **D** replaces an iron(II) ion in an irreversible reaction

(Total for Question 8 = 1 mark)

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

9 The sequence shown is the mechanism for a reaction in aqueous solution.

Step 1 $Ag^+ + Ce^{4+} \rightarrow Ag^{2+} + Ce^{3+}$

Step 2 $Ti^+ + Ag^{2+} \rightarrow Ti^{2+} + Ag^+$

Step 3 $Ti^{2+} + Ce^{4+} \rightarrow Ti^{3+} + Ce^{3+}$
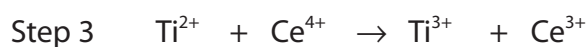
In the **overall** reaction

☒   **A**   the oxidation of Ag^+ is catalysed by Ce^{4+} ions

☒   **B**   the oxidation of Ag^+ is catalysed by Ti^{2+} ions

☒   **C**   the oxidation of Ti^+ is catalysed by Ag^+ ions

☒   **D**   the oxidation of Ti^+ is catalysed by Ag^{2+} ions

(Total for Question 9 = 1 mark)

10 How many σ bonds and π bonds are there in a molecule of benzene?

	σ bonds	π bonds
☒ **A**	6	3
☒ **B**	6	6
☒ **C**	12	3
☒ **D**	12	6

(Total for Question 10 = 1 mark)

11 Benzene reacts with fuming sulfuric acid to form benzenesulfonic acid.

Fuming sulfuric acid is

☒   **A**   sulfuric acid with a concentration of 98 %

☒   **B**   pure sulfuric acid

☒   **C**   concentrated sulfuric acid containing dissolved sulfur dioxide

☒   **D**   concentrated sulfuric acid containing dissolved sulfur trioxide

(Total for Question 11 = 1 mark)

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12 The structure of the amino acid isoleucine is shown.
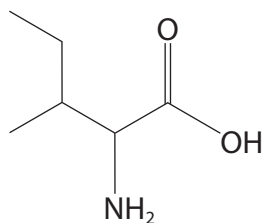
(a) What is the systematic name of isoleucine?

(1)

☒ **A** 2-amino-3-ethylbutanoic acid

☒ **B** 2-amino-3-methylpentanoic acid

☒ **C** 3-amino-2-ethylbutanoic acid

☒ **D** 3-amino-2-methylpentanoic acid

(b) What is the structure of isoleucine in a solution of pH = 2?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**
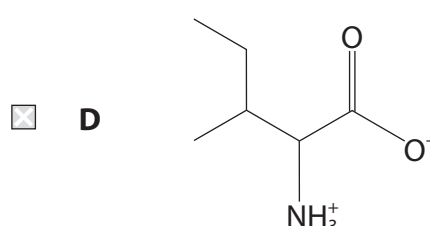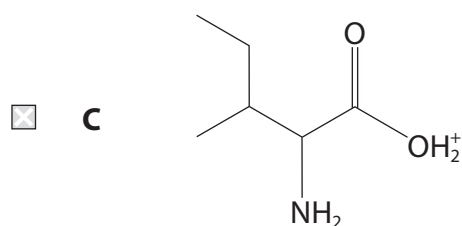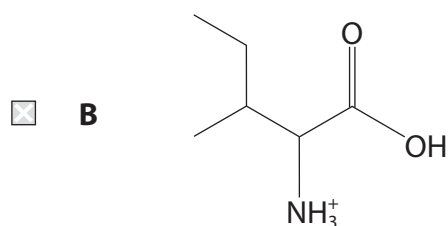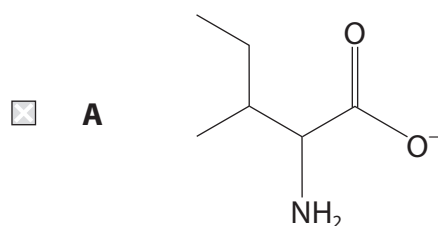
(Total for Question 12 = 2 marks)

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13 When dilute hydrochloric acid is added to butylamine and the solution is allowed to evaporate to dryness, a white solid forms.

What is the formula of the white solid?

☒ **A** $CH_3CH_2CH_2CH_2Cl$

☒ **B** $CH_3CH_2CH_2CH_2NH_3Cl$

☒ **C** $CH_3CH_2CH_2CONH_2$

☒ **D** $CH_3CH_2CH_2COOH$

(Total for Question 13 = 1 mark)

14 Amines may be prepared by the reduction of nitriles.

Identify the nitrile and the reducing agent used to prepare butylamine.

		Nitrile	Reducing agent
☒	**A**	propanenitrile	lithium tetrahydridoaluminate(III)
☒	**B**	propanenitrile	tin and concentrated hydrochloric acid
☒	**C**	butanenitrile	lithium tetrahydridoaluminate(III)
☒	**D**	butanenitrile	tin and concentrated hydrochloric acid

(Total for Question 14 = 1 mark)

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

P 7 1 8 7 3 A 0 8 3 2

15 The structure of crotonamide is shown.
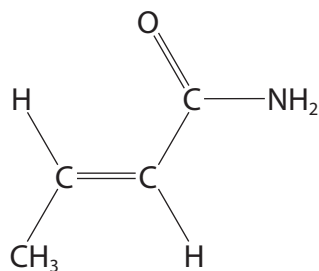
What is the repeat unit of the polymer formed from crotonamide?

☒ **A**

☒ **B**

☒ **C**

☒ **D**
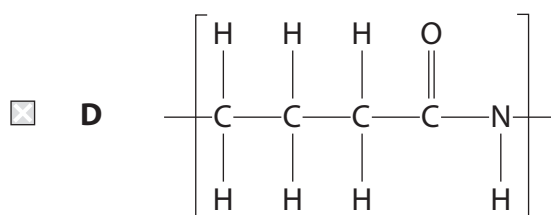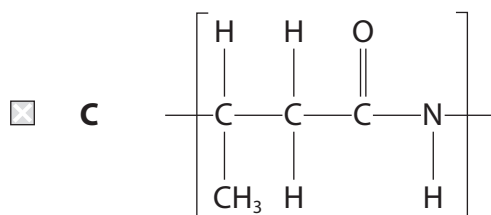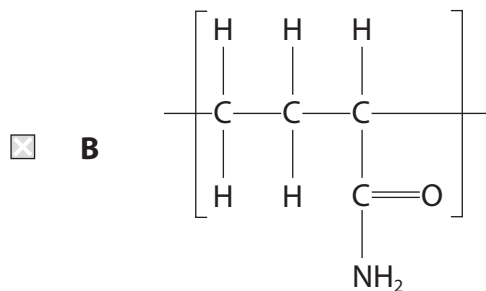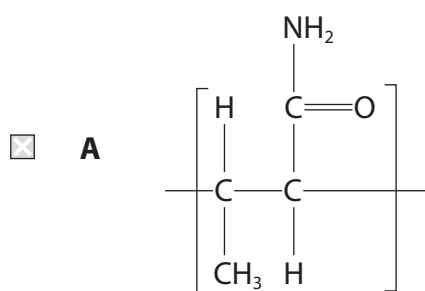
(Total for Question 15 = 1 mark)

16 The structure of a hydrocarbon is shown.
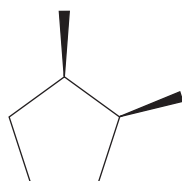
How many peaks will there be in the ^{13}C NMR spectrum of this compound?

☒ **A** four

☒ **B** five

☒ **C** six

☒ **D** seven

(Total for Question 16 = 1 mark)

17 The structures of cocaine and its metabolite benzoylecgonine are shown.

cocaine	benzoylecgonine
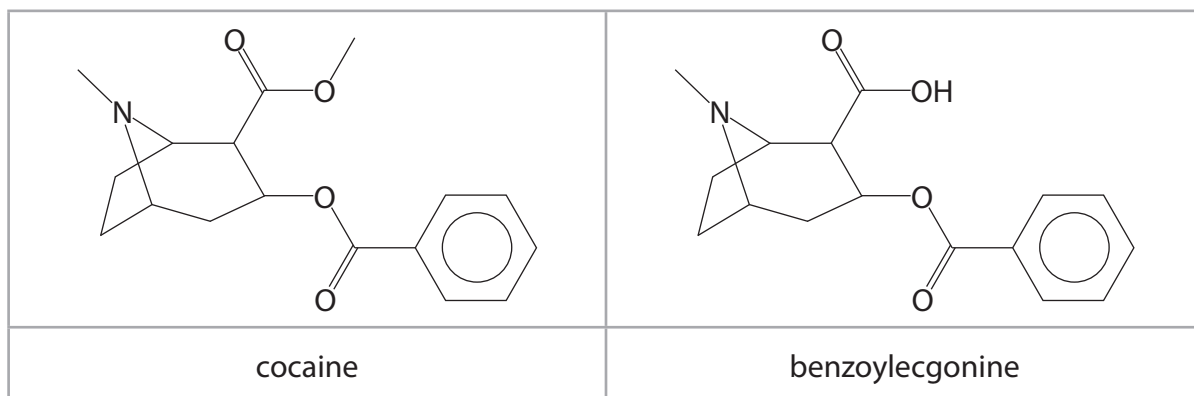
How would you expect the solubility of cocaine in water and the pH of its aqueous solution to compare with benzoylecgonine?

	Solubility in water	pH of aqueous solution
☒ **A**	cocaine more soluble	cocaine higher pH
☒ **B**	cocaine more soluble	cocaine lower pH
☒ **C**	cocaine less soluble	cocaine higher pH
☒ **D**	cocaine less soluble	cocaine lower pH

(Total for Question 17 = 1 mark)

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

18 The use of recrystallisation to purify a chemical compound depends on how its solubility in the chosen solvent varies with temperature.

How should the solubility of the chemical compound depend on temperature?

	High temperature	Low temperature
☒ **A**	soluble	soluble
☒ **B**	soluble	insoluble
☒ **C**	insoluble	soluble
☒ **D**	insoluble	insoluble

(Total for Question 18 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

19 This question is about the chemistry of vanadium.

The standard electrode potentials of some vanadium species are shown.

Electrode system	$E^{\ominus}$ / V
$V^{2+}(aq) + 2e^- \rightleftharpoons V(s)$	−1.18
$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$	−0.26
$VO^{2+}(aq) + 2H^+(aq) + e^- \rightleftharpoons V^{3+}(aq) + H_2O(l)$	+0.34
$VO_3^-(aq) + 4H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + 2H_2O(l)$	+1.00

(a) Explain the highest stable oxidation state formed by vanadium, by referring to its electronic configuration.

(3)

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(b) A student suggests that the ion VO^{2+} may be converted into V^{3+} using sodium thiosulfate, $Na_2S_2O_3$, with no other vanadium species being formed by reduction.

(i) Justify the use of sodium thiosulfate for this reaction by writing the relevant equations and calculating their $E^{\ominus}_{cell}$ values.

Use the standard electrode potentials given in the table and values from your Data Booklet.
State symbols are not required in the equations.

(4)

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(ii) Explain why nickel, Ni, is **not** a suitable reagent to convert VO^{2+} into V^{3+}, with no other vanadium species being formed.

(2)

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(c) Most vanadium produced is used to make a steel alloy called ferrovanadium. The vanadium content of ferrovanadium may be determined by a titration method.

Procedure

- The sample of ferrovanadium is dissolved in chloric(V) acid. The vanadium species formed is VO_3^-.

- The resulting solution is transferred to a 250.0 cm^3 volumetric flask, washings added and the solution made up to the mark with distilled water and mixed.

- Using a pipette, 25.0 cm^3 of the solution is transferred to a conical flask and 25.0 cm^3 of a 0.250 mol dm^{-3} solution of iron(II) sulfate, FeSO$_4$, is added. The iron(II) ions react with the VO_3^- ions:

$$VO_3^- + 4H^+ + Fe^{2+} \rightleftharpoons VO^{2+} + 2H_2O + Fe^{3+}$$
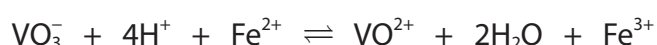
- The resulting solution is titrated against potassium manganate(VII) to determine the amount of iron(II) ions remaining.

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$
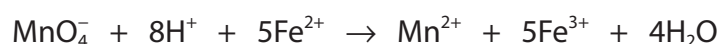
In an experiment, the mass of ferrovanadium used was 4.87 g, the concentration of potassium manganate(VII) was 0.0195 mol dm^{-3} and a mean titre of 22.50 cm^3 was obtained.

(i) Give the colour of the solution at the end-point of the titration.

(1)

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(ii) Suggest why the VO^{2+} ions formed do **not** affect the titration.

(2)

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(iii) Calculate the percentage by mass of vanadium in the ferrovanadium.

(7)

(d) In the manufacture of sulfuric acid, vanadium(V) oxide, V_2O_5, is the catalyst used in the conversion of sulfur dioxide to sulfur trioxide:

$$2SO_2 \; + \; O_2 \; \rightleftharpoons \; 2SO_3$$
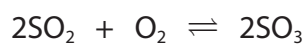
Write **two** equations to show a possible mechanism for this reaction.
State symbols are not required.

(2)

(Total for Question 19 = 21 marks)

*20 Delocalised electron systems are important in determining the chemical properties of some compounds.

Compare and contrast the chemical reactions of bromine with benzene and cyclohexene, and with benzene and phenol, by considering the effects of delocalised electrons.

Detailed descriptions of the bonds or of the reaction mechanisms involved are **not** required.

(6)

(Total for Question 20 = 6 marks)

P71873A01732

21 Coniine is the toxic compound present in poison hemlock.
The structure of coniine is shown, with R representing an alkyl group.
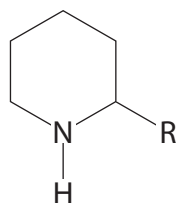
coniine

(a) A sample of 0.235 g of coniine was vaporised at 185 °C and 105 000 Pa.
The volume of the vapour was 67.1 cm^3.

(i) Show by calculation that the molar mass of coniine is 127 g mol^{-1}.

(4)

(ii) Deduce the molecular formula of the alkyl group R, using the structure of coniine and its molar mass. You **must** show your working.

(2)

(b) The table summarises the low resolution proton NMR data for the R group in coniine.

Proton environment	Chemical shift / ppm	Peak area
1	0.90	3
2	1.33	2
3	1.37	2

(i) Explain why only **one** of the two possible structural formulae of R can give these data.

(3)

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(ii) In the high resolution proton NMR data for the R group in coniine, the peak for proton environment 2 is a sextet.

Deduce the splitting patterns for proton environments 1 and 3, using this information and the information in the table.

(3)

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P 7 1 8 7 3 A 0 2 0 3 2

(c) Explain, using a diagram, which type of stereoisomerism is shown by coniine.
In your diagram use R to represent the alkyl group.

(2)

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(Total for Question 21 = 14 marks)

22 Many oxides of transition metals are used as coloured pigments.

(a) Viridian is a blue-green pigment with the formula $M_2O_3 \cdot 2H_2O$; M is not the symbol of the element.

When a sample of viridian is heated until all the water of crystallisation is removed, the mass is reduced by 19.15%.

Identify element M.

(4)

(b) Cobalt(II) oxide is used in the ceramics industry as an additive to produce blue glazes and enamels. Cobalt(II) oxide dissolves in sulfuric acid to give a pink aqueous solution of cobalt(II) sulfate. When concentrated hydrochloric acid is added to aqueous cobalt(II) sulfate, a dark blue solution forms.

(i) Name the type of reaction that occurs when concentrated hydrochloric acid is added to aqueous cobalt(II) sulfate.

(1)

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(ii) Write an **ionic** equation for the reaction that occurs when concentrated hydrochloric acid is added to aqueous cobalt(II) sulfate. State symbols are not required.

(2)

(iii) Explain why the shape of the complex ion changes when concentrated hydrochloric acid is added.

(2)

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(Total for Question 22 = 9 marks)

TOTAL FOR SECTION B = 50 MARKS

SECTION C

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

23   **Chemicals from Plants**

Plants are a rich source of useful chemicals, although their applications have often pre-dated the identification of the active compound. One of the best known examples of this is the use of willow bark extracts to reduce pain and fevers, a practice that is at least two thousand years old. The active compound in willow bark is salicin.
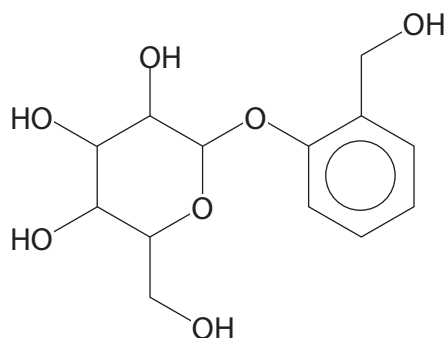
salicin

In the body, salicin is changed into salicylaldehyde and then salicylic acid. Salicylic acid may in turn be converted into 2-acetoxybenzenecarboxylic acid, a compound which is better known as aspirin, one of the most widely used medications in the world.
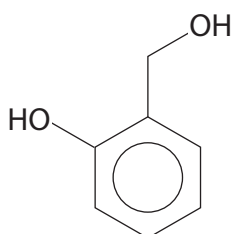
salicylaldehyde	salicylic acid	2-acetoxybenzenecarboxylic acid

(a) Calculate the percentage composition by mass of the elements in salicin.

(4)

(b) The first stage in the breakdown of salicin results in the formation of salicyl alcohol.

salicyl alcohol

Salicyl alcohol is readily oxidised in the laboratory to form salicylic acid.

(i) State the reagents and conditions needed for this oxidation.

(2)

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(ii) The boiling temperature of salicylaldehyde is 197 °C.

Suggest why this makes it very difficult to obtain salicylaldehyde by oxidising salicyl alcohol.

(2)

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(c) Aromatic aldehydes such as salicylaldehyde may be prepared in the laboratory by electrophilic substitution.
For example, benzaldehyde may be obtained by reacting benzene with a mixture of carbon monoxide and hydrogen chloride in the presence of aluminium chloride.
The mixture of carbon monoxide and hydrogen chloride reacts like methanoyl chloride.

(i) Write an equation for the formation of the electrophile from methanoyl chloride. Use displayed formulae.
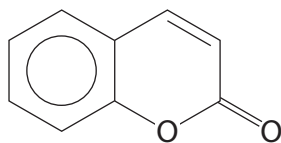
(1)

(ii) Draw the mechanism of the formation of benzaldehyde from benzene using the electrophile from (c)(i).
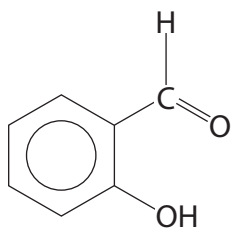
(3)

(d) Salicylaldehyde may be used in the synthesis of coumarin, a compound which occurs in many plants. Coumarin is in turn used to prepare warfarin, a compound prescribed to reduce blood clotting.
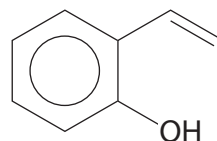
coumarin

One suggested synthesis of coumarin from salicylaldehyde involves the formation of an intermediate compound, **F**.
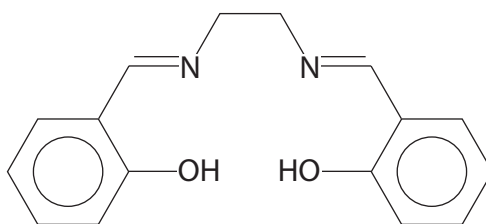
salicylaldehyde   compound **F**

Devise a synthesis of **F** using salicylaldehyde and bromoethane as the **only** organic starting materials.
Include any other reagents and intermediate compounds, and give essential reaction conditions.

(4)

(e) Salicylaldehyde combines with 1,2-diaminoethane in a condensation reaction to form salen ligand.

salen ligand

Salen ligand reacts with many metal ions to form very stable complexes which are useful catalysts.

(i) Draw a diagram of the complex that **one** salen ligand forms with a Ni^{2+} ion, showing the type of bonding involved.

(2)

(ii) Explain why the salen ligand complex of the Ni^{2+} ion is much more stable than the aqua complex of the same ion.

(2)

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(Total for Question 23 = 20 marks)

TOTAL FOR SECTION C = 20 MARKS

TOTAL FOR PAPER = 90 MARKS