**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, ruler

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*.
- 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.
- Check your answers if you have time at the end.

*Turn over* ▶

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 apparatus shown was used to measure the standard electrode potential for the reduction of $Cr_2O_7^{2-}$ ions to $Cr^{3+}$ ions in acid solution:

$$Cr_2O_7^{2-}(aq) \ + \ 14H^+(aq) \ + \ 6e^- \ \rightarrow \ 2Cr^{3+}(aq) \ + \ 7H_2O(l)$$
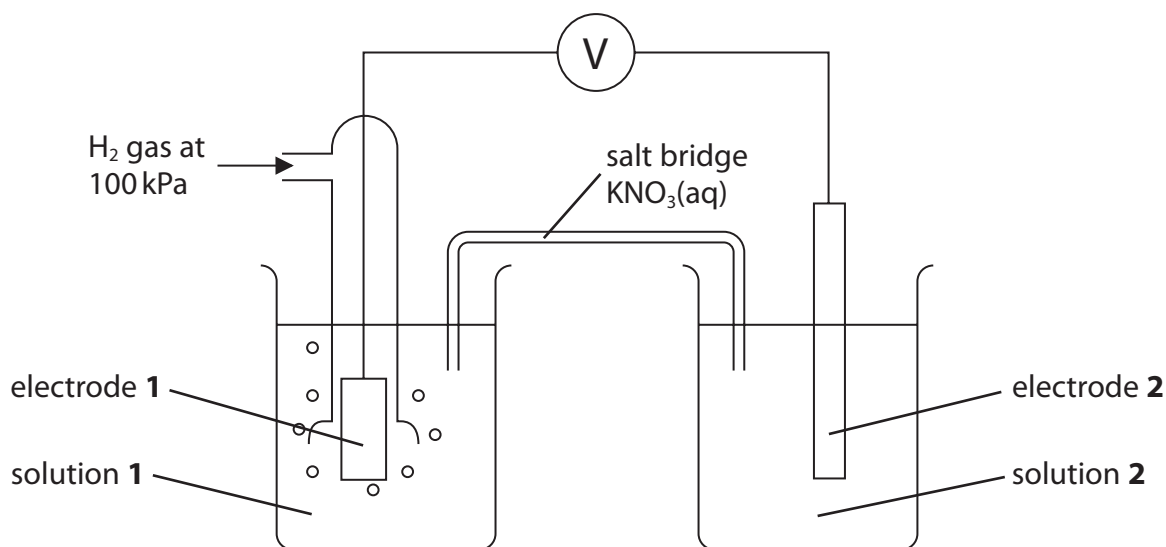


(a) Which material should be used for each electrode?

(1)

|  | | Electrode **1** | Electrode **2** |
|---|---|---|---|
| ⊠ | **A** | $Na_2Cr_2O_7$ | $Cr_2O_3$ |
| ⊠ | **B** | $H_2$ | $Cr$ |
| ⊠ | **C** | $Pt$ | $Cr$ |
| ⊠ | **D** | $Pt$ | $Pt$ |

(b) Solution **1** is

(1)

☒ **A** 0.33 mol dm$^{-3}$ H$_3$PO$_4$(aq)

☒ **B** 0.50 mol dm$^{-3}$ H$_2$SO$_4$(aq)

☒ **C** 1.00 mol dm$^{-3}$ HCl(aq)

☒ **D** 1.00 mol dm$^{-3}$ CH$_3$COOH(aq)

(c) Solution **2** contains 14.71 g of K$_2$Cr$_2$O$_7$.

What mass of Cr$_2$(SO$_4$)$_3$·18H$_2$O should also be used?

[$M_r$ values: K$_2$Cr$_2$O$_7$ = 294.2      Cr$_2$(SO$_4$)$_3$·18H$_2$O = 716.3]

(1)

☒ **A**   8.95 g

☒ **B** 17.91 g

☒ **C** 19.62 g

☒ **D** 35.82 g

(d) Solution **2** is **best** acidified with

(1)

☒ **A** H$_2$SO$_4$

☒ **B** HCl

☒ **C** HBr

☒ **D** H$_2$CrO$_4$

**(Total for Question 1 = 4 marks)**

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

**2**  The equation for a redox reaction is

$$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$$
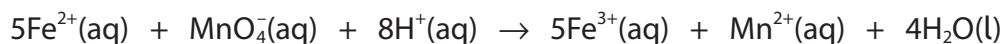
Which is the correct cell diagram to measure $E_{cell}^{\ominus}$ for this reaction?

☒ **A**  $Fe \mid Fe^{2+}, Fe^{3+} \parallel [MnO_4^- + 8H^+], [Mn^{2+} + 4H_2O] \mid Mn$

☒ **B**  $Fe \mid Fe^{2+}, Fe^{3+} \parallel [Mn^{2+} + 4H_2O], [MnO_4^- + 8H^+] \mid Mn$

☒ **C**  $Pt \mid Fe^{2+}, Fe^{3+} \parallel [MnO_4^- + 8H^+], [Mn^{2+} + 4H_2O] \mid Pt$

☒ **D**  $Pt \mid Fe^{2+}, Fe^{3+} \parallel [Mn^{2+} + 4H_2O], [MnO_4^- + 8H^+] \mid Pt$

**(Total for Question 2 = 1 mark)**

**3**  Some standard electrode potentials are shown.

| Electrode system | $E^{\ominus}$ / V |
|---|---|
| $Bk^{3+} + e^- \rightleftharpoons Bk^{2+}$ | −2.80 |
| $Cu^{2+} + e^- \rightleftharpoons Cu^+$ | +0.15 |
| $Bk^{4+} + e^- \rightleftharpoons Bk^{3+}$ | +1.67 |
| $Au^+ + e^- \rightleftharpoons Au$ | +1.69 |
| $Au^{2+} + e^- \rightleftharpoons Au^+$ | +1.80 |
| $Ag^{3+} + e^- \rightleftharpoons Ag^{2+}$ | +1.80 |
| $Ag^{2+} + e^- \rightleftharpoons Ag^+$ | +1.98 |
| $Cu^{3+} + e^- \rightleftharpoons Cu^{2+}$ | +2.40 |

Which of these disproportionation reactions is thermodynamically feasible under standard conditions?

☒ **A**  $2Bk^{3+} \rightarrow Bk^{2+} + Bk^{4+}$

☒ **B**  $2Cu^{2+} \rightarrow Cu^+ + Cu^{3+}$

☒ **C**  $2Au^+ \rightarrow Au + Au^{2+}$

☒ **D**  $2Ag^{2+} \rightarrow Ag^+ + Ag^{3+}$

**(Total for Question 3 = 1 mark)**

**4** Which is **true** of a hydrogen-oxygen fuel cell?

☒ **A** the cathode has a more positive potential than the anode

☒ **B** hydrogen is oxidised at the cathode

☒ **C** oxygen is reduced at the negative electrode

☒ **D** the cell potential is different when operating under alkaline or acidic conditions

**(Total for Question 4 = 1 mark)**

**5** Which of the following statements **best** explains carbon monoxide poisoning?

☒ **A** carbon monoxide binds irreversibly to haemoglobin

☒ **B** carbon monoxide forms stronger dative covalent bonds with haemoglobin than oxygen does

☒ **C** the formation of carboxyhaemoglobin leads to a large increase in the entropy of the system

☒ **D** carbon monoxide has a triple bond whereas oxygen has a double bond

**(Total for Question 5 = 1 mark)**

**6** Aqueous ammonia is added drop by drop to a solution of cobalt(II) chloride, $CoCl_2(aq)$, until in excess.

What would be the sequence of observations?

☒ **A** blue solution $\rightarrow$ pink precipitate $\rightarrow$ dark blue solution

☒ **B** pink solution $\rightarrow$ blue precipitate

☒ **C** blue solution $\rightarrow$ pink precipitate

☒ **D** pink solution $\rightarrow$ blue precipitate $\rightarrow$ yellow-brown solution

**(Total for Question 6 = 1 mark)**

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

**7** Some nickel(II) complex ions are formed by the addition of complexing agents to nickel(II) ions, $[Ni(H_2O)_6]^{2+}$, in aqueous solution.

On formation, which of these leads to the **most** positive increase in $\Delta S_{system}$?

⊠ **A** $[NiCl_4]^{2-}$

⊠ **B** $[Ni(EDTA)]^{2-}$

⊠ **C** $[Ni(C_2O_4)_2]^{2-}$

⊠ **D** $[Ni(H_2NCH_2CH_2NH_2)_3]^{2+}$

**(Total for Question 7 = 1 mark)**

**8** Which of the following is **not** true of the reactions occurring in the catalytic converter fitted to a car exhaust?

⊠ **A** they involve heterogeneous catalysis

⊠ **B** carbon monoxide is adsorbed onto the surface of the catalyst

⊠ **C** nitrogen is desorbed from the surface of the catalyst

⊠ **D** the products cause no harm to the environment

**(Total for Question 8 = 1 mark)**

**9** The reaction of ethanedioate ions, $C_2O_4^{2-}$, with manganate(VII) ions, $MnO_4^-$, in acidic solution involves autocatalysis.

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$
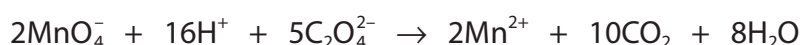
The catalyst in this reaction is

⊠ **A** $MnO_4^-$

⊠ **B** $H^+$

⊠ **C** $Mn^{2+}$

⊠ **D** $CO_2$

**(Total for Question 9 = 1 mark)**

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

**10** Iodide ions, $I^-$, are oxidised by peroxodisulfate(VI) ions, $S_2O_8^{2-}$.

$$2I^-(aq) \;+\; S_2O_8^{2-}(aq) \;\rightarrow\; I_2(aq) \;+\; 2SO_4^{2-}(aq)$$
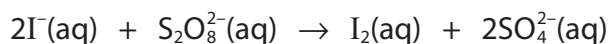
Which of the following statements is **true** of this reaction?

☒ **A**  both $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$ catalyse the reaction

☒ **B**  $Fe^{2+}(aq)$ catalyses the reaction but $Fe^{3+}(aq)$ does not

☒ **C**  $Fe^{3+}(aq)$ catalyses the reaction but $Fe^{2+}(aq)$ does not

☒ **D**  neither $Fe^{2+}(aq)$ nor $Fe^{3+}(aq)$ catalyses the reaction

**(Total for Question 10 = 1 mark)**

**11** Which of these could **not** be formed when excess benzene is heated with trichloromethane, $CHCl_3$, in the presence of an aluminium chloride catalyst?

☒ **A**
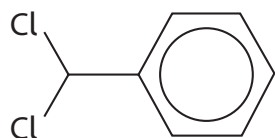
☒ **B**
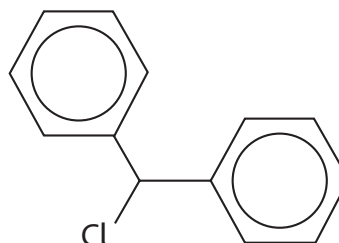
☒ **C**

☒ **D**
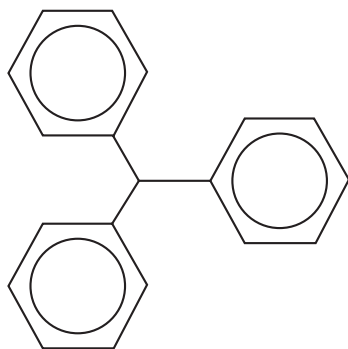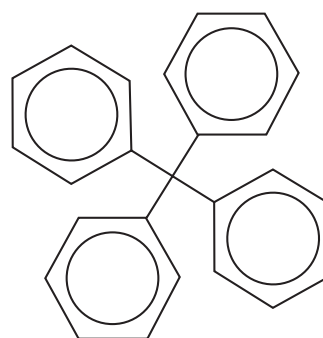
**(Total for Question 11 = 1 mark)**

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

**12** What is the molar mass, in $g\,mol^{-1}$, of the organic product when phenol reacts with **excess** bromine water?

- ☒ **A** 156.9
- ☒ **B** 172.9
- ☒ **C** 330.7
- ☒ **D** 488.5

**(Total for Question 12 = 1 mark)**

**13** Which sequence shows these compounds in order of **decreasing** basicity?

- ☒ **A** $C_6H_5NH_2 > CH_3CH_2CH_2NH_2 > NH_3$
- ☒ **B** $NH_3 > CH_3CH_2CH_2NH_2 > C_6H_5NH_2$
- ☒ **C** $CH_3CH_2CH_2NH_2 > NH_3 > C_6H_5NH_2$
- ☒ **D** $C_6H_5NH_2 > NH_3 > CH_3CH_2CH_2NH_2$

**(Total for Question 13 = 1 mark)**

**14** Which amine could **not** be prepared by the reduction of a nitrile?

- ☒ **A** $H_2N$— (straight-chain primary amine structure)
- ☒ **B** $H_2N$— (branched amine structure)
- ☒ **C** $H_2N$— (branched amine structure)
- ☒ **D** $H_2N$— (branched amine structure)
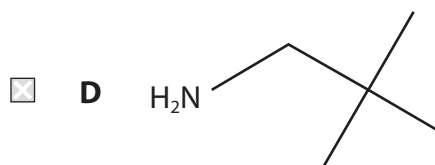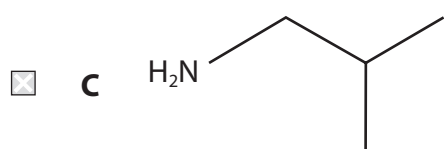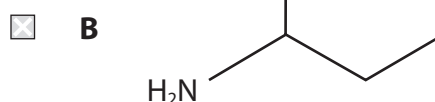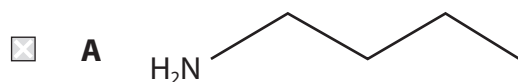
**(Total for Question 14 = 1 mark)**

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

**15** How many **different** amino acids form the repeat unit of the polymer shown?
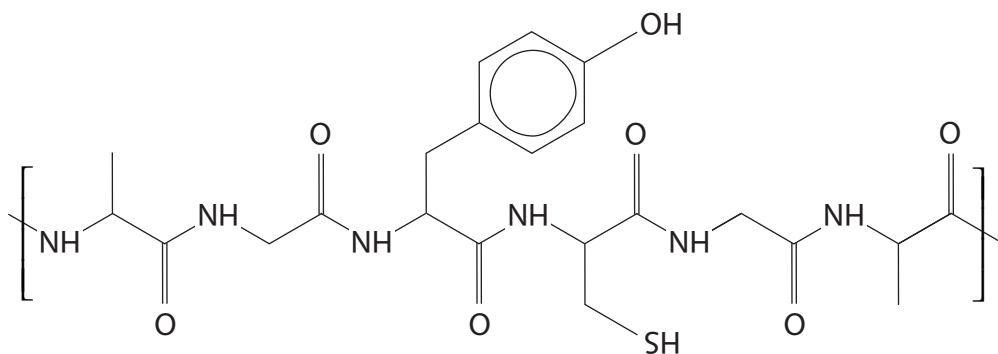


☒ **A** 3

☒ **B** 4

☒ **C** 5

☒ **D** 6

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

**16** Grignard reagents react with

☒ **A** water giving primary alcohols

☒ **B** all aldehydes giving secondary alcohols

☒ **C** ketones giving secondary or tertiary alcohols

☒ **D** carbon dioxide giving carboxylic acids

**(Total for Question 16 = 1 mark)**

**17** The melting temperature is determined for impure crystals of an organic compound. When compared with a data book value for the pure compound, the measured melting temperature

☒ **A** will be the same as the true value

☒ **B** will be higher than the true value

☒ **C** will be lower than the true value

☒ **D** could be higher or lower than the true value

**(Total for Question 17 = 1 mark)**

**TOTAL FOR SECTION A = 20 MARKS**

## SECTION B

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

**18** A series of reactions with iron and iron complexes was carried out.

Reaction **1**     A sample of iron was heated with hydrochloric acid and a pale green hydrated salt **A** with molar mass $198.8\,g\,mol^{-1}$ was crystallised from the solution.

Reaction **2**     Salt **A** was dissolved in water forming a pale green solution containing complex ion **B**. On addition of excess aqueous potassium cyanide, KCN, the solution turned yellow due to the formation of complex ion **C**.

Reaction **3**     Chlorine gas was bubbled through the solution containing complex ion **C** forming a red solution of complex ion **D**.
Salt **E**, the potassium salt of complex ion **D**, was then crystallised from the solution.

(a)  Deduce the formula of the hydrated salt **A**.
You **must** show your working.

(2)

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(b)  Give the **formula** of complex ion **B**.

(1)

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(c) Complex ion **C** has six cyanide ligands.
   Draw the structure of **C**, clearly showing its three-dimensional shape.

**(1)**

(d) The percentage composition by mass of salt **E** is

$$K = 35.6\% \qquad Fe = 17.0\% \qquad C = 21.9\% \qquad N = 25.5\%$$

Calculate the empirical formula of salt **E**.

**(3)**

(e) Write the **ionic** equation for the reaction of complex ion **C** with chlorine to form complex ion **D**.

(2)

(f) Complete the table, using ✓ as appropriate, to identify the type of each reaction.

(2)

|  | Neutralisation | Ligand exchange | Redox |
|---|---|---|---|
| Reaction 2 |  |  |  |
| Reaction 3 |  |  |  |

**(Total for Question 18 = 11 marks)**

**19** This question is about benzene, $C_6H_6$, a colourless liquid first isolated in 1825, and some related compounds.

Three $C_6H_6$ structures proposed in the 1860s are shown.

| Kekulé structure | Dewar structure | Ladenburg structure |
|---|---|---|
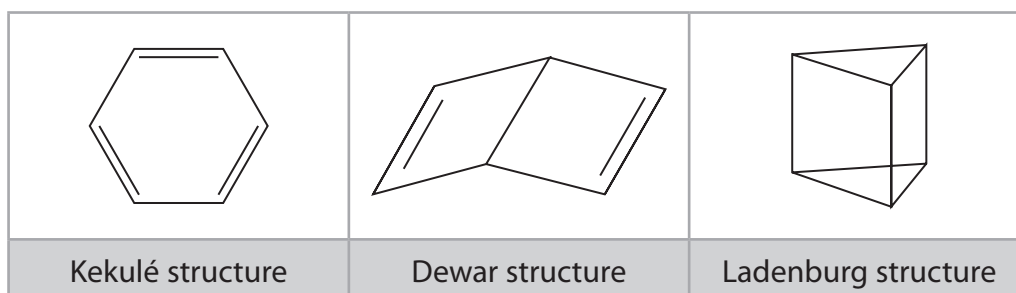
The delocalised model for the structure of benzene has been accepted since the 1930s following the study of its X-ray diffraction pattern and the understanding of electron delocalisation in bonding theory.

The Dewar and Ladenburg structures have since been isolated as stable compounds but there is no compound with the Kekulé structure.
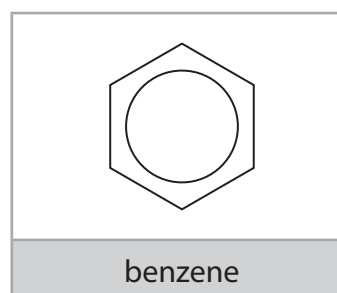
benzene

(a) Describe a **chemical** test, including the result, that could distinguish the Dewar structure from benzene.

**(2)**

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(b) State **one** similarity and **one** difference you would expect in the **low** resolution proton NMR spectrum of the Ladenburg structure and that of benzene.

You **must** include data from the Data Booklet to support your answer.

**(2)**

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(c) Explain how X-ray diffraction shows that benzene has a delocalised structure and **not** a Kekulé structure.

(2)

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(d) The Ladenburg and Dewar structures both isomerise to benzene.
The enthalpy changes are $-376\,kJ\,mol^{-1}$ and $-297\,kJ\,mol^{-1}$ respectively.

(i) Draw a **labelled** enthalpy level diagram showing the relative thermodynamic stability of the Ladenburg structure, the Dewar structure and benzene.
Include the enthalpy change values in $kJ\,mol^{-1}$.
Your diagram does **not** need to be to scale.

(2)
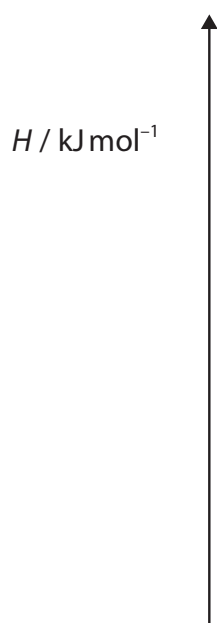
$H\,/\,kJ\,mol^{-1}$

(ii) Give a possible reason why the isomerisation of the Dewar structure to benzene has a lower activation energy than that of the Ladenburg structure to benzene.

(1)

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(e) The enthalpy change of hydrogenation of hex-3-ene is $-118\,\text{kJ}\,\text{mol}^{-1}$.
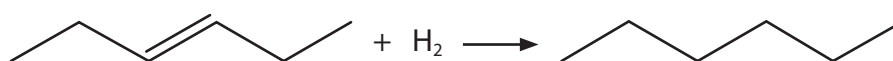


The table shows the enthalpy changes of hydrogenation of two further alkenes containing six carbon atoms.

| Alkene | Enthalpy change of hydrogenation / $\text{kJ}\,\text{mol}^{-1}$ |
|---|---|
| <br>*E*-hexa-1,4-diene | −236 |
| <br>*E*-hexa-1,3-diene | −214 |

Use your knowledge of benzene thermochemistry to suggest explanations for **both** of these enthalpy changes of hydrogenation in relation to the value for hex-3-ene.

(2)

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(f) Methylbenzene, $C_6H_5CH_3$, reacts with ethanoyl chloride, $CH_3COCl$, in the presence of the catalyst aluminium chloride, $AlCl_3$, to form a mixture of organic products with the formula $CH_3COC_6H_4CH_3$.

$$C_6H_5CH_3 \ + \ CH_3COCl \ \rightarrow \ CH_3COC_6H_4CH_3 \ + \ HCl$$
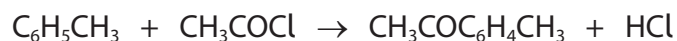
(i) Draw the **skeletal** formulae of **three** different arenes with the formula $CH_3COC_6H_4CH_3$.

(2)

(ii) The $^{13}C$ NMR spectrum of **one** of these arenes, compound **X**, is shown.



two peaks very close in chemical shift

200   180   160   140   120   100   80   60   40   20   0

$\delta$ / ppm
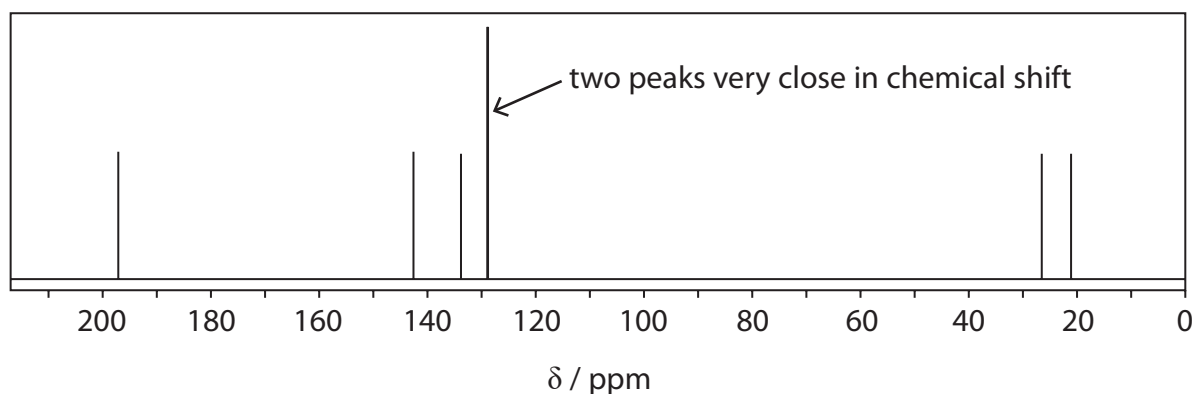
Identify compound **X**.
Use the number of peaks on the $^{13}C$ NMR spectrum to justify your answer.

(2)

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(iii) Complete the diagram, including curly arrows, to show the mechanism for the formation of compound **X** in this reaction.
Include an equation for the regeneration of the catalyst.

**(4)**

$$CH_3COCl \ + \ AlCl_3 \ \rightarrow \ CH_3CO^+ \ + \ AlCl_4^-$$
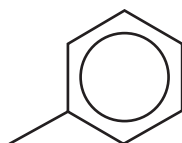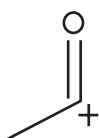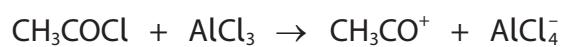
**(Total for Question 19 = 19 marks)**

*Turn over* ▶

**20** This question is about titanium(III) chloride, $TiCl_3$.

(a) Titanium(III) chloride is used as a catalyst in the production of poly(propene).

State the property of transition metals, such as titanium, that makes their **compounds** effective catalysts.

**(1)**

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(b) When dissolved in tetrahydrofuran (THF), titanium(III) chloride forms a blue solution containing complex **Y**.
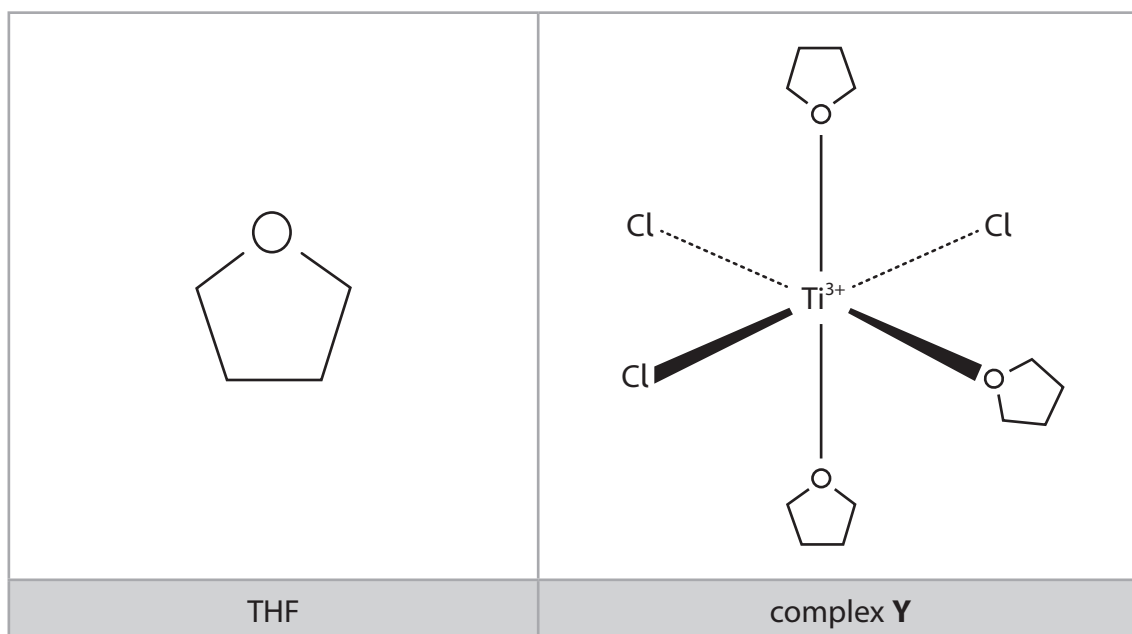


| THF | complex **Y** |

(i) THF acts as a monodentate ligand in complex **Y**.

State the meaning of the terms **monodentate** and **ligand**.

**(2)**

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(ii) Complex **Z** is a stereoisomer of complex **Y**.

Complete the diagram to show the arrangement of the ligands in complex **Z**.

**(1)**
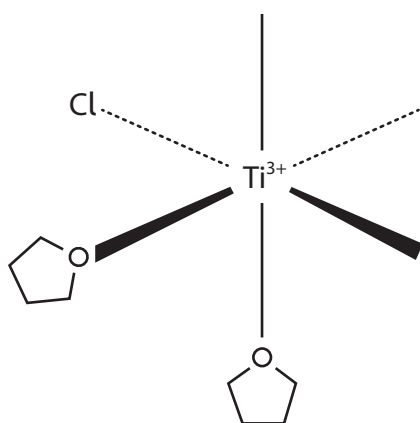


complex **Z**

(c) A student determines the change in oxidation number of **nitrogen** when a solution of magnesium nitrate, $Mg(NO_3)_2$, is titrated with aqueous titanium(III) chloride.

**Procedure**

Step **1** Using a volumetric flask, prepare $100.0\,cm^3$ of an aqueous solution containing $0.750\,g$ of solid $Mg(NO_3)_2 \cdot 6H_2O$.

Step **2** Pipette $10.0\,cm^3$ of the solution from Step **1** into a conical flask and add a few drops of alizarin indicator.
Add $2\,cm^3$ of concentrated hydrochloric acid and heat the mixture.

Step **3** Fill a burette with $0.0850\,mol\,dm^{-3}$ aqueous titanium(III) chloride and titrate the contents of the conical flask from Step **2** while continuing to heat the mixture.

During the titration, $Ti^{3+}$ ions are oxidised to $TiO^{2+}$ ions

$$Ti^{3+} \ + \ H_2O \ \rightarrow \ TiO^{2+} \ + \ 2H^+ \ + \ e^-$$

Alizarin indicator is green in the presence of aqueous $Ti^{3+}$ and yellow in the presence of aqueous $TiO^{2+}$.

The end-point of the titration is reached on the addition of $20.70\,cm^3$ of aqueous titanium(III) chloride.

(i) State the colour **change** that would be observed at the end-point of the titration.

(1)

From ................................................................................................ to ................................................................................................

(ii) Use the results to determine the **final** oxidation state of nitrogen in the titration.
You **must** show your working.

[$M_r$ value: Mg(NO$_3$)$_2$·6H$_2$O = 256.3]

**(5)**

(iii) Write the overall **ionic** equation for the titration reaction using your answer to (c) (ii) and the relevant half-equations from the list below.

(2)

$$TiO^{2+} + 2H^+ + e^- \rightleftharpoons Ti^{3+} + H_2O \qquad E^\ominus = +0.10\,V$$

$$NO_3^- + 2H^+ + e^- \rightleftharpoons NO_2 + H_2O \qquad E^\ominus = +0.80\,V$$

$$NO_3^- + 3H^+ + 2e^- \rightleftharpoons HNO_2 + H_2O \qquad E^\ominus = +0.94\,V$$

$$NO_3^- + 4H^+ + 3e^- \rightleftharpoons NO + 2H_2O \qquad E^\ominus = +0.96\,V$$
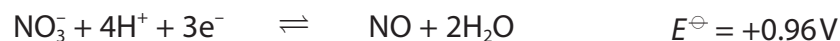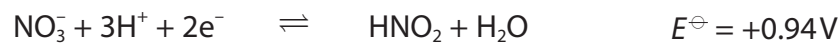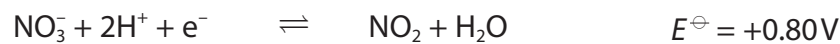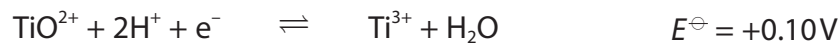
(iv) Use the electrode potential data provided to calculate $E^\ominus_{cell}$ for the overall titration reaction.

(1)

(v) Suggest why the contents of the conical flask are heated.

(1)

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*(vi) The student's teacher said,

*"As TiCl$_3$ is blue and TiO$^{2+}$ ions are colourless in aqueous solution, the titration can be carried out **without** an alizarin indicator."*

Assess the teacher's statement.
In your answer you should
- identify, by name or formula, a coloured complex ion expected to be present when TiCl$_3$ dissolves in water
- explain how the colour of this complex ion arises
- suggest why the titration may be more accurate **with** an alizarin indicator.

(6)

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**(Total for Question 20 = 20 marks)**

**TOTAL FOR SECTION B = 50 MARKS**

P67131A02432

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

**21** Organic molecules are an important source of colour both in the natural world and in a wide range of industrial applications.

Curcumin contributes to the yellow colour of turmeric spice and is used as an additive in cosmetics and foods. It has been suggested that curcumin can act as an antioxidant and anticancer agent, through reactions with free radicals and proteins, and may also inhibit Alzheimer's disease by complexing to toxic metal ions.
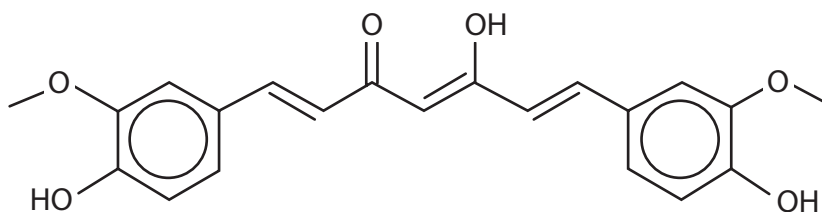


curcumin

Azo dyes are synthetic compounds that do not occur naturally. They can be used to colour textiles such as cotton. The acid-base indicator methyl red is an azo dye.
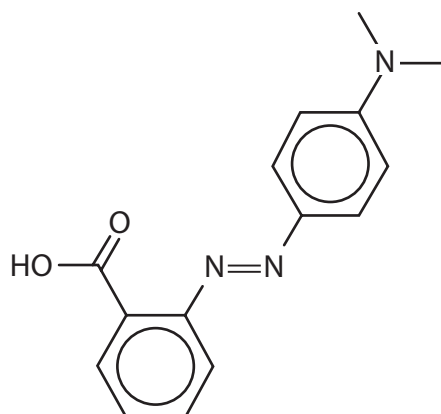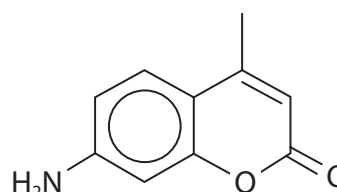


methyl red

Indigotin is used to dye denim a blue colour and coumarin 440 is used to generate blue light in lasers. Both dyes occur naturally in plants but can be synthesised in the laboratory.
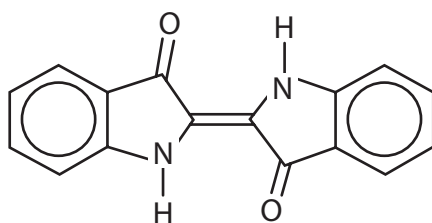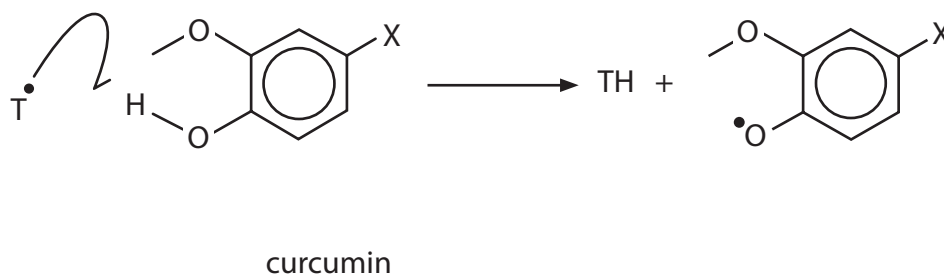


indigotin          coumarin 440

(a) The equation shows the reaction between a free radical T• and curcumin (shown by a simplified structure).
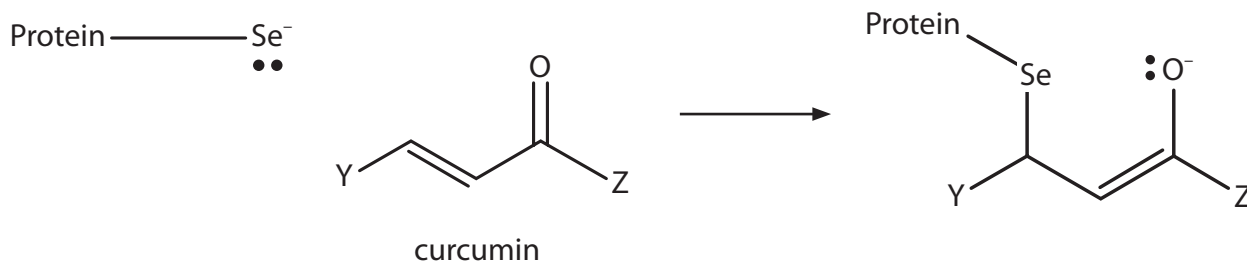


curcumin

Complete the left-hand side of the equation by adding curly half-arrows.

(1)

(b) Selenide anions attached to protein side-chains may undergo nucleophilic addition reactions with curcumin.

Complete the mechanism for one of the steps in such a reaction, adding curly arrows to the simplified structures shown.

(2)



curcumin

(c) Curcumin anions can act as bidentate ligands in metal-curcumin (M-curc) complexes. The oxygen atoms of the curc ligand occupy adjacent coordination sites in the complex, as shown.
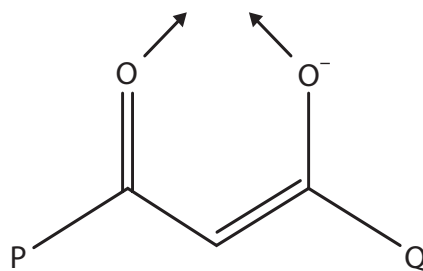


curcumin anion

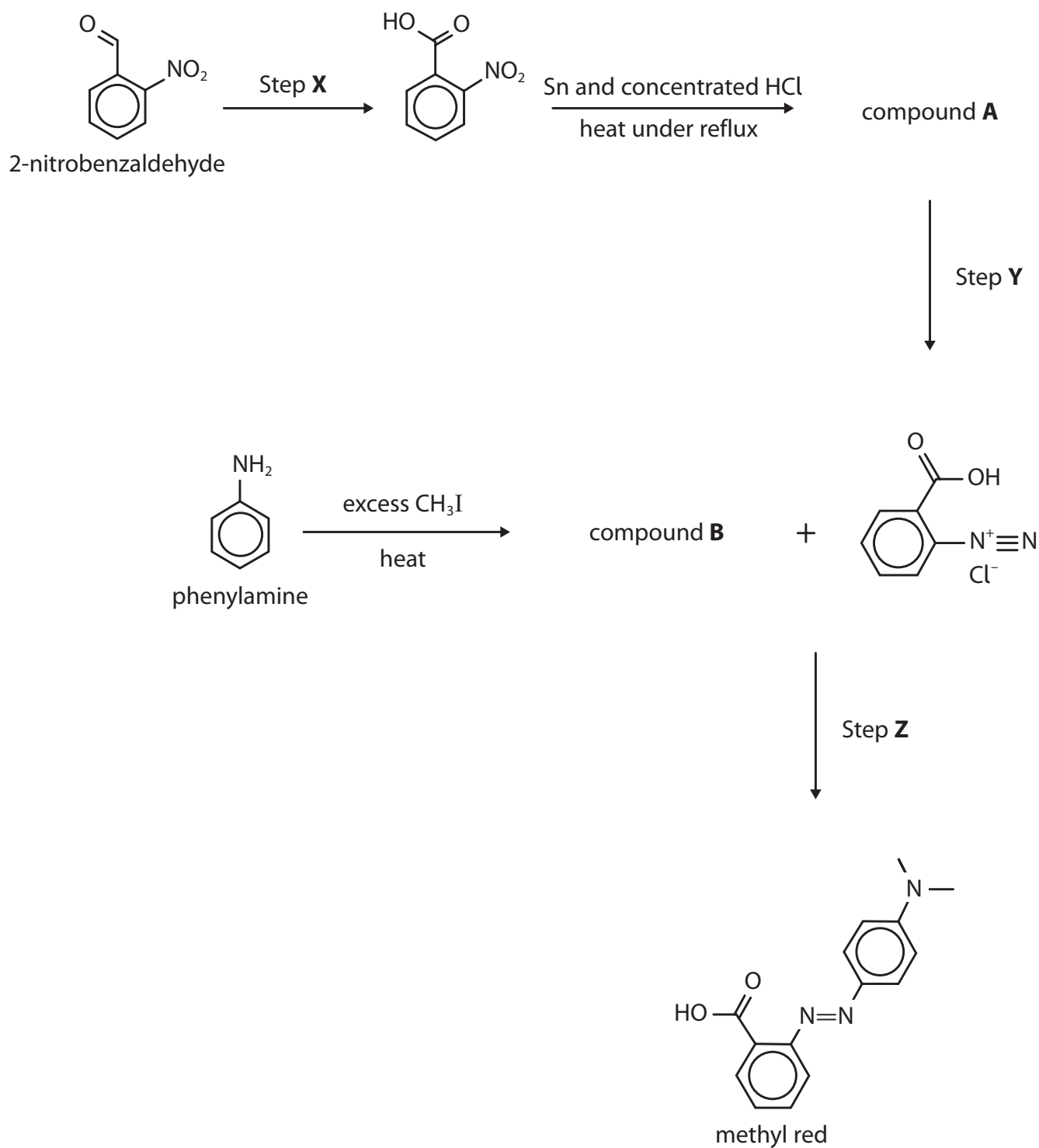Complete the table relating to two M-curc complexes.

**(2)**

|  | $[Au(curc)_2]^+$ | $[Al(curc)(C_2H_5OH)_2(NO_3)_2]$ |
|---|---|---|
| Coordination number | 4 |  |
| O—M—O bond angle | 90° |  |
| Shape |  | octahedral |
| Charge on metal ion |  | +3 |

(d) An incomplete synthesis for methyl red starting from 2-nitrobenzaldehyde and phenylamine is shown.



2-nitrobenzaldehyde

Step **X**

Sn and concentrated HCl
heat under reflux

compound **A**

Step **Y**

NH₂

phenylamine

excess CH₃I

heat

compound **B**   +

Step **Z**

methyl red

(i) State the reagents and conditions needed in Step **X**.

**(2)**

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(ii) Draw the structure of compound **A**.

**(1)**

(iii) State the reagents needed in Step **Y**.

**(1)**

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(iv) Draw the structure of compound **B**.

**(1)**

(v) The temperature used in Steps **Y** and **Z** should be kept as close to 5 °C as possible. State why the temperature should be neither higher nor lower than 5 °C.
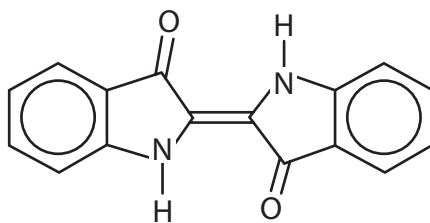
**(2)**

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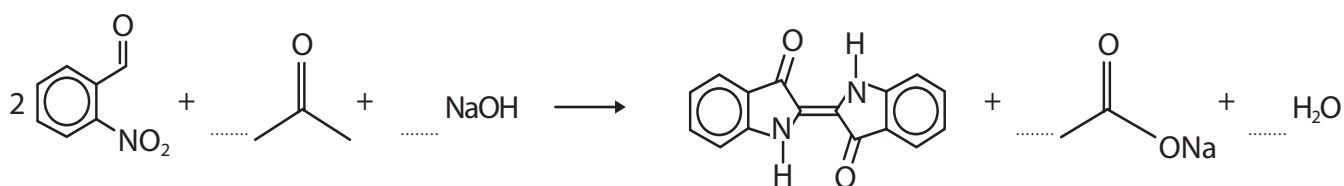
(e) Indigotin can be synthesised from 2-nitrobenzaldehyde and propanone in aqueous sodium hydroxide.



indigotin

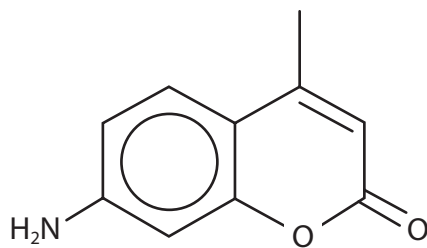(i) Complete the equation for this reaction.

**(2)**



(ii) Calculate the mass of 2-nitrobenzaldehyde required to make 10.0 g of indigotin from this reaction when the percentage yield is 85.0 %.

**(3)**

(f) Give the structure of the **organic** product of each of the following reactions of coumarin 440.



coumarin 440

(i) Hydrolysis with **excess** aqueous sodium hydroxide.

**(2)**

(ii) Condensation with ethanoyl chloride.

**(1)**

**(Total for Question 21 = 20 marks)**

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