

Please check the examination details below before entering your candidate information

Candidate surname					Other names				
Centre Number					Candidate Number				
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Pearson Edexcel International Advanced Level

Friday 12 January 2024

Morning (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 ball-point pen.
- If pencil is used for diagrams/sketches/graphs it must be dark (HB or B).
- **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 ►

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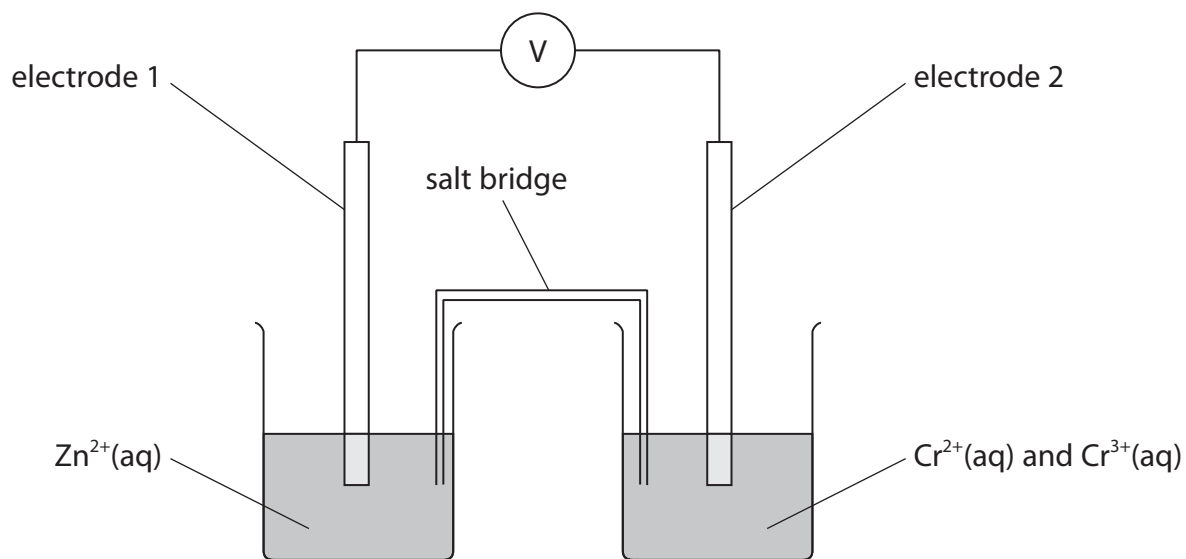
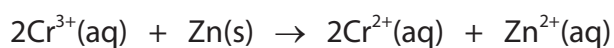
SECTION A

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 The apparatus can be used to measure $E_{\text{cell}}^{\ominus}$ for the reaction shown.



- (a) Which electrodes are used for this cell?

(1)

	electrode 1	electrode 2
<input type="checkbox"/> A	platinum	platinum
<input type="checkbox"/> B	platinum	chromium
<input type="checkbox"/> C	zinc	chromium
<input type="checkbox"/> D	zinc	platinum



- (b) A student wishes to measure the standard cell potential, $E_{\text{cell}}^{\ominus}$, of this cell.
The right-hand cell requires Cr^{3+} and Cr^{2+} ions.

What mass of $\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ must be dissolved in 1.00 dm^3 of deionised water to give the concentration of Cr^{3+} ions required to measure this $E_{\text{cell}}^{\ominus}$?

(1)

- ☐ A 52.0 g
☐ B 196 g
☐ C 358 g
☐ D 716 g

- (c) What can be deduced from the fact that, for this reaction, $E_{\text{cell}}^{\ominus}$ is positive?

(1)

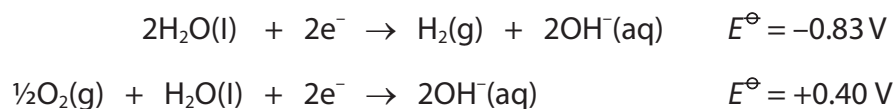
- ☐ A ΔS_{total} and $\ln K$ are positive
☐ B ΔS_{total} and $\ln K$ are negative
☐ C ΔS_{total} is positive and $\ln K$ is negative
☐ D ΔS_{total} is negative and $\ln K$ is positive

(Total for Question 1 = 3 marks)

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



2 The half-equations for a hydrogen-oxygen fuel cell in **alkaline** solution are shown.



(a) The equation for the overall cell reaction is

(1)

- ☐ **A** $3\text{H}_2\text{O(l)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{H}_2\text{(g)} + 4\text{OH}^-\text{(aq)}$
- ☐ **B** $\text{H}_2\text{(g)} + 4\text{OH}^-\text{(aq)} \rightarrow 3\text{H}_2\text{O(l)} + \frac{1}{2}\text{O}_2\text{(g)}$
- ☐ **C** $\text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{H}_2\text{O(l)}$
- ☐ **D** $\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)}$

(b) Calculate E^\ominus_{cell} for the reaction occurring in the hydrogen-oxygen fuel cell, under alkaline conditions.

(1)

- ☐ **A** -1.23 V
- ☐ **B** -0.43 V
- ☐ **C** $+0.43\text{ V}$
- ☐ **D** $+1.23\text{ V}$

(Total for Question 2 = 2 marks)

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



3 Which successive ionisation energies (in kJ mol^{-1}) are most likely to be those of a transition element?

- ☐ A 578 1817 2745 11 578 14 831
- ☐ B 759 1561 2958 5290 7236
- ☐ C 789 1577 3232 4356 16 091
- ☐ D 801 2427 3660 25 026 32 828

(Total for Question 3 = 1 mark)

4 Which sequence shows the ions in order of increasing strength as a reducing agent? Refer to your Data Booklet.

- ☐ A $\text{V}^{2+} < \text{Fe}^{2+} < \text{Cr}^{2+}$
- ☐ B $\text{Cr}^{2+} < \text{Fe}^{2+} < \text{V}^{2+}$
- ☐ C $\text{Cr}^{2+} < \text{V}^{2+} < \text{Fe}^{2+}$
- ☐ D $\text{Fe}^{2+} < \text{V}^{2+} < \text{Cr}^{2+}$

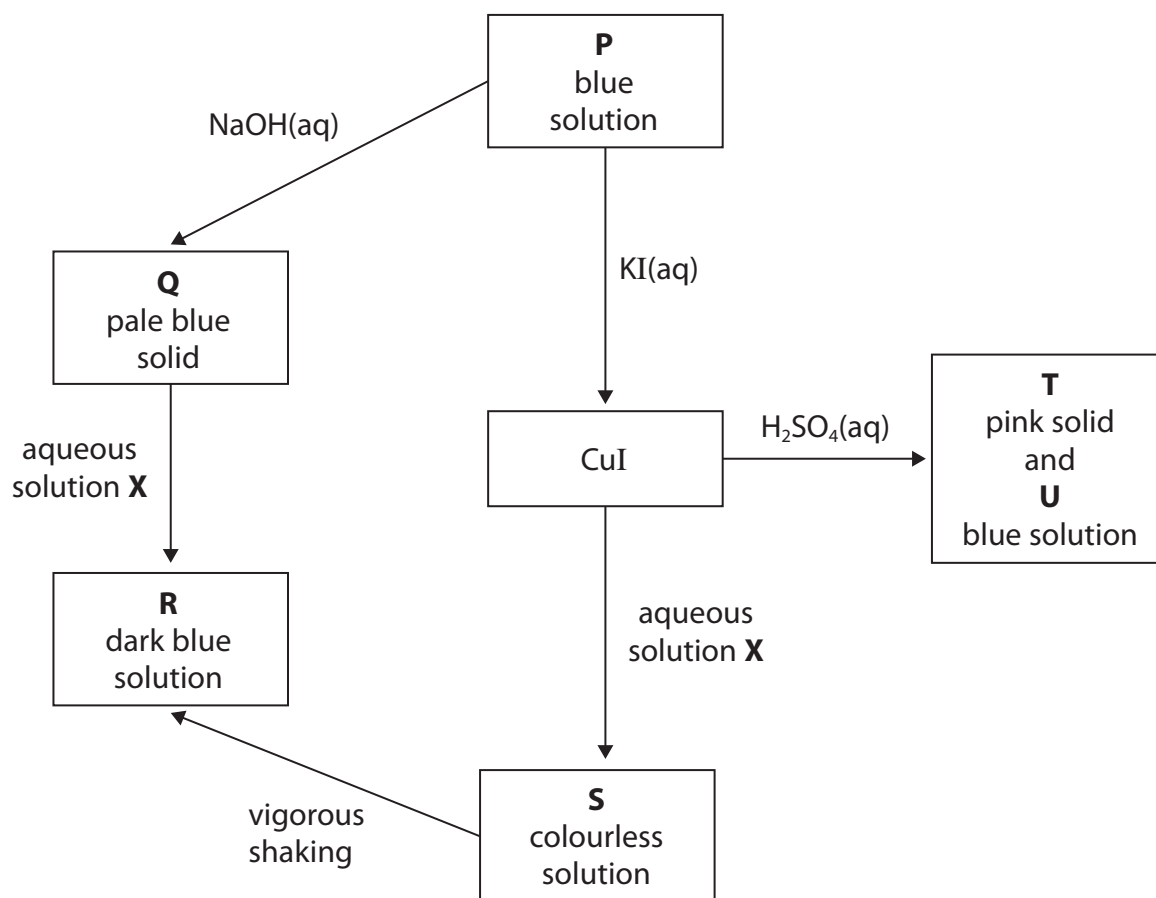
(Total for Question 4 = 1 mark)

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5 This question concerns the chemistry of copper.

In the reaction sequence, the substances P, Q, R, S, T and U contain copper in various oxidation states.



(a) What are the electronic structures of the three copper species?

(1)

	Cu	Cu ⁺	Cu ²⁺
<input type="checkbox"/> A	[Ar] 3d ⁹ 4s ²	[Ar] 3d ⁹ 4s ¹	[Ar] 3d ⁹
<input type="checkbox"/> B	[Ar] 3d ⁹ 4s ²	[Ar] 3d ⁸ 4s ²	[Ar] 3d ⁷ 4s ²
<input type="checkbox"/> C	[Ar] 3d ¹⁰ 4s ¹	[Ar] 3d ⁹ 4s ¹	[Ar] 3d ⁸ 4s ¹
<input type="checkbox"/> D	[Ar] 3d ¹⁰ 4s ¹	[Ar] 3d ¹⁰	[Ar] 3d ⁹



(b) Which rows show the substances with their correct oxidation states?

(1)

		Cu(0)	Cu(I)	Cu(II)
<input type="checkbox"/>	A	S	U	P
<input type="checkbox"/>	B	S	R	Q
<input type="checkbox"/>	C	T	S	P
<input type="checkbox"/>	D	T	U	Q

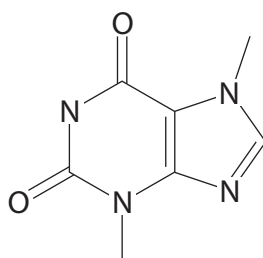
(c) Aqueous solution **X** contains

(1)

- ☐ **A** H_2SO_4
- ☐ **B** KI
- ☐ **C** NaOH
- ☐ **D** NH_3

(Total for Question 5 = 3 marks)

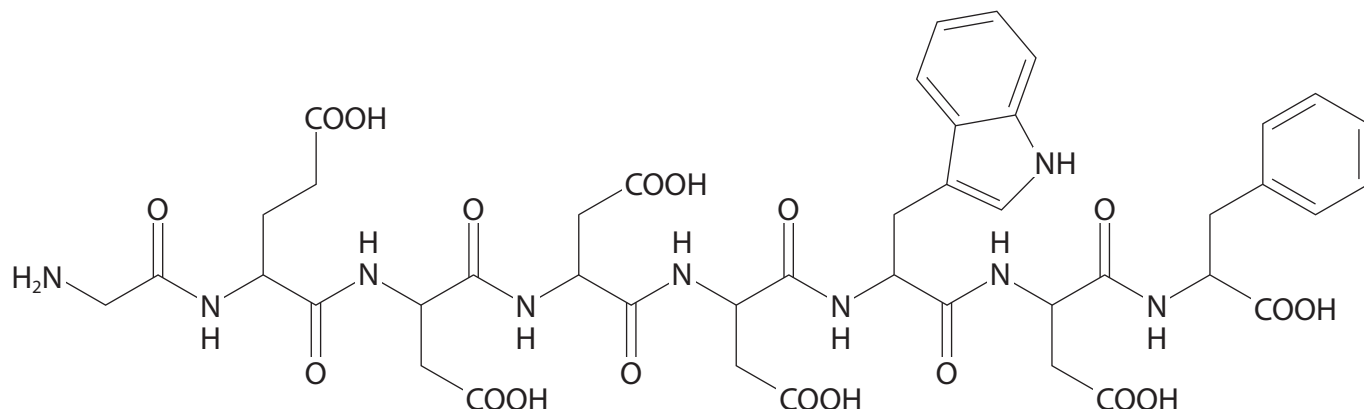
- 6 The diagram shows the skeletal structure of theobromine, which has a bitter taste and is found in chocolate and tea leaves.



Which of the functional groups listed is **not** present in the structure?

- ☐ **A** alkyl
- ☐ **B** amide
- ☐ **C** amine
- ☐ **D** ketone

(Total for Question 6 = 1 mark)



How many **different** types of amino acid have joined to form the octapeptide?

- ☐ **A** 4
- ☐ **B** 5
- ☐ **C** 6
- ☐ **D** 8

(Total for Question 7 = 1 mark)

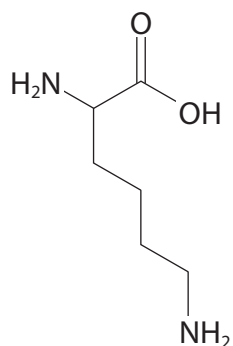
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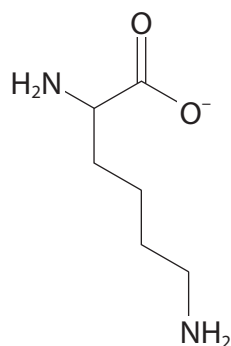
- 8 Which shows the structure of the amino acid lysine as a solid, and in solution at high pH?



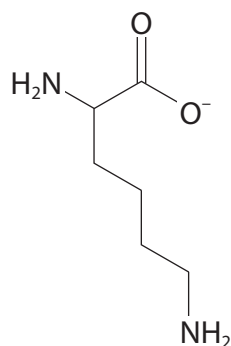
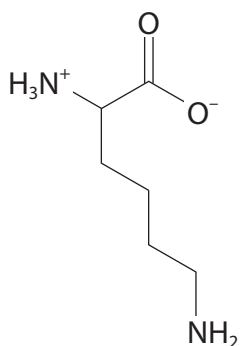
A



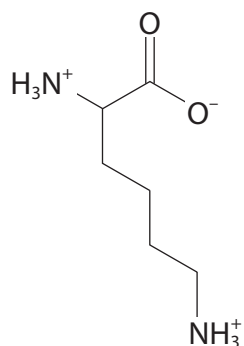
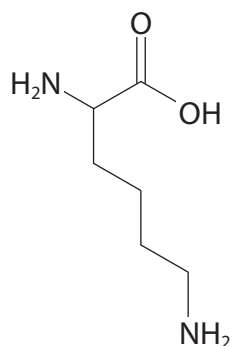
High pH solution



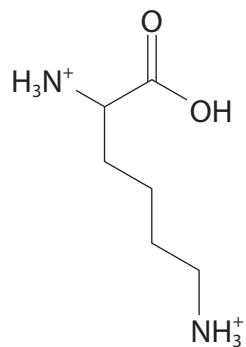
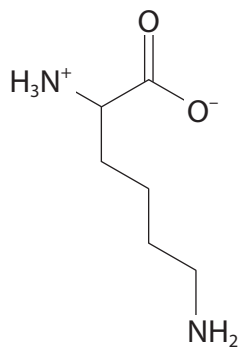
B



C



D



(Total for Question 8 = 1 mark)

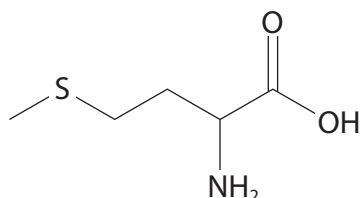


9 A dipeptide has the molecular formula $C_7H_{12}N_2O_3$.

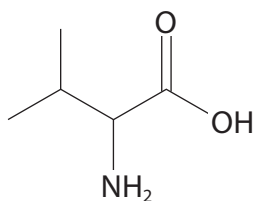
The dipeptide is hydrolysed to form two amino acids. One of the amino acids produced does not have a chiral centre.

What is the structure of the other amino acid which does have a chiral centre?

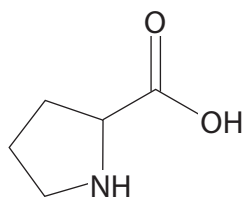
☐ A



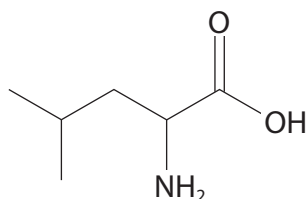
☐ B



☐ C



☐ D

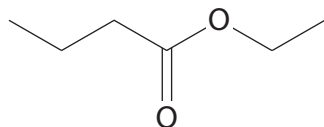


(Total for Question 9 = 1 mark)

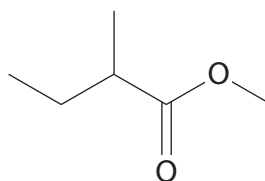
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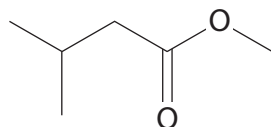
- 10 The aroma of strawberries is due to a number of volatile compounds, including the four isomeric esters shown.



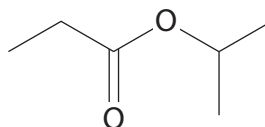
ester **P**



ester **Q**



ester **R**



ester **S**

- (a) Which of the esters have five peaks in their ^{13}C NMR spectrum?

(1)

- ☐ **A** **P** only
- ☐ **B** **Q** and **R** only
- ☐ **C** **R** and **S** only
- ☐ **D** **Q**, **R** and **S** only

- (b) Which of the esters will **not** have a doublet in its high resolution proton NMR spectrum?

(1)

- ☐ **A** **P**
- ☐ **B** **Q**
- ☐ **C** **R**
- ☐ **D** **S**

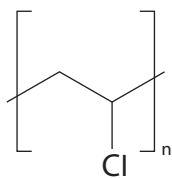
- (c) Which of the esters could rotate the plane of plane-polarised monochromatic light?

(1)

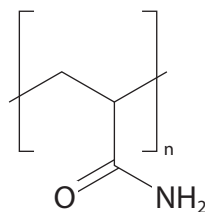
- ☐ **A** **Q** only
- ☐ **B** **Q** and **R**
- ☐ **C** **Q**, **R** and **S**
- ☐ **D** **R** and **S**

(Total for Question 10 = 3 marks)

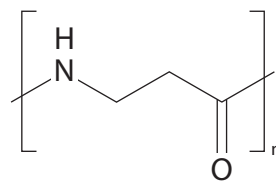
11 The formulae of three synthetic polymers, **X**, **Y** and **Z**, are shown.



X



Y



Z

Which are made by addition polymerisation reactions?

- ☐ **A** **X**, **Y** and **Z**
- ☐ **B** **X** and **Y**
- ☐ **C** **X** and **Z**
- ☐ **D** **Y** and **Z**

(Total for Question 11 = 1 mark)

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12 Sodium thiosulfate can be used to determine the concentration of an iodine solution by titration using starch indicator.

- (a) 5.00 g of sodium thiosulfate was dissolved in deionised water and the solution made up to 250.0 cm³ in a volumetric flask.

The volumetric flask has an uncertainty of $\pm 0.25 \text{ cm}^3$.

What is the minimum uncertainty of the balance required to match the uncertainty of the volumetric flask?

Assume two weighings are needed.

(1)

- ☐ **A** $\pm 0.0025 \text{ g}$
- ☐ **B** $\pm 0.005 \text{ g}$
- ☐ **C** $\pm 0.01 \text{ g}$
- ☐ **D** $\pm 0.05 \text{ g}$

- (b) The titration was carried out with sodium thiosulfate in the burette and starch was added just before the end-point.

What would be the colour of the solution in the conical flask at the end-point?

(1)

- ☐ **A** blue-black
- ☐ **B** brown
- ☐ **C** colourless
- ☐ **D** yellow

(Total for Question 12 = 2 marks)

TOTAL FOR SECTION A = 20 MARKS

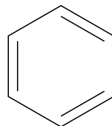


P 7 3 4 5 7 R A 0 1 3 3 6

SECTION B

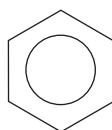
Answer ALL the questions. Write your answers in the spaces provided.

- 13 In 1865, Friedrich August Kekulé suggested a structure for benzene which consisted of alternating single and double carbon-carbon bonds.



Kekulé structure

However, modern analytical techniques indicate a structure in which the electrons are delocalised.



delocalised structure

- (a) Explain how the results of X-ray diffraction experiments on benzene suggest a delocalised structure rather than the Kekulé structure.

(2)

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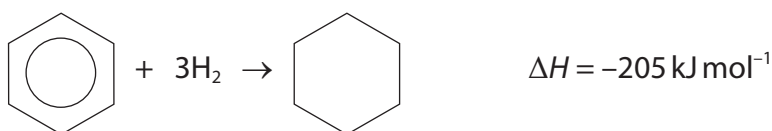
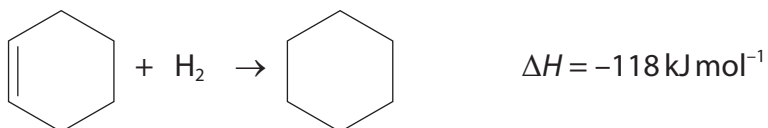
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- (b) The compound 1,2-dichlorobenzene exists as only one structure.
Explain how this supports the delocalised structure of benzene rather than the Kekulé structure.

(2)

- (c) State how the enthalpy changes of hydrogenation for cyclohexene and benzene provide evidence for the delocalised structure.



(1)

- (d) Describe the structure of benzene in terms of the atomic orbitals involved, the bonds formed and the delocalised electrons.

(3)

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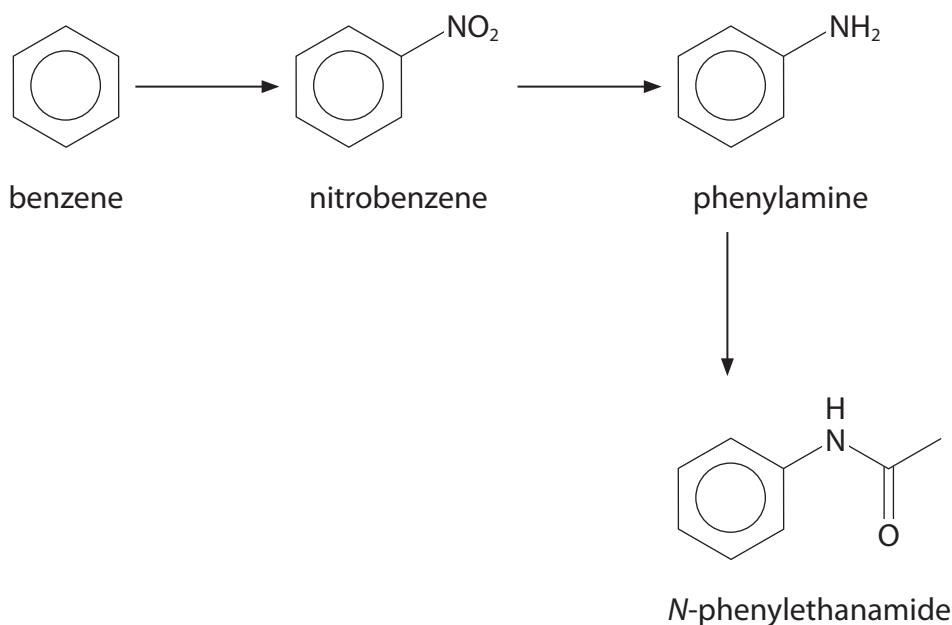
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(Total for Question 13 = 8 marks)



- 14 *N*-phenylethanamide, historically used as a painkiller, can be synthesised from benzene as shown.



- (a) Concentrated nitric acid reacts with a second reagent to produce an electrophile. This electrophile reacts with benzene to form nitrobenzene.

- (i) Identify, by name or formula, the second reagent and the electrophile.

(2)



- (ii) Draw the mechanism for the reaction between the electrophile and benzene to form nitrobenzene.

(3)

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- (b) (i) Identify, by name or formula, the reagent(s) required to convert nitrobenzene into phenylamine.

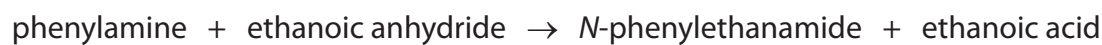
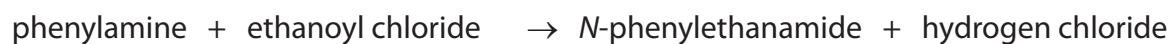
(1)

- (ii) State the type of reaction occurring during this step.

(1)



















*(c) In the final step of the synthesis, phenylamine reacts with either ethanoyl chloride or ethanoic anhydride.



Ethanoyl chloride is considerably more reactive than ethanoic anhydride.

Hazard symbols for reactants and products are shown.

Compound	Hazards
phenylamine	   
ethanoic anhydride	   
ethanoyl chloride	  

Compound	Hazards
N-phenylethanamide	
ethanoic acid	 
hydrogen chloride	 

Assess the advantages and disadvantages of the use of ethanoic anhydride rather than ethanoyl chloride for this reaction.

Consider the hazards associated with the reactants and products, and the atom economy of each reaction.

(6)

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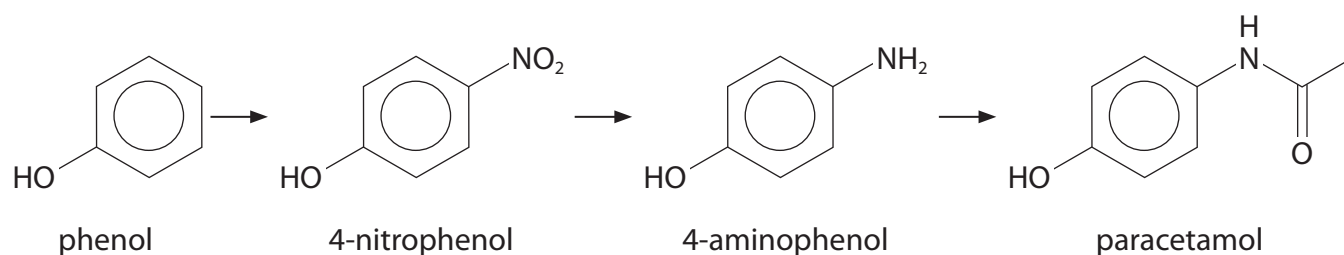
- (d) The overall yield for the synthesis of *N*-phenylethanamide from benzene was found to be 35.2%.

Calculate the minimum volume of benzene, in cm^3 , required to make 10.0 g of *N*-phenylethanamide.

[Density of benzene = 0.879 g cm^{-3}]

(4)

- (e) Another painkiller, paracetamol, can be synthesised from phenol in a similar sequence. Phenol is nitrated by dilute nitric acid.



Explain why the nitration of phenol requires much milder conditions than the formation of nitrobenzene.

(2)

(Total for Question 14 = 19 marks)



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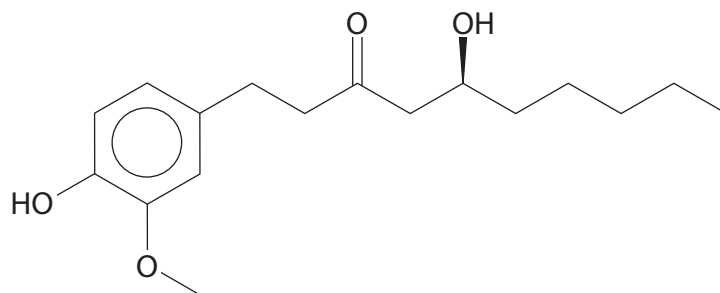
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- 15** (a) Gingerol is a compound found in fresh ginger that activates spice receptors on the tongue, giving raw ginger a hot taste. The skeletal formula of gingerol is shown.



gingerol

- (i) Give the molecular formula of gingerol.

(1)

- (ii) The OH group is shown attached to the carbon chain by a wedge-shaped bond. Suggest why the bond between the carbon chain and the OH group is shown as a wedge.

(2)



- (b) Cooking fresh ginger converts gingerol into zingerone, which is less pungent and has a sweeter flavour.

Zingerone can be formed in a four-step synthesis from coniferyl alcohol.

Step **2** in the synthesis involves a Grignard Reagent, while Steps **1**, **3** and **4** are redox reactions.

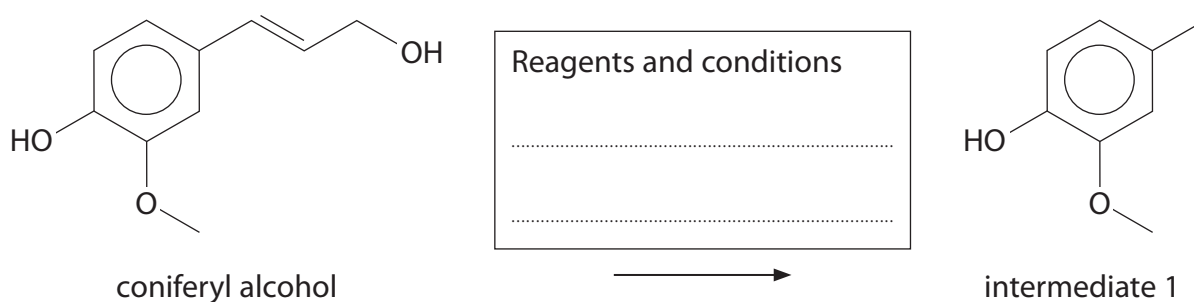
The synthesis is shown with the structures of the intermediate compounds incomplete.

Complete this four-step synthesis of zingerone from coniferyl alcohol.

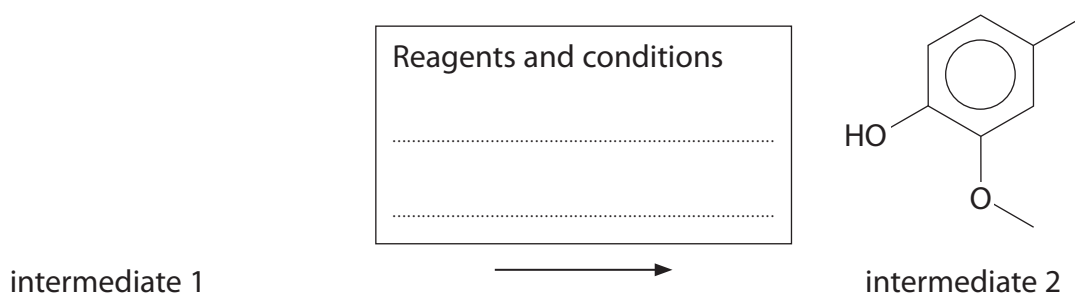
Include in your answer completed structures of the intermediate compounds and the reagents and conditions required.

(7)

Step 1



Step 2



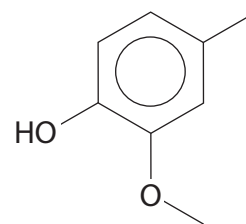
Step 3

intermediate 2

Reagents and conditions

.....

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intermediate 3

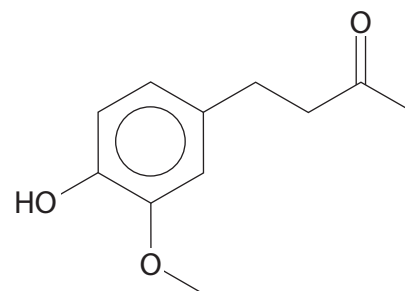
Step 4

intermediate 3

Reagents and conditions

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zingerone

(Total for Question 15 = 10 marks)

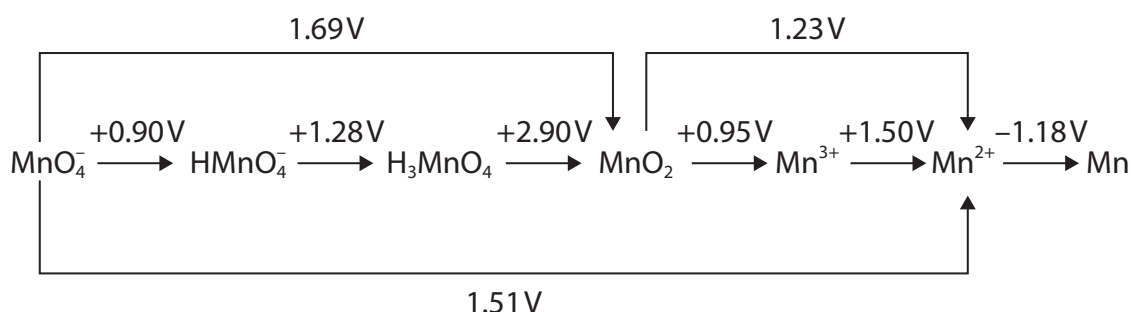


P 7 3 4 5 7 R A 0 2 5 3 6

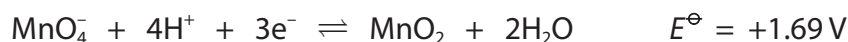
16 A Latimer diagram for a chemical element is a summary of the standard electrode potential data for that element.

In a Latimer diagram, the form of the element with the highest oxidation state is on the left, with successively lower oxidation states to the right.

A Latimer diagram for manganese at pH = 0 is shown.



The diagram shows that the standard electrode potential for the reduction of MnO_4^- to MnO_2 , in acidic conditions, is +1.69V.



- (a) (i) Justify the assignment of the oxidation state of +5 to manganese in H_3MnO_4 using oxidation numbers.

(1)

- (ii) Write an equation for the reaction of H_3MnO_4 in acidic solution to give ions containing manganese(VI) and manganese(IV).
Use the Latimer diagram to obtain the formulae of the ions produced.
State symbols are not required.

(2)



- (iii) Deduce whether or not this disproportionation reaction is thermodynamically feasible by calculating E^\ominus for the reaction.

(2)

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- (b) Before use in titration experiments, potassium manganate(VII) solutions must be standardised. One method uses ethanedioate ions to find the exact concentration of the manganate(VII) ions.

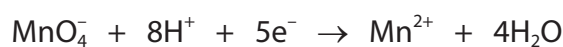
250.0 cm³ of a standard solution contained 1.915 g of sodium ethanedioate, Na₂C₂O₄.

A potassium manganate(VII) solution of approximately 0.02 mol dm⁻³ was standardised using this solution.

Excess sulfuric acid was added to 25.0 cm³ portions of the potassium manganate(VII) solution which were titrated with the sodium ethanedioate solution.

The mean titre was 22.95 cm³.

The relevant ionic half-equations are shown.



- (i) State the colour change at the end-point of the titration.

(1)

- (ii) Calculate the accurate concentration of the potassium manganate(VII), in mol dm⁻³, giving your answer to an appropriate number of significant figures.

(4)



- (iii) A second titration carried out without the addition of sulfuric acid resulted in the formation of a brown suspension.

Explain how the value of the mean titre would be affected, if at all, by the reaction that forms this suspension.

Use the Data Booklet as a source of information.

There is no need to calculate E_{cell} values.

(3)

(Total for Question 16 = 13 marks)

TOTAL FOR SECTION B = 50 MARKS



SECTION C

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

- 17** Transition metal compounds can show a number of different types of isomerism. Hydration isomerism is where different numbers of water molecules act as ligands. The name chromium(III) chloride is given to several chemical compounds with the formula $\text{CrCl}_3 \cdot x\text{H}_2\text{O}$, including a number of hydration isomers.

- (a) Anhydrous chromium(III) chloride, CrCl_3 , is a violet solid which can react with water to produce three isomers.

$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}3\text{Cl}^-$ is violet.

$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}2\text{Cl}^- \cdot \text{H}_2\text{O}$ is pale green.

$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+\text{Cl}^- \cdot 2\text{H}_2\text{O}$ is dark green.

- (i) Explain why the three isomers have different colours.

(3)

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- (ii) You are provided with three equimolar solutions of the three isomers.
Suggest how you would quantitatively determine the relative numbers of free chloride ions in the three isomers using the standard test for a chloride ion.

(5)

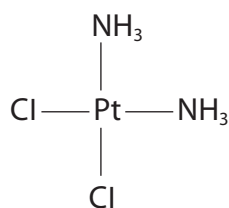
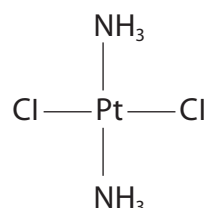
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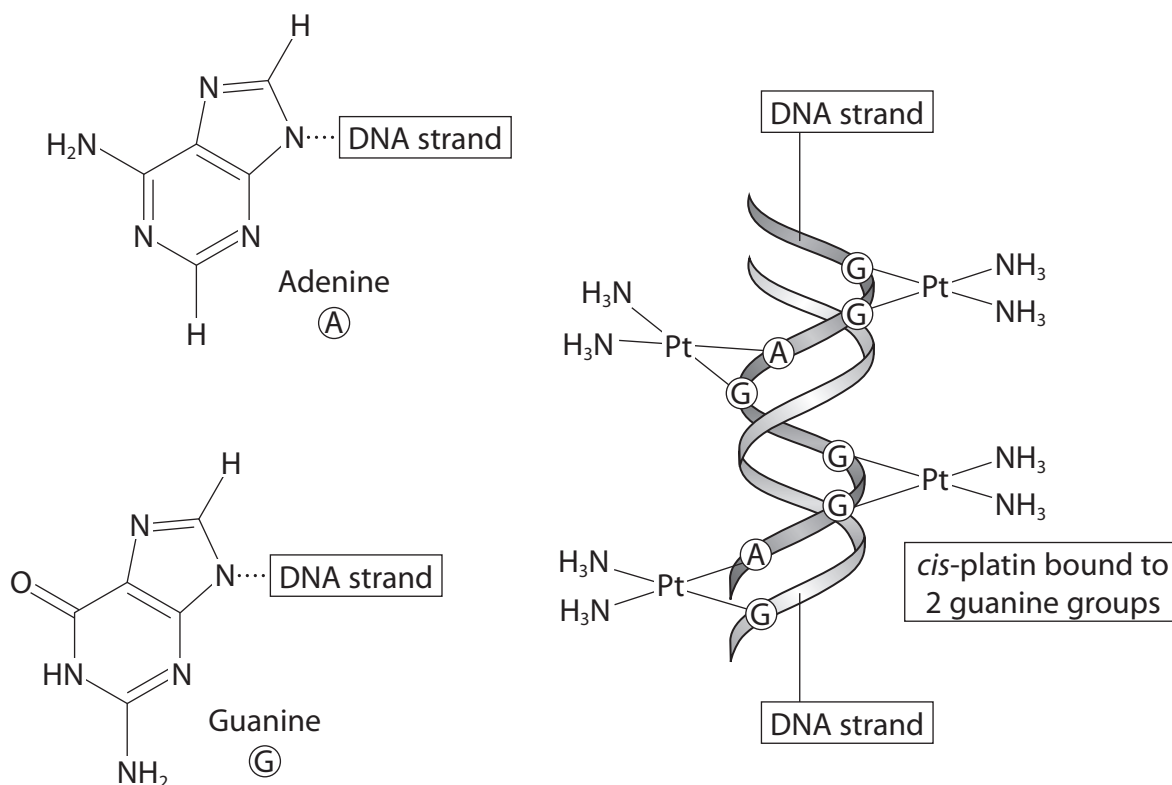
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- (b) Complexes can exhibit both cis-trans and optical isomerism. The cis- and trans-isomers of diamminedichloroplatinum(II) are commonly known as *cis-platin* and *trans-platin*.

*cis-platin**trans-platin*

In chemotherapy medication, *cis-platin* is used to treat a number of cancers including testicular cancer and breast cancer, while *trans-platin* has no beneficial effect against cancer. The cis-isomer is effective because it binds with the deoxyribonucleic acid (DNA) molecules in a cancerous cell through adenine and guanine groups. This interferes with the replication of the cell and results in its destruction.



This works in three steps.

Step 1 Slow substitution of one chloride ligand by a water.

Step 2 This water ligand is easily displaced by guanine or adenine in the DNA strand.

Step 3 Finally the second chloride ligand is displaced by a different guanine or adenine from a different part of the strand.



- (i) Write the balanced equation for Step 1.
State symbols are not required.

(1)

- (ii) Describe how guanine and adenine can bind to the platinum ion.

(1)

- (iii) *trans*-Platin binds to DNA.
Suggest why this does not damage the DNA.

(2)

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(c) Reinecke's salt has the formula $\text{NH}_4[\text{Cr}(\text{SCN})_x(\text{NH}_3)_y] \cdot z\text{H}_2\text{O}$. The anion exists as a trans-isomer.

It contains 14.67% chromium, 36.23% sulfur, 4.51% oxygen and 27.65% nitrogen by mass.

- (i) Calculate the values x , y and z in Reinecke's salt.
You **must** show your working.

(3)

- (ii) Draw a diagram of the **anion** of Reinecke's salt showing its three-dimensional shape.

(2)



- (d) (i) Explain why the tetrahedral complex $[\text{Co}(\text{NH}_3)\text{ClBrI}]$ exists as two optical isomers.

(2)

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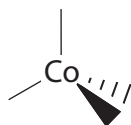
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- (ii) Complete the diagram showing the **two** optical isomers of the tetrahedral complex.

(1)



Co

(Total for Question 17 = 20 marks)

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



P 7 3 4 5 7 R A 0 3 5 3 6

