Candidate surname | Other names

Centre Number | Candidate Number

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 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 ▶

P71888A0132

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 In which species does the transition metal have the **lowest** oxidation number?

☒ **A** $[Cu(NH_3)_2]^+$

☒ **B** $[Fe(CN)_6]^{3-}$

☒ **C** $MnSO_4$

☒ **D** $Ni(CO)_4$

(Total for Question 1 = 1 mark)

2 A complex ion of chromium(III) has the formula $[CrCl_2(NH_2CH_2CH_2NH_2)_2]^x$, where x is the overall charge.

(a) What is the coordination number of chromium(III) in this complex ion?

(1)

☒ **A** 2

☒ **B** 3

☒ **C** 4

☒ **D** 6

(b) What is the overall charge on this complex ion?

(1)

☒ **A** 0

☒ **B** +1

☒ **C** +2

☒ **D** +3

(Total for Question 2 = 2 marks)

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

P 7 1 8 8 8 A 0 2 3 2

3 Which complex ion is colourless?

☒ **A** $[Al(H_2O)_6]^{3+}$

☒ **B** $[Cu(H_2O)_6]^{2+}$

☒ **C** $[Fe(H_2O)_6]^{3+}$

☒ **D** $[Ni(H_2O)_6]^{2+}$

(Total for Question 3 = 1 mark)

4 Which metal hydroxide precipitate is soluble in **both** excess aqueous ammonia and excess aqueous sodium hydroxide?

☒ **A** $Cu(OH)_2$

☒ **B** $Fe(OH)_2$

☒ **C** $Ni(OH)_2$

☒ **D** $Zn(OH)_2$

(Total for Question 4 = 1 mark)

5 The formula of hydrated copper(II) bromide is $CuBr_2 \cdot 4H_2O$.

What is the percentage, by mass, of water of crystallisation in this compound?

☒ **A** 6.10%

☒ **B** 8.06%

☒ **C** 24.4%

☒ **D** 32.2%

(Total for Question 5 = 1 mark)

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

6 The diagram shows how the relative colour intensity of an aqueous solution containing 0.001 mol of chromium(III) ions varies with increasing amounts of cyanide ions, CN^-.

Relative colour intensity (y-axis, 0–8) vs Amount of ligand/mol (x-axis, 0–0.008)
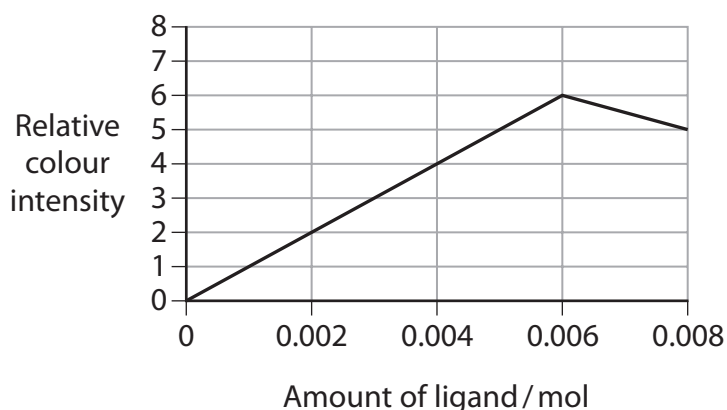
Chromium(III) ions form a complex ion with $EDTA^{4-}$ with a greater relative colour intensity than the complex ion formed with cyanide ions.

Which diagram shows the change in relative colour intensity when increasing amounts of $EDTA^{4-}$ are added to an aqueous solution containing 0.001 mol chromium(III) ions?

☒ **A**

Relative colour intensity vs Amount of ligand/mol

☒ **B**

Relative colour intensity vs Amount of ligand/mol

☒ **C**

Relative colour intensity vs Amount of ligand/mol

☒ **D**

Relative colour intensity vs Amount of ligand/mol
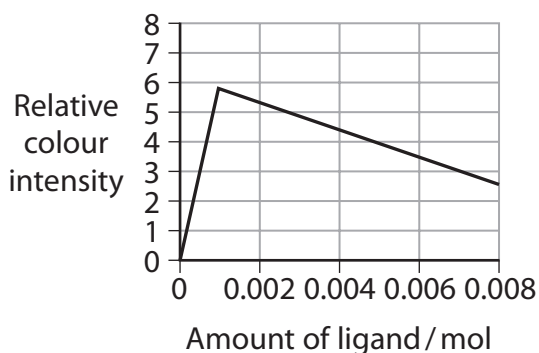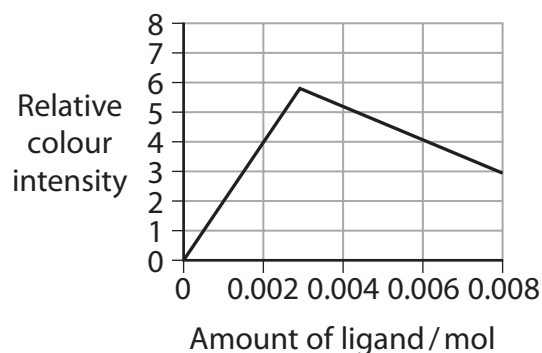
(Total for Question 6 = 1 mark)

7 Persulfate ions react slowly with iodide ions at room temperature unless a catalyst of Fe^{2+} or Fe^{3+} is added to the reaction mixture.

$$S_2O_8^{2-}(aq) \ + \ 2I^-(aq) \ \rightarrow \ 2SO_4^{2-}(aq) \ + \ I_2(aq)$$

Which of these is the most likely reason why this reaction is slow without a catalyst?

☒ **A** $E_{cell}^{\ominus}$ is positive

☒ **B** Δ_rH is positive

☒ **C** ΔS_{total} is positive

☒ **D** activation energy is high

(Total for Question 7 = 1 mark)

8 The cell diagram for an electrochemical cell is shown.

$$Pt(s) \,|\, Fe^{2+}(aq), Fe^{3+}(aq) \,||\, Br_2(aq), 2Br^-(aq) \,|\, Pt(s) \qquad E_{cell}^{\ominus} = +0.32\,V$$

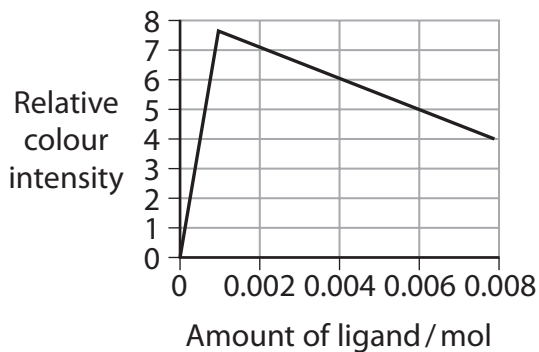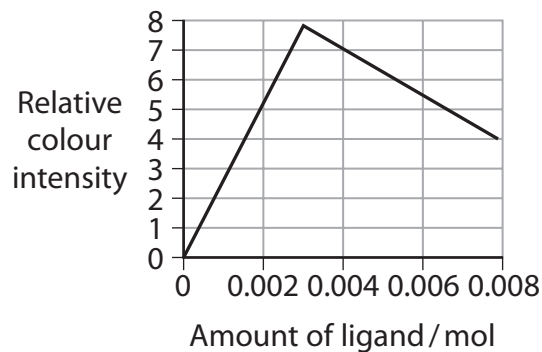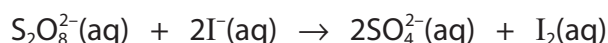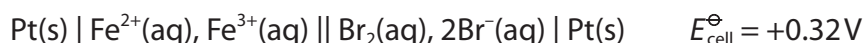What are the half-equations for the reactions that occur in the half-cells?

	Half-equation in left-hand half-cell	Half-equation in right-hand half-cell
☒ **A**	$Fe^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) \ + \ e^-$	$2Br^-(aq) \rightleftharpoons Br_2(aq) \ + \ 2e^-$
☒ **B**	$Fe^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) \ + \ e^-$	$Br_2(aq) \ + \ 2e^- \rightleftharpoons 2Br^-(aq)$
☒ **C**	$Fe^{3+}(aq) \ + \ e^- \rightleftharpoons Fe^{2+}(aq)$	$2Br^-(aq) \rightleftharpoons Br_2(aq) \ + \ 2e^-$
☒ **D**	$Fe^{3+}(aq) \ + \ e^- \rightleftharpoons Fe^{2+}(aq)$	$Br_2(aq) \ + \ 2e^- \rightleftharpoons 2Br^-(aq)$

(Total for Question 8 = 1 mark)

9 What is the minimum volume, in cm^3, of oxygen needed for the complete combustion of a mixture of $50\,cm^3$ of propene and $50\,cm^3$ of but-1-ene gases?

All gas volumes are measured at the same temperature and pressure.

☒ **A** 225

☒ **B** 300

☒ **C** 525

☒ **D** 700

(Total for Question 9 = 1 mark)

10 A sample of air contains 405 parts per million (ppm) of carbon dioxide.

What is the approximate volume, in cm^3, of carbon dioxide in $250\,cm^3$ of this air?

☒ **A** 0.001

☒ **B** 0.01

☒ **C** 0.1

☒ **D** 1

(Total for Question 10 = 1 mark)

11 This question is about the infrared and proton NMR spectra of the amino acid valine.
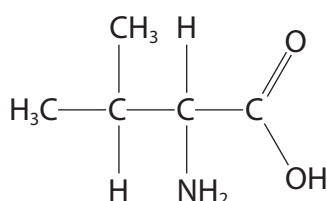
(a) Which of these wavenumber ranges would you **not** expect to have an absorption in the infrared spectrum of valine?

(1)

☒ **A** $3500 - 3300\,cm^{-1}$

☒ **B** $3095 - 3010\,cm^{-1}$

☒ **C** $2962 - 2853\,cm^{-1}$

☒ **D** $1725 - 1700\,cm^{-1}$

(b) What are the expected splitting patterns in the high resolution proton NMR spectrum of valine for the protons shown in bold?

(1)

		Splitting pattern for C**H**$_3$ protons	Splitting pattern for $(CH_3)_2$C**H** proton
☒	**A**	doublet	octet
☒	**B**	doublet	septet
☒	**C**	singlet	octet
☒	**D**	singlet	septet

(Total for Question 11 = 2 marks)

12 Grignard reagents are used to increase the length of the carbon chain in organic molecules.

(a) What type of reaction occurs with a Grignard reagent?

(1)

☒ **A** electrophilic addition

☒ **B** free radical substitution

☒ **C** oxidation

☒ **D** nucleophilic addition

(b) Benzaldehyde reacts with a Grignard reagent, followed by hydrolysis, to form 2-methyl-1-phenylbutan-1-ol.
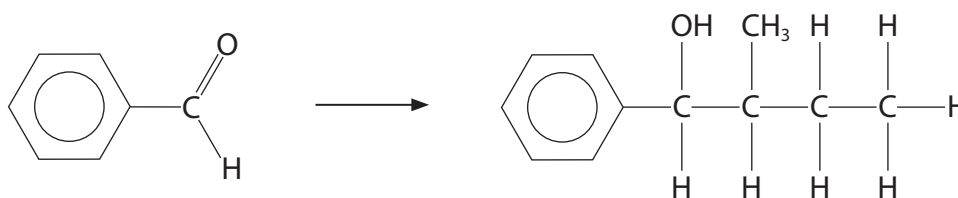
What is the formula of this Grignard reagent?

(1)

☒ **A** $CH_3CH_2CH_2CH_2MgBr$

☒ **B** $CH_3CH_2CH(CH_3)MgBr$

☒ **C** $(CH_3)_2CHCH_2MgBr$

☒ **D** $(CH_3)_3CMgBr$

(Total for Question 12 = 2 marks)

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

13 A student hydrolysed a section of a protein and then used thin-layer chromatography to analyse the amino acids produced.

The chromatogram is shown.

solvent front

X

baseline
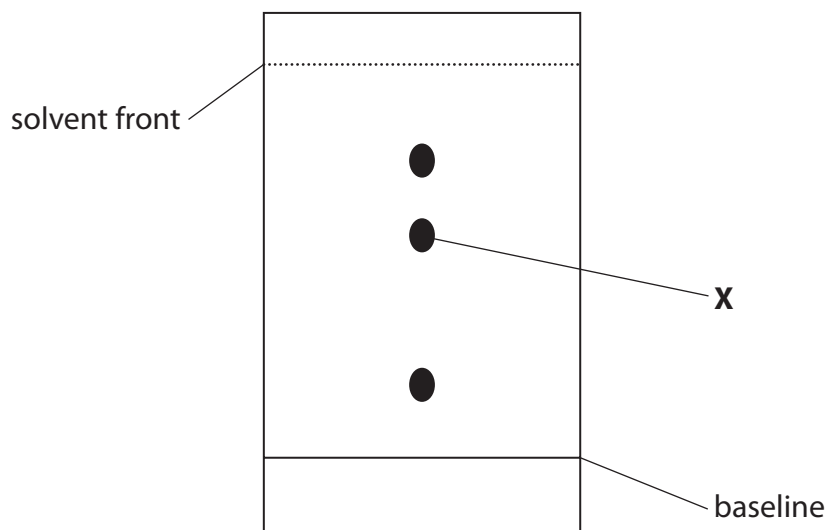
What is the best estimate of the R_f value of the amino acid labelled **X**?

☒ **A** 0.2

☒ **B** 0.4

☒ **C** 0.6

☒ **D** 0.8

(Total for Question 13 = 1 mark)

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

14 A polyamide has the repeat unit
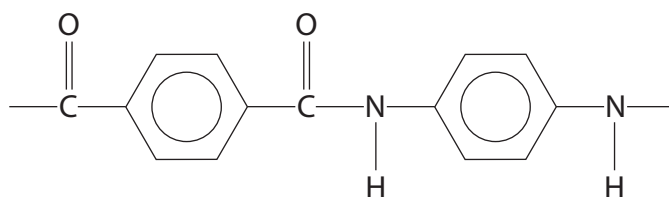
Which of these monomers can form this polyamide?

☒ **A**   only

☒ **B**   only

☒ **C**   and

☒ **D**   and
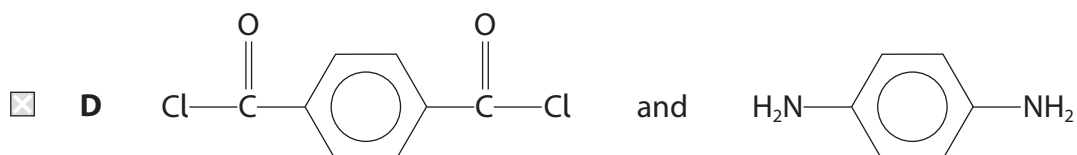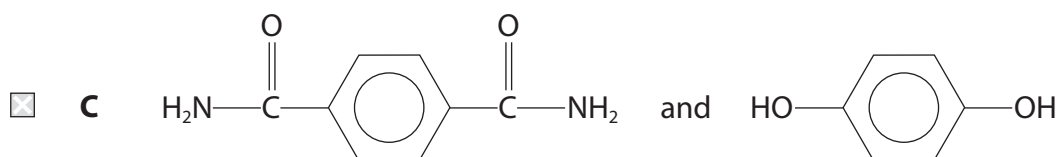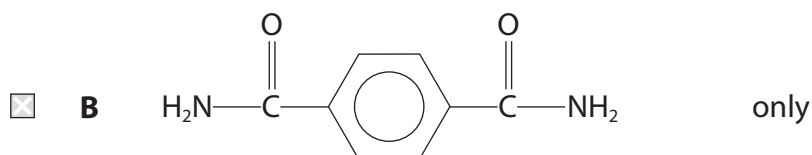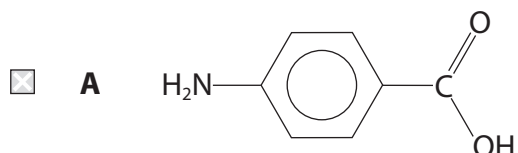
(Total for Question 14 = 1 mark)

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

15 A reaction scheme for the preparation of an azo dye from phenylamine is shown.
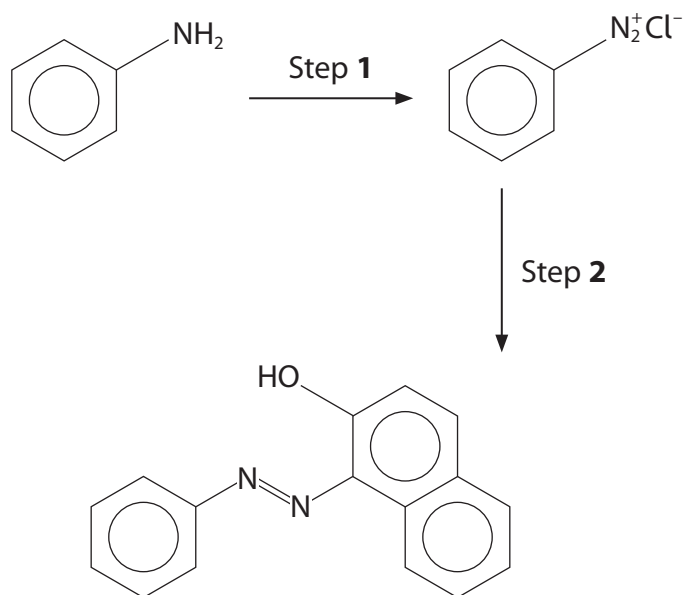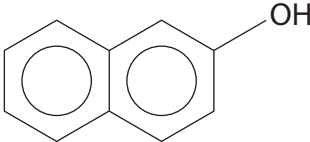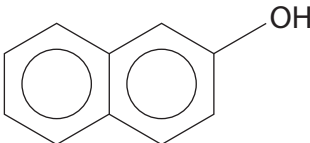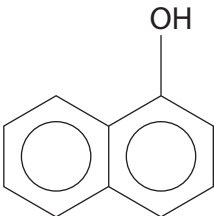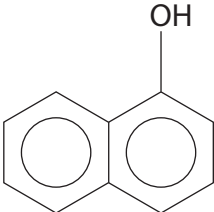
(a) What are the reagents and condition for Step **1**?

(1)

⊠ **A** $NaNO_2$ and HCl at 5 °C

⊠ **B** $NaNO_3$ and HCl at 5 °C

⊠ **C** $NaNO_2$ and HCl at 50 °C

⊠ **D** $NaNO_3$ and HCl at 50 °C

(b) Which reagent and condition are used for Step **2**?

(1)

Reagent	Condition
☒ **A** OH (naphthalen-2-ol structure)	acidic
☒ **B** OH (naphthalen-2-ol structure)	alkaline
☒ **C** OH (naphthalen-1-ol structure)	acidic
☒ **D** OH (naphthalen-1-ol structure)	alkaline

(Total for Question 15 = 2 marks)

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

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

16 The organic compound 4-aminophenol can behave as an acid and a base.

$$HO \!-\!\! \bigcirc \!-\! NH_2$$
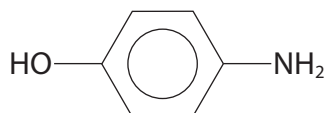
What is formed when 4-aminophenol reacts with hydrochloric acid?

☒ **A** $HO \!-\!\! \bigcirc \!-\! NH_3^+$

☒ **B** $^+H_2O \!-\!\! \bigcirc \!-\! NH_2$

☒ **C** $^-O \!-\!\! \bigcirc \!-\! NH_2$

☒ **D** $^-O \!-\!\! \bigcirc \!-\! NH^-$
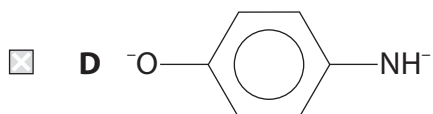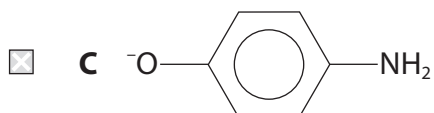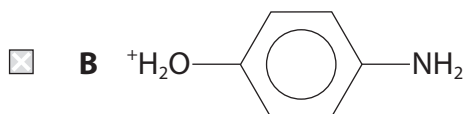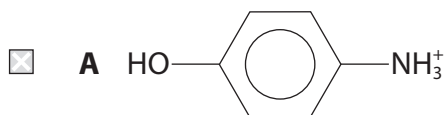
(Total for Question 16 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

17 Organic compounds can be analysed using a combination of qualitative analysis, quantitative analysis and spectroscopic techniques.

(a) An organic compound **A** contains carbon, hydrogen and oxygen only and has a molar mass of $136\,g\,mol^{-1}$.

Complete combustion of 5.26 g of **A** in dry oxygen produces 15.3 g of carbon dioxide and 4.18 g of water.

Show that the formula of **A** is $C_9H_{12}O$.
You **must** show all your working.

(4)

(b) Compound **A**, $C_9H_{12}O$, contains a benzene ring and **one** side-chain.

A is oxidised when heated with acidified potassium dichromate(VI) to produce a compound **B** which reacts with iodine and aqueous sodium hydroxide to give a pale yellow solid, **C**.

When **A** reacts with concentrated phosphoric(V) acid, it forms a mixture of two **structural** isomers, **D** and **E**, both of which decolourise bromine water.

D exists as geometric isomers but **E** does not.

Draw the structures of compounds **A** to **E**.

(5)

Structure
A
B
C
D
E

(c) Compound **F** is a structural isomer of **A** which also has a benzene ring and one side-chain.

F is **not** oxidised when heated with acidified potassium dichromate(VI). The ^{13}C NMR spectrum of **F** has six peaks.

Draw the structure of **F**. Justify your answer by labelling the six different carbon environments.

(2)

(d) Compound **G** is a structural isomer of **A** which also has a benzene ring and one side-chain.

The mass spectrum of **G** has a peak at $m/z = 107$.

Deduce the structure of **G**. Justify your answer.

(2)

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(Total for Question 17 = 13 marks)

18 Vanadium forms compounds with oxidation states +2, +3, +4 and +5.

(a) State the oxidation number of vanadium in Na_3VO_4.

(1)

....

(b) In aqueous solution, vanadium(II) exists as $[V(H_2O)_6]^{2+}$ but vanadium(V) exists as $[VO_2(H_2O)_4]^+$.

Explain why vanadium(V) does **not** exist as $[V(H_2O)_6]^{5+}$.

(3)

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(c) Hydrated potassium vanadium(III) sulfate contains 7.9% potassium, 10.2% vanadium, 12.9% sulfur, 4.8% hydrogen and 64.2% oxygen.

Calculate the empirical formula of this compound and hence write the overall formula showing the potassium (K^+), vanadium (V^{3+}) and sulfate (SO_4^{2-}) ions and the water of crystallisation.

(3)

(d) An acidified aqueous solution of potassium manganate(VII) oxidises vanadium(III) ions.

In an experiment, 10.0 cm^3 portions of a solution containing 0.132 mol dm^{-3} vanadium(III) ions are titrated against 0.0200 mol dm^{-3} potassium manganate(VII) in acidic conditions.

The mean titre is 26.40 cm^3.

(i) Calculate the ratio of the number of moles of manganate(VII) ions, MnO_4^-, to the number of moles of vanadium(III) ions, V^{3+}, in this oxidation.

You **must** show all your working.

(3)

(ii) Write the equation for the reaction between manganate(VII) ions and vanadium(III) ions in acidic solution.
State symbols are not required.

(2)

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

*(e) Vanadium(V) ions, VO_2^+, in acidic solution may be reduced step by step through its oxidation states.

Compare and contrast the use of iron and tin in this reduction process.
Include equations and $E_{cell}^{\ominus}$ values for any reactions that occur.
State symbols are not required.

(6)

Use only data from these tables.

Vanadium systems

Electrode system	$E^{\ominus}$ / V
$V^{3+}(aq) \ + \ e^- \ \rightleftharpoons \ V^{2+}(aq)$	−0.26
$VO^{2+}(aq) \ + \ 2H^+(aq) \ + \ e^- \ \rightleftharpoons \ V^{3+}(aq) \ + \ H_2O(l)$	+0.34
$VO_2^+(aq) \ + \ 2H^+(aq) \ + \ e^- \ \rightleftharpoons \ VO^{2+}(aq) \ + \ H_2O(l)$	+1.00

Reducing agents

Electrode system	$E^{\ominus}$ / V
$Fe^{2+}(aq) \ + \ 2e^- \ \rightleftharpoons \ Fe(s)$	−0.44
$Sn^{2+}(aq) \ + \ 2e^- \ \rightleftharpoons \ Sn(s)$	−0.14

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(Total for Question 18 = 18 marks)

P71888A01932

19 This question is about some organic nitrogen compounds.

(a) Phenol reacts with dilute nitric acid at room temperature to form a mixture of 2-nitrophenol and 4-nitrophenol.
The reaction is an electrophilic substitution.

(i) Draw a mechanism for the reaction to form 2-nitrophenol.
Assume that NO_2^+ is the electrophile.

(3)

(ii) Benzene requires a mixture of concentrated nitric acid and concentrated sulfuric acid at 60 °C to form nitrobenzene.

Explain why phenol requires milder conditions for nitration than benzene.

(2)

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....

(b) Devise a synthesis of *N*-phenylethylethanamide from (bromomethyl)benzene **without** the use of a Grignard reagent.
Include reagents, conditions and the structures of the intermediate compounds.

(bromomethyl)benzene

N-phenylethylethanamide

(5)
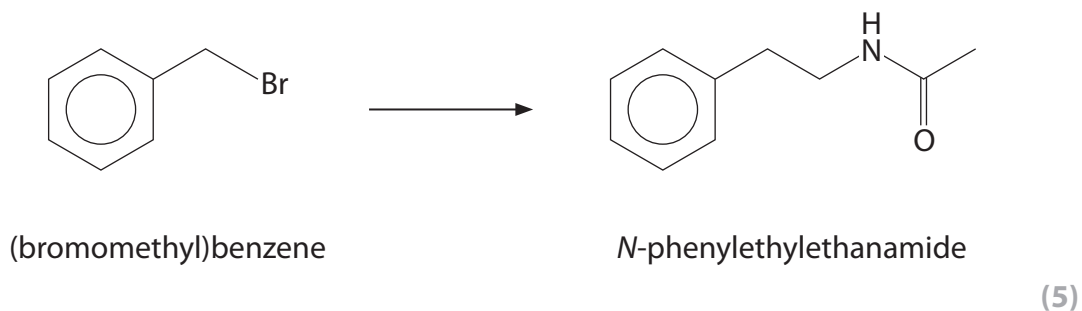
(c) Phenylalanine is a naturally-occurring amino acid found in meat, milk and eggs. It is used to form the artificial sweetener known as aspartame.
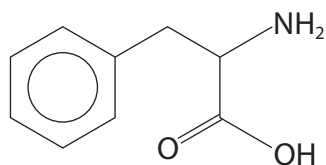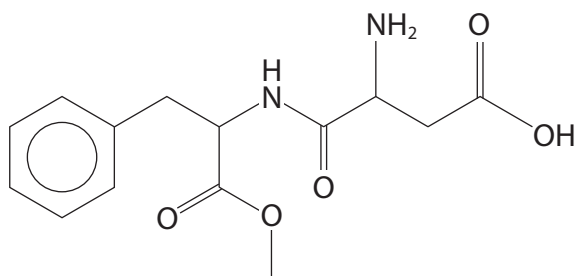
phenylalanine   aspartame

(i) Complete the structure of the zwitterion of phenylalanine.

(1)
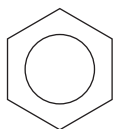
(ii) Draw the structure of the dipeptide formed from phenylalanine.

(1)

(iii) Give the molecular formula of aspartame.

(1)

(iv) Circle the **two** chiral carbon atoms in aspartame on the structure shown.

(1)
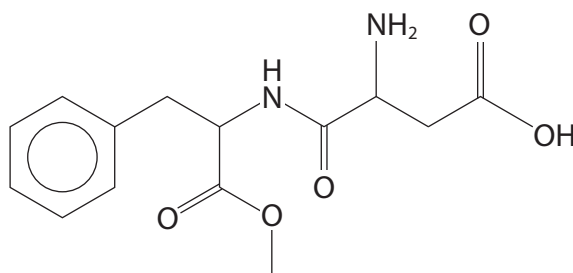
(v) Aspartame is hydrolysed by hydrochloric acid in the stomach.

Draw the structures of the three organic products formed from the complete acid hydrolysis of aspartame.

(3)

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

(vi) A can of a fizzy drink contains 53 mg of aspartame per 100 cm^3 of drink.

Calculate the number of molecules of aspartame in a 330 cm^3 can of the drink.
Give your answer to an appropriate number of significant figures.

[Molar mass aspartame = 294 g mol^{-1}
Avogadro constant = 6.02×10^{23} mol^{-1}]

(3)

(Total for Question 19 = 20 marks)

TOTAL FOR SECTION B = 51 MARKS

SECTION C

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

20

> **Manganese and some of its compounds**
>
> Manganese is the twelfth most abundant element in the Earth's crust and it is an essential element for all living organisms.
>
> Manganese is a transition metal and it can form compounds with oxidation states +2, +3, +4, +5, +6 and +7, although not all these are stable and some readily undergo disproportionation.
>
> Some compounds and ions containing manganese are effective heterogeneous and homogeneous catalysts.
>
> Alkaline batteries have a manganese(IV) oxide cathode and are used in digital cameras and toys. They have a similar voltage to traditional zinc-carbon batteries but have a higher energy density and last longer.

(a) Some of the properties of manganese and its compounds depend on electronic configurations.

(i)   Complete the electronic configurations for a manganese atom and a manganese(II) ion, using the electron-in-boxes notation.

(1)

Mn atom: [Ar]

3d   4s

Mn^{2+} ion: [Ar]
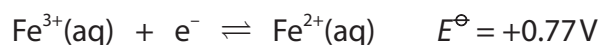
3d   4s

(ii) The standard electrode potentials, $E^{\ominus}$, for the half-cells involving the oxidation states +3 and +2 for manganese and iron are shown.

$$Mn^{3+}(aq) + e^- \rightleftharpoons Mn^{2+}(aq) \qquad E^{\ominus} = +1.49V$$

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq) \qquad E^{\ominus} = +0.77V$$

Explain, in terms of electronic configurations, why the $E^{\ominus}$ value for the Mn^{2+}/Mn^{3+} half-cell is significantly higher than that for the Fe^{2+}/Fe^{3+} half-cell.

(3)

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(b) Manganese(IV) oxide, MnO_2, is an oxidising agent and a catalyst.

(i) Chlorine can be prepared in a laboratory by reacting manganese(IV) oxide with concentrated hydrochloric acid.

$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$$

Explain, in terms of oxidation numbers, why this is a redox reaction.

(2)

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(ii) Manganese(IV) oxide catalyses the decomposition of hydrogen peroxide.

$$2H_2O_2(aq) \rightarrow 2H_2O(aq) + O_2(g)$$
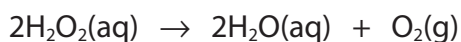
$100\,cm^3$ of a solution of hydrogen peroxide decomposed to produce $86.0\,cm^3$ of oxygen gas, measured at room temperature and pressure (r.t.p.).

Calculate the concentration of the hydrogen peroxide solution in $mol\,dm^{-3}$.

[Molar volume of gas at r.t.p. $= 24.0\,dm^3\,mol^{-1}$]

(2)

(c) Potassium manganate(VI), K_2MnO_4, is a green solid.
In acidic solution, the manganate(VI) ions disproportionate to form manganate(VII) ions and manganese(IV) oxide.

Write the **ionic** equation for this disproportionation.
State symbols are not required.

(1)

(d) Manganate(VII) ions react with ethanedioate ions in acidic solution.

$$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$$
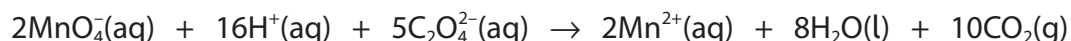
Two experiments were carried out:

Experiment 1
Aqueous potassium manganate(VII) was added to a mixture of excess ethanedioic acid and sulfuric acid. The concentration of the manganate(VII) ions was determined as the reaction progressed.
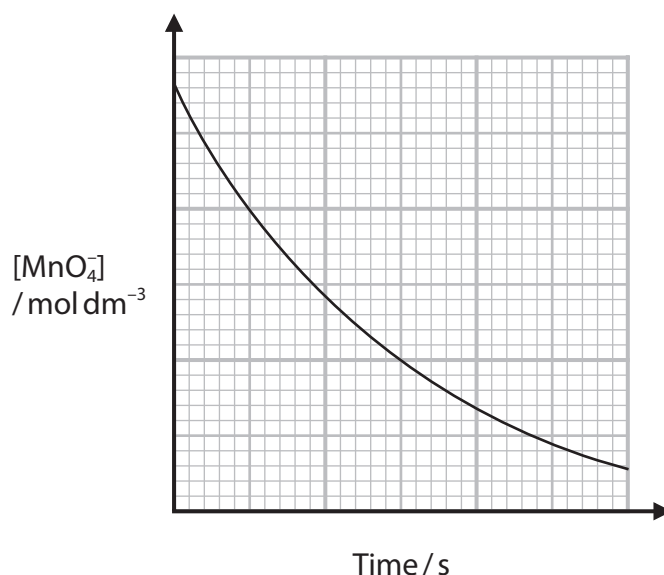
Experiment 2
The same volumes and concentrations of solutions as in **Experiment 1** were used but some solid manganese(II) sulfate was dissolved in the ethanedioic acid and sulfuric acid mixture before adding the potassium manganate(VII) solution.

Graphs of the concentration of manganate(VII) ions against time are shown.

Experiment 1

$[MnO_4^-]$ $/mol\,dm^{-3}$

Time/s

Experiment 2

$[MnO_4^-]$ $/mol\,dm^{-3}$

Time/s
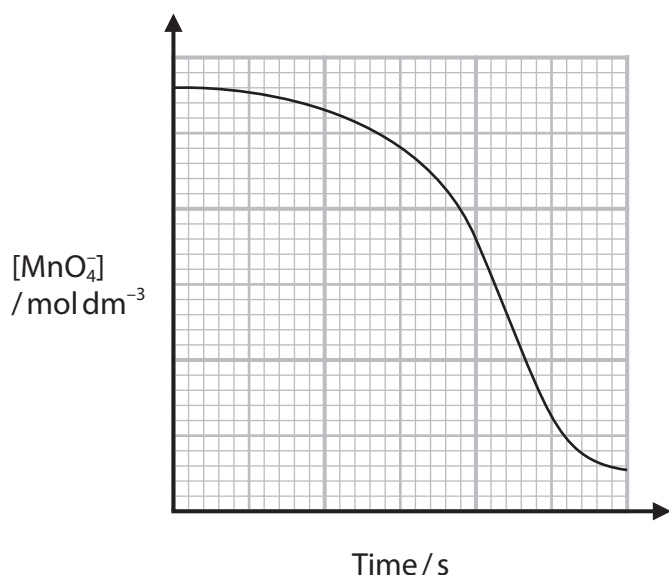
Explain, in terms of catalysis, why the graphs have different shapes.

(3)

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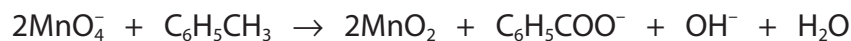
(e) Methylbenzene is oxidised to benzoic acid by heating under reflux with an alkaline solution of potassium manganate(VII).

In an experiment, 1.73 g of methylbenzene was mixed with 7.00 g of potassium manganate(VII) and excess potassium hydroxide solution.

The overall equation is

$$2MnO_4^- \ + \ C_6H_5CH_3 \ \rightarrow \ 2MnO_2 \ + \ C_6H_5COO^- \ + \ OH^- \ + \ H_2O$$

(i) Show that the potassium manganate(VII) is in excess.

[Molar masses / g mol^{-1}: $C_6H_5CH_3 = 92$ $KMnO_4 = 158$]

(3)

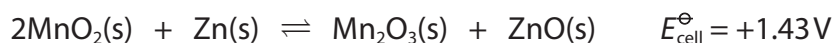(ii) State how the benzoate ions, $C_6H_5COO^-$, can be converted into benzoic acid.

(1)

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(f) Alkaline batteries consist of an anode made of a zinc alloy, a cathode made of manganese(IV) oxide and an electrolyte of aqueous potassium hydroxide.

The overall equation for the reaction in the cell is

$$2MnO_2(s) \; + \; Zn(s) \; \rightleftharpoons \; Mn_2O_3(s) \; + \; ZnO(s) \qquad E^{\ominus}_{cell} = +1.43\,V$$

(i) Write the half-equations for the reactions at the anode and the cathode.

(2)

anode half-equation:

cathode half-equation:

(ii) The standard electrode potential for the Zn/ZnO half-cell is −1.28 V.

Calculate the standard electrode potential for the MnO_2/Mn_2O_3 half-cell.

(1)

(Total for Question 20 = 19 marks)

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