Please check the examination details k	below before ento	ering your candidate information		
Candidate surname Other names		Other names		
Pearson Edexcel International Advanced Level	entre Number	Candidate Number		
Tuesday 9 June	e 202	0		
Morning (Time: 1 hour 45 minutes)	Paper R	Reference WCH15/01		
Chemistry International Advanced Level Unit 5: Transition Metals and Organic Nitrogen Chemistry				
Candidates must have: Scientific		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.
- For the question marked with an asterisk (\*), marks will be awarded for your ability to structure your answer logically showing 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 your working in calculations and include units where appropriate.
- Check your answers if you have time at the end.

Turn over ▶



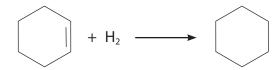
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### **SECTION A**

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 enthalpy change of hydrogenation of cyclohexene is  $-120 \, \text{kJ mol}^{-1}$ .



What is the approximate enthalpy change of hydrogenation of benzene, in kJ mol<sup>-1</sup>?

- **■ B** -210
- **C** −360
- **D** −510

(Total for Question 1 = 1 mark)

**2** Which orbitals overlap to form the ring of delocalised electrons in benzene and what type of bond is formed?

X A

■ B

X C

□ D

Orbitals overlapping	Type of bond
р	π
р	σ
s and p	π
s and p	σ

(Total for Question 2 = 1 mark)

3 Which reagent and catalyst will convert benzene into phenylethanone?

	Reagent Catalyst		Catalyst
×	A	ethanal	aluminium chloride
×	В	ethanal	platinum
×	C	ethanoyl chloride	aluminium chloride
X	D	ethanoyl chloride	platinum

(Total for Question 3 = 1 mark)

4 Chlorine reacts with methylbenzene in the presence of ultraviolet light.

Which of these is a product of this reaction?

⊠ B

**⊠** C

 $\boxtimes$  D

(Total for Question 4 = 1 mark)

- How many isomers containing a benzene ring are there with the molecular formula  $C_6H_3(NO_2)_2OH$ ?
  - A 4
  - **■ B** 5

(Total for Question 5 = 1 mark)

6 Phenol reacts with ethanoyl chloride to form phenyl ethanoate.

phenol

phenyl ethanoate

$$M_{\rm r} = 94$$

$$M_{\rm r} = 136$$

In an experiment, 3.67 g of phenyl ethanoate was formed, giving a yield of 85.0 %.

What was the starting mass of phenol?

- A 2.16g
- B 2.54 g

(Total for Question 6 = 1 mark)

**7** A hydrocarbon contains 91.3 % by mass of carbon.

Which of these could be the molecular formula of this compound?

- $\triangle$  A  $C_6H_6$
- $\blacksquare$  **B**  $C_7H_8$
- □ C<sub>9</sub>H<sub>12</sub>

(Total for Question 7 = 1 mark)

- **8** What is an organic product of the reaction between ethylamine and chloroethane?
  - NH₂CH₂COCl
  - $\blacksquare$  **B**  $C_2H_5NH_4^+Cl^-$
  - C C<sub>2</sub>H<sub>5</sub>NHCOC<sub>2</sub>H<sub>5</sub>
  - $\square$  **D**  $(C_2H_5)_2NH_2^+Cl^-$

(Total for Question 8 = 1 mark)

**9** Which pair of monomers can form this polymer?

X	Δ

 $\mathbb{X}$  B

 $\times$  C

 $\boxtimes$  D

Monomer 1	Monomer 2	
HOC <sub>6</sub> H₄OH	HOOCCH <sub>2</sub> CH <sub>2</sub> COOH	
HOCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	HOOCCH <sub>2</sub> CH <sub>2</sub> COOH	
HOCH₂C <sub>6</sub> H₄COOH	HOCH <sub>2</sub> CH <sub>2</sub> COOH	
HOOCC <sub>6</sub> H <sub>4</sub> COOH	HOCH <sub>2</sub> CH <sub>2</sub> OH	

(Total for Question 9 = 1 mark)

**10** Part of the structure of a protein is shown.

How many different amino acids were used to form this part of the structure?

- A 3
- B 4
- **■ D** 6

(Total for Question 10 = 1 mark)

- **11** Which organic compound reacts with a Grignard reagent to give a product that forms a secondary alcohol on hydrolysis?
  - **A** carbon dioxide
  - B ethanal
  - C methanal
  - **D** propanone

(Total for Question 11 = 1 mark)

12 A compound with the formula  $C_6H_{14}$  gives a  $^{13}C$  NMR spectrum with four peaks.

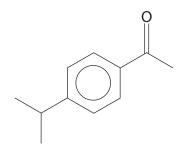
Which compound gives this spectrum?

- X B

- ⊠ C
- ×

(Total for Question 12 = 1 mark)

**13** Cuminone is used as a flavouring.



cuminone

What is the molecular formula of cuminone?

- $\triangle$  **A**  $C_{10}H_{13}O$
- $lacktriangleq B C_{10}H_{15}O$
- $\square$  **C**  $C_{11}H_{14}O$
- $\square$  **D**  $C_{11}H_{16}O$

(Total for Question 13 = 1 mark)

- 14 Which species contains an element with the same oxidation number as bromine in KBrO<sub>3</sub>?
  - $\square$  A  $N_2O_5$
  - B KMnO<sub>4</sub>

  - $\square$  **D** Na<sub>2</sub>SO<sub>3</sub>

(Total for Question 14 = 1 mark)

- **15** Which is a redox reaction?
  - $\square$  **A**  $Cr_2O_7^{2-} + 2C \rightarrow Cr_2O_3 + CO_3^{2-} + CO$
  - $\blacksquare$  **B**  $CrO_2Cl_2 + 4OH^- \rightarrow CrO_4^{2-} + 2Cl^- + 2H_2O$
  - $\square$  **C**  $Cr_2O_7^{2-} + 2HCl \rightarrow 2CrO_3Cl^- + H_2O$
  - $\square$  **D**  $2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$

(Total for Question 15 = 1 mark)

**16** The electronic configuration of the atoms of an element is 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>3d<sup>5</sup>4s<sup>1</sup>.

What is the maximum oxidation number shown in compounds of this element?

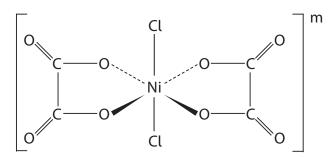
- **■ A** +1
- **B** +5
- **C** +6
- **■ D** +7

(Total for Question 16 = 1 mark)

- **17** Which of the following species will **not** act as a ligand in the formation of a complex ion?
  - A CH<sub>3</sub>NH<sub>2</sub>
  - B CN<sup>-</sup>
  - C NH<sub>3</sub>
  - $\square$  **D** NH<sub>4</sub><sup>+</sup>

(Total for Question 17 = 1 mark)

18 What is the coordination number of the nickel(II) ion and the overall charge, m, of this complex?



		nickel(II) ion	complex
X	A	2	0
X	В	2	4–
X	C	6	0
X	D	6	4–

(Total for Question 18 = 1 mark)

**19** In acidic conditions, manganate(VII) ions are reduced to manganese(II) ions, Mn<sup>2+</sup>.

In neutral conditions, manganate(VII) ions are reduced to manganese(IV) oxide, MnO<sub>2</sub>.

22.0 cm<sup>3</sup> of a solution of manganate(VII) ions were needed to oxidise 25.0 cm<sup>3</sup> of a solution of iron(II) ions to iron(III) ions in acidic conditions.

The same solution of manganate(VII) ions is used to oxidise 25.0 cm<sup>3</sup> of the same solution of iron(II) ions in **neutral** conditions.

By considering the oxidation number changes involved, it may be shown that the volume of the manganate(VII) solution required, in neutral conditions, is

- 12.6 cm<sup>3</sup> X
- 13.2 cm<sup>3</sup>
- X 36.7 cm<sup>3</sup>
- 38.5 cm<sup>3</sup>

(Total for Question 19 = 1 mark)

**20** A solution contains  $19.6\,\mathrm{g}\;\mathrm{dm}^{-3}\,\mathrm{of}\;\mathrm{chromium}(III)\;\mathrm{sulfate},\;\mathrm{Cr_2(SO_4)_3}$ .

What is the concentration, in mol dm<sup>-3</sup>, of sulfate ions in this solution?

[Molar mass  $Cr_2(SO_4)_3 = 392 \text{ g mol}^{-1}$ ]

- **■ B** 0.10
- **■ C** 0.15
- **■ D** 0.25

(Total for Question 20 = 1 mark)

**TOTAL FOR SECTION A = 20 MARKS** 

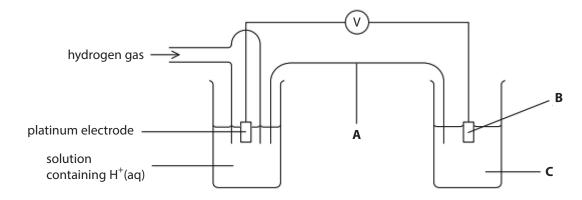
## **SECTION B**

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

- 21 This question is about electrochemical cells.
  - (a) The half-equation for an iron(III) / iron(II) half-cell is

$$Fe^{3+}(aq) + e^{-} \Rightarrow Fe^{2+}(aq)$$

The standard electrode potential of this half-cell is measured using the apparatus shown.



The measurement is made under standard conditions.

Identify, by name or formula, the substances needed in the salt bridge and in the right-hand half-cell to measure the standard electrode potential.

(3)

- A Salt bridge containing a solution of
- **B** Electrode made of
- **C** Solution containing



(b) The cell diagram for an electrochemical cell is

Pt | [Mn<sup>2+</sup> + 4H<sub>2</sub>O], [MnO<sub>4</sub><sup>-</sup> + 8H<sup>+</sup>] | [BiO<sub>3</sub><sup>-</sup> + 6H<sup>+</sup>], [Bi<sup>3+</sup> + 3H<sub>2</sub>O] | Pt 
$$E_{cell}^{\Theta}$$
 = +0.09 V

Write the half-equations for the two half-cells and hence the overall ionic equation for the reaction that occurs.

State symbols are not required.

(3)

(c) The standard electrode potential,  $E^{\Theta}$ , for the chromium(III)/chromium half-cell is -0.74 V.

$$Cr^{3+}(aq) + 3e^{-} \rightleftharpoons Cr(s)$$

The effect on the electrode potential, *E*, of changing the concentration of the ions in the half cell is calculated using the equation

$$E = E^{\Theta} + \frac{RT}{96500 \times n} \ln[Cr^{3+}(aq)]$$

where n is the number of electrons in the half-equation, T is the temperature in kelvin and R is the gas constant.

Calculate the electrode potential of the half-cell at 298 K when the concentration of chromium(III) ions is  $0.0100\,\mathrm{mol}\ dm^{-3}$ .

(2)

(Total for Question 21 = 8 marks)

- **22** This question is about aromatic amines and amino acids.
  - (a) A synthesis of phenylamine is shown.

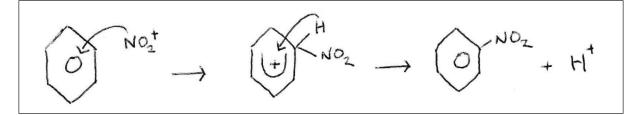
$$\begin{array}{c|c} & \text{Step 1} \\ \hline \end{array} \begin{array}{c} & \text{Step 2} \\ \hline \end{array}$$

nitrobenzene

phenylamine

(i) Benzene is converted into nitrobenzene in Step 1 using a mixture of concentrated nitric acid and concentrated sulfuric acid. The electrophile is NO<sub>2</sub><sup>+</sup>.

A student drew a mechanism for the reaction.



Describe the three changes needed to correct this student's mechanism.

(3)

Change 1
Change 2
Change 3

(i	ii) Give the reagents for Step <b>2</b> .	(1)
(b) P	henylamine is a base.	
(i	Explain why phenylamine is a weaker base than ammonia.	(3)
(i	ii) State what is <b>seen</b> when a few drops of an aqueous solution of phenylamine are added to an aqueous solution containing Cu <sup>2+</sup> ions.	(1)



(c) Azo violet is used as a dye and an indicator.
A synthesis of azo violet from 1-amino-4-nitrobenzene is shown.

1-amino-4-nitrobenzene

(i) Give the reagents and condition for Step 1.

(2)

(ii) Deduce the structure of the organic compound needed to produce azo violet in Step 2.

(1)

(iii) Give a reason why azo violet exists as geometric isomers.

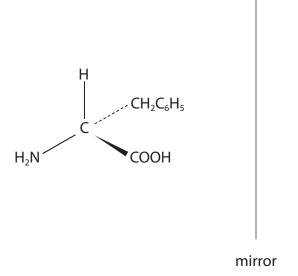
(1)

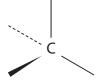
(d) Phenylalanine is an amino acid that exists as optical isomers.

The structure of one of the optical isomers is shown.

Complete the diagram to show the other optical isomer of phenylalanine.

(1)





(Total for Question 22 = 13 marks)

- 23 This question is about some organic compounds.
  - (a) A mixture of methane and ethane with a total volume of 25.0 cm<sup>3</sup> required 65.0 cm<sup>3</sup> of oxygen for complete combustion.

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

Determine the percentage, by volume, of methane in the mixture.

(4)



(b) Devise a reaction scheme to convert butan-2-ol into 1-amino-2-methylbutan-2-ol in **three** steps.

1-amino-2-methylbutan-2-ol

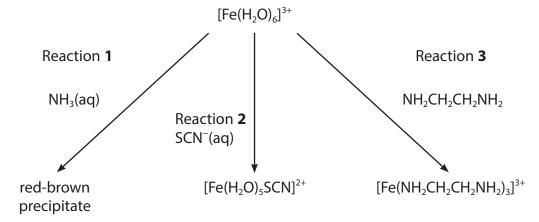
Include the reagents, conditions and equations for each of the steps.

For any oxidation or reduction use [O] and [H] respectively.

(6)

(Total for Question 23 = 10 marks)

- **24** This question is about transition metals and their compounds.
  - (a) Three reactions were carried out on a solution containing  $[Fe(H_2O)_6]^{3+}$  ions.



(i) Complete the equation for Reaction 1. State symbols are not required.

(2)

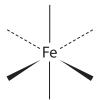
$$[\text{Fe}(\text{H}_2\text{O})_6]^{3+} \ + \ ..... \ \text{NH}_3 \ \rightarrow$$

(ii) State the type of reaction occurring in Reaction 2.

(1)

(iii) Complete the diagram to show the structure of the complex ion formed in Reaction 3, showing all of the atoms.

(2)



- (b) Vanadium can exist in the oxidation states +2, +3, +4 and +5.
  - (i) Complete the table to show the colours of the ions that each of these oxidation states has in aqueous solution.

(2)

Oxidation state of vanadium	Colour of the ions in aqueous solution
+2	mauve
+3	
+4	
+5	

(ii) Two vanadium species exist in equilibrium in an aqueous solution.

$$VO_3^-(aq) + H_2O(I) \Rightarrow VO_2^+(aq) + 2OH^-(aq)$$

Deduce whether or not this is a redox reaction.

Justify your answer in terms of oxidation numbers.

a.	-	70.	
1	ч	- 1	
	-	- 1	

		- XXXXXXX

(iii) Predict the oxidising agent that could convert vanadium(II) ions to vanadium(III) ions and then vanadium(IV) ions, but **not** to vanadium(V) ions, under standard conditions.

Only use data from the tables shown.

Include equations and  $E_{\text{cell}}^{\Theta}$  values for the two reactions that occur.

(5)

# Vanadium systems

Electrode system	E <sup>⊕</sup> / V
$V^{3+}(aq) + e^{-} \Rightarrow V^{2+}(aq)$	-0.26
$VO^{2+}(aq) + 2H^{+}(aq) + e^{-} \Rightarrow V^{3+}(aq) + H_2O(I)$	+0.34
$VO_2^+(aq) + 2H^+(aq) + e^- \Rightarrow VO^{2+}(aq) + H_2O(l)$	+1.00

# Oxidising agents

Electrode system	E <sup>⊕</sup> / V
$Cu^{2+}(aq) + e^- \Rightarrow Cu^+(aq)$	+0.15
$NO_3^-(aq) + 2H^+(aq) + e^- \Rightarrow NO_2(g) + H_2O(l)$	+0.80
$\frac{1}{2}Br_2(aq) + e^- \Rightarrow Br^-(aq)$	+1.09



*(c)	Transition metals, their compounds and their ions can act as heterogeneous and homogeneous catalysts.	
	Compare and contrast these two types of catalytic behaviour.	
	Include one specific example from transition metal chemistry of each of these types of catalyst and a reaction in which it is used.	(6)
		(6)



(Total for Question 24 = 19 marks)
TOTAL FOR SECTION B = 50 MARKS



#### **SECTION C**

## Answer ALL the questions.

## Write your answers in the spaces provided.

25

#### The Lanthanides

The lanthanides form a series in the Periodic Table comprising the elements from lanthanum, La (Z = 57) to lutetium, Lu (Z = 71). They have important uses as elements and compounds, for example, in the screens, circuits and speakers of smartphones. These elements have some similar properties to d-block elements.

Many of the lanthanide elements are obtained by heating their trichlorides or trifluorides with calcium at 1000°C.

These elements form part of the f-block of the Periodic Table as the last electron added enters an f-orbital. There are seven f-orbitals in the f-subshell.

The electronic configurations of the atoms consist of the electronic configuration of xenon followed by electrons in the 4f and 6s orbitals and sometimes the 5d orbitals. For example:

samarium, Sm [Xe]4f<sup>6</sup>6s<sup>2</sup>

europium, Eu [Xe]4f<sup>7</sup>6s<sup>2</sup>

gadolinium, Gd [Xe]4f<sup>7</sup>5d<sup>1</sup>6s<sup>2</sup>

terbium, Tb [Xe]4f<sup>9</sup>6s<sup>2</sup>

All of the lanthanides form ions with a charge of 3+ and the ionic radii of these ions decrease as the atomic number of the element increases.

The lanthanides form complex ions, for example,  $[Ce(H_2O)_9]^{3+}$  and  $[Yb(H_2O)_8]^{3+}$ .

Many of the complex ions formed from the elements in the lanthanide series are coloured and this colour is caused by f–f transitions.

Cerium(IV) ammonium nitrate is yellow in aqueous solution and gives a red colour with all alcohols.

Cerium(IV) ammonium sulfate is used in redox titrations with ferroin as the indicator. The colour change is red to yellow.

Use your knowledge of d-block elements to help you to answer the questions.

(a) Write the equation for the reduction of holmium(III) fluoride, HoF <sub>3</sub> , by calcium. State symbols are not required.	(1)
<ul> <li>(b) The electronic configuration of xenon is 1s²2s²2p63s²3p63d¹04s²4p64d¹05s²5p6.</li> <li>(i) Suggest a reason why gadolinium has the electronic configuration [Xe]4f<sup>7</sup>5d¹6s² rather than [Xe]4f86s².</li> </ul>	(1)
(ii) Complete the electronic configuration of Sm <sup>3+</sup> .	(1)
(c) (i) Explain why the ionic radius of a thulium ion, Tm³+, is less than that of a cerium ion, Ce³+.  Tm³+ 0.095 nm  Ce³+ 0.111 nm	
Ce 0.111 nm	(2)

(ii) Suggest a reason why the complex ions of the lanthanides can contain mo ligands than those of the transition metals.	(1)
(d) Explain why solutions containing $[La(H_2O)_9]^{3+}$ are colourless.	(2)
(e) Hydrated cerium(IV) ammonium nitrate contains $Ce^{4+}$ , $NH_4^+$ and $NO_3^-$ ions and some water of crystallisation.	
(i) Hydrated cerium(IV) ammonium nitrate contains 23.97% cerium, 19.18% nitrogen, 2.05% hydrogen and 54.80% oxygen by mass.	
Calculate the empirical formula of this compound and hence write the overall formula showing the cerium, ammonium and nitrate ions and the water of crystallisation.	(3)

(ii)	An organic compound, <b>X</b> , with the molecular formula C <sub>7</sub> H <sub>16</sub> O did not react with acidified potassium dichromate(VI) solution but gave a red colour with cerium(IV) ammonium nitrate solution. <b>X</b> exists as a pair of optical isomers.	
	Deduce a possible structure of <b>X</b> . Justify your answer.	(4)

(f) The amount of paracetamol in a tablet can be determined using a titration with cerium(IV) ions.

The tablets are crushed and then hydrolysed in acid to form 4-aminophenol.

$$HO \longrightarrow N \longrightarrow C \longrightarrow CH_3 + H_2O \longrightarrow HO \longrightarrow NH_2 + CH_3COOH$$
paracetamol 4-aminophenol

4-aminophenol is oxidised by cerium(IV) ions.

$$HO \longrightarrow NH_2 + 2Ce^{4+} \longrightarrow O \longrightarrow NH + 2Ce^{3+} + 2H^+$$

## Outline procedure

- Two tablets containing paracetamol were crushed and 0.800 g of the powder was added to dilute sulfuric acid.
- The mixture was heated under reflux until the hydrolysis was complete.
- The solution was made up to 100.0 cm<sup>3</sup> in a volumetric flask.
- 25.0 cm<sup>3</sup> portions of the solution were titrated against acidified 0.100 mol dm<sup>-3</sup> Ce<sup>4+</sup> using ferroin the indicator.

## Result

The mean titre was 21.70 cm<sup>3</sup>.

Calculate the percentage by mass of paracetamol in the tablets. Give your answer to an appropriate number of significant figures.

(5)

(Total for Question 25 = 20 marks)

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

