Please check the examination details below b	pefore entering your candidate information
Candidate surname	Other names
Centre Number Candidate Number  Pearson Edexcel Interna	
Tuesday 24 October 2	.023
N(C)[1][[C] ( [][[C] ( [] ( [] ( [] ( [] ( []	wcH15/01
Chemistry International Advanced Leve UNIT 5: Transition Metals ar 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 ▶







#### **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  $\boxtimes$ . If you change your mind, put a line through the box  $\boxtimes$  and then mark your new answer with a cross  $\boxtimes$ .

- 1 Which of these is a d-block element but is not a transition element?
  - **A** cobalt
  - B copper
  - C nickel
  - **D** zinc

(Total for Question 1 = 1 mark)

- 2 In which of these pairs does the transition metal have the same oxidation number?
  - $\triangle$  A CrO<sub>2</sub>Cl<sub>2</sub> and [Cr(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup>
  - $\blacksquare$  **B**  $[Cu(NH_3)_2]^+$  and  $[CuCl_4]^{2-}$
  - C Mn<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub>
  - $\square$  **D**  $VO_3^-$  and  $VO_2^+$

(Total for Question 2 = 1 mark)

**3** What is the co-ordination number of chromium in the complex ion shown?

- **B** 3
- X C 4
- □ 6

(Total for Question 3 = 1 mark)

**4** Aqueous sodium hydroxide and aqueous ammonia are added, until they are in excess, to separate portions of a pale green aqueous solution **E**.

Test	Observations
Aqueous sodium hydroxide is added to <b>E</b>	Green precipitate forms
	No further change in excess
	Green precipitate forms
Aqueous ammonia is added to <b>E</b>	Green precipitate dissolves in excess to form a pale blue solution

Which ion is present in **E**?

- A Cu<sup>2+</sup>
- B Fe<sup>2+</sup>
- C Ni<sup>2+</sup>

(Total for Question 4 = 1 mark)

5 A **small** amount of aqueous ammonia is added to an aqueous solution containing zinc ions. A white precipitate forms.

Which is the equation for this reaction?

- $\square$  **A**  $[Zn(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Zn(OH)_2(H_2O)_4]^{2+} + 2NH_4^+$

- $\square$   $[Zn(H_2O)_6]^{2+} + 4NH_3 \rightarrow Zn(NH_3)_4(H_2O)_2 + 2H_2O + 2H_3O^+$

(Total for Question 5 = 1 mark)

**6** Acidified manganate(VII) ions react with ethanedioate ions.

$$2MnO_{4}^{-} \ + \ 16H^{\scriptscriptstyle +} \ + \ 5C_{2}O_{4}^{2-} \ \rightarrow \ 2Mn^{2+} \ + \ 8H_{2}O \ + \ 10CO_{2}$$

The rate of this reaction increases then decreases.

What are the reasons for these changes in rate of reaction?

		Reason rate increases	Reason rate decreases
×	A	Mn <sup>2+</sup> acts as a catalyst	kinetic energy of particles decreases
X	В	Mn <sup>2+</sup> acts as a catalyst	concentration of reactants decreases
X	C	MnO <sub>4</sub> acts as a catalyst	kinetic energy of particles decreases
×	D	MnO <sub>4</sub> acts as a catalyst	concentration of reactants decreases

(Total for Question 6 = 1 mark)

- **7**  $E_{\text{cell}}^{\Theta}$  is directly proportional to
  - $\triangle$  **A**  $\triangle_r H$  and  $\ln K$
  - $\boxtimes$  **B**  $\triangle_{r}H$  and  $\ln RT$
  - lacksquare **C**  $\Delta S_{\text{total}}$  and  $\ln K$
  - $lacktriangleq \mathbf{D} \quad \Delta S_{\text{total}} \text{ and } \ln RT$

(Total for Question 7 = 1 mark)

**8** Standard electrode potentials can also be given an alternative name. The electrochemical series lists standard electrode potentials in order.

Which of these is correct?

		Alternative name for standard electrode potential	Order of standard electrode potentials in the electrochemical series
X	Α	standard reduction potential	most negative to most positive
X	В	standard reduction potential	most positive to most negative
X	c	standard cell potential	most negative to most positive
×	D	standard cell potential	most positive to most negative

(Total for Question 8 = 1 mark)

**9** The half-equation for the reaction taking place at the positive electrode in an **alkaline** hydrogen-oxygen fuel cell is

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

What is the half-equation for the reaction taking place at the negative electrode?

$$\blacksquare$$
 A H<sub>2</sub> + 2OH<sup>-</sup>  $\rightarrow$  2H<sub>2</sub>O + 2e<sup>-</sup>

$$\square$$
 **C**  $H_2 \rightarrow 2H^+ + 2e^-$ 

$$\square$$
 **D** H<sub>2</sub> + H<sub>2</sub>O  $\rightarrow$  3H<sup>+</sup> + OH<sup>-</sup> + 2e<sup>-</sup>

(Total for Question 9 = 1 mark)

**10** The emf,  $E_{\text{cell}}^{\Theta}$ , of a cell is +0.57V.

The numerical values of the standard electrode potentials of the two half-cells joined in this cell are 0.17V and 0.40V.

What are the signs of the standard electrode potentials of the right-hand half-cell and the left-hand half-cell?

	Sign of standard electrode potential							
in left-hand half-cell in right-hand half-c								
	negative	negative						
	negative	positive						
	positive	negative						
)	positive	positive						

(Total for Question 10 = 1 mark)

- **11** An electrochemical cell is set up:
  - a half-cell is made from a piece of zinc and a solution of zinc chloride, ZnCl<sub>2</sub>
  - a second half-cell is made from a piece of metal G and a solution of its chloride, GCl<sub>2</sub>
  - the two half-cells are connected and a current allowed to pass for some time.

The zinc electrode increased in mass by 1.635 g.

The electrode of metal **G** decreased in mass by 0.6075 g.

What is metal **G**?

X

X

X

Α

C

D

- A copper
- B iron
- C magnesium
- **D** manganese

(Total for Question 11 = 1 mark)



- **12** Which of these is the **weakest** base?
  - **A** ammonia
  - **B** butylamine
  - C ethylamine
  - **D** phenylamine

(Total for Question 12 = 1 mark)

13 The amino acid 2-aminopropanoic acid exists as a zwitterion at pH 6.0

What will be the structure of 2-aminopropanoic acid at pH 9.0?

- ☑ A H,NCH(CH,)COOH
- B H<sub>3</sub>NCH(CH<sub>3</sub>)COO<sup>-</sup>
- D H<sub>3</sub>N+CH(CH<sub>3</sub>)COO-

(Total for Question 13 = 1 mark)

- **14** An organic compound, **J**, reacts with
  - sodium hydroxide to form an ionic compound
  - hydrogen in the presence of a nickel catalyst
  - ethanol in the presence of sulfuric acid.

Which of these could be the structure of **J**?

- A CH₂=CHCOOH
- $\square$  **B**  $C_{6}H_{5}OH$
- ☑ D CH,COOH

(Total for Question 14 = 1 mark)



**15** A reaction scheme for the preparation of an azo dye is shown.

(a) Step **1** takes place using a mixture of concentrated nitric acid and concentrated sulfuric acid at 55°C.

Why is the reaction **not** carried out at 80°C?

(1)

- A further substitution by a nitro group occurs
- B nitrobenzene decomposes
- Substitution by SO₃H occurs
- D the nitric acid decomposes
- (b) How is Step 2 carried out?

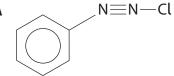
- (1)
- A Sn, concentrated HCl(aq) and NaOH(aq) are added together
- Sn, dilute HCl(aq) and NaOH(aq) are added together
- Sn and concentrated HCl(aq) are added first, then NaOH(aq) is added at the end
- Sn and dilute HCl(aq) are added first, then NaOH(aq) is added at the end

(c) Step 3 takes place using sodium nitrite and dilute hydrochloric acid at 5°C.

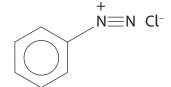
Which is the structure of Intermediate **L**?

(1)

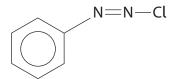




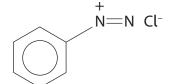
**⋈** B



**⊠** C



■ D



(d) The reactant in Step 4 is phenol.

What condition is needed for this reaction?

(1)

- A acidic
- **B** alkaline
- **C** ethanolic
- **D** neutral

(Total for Question 15 = 4 marks)

**16** A 10 cm<sup>3</sup> mixture of methane and argon is ignited.

The methane requires 4 cm<sup>3</sup> of oxygen for complete combustion.

What is the volume of argon, in cm<sup>3</sup>, in the mixture?

All volumes are measured at the same temperature and pressure.

- B 4

X

X

X

X

(Total for Question 16 = 1 mark)

17 When  $10 \text{ cm}^3$  of but-1-ene,  $C_4H_8$ , is ignited with excess oxygen, there is an overall decrease in volume of  $x \text{ cm}^3$ .

All gas volumes are measured at room temperature and pressure.

$$C_4H_8(g) + 6O_2(g) \rightarrow 4CO_2(g) + 4H_2O(l)$$

A further decrease of  $y \text{ cm}^3$  takes place on the addition of aqueous sodium hydroxide as carbon dioxide is removed.

What are the values of *x* and *y*?

	Value of x	Value of y
A	30	40
В	30	80
C	40	40
D	40	80

(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** This question is about electrochemical cells and redox reactions.
  - (a) Draw a labelled diagram of the apparatus you would use to measure the standard electrode potential of a Cu<sup>2+</sup>(aq) | Cu(s) electrode with a standard hydrogen electrode. Include essential conditions.

(5)



(b) The standard electrode potentials for two half-cells are shown.

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \Rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$
  $E^{\oplus} = +1.33V$ 

$$Cl_{2}(g) + 2e^{-} \Rightarrow 2Cl^{-}(aq)$$
  $E^{\Theta} = +1.36V$ 

(i) Explain, in terms of electrode potentials, why acidified dichromate(VI) ions react with **concentrated** hydrochloric acid to form chlorine, even though  $E_{cell}^{\Theta} = -0.03 \text{ V}$ .

(3)

- - (ii) Write the cell diagram, using the conventional representation of half-cells, for the reaction to produce chlorine.

(2)



(c) When  $25.0\,\mathrm{cm^3}$  of a  $0.100\,\mathrm{mol\,dm^{-3}}$  solution of  $\mathrm{X_2O_5}$  reacts with a reducing agent, X is reduced to a lower oxidation state.

To oxidise X back to its original oxidation state required 50.0 cm<sup>3</sup> of 0.0200 mol dm<sup>-3</sup> acidified potassium manganate(VII) solution.

The half-equation for acidified manganate(VII) is

$${\rm MnO_4^-} + {\rm 8H^+} + {\rm 5e^-} \rightarrow {\rm Mn^{2+}} + {\rm 4H_2O}$$

Calculate the oxidation state of X after it has been reduced.

(3)

(Total for Question 18 = 13 marks)



- **19** This question is about compounds and complex ions of iron.
  - (a) A compound of iron contains, by mass, 39.5% potassium, 28.2% iron and 32.3% oxygen.

Calculate the empirical formula of this compound.

(2)

(b) The reaction between iodide ions and persulfate ions is thermodynamically feasible under standard conditions. The reaction is very slow but is catalysed by the presence of  $Fe^{2+}$  ions.

$$2I^{-}(aq) + S_{2}O_{8}^{2-}(aq) \rightarrow I_{2}(s) + 2SO_{4}^{2-}(aq)$$

(i) Give a reason why the activation energy for this reaction is high in the absence of a catalyst.

(1)

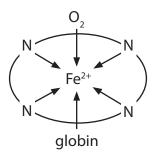
(ii) Write the ionic equations for the reactions that occur when the catalyst of  $Fe^{2+}$  ions is added. State symbols are not required.

(2)

(c) In aqueous solution, iron(II) exists as the complex ion $[Fe(H_2O)_6]^{2+}$ . (i) Explain how water acts as a monodentate ligand.	(2)
(ii) Explain the shape of the $[Fe(H_2O)_6]^{2+}$ complex ion.	(2)
(ii) Explain the shape of the [Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> complex ion.	(2)



(d) Haemoglobin is an iron(II) complex which carries oxygen around the body. Part of the structure of oxyhaemoglobin is shown.



The four nitrogen atoms are part of a multidentate ligand in the haem group.

Explain, in terms of the iron(II) complex, why carbon monoxide is toxic.

(2)

(a) E+k	hanodioato l	iaande roac	t with iron(	I) ions in a	arroone co	lution

$$[Fe(H_2O)_6]^{2+} + 2C_2O_4^{2-} \rightarrow [Fe(C_2O_4)_2(H_2O)_2]^{2-} + 4H_2O_4$$

Explain, in terms of entropy, why this reaction is feasible.

(2)



(f) Potassium dichromate(VI) oxidises iron(II) ions to iron(III) ions in acid solution.

$$\text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O}$$

Iron(III) ions do not react with acidified potassium dichromate(VI).

A solution  $\mathbf{Y}$  contains 6.28 g dm<sup>-3</sup> of iron as a mixture of iron(II) ions and iron(III) ions.

 $50\,\mathrm{cm^3}$  of dilute sulfuric acid is added to a  $25.0\,\mathrm{cm^3}$  portion of **Y** and it is titrated with a solution containing  $2.56\,\mathrm{g\,dm^{-3}}$  of dichromate(VI) ions,  $\mathrm{Cr_2O_7^{2^-}}$ . The titration is repeated until concordant results are obtained.

The mean titre is 22.55 cm<sup>3</sup>.

Calculate the percentage of iron present as **iron(III)** ions in Y.

(5)

(Total for Question 19 = 18 marks)



- **20** This question is about benzene and some of its compounds.
  - (a) Benzene reacts with bromine in the presence of an iron(III) bromide catalyst to form bromobenzene.



(i) Draw the mechanism for this reaction, including the formation of the electrophile.

(4)



*(ii)	ii) Compare and contrast the reaction of benzene with bromine with the reactions of cyclohexene with bromine and of phenol with bromine.					
	Include reasons for any differences.					
	Detailed mechanisms for these reactions are <b>not</b> required.	(4)				
		(6)				



(b) Devise a synthesis to convert bromobenzene into benzamide.

Include reagents, conditions and the structures of the intermediate compounds.

(7)

- (c) Semi-aromatic polyamides have high melting temperatures, high strength and rigidity and are resistant to chemical attack so they have many applications in engineering.
  - (i) Draw the repeat unit of the polyamide formed from the monomers shown.

$$H_2N(CH_2)_6NH_2$$
 and

(1)

(ii) Explain why polyamides have higher melting temperatures than polyalkenes.

(2)

(Total for Question 20 = 20 marks)

**TOTAL FOR SECTION B = 51 MARKS** 



#### **SECTION C**

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

## Salicylic acid

Salicin was extracted from the bark of willow trees in the first half of the 19th century. About 30 years later, scientists showed that salicin was converted into salicylic acid in the body.

Salicylic acid was given to patients with fevers and their symptoms were reduced. However, it caused severe irritation to the lining of the mouth, oesophagus and stomach.

In the 1890s Hoffmann converted salicylic acid into acetylsalicylic acid, which is commonly known as aspirin and is still used to treat fevers and as a painkiller.

Salicylic acid may also be converted into methyl salicylate. This is the active ingredient in oil of wintergreen, which is applied externally to treat joint and muscle pain.

21

(a) Give the IUPAC name for salicylic acid.

(1)

- (b) Acetylsalicylic acid is formed when salicylic acid reacts with ethanoic anhydride, (CH<sub>3</sub>CO)<sub>2</sub>O.
  - (i) **Name** the three functional groups in acetylsalicylic acid.

(1)

(ii) Write the equation for the reaction of salicylic acid and ethanoic anhydride.

(1)

(iii) 2.00 g of salicylic acid produced a 74.8% yield of acetylsalicylic acid.

Calculate the mass of acetylsalicylic acid formed.

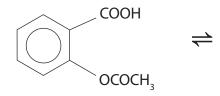
[ $M_r$  values: salicylic acid = 138 acetylsalicylic acid = 180]

(3)



- (c) Acetylsalicylic acid is only slightly soluble in water. It has a  $K_3$  value of  $2.8 \times 10^{-4}$  mol dm<sup>-3</sup>.
  - (i) Complete the equation to show the dissociation of acetylsalicylic acid in aqueous solution.

(1)



(ii) The dissociation of acetylsalicylic acid is different in the acidic conditions found in the stomach compared with the slightly alkaline conditions in the small intestine.

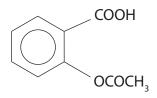
Explain this difference in dissociation.


(d) Identify, by name or formula, the reagent needed to convert salicylic acid into methyl salicylate.

(1)

(e) The high resolution proton (¹H) NMR spectra of acetylsalicylic acid and methyl salicylate both contain four peaks from the protons on the benzene ring and two other peaks from the OH and CH<sub>3</sub> protons in the side chains.

Complete the table to give the chemical shift ranges that you would expect for each type of proton in the side chains of the molecules.



acetylsalicylic acid

methyl salicylate

(2)

	Acetylsalicylic acid		Methyl s	alicylate
Type of proton	ОН	CH <sub>3</sub>	ОН	CH <sub>3</sub>
Chemical shift / ppm				

(f) Acetylsalicylic acid in aspirin tablets is hydrolysed by excess sodium hydroxide.

$$CH_3COOC_6H_4COOH + 2NaOH \rightarrow CH_3COONa + HOC_6H_4COONa + H_2O$$

The unreacted sodium hydroxide may be titrated with a standard solution of hydrochloric acid to determine the percentage of acetylsalicylic acid in the tablets.

Aspirin tablets can be analysed using the outline procedure:

- add 25.0 cm<sup>3</sup> of 1.00 mol dm<sup>-3</sup> sodium hydroxide to a known mass of powdered aspirin tablets
- heat the mixture for 10 minutes to hydrolyse the aspirin
- cool the mixture, make the solution up to 250.0 cm<sup>3</sup> in a volumetric flask and mix it thoroughly
- pipette 25.0 cm³ of the hydrolysed solution into a conical flask and titrate it against 0.100 mol dm⁻³ hydrochloric acid using phenolphthalein indicator
- repeat the titration until concordant values are obtained.

#### Results

Mass of aspirin tablets used = 0.760 g

Mean titre =  $16.95 \, \text{cm}^3$ 

The table shows the percentage by mass of acetylsalicylic acid in four brands of aspirin tablets.

Brand of aspirin tablets	Percentage of acetylsalicylic acid / %
А	92.2
В	95.4
С	97.5
D	99.6



Determine which brand of aspirin tablets was analysed.

You **must** show your working.

(6)

(Total for Question 21 = 19 marks)

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

