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| Surname | Other names |
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| <h1 style="margin: 0;">Chemistry</h1> <h2 style="margin: 0;">Advanced</h2> <h3 style="margin: 0;">Unit 5: General Principles of Chemistry II – Transition Metals and Organic Nitrogen Chemistry (including synoptic assessment)</h3> | |
| Monday 19 June 2017 – Morning Time: 1 hour 40 minutes | Paper Reference 6CH05/01 |
| You must have: Data Booklet Scientific calculator | 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.*
- Questions labelled with an **asterisk** (*) are ones where the quality of your written communication will be assessed
– *you should take particular care with your spelling, punctuation and grammar, as well as the clarity of expression, on these questions.*
- A Periodic Table is printed on the back cover of this paper.

Advice

- Read each question carefully before you start to answer it.
- Keep an eye on the time.
- 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 Which species contains an element with the same oxidation number as vanadium has in NH_4VO_3 ?

- A $[\text{AlH}_4]^-$
 B K_2MnO_4
 C NaClO_3
 D $[\text{Fe}(\text{CN})_6]^{4-}$

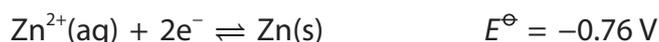
(Total for Question 1 = 1 mark)

2 Which of the following is **not** a disproportionation reaction?

- A $2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$
 B $6\text{KOH} + 3\text{I}_2 \rightarrow \text{KIO}_3 + 5\text{KI} + 3\text{H}_2\text{O}$
 C $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$
 D $2\text{CuI} \rightarrow \text{CuI}_2 + \text{Cu}$

(Total for Question 2 = 1 mark)

3 The half-equation of a standard half-cell containing $\text{Zn}^{2+}(\text{aq})|\text{Zn}(\text{s})$ is



This is connected to a standard hydrogen electrode in a circuit and a current flows. At the zinc electrode

- A zinc atoms are reduced.
 B zinc ions are reduced.
 C zinc atoms are oxidized.
 D zinc ions are oxidized.

(Total for Question 3 = 1 mark)

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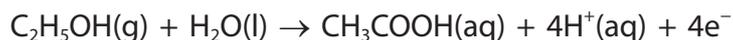
4 Use the data provided to deduce the species which reacts with $V^{3+}(aq)$ to form $VO^{2+}(aq)$.

| Electrode reaction | Standard electrode potential/V |
|--|--------------------------------|
| $Fe^{2+}(aq) + 2e^{-} \rightleftharpoons Fe(s)$ | -0.44 |
| $VO^{2+}(aq) + 2H^{+}(aq) + e^{-} \rightleftharpoons V^{3+}(aq) + H_2O(l)$ | +0.34 |
| $Ag^{+}(aq) + e^{-} \rightleftharpoons Ag(s)$ | +0.80 |

- A $Fe^{2+}(aq)$
- B $Fe(s)$
- C $Ag^{+}(aq)$
- D $Ag(s)$

(Total for Question 4 = 1 mark)

5 In a fuel cell breathalyser, the following reaction occurs at one electrode.



The reaction occurring at the other electrode is

- A $4H^{+}(aq) + O_2(g) + 4e^{-} \rightarrow 2H_2O(l)$
- B $2H_2(g) + 2O_2(g) + 4e^{-} \rightarrow 4OH^{-}(aq)$
- C $4OH^{-}(aq) \rightarrow 2H_2(g) + 2O_2(g) + 4e^{-}$
- D $2H_2O(l) \rightarrow 4H^{+}(aq) + O_2(g) + 4e^{-}$

(Total for Question 5 = 1 mark)

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



- 6 Dilute aqueous sodium hydroxide and dilute aqueous ammonia are added to separate samples of aqueous nickel(II) chloride. In each case a green precipitate forms. What would be observed when excess alkali is added to the green precipitate?

| | Addition of excess NaOH(aq) | Addition of excess NH ₃ (aq) |
|----------------------------|--|---|
| <input type="checkbox"/> A | Precipitate remains | Precipitate remains |
| <input type="checkbox"/> B | Precipitate remains | Precipitate dissolves to form a blue solution |
| <input type="checkbox"/> C | Precipitate dissolves to form a green solution | Precipitate remains |
| <input type="checkbox"/> D | Precipitate dissolves to form a green solution | Precipitate dissolves to form a blue solution |

(Total for Question 6 = 1 mark)

- 7 In the reaction of sodium thiosulfate solution with iodine, the half-equation for the reaction of the thiosulfate ions is

- A $S_2O_3^{2-} + 3H_2O \rightarrow 2SO_3^{2-} + 6H^+ + 4e^-$
- B $S_2O_3^{2-} + 3H_2O + 4e^- \rightarrow 2SO_3^{2-} + 6H^+$
- C $2S_2O_3^{2-} + 2e^- \rightarrow S_4O_6^{2-}$
- D $2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$

(Total for Question 7 = 1 mark)

- 8 In the titration of sodium thiosulfate solution with iodine, starch indicator is added near the end-point. This is because

- A there is no warning of the end-point if starch is added at the start.
- B high concentrations of iodine decompose the starch.
- C the blue-black colour showing the presence of iodine would not be seen.
- D an insoluble complex forms between starch and high concentrations of iodine.

(Total for Question 8 = 1 mark)

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9 Evidence that the carbon-carbon bonds in benzene are all the same length is provided by

- A X-ray diffraction.
- B infrared spectroscopy.
- C a comparison of the enthalpy changes for the addition of hydrogen to benzene and the theoretical compound cyclohexa-1,3,5-triene.
- D a comparison of the rates of reaction of benzene and alkenes with bromine.

(Total for Question 9 = 1 mark)

10 The product of the reaction of benzene with sulfur trioxide dissolved in concentrated sulfuric acid is

- A $C_6H_5SO_3$
- B $C_6H_5SO_3H$
- C $C_6H_5SO_4$
- D $C_6H_5HSO_4$

(Total for Question 10 = 1 mark)

11 Benzene reacts with ethanoyl chloride in the presence of aluminium chloride. The equation for the reaction of ethanoyl chloride with aluminium chloride is

- A $CH_3COCl + AlCl_3 \rightarrow [CH_3CO]^- + AlCl_4^+$
- B $CH_3COCl + AlCl_3 \rightarrow [CH_3CO]^+ + AlCl_4^-$
- C $CH_3COOCl + AlCl_3 \rightarrow [CH_3COO]^- + AlCl_4^+$
- D $CH_3COOCl + AlCl_3 \rightarrow [CH_3COO]^+ + AlCl_4^-$

(Total for Question 11 = 1 mark)

12 In the high resolution proton nmr spectrum of butanone, $C_2H_5COCH_3$, there will be

- A one doublet and two triplets.
- B one quartet and one sextet.
- C one singlet, one triplet and one quartet.
- D one singlet, one doublet and one triplet.

(Total for Question 12 = 1 mark)



13 The compounds $C_2H_5COOCH_3$ and $CH_3COOC_2H_5$ are most easily differentiated by the

- A infrared spectra outside the fingerprint region.
- B fragmentation patterns in their mass spectra.
- C splitting patterns in their high resolution nmr spectra.
- D numbers of peaks in their low resolution nmr spectra.

(Total for Question 13 = 1 mark)

14 The infrared spectrum of an organic compound with molecular formula $C_8H_8O_2$ has a strong peak in the range $1700-1680\text{ cm}^{-1}$ and a broad peak above 3300 cm^{-1} .

The compound could be

- A $H_3CC_6H_4COOH$
- B $C_6H_5CH_2COOH$
- C $C_6H_5COOCH_3$
- D $HOC_6H_4COCH_3$

(Total for Question 14 = 1 mark)

15 An organic compound is very soluble in water forming an alkaline solution that reacts with copper(II) ions to give a coloured product.

The compound is most likely to be

- A $C_4H_9NH_2$
- B C_4H_9CN
- C $C_6H_5NH_2$
- D $C_6H_5NO_2$

(Total for Question 15 = 1 mark)

16 The polymer poly(ethenol), which has the formula $\{CH_2CH(OH)\}_n$ is used to make capsules for liquid detergents because

- A it is inert.
- B it is water-soluble.
- C London forces between its molecules are very strong.
- D it neutralises acids that could harm fabrics.

(Total for Question 16 = 1 mark)

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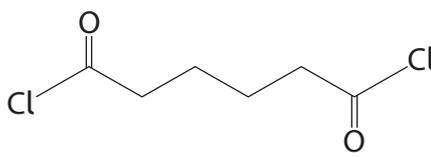
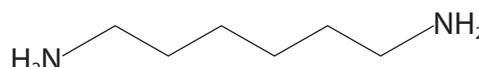
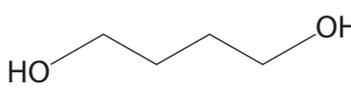
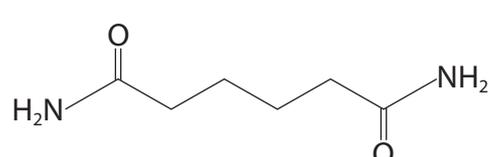
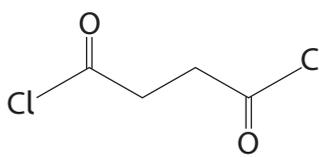
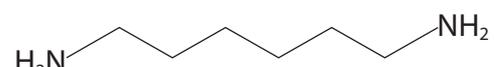
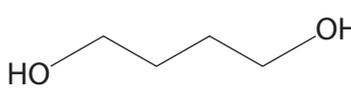
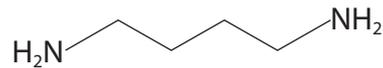
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17 The formula of the repeat unit of a polymer is $[-OC(CH_2)_4CONH(CH_2)_6NH-]$.

The polymer is formed by the reaction of

- A  and 
- B  and 
- C  and 
- D  and 

(Total for Question 17 = 1 mark)

18 On combustion, 0.50 mol of a primary alcohol produced 45 g of water and 88 g of carbon dioxide.

The alcohol could be

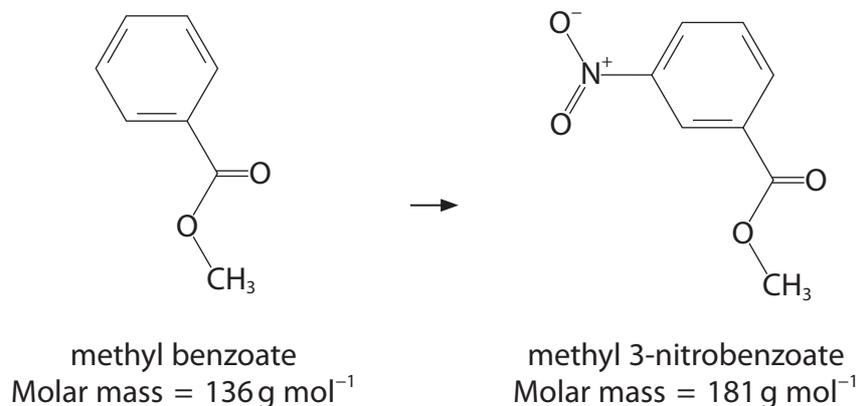
- A ethanol
- B propan-1-ol
- C butan-1-ol
- D pentan-1-ol

(Total for Question 18 = 1 mark)

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- 19 Crystals of methyl 3-nitrobenzoate can be prepared by nitration of methyl benzoate. The reaction is carried out in a flask surrounded by ice, and the product is purified by recrystallization from ethanol.



- (a) In this preparation, 2.00 g of methyl benzoate produced 1.50 g of methyl 3-nitrobenzoate. The percentage yield is

(1)

- A 82.9
- B 75.0
- C 56.4
- D 15.0

- (b) In the recrystallization step, the highest yield will be obtained when

(1)

- A using excess ethanol to dissolve the crude solid.
- B heating the ethanol to 20°C below its boiling temperature.
- C slowly filtering the hot mixture to remove insoluble impurities.
- D crystallizing the filtrate using an ice bath.

(Total for Question 19 = 2 marks)

TOTAL FOR SECTION A = 20 MARKS

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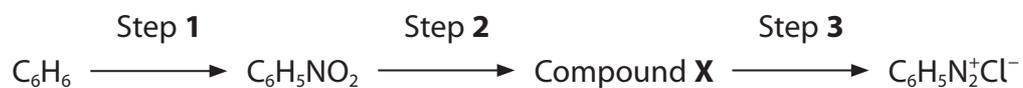
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SECTION B

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

20 Benzenediazonium chloride, $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$, can be prepared from benzene in a series of steps.



(a) (i) Identify the substances that are used to convert benzene into $\text{C}_6\text{H}_5\text{NO}_2$ in Step 1. (1)

(ii) Give the mechanism of the reaction taking place in Step 1, including one or more equations for the formation of the electrophile. (4)

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(iii) Identify compound **X** and state the reagents needed to prepare it in Step 2. (2)

Compound **X**

Reagents

(iv) State the reagents and condition needed to convert compound **X** into benzenediazonium chloride in Step 3. (2)

Reagents

Condition

(b) Benzenediazonium chloride is used to prepare dyes.

Write an equation for a reaction of benzenediazonium chloride with a compound of your choice in which the product is a dye. Show the structure of the dye in your equation.

(2)

(c) Benzenediazonium chloride can be converted into benzoic acid, C_6H_5COOH , in two steps. The first step is a substitution reaction to produce the nitrile, C_6H_5CN . State the reagent needed for the second step. (1)

.....



(d) An aqueous solution of benzenediazonium chloride decomposes when it is warmed. The products of decomposition are a colourless unreactive gas, hydrochloric acid and an aryl (aromatic) compound. A white precipitate forms when bromine water is added to this aryl compound.

(i) Write a balanced equation showing the decomposition of an aqueous solution of benzenediazonium chloride. State symbols are not required.

(2)

(ii) Give the formula of the white precipitate.

(1)

(Total for Question 20 = 15 marks)



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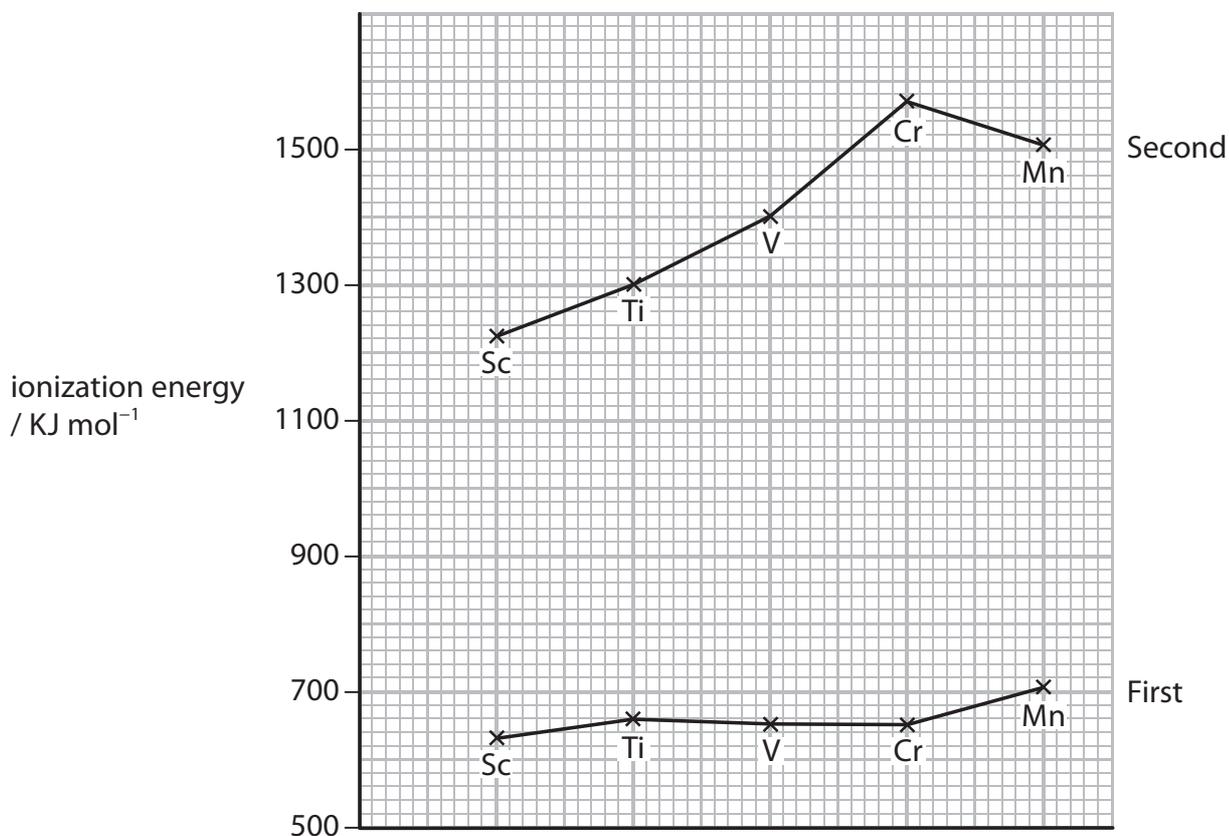
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P 4 8 0 7 0 A 0 1 3 2 8

21 This question is about the chemistry of chromium.

- (a) The graph below shows the first and second ionization energies of the elements scandium to manganese.



- (i) Explain why the values for the **first** ionization energies are very similar.

(2)

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*(ii) The electronic configuration of a chromium atom is $[\text{Ar}] 3d^5 4s^1$

By considering the electronic configurations of the singly charged ions of vanadium, chromium and manganese, suggest why the second ionization energy of chromium is higher than the corresponding values for vanadium and manganese.

(3)

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P 4 8 0 7 0 A 0 1 5 2 8

(b) The table below shows the formulae of ions of chromium which exist in aqueous solution.

| Ion | Oxidation number of chromium | Colour in aqueous solution |
|--|------------------------------|----------------------------|
| $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ | +2 | Blue |
| $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ | | |
| CrO_4^{2-} | | |
| $\text{Cr}_2\text{O}_7^{2-}$ | | |

(i) Complete the table above by adding the missing oxidation numbers and colours. (3)

*(ii) Explain why the $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ ion is coloured. (4)

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- (iii) A solution containing aqueous Cr^{3+} ions reacts with zinc in suitable conditions to form Cr^{2+} ions and Zn^{2+} ions.

Draw a diagram of a cell that can be used to measure $E_{\text{cell}}^{\ominus}$ for the reaction.
State the conditions which are necessary.

(3)

- (iv) Use your Data booklet to calculate $E_{\text{cell}}^{\ominus}$.

(2)

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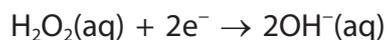
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- (c) A solution containing $\text{Cr}^{3+}(\text{aq})$ ions is oxidized by hydrogen peroxide in the presence of hydroxide ions to form CrO_4^{2-} ions.

The half-equation for the reduction of hydrogen peroxide is



- (i) Write the half-equation for the oxidation of $\text{Cr}^{3+}(\text{aq})$ in the presence of hydroxide ions to form CrO_4^{2-} ions.

(1)

- (ii) Hence write the overall equation for this reaction.

(1)

- (d) Write the equation for the reaction of chromate(VI) ions with hydrogen ions.

(1)

(Total for Question 21 = 20 marks)



22 This question is about some naturally occurring amino acids, which have the formula $\text{RCH}(\text{NH}_2)\text{COOH}$.

(a) Amino acids can exist as zwitterions. What is meant by the term zwitterion?

(1)

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.....

(b) In the amino acid serine, the formula of the R group is $-\text{CH}_2\text{OH}$.

The structure of serine varies with pH. Draw its structure at pH 1.0 and at pH 10.0.

(2)

| | |
|---------------------|----------------------|
| | |
| Structure at pH 1.0 | Structure at pH 10.0 |

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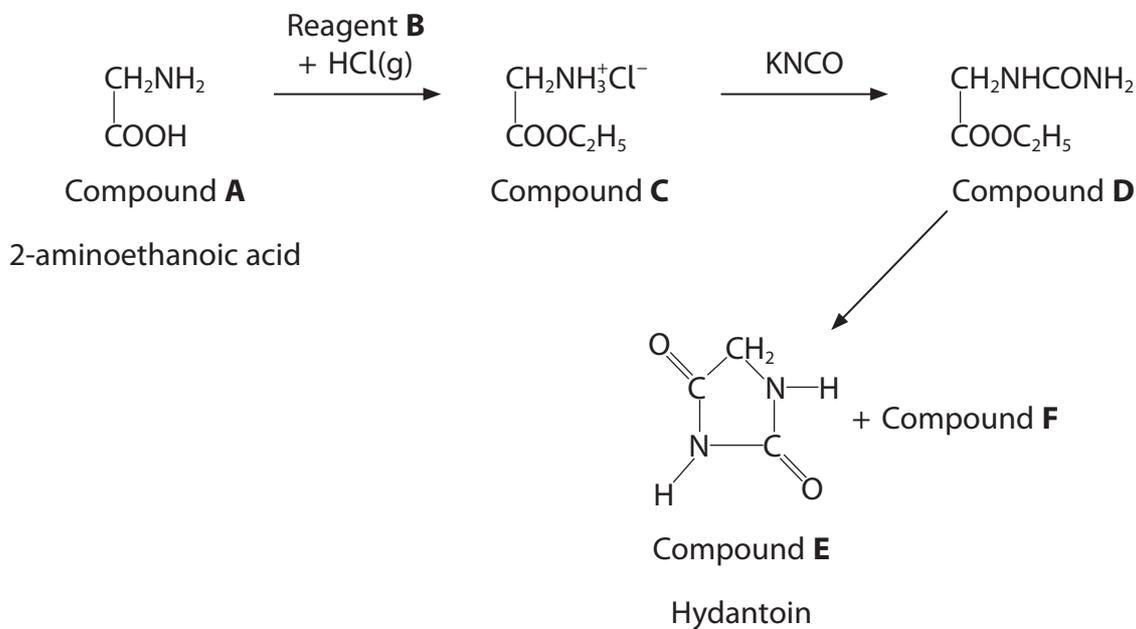
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- (c) In the amino acid alanine, the formula of the R group is $-\text{CH}_3$. Alanine can polymerize forming a condensation polymer. Draw a section of this polymer showing **two** repeat units, displaying the link between them.

(2)

- (d) Compound **A** is the amino acid 2-aminoethanoic acid. It can be converted in three steps into a cyclic compound, **E**, called hydantoin.



- (i) State a property shown by all naturally occurring amino acids **except** for 2-aminoethanoic acid.

(1)



(ii) Name the **two** types of reaction which are occurring when 2-aminoethanoic acid is converted into compound **C**.

(2)

(iii) Suggest the identity of the other organic product, compound **F**, which forms when compound **D** is converted into compound **E**.

(1)

(iv) When compound **E** reacts with hot dilute hydrochloric acid, 2-aminoethanoic acid is formed again, along with other products.

Suggest the type of reaction which is occurring.

(1)

(v) Suggest the identity of the **two** products which also form in the reaction in (d)(iv).

(2)

(Total for Question 22 = 12 marks)

TOTAL FOR SECTION B = 47 MARKS

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- (ii) The ion $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ has stereoisomers. Name the type of stereoisomerism and explain how their structures differ.

The different structures may be shown on a diagram.

(2)

.....

.....

.....

.....

- (c) Write the equation for the ligand exchange reaction of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ with excess chloride ions from concentrated hydrochloric acid. State symbols are not required.

State the shape of the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ion, and suggest the shape of the copper complex ion produced.

(3)

Equation

Shape of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$

Shape of complex ion produced

- (d) (i) Explain the difference between monodentate and hexadentate ligands.

(2)

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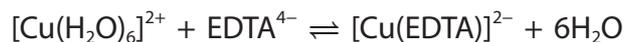
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- *(ii) EDTA⁴⁻ forms very stable complex ions. In solution, its reaction with copper ions can be represented as shown.



Explain why the equilibrium constant for this reaction is greater than that for the reaction of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ with a monodentate ligand.

(2)

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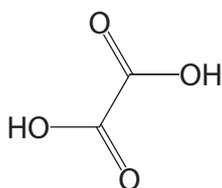
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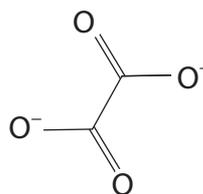
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- (e) Crystals of a hydrated salt were prepared by reacting a solution containing iron(II) ions with a mixture of ethanedioic acid, $(\text{COOH})_2$ and potassium ethanedioate, $\text{K}_2(\text{COO})_2$ or $\text{K}_2\text{C}_2\text{O}_4$.



ethanedioic acid



ethanedioate ion

The resulting mixture was reacted with hydrogen peroxide, which oxidized the iron(II) ions and, after a suitable procedure was carried out, coloured crystals were produced.

The crystals contain a complex ion and the formula of the crystals can be written as $\text{K}_x\text{Fe}_y(\text{C}_2\text{O}_4)_z(\text{H}_2\text{O})_n$

The crystals were analysed.

- (i) The percentage of water in 2.00 g of the crystals was measured by gentle heating until the mass was constant. The final mass was 1.78 g. Calculate the percentage by mass of water in the crystals.

(1)



- (ii) The percentage by mass of ethanedioate ions in the crystals was found by titrating an acidified solution containing 0.150 g of the crystals with a solution of $0.0100 \text{ mol dm}^{-3}$ potassium manganate(VII). The titre was 36.60 cm^3 .

The ethanedioate ions were oxidized by the manganate(VII) ions. The reactions which occur are



Use the titration results to calculate the percentage by mass of ethanedioate ions in the crystals.

(4)

- (iii) To find the percentage by mass of iron in the crystals, they were first heated with concentrated sulfuric acid to decompose the ethanedioate ions, taking suitable safety precautions.

The iron ions in solution were then reduced to iron(II) ions with a suitable metal and these ions were then titrated with $0.0100 \text{ mol dm}^{-3}$ potassium manganate(VII) solution. The iron(II) ions were oxidized to iron(III) ions in the titration.

Why must the ethanedioate ions be decomposed before determining the concentration of iron(II) ions?

(1)

.....

.....



(iv) The percentage by mass of iron was found to be 11.4%.

Use this value, and the percentages of water and ethanedioate ions you have calculated, to deduce the percentage by mass of potassium in the crystals.

(1)

| Species | Percentage by mass |
|-------------------|--------------------|
| water | |
| ethanedioate ions | |
| iron | 11.4 |
| potassium | |

(v) The percentage by mass shows the **mass** of each species in 100g.

Calculate the number of **moles** of each species in 100g of the crystals and hence the ratio in moles.

(2)

| Species | Number of moles in 100g | Mole ratio |
|-------------------|-------------------------|------------|
| water | | |
| ethanedioate ions | | |
| iron | | |
| potassium | | |

(vi) Suggest a formula, including the charge, for the complex ion present in the crystals.

(1)

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(vii) Draw a diagram showing how **one** ethanedioate ligand is bonded to the central metal ion.

(1)

(Total for Question 23 = 23 marks)

TOTAL FOR SECTION C = 23 MARKS

TOTAL FOR PAPER = 90 MARKS

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