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Pearson Edexcel
International
Advanced Level

Centre Number

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Candidate Number

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Chemistry

Advanced

Unit 6: Chemistry Laboratory Skills II

Tuesday 17 May 2016 – Morning

Time: 1 hour 15 minutes

Paper Reference

WCH06/01

Candidates may use a calculator.

Total Marks

Instructions

- Use **black** ink or 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 50.
- The marks for **each** question are shown in brackets
– *use this as a guide as to how much time to spend on each question.*
- You will be assessed on your ability to organise and present information, ideas, descriptions and arguments clearly and logically, including your use of grammar, punctuation and spelling.
- 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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Answer ALL the questions. Write your answers in the spaces provided.

- 1 A series of tests is carried out on aqueous solutions, **X**, **Y** and **Z**. Each solution contains a compound of a different d-block element.

(a) Tests **A** and **B**, described in the table, are carried out on solution **X**.

	Test	Observations
A	To 1 cm ³ of solution X in a test tube, add dilute sodium hydroxide solution, drop by drop, until no further change occurs. Shake the test tube gently as you add the dilute sodium hydroxide solution.	A white precipitate forms initially. The white precipitate dissolves in excess sodium hydroxide solution to form a colourless solution.
B	To 1 cm ³ of solution X in a test tube, add dilute aqueous ammonia solution, drop by drop, until no further change occurs. Shake the test tube gently as you add the aqueous ammonia solution.	A white precipitate forms initially. The white precipitate dissolves in excess aqueous ammonia solution to form a colourless solution.

- (i) Write the formula of the complex ion that is present at the **end** of Test **A**. (1)

- (ii) Write the formula of the complex ion that is present at the **end** of Test **B**. (1)

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(b) Test **C**, described in the table, is carried out on solution **Y**.

	Test	Observations
C	<p>To 2 cm³ of solution Y in a boiling tube, add dilute sodium hydroxide solution, drop by drop, until no further change occurs.</p> <p>Next add 2 cm³ more of dilute sodium hydroxide solution and 5 cm³ of hydrogen peroxide solution.</p> <p>Shake the tube gently and stand it in a beaker of hot water for a few minutes.</p>	<p>A green precipitate forms initially.</p> <p>The green precipitate dissolves to form a green solution.</p> <p>A yellow solution forms.</p>

(i) Write an ionic equation, including state symbols, for the formation of the green precipitate in Test **C**.

(1)

(ii) Give the oxidation numbers, including signs, of the d-block element in Test **C**.

(2)

Before the addition of hydrogen peroxide

At the end of Test **C**



(c) Test **D**, described in the table, is carried out on solution **Z**.

	Test	Observations
D	To 2 cm ³ of solution Z in a test tube, add an equal volume of dilute sodium hydroxide solution. Then add 10 drops of aqueous hydrogen peroxide solution.	An off-white precipitate forms initially. The off-white precipitate darkens.

Give the **formula** of the d-block metal cation present in solution **Z**.

(1)

(Total for Question 1 = 6 marks)



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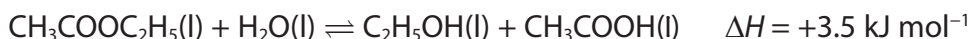
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- 2 Ethyl ethanoate, $\text{CH}_3\text{COOC}_2\text{H}_5$, is hydrolysed in the presence of a catalyst of dilute hydrochloric acid, $\text{HCl}(\text{aq})$, according to the equation below.



In an experiment carried out by a teacher to determine the equilibrium constant, K_c , the following steps are carried out.

- 15.0 cm^3 (0.153 mol) of ethyl ethanoate and 10.0 cm^3 dilute hydrochloric acid, concentration 1.00 mol dm^{-3} , are mixed together. In this pre-equilibrium mixture, there is 0.556 mol of water.
- The mixture is left for several days, at room temperature and pressure, to reach equilibrium.
- Using a pipette, several 5.00 cm^3 samples are taken from the 25.0 cm^3 of equilibrium mixture.
- Each 5.00 cm^3 sample is titrated with dilute sodium hydroxide solution from a burette. The concentration of the sodium hydroxide solution is $0.500 \text{ mol dm}^{-3}$.
- The mean titre of sodium hydroxide is 42.40 cm^3 . This neutralizes both the hydrochloric acid catalyst **and** the ethanoic acid in 5.0 cm^3 of the equilibrium mixture.

- (a) (i) Show that the 25.0 cm^3 of equilibrium mixture contains 0.0960 mol of CH_3COOH .

(3)

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- (ii) Deduce the number of moles of each of the other components in the equilibrium mixture.

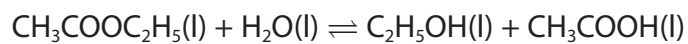
(3)

Equilibrium moles of C_2H_5OH = mol

Equilibrium moles of $CH_3COOC_2H_5$ = mol

Equilibrium moles of H_2O = mol

- (iii) Give the expression for the equilibrium constant, K_c , for the reaction



(1)



- (iv) The equilibrium constant, K_c , is defined in terms of the concentrations in the equilibrium mixture. However, in this case, K_c can be calculated using moles rather than concentrations.

Calculate the value of K_c from the data in parts (a)(i) and (a)(ii).

Give your answer to **three** significant figures.

(2)

$K_c =$

- (v) Explain why it is possible, in this case, to calculate K_c using moles rather than concentrations.

(1)

- (b) The experiment was repeated by a student whose value for K_c differed from the value calculated in (a)(iv).

The student made several suggestions to explain this.

State and explain how, if at all, each suggestion would affect the K_c value obtained by the student, compared with that from (a)(iv).

- (i) **Suggestion 1** – The concentration of the sodium hydroxide solution used by the student was less than $0.500 \text{ mol dm}^{-3}$.

(2)

How the student's value of K_c compared with that from (a)(iv)

Explanation

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- (ii) **Suggestion 2** – The mixture had been left in a warm part of the laboratory and the equilibrium had been reached at a temperature above room temperature. (2)

How the student's value of K_c compared with that from (a)(iv)

Explanation

- (c) A second student repeated the original experiment using exactly the same method. However, when using the pipette and the burette, the readings were taken from the **top** of the meniscus.

- (i) How, if at all, will this affect the volume of the equilibrium mixture delivered from the pipette? Justify your answer. (1)

- (ii) How, if at all, will this affect the volume of sodium hydroxide solution delivered from the burette? Justify your answer. (1)

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(iii) One of the student's titres was 42.60 cm^3 of sodium hydroxide solution.
The burette has a maximum uncertainty of $\pm 0.05 \text{ cm}^3$ for each reading.

Calculate the percentage uncertainty in this titre.

(1)

Percentage uncertainty =%

(Total for Question 2 = 17 marks)

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- 3 Six students attempted to carry out a two-stage synthesis of nitrobenzoic acids starting from ethyl benzoate, $C_6H_5COOCH_2CH_3$.

There are two parts to the synthesis.

- In the first part, ethyl benzoate is hydrolysed to form benzoic acid, C_6H_5COOH .
- In the second part, benzoic acid is nitrated.

Part 1 – Hydrolysis of ethyl benzoate

The students were provided with the method outlined in the steps below.

Step 1 Mix in a flask 6.0 cm^3 ethyl benzoate (density = 1.05 g cm^{-3}) with an excess of aqueous sodium hydroxide solution (made by dissolving 2 g of sodium hydroxide in 25 cm^3 water).

Heat the mixture under reflux for 30 minutes.

Step 2 Pour the contents of the flask into a beaker and add 1 mol dm^{-3} dilute hydrochloric acid until the solution is acidic to universal indicator paper. Crystals of benzoic acid will form.

Step 3 Filter off the crystals under reduced pressure.

Step 4 Dissolve the crystals in the minimum volume of boiling water and then filter.

Step 5 Allow the solution to cool so that crystals of benzoic acid form. Filter off the crystals.

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(a) Student **A** followed the method exactly and obtained 0.021 mol of benzoic acid crystals.

Calculate the percentage yield of the benzoic acid obtained by Student **A**.

[Molar mass of ethyl benzoate = 150 g mol^{-1}]

(2)

Percentage yield = %

(b) Student **B** dissolved just 1 g of sodium hydroxide instead of 2 g. This student carried on with the experiment.

Show, by calculation, that Student **B** did **not** have an excess of sodium hydroxide.

(2)

(c) Student **C** dissolved 10 g of sodium hydroxide instead of 2 g. This student noticed the mistake and started the experiment again.

Explain why Student **C** did not need to start again.

(1)



- (d) Student **D** decided to miss out **Steps 4** and **5**. This student's mass of crystals was greater than the mass of crystals obtained by Student **A**.

The benzoic acid obtained by Student **A** had fewer impurities than the benzoic acid obtained by Student **D**.

Name the procedure described in step 4 and 5, and explain why the benzoic acid prepared by Student **A** was purer than that obtained by Student **D**.

(1)

- (e) Student **E** decided not to carry out **Steps 2, 3, 4** and **5**. Instead, Student **E** evaporated off the water after **Step 1** and found that 4.6 g of crystals had been formed, which was more than the mass obtained by Student **A**.

One reason why Student **E** obtained a greater mass of crystals than Student **A** was that the product was not benzoic acid.

Give the structural formula of the organic product that Student **E** obtained.

(1)

- (f) Student **F** ran out of time and filtered the solution in **Step 5** before it had cooled properly. A low yield was obtained.

Explain why Student **F**'s failure to cool fully the solution resulted in a **low yield**.

(1)

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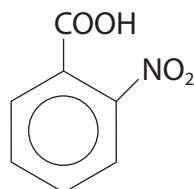
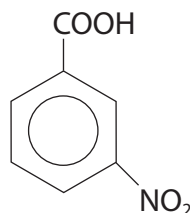
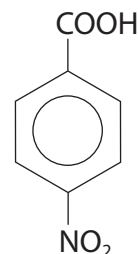
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Part 2 – Nitration of benzoic acid

The students nitrated the benzoic acid and used chromatography to separate the three organic products.

The students suspected that the three products were isomers with the structures shown below, labelled **P**, **Q** and **R**.

**P****Q****R**

- (g) A student measured the melting temperature range of **one** of the separated products (**Sample 1**).

The student then recrystallized the sample and took the melting temperature range of the recrystallized product (**Sample 2**).

The student's results are shown below.

Sample 1 melting temperature range before recrystallization was 136°C to 140°C

Sample 2 melting temperature range after recrystallization was 144°C to 146°C

The melting temperatures for the three structural isomers from a database are shown below.

- 2-nitrobenzoic acid (**P**) 148°C
- 3-nitrobenzoic acid (**Q**) 142°C
- 4-nitrobenzoic acid (**R**) 241°C



(i) Why are the melting temperatures of **Sample 1** and **Sample 2** different? (1)

.....

.....

(ii) Suggest which isomer is present in these samples. Justify your answer. (2)

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- (h) (i) Can the number of peaks in the low resolution proton nmr spectroscopy be used to distinguish between the three isomers **P**, **Q** and **R**?
Justify your answer.

(2)

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- (ii) In a mass spectrum, which m/e value could be used to confirm that only mono-nitration occurred in this reaction?

(1)

 m/e value =**(Total for Question 3 = 14 marks)**

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- 4 Vanadium is a transition metal and forms ions in which it has oxidation numbers +2, +3, +4 and +5.

Part 1

Two students want to make solutions containing ions in which vanadium has oxidation numbers of +3 and +4.

Both students start with solid ammonium vanadate(V), NH_4VO_3 .

The first student decides to make an aqueous solution containing vanadium(III) ions, $\text{V}^{3+}(\text{aq})$.

- (a) First, the student heats solid ammonium vanadate(V) to make vanadium(V) oxide, ammonia and steam.

- (i) Write a balanced equation for this decomposition of ammonium vanadate(V).
State symbols are not required.

(1)

- (ii) How would the student confirm that this decomposition is complete?

(1)

- (b) The student then reduces the vanadium(V) oxide to vanadium(III) oxide, V_2O_3 , by passing hydrogen over the heated oxide.

Identify the hazard associated with this procedure.

(1)

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(c) The student reacts 1.498 g of vanadium(III) oxide, $V_2O_3(s)$, completely with an **excess** of sulfuric acid, $H_2SO_4(aq)$, to make 250 cm^3 of a solution, T, containing aqueous vanadium(III) ions, $V^{3+}(aq)$.

(i) Calculate the concentration, in mol dm^{-3} , of vanadium(III) ions, $V^{3+}(aq)$, in the solution T.

(2)

Concentration = mol dm^{-3}

(ii) Give the **formulae** of **two** ions that would be present in high concentration in solution T, apart from vanadium(III) ions, $V^{3+}(aq)$ ions.

(1)

..... ions **and** ions

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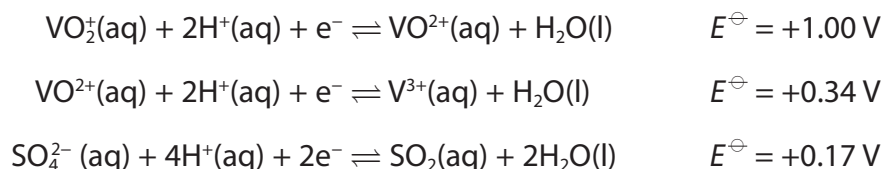
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- (d) The second student decides to make a solution containing $\text{VO}^{2+}(\text{aq})$ ions, in which vanadium has an oxidation number of +4.

The student dissolves the ammonium vanadate(V) in dilute sulfuric acid. In this solution, the vanadium species is $\text{VO}_2^+(\text{aq})$. The student needs to reduce the $\text{VO}_2^+(\text{aq})$ ions to $\text{VO}^{2+}(\text{aq})$ ions.

The teacher suggests using sulfur dioxide as the reducing agent and supplies the student with the following standard electrode potential values.



- (i) These data suggest that a step-wise reduction of an acidified solution of $\text{VO}_2^+(\text{aq})$ ions, using sulfur dioxide, $\text{SO}_2(\text{aq})$, will initially produce $\text{VO}^{2+}(\text{aq})$ ions and then $\text{V}^{3+}(\text{aq})$ ions in solution.

By calculating the relevant E_{cell}^\ominus values for any reactions that you predict will occur, show that such a step-wise reduction is possible.

(2)



- (ii) When the student bubbles sulfur dioxide into a solution containing acidified $\text{VO}_2^+(\text{aq})$ ions, $\text{VO}^{2+}(\text{aq})$ ions are obtained, rather than $\text{V}^{3+}(\text{aq})$ ions.

Suggest why $\text{VO}^{2+}(\text{aq})$ ions are produced, rather than the $\text{V}^{3+}(\text{aq})$ ions predicted in (d)(i).

(1)

- (iii) Construct the overall equation for the reduction of acidified $\text{VO}_2^+(\text{aq})$ ions to $\text{VO}^{2+}(\text{aq})$ ions by aqueous sulfur dioxide, $\text{SO}_2(\text{aq})$.
State symbols are not required.

(1)

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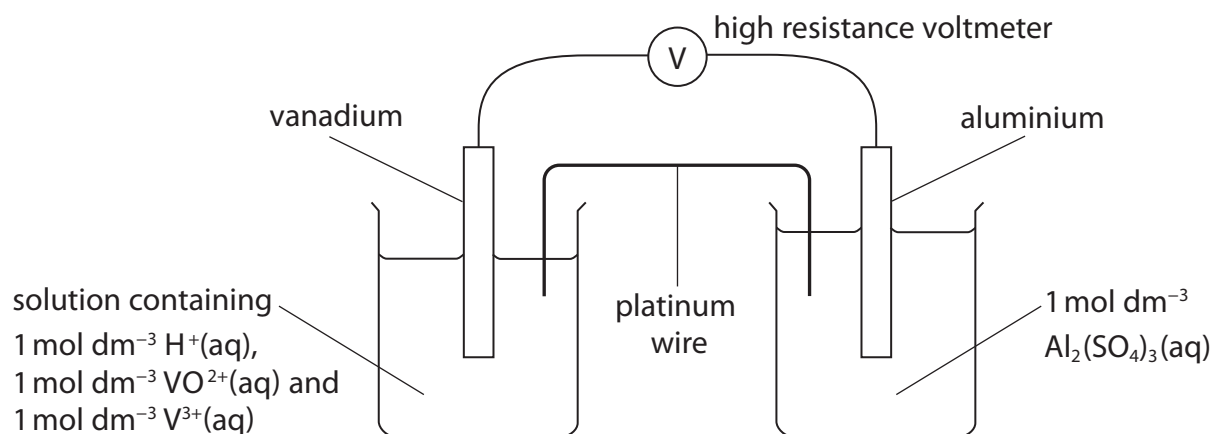
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Part 2

Having made solutions of $\text{VO}^{2+}(\text{aq})$ and $\text{V}^{3+}(\text{aq})$ ions, the students decide to measure the standard cell potential between the $\text{VO}^{2+}(\text{aq}) / \text{V}^{3+}(\text{aq})$ and $\text{Al}^{3+}(\text{aq}) / \text{Al}(\text{s})$ half-cells.

The students set up the apparatus below to measure this standard cell potential. The solutions were at 25°C .



- (e) Identify **three** mistakes in the way the cell has been set up and state what modifications should be made to correct them. Write your answers in the table below.

(3)

Mistake in set-up	Modification needed to correct mistake

(Total for Question 4 = 13 marks)

TOTAL FOR PAPER = 50 MARKS

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