HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME		**CT GROUP**	**21S**
CENTRE NUMBER		**INDEX NUMBER**	

CHEMISTRY

9729/02

Paper 2 Structured Questions

29 August 2022

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your **name**, **CT group, centre number** and **index number** clearly in the spaces above.

Write in dark blue or black pen.

You may use a HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer all questions in the spaces provided in the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	/ 11
2	/ 9
3	/ 13
4	/ 15
5	/ 27
Deductions	
Total	/ 75

Answer **all** the questions in the spaces provided.

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1 Fossil fuels which are found in deposits have been formed from plants and animals that lived millions of years ago.

When fossil fuels are burned in internal combustion engines, CO_2 and H_2O are the main products, with NO and SO_2 also being formed.

(a) (i) What class of compound, present in fossil fuels, produces CO_2 and H_2O on combustion?

……[1]

(ii) NO and NO_2, collectively known as oxides of nitrogen, are pollutants that are also formed during combustion in motor vehicles. Write equations to show how each of these two gases are formed in vehicle engines.

……

……[1]

(iii) State one harmful effect of oxides of nitrogen on the environment.

……[1]

To meet emission standards in Singapore, sulfur emissions from cars have to be lower than 50 parts per million (ppm). This means that there should be less than 50 molecules of SO_2 for every 1×10^6 molecules of gas in the fuel exhaust for it to meet regulations.

(b) (i) A sample of fuel was combusted at 900 °C and 10.0 bar. At the end of the reaction, 63.2 dm^3 of gas was collected under the same conditions.

Determine the amount of gas, in moles, produced by combustion of the fuel sample.

[2]

(ii) Given that 0.0183 g of SO_2 was produced in **(b)(i)**, calculate the concentration of SO_2, in parts per million, and explain whether the fuel exhaust meets the sulfur emission standards.

[2]

(c) Describe the reactions, if any, of SO_3, Na_2O and Al_2O_3 with water. Include the approximate pH value of any resulting solutions, and write equations for any reactions that occur.

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……[4]

[Total: 11]

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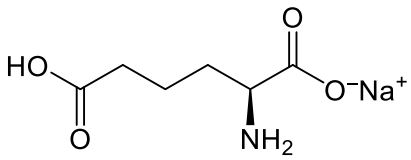
2 Monosodium glutamate (MSG) is a natural flavour enhancer present in foods. Naturally occurring MSG can be extracted from seaweed and is commonly manufactured on a large scale by fermenting sugars.



MSG

(a) (i) A chemist proposed to synthesise MSG using the following reaction scheme. Draw intermediates **A** and **B**, and state the reagents and conditions for step 1 and step 2.

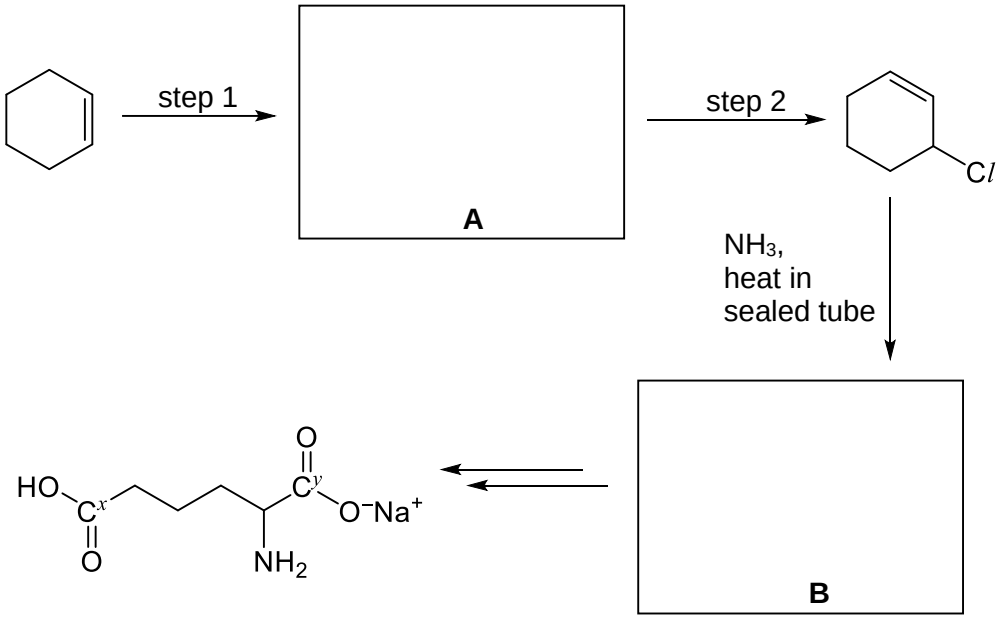


Fig. 2.1

step 1: ……

step 2: ……
[4]

(ii) In the final step of the reaction scheme, the $–C^yO_2H$ group is deprotonated instead of the $–C^xO_2H$ group. Explain why this is so.

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……[2]

DO NOT WRITE IN THIS MARGIN

(iii) Food flavours enhanced by the MSG synthesised in the laboratory according to Fig. 2.1 might taste differently from flavours enhanced by naturally occurring MSG. Suggest why this is so.

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……[1]

(b) High sodium content food is linked to increased risk of heart disease. Some health experts recommend using MSG instead of table salt (NaC*l*) to flavour food so as to reduce sodium intake. With the aid of suitable calculations, show that 1 g of MSG helps achieve lower sodium intake than 1 g of table salt.

[2]

[Total: 9]

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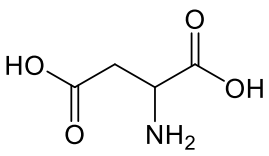
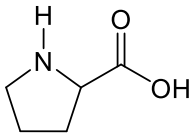
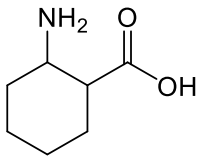
3 The structures of amino acids **A** to **D** are given below.



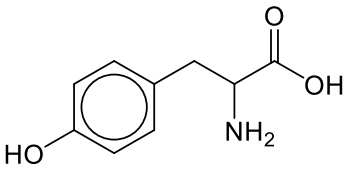
A



B



C



D

(a) Identify the amino acid that is **not** an α-amino acid.

..... [1]

(b) On complete hydrolysis, a tripeptide gave the other three amino acids not identified in **(a)** in equimolecular amounts.

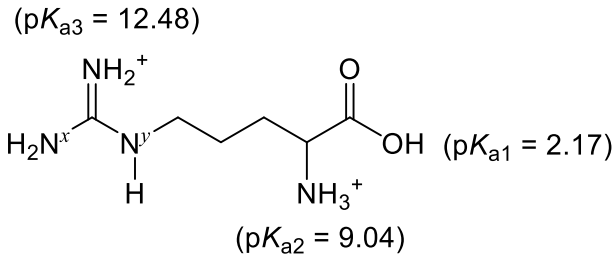
Draw the structural formula of one such tripeptide at pH 1 and pH 14.

At pH 1:

At pH 14:

[3]

(c) The pK_a values of the acidic groups in a fully protonated arginine are labelled below.



fully protonated arginine

(i) Given that N^x and N^y are both sp^2 hybridised, suggest why they are both very weak bases.

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.....[1]

When a 10.0 cm^3 sample of the fully protonated arginine is titrated against 0.100mol dm^{-3} NaOH, the following titration curve is obtained.

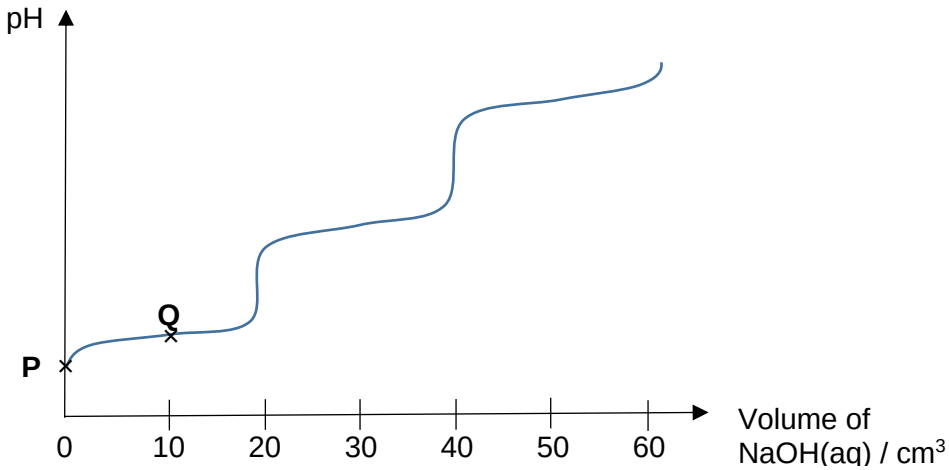

Fig. 3.1

(ii) Calculate the concentration of arginine in the 10.0 cm^3 sample.

[1]

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(iii) Calculate the pH of the solution at point **P** (ignore the effects of the second and third acid dissociations on the pH).

[2]

(iv) Determine the pH at point **Q**.

[1]

(v) Explain, using an equation and the relevant ionic forms of arginine, why the pH changes only gradually around point **Q** as aqueous NaOH is added.

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.....[3]

(vi) The isoelectric point is the pH at which the net electrical charge on an amino acid is zero.

On the titration curve in Fig. 3.1, label the isoelectric point of arginine clearly with an "X".

[1]

[Total: 13]

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4 (a) A nickel(II) complex is prepared by adding excess aqueous ammonia to an aqueous solution of nickel(II) ions.

The water ligands are replaced by ammonia ligands in this reaction.

$$[Ni(H_2O)_6]^{2+}(aq) + 6NH_3(aq) \rightleftharpoons [Ni(NH_3)_6]^{2+}(aq) + 6H_2O(l)$$

(i) What is meant by the term *ligand*?

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..... [1]

(ii) Explain why complexes of nickel(II) are coloured, and why the aqueous solution of nickel(II) changes colour when excess aqueous ammonia is added.

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.....[3]

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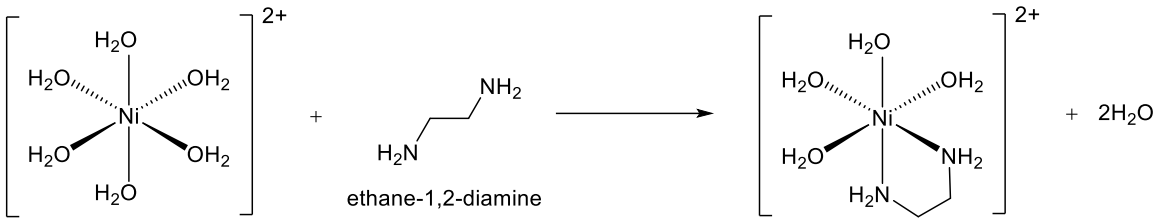
(b) Ethane-1,2-diamine, en, is a bidentate ligand, which can form 2 coordinate bonds to nickel(II) simultaneously.



When an excess of ethane-1,2-diamine is added to an aqueous solution of $[Ni(NH_3)_6]^{2+}$, the following equilibrium is established.

equation 4.1 $[Ni(NH_3)_6]^{2+}(aq) + 3en(aq) \rightleftharpoons [Ni(en)_3]^{2+}(aq) + 6NH_3(aq)$

Table 4.1 shows the standard enthalpy and entropy changes for equation 4.1 at 298 K.

Table 4.1

$\Delta H^{\ominus}_r$ / kJ mol^{-1}	–17.0
$\Delta S^{\ominus}_r$ / J K^{-1} mol^{-1}	+121

(i) Explain why equation 4.1 shows a large **and** positive value for $\Delta S^{\ominus}_r$.

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.....

.....[2]

(ii) Calculate $\Delta G^{\ominus}_r$ for equation 4.1.

[1]

(iii) State what the $\Delta G^{\ominus}_r$ value indicates about the position of equilibrium for equation 4.1. Hence, identify which ligand bonds preferentially with Ni^{2+}.

.....

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.....

.....[2]

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(iv) Bidentate ligands, like ethane-1,2-diamine, form coordinate bonds with metal centres very quickly compared to a similar reaction with ammonia ligands.

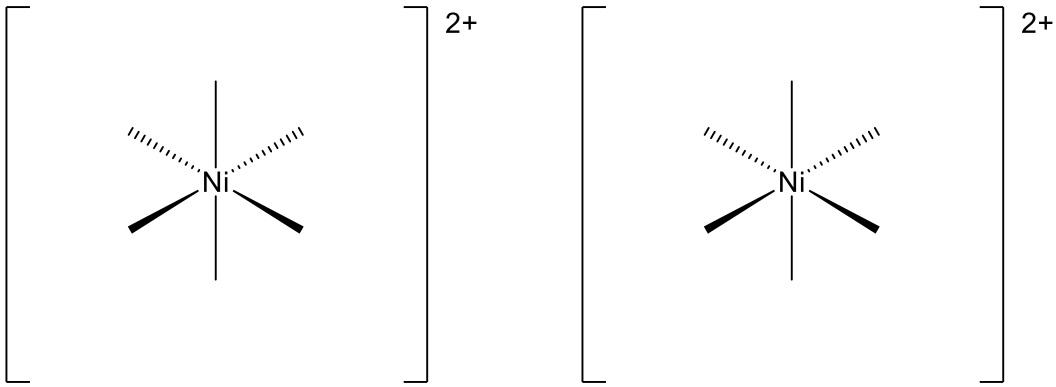
Suggest a reason for the rapid rate of reaction.

……

……[1]

(c) (i) The $[Ni(en)_3]^{2+}$ complex, formed in equation 4.1, is chiral.

Complete the drawings below to show the 3-dimensional structures of the two enantiomers of $[Ni(en)_3]^{2+}$.



[2]

(ii) Explain why $[Ni(en)_3]^{2+}$ is considered chiral.

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……[1]

(iii) Describe **one** similarity and **one** difference between the enantiomers of a $[Ni(en)_3]^{2+}$ containing compound in terms of their physical properties.

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……[2]

[Total: 15]

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5 (a) Iron and its compounds are commonly used as homogeneous or heterogeneous catalysts to speed up reactions.

(i) Explain, with the aid of a Boltzmann distribution diagram, the effect on a rate constant of adding a catalyst.

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..... [3]

(ii) State the electronic configuration of an iron atom.

..... [1]

(iii) Complete Table 5.1 to show an example of a reaction where iron or its compound acts as a homogeneous catalyst or heterogeneous catalyst. State the identity of the catalyst used in each case, and briefly explain why it can act as this type of catalyst.

Table 5.1

	homogeneous catalysis	heterogeneous catalysis
balanced equation for catalysed reaction		
catalyst used		
reason why iron or its compound could act as this type of catalyst		

[4]

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Two methods for the electrochemical synthesis of H_2O_2 are described in **(b)** and **(c)**.

(b) Fig. 5.1 shows a conventional fuel cell that produces H_2O_2 via a two-electron reduction of oxygen.

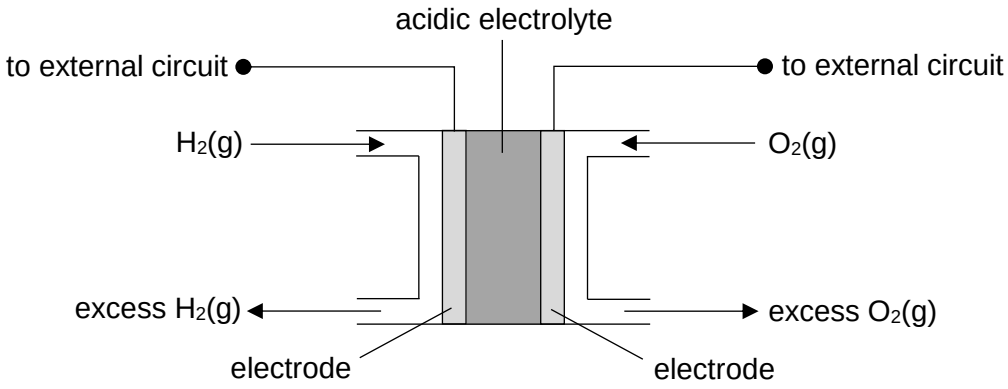

Fig. 5.1

The two half-equations involved in the electrode reactions are

half-equation 1 $H_2(g) \rightarrow 2H^+(aq) + 2e^-$

half-equation 2 $O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O_2(aq)$

A competing reaction can also occur at the cathode, where water is produced instead via a four-electron reduction of oxygen.

half-equation 3 $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

Water may also be produced by the further reduction of H_2O_2 as shown.

half-equation 4 $H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$

(i) Define the term *standard electrode potential*.

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……[1]

(ii) **On Fig. 5.1**, label the polarity of each electrode and draw the direction of electron flow when the overall reaction as shown by half-equations 1 and 2 occurs. [2]

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In this fuel cell, the cathode is coated with a catalyst. Depending on the transition metal catalyst used, **one** of the two mechanisms in Table 5.2 occurs.

In each mechanism, ∗ represents an unoccupied active site on the catalyst, while ∗OOH represents O–O–H adsorbed on the catalyst surface.

Table 5.2

mechanism 1	mechanism 2
$* + O_2(g) + H^+(aq) + e^- \rightarrow *OOH$ $*OOH + H^+(aq) + e^- \rightarrow H_2O(l) + O*$ $O* + H^+(aq) + e^- \rightarrow *OH$ $*OH + H^+(aq) + e^- \rightarrow H_2O(l) + *$	$* + O_2(g) + H^+(aq) + e^- \rightarrow *OOH$ $*OOH + H^+(aq) + e^- \rightarrow H_2O_2(aq) + *$

(iii) State which half-equation, 1 to 4, is represented by the two mechanisms in Table 5.2.

mechanism 1: ……..

mechanism 2: …….. [1]

(iv) The extent to which the O–O single bond is preserved in the mechanism determines whether H_2O_2 or H_2O is produced at the cathode. By considering the equations in Table 5.2 and the effect of adsorption, suggest why this is so.

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……[2]

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Question 5 continues on Page 17.

(c) Fig. 5.2 shows an electrolytic cell that produces H_2O_2 via a two-electron oxidation of water. Similar to the method described in **(b)**, a catalyst is coated on the electrode surface for the selective oxidation of water.

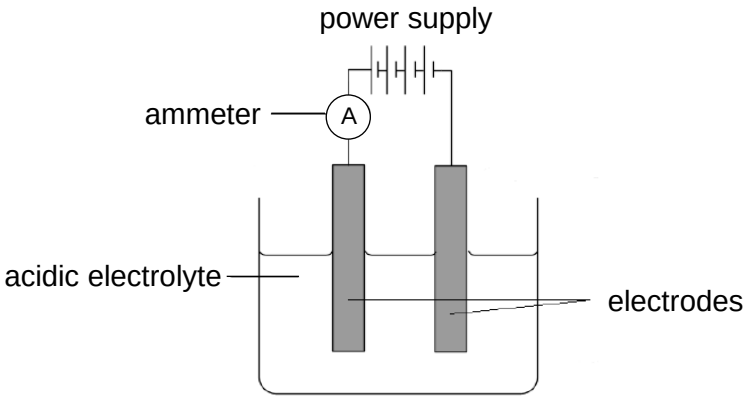

Fig. 5.2

The two half-equations which are involved in the electrode reactions are

half-equation 5 $2H^+(aq) + 2e^- \rightarrow H_2(g)$

half-equation 6 $2H_2O(l) \rightarrow H_2O_2(aq) + 2H^+(aq) + 2e^-$

(i) Write an equation, with state symbols, for a possible competing reaction at the anode. Use the *Data Booklet* to explain whether this reaction is more or less likely to occur than half-equation 6.

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.....[3]

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The amount of H_2O_2 produced in the electrolysis may be determined via a reaction with acidified cerium(IV) sulfate, $Ce(SO_4)_2$.

In this reaction, O_2 is produced and yellow $Ce^{4+}(aq)$ ions are reduced to colorless $Ce^{3+}(aq)$ ions. The concentration of $Ce^{4+}(aq)$ can be determined by measuring the absorbance of the solution at 316 nm.

(ii) Write an ionic equation for the reaction between H_2O_2 and $Ce(SO_4)_2$.

..... [1]

(iii) $\Delta G^{\ominus}$ for the overall reaction in **(c)(ii)** is -179.5 kJ mol^{-1}. Calculate the standard cell potential for this reaction, and hence the standard electrode potential for Ce^{4+}/Ce^{3+}.

[2]

The effectiveness of H_2O_2 production may be determined by calculating the Faradaic efficiency (FE) as shown

$$\text{FE} = \frac{n_{H_2O_2}\,\text{detected}}{\text{theoretical maximum } n_{H_2O_2}} \times 100\%$$

An experiment to determine the FE was conducted as follows.

1. A constant current of 1.00×10^{-4} A was passed through the electrolysis cell consisting of 100 cm^3 acidic electrolyte.
2. After an hour, the power supply was disconnected and the electrolyte was stirred.
3. 1.00×10^{-4} mol dm^{-3} acidified $Ce(SO_4)_2$ was prepared and its absorbance at 316 nm was found to be 0.567.
4. 100 cm^3 of the acidified $Ce(SO_4)_2$, which was in excess, was added to the 100 cm^3 electrolyte.
5. At the end of the reaction, the absorbance of the mixture in step 4 was measured again at 316 nm, and found to be 0.200.

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(iv) Calculate the theoretical maximum amount, in moles, of H_2O_2 that can be produced in this electrolysis, based on half-equation 6.

[2]

(v) Given that the measured absorbance is directly proportional to the concentration of $Ce^{4+}(aq)$, calculate the final concentration of $Ce^{4+}(aq)$ in the 200 cm^3 reaction mixture in step 4.

[1]

(vi) Hence, calculate the amount, in moles, of $Ce^{4+}(aq)$ which reacted with the 100 cm^3 electrolyte in step 4.

[2]

(vii) Use your answers from **(c)(ii)**, **(c)(iv)** and **(c)(vi)** to calculate the actual amount, in moles, of H_2O_2 produced in this electrolysis and the FE.

[2]

[Total: 27]