**1** Vanadium exists in different oxidation states which can be interconverted using suitable oxidising and reducing agents.

(a) Use relevant standard electrode potential values, on page 14 of the Data Booklet, to complete the table below in which two $E^{\ominus}$ values are missing.

(1)

Half-equation	$E^{\ominus}$ / V
$V^{2+}(aq) + 2e^- \rightleftharpoons V(s)$	
$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$	
$VO^{2+}(aq) + 2H^+(aq) + e^- \rightleftharpoons V^{3+}(aq) + H_2O(l)$	+0.34
$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$	+1.00

(b) The standard electrode potential of $V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$ is measured using the apparatus below.
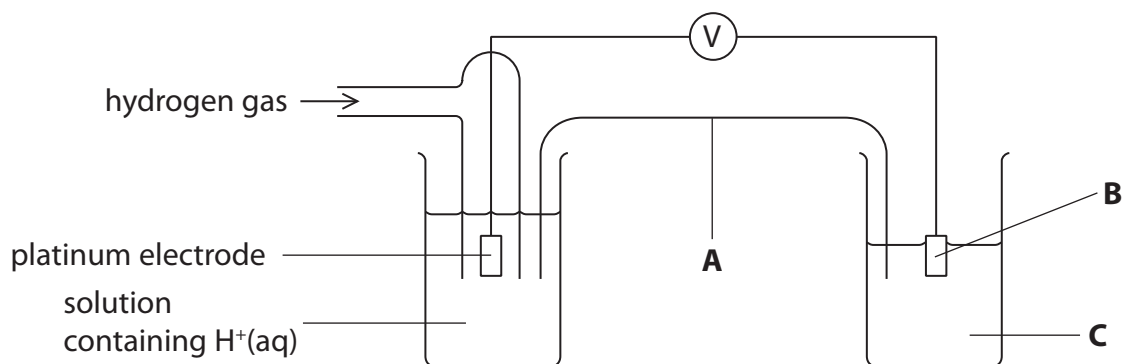
(i) Identify, by name or formula, the substances needed in the salt bridge and the right-hand half-cell to measure the standard electrode potential.

(3)

A Salt bridge containing a solution of

....

B Electrode made of

....

C Solution containing

....

(ii) State the **three** standard conditions needed for this measurement.

(2)

1 ....

2 ....

3 ....

*(c) A solution containing iodide ions, I^-, was added to an acidified solution containing vanadium(V) ions, VO_2^+.

Predict the oxidation state of the vanadium ions left at the end of the reaction. Justify your prediction by calculating the $E_{cell}^{\ominus}$ for any relevant reaction(s).

Write the ionic equation for any reaction(s) occurring. State symbols are not required.

(5)

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(Total for Question = 11 marks)

2 This question is about vanadium and its ions.

(a) Consider the data below.

Electrode system	Standard electrode potential $E^{\ominus}$/ V
$V^{2+}(aq)\|V(s)$	−1.18
$V^{3+}(aq), V^{2+}(aq)\|Pt$	−0.26

(i) Draw a labelled diagram showing how to set up a cell, using the two electrode systems in the table above, in order to measure $E^{\ominus}_{cell}$.
Include standard conditions in your labelling.

(3)

(ii) Write an equation for the reaction in this cell. State symbols are not required.

(2)

(b) (i) Complete the table below with the missing standard electrode potentials.
Use the table starting on page 14 of your Data Booklet.

(1)

Electrode system	Standard electrode potential $E^{\ominus}$/ V
$[VO^{2+}(aq) + 2H^+(aq)], [V^{3+}(aq) + H_2O(l)]\|Pt$	
$[VO_2^+(aq) + 2H^+(aq)], [VO^{2+}(aq) + H_2O(l)]\|Pt$	
$I_2(aq),2I^-(aq)\|Pt$	+0.54
$[2H^+(aq) + O_2(g)], [H_2O_2(aq)]\|Pt$	+0.68

(ii) The colours of the different oxidation states of vanadium are shown below.

Oxidation state	Colour
+5	yellow
+4	blue
+3	green
+2	violet

For each of the following experiments, **A** and **B**, calculate the $E^{\ominus}$ value for the proposed reaction. Use your answers to predict whether or not a reaction occurs in each case.

Give the formula of the vanadium product formed where a reaction occurs and give **one** observation you would make in each experiment.

(6)

Experiment A: Hydrogen peroxide is added to an aqueous solution containing VO_2^+ ions.

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Experiment B: An aqueous solution of potassium iodide is added to an aqueous solution containing VO^{2+} ions.

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(c) An experiment was carried out to determine the percentage purity of a sample of ammonium vanadate(V), NH_4VO_3.

An impure sample of ammonium vanadate(V) with mass 0.150 g was dissolved in dilute sulfuric acid. This produced a solution containing VO_2^+ ions. Excess zinc powder was added to the solution, and this reduced the VO_2^+ ions to V^{2+} ions.

The solution containing V^{2+} ions was titrated with potassium manganate(VII) of concentration 0.0200 mol dm^{-3}. The manganate(VII) ions oxidized the V^{2+} back to VO_2^+. The volume of potassium manganate(VII) required was 35.50 cm^3.

(i) The manganate(VII) ions react as shown:

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

Show, by writing the appropriate half equation or otherwise, that 5 mol V^{2+} react with 3 mol MnO_4^-.

(1)

(ii) Calculate the number of moles of manganate(VII) ions used in the titration.

(1)

(iii) Calculate the number of moles of VO_2^+ in the original solution, and hence the percentage purity of the sample of NH_4VO_3. Give your answer to **three** significant figures.

Molar mass of $NH_4VO_3 = 116.9$ g mol^{-1}.

(3)

(Total for Question = 17 marks)

3 Hydrogen-oxygen fuel cells can operate in acidic or alkaline conditions.
One such commercial cell uses porous platinum electrodes in contact with
concentrated aqueous potassium hydroxide solution, KOH(aq).

(a) Use relevant standard electrode potential values, on pages 15 and 17 of the Data
Booklet, to complete the table below in which two $E^{\ominus}$ values are missing.

(2)

Half-equation	$E^{\ominus}$ / V
$2H_2O(l) + 2e^- \rightleftharpoons 2OH^-(aq) + H_2(g)$	−0.83
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	

(b) (i) Fill in the boxes to identify, by name or formula, the substances used in the **standard** hydrogen electrode.

(2)

platinum
electrode
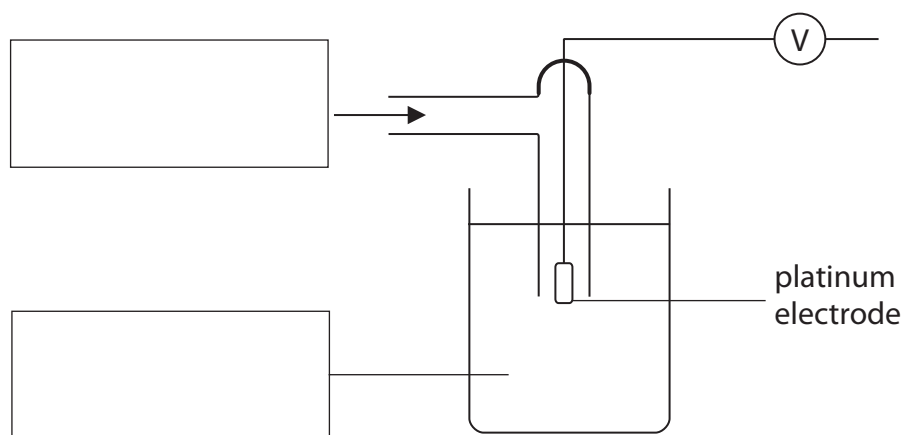
(ii) State **three** conditions that are necessary for a standard hydrogen electrode.

(2)

1. ....

2. ....

3. ....

(c) Write appropriate half-equations and use them to derive an overall equation for the reaction which occurs when an **alkaline** hydrogen-oxygen fuel cell operates.

(2)

(d) Use the $E^{\ominus}$ values from the table in part (a) to calculate the $E^{\ominus}_{cell}$ for a hydrogen-oxygen fuel cell operating in alkaline conditions.

(1)

(e) Suggest why the $E^{\ominus}_{cell}$ for a hydrogen-oxygen fuel cell, operating in **acidic** conditions, is identical to that of an alkaline fuel cell.

(1)

....

....

(f) Give **one** reason (other than cost implications) why the platinum electrodes are made by coating porous material with platinum rather than by using platinum rods.

(1)

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....

(g) Suggest **one** disadvantage of using a hydrogen-oxygen fuel cell compared with a rechargeable battery when providing electrical energy for a motor vehicle.

(1)

....

....

(Total for Question = 12 marks)

4 Hydrogen combines rapidly with oxygen in the presence of a platinum catalyst:

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l)$$
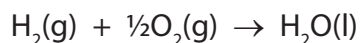
The reaction is highly exothermic.

(a) Use the thermochemical data from the data booklet to obtain the enthalpy change for this reaction under standard conditions.

(1)

.... kJ mol^{-1}

(b) The same reaction occurs, also with a platinum catalyst, in a fuel cell.

(i) Write the two ionic half equations which occur in an **alkaline** fuel cell. Include state symbols.

(3)

Equation 1

Equation 2

(ii) The alkali in an alkaline fuel cell serves the same purpose as the acid in an acid fuel cell. State this purpose.

(1)

....

....

*(iii) Platinum catalyses both the direct combination of hydrogen with oxygen and the reactions in the fuel cell. By considering the way in which the catalyst lowers the activation energy, suggest two **similarities** in these processes.

(2)

Similarity 1 ....

....

....

Similarity 2 ....

....

....

(c) The use of hydrogen as a fuel, both in fuel cells and in direct combustion reactions, is seen as an important potential alternative to fossil fuels.

(i) State what is considered to be the main advantage of hydrogen compared with fossil fuels, bearing in mind that most hydrogen is obtained from fossil fuels.

(1)

....

....

*(ii) Explain the main advantage of using a fuel cell over direct combustion of hydrogen.

(2)

....

....

....

....

(iii) State a disadvantage of using a hydrogen fuel cell compared with direct combustion of hydrogen.

(1)

....

....

(iv) Suggest **two** advantages of using an ethanol fuel cell rather than a hydrogen fuel cell.

(2)

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(Total for Question = 13 marks)