CHEMISTRY

Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.

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

This document consists a total of **16** printed pages.

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1 This Question tests up to, and mainly Chapter 20 (Electrochemistry).

(a) A student creates a simple electrolysis setup. 1 platinum anode and 1 platinum cathode was placed in a solution containing dilute sodium chloride, with a constant current of 0.500 A passed through the circuit.

(i) Using relevant standard electrode potentials from the *Data Booklet*, explain the effect of the electrolysis on the pH of the solution. [2]

(ii) Sketch a graph of the mass of the solution against time elapsed since the current was passed through the circuit. [2]

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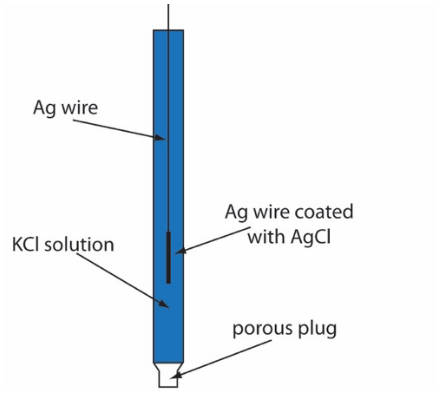
(b) Apart from the standard hydrogen electrode, there are other standard electrodes used in analytical chemistry too.

One such electrode is the silver chloride electrode. A diagram of the silver chloride electrode is shown below.



The relevant half-equation taking place in this electrode is:

Equation 1: $AgCl\,(s) + e^- \rightleftharpoons Ag\,(s) + Cl^-\,(aq)$

(i) The porous plug is meant for a salt bridge to be connected to the analyte (solution to be tested).

Complete the diagram above to show how you would measure the potential of this electrode relative to the standard hydrogen electrode. [2]

(ii) Given that the standard electrode (reduction) potential of **Equation 1** is +0.22249 V, using relevant data from the *Data Booklet*, calculate the change in the Gibbs' Free Energy of the dissolution of silver chloride at 25 degrees Celsius. [3]

(iii) A modification of the silver chloride electrode is to use a saturated solution of potassium chloride instead of a concentration of 1.00 mol dm^{-3}.

Suggest a benefit of doing so. [1]

(iv) Compare the electrode potential of **Equation 1** when a saturated solution of potassium chloride is used as the aqueous media to when a solution of 1.00 mol dm^{-3} potassium chloride is used. Provide a reason for your answer. [1]

(v) Suggest a benefit of using the silver chloride electrode over the standard hydrogen electrode. [1]

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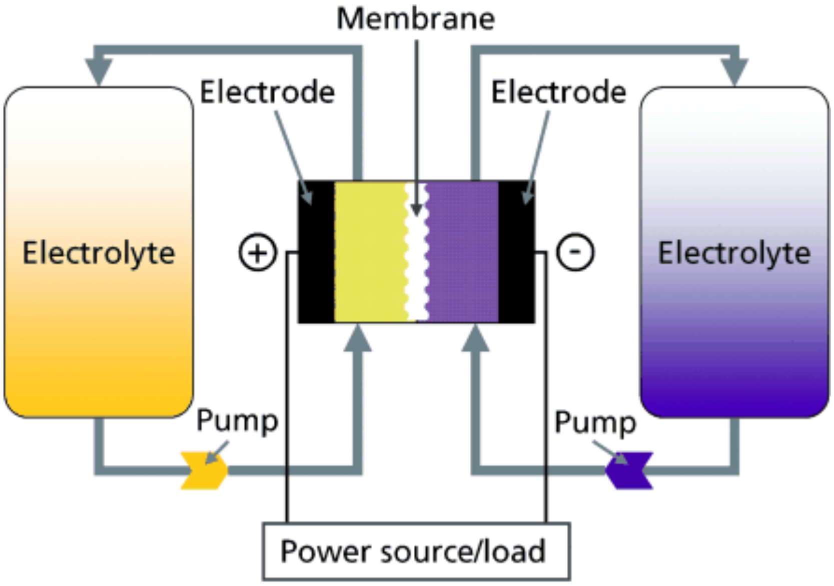
(c) Rechargeable batteries are now seen to be eco-friendly alternatives to conventional batteries made of manganese.

The diagram below illustrates the model of a rechargeable battery.



One such rechargeable battery is the zinc-cerium battery, developed in 2000 in the UK.

The solvent used in this system is methanesulfonic acid (CH_3SO_3H).

Relevant data is provided below:

Ce^{4+} (aq) + e^- $\rightleftharpoons$ Ce^{3+} (aq) $E^\ominus = +1.44$ V

The power source draws electricity from the setup.

(i) Based on the diagram above, state which electrode should be the zinc electrode. Calculate the discharge voltage at standard conditions. [1]

A scientist set up a small zinc-cerium battery with the following specifications.

Volume of negative electrolyte (Electrolyte at negative terminal)	20.0 dm^3
Volume of positive electrolyte (Electrolyte at positive terminal)	10.0 dm^3
Concentration of $Zn(CH_3SO_3)_2$ / mol dm^{-3}	1.500
Concentration of $Ce(CH_3SO_3)_3$ / mol dm^{-3}	1.050
Concentration of $Ce(CH_3SO_3)_4$ / mol dm^{-3}	0.840
Mass of zinc electrode	2.00 kg

Part (c) continues on the next page.

(ii) Assume that this battery has no side reactions and is 100% efficient.

If this battery were to be charged to its fullest, how much charge needs to be supplied to the battery? Give your answer in mAh (milli-ampere hours). [3]

It would help to show that 1 mAh = 3.6 C.

(iii) Hence, calculate the charge capacity of this battery in mAh. [3]

(iv) What is the percentage charge of this battery? [1]

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[Total: 20]

2 **(a)** Explain why the hydrogen-halogen bond is weaker down the group for halogens. Hence describe the observations when the respective hydrogen halides are heated. [3]

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(b) Explain the trend in the boiling points of the hydrogen-halides. [3]

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(c) Explain the link between the trend of the decomposition temperature of the Group II carbonates and the disparity between their theoretically calculated and experimentally measured lattice energies. [5]

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(d) Element **E** is an element in the third period of the periodic table.

When element **E** is left in open air, its oxide **A** is formed. The oxidation state of **E** in **A** is its maximum. When **A** is dissolved in water, a solution of a different pH is formed due to formation of **B**. When potassium carbonate is slowly added into the solution until no further change, no precipitate is observed, but **C** is formed.

Dissolving the salt **C** in water results in an alkaline solution being formed.

E can be heated in chlorine gas to form **D**. Increasing the pressure of chlorine gas will result in **F** being formed. **F** also dissolves in water to form **B**, but a solution of a low pH results instead.

(i) Deduce the element **E**, and species **A** to **D** and **F**. [7]

(ii) Write balanced chemical equations for all reactions taking place in the description. [7]

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(e) Aluminium isopropoxide is a reducing and oxidising agent in organic chemistry. To prepare aluminium isopropoxide, some aluminium is dissolved in a solution of isopropanol.

Analysis discovers that aluminium isopropoxide contains A*l*—O bonds.

(i) Explain why aluminium can form covalent bonds with oxygen. [2]

(ii) Aluminium isopropoxide can also be formed through aluminium chloride. Describe what happens when a few drops of water is added to anhydrous aluminium chloride. [1]

(iii) When aluminium is added into a solution of sodium hydroxide, a gas is evolved after some time. The gas extinguishes a lighted splint with a 'pop'. The aluminium dissolves and forms a colourless solution.

Construct an ionic equation accounting for the observations. [2]

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[Total: 30]

3 (a) The peroxysulfate ($S_2O_8^{2-}$) ion is a very strong oxidising agent.

When a solution of potassium peroxysulfate is added into a solution of potassium iodide, a yellow colouration is observed. After some time, the solution turns brown.

When a drop of dilute iron(II) sulfate is added, the solution immediately turns brown.

Using relevant standard electrode potential values, explain the above observations. [3]

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(b) A dilute solution of iron(II) sulfate is light green in colour. In contrast, a solution of iron(III) is yellow in colour.

Explain why these solutions are coloured using the crystal field theory, and why solutions of iron(II) and iron(III) ions are different in colour. [3]

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(c) Potassium ferrioxalate ($K_3[Fe(C_2O_4)_3]$) crystals are green in colour. The ferrioxalate ion has an octahedral geometry with respect to the iron(III) centre.

The oxalate ion contains 1 C—C bond and is symmetrical. It acts as a bidentate ligand.

(i) The ferrioxalate ion has 2 enantiomers. Draw the 3 dimensional structures of the 2 enantiomers. [3]

(ii) To make a solution of potassium ferrioxalate, ferric oxalate ($Fe_2(C_2O_4)_3$) needs to be prepared first. Ferric oxalate is yellow in colour.

Explain why there is a difference in colour between both iron(III) and oxalate containing species. [1]

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(d) When iron(III) hydroxide is treated with sodium hypochlorite (NaOC*l*) in aqueous sodium hydroxide, a violet colouration is observed. Subsequently, the violet solution is treated with barium chloride, in which a brown precipitate is formed.

The brown precipitate contains 3 elements.

(i) Given that the brown precipitate contains 53.4% barium and 24.9% oxygen by mass, determine the empirical formula of this brown precipitate. [2]

(ii) Hence, construct 2 equations for the reactions taking place above. [2]

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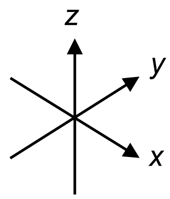
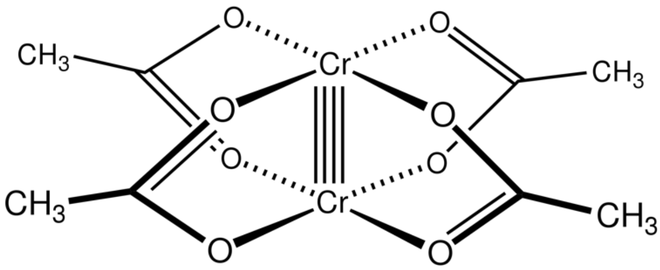
(e) Chromium(II) acetate is a non-ionic compound despite its name. Its molecular formula is $Cr_2(CH_3CO_2)_4$.

The structure of chromium(II) acetate is shown below.





(i) On the structure above, indicate the co-ordinate bond(s) by circling the bond(s). [1]

(ii) Copy and use the x-y-z axes printed on the top right of the structure in its given orientation. On separate axes, draw all the 5 *d* orbitals of chromium. [2]

You must not change the orientation of the axes.

(iii) The chromium-chromium bond has 4 covalent bonds, containing 1 sigma bond, 2 pi bonds, and 1 delta bond.

The delta bond is formed through a side-on overlap of 2 orbitals with 4 lobes.

By considering the given orientation of the axes in the structure and your answer in **(ii)**, state which orbital(s) in the chromium atom are involved in:

- the sigma bond,
- the 2 pi bonds, and
- the delta bond of the Cr—Cr bond. [2]

(iv) Chromium(II) acetate is insoluble in water. It can be prepared through a precipitation reaction between the chromium(II) ion and acetate ion. State how you would obtain the chromium(II) ion from a solution of chromium(III) sulfate. [1]

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