A2 Electrochemistry

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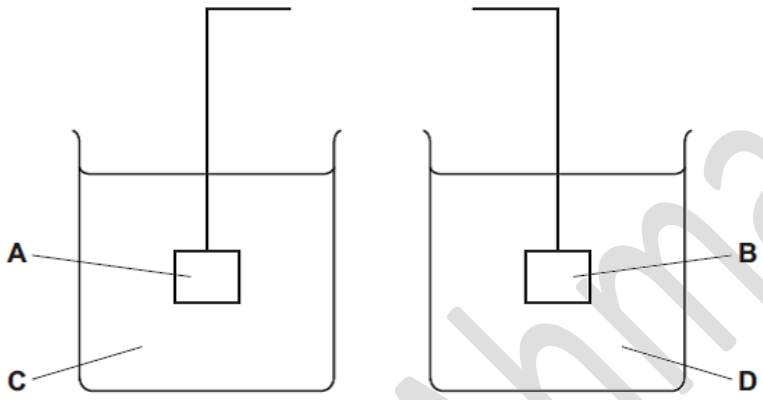
Electrochemistry

(b) The following diagram shows the apparatus used to measure the standard electrode potential, $E^{\ominus}$, of a cell composed of a Cu(II)/Cu electrode and an Fe(II)/Fe electrode.

(i) Finish the diagram by adding components to show the complete circuit. Label the components you add.



(ii) In the spaces below, identify or describe what the four letters **A-D** represent.

A .....

B .....

C .....

D .....

(iii) Use the *Data Booklet* to calculate the $E^{\ominus}$ for this cell.

.....

(iv) Predict how the size of the overall cell potential would change, if at all, as the concentration of solution **C** is increased.
Explain your reasoning.

.....

.....

.....

[8]

(c) The iron(II) complex *ferrous bisglycinate hydrochloride* is sometimes prescribed, in capsule form, to treat iron deficiency or anaemia.
A capsule containing 500 mg of this iron(II) complex was dissolved in dilute H_2SO_4 and titrated with 0.0200 mol dm^{-3} $KMnO_4$.
18.1 cm^3 of $KMnO_4$ solution were required to reach the end point.

The equation for the titration reaction is as follows.

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

(i) Describe how you would recognise the end point of this titration.

.....

(ii) Calculate

- the number of moles of Fe^{2+} in the capsule,

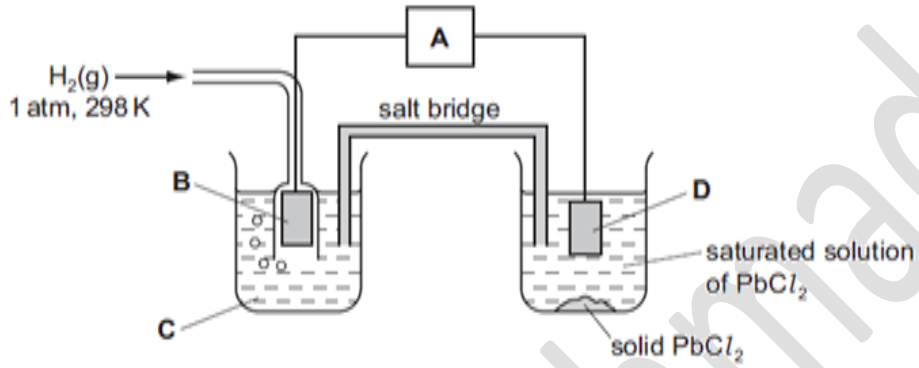
- the mass of iron in the capsule,

- the molar mass of the iron(II) complex, assuming 1 mol of the complex contains 1 mol of iron.

[4]

2 Lead(II) chloride, $PbCl_2$, can be used in the manufacture of some types of coloured glass.

$PbCl_2$ is only sparingly soluble in water. The $[Pb^{2+}]$ in a saturated solution of $PbCl_2$ can be estimated by measuring the cell potential, E_{cell}, of the following cell.



(a) In the spaces below, identify what the four letters **A-D** in the above diagram represent.

A ..... B .....

C ..... D .....

[4]

(b) In a saturated solution of $PbCl_2$, $[PbCl_2(aq)] = 3.5 \times 10^{-2}$ mol dm^{-3}.

(i) The $E^{\ominus}$ for the Pb^{2+}/Pb electrode is -0.13 V. Predict the potential of the right-hand electrode in the diagram above. Indicate this by placing a tick in the appropriate box in the table below.

electrode potential / V	place **one tick only** in this column
−0.17	
−0.13	
−0.09	
0.00	

Explain your answer.

.....

.....

(c) The behaviours of $PbCl_2$ and $SnCl_2$ towards reducing agents are similar, but their behaviours towards oxidising agents are very different.

(i) Illustrate this comparison by quoting and comparing relevant $E^\ominus$ values for the two metals and their ions. Explain what the relative $E^\ominus$ values mean in terms of the ease of oxidation or reduction of these compounds.

.....

.....

.....

.....

.....

.....

(ii) Writing a balanced molecular or ionic equation in each case, suggest a reagent to carry out each of the following reactions.

the reduction of $PbCl_2$

.....

the oxidation of $SnCl_2$

.....

[5]

s/14/qp42

(c) When aqueous solutions of KI and $K_2S_2O_8$ are mixed almost no reaction occurs, but when a few drops of $Fe^{2+}(aq)$ or $Fe^{3+}(aq)$ are added, iodine, $I_2(aq)$, is produced at a steady rate.

(i) Write an equation for the overall reaction.

.....

(ii) State the precise role of the iron ions during this reaction.

.....

(iii) By means of equations or otherwise, explain why the presence of *either* Fe^{2+} *or* Fe^{3+} is able to speed up the reaction.

.....

.....

.....

[3]

s/14/qp42

2 (a) (i) With the aid of a fully-labelled diagram, describe the standard hydrogen electrode.

(ii) Use the *Data Booklet* to calculate the standard cell potential for the reaction between Cr^{2+} ions and $Cr_2O_7^{2-}$ ions in acid solution, and construct a balanced equation for the reaction.

$E^{\ominus}_{cell}$ = ... V

equation .....

(iii) Describe what you would see if a blue solution of Cr^{2+} ions was added to an acidified solution of $Cr_2O_7^{2-}$ ions until reaction was complete.

.....

.....

[8]

s/13/qp42

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

1 **(a)** What is meant by the term *standard electrode potential*, SEP?

.....

.....

[2]

(b) Draw a fully labelled diagram of the apparatus you could use to measure the SEP of the Fe^{3+}/Fe^{2+} electrode.

[5]

(c) The reaction between Fe^{3+} ions and I^- ions is an equilibrium reaction.

$$2Fe^{3+}(aq) + 2I^-(aq) \rightleftharpoons 2Fe^{2+}(aq) + I_2(aq)$$

(i) Use the *Data Booklet* to calculate the $E^{\ominus}_{cell}$ for this reaction.

.....

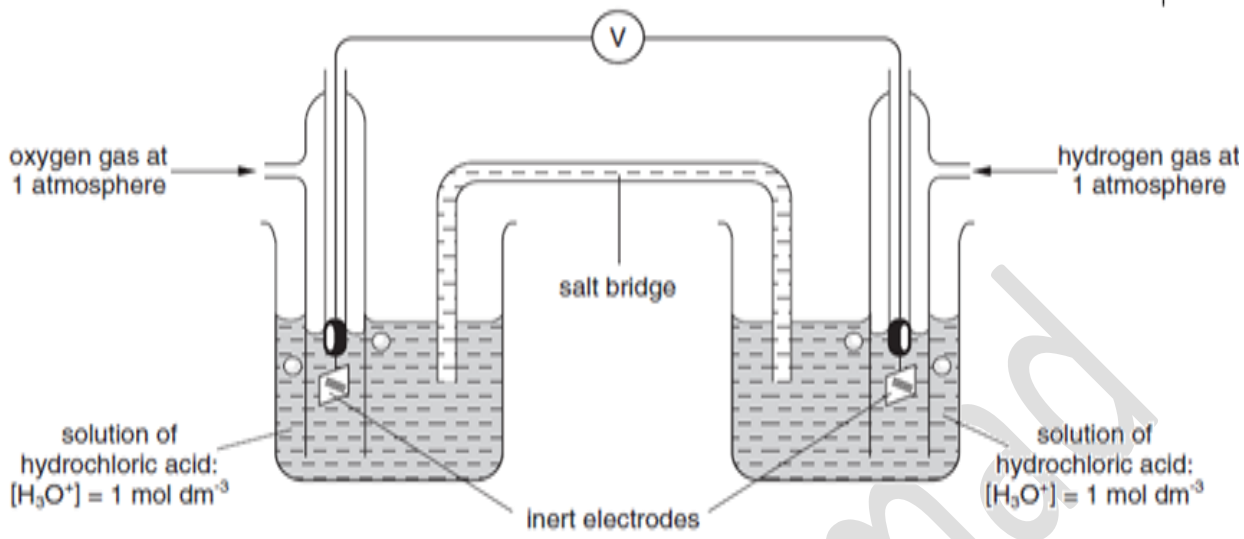
(ii) Hence state, with a reason, whether there will be more products or more reactants at equilibrium.

.....

.....

Use

2 The diagram shows a laboratory illustration of a simple hydrogen-oxygen fuel cell.



(a) Write the half equation for the reaction occurring at the left hand (oxygen) electrode when the cell operates.

.....

..... [1]

(b) State the polarity (+ or –) of the left hand (oxygen) electrode. ..... [1]

(c) Use the *Data Booklet* to calculate the voltage produced by this cell.

..... [1]

(d) Only a very small current can be drawn from this laboratory cell. Suggest **one** way in which it could be modified to enable a larger current to be drawn from it.

.....

..... [1]

(e) A fuel cell in an orbiting satellite is required to produce a current of 0.010 A for 400 days. Calculate the mass of hydrogen that will be needed.

.....

.....

..... [3]

(f) State **one** advantage, and **one** disadvantage of using fuel cells to power road vehicles compared to hydrocarbon fuels such as petrol.

advantage: .....

.....

disadvantage: .....

..... [2]

[Total: 9]

w/04/qp4

2 **(a)** What do you understand by the term *standard electrode potential*?

.....

..... [2]

(b) By reference to relevant $E^{\ominus}$ data in the *Data Booklet*, explain how the halogen/halide electrode potentials relate to the relative reactivity of the halogens as oxidising agents.

.....

.....

..... [2]

(c) Use data from the *Data Booklet* to construct redox equations, and calculate the standard cell potentials, for the reactions between

(i) Acidified $H_2O_2(aq)$ and KI(aq),

.....

(ii) $Cl_2(aq) + SO_2(aq)$.

.....

[4]

(d) Use data from the *Data Booklet* to predict the likely product of the reaction between $I_2(aq)$ and tin metal, writing a balanced equation for the reaction.

..... [2]

[Total: 10]

w/05/qp4

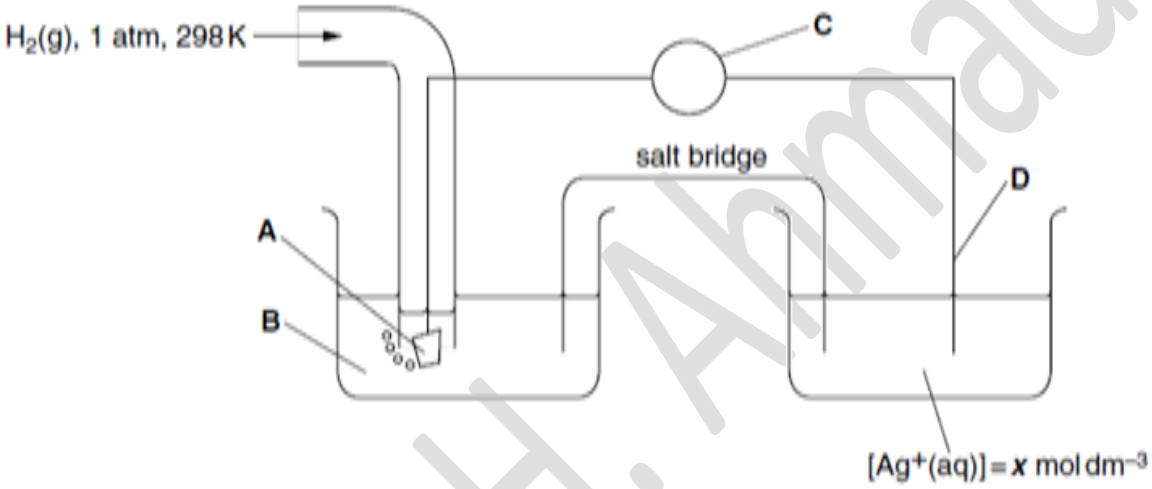
1 Silver bromide, AgBr, is widely used in photography. In a photographic film, AgBr crystals are precipitated into a gelatine base as 'grains' of diameter about 1×10^{-6} m.

(a) Calculate the approximate number of silver ions contained in a grain of AgBr of mass 2.5×10^{-12} g.

.....

..... [2]

(b) AgBr is only sparingly soluble in water. The $[Ag^+]$ in a saturated solution of AgBr can be estimated by measuring the E_{cell} of the following cell.



(I) In the spaces below, identify what the four letters **A** – **D** in the above diagram represent.

A ..... **C** .....

B ..... **D** .....

(II) Predict how the potential of the right hand electrode might vary as $[Ag^+]$ is decreased.

.....

In its saturated solution, $[AgBr(aq)] = 7.1 \times 10^{-7}$ mol dm^{-3}.

(III) Write an expression for the solubility product of AgBr, and calculate its value, including units.

.....

.....

[7]

w/05/qp4

3 Potassium manganate(VII) and potassium dichromate(VI) are both used as oxidising agents in acidic solution.

(a) Using data from the *Data Booklet*, write *either* ionic *or* full equations for the reaction between

(i) $KMnO_4$ and $FeSO_4$ in dilute H_2SO_4,

(ii) $K_2Cr_2O_7$ and SO_2 in dilute H_2SO_4.

[3]

(b) $KMnO_4$ is often used in titrations to estimate reducing agents. It is added from a burette to a solution of the reducing agent.

(i) What colour is $KMnO_4$ solution?

.....

(ii) How is the end point in the titration recognised?

.....

(iii) A solution of 0.010 mol dm^{-3} $KMnO_4$ was used to estimate the amount of $FeSO_4$ in an iron dietary supplement tablet. The tablet was crushed under dilute H_2SO_4 and the $KMnO_4$ solution was added from the burette. It was found that 14.00 cm^3 were required.

Calculate the mass of $FeSO_4$ in the tablet.

.....

.....

.....

.....

[5]

3 **(a)** A transition element **X** has the electronic configuration [Ar] $4s^2$ $3d^3$.

(i) Predict its likely oxidation states.

.....

(ii) State the electronic configuration of the ion X^{3+}.

.....

[2]

(b) Potassium manganate(VII), $KMnO_4$, is a useful oxidising agent in titrimetric analysis.

(i) Describe how you could use a 0.0200 mol dm^{-3} solution of $KMnO_4$ to determine accurately the [Fe^{2+}] in a solution. Include in your description how you would recognise the end-point in the titration, and write an equation for the titration reaction.

.....

.....

.....

.....

.....

.....

(ii) A 2.00 g sample of iron ore was dissolved in dilute H_2SO_4 and all the iron in the salts produced was reduced to $Fe^{2+}(aq)$. The solution was made up to a total volume of 100 cm^3.

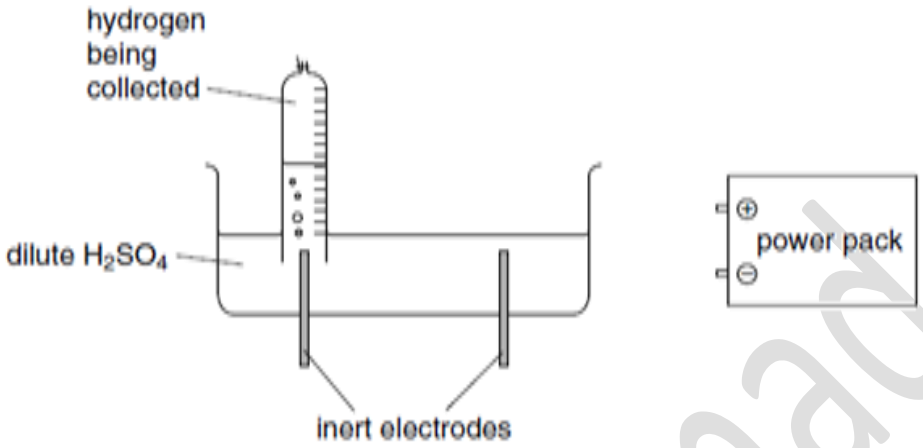
A 25.0 cm^3 portion of the solution required 14.0 cm^3 of 0.0200 mol dm^{-3} $KMnO_4$ to reach the end-point.

Calculate the percentage of iron in the ore.

.....

[8]

1 A student decided to determine the value of the Faraday constant by an electrolysis experiment. The following incomplete diagram shows the apparatus that was used.



(a) **(i)** Apart from connecting wires, what **two** additional pieces of equipment are needed for this experiment?

.....

.....

(ii) Complete the diagram, showing additional equipment connected in the circuit, and showing the powerpack connected to the correct electrodes.

(iii) List the measurements the student would need to make in order to use the results to calculate a value for the Faraday constant.

.....

.....

.....

.....

[7]

(b) **(i)** Using an equation, state the relationship between the Faraday constant, *F*, the Avogadro constant, *L*, and the charge on the electron, *e*.

.....

(ii) The value the student obtained was: 1 Faraday = 9.63×10^4 Coulombs

Use this value and your equation in **(b)(i)** to calculate the Avogadro constant (take the charge on the electron to be 1.60×10^{-19} Coulombs)

.....

.....

[2]

[Total: 9]

w/05/qp4

1 Magnesium is used extensively in the form of alloys as a constructional material due to its low density ($1.7\,g\,cm^{-3}$, compared to $7.8\,g\,cm^{-3}$ for iron). It is usually prepared by the electrolysis of magnesium chloride, $MgCl_2$, at a temperature a little above its melting point of 715 °C.

(a) Suggest the half-equation that represents the production of magnesium at the cathode during the electrolysis.

.....[1]

(b) What will be the product at the other electrode?

.....[1]

(c) Suggest **two** properties of its atoms that could explain why magnesium is less dense than iron.

.....

.....[2]

s/04/qp4

(c) The last oxide in Group IV, PbO_2, reacts with concentrated hydrochloric acid liberating chlorine gas.

Use the *Data Booklet* to calculate the $E^{\ominus}_{cell}$ and to write a balanced equation for this reaction.

.....

.....[2]

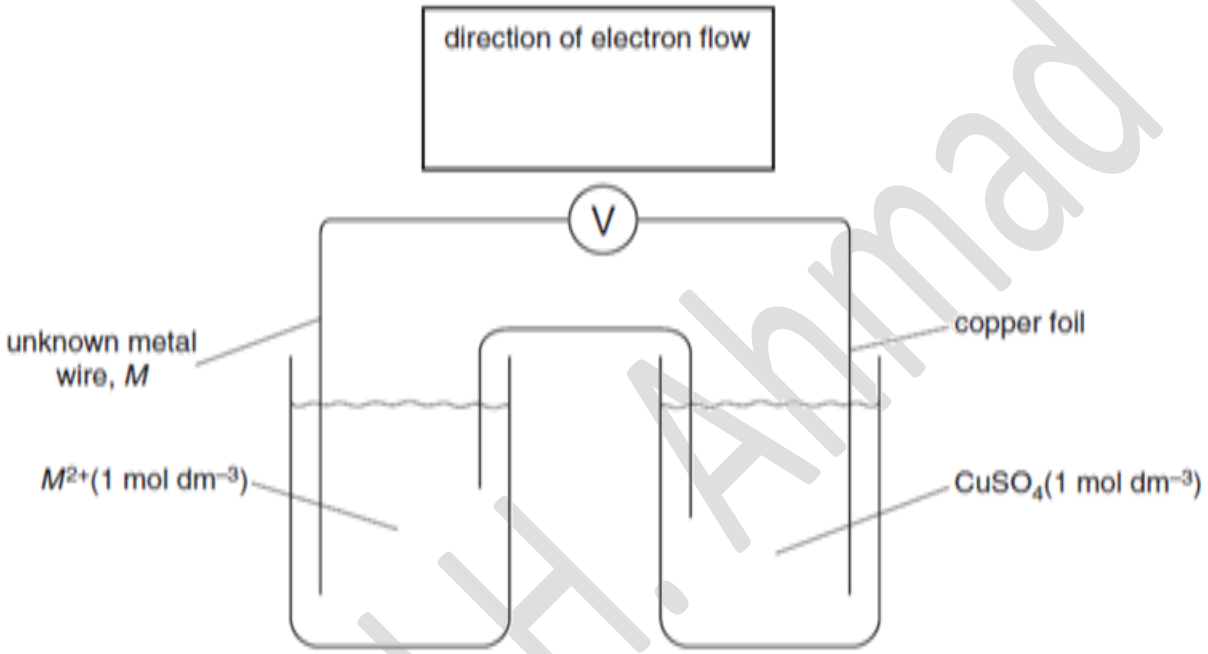
s/03/qp4

1 **(a)** What do you understand by the term *standard electrode potential*?

.....

.....[2]

(b) The following cell was set up between a copper electrode and an unknown metal electrode $M^{2+}(aq)/M(s)$. The standard cell potential was found to be 0.76 V, and the copper foil was the positive electrode.



(i) Use the *Data Booklet* to calculate the standard electrode potential of the $M^{2+}(aq)/M(s)$ system.

.....

(ii) Draw an arrow over the voltmeter symbol in the above diagram to show the direction of electron flow through the voltmeter.

(iii) Predict the outcomes of the following situations. Describe what you might see and write ionic equations for any reactions that occur.

I A rod of metal *M* is dipped into a solution of 1 mol dm^{-3} $CuSO_4$.

.....

.....

.....

II Dilute sulphuric acid is added to a beaker containing a powdered sample of metal *M*.

.....

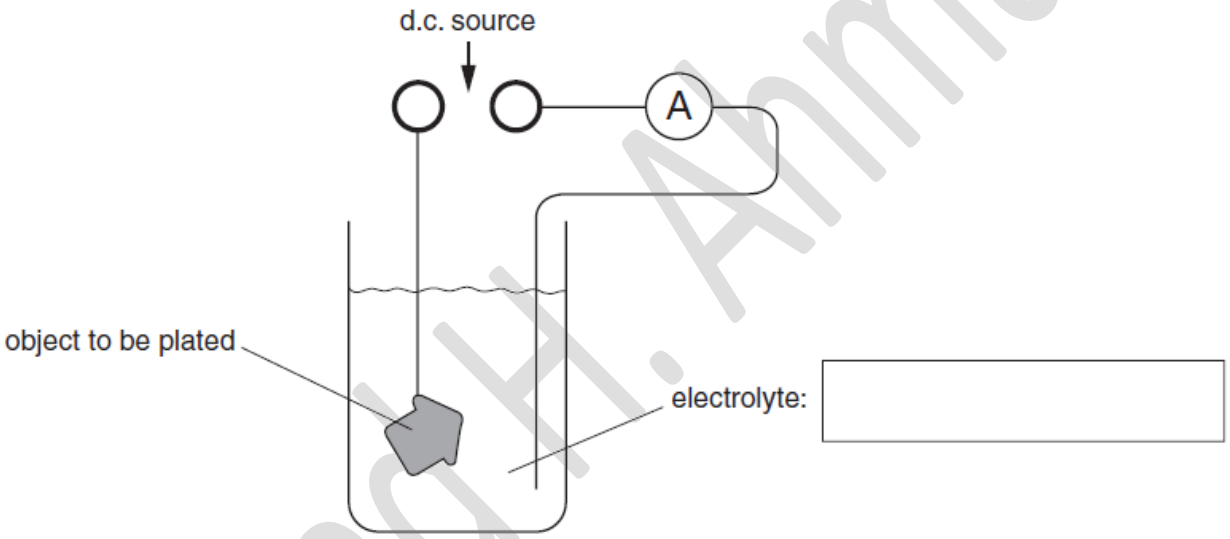
.....

.....

[6]

(c) Because of its increased scarcity, cheaper copper ornaments are no longer made from the solid metal, but from iron that has been copper plated.

(i) Complete the following diagram showing the set-up for a copper electroplating process. Show clearly the polarity (+/–) of the power source, and suggest a suitable electrolyte.



(ii) A current of 0.500 A is passed through the electroplating cell. Calculate the time required to deposit a mass of 0.500 g of copper on to the ornament.

.....

.....

.....

[5]

[Total : 13]

s/03/qp4

4 **(a)** Complete the electronic configuration of the Fe^{3+} ion.

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ ..... [1]

(b) By quoting suitable data from the *Data Booklet*, explain how $E^{\ominus}$ values can be used to show the relative oxidising abilities of

(i) the halogens Cl_2, Br_2, I_2,

.....

.....

(ii) the transition metal ions Cr^{3+}, Fe^{3+}, Co^{3+}.

.....

.....

[3]

(c) Use these $E^{\ominus}$ values to predict whether a reaction will occur when the following pairs of aqueous solutions are mixed. If a reaction occurs, write a balanced equation and calculate the $E^{\ominus}_{cell}$.

(i) $Fe^{3+}(aq)$ and $Cl^-(aq)$

.....

.....

(ii) $Co^{3+}(aq)$ and $Br^-(aq)$

.....

.....

(iii) $Cr^{2+}(aq)$ and $I_2(aq)$

.....

.....

[4]

[Total: 8]

s/02/qp4

(c) Draw a fully-labelled diagram of the apparatus you could use to measure the $E^{\ominus}$ of a cell composed of the Fe^{3+}/Fe^{2+} electrode and the Cu^{2+}/Cu electrode.

[5]

(d) The $E^{\ominus}$ for Cu^{2+}/Cu is +0.34 V. When $NH_3(aq)$ is added to the electrode solution, the $E_{electrode}$ changes.

(i) Describe the type of reaction taking place between $Cu^{2+}(aq)$ and $NH_3(aq)$.

.....

(ii) Write an equation for the reaction.

.....

(iii) Describe the change in the colour of the solution.

.....

(iv) Predict and explain how the $E_{electrode}$ might change on the addition of $NH_3(aq)$.

.....

.....

[4]

w/12/qp43

3 (a) Catalysts can be described as homogeneous or heterogeneous.

(i) What is meant by the terms *homogeneous* and *heterogeneous*?

.....

.....

(ii) By using iron and its compounds as examples, outline the different modes of action of homogeneous and heterogeneous catalysis.
Choose **one** example of each type, and for **each** example you should

- state what the catalyst is, and whether it is acting as a homogeneous or a heterogeneous catalyst,
- write a balanced equation for the reaction,
- outline how the catalyst you have chosen works to decrease the activation energy.

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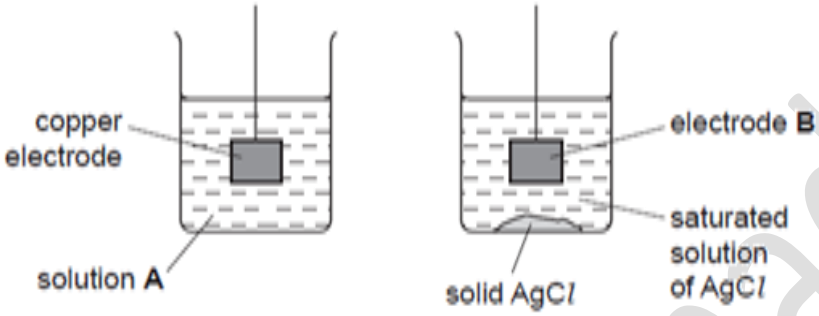
[8]

w/12/qp41

2 (a) The diagram below shows an incomplete experimental set-up needed to measure the E_{cell} of a cell composed of the standard Cu^{2+}/Cu electrode and an Ag^{+}/Ag electrode.



(i) State the chemical composition of

solution **A**, ...

electrode **B**. .....

(ii) Complete the diagram to show the whole experimental set-up.

[4]

(b) The above cell is not under standard conditions, because the $[Ag^{+}]$ in a saturated solution of AgCl is much less than 1.0 mol dm^{-3}. The $E_{electrode}$ is related to $[Ag^{+}]$ by the following equation.

equation 1 $\quad E_{electrode} = E^{\ominus}_{electrode} + 0.06 \log[Ag^{+}]$

(i) Use the *Data Booklet* to calculate the $E^{\ominus}_{cell}$ if the cell was operating under standard conditions.

$E^{\ominus}_{cell}$ = ... V

In the above experiment, the E_{cell} was measured at +0.17V.

(ii) Calculate the value of $E_{electrode}$ for the Ag^{+}/Ag electrode in this experiment.

.....

(iii) Use equation 1 to calculate $[Ag^{+}]$ in the saturated solution.

$[Ag^{+}]$ = ... mol dm^{-3}

[3]

w/12/qp41

1 **(a)** Write down what you would see, and write equations for the reactions that occur, when silicon(IV) chloride and phosphorus(V) chloride are separately mixed with water.

silicon(IV) chloride

.....

.....

phosphorus(V) chloride

.....

.....

[4]

(b) Iron(III) chloride, $FeCl_3$, is used to dissolve unwanted copper from printed circuit boards (PCBs) by the following reaction.

$$2FeCl_3(aq) + Cu(s) \rightarrow 2FeCl_2(aq) + CuCl_2(aq)$$

A solution in which $[Fe^{3+}(aq)]$ was originally equal to 1.50 mol dm^{-3} was re-used several times to dissolve copper from the PCBs, and was then titrated as follows.

A 2.50 cm^3 sample of the partially-used-up solution was acidified and titrated with 0.0200 mol dm^{-3} $KMnO_4$.
This oxidised any $FeCl_2$ in the solution back to $FeCl_3$.
It was found that 15.0 cm^3 of $KMnO_4(aq)$ was required to reach the end point.

(i) Construct an ionic equation for the reaction between Fe^{2+} and MnO_4^- in acid solution.

.....

(ii) State here the Fe^{2+} : MnO_4^- ratio from your equation in **(i)**. .....

(iii) Calculate the number of moles of MnO_4^- used in the titration.

(iv) Calculate the number of moles of Fe^{2+} in 2.50 cm^3 of the partially-used-up solution.

(v) Calculate the $[Fe^{2+}]$ in the partially-used-up solution.

(vi) Calculate the mass of copper that could still be dissolved by 100 cm^3 of the partially-used-up solution.

mass of copper = ... g
[6]

w/12/qp41

1 **(a)** Complete the electronic configurations of the following ions.

Cr^{3+}: $1s^2 2s^2 2p^6$.....

Mn^{2+}: $1s^2 2s^2 2p^6$.....

[2]

(b) Both $KMnO_4$ and $K_2Cr_2O_7$ are used as oxidising agents, usually in acidic solution.

(i) Use information from the *Data Booklet* to explain why their oxidising power increases as the $[H^+(aq)]$ in the solution increases.

.....

.....

.....

(ii) What colour changes would you observe when each of these oxidising agents is completely reduced?

- $KMnO_4$

  from ..... to .....

- $K_2Cr_2O_7$

  from..... to .....

[4]

(c) Manganese(IV) oxide, MnO_2, is a dark brown solid, insoluble in water and dilute acids. Passing a stream of $SO_2(g)$ through a suspension of MnO_2 in water does, however, cause it to dissolve, to give a colourless solution.

(i) Use the *Data Booklet* to suggest an equation for this reaction, and explain what happens to the oxidation states of manganese and of sulfur during the reaction.

.....

.....

.....

(ii) The pH of the suspension of MnO_2 is reduced.
Explain what effect, if any, this would have on the extent of this reaction.

.....

.....

[4]

(d) The main ore of manganese, pyrolusite, is mainly MnO_2. A solution of $SnCl_2$ can be used to estimate the percentage of MnO_2 in a sample of pyrolusite, using the following method.

- A known mass of pyrolusite is warmed with an acidified solution containing a known amount of $SnCl_2$.
- The excess $Sn^{2+}(aq)$ ions are titrated with a standard solution of $KMnO_4$.

In one such experiment, 0.100 g of pyrolusite was warmed with an acidified solution containing 2.00×10^{-3} mol Sn^{2+}. After the reaction was complete, the mixture was titrated with 0.0200 mol dm^{-3} $KMnO_4$, and required 18.1 cm^3 of this solution to reach the end point.

The equation for the reaction between $Sn^{2+}(aq)$ and $MnO_4^-(aq)$ is as follows.

$$2MnO_4^- + 5Sn^{2+} + 16H^+ \rightarrow 2Mn^{2+} + 5Sn^{4+} + 8H_2O$$

(i) Use the *Data Booklet* to construct an equation for the reaction between MnO_2 and Sn^{2+} ions in acidic solution.

.....

(ii) Calculate the percentage of MnO_2 in this sample of pyrolusite by the following steps.

- number of moles of MnO_4^- used in the titration

- number of moles of Sn^{2+} this MnO_4^- reacted with

- number of moles of Sn^{2+} that reacted with the 0.100 g sample of pyrolusite

- number of moles of MnO_2 in 0.100 g pyrolusite. Use your equation in **(i)**.

- mass of MnO_2 in 0.100 g pyrolusite

- percentage of MnO_2 in pyrolusite

percentage = ... %
[6]

[Total: 16]

5 Chlorine is manufactured by the electrolysis of brine, NaCl(aq). At the cathode, $H_2(g)$ and $OH^-(aq)$ are produced, but the product at the anode depends on the [NaCl(aq)] in the solution. Either $O_2(g)$ or $Cl_2(g)$ is produced.

(a) The equation for the cathode reaction is $2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$.

Starting from **neutral** NaCl(aq), write equations for the production at the anode of

(i) $O_2(g)$, ...

(ii) $Cl_2(g)$. .....

[2]

(b) For electrolysis to occur, the voltage applied to the cell must be at least as large as the $E^{\ominus}_{cell}$, as calculated from standard electrode potentials.
Use the *Data Booklet* to calculate $E^{\ominus}_{cell}$ for the production at the anode of

(i) $O_2(g)$, ...

(ii) $Cl_2(g)$. .....

[2]

(c) **(i)** By using **one** of the phrases *more positive*, *less positive* or *no change*, use the equations you wrote in **(a)** to deduce the effect of increasing $[Cl^-(aq)]$ on

- the E_{anode} for the production of $O_2(g)$, ...
- the E_{anode} for the production of $Cl_2(g)$. .....

(ii) Hence explain why the $Cl_2(g) : O_2(g)$ ratio increases as [NaCl(aq)] increases.

.....

.....[3]

(d) Sodium chlorate(V) is prepared commercially by electrolysing NaCl(aq) in a cell which allows the cathode and anode electrolytes to mix.
The cathode reaction is the same as that described in **(a)**.
The equation for the anode reaction is

$$Cl^-(aq) + 6OH^-(aq) - 6e^- \longrightarrow ClO_3^-(aq) + 3H_2O(l)$$

(i) Construct an ionic equation for the overall reaction.

.....

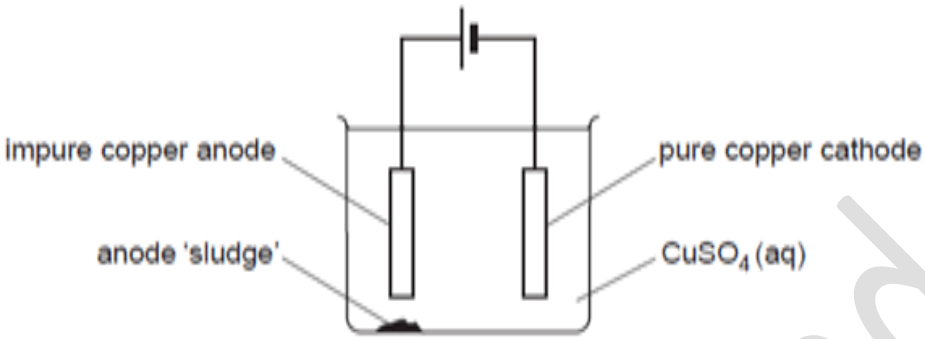
(ii) Calculate the mass of $NaClO_3$ that is produced when a current of 250 A is passed through the cell for 60 minutes.

mass of $NaClO_3$ = ... g [4]

[Total: 11]

w/10/qp43

3 The electrolytic purification of copper can be carried out in an apparatus similar to the one shown below.



The impure copper anode contains small quantities of metallic nickel, zinc and silver, together with inert oxides and carbon resulting from the initial reduction of the copper ore with coke. The copper goes into solution at the anode, but the silver remains as the metal and falls to the bottom as part of the anode 'sludge'. The zinc also dissolves.

(a) (i) Write a half equation including state symbols for the reaction of copper at the anode.

.....

(ii) Use data from the *Data Booklet* to explain why silver remains as the metal.

.....

(iii) Use data from the *Data Booklet* to predict what happens to the nickel at the anode.

.....

.....

(iv) Write a half equation including state symbols for the main reaction at the cathode.

.....

(v) Use data from the *Data Booklet* to explain why zinc is not deposited on the cathode.

.....

.....

(vi) Suggest why the blue colour of the electrolyte slowly fades as the electrolysis proceeds.

.....

.....

[7]

(b) Most of the current passed through the cell is used to dissolve the copper at the anode and precipitate pure copper onto the cathode. However, a small proportion of it is 'wasted' in dissolving the impurities at the anode which then remain in solution.
When a current of 20.0 A was passed through the cell for 10.0 hours, it was found that 225 g of pure copper was deposited on the cathode.

(i) Calculate the following, using appropriate data from the *Data Booklet*.

- number of moles of copper produced at the cathode

- number of moles of electrons needed to produce this copper

- number of moles of electrons that passed through the cell

(ii) Hence calculate the percentage of the current through the cell that has been 'wasted' in dissolving the impurities at the anode.

[4]

(c) Nickel often occurs in ores along with iron. After the initial reduction of the ore with coke, a nickel-iron alloy is formed.
Use data from the *Data Booklet* to explain why nickel can be purified by a similar electrolysis technique to that used for copper, using an impure nickel anode, a pure nickel cathode, and nickel sulfate as the electrolyte. Explain what would happen to the iron during this process.

.....

.....

.....

.....[2]

[Total: 13]

(d) Outline the role that Fe^{3+} ions play in catalysing the reaction between iodide ions and peroxydisulfate(VI) ions.

$$2I^- + S_2O_8^{2-} \longrightarrow I_2 + 2SO_4^{2-}$$

.....

.....

.....[2]

[Total: 14]

w/09/qp42

(d) Tin forms an oxide, **A**, that contains the metal in both oxidation states II and IV. The formula of **A** can be found by the following method.

- A sample of **A** was dissolved in $H_2SO_4(aq)$, producing solution **B**, which was a mixture of tin(II) sulfate and tin(IV) sulfate.
- A 25.0 cm^3 sample of solution **B** was titrated with 0.0200 mol dm^{-3} $KMnO_4$. 13.5 cm^3 of $KMnO_4$ was required to reach the end-point.
- Another 25.0 cm^3 sample of solution **B** was stirred with an excess of powdered zinc. This converted all the tin into tin(II). The excess of zinc powder was filtered off and the filtrate was titrated with 0.0200 mol dm^{-3} $KMnO_4$, as before. This time 20.3 cm^3 of $KMnO_4$ was required to reach the end-point.

The equation for the reaction occurring during the titration is as follows.

$$2MnO_4^- + 16H^+ + 5Sn^{2+} \longrightarrow 2Mn^{2+} + 8H_2O + 5Sn^{4+}$$

(i) Write a balanced equation for the reaction between Zn and Sn^{4+}.

.....

(ii) Use the *Data Booklet* to calculate the $E^\ominus$ values for the reactions between

- Zn and Sn^{4+}, ...
- MnO_4^- and Sn^{2+}.....

(iii) Use the results of the two titrations to calculate

- the number of moles of Sn^{2+} in the first titration sample,

.....

.....

- the number of moles of Sn^{2+} in the second titration sample.

.....

.....

(iv) Use the results of your calculation in **(iii)** to deduce the Sn^{2+}/Sn^{4+} ratio in the oxide **A**, and hence suggest the formula of **A**.

.....

.....

.....

[8]

(e) A major use of tin is to make 'tin plate', which is composed of thin sheets of mild steel electroplated with tin, for use in the manufacture of food and drinks cans. A tin coating of 1.0×10^{-5} m thickness is often used.

(i) Calculate the volume of tin needed to coat a sheet of steel 1.0 m × 1.0 m to this thickness, on one side only.

.....

.....

(ii) Calculate the number of moles of tin that this volume represents.
[The density of tin is 7.3 g cm^{-3}.]

.....

.....

.....

(iii) The solution used for electroplating contains Sn^{2+} ions. Calculate the quantity of electricity in coulombs needed to deposit the amount of tin you calculated in **(ii)**.

.....

.....

.....

[4]

w/09/qp41

5 Potassium manganate(VII) can be used to estimate the percentage of hydrogen peroxide in household bleach. The following unbalanced equation represents the reaction between them.

..... MnO_4^- + ... H_2O_2 + ... H^+ ⟶ ..... Mn^{2+} + ... H_2O + ... O_2

(a) Balance this equation by putting the appropriate numbers in the spaces above. [1]

(b) Use data from the *Data Booklet* to calculate the $E^{\ominus}_{cell}$ for the reaction.

.....[1]

(c) When 0.020 mol dm^{-3} $KMnO_4$(aq) was added from a burette into an acidified 25.0 cm^3 sample of H_2O_2, 15.0 cm^3 of $KMnO_4$ was required to reach the end-point.

(i) Describe what you would see during this titration, and also at the end-point.

.....

.....

(ii) Calculate the concentration of H_2O_2 in the sample.

.....

.....

.....

[4]

[Total: 6]

w/07/qp4

3 The following account describes the preparation of Péligot's salt, named after the 19th century French chemist who first made it.

Place 6.0 g of potassium dichromate(VI) in a 100 cm^3 beaker and add 8.0 g of concentrated hydrochloric acid and 1.0 cm^3 water. Warm the mixture gently; if carefully done the dichromate(VI) will dissolve without the evolution of chlorine. On cooling the beaker in an ice bath the solution will deposit long orange-red crystals of Péligot's salt.

An analysis of Péligot's salt showed that it contained the following percentages by mass:
K, 22.4%; Cr, 29.8%; Cl, 20.3%; O, 27.5%.

(a) Calculate the empirical formula of Péligot's salt.

[2]

(b) Suggest a balanced equation for the formation of Péligot's salt.

.....[1]

(c) The instructions suggest that strong heating might cause chlorine to be evolved.

(i) What *type of reaction* would produce chlorine in this system?

.....

(ii) Use the *Data Booklet* to identify relevant half equations and $E^\ominus$ values for the production of chlorine from the reaction between $K_2Cr_2O_7$ and HCl.

.....

.....

Use these equations to write the overall full ionic equation for this reaction.

.....

(iii) The use of **dilute** HCl(aq) does not result in the production of chlorine. Suggest why this is so.

.....

(iv) Use the *Data Booklet* to suggest a reason why it is **not** possible to prepare the bromine analogue of Péligot's salt by using HBr(aq) instead of HCl(aq).

.....

[6]

[Total: 9]

w/07/qp4

(c) The following information on half-reactions relates to the reaction between HNO_3 and an excess of $FeSO_4$.

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad E^\ominus = +0.77\,V$$

$$3H^+ + NO_3^- + 2e^- \rightarrow HNO_2 + H_2O \qquad E^\ominus = +0.94\,V$$

$$HNO_2 + H^+ + e^- \rightarrow NO + H_2O \qquad E^\ominus = +0.99\,V$$

(i) Suggest the formula of the nitrogen-containing final product of this reaction.

.....

(ii) Write an equation for the formation of this nitrogen-containing product.

s/12/qp41

3 **(a)** State the relationship between the Faraday constant, *F*, the charge on the electron, *e*, and the Avogadro number, *L*.

.....[1]

(b) If the charge on the electron, the A_r and the valency of copper are known, the value of the Avogadro number can be determined experimentally. This is done by passing a known current for a known time through a copper electrolysis cell, and weighing the mass of copper deposited onto the cathode.

(i) Draw a diagram of suitable apparatus for carrying out this experiment.
Label the following: power supply (with + and – terminals); anode; cathode; and ammeter.
State the composition of the electrolyte.

The following are the results obtained from one such experiment.

current passed through the cell	=	0.500 A
time current was passed through cell	=	30.0 min
initial mass of copper cathode	=	52.243 g
final mass of copper cathode	=	52.542 g

(ii) Use these data and relevant information from the *Data Booklet* to calculate a value of *L* to **3 significant figures**.

L = ...
[9]

(c) Use relevant information from the *Data Booklet* to identify the substances formed at the anode and at the cathode when aqueous solutions of the following compounds are electrolysed.

compound	product at anode	product at cathode
AgF		
$FeSO_4$		
$MgBr_2$		

[5]

[Total: 15]

s/11/qp43

8 The design and development of batteries has been a major research area in recent years.

(a) Lead-acid batteries, used in cars, are made up of a number of rechargeable cells in series, and were first developed in 1860. They have the disadvantage of a relatively high mass compared to the energy stored. During discharge, the electrode reactions in the cells of these batteries are as follows.

I $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$

II $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$

State which of these reactions occurs at the positive electrode in a lead-acid cell during discharge, explaining your answer.

.....

.....[1]

(b) Use the *Data Booklet* and the equations **I** and **II** above to calculate the voltage produced by a lead-acid cell under standard conditions.

[2]

(c) Nickel-metal hydride batteries were developed in the 1980s and have become increasingly common particularly for small devices such as mobile phones and digital cameras that need near-constant sources of electrical energy. These cells use nickel oxohydroxide (NiO(OH)) as one electrode and a hydrogen-absorbing alloy such as $LiNi_5$ as the other electrode.

One reaction that takes place in these batteries is

$$NiO(OH) + H_2O + e^- \rightleftharpoons Ni(OH)_2 + OH^-$$

(i) State the oxidation state of nickel in NiO(OH). .....

(ii) Suggest a likely advantage of these batteries compared with lead-acid batteries.

.....

.....

[2]

(d) Hydrogen fuel cells have been suggested as the next major advance in electrically powered vehicles. In these fuel cells hydrogen is oxidized to produce water, using a catalyst and inert electrodes.

(i) Suggest a material for the electrodes.

.....

(ii) Use your knowledge of hydrogen to suggest a disadvantage of these fuel cells in powering vehicles.

.....

.....

[2]

s/10/qp43

4 **(a)** Complete the electronic structures of the Cr^{3+} and Mn^{2+} ions.

Cr^{3+} $1s^2 2s^2 2p^6$ .....

Mn^{2+} $1s^2 2s^2 2p^6$ .....

[2]

(b) **(i)** Describe what observations you would make when dilute $KMnO_4(aq)$ is added slowly and with shaking to an acidified solution of $FeSO_4(aq)$ until the $KMnO_4$ is in a large excess.

.....

.....

.....

.....

.....

.....

(ii) Construct an ionic equation for the reaction that occurs.

.....

[4]

(c) By selecting relevant $E^{\ominus}$ data from the *Data Booklet* explain why acidified solutions of $Fe^{2+}(aq)$ are relatively stable to oxidation by air, whereas a freshly prepared precipitate of $Fe(OH)_2$ is readily oxidised to $Fe(OH)_3$ under alkaline conditions.

relevant $E^{\ominus}$ values and half equations

.....

.....

.....

.....

explanation

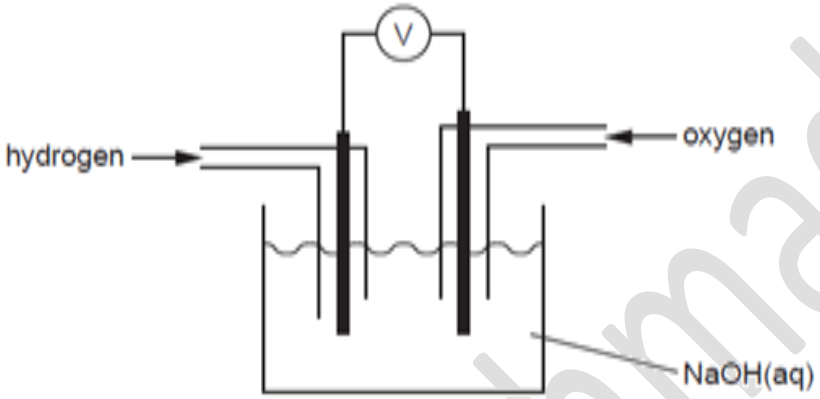
.....

.....

[4]

5 Although standard electrode potentials are measured for solutions where the concentrations of ions are 1.0 mol dm^{-3}, cells used as sources of battery power tend to operate with more concentrated solutions. This question concerns the electrode reactions involved in the hydrogen-oxygen fuel cell and the lead-acid car battery.

(a) In the hydrogen-oxygen fuel cell, $H_2(g)$ and $O_2(g)$ are fed onto two inert electrodes dipping into NaOH(aq).



The following reactions take place.

left hand electrode (cathode): $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$

right hand electrode (anode): $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

(i) Use the *Data Booklet* to calculate $E^{\ominus}_{cell}$ for this reaction.

.....

(ii) Construct an equation for the overall reaction.

.....

(iii) By using **one** of the phrases *more positive*, *more negative* or *no change*, deduce the effect of increasing $[OH^-(aq)]$ on the electrode potential of

- the left hand electrode .....
- the right hand electrode .....

(iv) Hence deduce whether the overall E_{cell} is likely to *increase*, *decrease* or *remain the same*, when $[OH^-(aq)]$ increases. Explain your answer.

.....

.....

(v) Suggest **one** other reason why a high [NaOH(aq)] is used in the fuel cell.

..... [6]

(b) In the cells of a lead-acid car battery the following reactions take place.

cathode: $Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^-$

anode: $PbO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Pb^{2+}(aq) + 2H_2O(l)$

(i) Use the *Data Booklet* to calculate $E^{\ominus}_{cell}$ for this reaction.

.....

(ii) Construct an equation for the overall reaction.

.....

The electrolyte in a lead-acid cell is $H_2SO_4(aq)$. Most of the $Pb^{2+}(aq)$ ions that are produced at the electrodes are precipitated as the highly insoluble $PbSO_4(s)$.

(iii) Construct an equation for the overall cell reaction in the presence of H_2SO_4.

.....

(iv) By considering the effect of decreasing $[Pb^{2+}(aq)]$ on the electrode potentials of the cathode and the anode, deduce the effect of the presence of $H_2SO_4(aq)$ in the electrolyte on the overall E_{cell}.
State whether the E_{cell} will *increase*, *decrease* or *remain the same*.

Overall E_{cell} will ..... .

Explain your answer.

.....

.....

[5]

[Total: 11]

s/10/qp41

(e) Copper powder dissolves in an acidified solution of sodium vanadate(V), $NaVO_3$, to produce a blue solution containing VO^{2+} and Cu^{2+} ions.
By using suitable half-equations from the *Data Booklet*, construct a balanced equation for this reaction.

..... [2]

s/09/qp4

2 **(a)** Describe the observations you would make when concentrated sulfuric acid is added to separate portions of NaC*l*(s) and NaBr(s). Write an equation for **each** reaction that occurs.

NaC*l*(s): observation .....

.....

equation

NaBr(s): observation .....

.....

equation

[4]

(b) By quoting relevant $E^{\ominus}$ data from the *Data Booklet*, explain how the observations you have described above relate to the relative oxidising power of the elements.

.....

.....

..... [2]

(c) By referring to relevant $E^{\ominus}$ data choose a suitable reagent to convert Br_2 into Br^-. Write an equation and calculate the $E^{\ominus}$ for the reaction.

.....

.....

..... [3]

[Total: 9]

s/09/qp4

(c) The relative stabilities of the $M^{2+}(aq)$ and $M^{4+}(aq)$ ions also vary down Group IV.

(i) Use the *Data Booklet* to illustrate this observation when M = Sn and M = Pb.

.....

.....

.....

(ii) Use the *Data Booklet* to predict the products formed, and write equations for the reactions occurring, when

- an equimolar mixture of $Sn^{2+}(aq)$ and $Sn^{4+}(aq)$ is added to $I_2(aq)$.

.....

.....

- an equimolar mixture of $Pb^{2+}(aq)$ and $Pb^{4+}(aq)$ is added to $SO_2(aq)$.

.....

.....

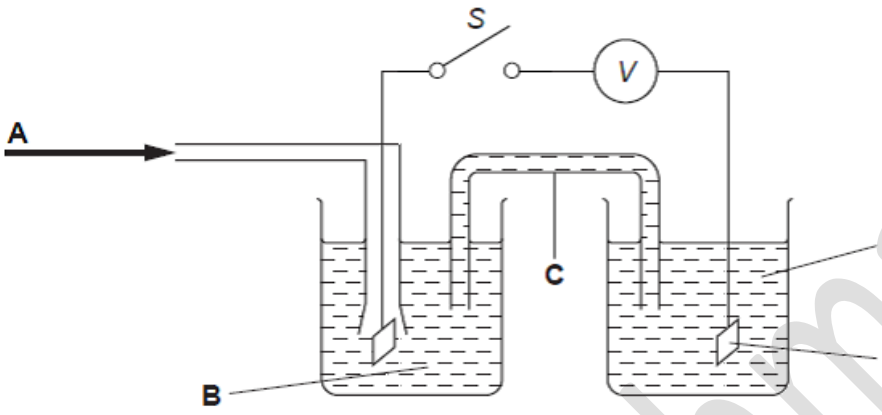
[4]

s/08/qp4

1 Chlorine gas and iron(II) ions react together in aqueous solution as follows.

$$Cl_2 + 2Fe^{2+} \rightarrow 2Cl^- + 2Fe^{3+}$$

(a) The following diagram shows the apparatus needed to measure the $E^{\ominus}_{cell}$ for the above reaction.



(i) In the spaces below, identify what the five letters **A – E** in the above diagram represent.

A .....

B .....

C .....

D .....

E .....

(ii) Use the *Data Booklet* to calculate the $E^{\ominus}_{cell}$ for this reaction, and hence decide which direction (left to right, or right to left) electrons would flow through the voltmeter *V* when switch *S* is closed.

$E^{\ominus}_{cell}$ = ... V

direction of electron flow .....

[7]

(ii) A solution of iron(III) chloride is used to dissolve unwanted copper from printed circuit boards.

When a copper-coated printed circuit board is immersed in $FeCl_3$(aq), the solution turns pale blue.

Suggest an equation for the reaction between copper and iron(III) chloride and use the Data Booklet to calculate the $E^{\ominus}$ for the reaction.

equation .....

$E^{\ominus}$ = ... V
[4]

s/08/qp4

1 Zinc chloride is one of the most important compounds of zinc. It is used in dry cell batteries, as a flux for soldering and tinning, as a corrosion inhibitor in cooling towers and in the manufacture of rayon.

(a) Draw a **fully labelled** diagram to show how you could use a standard hydrogen electrode to measure the standard electrode potential, $E^{\ominus}$, of zinc.

[6]

(b) The electrolysis of zinc chloride can give different electrode products, depending on the conditions used.
Suggest the products formed at each electrode in the following cases. One space has been filled in for you.

conditions	product at anode	product at cathode
$ZnCl_2$(l)	***chlorine***	
$ZnCl_2$(concentrated aqueous)		
$ZnCl_2$(dilute aqueous)		

[3]

s/07/qp4