ADVANCED GCE

CHEMISTRY A

Equilibria, Energetics and Elements

F325

Candidates answer on the question paper.

OCR Supplied Materials:
- *Data Sheet for Chemistry A* (inserted)

Other Materials Required:
- Scientific calculator

Wednesday 15 June 2011
Afternoon

Duration: 1 hour 45 minutes

Candidate forename		Candidate surname	

Centre number						Candidate number				

INSTRUCTIONS TO CANDIDATES

- The insert will be found in the centre of this document.
- Write your name, centre number and candidate number in the boxes above. Please write clearly and in capital letters.
- Use black ink. Pencil may only be used for graphs and diagrams where they appear.
- Read each question carefully. Make sure that you know what you have to do before starting your answer.
- Write your answer to each question in the space provided. Additional paper may be used if necessary but you must clearly show your candidate number, centre number and question number(s).
- Answer **all** the questions.
- Do **not** write in the bar codes.

INFORMATION FOR CANDIDATES

- The number of marks is given in brackets **[ ]** at the end of each question or part question.
- Where you see this icon you will be awarded marks for the quality of written communication in your answer.
  This means for example you should:
  - ensure that text is legible and that spelling, punctuation and grammar are accurate so that meaning is clear;
  - organise information clearly and coherently, using specialist vocabulary when appropriate.
- You may use a scientific calculator.
- A copy of the *Data Sheet for Chemistry A* is provided as an insert with this question paper.
- You are advised to show all the steps in any calculations.
- The total number of marks for this paper is **100**.
- This document consists of **24** pages. Any blank pages are indicated.

Answer **all** the questions.

1 Born–Haber cycles provide a model that chemists use to determine unknown enthalpy changes from known enthalpy changes. In this question, you will use a Born–Haber cycle to determine an enthalpy change of hydration.

(a) Magnesium chloride has a lattice enthalpy of –2493 kJ mol^{-1}.

Define in words the term *lattice enthalpy*.

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.... **[2]**

(b) The table below shows the enthalpy changes that are needed to determine the enthalpy change of hydration of magnesium ions.

enthalpy change	**energy/kJ mol^{-1}**
lattice enthalpy of magnesium chloride	–2493
enthalpy change of solution of magnesium chloride	–154
enthalpy change of hydration of chloride ions	–363

(i) Why is the enthalpy change of hydration of chloride ions exothermic?

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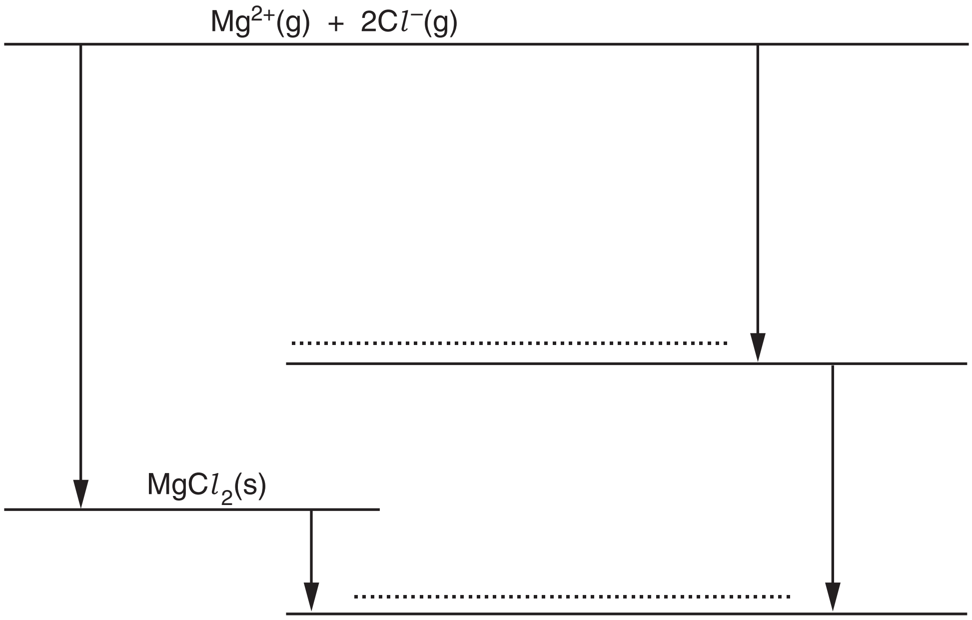
.... **[1]**

(ii) In this part, you will use the Born–Haber cycle to determine the enthalpy change of hydration of magnesium ions.

On the two dotted lines, add the species present, including state symbols.



[2]

(iii) Calculate the enthalpy change of hydration of magnesium ions.

answer = ... kJ mol^{-1} **[2]**

(c) The enthalpy change of hydration of magnesium ions is more exothermic than the enthalpy change of hydration of calcium ions.

Explain why.

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.... **[2]**

[Total: 9]

2 Nitric acid, HNO_3, is manufactured in large quantities. The main use of nitric acid is in the manufacture of fertilisers.

In its industrial preparation, nitric acid is produced in three main stages.

Stage 1
Ammonia is heated with oxygen in the air to form nitrogen monoxide, NO.

Stage 2
The hot nitrogen monoxide gas is then mixed with air and cooled under pressure. Nitrogen dioxide, NO_2, forms in a reversible reaction.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = -115\ \text{kJ mol}^{-1}$$

Stage 3
The nitrogen dioxide is reacted with water in a series of reactions to form nitric acid, HNO_3. The first of these reactions forms a mixture of nitric acid, HNO_3, and nitrous acid, HNO_2.

(a) In **Stage 2**, explain why the equilibrium mixture is both cooled **and** put under pressure.

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.... **[3]**

(b) Construct an equation for

- the reaction that takes place in **Stage 1**
- the first reaction that takes place in **Stage 3.**

Stage 1: ....

Stage 3: .... **[2]**

(c) An industrial chemist carries out some research into the $NO/O_2/NO_2$ equilibrium used in **Stage 2** of the manufacture of nitric acid.

- The chemist mixes together 0.80 mol NO(g) and 0.70 mol of O_2(g) in a container with a volume of 2.0 dm^3.
- The chemist heats the mixture and allows it to stand at constant temperature to reach equilibrium.
  The container is kept under pressure so that the total volume is maintained at 2.0 dm^3.
- At equilibrium, 75% of the NO has reacted.

(i) Write an expression for K_c for this equilibrium.

[1]

(ii) Calculate the equilibrium constant, K_c, including units, for this equilibrium.

K_c = ... units .... **[5]**

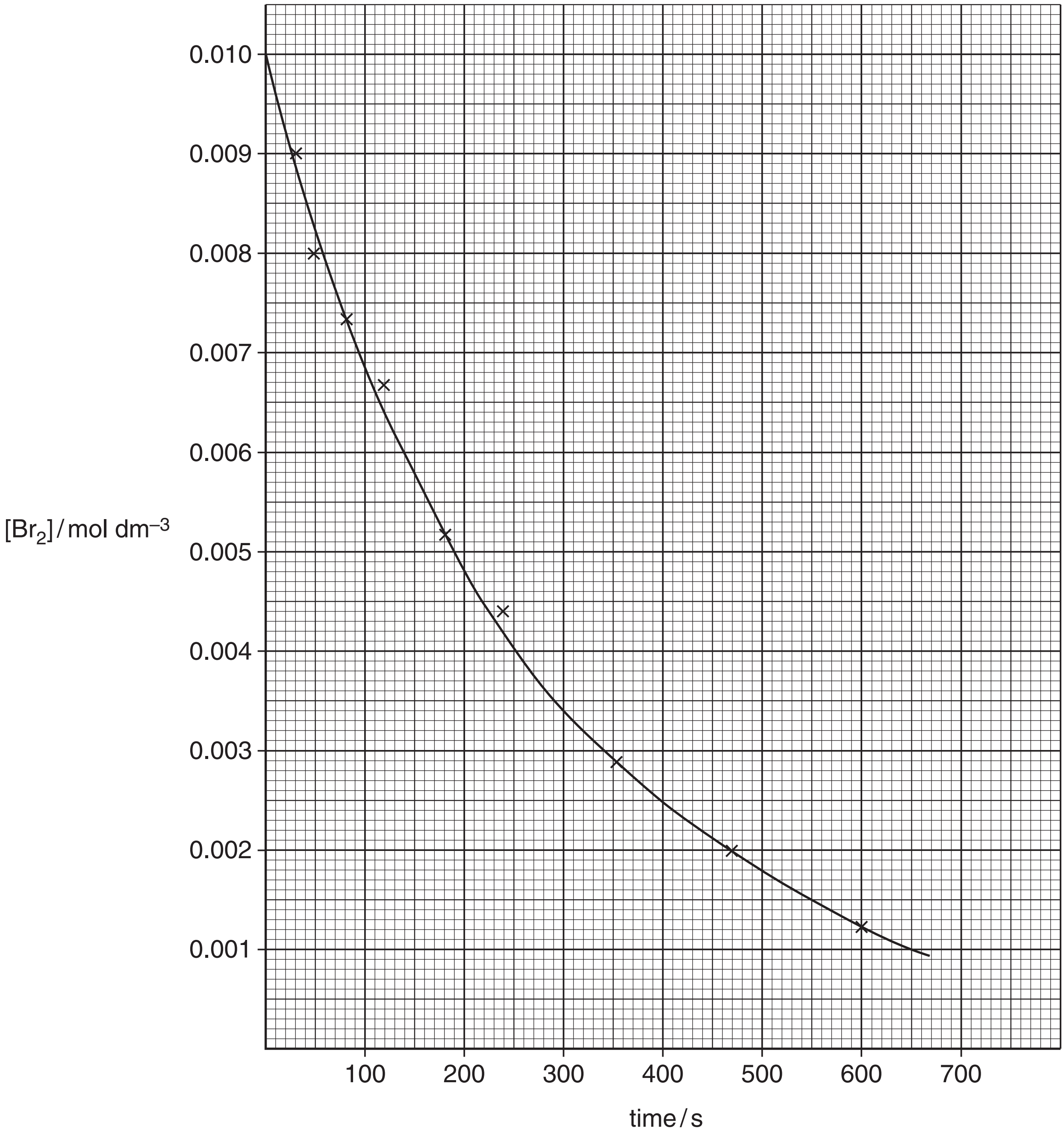
[Total: 11]

3 In aqueous solution, methanoic acid, HCOOH, reacts with bromine, Br_2.

$$HCOOH(aq) + Br_2(aq) \rightarrow 2H^+(aq) + 2Br^-(aq) + CO_2(g)$$

A student carried out an investigation on the rate of this reaction. The student used a large excess of methanoic acid which ensured that its concentration was effectively constant throughout. During the reaction, bromine is used up and its orange colour becomes less intense. The intensity of the bromine colour can be measured with a colorimeter to give the bromine concentration.

The graph below was plotted from the experimental results.



In this investigation, a large excess of methanoic acid was used. Under these conditions, the reaction is effectively zero-order with respect to methanoic acid.

- Using the graph, determine the order of reaction with respect to bromine.
- Using the graph, determine the initial rate of the reaction.
- Calculate the rate constant, *k*, for the reaction between methanoic acid and bromine under these conditions.

In your answer you should make clear how your conclusions fit with the experimental results, including working shown on the graph and units where appropriate.

[9]

[Total: 9]

4 Chemists and biochemists use pK_a values to compare the strengths of different acids. pK_a is a more convenient way of comparing acid strengths than K_a values.

pK_a values of several naturally occurring Brønsted–Lowry acids are shown in **Table 4.1** below.

common name and source	**systematic name**	**structural formula**	**pK_a (at 25°C)**
benzoic acid (from bark resin)	benzenecarboxylic acid	C_6H_5COOH	4.19
acetic acid (from vinegar)	ethanoic acid	CH_3COOH	4.76
pyruvic acid (formed during metabolism)	2-oxopropanoic acid	$CH_3COCOOH$	2.39
lactic acid (from milk)	2-hydroxypropanoic acid	$CH_3CHOHCOOH$	3.86

Table 4.1

(a) (i) What is meant by the term *Brønsted–Lowry acid*?

.... **[1]**

(ii) What is meant by the *strength* of an acid?

In your answer, include an equation for one of the acids in **Table 4.1**.

....

....

.... **[2]**

(iii) Place the four acids in **Table 4.1** in order of increasing strength.

weakest acid ....

↓ ....

....

strongest acid .... **[1]**

(iv) Aqueous benzoic acid was mixed with aqueous lactic acid. An equilibrium mixture was formed containing conjugate acid–base pairs.

Complete the equilibrium below to show the components in the equilibrium mixture.

$C_6H_5COOH + CH_3CHOHCOOH \rightleftharpoons$ .... + ... **[1]**

(b) Aqueous pyruvic acid was reacted with an aqueous solution of calcium hydroxide.

(i) Write an equation for this reaction.

.... **[1]**

(ii) Write an ionic equation for this reaction.

.... **[1]**

(c) The pH of an acid solution can be calculated from its pK_a value.

Calculate the pH of a 0.0150 mol dm^{-3} solution of pyruvic acid at 25 °C.

Show **all** your working.
Give the pH to **two** decimal places.

pH = ... **[4]**

(d) Oxalic acid (ethanedioic acid), $C_2H_2O_4$, is present in the leaves of rhubarb plants. Oxalic acid has two dissociations with pK_a = 1.23 and pK_a = 4.19.

(i) Draw the structure of oxalic acid.

[1]

(ii) Predict the equations that give rise to each dissociation.

pK_a = 1.23

pK_a = 4.19

[2]

(e) The 'magic tang' in many sweets is obtained by use of acid buffers. A sweet manufacturer carried out tasting tests with consumers and identified the acid taste that gives the 'magic tang' to a sweet.

The manufacturer was convinced that the 'magic tang' would give the company a competitive edge and he asked the company's chemists to identify the chemicals needed to generate the required taste. The chemists' findings would be a key factor in the success of the sweets.

The team of chemists identified that a pH of 3.55 was required and they worked to develop a buffer at this pH.

The chemists decided to use one of the acids in **Table 4.1** (page 8) and a salt of the acid to prepare this buffer.

- Deduce the chemicals required by the chemists to prepare this buffer.
- Calculate the relative concentrations of the acid and its salt needed by the chemist to make this buffer.
- Comment on the validity of the prediction that the pH of the sweet would give the sweets the 'magic tang'.

[6]

[Total: 20]

5 Chemists use three energy terms, enthalpy, entropy and free energy, to help them make predictions about whether reactions may take place.

(a) The table below shows five processes. Each process has either an increase in entropy or a decrease in entropy.

For each process, tick (✓) the appropriate box.

process		**increase in entropy**	**decrease in entropy**
A	$C_2H_5OH(l) \rightarrow C_2H_5OH(g)$		
B	$C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g)$		
C	$NH_4Cl(s) + aq \rightarrow NH_4Cl(aq)$		
D	$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$		
E	$2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$		

[2]

(b) At 1 atm (101 kPa) pressure, ice melts into water at 0 °C.

Complete the table below using the symbols '+', '–' or '0' to show the sign of ΔH and ΔS for the melting of ice at 0 °C and 1 atm.

For each sign, explain your reasoning.

energy change	**sign +, – or 0**	**reasoning**
ΔH		
ΔS		

[2]

(c) Much of the hydrogen required by industry is produced by reacting natural gas with steam:

$$CH_4(g) + H_2O(g) \longrightarrow 3H_2(g) + CO(g)$$

Standard entropies are given in the table below.

substance	$CH_4(g)$	$H_2O(g)$	$H_2(g)$	$CO(g)$
$S^{\ominus}$ / J K^{-1} mol^{-1}	186	189	131	198

(i) Calculate the standard entropy change, in J K^{-1} mol^{-1}, for this reaction of natural gas with steam.

$\Delta S^{\ominus}$ = ... J K^{-1} mol^{-1} **[2]**

(ii) State **two** large-scale uses for the hydrogen produced.

1. ....

2. .... **[1]**

(d) Ammonium chloride, NH_4Cl, can dissociate to form ammonia, NH_3, and hydrogen chloride, HCl.

$$NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$$

At 298 K, $\Delta H = +176\,kJ\,mol^{-1}$ and $\Delta G = +91.2\,kJ\,mol^{-1}$.

- Calculate ΔG for this reaction at 1000 K.
- Hence show whether this reaction takes place spontaneously at 1000 K.

Show **all** your working.

ΔG = ... $kJ\,mol^{-1}$ **[4]**

[Total: 11]

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TURN OVER FOR QUESTIONS 6, 7 AND 8

6 Nickel is a typical transition element in the d-block of the Periodic Table. Many nickel ions are able to interact with ligands to form complex ions, such as $[Ni(H_2O)_6]^{2+}$.

(a) Using the information about nickel above, explain the meaning of the terms *d-block element*, *transition element*, *ligand* and *complex ion*.

Include electron structures and diagrams in your answer.

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.... **[7]**

(b) A student dissolves nickel(II) sulfate in water. A green solution forms containing the complex ion $[Ni(H_2O)_6]^{2+}$.

The student then reacts separate portions of the green solution of nickel(II) sulfate as outlined below.

- Concentrated hydrochloric acid is added to the green solution of nickel(II) sulfate until there is no further change. The solution turns a lime-green colour and contains the four-coordinate complex ion **A**.
- Aqueous sodium hydroxide is added to the green solution of nickel(II) sulfate. A pale-green precipitate **B** forms.
- Concentrated aqueous ammonia is added to the green solution of nickel(II) sulfate until there is no further change. The solution turns a violet colour and contains the complex ion **C**.
  C has a molar mass of 160.7 $g\,mol^{-1}$.

(i) Draw a 3-D diagram for the $[Ni(H_2O)_6]^{2+}$ ion.
Show a value for the bond angles on your diagram.

[2]

(ii) Suggest the formulae of **A** and **B**.

A ....

B .... **[2]**

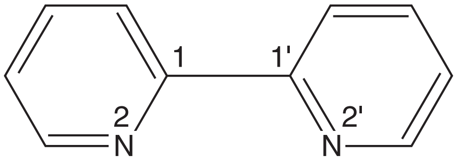
(iii) Deduce the formula of **C**.

C .... **[1]**

(iv) Write an equation for the formation of **C** from $[Ni(H_2O)_6]^{2+}$.

.... **[2]**

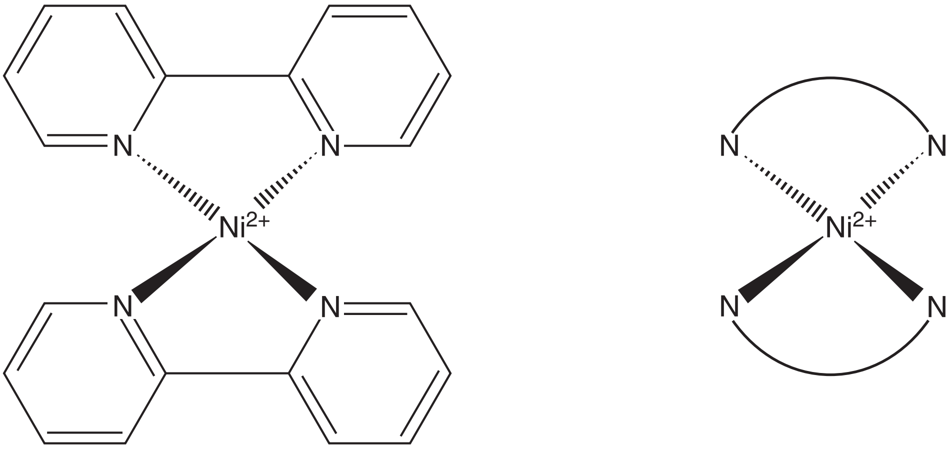
(c) 2,2'-Bipyridine (or 'bipy') is a bidentate ligand that forms complexes with many transition metals. The structure of 2,2'-bipyridine is shown below.



2,2'-bipyridine

In the naming of bipyridines, the numbering starts at the carbon atom that links to the other ring.

2,2'-Bipyridine forms a complex, $[Ni(bipy)_2]^{2+}$. The structure of $[Ni(bipy)_2]^{2+}$ is shown in **Fig 6.1** below.



structure

simplified diagram

$[Ni(bipy)_2]^{2+}$

Fig 6.1

(i) What is the molecular formula of 2,2'-bipyridine?

.... **[1]**

(ii) What is the coordination number of the $[Ni(bipy)_2]^{2+}$ complex ion?

.... **[1]**

(iii) 2,2'-Bipyridine forms a complex with the transition metal ruthenium with the formula $[Ru(bipy)_3]^{2+}$. This complex exists as two stereoisomers.

Draw 3-D diagrams to predict the structures for these stereoisomers of $[Ru(bipy)_3]^{2+}$. You can represent the 2,2'-bipyridine ligands as in the simplified diagram for $[Ni(bipy)_2]^{2+}$ in **Fig 6.1**.

[2]

(iv) 4,4'-Bipyridine (4,4'-bipy) can also form complexes with transition metal ions. Because of its structure, 4,4'-bipyridine can bridge between metal ions to form 'coordination polymers'. For example, nickel(II) can form a coordination polymer with 4,4'-bipyridine containing $\{[Ni(H_2O)_4(4,4'\text{-bipy})]^{2+}\}_n$ chains.

Draw a 3-D diagram to predict the repeat unit in this coordination polymer of nickel(II). Your diagram should show the complete structure of 4,4'-bipyridine and all coordinate bonds.

[3]

[Total: 21]

7 Nickel–cadmium cells (NiCd cells) have been extensively used as rechargeable storage cells. NiCd cells have been a popular choice for many electrical and electronic applications because they are very durable, reliable, easy-to-use and economical.

The electrolyte in NiCd cells is aqueous KOH. The standard electrode potentials for the redox systems that take place in NiCd cells are shown below.

$$Cd(OH)_2 + 2e^- \rightleftharpoons Cd + 2OH^- \qquad E^\ominus = -0.80\,V$$
$$NiO(OH) + H_2O + e^- \rightleftharpoons Ni(OH)_2 + OH^- \qquad E^\ominus = +0.45\,V$$

(a) Define the term *standard electrode potential*, including all standard conditions in your answer.

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.... **[2]**

(b) What is the standard cell potential of a NiCd cell?

answer = ... V **[1]**

(c) When a NiCd cell is being used for electrical energy, it is being discharged.

(i) Construct the overall cell reaction that takes place during discharge of a NiCd cell.

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.... **[2]**

(ii) Using oxidation numbers, show the species that have been oxidised and reduced during discharge of a NiCd cell.

oxidation ....

....

reduction ....

.... **[2]**

(d) NiCd cells are recharged using a battery charger.

(i) Suggest the reactions that take place in the NiCd cell during the recharging process.

....

.... **[1]**

(ii) As the cell approaches full charge, the aqueous KOH electrolyte starts to decompose, forming hydrogen gas at one electrode and oxygen gas at the other electrode.

Predict half-equations that might take place at each electrode for the decomposition of the electrolyte to form hydrogen and oxygen.

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.... **[2]**

[Total: 10]

8 Brass is an alloy which contains copper.
The percentage of copper in brass can be determined using the steps below.

Step 1	2.80 g of brass is reacted with an excess of concentrated nitric acid, HNO_3. The half-equations taking place are shown below. $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ $2HNO_3(l) + e^- \rightarrow NO_3^-(aq) + NO_2(g) + H_2O(l)$
Step 2	Excess aqueous sodium carbonate is added to neutralise any acid. The mixture effervesces and a precipitate forms.
Step 3	The precipitate is reacted with ethanoic acid to form a solution which is made up to 250 cm^3 with water.
Step 4	A 25.0 cm^3 sample of the solution is pipetted into a conical flask and an excess of aqueous potassium iodide is added. A precipitate of copper(I) iodide and a solution of iodine, $I_2(aq)$, forms.
Step 5	The resulting mixture is titrated with 0.100 mol dm^{-3} sodium thiosulfate to estimate the iodine present: $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$
Step 6	**Steps 4** and **5** are repeated to obtain an average titre of 29.8 cm^3.

- For **steps 1**, **2** and **4**, write ionic equations, including state symbols, for the reactions taking place.
- Determine the percentage, by mass, of copper in the brass.
  Give your answer to **one** decimal place.

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.... [9]

[Total: 9]

END OF QUESTION PAPER

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