THIS IS A NEW SPECIFICATION

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RECOGNISING ACHIEVEMENT

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

Thursday 17 June 2010
Afternoon

Duration: 1 hour 45 minutes

OCE/11144

F 3 2 5

Candidate Forename		Candidate Surname	

Centre Number						Candidate Number				

INSTRUCTIONS TO CANDIDATES

- Write your name clearly in capital letters, your Centre Number and Candidate Number in the boxes above.
- Use black ink. Pencil may be used for graphs and diagrams only.
- Read each question carefully and make sure that you know what you have to do before starting your answer.
- Answer **all** the questions.
- Do **not** write in the bar codes.
- 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).

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 **20** pages. Any blank pages are indicated.

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Answer **all** the questions.

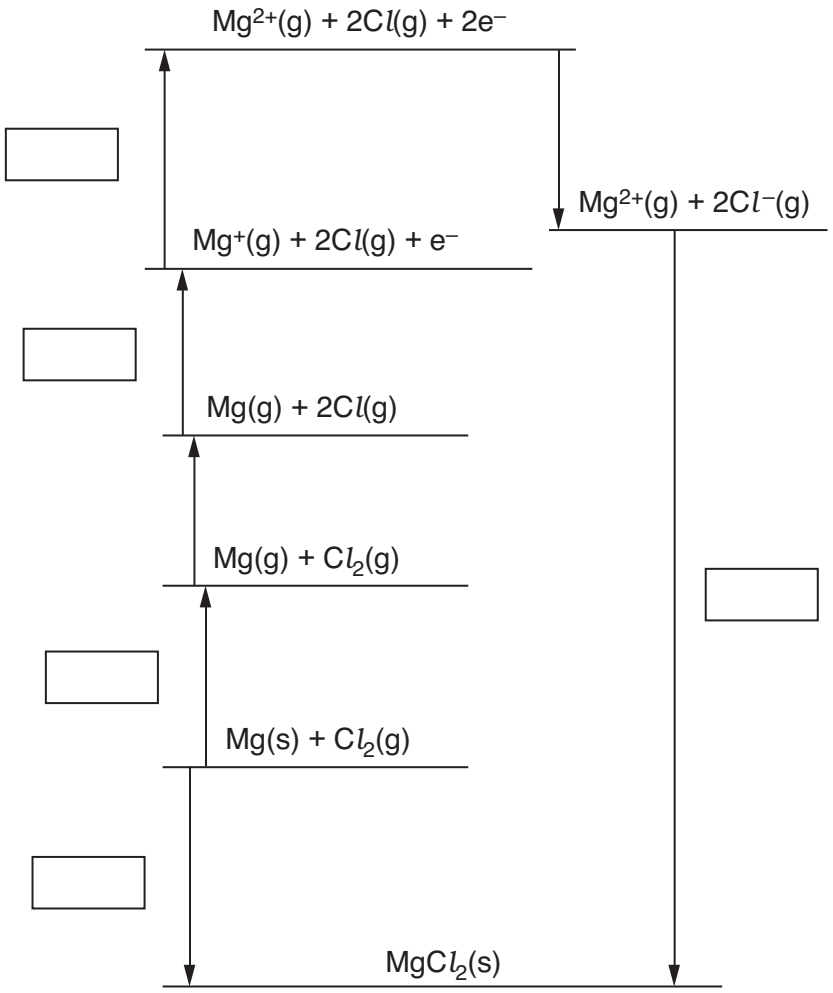
1 Lattice enthalpy can be used as a measure of ionic bond strength. Lattice enthalpies are determined indirectly using an enthalpy cycle called a Born–Haber cycle.

The table below shows the enthalpy changes that are needed to determine the lattice enthalpy of magnesium chloride, $MgCl_2$.

letter	enthalpy change	energy/ kJ mol^{-1}
A	1st electron affinity of chlorine	–349
B	1st ionisation energy of magnesium	+736
C	atomisation of chlorine	+150
D	formation of magnesium chloride	–642
E	atomisation of magnesium	+76
F	2nd ionisation energy of magnesium	+1450
G	lattice enthalpy of magnesium chloride	

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(a) On the cycle below, write the correct letter in each empty box.



[3]

(b) Use the Born–Haber cycle to calculate the lattice enthalpy of magnesium chloride.

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

(c) Magnesium chloride has stronger ionic bonds than sodium chloride.

Explain why.

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..... **[3]**

[Total: 8]

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2 In the presence of acid, $H^+(aq)$, aqueous bromate(V) ions, $BrO_3^-(aq)$, react with aqueous bromide ions, $Br^-(aq)$, to produce bromine, $Br_2(aq)$.

A student carried out an investigation into the kinetics of this reaction.

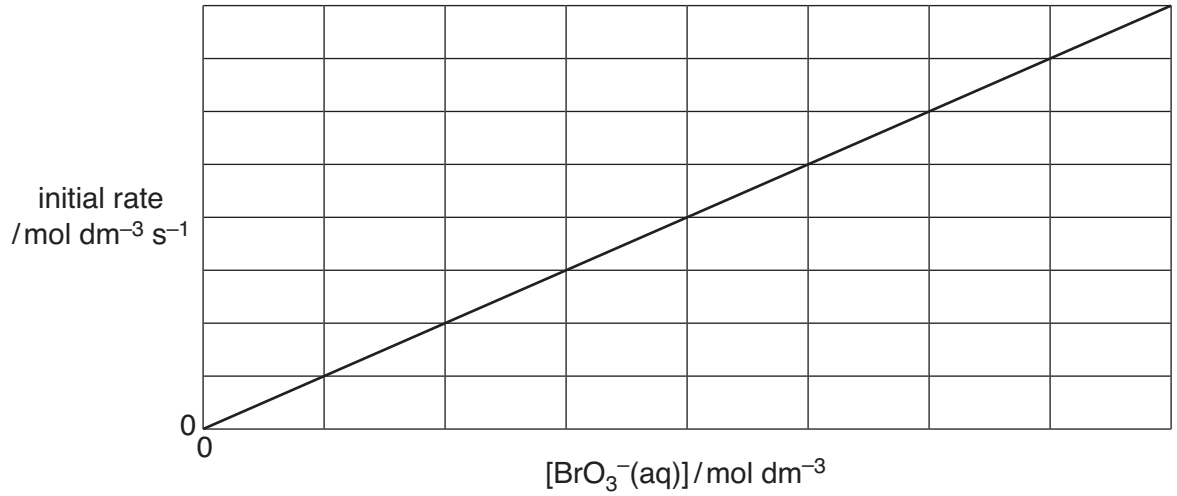
(a) Balance the ionic equation for this reaction.

$$BrO_3^- + \ldots\ldots Br^- + \ldots\ldots H^+ \longrightarrow \ldots\ldots Br_2 + \ldots\ldots H_2O$$

[1]

(b) The student investigated how different concentrations of $BrO_3^-(aq)$ affect the initial rate of the reaction.

A graph of initial rate against $[BrO_3^-(aq)]$ is shown below.



The student then investigated how different concentrations of $Br^-(aq)$ and $H^+(aq)$ affect the initial rate of the reaction.

The results are shown below.

$[BrO_3^-(aq)]$ / mol dm^{-3}	$[Br^-(aq)]$ / mol dm^{-3}	$[H^+(aq)]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
5.0×10^{-2}	1.5×10^{-1}	3.1×10^{-1}	1.19×10^{-5}
5.0×10^{-2}	3.0×10^{-1}	3.1×10^{-1}	2.38×10^{-5}
5.0×10^{-2}	1.5×10^{-1}	6.2×10^{-1}	4.76×10^{-5}

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- Using the results from the student's experiments, what conclusions can be drawn about the kinetics of this reaction? Justify your reasoning.

- Calculate the rate constant for this reaction, including the units.

In your answer you should make clear how your conclusions fit with the experimental results.

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3 The chemicals that we call 'acids' have been known for thousands of years. However, modern theories of acids have been developed comparatively recently. It wasn't until the early 1900s that the concept of dissociation became accepted by the scientific community and the concept of pH was introduced.

A student carried out a series of experiments with acids and alkalis.

(a) Propanoic acid, CH_3CH_2COOH, is a naturally occurring weak acid. The equation for the dissociation of propanoic acid is shown below.

$$CH_3CH_2COOH(aq) \rightleftharpoons H^+(aq) + CH_3CH_2COO^-(aq)$$

The student wanted to prove that propanoic acid is a weak acid. The student had access to a pH meter and 0.100 mol dm^{-3} propanoic acid.

- Explain how the student could prove that propanoic acid is a weak acid by taking a single pH measurement.
- Show how the student could then calculate the acid dissociation constant, K_a, for propanoic acid.

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..... **[4]**

(b) The student measured the pH of a solution of sodium hydroxide at 25 °C.
The measured pH was 13.46.

Calculate the concentration of the aqueous sodium hydroxide.

concentration = ... mol dm^{-3} **[2]**

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(c) A student made a buffer solution by mixing an excess of propanoic acid to an aqueous solution of sodium hydroxide at 25 °C. This buffer solution contains an equilibrium system that minimises changes in pH when small amounts of acids and alkalis are added.

- Explain why a buffer solution formed when an excess of propanoic acid was mixed with aqueous sodium hydroxide.

- Explain how this buffer solution controls pH when an acid or an alkali is added.



In your answer you should explain how the equilibrium system allows the buffer solution to control the pH.

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..... **[7]**

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(d) A student added nitric acid to propanoic acid. A reaction took place to form an equilibrium mixture containing two acid–base pairs.

Complete the equilibrium below and label the two conjugate acid–base pairs.

$HNO_3 + CH_3CH_2COOH \rightleftharpoons$ ..... + ...

[2]

(e) Finally, the student reacted an aqueous solution of propanoic acid with a reactive metal and with a carbonate.

(i) Write an equation for the reaction of aqueous propanoic acid with magnesium.

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

(ii) Write an ionic equation for the reaction of aqueous propanoic acid with aqueous sodium carbonate.

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

[Total: 17]

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QUESTION 4 STARTS ON PAGE 10

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4 Electrochemical cells have been developed as a convenient and portable source of energy.

The essential components of any electrochemical cell are two redox systems, one providing electrons and the other accepting electrons. The tendency to lose or gain electrons can be quantified using values called standard electrode potentials.

Standard electrode potentials for seven redox systems are shown in **Table 4.1**.
You may need to use this information throughout this question.

Table 4.1

redox system	equation	$E^{\ominus}$/V
1	$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0
2	$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
3	$SO_4^{2-}(aq) + 2H^+(aq) + 2e^- \rightleftharpoons SO_3^{2-}(aq) + H_2O(l)$	+0.17
4	$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.34
5	$Cl_2(aq) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
6	$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23
7	$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54

(a) An electrochemical cell can be made based on redox systems 2 and 4.

(i) Draw a labelled diagram to show how this cell can be set up in the laboratory.

[3]

(ii) State the charge carriers that transfer current

through the wire, ...

through the solution. ..... **[1]**

(iii) Write down the overall cell reaction.

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

(iv) Write down the cell potential.

cell potential ..... V **[1]**

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(b) Select from **Table 4.1**,

(i) a species which oxidises $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$,

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

(ii) a species which reduces $Fe^{3+}(aq)$ to $Fe^{2+}(aq)$ but does **not** reduce $Ag^{+}(aq)$ to Ag(s).

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

(c) Fuel cells are a type of electrochemical cell being developed as a potential source of energy in the future.

- State **one** important difference between a fuel cell and a conventional electrochemical cell.
- Write the equation for the overall reaction that takes place in a hydrogen fuel cell.
- State **two** ways that hydrogen might be stored as a fuel for cars.
- Suggest why some people consider that the use of hydrogen as a fuel for cars consumes more energy than using fossil fuels such as petrol and diesel.

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..... **[5]**

[Total: 13]

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5 Ammonia is one of our most important chemicals, produced in enormous quantities because of its role in the production of fertilisers.

Much of this ammonia is manufactured from nitrogen and hydrogen gases using the Haber process. The equilibrium is shown below.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92\,kJ\,mol^{-1}$$

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

[1]

(ii) Deduce the units of K_c for this equilibrium.

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

(b) A research chemist was investigating methods to improve the synthesis of ammonia from nitrogen and hydrogen at 500 °C.

- The chemist mixed together nitrogen and hydrogen and pressurised the gases so that their total gas volume was 6.0 dm^3.
- The mixture was allowed to reach equilibrium at constant temperature and without changing the total gas volume.
- The equilibrium mixture contained 7.2 mol N_2 and 12.0 mol H_2.
- At 500 °C, the numerical value of K_c for this equilibrium is 8.00×10^{-2}.

Calculate the amount, in mol, of ammonia present in the equilibrium mixture at 500 °C.

equilibrium amount of NH_3 = ... mol **[4]**

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(c) The research chemist doubled the pressure of the equilibrium mixture whilst keeping all other conditions the same. As expected the equilibrium yield of ammonia increased.

(i) Explain in terms of le Chatelier's principle why the equilibrium yield of ammonia increased.

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

(ii) Explain in terms of K_c why the equilibrium yield of ammonia increased.

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..... **[3]**

(d) For the industrial manufacture of ammonia, nitrogen and hydrogen gases are required in large quantities from readily available resources.

Various methods have been developed to obtain hydrogen gas for this process.

(i) Much of the hydrogen is obtained by reacting together natural gas (methane) and steam.

Construct an equation for this reaction.

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

(ii) Natural gas is a fossil fuel and the annual production of ammonia accounts for about 2% of all methane consumption. In the future, as fossil fuels become more depleted, the use of methane for ammonia production may become too expensive.

Suggest another process that might be used in the future to obtain hydrogen gas for the Haber process.

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

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(e) In the industrial production of ammonia, a temperature in the range 400–500 °C is used.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92\,kJ\,mol^{-1}$$

Standard entropies of $N_2(g)$, $H_2(g)$ and $NH_3(g)$ are given in the table below.

substance	$N_2(g)$	$H_2(g)$	$NH_3(g)$
S **/ J K^{-1} mol^{-1}**	191	131	192

(i) Show that the formation of ammonia from nitrogen and hydrogen gases should be feasible at room temperature (25 °C).

[6]

(ii) Explain, in terms of entropy, why this reaction is **not** feasible at very high temperatures.

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

(iii) Suggest why a temperature of 400–500 °C is used for ammonia production, despite the reaction being feasible at room temperature.

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

[Total: 22]

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6 Chromium shows typical properties of a transition element. The element's name comes from the Greek word 'Chroma' meaning colour because of its many colourful compounds.

(a) Write down the electron configuration of

(i) a Cr atom, ... **[1]**

(ii) a Cr^{3+} ion. ..... **[1]**

(b) An acidified solution containing orange $Cr_2O_7^{2-}$ ions reacts with zinc in a redox reaction to form a solution containing Zn^{2+} ions and blue Cr^{2+} ions.

The unbalanced half-equations are shown below.

$$Zn \longrightarrow Zn^{2+} + e^-$$

$$Cr_2O_7^{2-} + H^+ + e^- \longrightarrow Cr^{2+} + H_2O$$

Balance these equations and construct an overall equation for this reaction.

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..... **[3]**

(c) Aqueous solutions of Cr^{3+} ions contain ruby-coloured $[Cr(H_2O)_6]^{3+}$ complex ions. If an excess of concentrated ammonia solution is added, the solution changes to a violet colour as the hexaammine chromium(III) complex ion forms.

(i) What type of reaction has taken place?

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

(ii) Suggest an equation for this reaction.

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

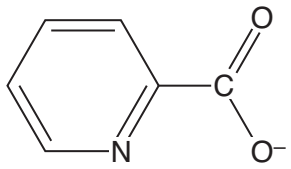
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(d) Chromium picolinate, $Cr(C_6H_4NO_2)_3$, is a bright red complex, used as a nutritional supplement to prevent or treat chromium deficiency in the human body.

In this complex,

- chromium has the +3 oxidation state,
- picolinate ions, $C_6H_4NO_2^-$, act as bidentate ligands.

The structure of the picolinate ion is shown below.



$Cr(C_6H_4NO_2)_3$ exists as a mixture of stereoisomers.

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

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

(ii) How is the picolinate ion able to act as a **bidentate** ligand?

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

(iii) Why does $Cr(C_6H_4NO_2)_3$ exist as a mixture of stereoisomers?
Draw diagrams of the stereoisomers as part of your answer.

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..... **[3]**

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(e) Compound **A** is an orange ionic compound of chromium with the percentage composition by mass N, 11.11%; H, 3.17%; Cr, 41.27%; O, 44.45%. Compound **A** does **not** have water of crystallisation.

On gentle heating, compound **A** decomposes to form three products, **B**, **C** and water.
B is a green oxide of chromium with a molar mass of 152.0 g mol^{-1}.
C is a gas. At RTP, each cubic decimetre of **C** has a mass of 1.17 g.

In the steps below, show all your working.

- Calculate the empirical formula of compound **A**.
- Deduce the ions that make up the ionic compound **A**.
- Identify substances **B** and **C**.
- Write an equation for the decomposition of compound **A** by heat.

[8]

[Total: 22]

TURN OVER FOR QUESTION 7

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7 Redox titrations using $KMnO_4$ in acidic conditions can be used to analyse reducing agents. Acidified $KMnO_4$ is a strong oxidising agent, readily removing electrons:

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

A student analysed a solution of hydrogen peroxide, $H_2O_2(aq)$, using a redox titration with $KMnO_4$ under acidic conditions. Under these conditions, H_2O_2 is a reducing agent.

The overall equation for the reaction is given below.

$$2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

(a) Deduce the simplest whole number half-equation for the oxidation of H_2O_2 under these conditions.

[2]

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(b) The student diluted 25.0 cm^3 of a solution of hydrogen peroxide with water and made the solution up to 250.0 cm^3. The student titrated 25.0 cm^3 of this solution with 0.0200 mol dm^{-3} $KMnO_4$ under acidic conditions. The volume of $KMnO_4$(aq) required to reach the end-point was 23.45 cm^3.

- Calculate the concentration, in g dm^{-3}, of the **undiluted** hydrogen peroxide solution.
- What volume of oxygen gas, measured at RTP, would be produced during this titration?

[6]

[Total: 8]

END OF QUESTION PAPER

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