Centre Number						Candidate Number				
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For Examiner's Use	
Examiner's Initials	
Question	Mark
1	
2	
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8	
TOTAL	

General Certificate of Education
Advanced Level Examination
June 2013

Chemistry CHEM5

Unit 5 Energetics, Redox and Inorganic Chemistry

Wednesday 19 June 2013 9.00 am to 10.45 am

For this paper you must have:
- the Periodic Table/Data Sheet provided as an insert (enclosed)
- a calculator.

Time allowed
- 1 hour 45 minutes

Instructions
- Use black ink or black ball-point pen.
- Fill in the boxes at the top of this page.
- Answer **all** questions.
- You must answer the questions in the spaces provided. Do not write outside the box around each page or on blank pages.
- All working must be shown.
- Do all rough work in this book. Cross through any work you do not want to be marked.

Information
- The marks for questions are shown in brackets.
- The maximum mark for this paper is 100.
- You are expected to use a calculator, where appropriate.
- The Periodic Table/Data Sheet is provided as an insert.
- Your answers to the questions in **Section B** should be written in continuous prose, where appropriate.
- You will be marked on your ability to:
  – use good English
  – organise information clearly
  – use scientific terminology accurately.

Advice
- You are advised to spend about 70 minutes on **Section A** and about 35 minutes on **Section B**.

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Section A

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

1 (a) Define the term *lattice enthalpy of dissociation*.

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(2 marks)

1 (b) Lattice enthalpy can be calculated theoretically using a perfect ionic model.

Explain the meaning of the term *perfect ionic model*.

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(1 mark)

(Extra space) .....

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1 (c) Suggest **two** properties of ions that influence the value of a lattice enthalpy calculated using a perfect ionic model.

Property 1 .....

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Property 2 .....

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(2 marks)

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1 (d) Use the data in the table to calculate a value for the lattice enthalpy of dissociation for silver chloride.

Enthalpy change	**Value / kJ mol^{-1}**
Enthalpy of atomisation for silver	+289
First ionisation energy for silver	+732
Enthalpy of atomisation for chlorine	+121
Electron affinity for chlorine	–364
Enthalpy of formation for silver chloride	–127

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(3 marks)

1 (e) Predict whether the magnitude of the lattice enthalpy of dissociation that you have calculated in part **(d)** will be less than, equal to or greater than the value that is obtained from a perfect ionic model. Explain your answer.

Prediction compared with ionic model .....

Explanation .....

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(2 marks)

10

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2 The enthalpy of hydration for the chloride ion is –364 kJ mol^{-1} and that for the bromide ion is –335 kJ mol^{-1}.

2 (a) By describing the nature of the attractive forces involved, explain why the value for the enthalpy of hydration for the chloride ion is more negative than that for the bromide ion.

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(3 marks)

2 (b) The enthalpy of hydration for the potassium ion is –322 kJ mol^{-1}. The lattice enthalpy of dissociation for potassium bromide is +670 kJ mol^{-1}.

Calculate the enthalpy of solution for potassium bromide.

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(2 marks)

Do not write outside the box

2 (c) The enthalpy of solution for potassium chloride is +17.2 kJ mol^{-1}.

2 (c) (i) Explain why the free-energy change for the dissolving of potassium chloride in water is negative, even though the enthalpy change is positive.

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(3 marks)

(Extra space) .....

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2 (c) (ii) A solution is formed when 5.00 g of potassium chloride are dissolved in 20.0 g of water. The initial temperature of the water is 298 K.

Calculate the final temperature of the solution.

In your calculation, assume that only the 20.0 g of water changes in temperature and that the specific heat capacity of water is 4.18 J K^{-1} g^{-1}.

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(5 marks)

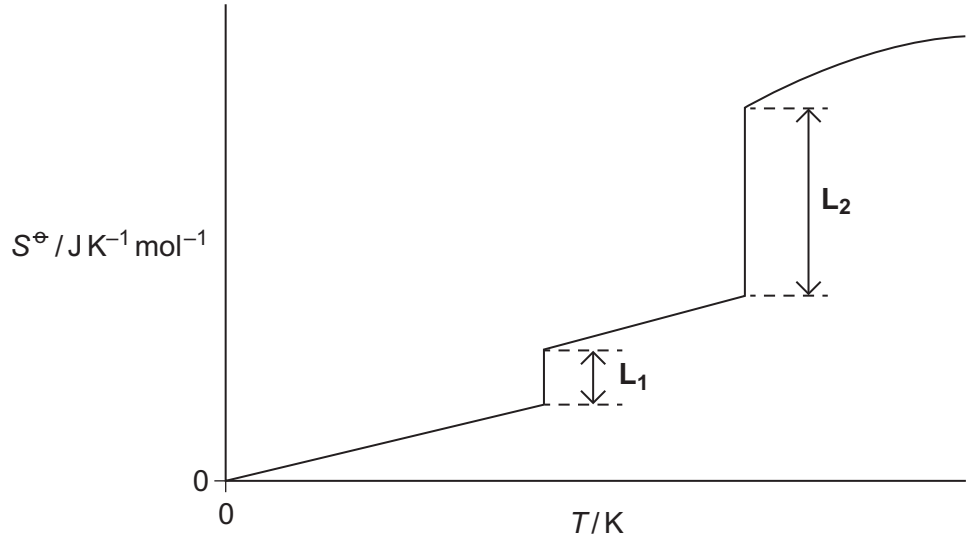
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Turn over ▶

Do not write outside the box

3 (a) **Figure 1** shows how the entropy of a molecular substance **X** varies with temperature.

Figure 1



3 (a) (i) Explain, in terms of molecules, why the entropy is zero when the temperature is zero Kelvin.

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(2 marks)

(Extra space) .....

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3 (a) (ii) Explain, in terms of molecules, why the first part of the graph in **Figure 1** is a line that slopes up from the origin.

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(2 marks)

(Extra space) .....

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Do not write outside the box

3 (a) (iii) On **Figure 1**, mark on the appropriate axis the boiling point (T_b) of substance **X**.

(1 mark)

3 (a) (iv) In terms of the behaviour of molecules, explain why $\mathbf{L_2}$ is longer than $\mathbf{L_1}$ in **Figure 1**.

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(2 marks)

(Extra space) .....

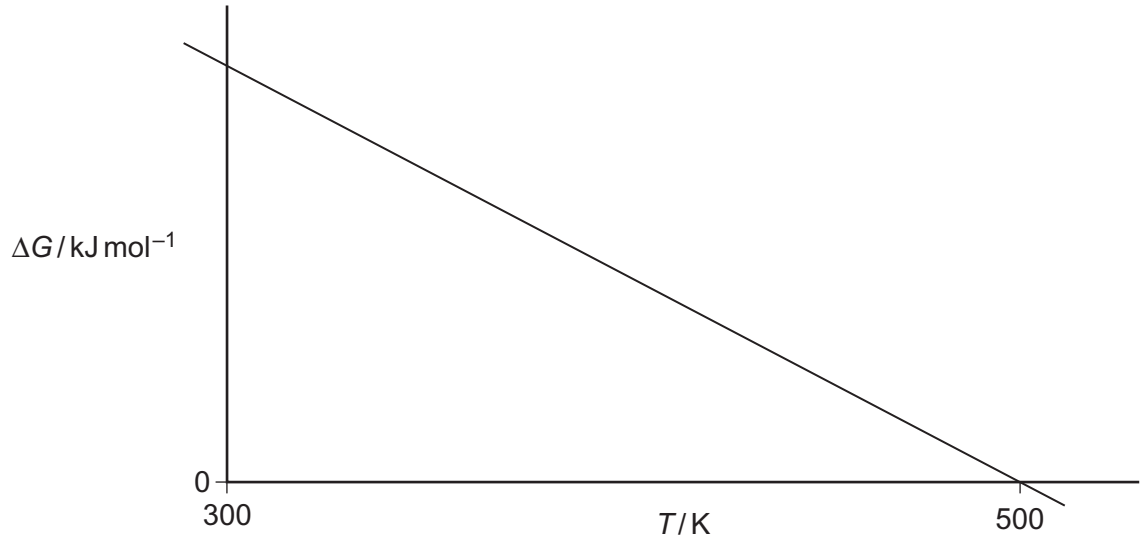
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Question 3 continues on the next page

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3 (b) **Figure 2** shows how the free-energy change for a particular gas-phase reaction varies with temperature.

Figure 2



3 (b) (i) Explain, with the aid of a thermodynamic equation, why this line obeys the mathematical equation for a straight line, $y = mx + c$.

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(2 marks)

3 (b) (ii) Explain why the magnitude of ΔG decreases as T increases in this reaction.

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(1 mark)

3 (b) (iii) State what you can deduce about the feasibility of this reaction at temperatures lower than 500 K.

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(1 mark)

Do not write outside the box

3 (c) The following reaction becomes feasible at temperatures above 5440 K.

$$H_2O(g) \longrightarrow H_2(g) + \tfrac{1}{2}O_2(g)$$

The entropies of the species involved are shown in the following table.

	$H_2O(g)$	$H_2(g)$	$O_2(g)$
S / J K^{-1} mol^{-1}	189	131	205

3 (c) (i) Calculate the entropy change ΔS for this reaction.

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(1 mark)

3 (c) (ii) Calculate a value, with units, for the enthalpy change for this reaction at 5440 K.

(If you have been unable to answer part **(c) (i)**, you may assume that the value of the entropy change is +98 J K^{-1} mol^{-1}. This is **not** the correct value.)

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(3 marks)

15

Do not write outside the box

4 Magnesium oxide, silicon dioxide and phosphorus(V) oxide are white solids but each oxide has a different type of structure and bonding.

4 (a) State the type of bonding in magnesium oxide.
Outline a simple experiment to demonstrate that magnesium oxide has this type of bonding.

Type of bonding .....

Experiment .....

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(3 marks)

4 (b) By reference to the structure of, and the bonding in, silicon dioxide, suggest why it is insoluble in water.

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(3 marks)

Do not write outside the box

4 (c) State how the melting point of phosphorus(V) oxide compares with that of silicon dioxide. Explain your answer in terms of the structure of, and the bonding in, phosphorus(V) oxide.

Melting point in comparison to silicon dioxide .....

Explanation .....

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(3 marks)

4 (d) Magnesium oxide is classified as a basic oxide.

Write an equation for a reaction that shows magnesium oxide acting as a base with another reagent.

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(2 marks)

4 (e) Phosphorus(V) oxide is classified as an acidic oxide.

Write an equation for its reaction with sodium hydroxide.

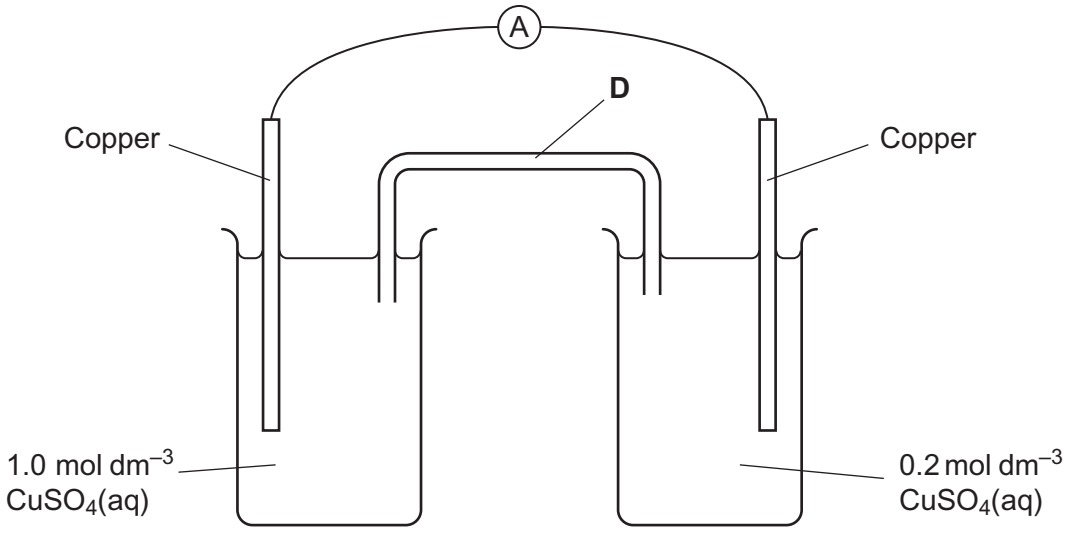
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(1 mark)

12

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5 An electrochemical cell is shown in the diagram. In this cell, the amount of copper in the electrodes is much greater than the amount of copper ions in the copper sulfate solutions.



5 (a) Explain how the salt bridge **D** provides an electrical connection between the two electrodes.

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(1 mark)

5 (b) Suggest why potassium chloride would **not** be a suitable salt for the salt bridge in this cell.

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(1 mark)

5 (c) In the external circuit of this cell, the electrons flow through the ammeter from right to left.

Suggest why the electrons move in this direction.

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(2 marks)

Do not write outside the box

5 (d) Explain why the current in the external circuit of this cell falls to zero after the cell has operated for some time.

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(1 mark)

5 (e) The simplified electrode reactions in a rechargeable lithium cell are

Electrode **A** $Li^+ + MnO_2 + e^- \longrightarrow LiMnO_2$ $E = -0.15\,V$

Electrode **B** $Li^+ + e^- \longrightarrow Li$

Electrode **B** is the negative electrode.

5 (e) (i) The e.m.f. of this cell is 2.90 V.

Use this information to calculate a value for the electrode potential of electrode **B**.

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(1 mark)

5 (e) (ii) Write an equation for the overall reaction that occurs when this lithium cell is being **recharged**.

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(2 marks)

5 (e) (iii) Suggest why the recharging of a lithium cell may lead to release of carbon dioxide into the atmosphere.

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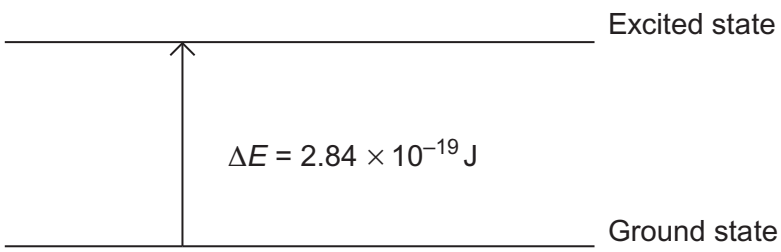
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(1 mark)

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Do not write outside the box

6 This diagram represents the energy change that occurs when a d electron in a transition metal ion is excited by visible light.



6 (a) Give the equation that relates the energy change ΔE to the Planck constant h and the frequency of the visible light v.

Use this equation and the information in the diagram to calculate a value for the frequency of the visible light, and state the units.
The Planck constant $h = 6.63 \times 10^{-34}$ J s.

Equation .....

Calculation .....

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(2 marks)

6 (b) Explain why this electron transition causes a solution containing the transition metal ion to be coloured.

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(2 marks)

Do not write outside the box

6 (c) The energy change shown in the diagram represents the energy of red light and leads to a solution that appears blue.
Blue light has a higher frequency than red light.

Suggest whether the energy change ΔE will be bigger, smaller or the same for a transition metal ion that forms a red solution. Explain your answer.

Energy change .....

Explanation .....

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(2 marks)

6 (d) State **three** different features of transition metal complexes that cause a change in the value of ΔE, the energy change between the ground state and the excited state of the d electrons.

Feature 1 .....

Feature 2 .....

Feature 3 .....

(3 marks)

9

Turn over for the next question

Do not write outside the box

Section B

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

7 An excess of a given reagent is added to each of the following pairs of aqueous metal ions.

For each metal ion, state the initial colour of the solution and the final observation that you would make.

In each case, write an overall equation for the formation of the final product from the initial aqueous metal ion.

7 (a) An excess of aqueous sodium carbonate is added to separate aqueous solutions containing $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$

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(5 marks)

7 (b) An excess of concentrated hydrochloric acid is added to separate aqueous solutions containing $[Cu(H_2O)_6]^{2+}$ and $[Co(H_2O)_6]^{2+}$

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(4 marks)

Do not write outside the box

7 (c) An excess of dilute aqueous sodium hydroxide is added to separate aqueous solutions containing $[Fe(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{3+}$

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(4 marks)

7 (d) An excess of dilute aqueous ammonia is added to separate aqueous solutions containing $[Al(H_2O)_6]^{3+}$ and $[Ag(H_2O)_2]^{+}$

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(4 marks)

17

Turn over for the next question

Do not write outside the box

8 This question explores some reactions and some uses of cobalt compounds.

8 (a) Ethanal is oxidised to ethanoic acid by oxygen. The equation for this reaction is

$$2CH_3CHO + O_2 \longrightarrow 2CH_3COOH$$

This redox reaction is slow at room temperature but speeds up in the presence of cobalt compounds.

Explain why a cobalt compound is able to act as a catalyst for this process.

Illustrate your explanation with **two** equations to suggest how, in the presence of water and hydrogen ions, Co^{3+} and then Co^{2+} ions could be involved in catalysing this reaction.

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(4 marks)

Do not write outside the box

8 (b) In aqueous solution, the $[Co(H_2O)_6]^{2+}$ ion reacts with an excess of ethane-1,2-diamine to form the complex ion **Y**.

8 (b) (i) Write an equation for this reaction.

Explain, in terms of the chelate effect, why the complex ion **Y** is formed in preference to the $[Co(H_2O)_6]^{2+}$ complex ion.

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(3 marks)

8 (b) (ii) Draw a diagram that shows the shape of the complex ion **Y** and shows the type of bond between the ethane-1,2-diamine molecules and the cobalt.

(3 marks)

Question 8 continues on the next page

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8 (c) Compound **Z** is a complex that contains only cobalt, nitrogen, hydrogen and chlorine.

A solid sample of **Z** was prepared by reaction of 50 cm^3 of 0.203 mol dm^{-3} aqueous cobalt(II) chloride with ammonia and an oxidising agent followed by hydrochloric acid.

When this sample of **Z** was reacted with an excess of silver nitrate, 4.22 g of silver chloride were obtained.

Use this information to calculate the mole ratio of chloride ions to cobalt ions in **Z**.

Give the formula of the complex cobalt compound **Z** that you would expect to be formed in the preparation described above.

Suggest **one** reason why the mole ratio of chloride ions to cobalt ions that you have calculated is different from the expected value.

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(5 marks)

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END OF QUESTIONS

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