Centre Number						Candidate Number				
Surname										
Other Names										
Candidate Signature										

For Examiner's Use	
Examiner's Initials	
Question	Mark
1	
2	
3	
4	
5	
6	
7	
TOTAL	

General Certificate of Education
Advanced Level Examination
January 2011

Chemistry CHEM5

Unit 5 Energetics, Redox and Inorganic Chemistry

Monday 31 January 2011 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.
- 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 accurate scientific terminology.

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

J A N 1 1 C H E M 5 0 1

Section A

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

1 Comparisons of lattice enthalpies from Born–Haber cycles with lattice enthalpies from calculations based on a perfect ionic model are used to provide information about bonding in crystals.

1 (a) Define the terms *enthalpy of atomisation* and *lattice dissociation enthalpy.*

Enthalpy of atomisation ....

....

....

Lattice dissociation enthalpy ....

....

....

(4 marks)

1 (b) Use the following data to calculate a value for the lattice dissociation enthalpy of sodium chloride.

Reaction	$\Delta H^\ominus$/ kJ mol^{-1}
$Na(s) \longrightarrow Na(g)$	+109
$Na(g) \longrightarrow Na^+(g) + e^-$	+494
$Cl_2(g) \longrightarrow 2Cl(g)$	+242
$Cl(g) + e^- \longrightarrow Cl^-(g)$	–364
$Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(s)$	–411

....

....

....

....

....

....

....

....

(3 marks)

1 (c) Consider the following lattice dissociation enthalpy ($\Delta H_L^\ominus$) data.

	NaBr	AgBr
$\Delta H_L^\ominus$(experimental) / kJ mol^{-1}	+733	+890
$\Delta H_L^\ominus$(theoretical) / kJ mol^{-1}	+732	+758

The values of $\Delta H_L^\ominus$ (experimental) have been determined from Born–Haber cycles.

The values of $\Delta H_L^\ominus$ (theoretical) have been determined by calculation using a perfect ionic model.

1 (c) (i) Explain the meaning of the term *perfect ionic model.*

....

....

....

....

(2 marks)

1 (c) (ii) State what you can deduce about the bonding in NaBr from the data in the table.

....

....

(1 mark)

1 (c) (iii) State what you can deduce about the bonding in AgBr from the data in the table.

....

....

(1 mark)

11

Turn over ▶

2 The balance between enthalpy change and entropy change determines the feasibility of a reaction. The table below contains enthalpy of formation and entropy data for some elements and compounds.

	$N_2(g)$	$O_2(g)$	NO(g)	C(graphite)	C(diamond)
$\Delta H_f^\ominus$ / kJ mol^{-1}	0	0	+90.4	0	+1.9
$S^\ominus$/J K^{-1} mol^{-1}	192.2	205.3	211.1	5.7	2.4

2 (a) Explain why the entropy value for the element nitrogen is much greater than the entropy value for the element carbon (graphite).

....

....

....

(2 marks)

2 (b) Suggest the condition under which the element carbon (diamond) would have an entropy value of zero.

....

(1 mark)

2 (c) Write the equation that shows the relationship between ΔG, ΔH and ΔS for a reaction.

....

(1 mark)

2 (d) State the requirement for a reaction to be feasible.

....

(1 mark)

2 (e) Consider the following reaction that can lead to the release of the pollutant NO into the atmosphere.

$$\tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow NO(g)$$

Use data from the table on page 4 to calculate the minimum temperature above which this reaction is feasible.

....

....

....

....

....

....

....

....

(5 marks)

2 (f) At temperatures below the value calculated in part **2 (e)**, decomposition of NO into its elements should be spontaneous. However, in car exhausts this decomposition reaction does **not** take place in the absence of a catalyst.
Suggest why this spontaneous decomposition does **not** take place.

....

....

(1 mark)

2 (g) A student had an idea to earn money by carrying out the following reaction.

$$C(graphite) \longrightarrow C(diamond)$$

Use data from the table on page 4 to calculate values for $\Delta H^\ominus$ and $\Delta S^\ominus$ for this reaction.
Use these values to explain why this reaction is **not** feasible under standard pressure at any temperature.

$\Delta H^\ominus$...

$\Delta S^\ominus$...

Explanation..

....

(3 marks)

14

Turn over ▶

3 There is a link between the properties of the oxides of the Period 3 elements and their structure and bonding. The table below shows the melting points of the oxides of some Period 3 elements.

	Na_2O	SiO_2	P_4O_{10}
T_m / K	1548	1883	573

3 (a) In terms of crystal structure and bonding, explain in each case why the melting points of sodium oxide and silicon dioxide are high.

Na_2O ....

....

....

SiO_2 ....

....

....

(4 marks)

3 (b) Predict whether the melting point of lithium oxide is higher than, the same as, or lower than the melting point of sodium oxide and explain your prediction.

Prediction...

Explanation...

....

....

(3 marks)

3 (c) Phosphorus(V) oxide has a lower melting point than sodium oxide.

3 (c) (i) State the structure of and bonding in phosphorus(V) oxide.

....

....

....

(2 marks)

3 (c) (ii) Explain why the melting point of phosphorus(V) oxide is low.

....

....

(1 mark)

3 (d) Separate samples of phosphorus(V) oxide and sodium oxide were reacted with water. In each case, predict the pH of the solution formed and write an equation for the reaction.

pH with P_4O_{10} ....

Equation ....

pH with Na_2O..

Equation ....

(4 marks)

3 (e) Write an equation for the reaction between Na_2O and P_4O_{10}
State the general type of reaction illustrated by this example.

Equation ....

Reaction type ....

(2 marks)

16

Turn over for the next question

4 Three characteristic properties of transition metals are complex formation, coloured ions and catalytic activity.

4 (a) State the feature of transition metals that gives rise to these characteristic properties.

....

(1 mark)

4 (b) State a fourth characteristic property of transition metals.

....

(1 mark)

4 (c) For each of the following shapes of complex, identify an appropriate example by drawing its structure.

4 (c) (i) a linear complex

(1 mark)

4 (c) (ii) a square planar complex

(1 mark)

4 (c) (iii) a tetrahedral complex

(1 mark)

Question 4 continues on the next page

Turn over ▶

4 (d) The chemical industry makes use of the catalytic activity of transition metal compounds. For example, vanadium(V) oxide is used as a heterogeneous catalyst in the Contact Process.

4 (d) (i) Write an equation for the overall reaction in the Contact Process.

....

(1 mark)

4 (d) (ii) Explain the meaning of the term *heterogeneous* as applied to a catalyst.

....

(1 mark)

4 (d) (iii) Write two equations to illustrate how vanadium(V) oxide acts as a catalyst in the Contact Process.

Equation 1 ....

Equation 2 ....

(2 marks)

4 (d) (iv) Suggest what is done to a heterogeneous catalyst such as vanadium(V) oxide to maximise its efficiency and how this is achieved.

....

....

....

(2 marks)

4 (e) The porphyrin ring is a multidentate ligand that is found in living systems complexed with iron(II) ions in haemoglobin and with cobalt(II) ions in vitamin B_{12}

4 (e) (i) Give the meaning of the term *multidentate.*

....

....

(1 mark)

4 (e) (ii) A porphyrin ring can be represented by the symbol PR. It reacts with aqueous iron(II) ions as shown in the equation below.
The enthalpy change for this reaction is approximately zero.

$$PR(aq) + [Fe(H_2O)_6]^{2+}(aq) \longrightarrow [FePR(H_2O)_2]^{2+}(aq) + 4H_2O(l)$$

Explain why the free-energy change for this reaction is negative.

....

....

....

....

(2 marks)

4 (e) (iii) In vitamin B_{12} the cobalt(II) ion is co-ordinated to a porphyrin ring, a cyanide (CN^-) ion and an additional unidentate ligand. The cyanide ion is very toxic.

Predict the co-ordination number of the cobalt ion in vitamin B_{12}
Suggest why vitamin B_{12} is **not** toxic.

Co-ordination number ....

Reason why vitamin B_{12} is **not** toxic

....

....

(2 marks)

16

5 (a) Lithium ion cells are used to power cameras and mobile phones.
A simplified representation of a cell is shown below.

$$\mathrm{Li} \mid \mathrm{Li^+} \parallel \mathrm{Li^+}\ ,\ \mathrm{CoO_2} \mid \mathrm{LiCoO_2} \mid \mathrm{Pt}$$

The reagents in the cell are absorbed onto powdered graphite that acts as a support medium. The support medium allows the ions to react in the absence of a solvent such as water.

The half-equation for the reaction at the positive electrode can be represented as follows.

$$\mathrm{Li^+} + \mathrm{CoO_2} + \mathrm{e^-} \longrightarrow \mathrm{Li^+[CoO_2]^-}$$

5 (a) (i) Identify the element that undergoes a change in oxidation state at the positive electrode and deduce these oxidation states of the element.

Element ....

Oxidation state 1 ....

Oxidation state 2 ....

(3 marks)

5 (a) (ii) Write a half-equation for the reaction at the negative electrode during operation of the lithium ion cell.

....

(1 mark)

5 (a) (iii) Suggest two properties of platinum that make it suitable for use as an external electrical contact in the cell.

Property 1..

Property 2 ....

(2 marks)

5 (a) (iv) Suggest **one** reason why water is **not** used as a solvent in this cell.

....

....

(1 mark)

5 (b) The half-equations for two electrodes used to make an electrochemical cell are shown below.

$$ClO_3^-(aq) + 6H^+(aq) + 6e^- \longrightarrow Cl^-(aq) + 3H_2O(l) \qquad E^\ominus = +1.45\ V$$

$$SO_4^{2-}(aq) + 2H^+(aq) + 2e^- \longrightarrow SO_3^{2-}(aq) + H_2O(l) \qquad E^\ominus = +0.17\ V$$

5 (b) (i) Write the conventional representation for the cell using platinum contacts.

....

(2 marks)

5 (b) (ii) Write an overall equation for the cell reaction and identify the oxidising and reducing agents.

Overall equation ....

....

....

Oxidising agent ....

Reducing agent ....

(3 marks)

12

Turn over for the next question

Section B

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

6 Aqueous metal ions can be identified by test-tube reactions.

For each of the following, describe what you would observe.

Write an equation or equations for any reactions that occur.

6 (a) The addition of aqueous sodium carbonate to a solution containing $[Fe(H_2O)_6]^{3+}$(aq) ions.

....

....

....

....

....

....

(4 marks)

6 (b) The addition of aqueous sodium hydroxide, dropwise until in excess, to a solution containing $[Al(H_2O)_6]^{3+}$(aq) ions.

....

....

....

....

....

....

(4 marks)

6 (c) The addition of dilute aqueous ammonia, dropwise until in excess, to a solution containing $[Cu(H_2O)_6]^{2+}(aq)$ ions.

....

....

....

....

....

....

(4 marks)

6 (d) The addition of concentrated hydrochloric acid, dropwise until in excess, to a solution containing $[Cu(H_2O)_6]^{2+}(aq)$ ions.

....

....

....

....

(2 marks)

14

Turn over for the next question

7 Hydrogen peroxide is used as an oxidising agent in the preparation of transition metal complexes.

7 (a) Consider the following reaction scheme. All the complexes are in aqueous solution.

$$[Co(H_2O)_6]^{2+} \xrightarrow{\text{Reaction } \mathbf{1}} \text{cobalt(II) complex} \xrightarrow[H_2O_2]{\text{Reaction } \mathbf{2}} [Co(NH_3)_6]^{3+}$$

7 (a) (i) Identify a reagent for Reaction **1** and describe the colour change that occurs.

....

....

....

....

(3 marks)

7 (a) (ii) State the colour of the final solution formed in Reaction **2**.

....

(1 mark)

7 (b) Consider the following reaction scheme. All the complexes are in aqueous solution.

$$[Cr(H_2O)_6]^{3+} \xrightarrow[\text{Excess NaOH(aq)}]{\text{Reaction } \mathbf{3}} \text{chromium(III) complex} \xrightarrow[H_2O_2]{\text{Reaction } \mathbf{4}} CrO_4^{2-}$$

7 (b) (i) For Reaction **3**, state the colour of the initial and of the final solution and write an equation for the reaction.

....

....

....

....

(4 marks)

7 (b) (ii) Write a half-equation for the reduction of hydrogen peroxide to hydroxide ions.

Deduce an overall equation for Reaction **4** and state the colour of the final solution.

....

....

....

....

....

....

(4 marks)

Question 7 continues on the next page

Turn over ▶

7 (c) The concentration of a hydrogen peroxide solution can be determined by titration with acidified potassium manganate(VII) solution. In this reaction the hydrogen peroxide is oxidised to oxygen gas.

A 5.00 cm^3 sample of the hydrogen peroxide solution was added to a volumetric flask and made up to 250 cm^3 of aqueous solution. A 25.0 cm^3 sample of this diluted solution was acidified and reacted completely with 24.35 cm^3 of 0.0187 mol dm^{-3} potassium manganate(VII) solution.

Write an equation for the reaction between acidified potassium manganate(VII) solution and hydrogen peroxide.
Use this equation and the results given to calculate a value for the concentration, in mol dm^{-3}, of the original hydrogen peroxide solution.
(If you have been unable to write an equation for this reaction you may assume that 3 mol of $KMnO_4$ react with 7 mol of H_2O_2. This is **not** the correct reacting ratio.)

....

....

....

....

....

....

....

....

....

....

(5 marks)

(Extra space) ....

....

17

END OF QUESTIONS

There are no questions printed on this page

DO NOT WRITE ON THIS PAGE
ANSWER IN THE SPACES PROVIDED