

Wednesday 12 June 2013 – Afternoon

A2 GCE CHEMISTRY A

F325/01 Equilibria, Energetics and Elements

Candidates answer on the Question Paper.

OCR supplied materials:

• Scientific calculator

• Data Sheet for Chemistry A (inserted)

Duration: 2 hours



Candidate forename		Candidate surname	
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Centre number	Candidate number		
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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. HB pencil may be used for graphs and diagrams only.
- Answer **all** the questions.
- Read each question carefully. Make sure you know what you have to do before starting your answer.
- Write your answer to each question in the space provided. If additional space is required, you should use the lined pages at the end of this booklet. The question number(s) must be clearly shown.
- 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.

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Answer all the questions.

- **1** Born–Haber cycles can be used to determine lattice enthalpies of ionic compounds.
 - (a) Define, in words, the term *lattice enthalpy*.



- (b) The Born–Haber cycle below can be used to determine the lattice enthalpy of calcium oxide. The cycle includes the values for the enthalpy changes of the steps labelled **A**–**G**.
 - (i) Complete the Born–Haber cycle by adding the species present on the two dotted lines.

Include state symbols.



(ii) Name the enthalpy changes for the following steps in the Born–Haber cycle.
step A
step C
step G

(iii) Calculate the lattice enthalpy of calcium oxide.

answer = kJ mol⁻¹ [2]

(c) Describe and explain the factors that affect the values of lattice enthalpies.

[3] [Total: 12] 2 In aqueous solution, benzenediazonium chloride, $C_6H_5N_2Cl$, decomposes above 10 °C.

$$C_6H_5N_2Cl(aq) + H_2O(l) \rightarrow C_6H_5OH(aq) + N_2(g) + HCl(aq)$$

A student investigates the rate of this reaction using an excess of water at 50 °C. The student takes measurements at intervals during the reaction and then plots his experimental results to give the graph shown below.



(iii) What would be the effect, if any, on the half-life of this reaction of doubling the initial concentration of $C_6H_5N_2Cl$?

.....[1]

- (b) The student predicts that the rate equation is: rate = $k[C_6H_5N_2Cl]$.
 - (i) Using the graph and this rate equation, determine the rate of reaction after 40 s.

Show your working on the graph.

rate =[3]

(ii) Calculate the rate constant, *k*, for this reaction and give its units.

(c) The order of this reaction with respect to H_2O is effectively zero.

Explain why.

[1] [Total: 10] **3** Hydrogen and iodine react together in a reversible reaction:

 $H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \Delta H = -9 \text{ kJ mol}^{-1}$

A chemist mixes together 2.00×10^{-3} mol H₂(g) and 4.00×10^{-3} mol I₂(g) in a 1.00 dm³ container. The chemist seals the container.

The mixture is heated and left to reach equilibrium.

At equilibrium, the mixture contains 3.00 \times $10^{-4}\,mol$ of $\rm H_2.$

(a) Calculate the equilibrium constant, $K_{\rm c}$, including units, if any, for this equilibrium.

Give your answer to three significant figures.

(i) The chemist uses 3.00×10^{-3} mol H₂(g) instead of 2.00×10^{-3} mol H₂(g).

Predict whether the amounts of $H_2(g)$, $I_2(g)$ and HI(g) in the equilibrium mixture would be greater, smaller or the same as in the original experiment.

Answer by placing ticks in the appropriate boxes of the table below.

	H ₂ (g)	I ₂ (g)	HI(g)
Greater			
Smaller			
The same			

(ii) The chemist heats the mixture to a higher temperature at constant pressure.

Explain whether the value of K_c would be greater, smaller or the same.

(iii) The chemist increases the pressure of the mixture at constant temperature.

Explain whether the value of K_c would be greater, smaller or the same.

......[1]

[Total: 9]

[2]

- 4 This question looks at pH values and reactions of acids, bases and buffers.
 - (a) 0.14 mol dm⁻³ solutions of hydrochloric acid, HC*l*, and chloric(I) acid, HC*l*O (p $K_a = 7.43$), have different pH values.

Explain why the pH values are different and calculate the pH of 0.14 mol dm^{-3} solutions of HCl and HClO to **two decimal places**.

Show any working in calculations.

(b) Aluminium powder is added to aqueous ethanoic acid, CH₃COOH. Write full and ionic equations for the reaction that takes place. full equation

(c) Calculate the pH of a 0.40 mol dm^{-3} solution of NaOH.

- (d) In biochemistry, buffer solutions based on methanoic acid can be used in the analysis of urine samples.
 - (i) Explain what is meant by the term *buffer solution*.

Describe how a buffer solution based on methanoic acid can act as a buffer.



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

[7]

[2]

(ii) A chemist prepares a buffer solution by mixing together the following:

200 cm³ of 3.20 mol dm⁻³ HCOOH ($K_a = 1.70 \times 10^{-4}$ mol dm⁻³) and 800 cm³ of 0.500 mol dm⁻³ NaOH.

The volume of the buffer solution is $1.00 \, \text{dm}^3$.

- Explain why a buffer solution is formed when these two solutions are mixed together.
- Calculate the pH of this buffer solution.

Give your answer to two decimal places.

[6]

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5 Iron is heated with chlorine to form an orange–brown solid, **A**.

Solid **A** is dissolved in water to form an orange–brown solution, **X**, containing the complex ion $[Fe(H_2O)_{cl}]^{3+}$.

Separate portions of solution **X** are reacted as shown in **Experiments 1–4** below.

Experiment 1

Aqueous sodium hydroxide is added to solution **X**. An orange–brown precipitate **B** forms.

Experiment 2

Excess zinc powder is added to solution **X** and the mixture is heated. The excess zinc is removed leaving a pale-green solution containing the complex ion **C** and aqueous Zn^{2+} ions.

Experiment 3

An excess of aqueous potassium cyanide, KCN(aq), is added to solution **X**. The solution turns a yellow colour and contains the complex ion **E**. **E** has a molar mass of 211.8 g mol^{-1} .

Experiment 4

An aqueous solution containing ethanedioate ions, $(COO^{-})_2$, is added to solution **X**. A coloured solution forms containing a mixture of optical isomers **F** and **G**.

The structure of the ethanedioate ion is shown below.



(a)	Wri	te an equation for the formation of solid A .	
			[1]
(b)	In E	Experiment 1, write an ionic equation for the formation of precipitate B.	
			[1]
(c)	In E	Experiment 2,	
	(i)	write an equation for the formation of complex ion ${f C}$	
			[2]
	(ii)	state the type of reaction taking place.	
			[1]

(d)	In E	Experiment 3,
	(i)	write an equation for the formation of complex ion E
		[2]
	(ii)	state the type of reaction taking place.
		[1]
(e) In Experiment 4, optical isomers F and G are formed.		

Show the 3-D shapes of **F** and **G**.

In your diagrams, show the ligand atoms that are bonded to the metal ions and any overall charges.

[3]

(f) In a separate experiment, iron metal is heated with potassium nitrate, KNO₃, a strong oxidising agent. A reaction takes place and the resulting mixture is poured into water. A dark red solution forms containing ferrate(VI) ions. The ferrate(VI) ion has a 2– charge.

Suggest a possible formula for the ferrate(VI) ion.

.....[1]

[Total: 12]

6 The equation for the reaction of CO₂ and H₂O to produce glucose, C₆H₁₂O₆, and O₂ is shown below.

$$6CO_{2}(g) + 6H_{2}O(I) \rightarrow C_{6}H_{12}O_{6}(s) + 6O_{2}(g) \Delta H = +2879 \text{ kJ mol}^{-1}; \Delta S = -256 \text{ J K}^{-1} \text{ mol}^{-1}$$

Standard entropies are given in the table below.

Substance	CO ₂ (g)	H ₂ O(I)	O ₂ (g)
S° / J K ⁻¹ mol ⁻¹	214	70	205

(a) (i) Calculate the standard entropy of glucose.

 S^{\oplus} = JK⁻¹ mol⁻¹ [2]

(ii) Calculate ΔG , in kJ mol⁻¹, at 25 °C.

Show all your working.

$\Delta G = \dots \text{kJmol}^{-1} [2]$

(iii) Explain why this reaction is **not** feasible at **any** temperature.

(b) Although the reaction between CO_2 and H_2O to form $C_6H_{12}O_6$ and O_2 appears not to be feasible, plants are able to make the reaction take place spontaneously by photosynthesis.

Each year, 3.4×10^{18} kJ of solar energy is taken in by all the plants on the Earth to make photosynthesis take place.

Calculate the mass of carbon dioxide that is removed each year from the atmosphere by photosynthesis on Earth.

[Total: 7]

7 Standard electrode potentials for seven redox systems are shown in **Table 7.1**. You may need to use this information in parts (a)–(d) of this question.

Redox system				E ^e /V
1	Mg ²⁺ (aq) + 2e ⁻	\rightleftharpoons	Mg(s)	-2.37
2	Cu ²⁺ (aq) + 2e ⁻	\rightleftharpoons	Cu(s)	+0.34
3	Al ³⁺ (aq) + 3e ⁻			-1.66
4	Fe ³⁺ (aq) + e ⁻	\rightleftharpoons	Fe ²⁺ (aq)	+0.77
5	I ₂ (aq) + 2e ⁻			+0.54
6	<i>Čl</i> ₂(g) + 2e [−]			+1.36
7	ClO-(aq) + 2H+(aq) + e-	\rightleftharpoons	$\frac{1}{2}Cl_{2}(g) + H_{2}O(I)$	+1.63

Table 7.1

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

(b) An electrochemical cell can be made based on redox systems 1 and 2.

Write down the standard cell potential of this cell.

standard cell potential = V [1]

- (c) Using redox systems 3, 4 and 5 only in Table 7.1, predict three reactions that might be feasible.
 - (i) Write the overall equation for each predicted reaction.

.....[3]

(ii) Give two reasons why it is uncertain whether reactions predicted from E° values may actually take place.[2] (d) In aqueous acid, $Cl^{-}(aq)$ ions react with $ClO^{-}(aq)$ ions to form chlorine gas, $Cl_{2}(g)$. In aqueous alkali, chlorine gas, $Cl_{2}(g)$, reacts to form $Cl^{-}(aq)$ and $ClO^{-}(aq)$ ions. Explain this difference. Use Table 7.1 to help you with your answer.[4] (e) In acidic conditions, Sn^{2+} ions react with IO_3^{-} ions to produce iodine and Sn^{4+} ions. (i) What is the oxidising agent in this reaction? Explain your answer.[1] Construct an equation for this reaction. (ii)

.....[2]

8 Dimethylglyoxime, DMGH, can be used to analyse nickel(II) compounds.

An excess of a solution of DMGH is added to an acidic solution of a nickel(II) compound. Aqueous ammonia is added which precipitates out a nickel(II) complex, Ni(DMG)₂, as a red solid.

A sample of a hydrated nickel(II) salt is analysed using the procedure below.

Step 1

2.50 g of the hydrated nickel(II) salt is dissolved in dilute acid. An excess of an aqueous solution of DMGH is added.

Step 2

An excess of aqueous ammonia is added and the mixture is heated. A red precipitate of Ni(DMG)₂ forms.

An equation for the reaction is shown below.

 $Ni^{2+}(aq) + 2DMGH(aq) + 2NH_3(aq) \rightarrow Ni(DMG)_2(s) + 2NH_4^+(aq)$ red precipitate

Step 3

The red precipitate is filtered, washed with water, dried and then weighed. The precipitate of Ni(DMG)₂ has a mass of 2.57 g. Assume that all Ni²⁺(aq) ions have been converted into Ni(DMG)₂(s). M[Ni(DMG)₂] = 288.7 g mol⁻¹.

Step 4

A second 2.50g sample of the hydrated nickel(II) salt is heated in a crucible to remove the water of crystallisation.

1.38g of the anhydrous salt remains.

(a) Complete the electron configurations of nickel as the element and in the +2 oxidation state.

nickel as the element:	1s ² 2s ² 2p ⁶
nickel in the +2 oxidation state:	1s ² 2s ² 2p ⁶

(b) The structure of $Ni(DMG)_2$ is shown below.



(i) State and explain the role of ammonia in **step 2** of this experiment.

	[1]
(ii)	State the coordination number of Ni in Ni(DMG) ₂ .
	[1]
(iii)	Why does the Ni(DMG) ₂ complex have no overall charge?
	[1]
(iv)	Draw the structure of dimethylglyoxime, DMGH.

[1]

(c) Determine a possible formula of the hydrated nickel(II) salt.

Your answer **must** show relevant working.

[Total: 13]

ADDITIONAL ANSWER SPACE

If additional answer space is required, you should use the following lined page(s). The question number(s) must be clearly shown in the margins.

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