OCR
RECOGNISING ACHIEVEMENT

# Wednesday 13 June 2012 – Morning

## A2 GCE CHEMISTRY A

**F325** Equilibria, Energetics and Elements

Candidates answer on the Question Paper.

**OCR supplied materials:**
- *Data Sheet for Chemistry A* (inserted)

**Other materials required:**
- Scientific calculator

**Duration:** 2 hours

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|---|---|---|---|
| Candidate forename | | Candidate surname | |

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

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**Turn over**

Answer **all** the questions.

**1** Lattice enthalpy can be used as a measure of ionic bond strength. Lattice enthalpies can be determined indirectly using Born–Haber cycles.

The table below shows the enthalpy changes that are needed to determine the lattice enthalpy of lithium fluoride, LiF.

| **enthalpy change** | **energy / kJ mol$^{-1}$** |
|---|---|
| 1st electron affinity of fluorine | –328 |
| 1st ionisation energy of lithium | +520 |
| atomisation of fluorine | +79 |
| atomisation of lithium | +159 |
| formation of lithium fluoride | –616 |

**(a)** Define the term *lattice enthalpy*.

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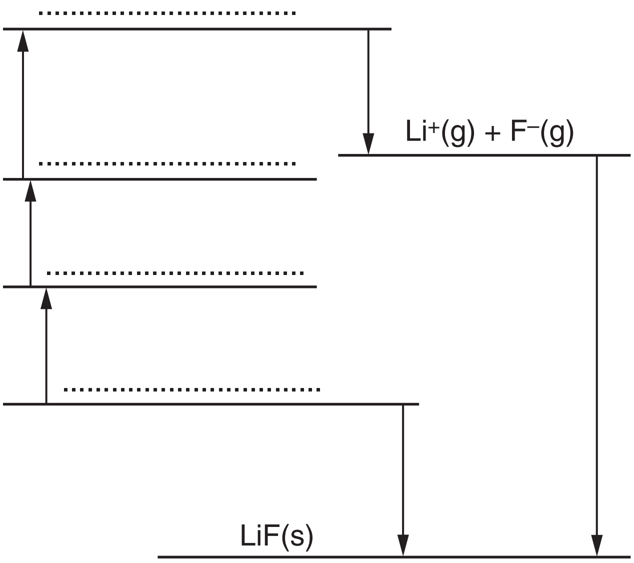
**(b)** The diagram below shows an incomplete Born–Haber cycle that would allow the lattice enthalpy of lithium fluoride to be determined.

**(i)** On the four dotted lines, add the species present, including state symbols.



**[4]**

**(ii)** Calculate the lattice enthalpy of lithium fluoride.

lattice enthalpy = ........................................... kJ mol$^{-1}$ **[2]**

**(c)** The change that produces lattice enthalpy is spontaneous but has a negative entropy change.

Why is this change able to take place spontaneously?

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**(d)** The lattice enthalpies of sodium fluoride, sodium chloride and magnesium fluoride are shown below.

| **compound** | **lattice enthalpy / kJ mol$^{-1}$** |
|---|---|
| sodium fluoride | –918 |
| sodium chloride | –780 |
| magnesium fluoride | –2957 |

Explain the differences between these lattice enthalpies.

*In your answer, your explanation should show how different factors affect lattice enthalpy.*

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**[Total: 12]**

**2** A chemist carries out an investigation on the equilibrium system shown below.

$$2CO(g) + 2NO(g) \rightleftharpoons 2CO_2(g) + N_2(g) \qquad \Delta H = -788\,kJ\,mol^{-1}$$

The chemist mixes 0.46 mol of CO with 0.45 mol of NO. The mixture is left to reach equilibrium at constant temperature.

The student analyses the equilibrium mixture and finds that 0.25 mol NO remains. The total volume of the equilibrium mixture is 1.0 $dm^3$.

**(a)** **(i)** Write the $K_c$ expression for this equilibrium.

**[1]**

**(ii)** What are the units of this equilibrium constant?

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**(iii)** Determine the value of $K_c$ for this equilibrium mixture.

Show all your working.

$K_c$ = ........................................................ **[4]**

**(iv)** What does your value of $K_c$ suggest about the position of equilibrium in this experiment?

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**(b)** The chemist increases **both** the temperature and the pressure of the equilibrium mixture. The mixture is left to reach equilibrium again.

**(i)** What is the effect, if any, on the value of $K_c$? Explain your answer.

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**(ii)** Explain why it is difficult to predict what would happen to the position of equilibrium after these changes in temperature and pressure.

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**[Total: 10]**

**3** Butanoic acid, $CH_3(CH_2)_2COOH$, is the 'butter acid', formed when butter turns rancid and tastes sour. A student prepares an aqueous solution of butanoic acid with a concentration of $0.250\,mol\,dm^{-3}$.

The $K_a$ of butanoic acid is $1.51 \times 10^{-5}\,mol\,dm^{-3}$.

**(a)** **(i)** Write the expression for the acid dissociation constant of butanoic acid.

**[1]**

**(ii)** Calculate the p$K_a$ of butanoic acid.

p$K_a$ = ........................................................ **[1]**

**(iii)** Calculate the pH of the $0.250\,mol\,dm^{-3}$ butanoic acid.

Give your answer to **two** decimal places.

pH = ........................................................ **[3]**

**(b)** The student adds aqueous butanoic acid to magnesium.

The student then adds aqueous butanoic acid to aqueous sodium carbonate.

**(i)** Write the ionic equation for the reaction between aqueous butanoic acid and magnesium.

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**(ii)** Write the ionic equation for the reaction between aqueous butanoic acid and aqueous sodium carbonate.

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**(c)** The student adds 50.0 $cm^3$ of 0.250 mol $dm^{-3}$ butanoic acid to 50.0 $cm^3$ of 0.0500 mol $dm^{-3}$ sodium hydroxide. A buffer solution forms.

**(i)** Explain why a buffer solution forms.

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**(ii)** Calculate the pH of the buffer solution.

The $K_a$ of butanoic acid is $1.51 \times 10^{-5}$ mol $dm^{-3}$.

Give your answer to **two** decimal places.

pH = ........................................................ **[5]**

**(d)** The student adds methanoic acid, HCOOH ($K_a = 1.82 \times 10^{-4}$ mol $dm^{-3}$), to butanoic acid. A reaction takes place to form an equilibrium mixture containing two acid–base pairs.

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

$HCOOH + CH_3(CH_2)_2COOH \rightleftharpoons$ ................................. + ....................................

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**[2]**

**[Total: 16]**

**4** Nitrogen dioxide reacts with ozone as shown below.

$$2NO_2(g) + O_3(g) \rightarrow N_2O_5(g) + O_2(g)$$

**(a)** The kinetics of the reaction between $NO_2$ and $O_3$ was investigated and the following experimental results were obtained.

| **experiment** | **$[NO_2(g)]$ / mol dm$^{-3}$** | **$[O_3(g)]$ / mol dm$^{-3}$** | **initial rate / mol dm$^{-3}$ s$^{-1}$** |
|---|---|---|---|
| 1 | 0.00150 | 0.00250 | $4.80 \times 10^{-8}$ |
| 2 | 0.00225 | 0.00250 | $7.20 \times 10^{-8}$ |
| 3 | 0.00225 | 0.00500 | $1.44 \times 10^{-7}$ |

**(i)** Determine the rate equation and rate constant for the reaction of $NO_2(g)$ and $O_3(g)$.

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

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**(ii)** Suggest a possible two-step mechanism for this reaction.

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**(b)** The feasibility of the reaction between $NO_2$ and $O_3$ is influenced by the enthalpy change and entropy change of the reaction and the temperature.

$$2NO_2(g) + O_3(g) \rightarrow N_2O_5(g) + O_2(g) \qquad \Delta H = -198\,\text{kJ mol}^{-1}$$
$$\Delta S = -168\,\text{J K}^{-1}\,\text{mol}^{-1}$$

**(i)** Explain why this reaction has a negative entropy change.

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**(ii)** Calculate the value of $\Delta G$, in kJ mol$^{-1}$, at 25 °C for the reaction of $NO_2$ with $O_3$.

$\Delta G$ = .......................................... kJ mol$^{-1}$ **[3]**

**(iii)** State and explain how the feasibility of this reaction will change with increasing temperature.

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**[Total: 17]**

**5** Iron, copper and platinum are examples of transition elements.

**(a)** Define the term *transition element*.

Show that iron fits this definition by use of full electron configurations of iron as the element and in its common oxidation states.

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**(b)** Describe **one** precipitation reaction and **one** ligand substitution reaction of copper in the +2 oxidation state.

Your answer should include reagents, relevant observations and balanced equations.

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**(c)** Platinum is an extremely unreactive transition element. However, platinum does take part in a redox reaction with '*aqua regia*', a mixture of concentrated hydrochloric and nitric acids. Two products of this reaction are hexachloroplatinic acid, $H_2PtCl_6$, and nitrogen dioxide, $NO_2$.

**(i)** Use oxidation states to show that this is a redox reaction.

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**(ii)** Write an equation for the reaction of platinum metal with *aqua regia*.

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**(d)** Ammonium hexachloroplatinate, $(NH_4)_2PtCl_6$, is a complex of platinum used in platinum plating. Ammonium hexachloroplatinate contains the hexachloroplatinate ion.

Draw a 3-D diagram to show the shape of a hexachloroplatinate ion.

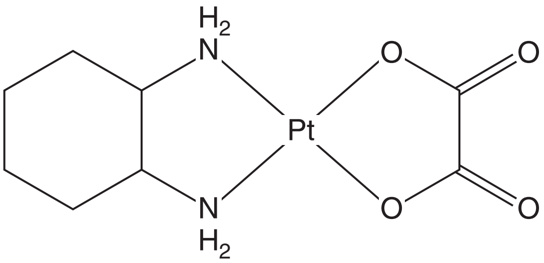
On your diagram, show

- the charge on the ion
- the value of the bond angle.

**[3]**

**(e)** Oxaliplatin is a neutral complex of platinum(II) used in cancer treatment.

A molecule of oxaliplatin has a square planar shape about the metal ion with two bidentate ligands. The structure of oxaliplatin is shown below.



**(i)** What is meant by a *bidentate ligand*?

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**(ii)** In the boxes below, show the structures of the two bidentate ligands in oxaliplatin.

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**[2]**

**[Total: 21]**

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TURN OVER FOR QUESTION 6

**6** Standard electrode potentials for eight redox systems are shown in **Table 6.1**.

You will need to use this information throughout this question.

| redox system | half-equation | $E^\ominus$/V |
|---|---|---|
| **1** | $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$ | 0.00 |
| **2** | $Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ | +0.77 |
| **3** | $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$ | +1.33 |
| **4** | $O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$ | +1.23 |
| **5** | $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ | +0.34 |
| **6** | $CO_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons HCOOH(aq)$ | –0.22 |
| **7** | $HCOOH(aq) + 2H^+(aq) + 2e^- \rightleftharpoons HCHO(aq) + H_2O(l)$ | +0.06 |
| **8** | $Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$ | –0.74 |

**Table 6.1**

**(a)** A student sets up a standard cell in the laboratory based on redox systems **2** and **8**. His circuit allows him to measure the standard cell potential.

**(i)** Draw a labelled diagram to show how the student could have set up this cell to measure its standard cell potential.

**[3]**

**(ii)** Write down the overall cell reaction.

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**(iii)** Write down the standard cell potential.

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

**(b)** Select from **Table 6.1**, the strongest oxidising agent.

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**(c)** Using the redox systems in **Table 6.1**, construct an equation for a reaction between acidified dichromate(VI) ions and methanoic acid, HCOOH.

Rather than using [O] or [H], your equation must show the actual reactants and products.

**[2]**

**(d)** A student added some chromium metal to an acidified solution containing copper(II) ions. A reaction took place. The student concluded that 'chromium is more reactive than copper'.

**(i)** Explain, in terms of their electrode potentials, why 'chromium is more reactive than copper' in this reaction.

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**(ii)** When this experiment was carried out, the student observed some bubbles of a gas.

Suggest an explanation for this observation.

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**(e)** Methanoic acid, HCOOH, has the common name of 'formic acid'. Direct-Formic Acid Fuel Cells (DFAFCs) are being developed for use in small, portable electronics such as phones and laptop computers.

In this fuel cell, methanoic acid (the fuel) reacts with oxygen to generate a cell potential.

**(i)** Predict the standard cell potential of a DFAFC.

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

**(ii)** Suggest **two** advantages of using methanoic acid as the fuel in a fuel cell rather than hydrogen.

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**[Total: 14]**

**7** Potassium manganate(VII) can be prepared in the laboratory by a two-step synthesis starting from manganese(IV) oxide.

***Step 1***

In this step, manganese(IV) oxide is heated strongly with potassium hydroxide and potassium chlorate(V), a powerful oxidising agent.

Manganese(IV) oxide, $MnO_2$, is oxidised to manganate(VI) ions.

***Step 2***

Potassium manganate(VI) is separated from the alkaline mixture from **step 1** as a green solid.

In this step, potassium manganate(VI) is heated in water. Manganate(VI) ions disproportionate forming manganate(VII) ions and a precipitate of manganese(IV) oxide.

**(a)** In **step 1**, a redox reaction takes place.

Add the correct number of electrons to the correct sides of the incomplete oxidation and reduction half-equations shown below.

$$MnO_2 + 4OH^- \rightarrow MnO_4^{2-} + 2H_2O$$

$$3H_2O + Cl O_3^- \rightarrow 6OH^- + Cl^-$$

**[2]**

**(b)** In **step 2**, an equilibrium is set up.

$$3MnO_4^{2-}(aq) + 2H_2O(l) \rightleftharpoons 2MnO_4^-(aq) + MnO_2(s) + 4OH^-(aq)$$

The equilibrium position can be shifted by bubbling carbon dioxide gas through the mixture.

Suggest, with the aid of an equation, how the equilibrium position shifts.

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**(c)** Aqueous potassium manganate(VII), $KMnO_4$, in acidic conditions can be used in analysis.

A student analyses a sample of sodium sulfite, $Na_2SO_3$, using the following method.

- The student dissolves 0.720 g of impure sodium sulfite in water.
- The solution is made up to 100.0 $cm^3$.
- The student titrates 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 is 26.2 $cm^3$.

The equation for the reaction is shown below.

$$2MnO_4^- + 6H^+ + 5SO_3^{2-} \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$

Determine the percentage purity of the sample of sodium sulfite.

percentage purity = ...................................................... % **[5]**

**[Total: 10]**

**END OF QUESTION PAPER**

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