Wednesday 1 February 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

Candidate forename		Candidate surname	

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. 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.

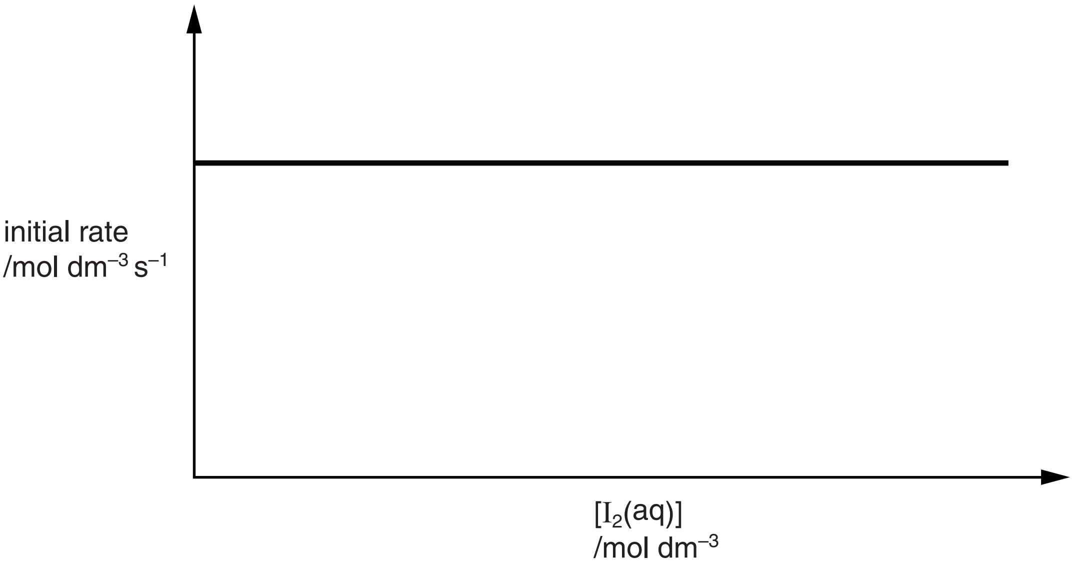
Turn over

Answer **all** the questions.

1 A student investigates the reaction between iodine, I_2, and propanone, $(CH_3)_2CO$, in the presence of aqueous hydrochloric acid, $HCl(aq)$.

The results of the investigation are shown below.

Rate–concentration graph



Results of initial rates experiments

experiment	$[(CH_3)_2CO(aq)]$ / mol dm^{-3}	$[HCl(aq)]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	1.50×10^{-3}	2.00×10^{-2}	2.10×10^{-9}
2	3.00×10^{-3}	2.00×10^{-2}	4.20×10^{-9}
3	3.00×10^{-3}	5.00×10^{-2}	1.05×10^{-8}

(a) Determine the orders with respect to I_2, $(CH_3)_2CO$ and HCl, the rate equation and the rate constant for the reaction.

Explain all of your reasoning.

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.... **[9]**

(b) The student then investigates the reaction of hydrogen, H_2, and iodine monochloride, ICl.

The equation for this reaction is shown below.

$$H_2(g) + 2ICl(g) \rightarrow 2HCl(g) + I_2(g)$$

The rate equation for this reaction is shown below.

$$\text{rate} = k[H_2(g)]\,[ICl(g)]$$

Predict a possible two-step mechanism for this reaction. The first step should be the rate-determining step.

step 1 ....

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

[Total: 11]

2 Lattice enthalpies can be calculated indirectly using Born–Haber cycles.

Table 2.1 shows enthalpy changes needed to calculate the lattice enthalpy of sodium oxide, Na_2O.

letter	**enthalpy change**	**energy /kJ mol^{-1}**
A	1st electron affinity of oxygen	–141
B	2nd electron affinity of oxygen	+790
C	1st ionisation energy of sodium	+496
D	atomisation of oxygen	+249
E	atomisation of sodium	+108
F	formation of sodium oxide	–414
G	lattice enthalpy of sodium oxide	

Table 2.1

(a) Define the term *lattice enthalpy*.

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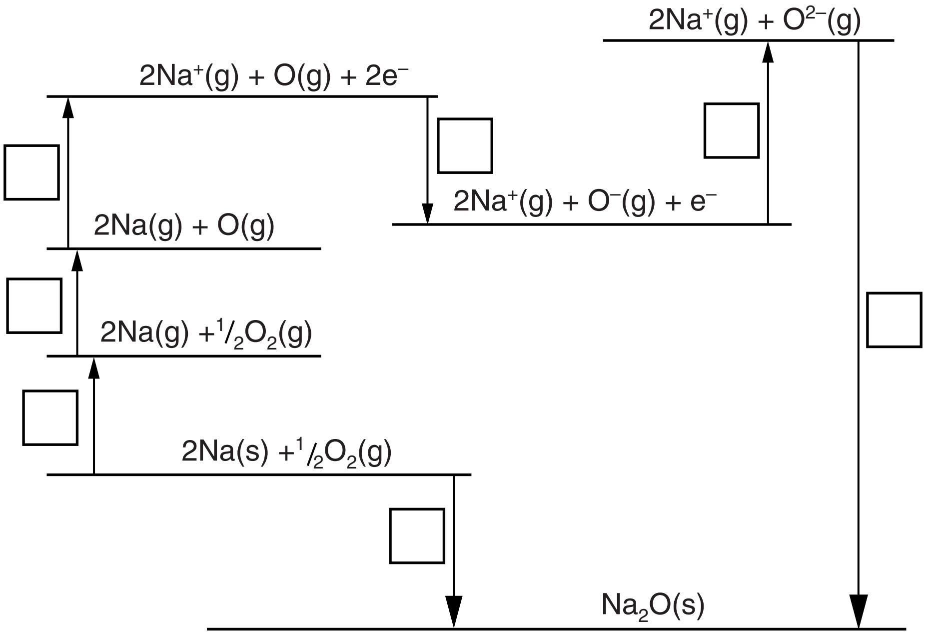
.... **[2]**

(b) The Born–Haber cycle below links the lattice enthalpy of sodium oxide with its enthalpy change of formation.

(i) On the Born–Haber cycle, write the correct letter from **Table 2.1** in each box.



[3]

(ii) Calculate the lattice enthalpy of sodium oxide, **G**.

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

(c) Explain why it is difficult to predict whether the lattice enthalpy of magnesium sulfide would be more or less exothermic than the lattice enthalpy of sodium oxide.

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.... **[3]**

(d) A student wanted to determine the lattice enthalpy of sodium carbonate, Na_2CO_3. Unfortunately this is very difficult to do using a similar Born–Haber cycle to that used for sodium oxide in **(b)**.

(i) Suggest why this is very difficult.

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.... **[1]**

(ii) The student thought that he could determine the lattice enthalpy of Na_2CO_3 using a Born–Haber cycle that links lattice enthalpy with enthalpy change of solution.
The enthalpy change of solution of Na_2CO_3 is exothermic.

- Sketch this Born–Haber cycle,
- Explain how the lattice enthalpy of Na_2CO_3 could be calculated from the enthalpy changes in the cycle.

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.... **[3]**

[Total: 14]

3 Cobalt is a transition element. Solid compounds of cobalt are often complexes and in solution, complex ions are formed.

(a) In its complexes, the common oxidation numbers of cobalt are +2 and +3.

Complete the electron configurations of cobalt as the element and in the +3 oxidation state:

cobalt as the element: $1s^2\ 2s^2\ 2p^6$ ....

cobalt in the +3 oxidation state: $1s^2\ 2s^2\ 2p^6$ .... **[2]**

(b) State **one** property of cobalt(II) and cobalt(III), other than their ability to form complex ions, which is typical of ions of a transition element.

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.... **[1]**

(c) Complex ions contain ligands.

State the meaning of the term *ligand*.

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.... **[1]**

(d) Aqueous cobalt(II) sulfate, $CoSO_4(aq)$, takes part in the following reactions.

For each reaction, state the formula of the transition element species formed and the type of reaction taking place.

(i) Aqueous cobalt(II) sulfate, $CoSO_4(aq)$, reacts with aqueous sodium hydroxide.

transition element species formed: ....

type of reaction: .... **[2]**

(ii) Aqueous cobalt(II) sulfate, $CoSO_4(aq)$, reacts with concentrated hydrochloric acid.

transition element species formed: ....

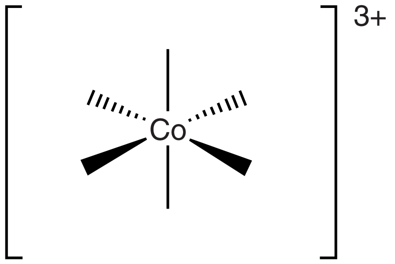
type of reaction: .... **[2]**

(e) Cobalt(III) chloride, $CoCl_3$, reacts with ammonia to form a range of complexes. These complexes contain different amounts of ammonia. Information about these complexes is summarised below.

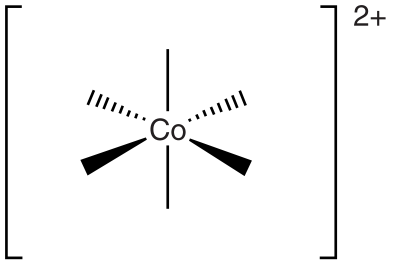
The complex ions **C** and **D** are stereoisomers.

complex	**formula**	**formula of complex**
A	$CoCl_3(NH_3)_6$	$[Co(NH_3)_6]^{3+}\ 3Cl^-$
B	$CoCl_3(NH_3)_5$	$[Co(NH_3)_5Cl]^{2+}\ 2Cl^-$
C	$CoCl_3(NH_3)_4$	$[Co(NH_3)_4Cl_2]^+\ Cl^-$
D	$CoCl_3(NH_3)_4$	$[Co(NH_3)_4Cl_2]^+\ Cl^-$

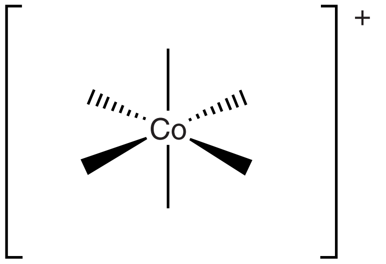
(i) Complete the diagrams below to suggest possible structures for the complex ion in complexes **A** to **D**.



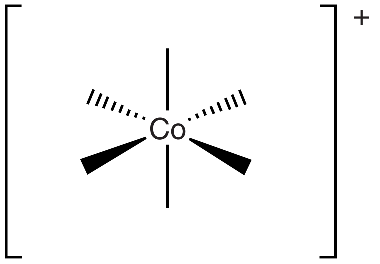
complex ion in A



complex ion in B



complex ion in C



complex ion in D

[4]

(ii) Chemists provided evidence for the formulae of these complexes from their reactions with aqueous silver nitrate. Aqueous silver nitrate reacts with aqueous halide ions in a precipitation reaction.

An excess of silver nitrate solution was reacted with 0.0100 mol of one of the complexes **A** to **D**. 2.868 g of a precipitate was formed.

Determine which complex was reacted.

In your answer you should explain how the result of the experiment would allow the formula of the complex to be identified.

[3]

[Total: 15]

4 This question looks at acids, bases and buffer solutions.

(a) Nitric acid, HNO_3, is a strong Brønsted–Lowry acid.
Nitrous acid, HNO_2, is a weak Brønsted–Lowry acid with a K_a value of $4.43 \times 10^{-4}\,mol\,dm^{-3}$.

(i) What is the difference between a strong acid and a weak acid?

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.... **[1]**

(ii) What is the expression for the acid dissociation constant, K_a, of nitrous acid, HNO_2?

[1]

(iii) Calculate the pH of $0.375\,mol\,dm^{-3}$ nitrous acid, HNO_2.

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

pH = ... **[2]**

(iv) A student suggests that an acid–base equilibrium is set up when nitric acid is mixed with nitrous acid.

Complete the equation for the equilibrium that would be set up and label the conjugate acid–base pairs.

HNO_3 + HNO_2 $\rightleftharpoons$ .... + ...

....

[2]

(b) Calcium hydroxide, $Ca(OH)_2$, is a strong Brønsted–Lowry base.

(i) Explain what is meant by the term *Brønsted–Lowry base*.

....

.... **[1]**

(ii) Calculate the pH of 0.0400 mol dm^{-3} $Ca(OH)_2$.

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

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

(c) Aqueous calcium hydroxide is added to nitrous acid, HNO_2.

Write the overall equation and the ionic equation for the reaction that takes place.

overall: ....

ionic: .... **[2]**

(d) Carbonic acid, H_2CO_3, is a weak Brønsted–Lowry acid formed when carbon dioxide dissolves in water. Healthy blood is buffered to a pH of 7.40. The most important buffer solution in blood is a mixture of carbonic acid and hydrogencarbonate ions, HCO_3^-.

(i) Explain how the carbonic acid–hydrogencarbonate mixture acts as a buffer in the control of blood pH.

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

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(ii) Healthy blood at a pH of 7.40 has a hydrogencarbonate : carbonic acid ratio of 10.5 : 1. A patient is admitted to hospital. The patient's blood pH is measured as 7.20.

Calculate the hydrogencarbonate : carbonic acid ratio in the patient's blood.

[5]

[Total: 22]

5 Redox reactions can be used to generate electrical energy from electrochemical cells.

(a) A student carries out an investigation based on the redox systems shown in **Table 5.1** below.

	redox system	$E^{\ominus}$**/V**
1	$Ni^{2+}(aq) + 2e^{-} \rightleftharpoons Ni(s)$	–0.25
2	$Fe^{3+}(aq) + e^{-} \rightleftharpoons Fe^{2+}(aq)$	+0.77
3	$Cr^{3+}(aq) + 3e^{-} \rightleftharpoons Cr(s)$	–0.74

Table 5.1

The student sets up two standard cells to measure two standard cell potentials.

- **Cell A** is based on redox systems **1** and **2**.
- **Cell B** is based on redox systems **1** and **3**.

(i) Draw a labelled diagram to show how the student could have set up **Cell A**, based on redox systems **1** and **2**, to measure the standard cell potential.

[3]

(ii) For each standard cell below,

- what would be the standard cell potential?
- what would be the sign of the Ni electrode?

Cell A based on redox system **1** and **2**:

standard cell potential = ... V

sign of Ni electrode, + or – = ...

Cell B based on redox system **1** and **3**:

standard cell potential = ... V

sign of Ni electrode, + or – = ...

[2]

(b) The student left each cell in **(a)** connected for a length of time.

For each cell, the student weighed the nickel electrode before connecting the cell and after the cell had been disconnected.

The student made the following observations.

- In **Cell A**, the nickel electrode lost mass.
- In **Cell B**, the nickel electrode gained mass.
- In **both** cells, the measured cell potential slowly changed.

Explain these observations. Include equations in your answer.

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.... **[3]**

(c) Nickel metal hydride cells (NiMH cells) are being developed for possible use in cars.
In a NiMH cell, an alloy is used to absorb hydrogen as a metal hydride. For simplicity, the alloy can be represented as M and the metal hydride as MH.

The overall cell reaction in a NiMH cell is shown below.

$$\mathrm{MH + NiO(OH) \rightarrow M + Ni(OH)_2}$$

The half-equation at one electrode is shown below.

$$\mathrm{NiO(OH) + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-}$$

(i) Deduce the half-equation at the other electrode.

.... **[1]**

(ii) State a method, other than absorption, that is being developed to store hydrogen for possible use as a fuel in cars.

.... **[1]**

[Total: 10]

6 Free energy changes can be used to predict the feasibility of processes.

(a) Write down the equation that links the free energy change with the enthalpy change and temperature.

.... **[1]**

(b) You are provided with equations for five processes.

For each process, predict the sign of Δ*S*.

process	**sign of Δ*S***
$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$	
$NaCl(s) + (aq) \rightarrow NaCl(aq)$	
$H_2O(l) \rightarrow H_2O(s)$	
$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$	
$CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4{\bullet}5H_2O(s)$	

[2]

(c) Ammonia can be oxidised as shown in the equation below.

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

Standard entropies are given in the table below.

substance	$NH_3(g)$	$O_2(g)$	$NO(g)$	$H_2O(g)$
$S^{\ominus}$ / J K^{-1} mol^{-1}	192	205	211	189

Calculate the standard entropy change, in J K^{-1} mol^{-1}, for this oxidation of ammonia.

$\Delta S^{\ominus}$ = ... J K^{-1} mol^{-1} **[2]**

(d) The exothermic reaction below occurs spontaneously at low temperatures but does **not** occur at very high temperatures.

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

Explain why.

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.... **[2]**

(e) An ore of iron contains iron(III) oxide, Fe_2O_3.
Iron is extracted from this ore by heating with carbon.
The equation below shows one of the reactions which takes place.

$$Fe_2O_3(s) + 3C(s) \rightarrow 2Fe(s) + 3CO(g)$$

$\Delta S = +543\,J\,K^{-1}\,mol^{-1}$ and $\Delta H = +493\,kJ\,mol^{-1}$

Calculate the minimum temperature at which this reaction becomes feasible.

Show **all** your working.

minimum temperature = ... **[3]**

[Total: 10]

7 Dinitrogen tetroxide, $N_2O_4(g)$, and nitrogen dioxide, $NO_2(g)$, coexist in the following equilibrium.

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad \Delta H = -57\,\text{kJ mol}^{-1}$$

A chemist adds 4.00 mol NO_2 to a container with a volume of 2.00 dm^3. The container is sealed, heated to a constant temperature and allowed to reach equilibrium.

The equilibrium mixture contains 3.20 mol NO_2.

(a) Calculate the value for K_c under these conditions.

[5]

(b) The experiment is repeated but the pressure in the container is doubled.

Explain in terms of K_c the effect on the concentrations of NO_2 and N_2O_4 when the mixture has reached equilibrium.

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.... **[3]**

[Total: 8]

8 Haematite is the main ore of iron. The percentage of iron in a sample of haematite can be determined using the method below.

Method

Stage 1. An excess of concentrated hydrochloric acid is added to a 3.25 g sample of haematite. The iron(III) oxide in the haematite reacts to form a solution containing Fe^{3+} ions.

Stage 2. An excess of aqueous tin(II) chloride is added. Sn^{2+} reduces the Fe^{3+} present to Fe^{2+}. Excess Sn^{2+} is removed.

Stage 3. The solution is diluted and made up to 250.0 cm^3 in a volumetric flask.

Stage 4. A 25.0 cm^3 sample of this solution is pipetted into a conical flask.

Stage 5. The solution in the conical flask is titrated with 0.0200 mol dm^{-3} aqueous potassium dichromate(VI), $K_2Cr_2O_7$.
The Fe^{2+} ions are oxidised to Fe^{3+} ions.

Stage 6. Stages 4 and **5** are repeated to obtain an average titre of 26.5 cm^3.

You are provided with the following electrode potentials.

You may need to use this information throughout this question.

$$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq) \qquad E^\ominus = +0.15\,V$$
$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq) \qquad E^\ominus = +0.77\,V$$
$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l) \qquad E^\ominus = +1.33\,V$$
$$Cl_2(aq) + 2e^- \rightleftharpoons 2Cl^-(aq) \qquad E^\ominus = +1.36\,V$$
$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l) \qquad E^\ominus = +1.51\,V$$

(a) Write an equation for the reaction between iron(III) oxide and concentrated hydrochloric acid, occurring in **Stage 1**.

.... **[1]**

(b) Write equations for the reactions involving iron ions in **Stages 2** and **5**.

Stage 2 ....

Stage 5 .... **[2]**

(c) Calculate the percentage by mass of iron in the haematite ore.

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

(d) Aqueous potassium manganate(VII), $KMnO_4$(aq), is **not** suitable for titrating the solution in this method. Aqueous potassium dichromate(VI), $K_2Cr_2O_7$(aq), is used instead.

Suggest and explain why potassium dichromate(VI), $K_2Cr_2O_7$, is suitable for this titration whereas potassium manganate(VII), $KMnO_4$, is not suitable.

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.... **[2]**

[Total: 10]

END OF QUESTION PAPER

ADDITIONAL PAGE

If additional space is required, you should use the lined pages below. The question number(s) must be clearly shown.

ADDITIONAL PAGE

ADDITIONAL PAGE

RECOGNISING ACHIEVEMENT