OCR
RECOGNISING ACHIEVEMENT

Wednesday 12 June 2013 – Afternoon

A2 GCE CHEMISTRY A

F325/01 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	Max	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.

DC (NH/SW) 57634/4

OCR is an exempt Charity

Turn over

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*.

FORMATION OF 1 MOLE OF COMPOUND ✓

FROM ITS GASEOUS IONS UNDER S.C. ✓

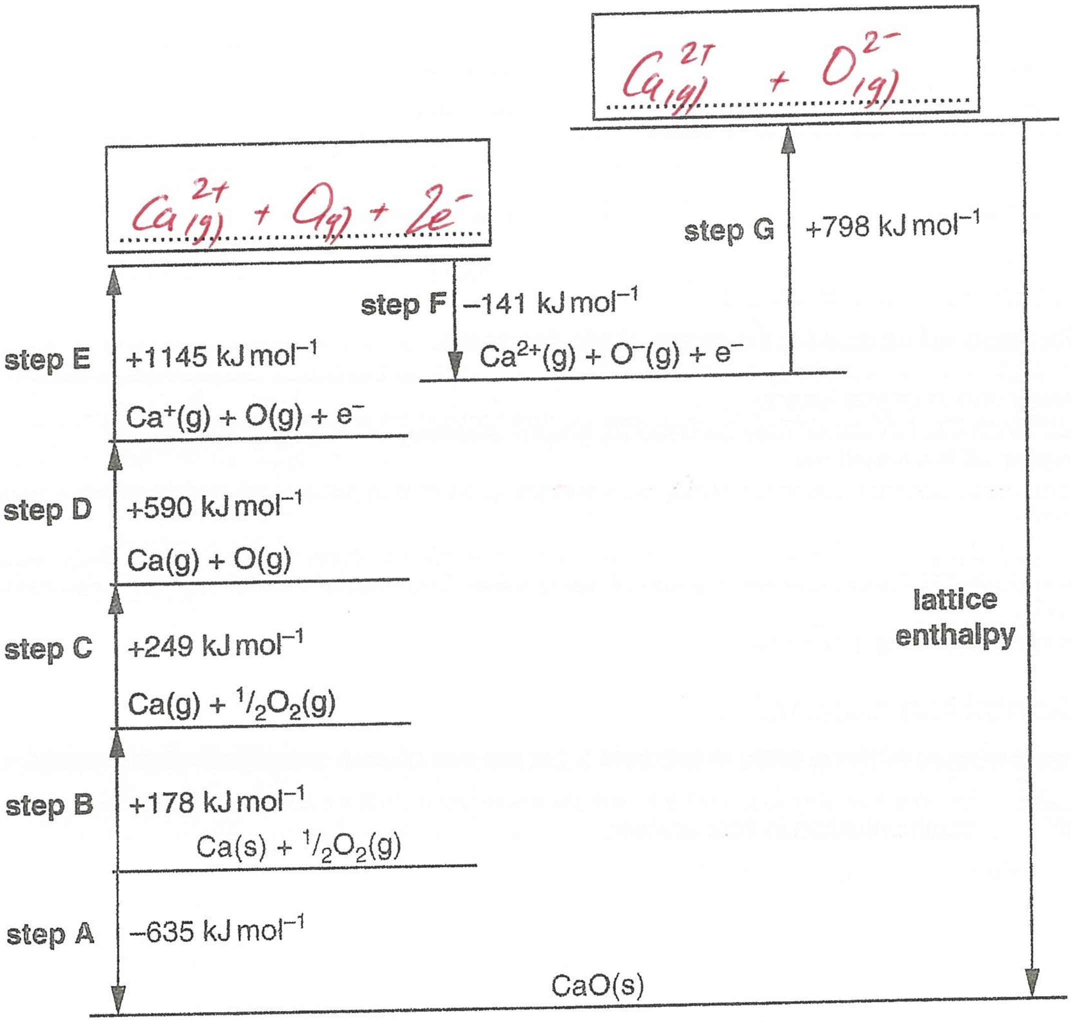
....

.... [2]

(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.



[2]

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

- **step A**

ENTHALPY CHANGE OF FORMATION

- **step C**

ENTHALPY CHANGE OF ATOMISATION OF OXYGEN

- **step G**

2ND ELECTRON AFFINITY OF OXYGEN

[3]

(iii) Calculate the lattice enthalpy of calcium oxide.

$-635 - (178 + 249 + 590 + 1145 + {}^{-}141 + 798)$

answer = -3454 kJ mol^{-1} **[2]**

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

SIZE OF ION :- AS SIZE ↓ CHARGE DENSITY ↑ ✓

ATTRACTION ↑ ∴ LE MORE EXOTHERMIC

CHARGE OF ION :-

AS CHARGE ↑, CHARGE DENSITY ↑ ✓

ATTRACTION ↑ ∴ L.E. MORE EXOTHERMIC

✓

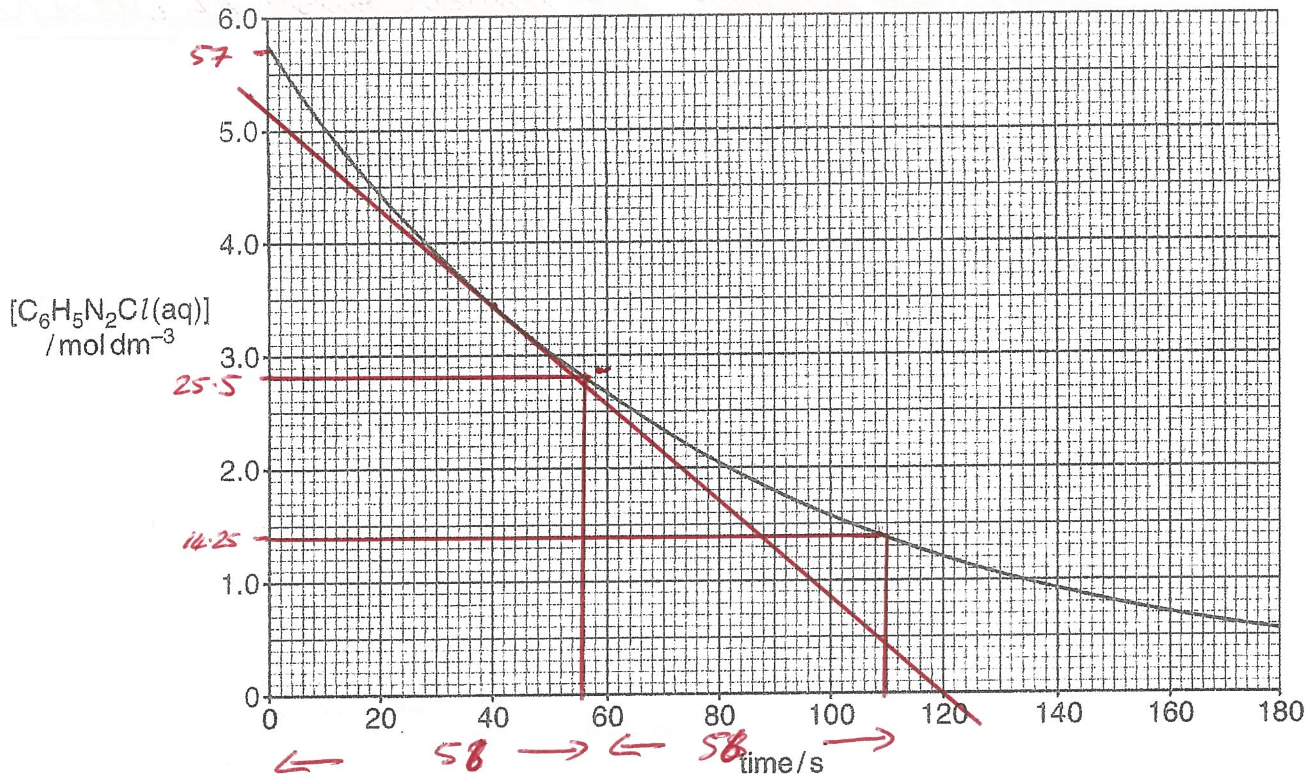
[3]

[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.



(a) The student uses half-life to suggest the order of reaction with respect to $C_6H_5N_2Cl$.

(i) What is meant by the *half-life* of a reaction?

TIME TAKEN FOR CONC^n TO HALVE

.... [1]

(ii) Confirm the order of reaction with respect to $C_6H_5N_2Cl$.

Show your working on the graph.

2 HALVE LIVES DRAWN ✓ (~56)

1ST ORDER-HAS A CONSTANT ½ LIFE ✓

.... [2]

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

NO EFFECT .... [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. MEANS AT 40

Show your working on the graph. TANGENT DRAWN ✓

$$RATE = \frac{\Delta Y}{\Delta X} = \frac{5.2}{120} = 0.043\dot{3}$$

✓ ✓

rate = $0.04\dot{3}$ units $Mol\,dm^{-3}\,s^{-1}$ [3]

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

$$k = \frac{RATE}{[C_6H_5N_2Cl]}$$

$$= \frac{0.043}{3.45}$$ ✓

CONC^n AT TANGENT = 3.45

RATE = $0.04\dot{3}$ (bi)

k = 0.0126 units s^{-1} ✓ [2]

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

Explain why.

WATER IS IN EXCESS ∴ DOESN'T CHANGE

....

.... [1]

[Total: 10]

3 Hydrogen and iodine react together in a reversible reaction: EXOTHERMIC

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

A chemist mixes together 2.00×10^{-3} mol $H_2(g)$ and 4.00×10^{-3} mol $I_2(g)$ in a 1.00 dm^3 container.
The chemist seals the container.
The mixture is heated and left to reach equilibrium.

$[\ ]_{EQ} \div 1$

At equilibrium, the mixture contains 3.00×10^{-4} mol of H_2.

(a) Calculate the equilibrium constant, K_c, including units, if any, for this equilibrium.

Give your answer to three significant figures.

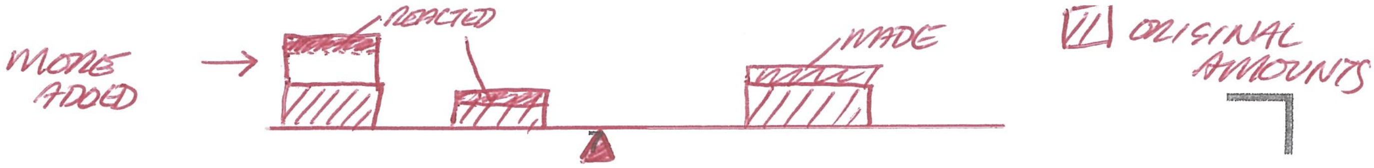
	H_2 +	I_2 ⇌	$2HI$
START	2×10^{-3}	4×10^{-3}	0
REACTED	1.7×10^{-3}	1.7×10^{-3}	
EQ	3×10^{-4}	2.3×10^{-3} ✓	$\xrightarrow{\times 2}$ 3.4×10^{-3} ✓
[EQ]	3×10^{-4}	2.3×10^{-3}	3.4×10^{-3}

$$K_c = \frac{[HI]^2}{[H_2][I_2]} \qquad \frac{(3.4\times10^{-3})^2}{3\times10^{-4} \times 2.3\times10^{-3}} ✓$$

$$= 16.8$$

K_c = 16.8 ✓ units NONE ✓ **[5]**

3SF



(b) The chemist repeats the experiment several times. In each experiment, the chemist makes one change.

(i) The chemist uses 3.00×10^{-3} mol $H_2(g)$ instead of 2.00×10^{-3} mol $H_2(g)$. MORE H_2 USED.

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			

[2]

(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.

K_c SMALLER

FORWARD REACTION IS EXOTHERMIC

(REVERSE RXN SO [P]↓ [R]↑) [1]

(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.

NO CHANGE AS ONLY T AFFECTS K_c

[1]

[Total: 9]

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 (pK_a = 7.43), have different pH values.

S.A. W.A.

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

Show any working in calculations.

HCL IS STRONG ACID

$pH = -\log 0.14$

$= 0.85$ ✓

HClO IS WEAK ACID ✓

$10^{-7.43} = 3.7 \times 10^{-8}$ ✓

$[H^+] = \sqrt{Ka \times [HClO]}$

$= \sqrt{3.7 \times 10^{-8} \times 0.14}$ ✓

$= 5.18 \times 10^{-9}$

$pH = -\log 5.18 \times 10^{-9}$

$= 4.14$ ✓

[5]

(b) Aluminium powder is added to aqueous ethanoic acid, CH_3COOH.

Write full and ionic equations for the reaction that takes place.

full equation $Al + 3CH_3COOH \rightarrow (CH_3COO)_3Al + 1\frac{1}{2}H_2$

ionic equation $Al + 3H^+ \rightarrow Al^{3+} + 1\frac{1}{2}H_2$ [2]

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

$$[H^+] = \frac{1\times10^{-14}}{0.4}$$

$$= 2.5\times10^{-14}$$ ✓

$$pH = -\log 2.5\times10^{-14}$$

$$= 13.6$$

[2]

(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*. — (NOT HOW ITS MADE)

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.

BUFFER MINIMISE CHANGES IN PH ✓

WITH SMALL ADD^n OF H^+ OR OH^- ✓

$HCOOH \rightleftharpoons H^+ + HCOO^-$ ✓

$+H^+$ EQ^M SHIFTS TO LHS ✓

BY REACTING WITH $HCOO^-$ ✓

$+OH^-$ EQ^M SHIFTS TO RHS ✓

$H^+ + OH^- \rightarrow H_2O$ ✓

[7]

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

200 cm^3 of 3.20 mol dm^{-3} HCOOH (K_a = 1.70 × 10^{-4} mol dm^{-3}) and
800 cm^3 of 0.500 mol dm^{-3} NaOH.

The volume of the buffer solution is 1.00 dm^3. ÷1 FOR [ ]$_{EQ}$^{m}

- 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.

$HCOOH + NaOH \longrightarrow HCOONa + H_2O$ ✓

V =	0.2	0.8		
c =	3.2	0.5		
MOLES = START	0.64 XS	0.40 L.R.		
REACTED	0.40	0.40		
MOLES EQ^m	0.24	0	0.40	+ 0.40
[ ]$_{EQ}$^{m}	0.24 ✓	0	0.40 ✓	0.40

HCOOH AND HCOO$^-$ PRESENT ∴ BUFFER MADE. ✓

$$[H^+] = \frac{K_a\,[HCOOH]}{[HCOO^-]}$$ ✓

$$= \frac{1.7\times10^{-4} \times 0.24}{0.40}$$

$$= 1.02\times10^{-4}$$

$$pH = -\log 1.02\times10^{-4}$$

$$= 3.99$$ ✓

[6]

[Total: 22]

Fe^{3+}

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 $[Fe(H_2O)_6]^{3+}$.

Fe^{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.

$Fe(OH)_3$

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.

Fe^{2+} scz D.

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}.

$[Fe(CN)_6]^{3+}$

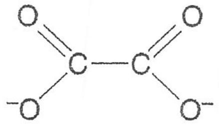
Fe^{3+}

$211.8 - 55.8 = \frac{156}{26} = 6$

Mr of CN → 26

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) Write an equation for the formation of solid **A**.

$2Fe + 3Cl_2 \rightarrow 2FeCl_3$ ..... [1]

(b) In **Experiment 1**, write an ionic equation for the formation of precipitate **B**.

$Fe^{3+}_{(aq)} + 3OH^-_{(aq)} \rightarrow Fe(OH)_{3(s)}$ ..... [1]

(c) In **Experiment 2**,

(i) write an equation for the formation of complex ion **C**

$2[Fe(H_2O)_6]^{3+} + Zn \rightarrow 2[Fe(H_2O)_6]^{2+} + Zn^{2+}$ ..... [2]

(ii) state the type of reaction taking place.

REDOX ..... [1]

(d) In **Experiment 3**,

(i) write an equation for the formation of complex ion **E** ✓

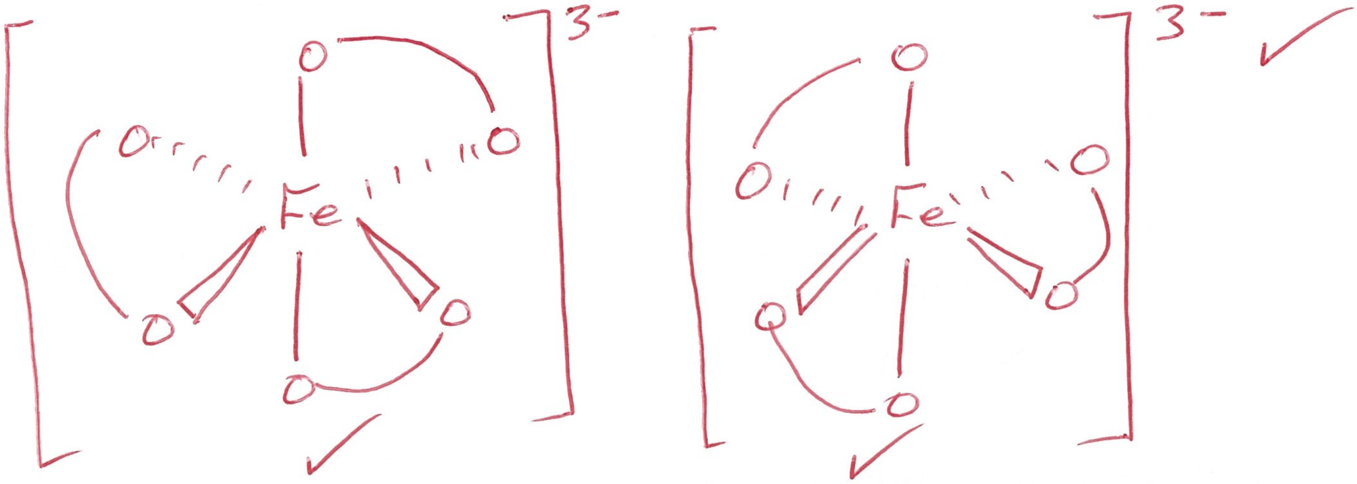
$[Fe(H_2O)_6]^{3+} + 6CN^- \rightarrow [Fe(CN)_6]^{3+} + 6H_2O$ ✓ [2]

(ii) state the type of reaction taking place.

LIGAND SUBSTITUTION ✓ [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, KNO_3, 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.

FeO_4^{2-} [1]

[Total: 12]

6 The equation for the reaction of CO_2 and H_2O to produce glucose, $C_6H_{12}O_6$, and O_2 is shown below.

$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(s) + 6O_2(g)$ $\Delta H = +2879\,\text{kJ mol}^{-1}$; $\Delta S = -256\,\text{J K}^{-1}\,\text{mol}^{-1}$

Standard entropies are given in the table below.

×6 ×6 ×6

Substance	$CO_2(g)$	$H_2O(l)$	$O_2(g)$
$S^\ominus$ / J K^{-1} mol^{-1}	214	70	205

1284 420 1230

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

$\Delta S = S_p - S_r$

$-256 = (1230 + X) - (1284 + 420)$ ✓

$-256 = 1230 + X - 1704$

$X = -256 - 1230 + 1704$

$= 218$

$S^\ominus$ = 218 ✓ J K^{-1} mol^{-1} **[2]**

(ii) Calculate ΔG, in kJ mol^{-1}, at 25 °C.

Show all your working.

$\Delta G = \Delta H - T\Delta S$

$= +2879 - (298 \times -0.256)$

$= 2879 + 76.288$

$= 2955$

ΔG = 2955 kJ mol^{-1} **[2]**

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

$\Delta G = \Delta H - T\Delta S$

(+)VE − (−)VE

ΔH IS (+)VE. TΔS IS (−)VE

∴ ΔG WILL ALWAYS BE (+)VE **[1]**

∴ NOT FEASIBLE

(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.

2879 KJ REMOVES 6 MOLES CO_2

$\frac{3.4 \times 10^{18}}{2879} \times 6 = 7.09 \times 10^{15}$ MOLES CO_2 REMOVED

MASS = $7.09 \times 10^{15} \times 44$

$= 3.12 \times 10^{17}$ g

mass of CO_2 = 3.12×10^{17} g **[2]**

[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				**$E^\ominus$ / V**
1	$Mg^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Mg(s)$	–2.37
2	$Cu^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Cu(s)$	+0.34
3	$Al^{3+}(aq) + 3e^-$	$\rightleftharpoons$	$Al(s)$	–1.66
4	$Fe^{3+}(aq) + e^-$	$\rightleftharpoons$	$Fe^{2+}(aq)$	+0.77
5	$I_2(aq) + 2e^-$	$\rightleftharpoons$	$2I^-(aq)$	+0.54
6	$Cl_2(g) + 2e^-$	$\rightleftharpoons$	$2Cl^-(aq)$	+1.36
7	$ClO^-(aq) + 2H^+(aq) + e^-$	$\rightleftharpoons$	$\frac{1}{2}Cl_2(g) + H_2O(l)$	+1.63

Table 7.1

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

THE EMF OF A ½ CELL COMPARED WITH HYDROGEN ½ CELL ✓

298K / 1ATM / 1moldm^{-3} ✓

[2]

(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 = 2.71 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.

$AL + 3Fe^{3+} \longrightarrow AL^{3+} + 3Fe^{2+}$

$2AL + 3I_2 \longrightarrow 2AL^{3+} + 6I^-$

$2I^- + 2Fe^{3+} \longrightarrow I_2 + 2Fe^{2+}$ [3]

(ii) Give **two** reasons why it is uncertain whether reactions predicted from $E^\ominus$ values may actually take place.

HIGH ACTIVATION ENERGY ✓

CONCENTRATIONS NOT STANDARD ✓

[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.

aq ⑦ ClO^-/Cl_2 IS MORE (+)VE THAN ⑥ Cl^-/Cl_2 ✓
∴ ⑦ ClO^-/Cl_2 MOVES TO RHS + ⑥ Cl^-/Cl_2
MOVES TO LHS ✓
ALKALINE OH^- REACTS WITH H^+ IN ⑦ ClO^-/Cl_2 ✓
MOVES EQ^{m} TO LHS ✓ AND BECOMES
MORE (−)VE THAN ⑥ Cl^-/Cl_2 ✓ [4]

MAX 4 MARKS

(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.

IO_3^- (+5) IS REDUCED TO I_2 (0) ∴ OXIDISES
Sn^{2+} (+2) TO Sn^{4+} (+4)

[1]

(ii) Construct an equation for this reaction.

$$5Sn^{2+} + 2IO_3^- + 12H^+ \rightarrow I_2 + 5Sn^{4+} + 6H_2O$$

[2]

[Total: 15]

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.

SAME MOLES.

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.

SAME MOLES

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

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 Ni^{2+}(aq) ions have been converted into $Ni(DMG)_2$(s).
$M[Ni(DMG)_2]$ = 288.7 g mol^{-1}. Mr

MOLES OF ~~HYDRATED SALT~~ PPT.

SAME MOLES

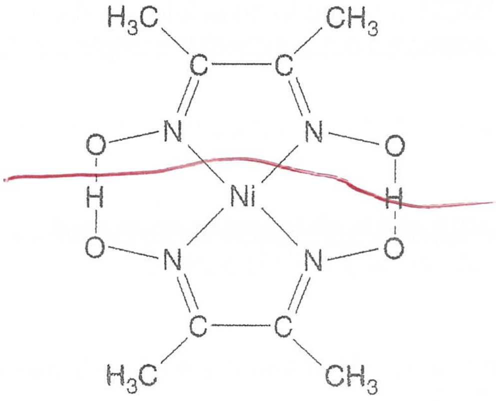
Step 4 —HYDRATED SALT.
A second 2.50 g sample of the hydrated nickel(II) salt is heated in a crucible to remove the water of crystallisation.
1.38 g of the anhydrous salt remains. —ANHYDROUS SALT DIFF = H_2O

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

nickel as the element: $1s^2 2s^2 2p^6$ $3s^2 3p^6 4s^2 3d^8$

nickel in the +2 oxidation state: $1s^2 2s^2 2p^6$ $3s^2 3p^6 3d^8$ [2]

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



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

ACCEPTS A PROTON FROM DMGH ∴

ACTS AS A BASE

[1]

(ii) State the coordination number of Ni in $Ni(DMG)_2$.

4

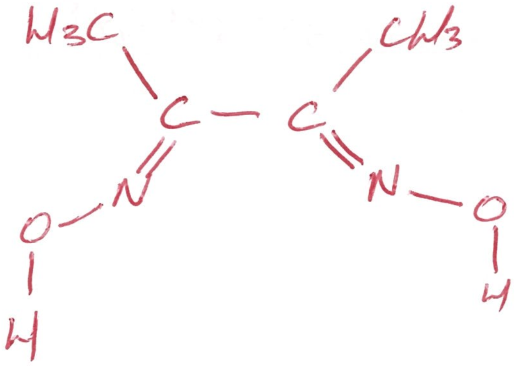
[1]

(iii) Why does the $Ni(DMG)_2$ complex have no overall charge?

DMG HAS -1 CHARGE $\times 2 = -2$

Ni^{2+} HAS $+2$ CHARGE ∴ CANCEL OUT **[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.

MOLES RED PPT $= \frac{2.57}{288.7} = 8.9 \times 10^{-3}$ ✓

MOLES HYDRATED SALT IN 2.5g $= 8.9 \times 10^{-3}$ (1:1 RATIO)

MOLES ANHYDROUS SALT $= 8.9 \times 10^{-3}$ (1:1 RATIO)

∴ Mr HYDRATED SALT (METAL + ANION + H_2O) $= \frac{2.5}{8.9 \times 10^{-3}} = 280.9$ ✓

Mr ANHYDROUS SALT (METAL + ANION) $= \frac{1.38}{8.9 \times 10^{-3}} = 155.0$ ✓

Mr (MASS OF ALL) xH_2O (H_2O ONLY) $= 280.9 - 155.0 = 125.9$ ✓

$H_2O = 125.9/18 = 7$ ∴ $7H_2O$ ✓

Mr ANION $= 155 - 58.7 = 96.3$

COMMON IONS: CO_3^{2-} SO_4^{2-} ($NO_3^{1-} \times 2$) ✓

60 96.3 (✓✓) 122

∴ $NiSO_4 \cdot 7H_2O$ ✓

[7]

[Total: 13]

END OF QUESTION PAPER

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.