

Mon

MAK Jan 2012

A2 GCE CHEMISTRY A

F325 Equilibria, Energetics and Elements

Candidates answer on the Question Paper.

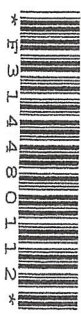
OCR supplied materials:

- *Data Sheet for Chemistry A* (inserted)

Duration: 2 hours

Other materials required:

- Scientific calculator



Candidate forename	<i>MAK</i>	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.

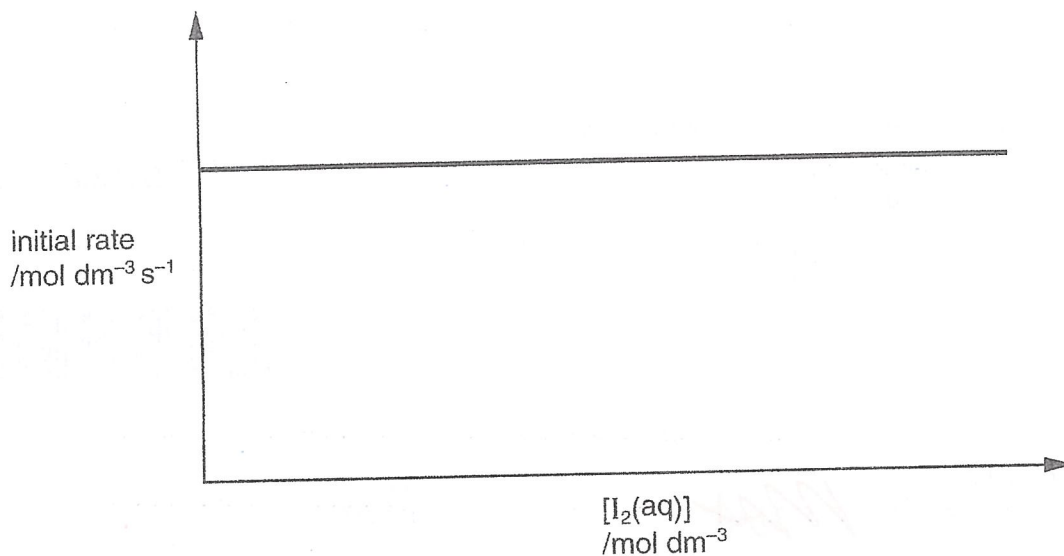


Answer **all** the questions.

- 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.

$[I_2]$ NO CHANGE IN RATE WITH CHANGE IN $[I_2]$

\therefore ZERO ORDER

$[(CH_3)_2CO]$ 1-2 $\times 2$, RATE $\times 2 \therefore$ 1ST ORDER

$[HCl]$ 2-3 $\times 2.5$ RATE $\times 2.5 \therefore$ 1ST ORDER

$r = k [(CH_3)_2CO] [HCl]$

$k = 7 \times 10^{-5} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$



- 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	

$\times 2 + 992$

$\times 2 + 216$

Table 2.1

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

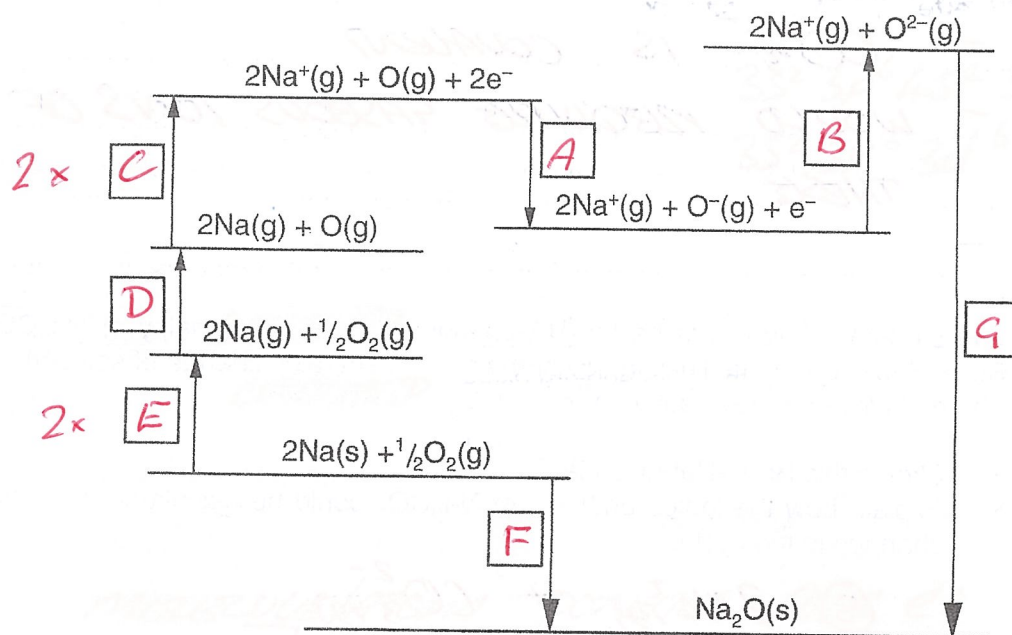
FORMATION OF 1 MOLE OF COMPOUND
FROM GASEOUS IONS
(UNDER S.C.)

[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.



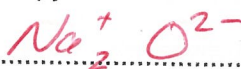
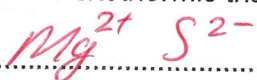
[3]

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

$$\Delta H_{LE}^{\ominus} = -414 - (1084 - 216 + 249 + 992 + 790 - 141)$$

answer = -2520 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.



Mg²⁺ HAS GREATER CHARGE DENSITY. ∴ GREATER
ATTRACTION.

S²⁻ HAS A SMALLER CHARGE DENSITY. ∴ WEAKER
ATTRACTION.

[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.

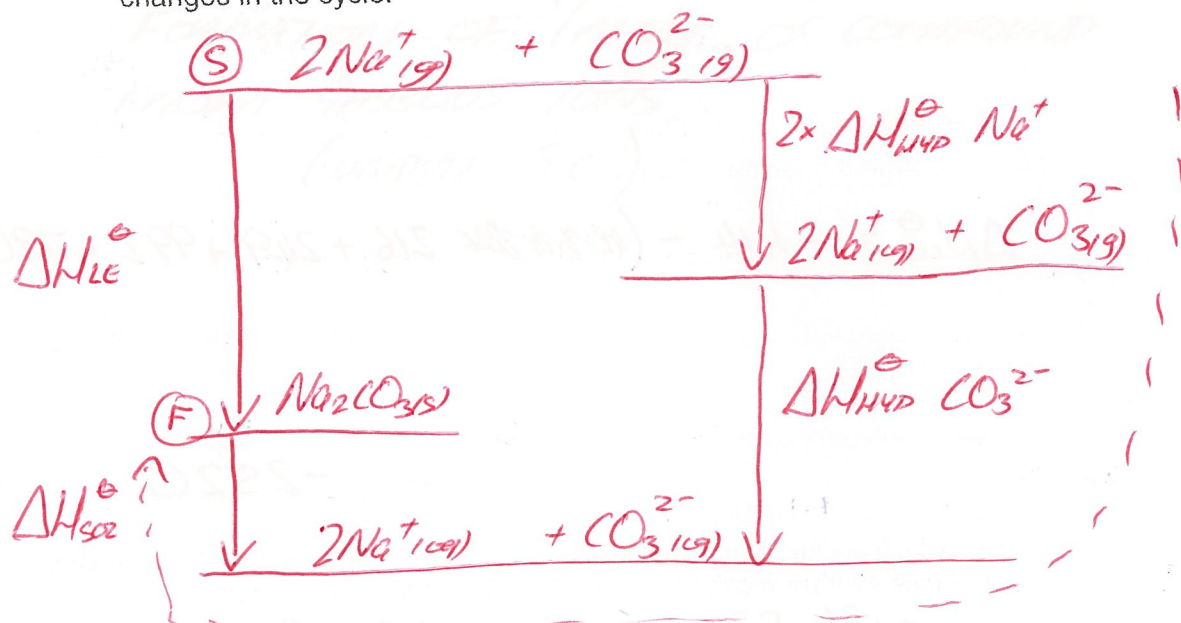
- CO_3^{2-} IS COVALENT

- WOULD REQUIRE GASEOUS IONS OF THESE

[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.



$$\Delta H_{IE}^{\ominus} = 2 \times \Delta H_{\text{hyd}}^{\ominus} \text{Na}^{\oplus} + \Delta H_{\text{hyd}}^{\ominus} \text{CO}_3^{2-} - \Delta H_{\text{sol}}^{\ominus} \text{Na}_2\text{CO}_3$$

[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: $1s^2 2s^2 2p^6$ $3s^2 3p^6 4s^2 3d^7$

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

..... CATALYST

..... COLOURED

..... [1]

- (c) Complex ions contain ligands.

State the meaning of the term *ligand*.

..... MOLECULE/ATOM DONATES PAIR e^s

..... FORMING DATIVE COV BOND WITH T.M.

..... [1]

- (d) Aqueous cobalt(II) sulfate, $\text{CoSO}_4(\text{aq})$, 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, $\text{CoSO}_4(\text{aq})$, reacts with aqueous sodium hydroxide.

transition element species formed: $\text{Co}(\text{OH})_2$

type of reaction: PRECIPITATION [2]

- (ii) Aqueous cobalt(II) sulfate, $\text{CoSO}_4(\text{aq})$, reacts with concentrated hydrochloric acid.

transition element species formed: $[\text{CoCl}_4]^{2-}$

type of reaction: $\text{LIGAND SUBSTITUTION}$ [2]

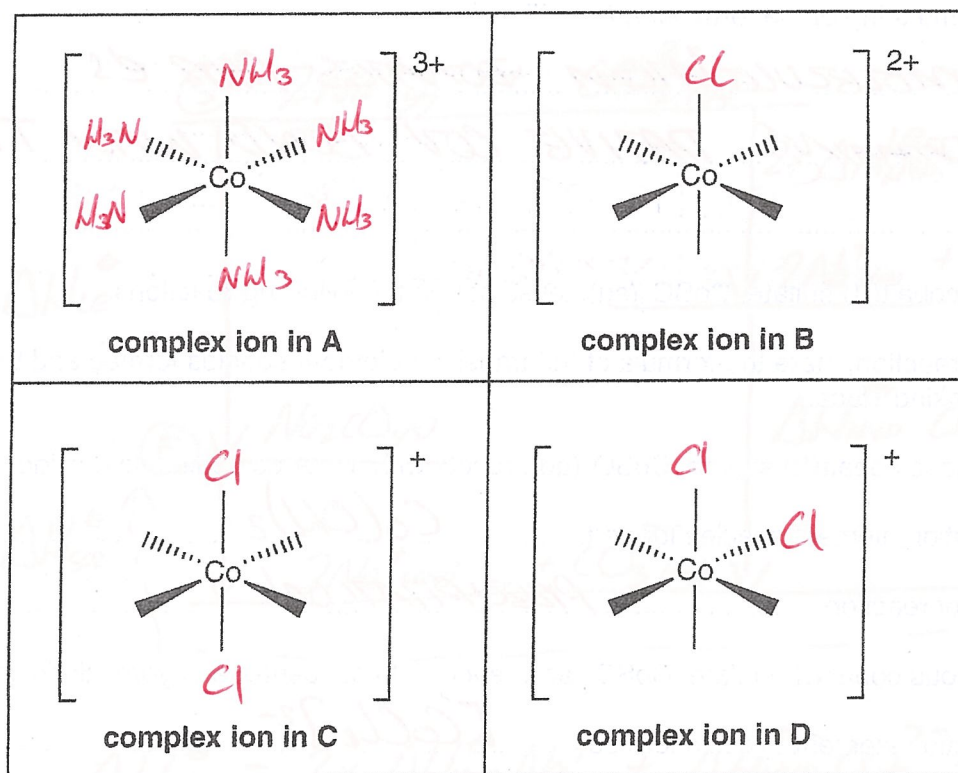


- (e) Cobalt(III) chloride, CoCl_3 , reacts with ammonia to form a range of complexes. These complexes contain different amounts of ammonia. Information about these complexes is summarised below.

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

complex	formula	formula of complex
A	$\text{CoCl}_3(\text{NH}_3)_6$	$[\text{Co}(\text{NH}_3)_6]^{3+} 3\text{Cl}^-$
B	$\text{CoCl}_3(\text{NH}_3)_5$	$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} 2\text{Cl}^-$
C	$\text{CoCl}_3(\text{NH}_3)_4$	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ \text{Cl}^-$
D	$\text{CoCl}_3(\text{NH}_3)_4$	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ \text{Cl}^-$

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

$$\begin{aligned} \text{PPT IS AgCl} & \therefore \text{MOLES AgCl} \\ &= \frac{2.868}{143.3} = 0.02 \text{ MOLES.} \end{aligned}$$

$$\begin{array}{ccc} 0.01 \text{ MOLE COMPLEX} & \rightarrow & 0.02 \text{ MOLES PPT} \\ 1 & : & 2 \end{array}$$

~~COMPLEX~~ ^{LET} B HAS 2 FREE Cl^- IONS PER MOLE OF COMPLEX ION.

[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 $4.43 \times 10^{-4} \text{ mol dm}^{-3}$.

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

STRONG ACIDS DISSOCIATE FULLY
WEAK " " PARTIALLY

[1]

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

$$K_a = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]}$$

[1]

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

Give your answer to two decimal places.

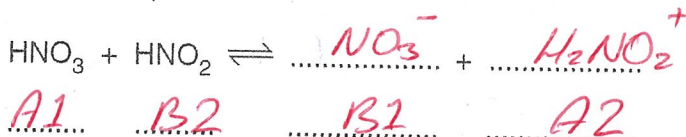
$$\begin{aligned} [\text{H}^+]^2 &= 4.43 \times 10^{-4} \times 0.375 \\ &= 1.66 \times 10^{-4} \\ [\text{H}^+] &= 0.0129 \\ \text{pH} &= -\log 0.0129 \end{aligned}$$

pH = 1.89 [2]

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

STRONGER ACID.

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



[2]



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

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

PROTON ACCEPTOR

[1]

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

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

$$[\text{OH}^-] = 0.08$$

$$[\text{H}^+] = \frac{1 \times 10^{-14}}{0.08}$$

$$= 1.25 \times 10^{-13}$$

$$\text{pH} = -\log 1.25 \times 10^{-13}$$

pH = 12.90 [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: $\text{Ca}(\text{OH})_2 + 2\text{HNO}_2 \rightarrow \text{Ca}(\text{NO}_2)_2 + 2\text{H}_2\text{O}$

ionic: $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$ [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.



ADDITION OF H^+

EQ^m SHIFTS TO LHS TO REMOVE
ADDED H^+ IONS BY REACTING WITH HCO_3^-

ADDITION OF OH^-

REACTS WITH H^+ IONS FORMING H_2O
THIS \downarrow $[\text{H}^+]$ IN EQ^m

EQ^m SHIFTS TO RHS TO REPLACE
THE USED H^+ IONS.

[5]



- (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.

pH 7.40

$$K_a = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

$$= \frac{3.98 \times 10^{-8} \times 10.5}{1}$$

$$= 4.18 \times 10^{-7}$$

$$[H^+] = 10^{-7.4}$$

$$= 3.98 \times 10^{-8}$$

pH 7.20

$$4.18 \times 10^{-7} = 6.31 \times 10^{-8} \times \frac{[HCO_3^-]}{[H_2CO_3]}$$

$$[H^+] = 10^{-7.2}$$

$$= 6.31 \times 10^{-8}$$

$$\frac{4.18 \times 10^{-7}}{6.31 \times 10^{-8}} = \frac{[HCO_3^-]}{[H_2CO_3]}$$

$$= \frac{6.6}{1}$$

$$\therefore 6.6 : 1$$



[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.

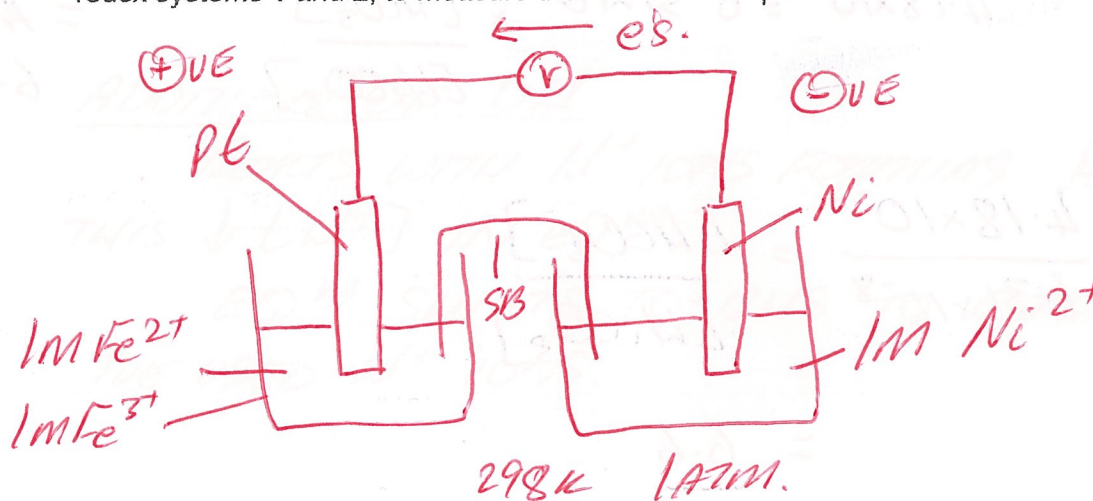
	redox system	E^\ominus/V
1	$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Ni}(\text{s})$	-0.25
2	$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$	+0.77
3	$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Cr}(\text{s})$	-0.74

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 = 1.02V V

sign of Ni electrode, + or - = (-)VE

Cell B based on redox system 1 and 3:

standard cell potential = 0.49V V

sign of Ni electrode, + or - = (+)VE

[2]



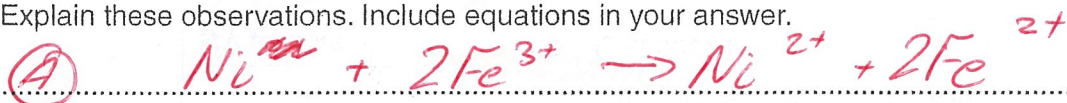
- (b) The student left each cell in (a) connected for a length of time.

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.



Ni USED UP.



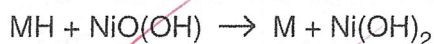
Ni BEING PRODUCED.

CONCⁿ OF IONS CHANGE OVER TIME

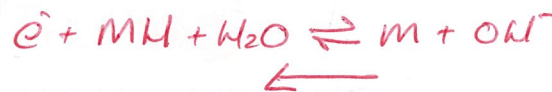
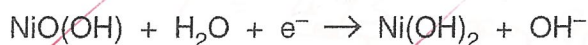
[3]

- (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.



The half-equation at one electrode is shown below.



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



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

ADSORPTION [1]

LIQUID UNDER PRESSURE.

[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.

..... $\Delta G = \Delta H - T\Delta S$ [1]

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

For each process, predict the sign of ΔS .

process	sign of ΔS
$2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$	-
$\text{NaCl}(\text{s}) + (\text{aq}) \rightarrow \text{NaCl}(\text{aq})$	+
$\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{s})$	-
$\text{Mg}(\text{s}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{MgSO}_4(\text{aq}) + \text{H}_2(\text{g})$	+
$\text{CuSO}_4(\text{s}) + 5\text{H}_2\text{O}(\text{l}) \rightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s})$	-

[2]

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



Standard entropies are given in the table below.

substance	$\text{NH}_3(\text{g})$	$\text{O}_2(\text{g})$	$\text{NO}(\text{g})$	$\text{H}_2\text{O}(\text{g})$
$S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$	192	205	211	189

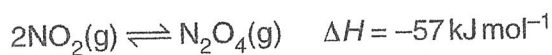
Calculate the standard entropy change, in $\text{J K}^{-1} \text{mol}^{-1}$, for this oxidation of ammonia.

$$\begin{aligned} \Delta S^\ominus &= S^\ominus_{\text{P}} - S^\ominus_{\text{R}} \\ &= (4 \times 211) + (6 \times 189) - (5 \times 205) - (4 \times 192) \\ &= +185 \text{ J mol}^{-1} \text{K}^{-1} \end{aligned}$$

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



- 7 Dinitrogen tetroxide, $\text{N}_2\text{O}_4(\text{g})$, and nitrogen dioxide, $\text{NO}_2(\text{g})$, coexist in the following equilibrium.



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.

	2NO_2	\rightleftharpoons	N_2O_4
START	4		0
EQ ^m	3.2		0.4
REACTED	0.8		
[] _{EQ}	1.6		0.2

$$\begin{aligned}
 K_c &= \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} \\
 &= \frac{0.2}{(1.6)^2} \\
 &= 7.81 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3
 \end{aligned}$$

[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.

K_c DOES NOT CHANGE

$$K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} \quad \uparrow P \times 2, \quad V_{\text{O}_2} = \frac{1}{2}$$

$$\therefore \text{CONC} \times 2$$

$$[\text{N}_2\text{O}_4] \times 2$$

$$[\text{NO}_2] \times 2^2 = \times 4$$

[3]

[Total: 8]

$\therefore [\text{NO}_2] \downarrow \quad [\text{N}_2\text{O}_4] \uparrow$ TO MAINTAIN K_c
ie EQ^m MOVES TO RHS



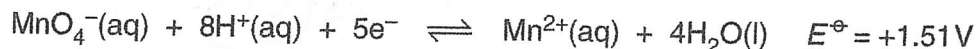
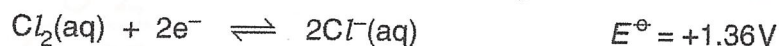
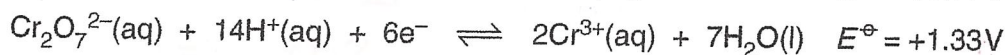
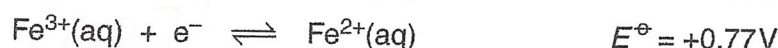
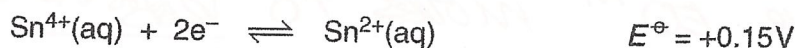
- 8 Haematite is the main ore of iron. The percentage of iron in a sample of haematite can be determined using the method below.

Method

- Stage 1.** An excess of concentrated hydrochloric acid is added to a 3.25g 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 $0.0200\text{ mol dm}^{-3}$ aqueous potassium dichromate(VI), $\text{K}_2\text{Cr}_2\text{O}_7$. 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.

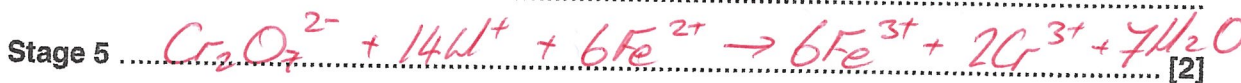
You may need to use this information throughout this question.



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



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



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

$$\text{Moles } \text{Cr}_2\text{O}_7^{2-} = C \times V = 0.02 \times 0.0265 \\ = 5.30 \times 10^{-4}$$

$$\text{Moles } \text{Fe}^{2+} \text{ IN } 25\text{cm}^3 = 5.30 \times 10^{-4} \times 6 \\ = 3.18 \times 10^{-3}$$

$$\text{Moles } \text{Fe}^{2+} \text{ IN } 250\text{cm}^3 = 3.18 \times 10^{-3} \times 10 \\ = 3.18 \times 10^{-2}$$

$$\text{Mass Fe} = 55.8 \times 3.18 \times 10^{-2} \\ = 1.77444\text{g}$$

$$\% = \frac{1.77444}{3.25} \times 100$$

percentage iron = 54.6% % [5]

- (d) Aqueous potassium manganate(VII), $\text{KMnO}_4(\text{aq})$, is **not** suitable for titrating the solution in this method. Aqueous potassium dichromate(VI), $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$, is used instead.

Suggest and explain why potassium dichromate(VI), $\text{K}_2\text{Cr}_2\text{O}_7$, is suitable for this titration whereas potassium manganate(VII), KMnO_4 , is not suitable.

$\text{MnO}_4^- / \text{Mn}^{2+}$ IS MORE (+) VS THAN Cl^-

$\therefore 2\text{Cl}^- \rightarrow \text{Cl}_2$

$\text{Cr}_2\text{O}_7^{2-} / \text{Cr}^{3+}$ IS NOT - \therefore WOULD NOT

INTERFERE WITH Cl^-

[2]

[Total: 10]

END OF QUESTION PAPER



