OCR
RECOGNISING ACHIEVEMENT

Tuesday 22 January 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

F3144801133

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 page 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 **20** pages. Any blank pages are indicated.

Answer **all** the questions.

1 This question refers to chemistry of d-block elements in Period 4 (Sc–Zn).

(a) For each statement below, select the symbols of the correct element(s).

(i) The element that has atoms containing six electrons in the 3d sub-shell.

Fe [1]

(ii) Two elements that have atoms with two unpaired d electrons.

Ti and Ni [2]

(iii) The element with ions that form a blue complex with chloride ions.

Co [1]

(iv) The element **X** that forms an oxide with the formula X_3O_4 with the molar mass of $228.7\,g\,mol^{-1}$.

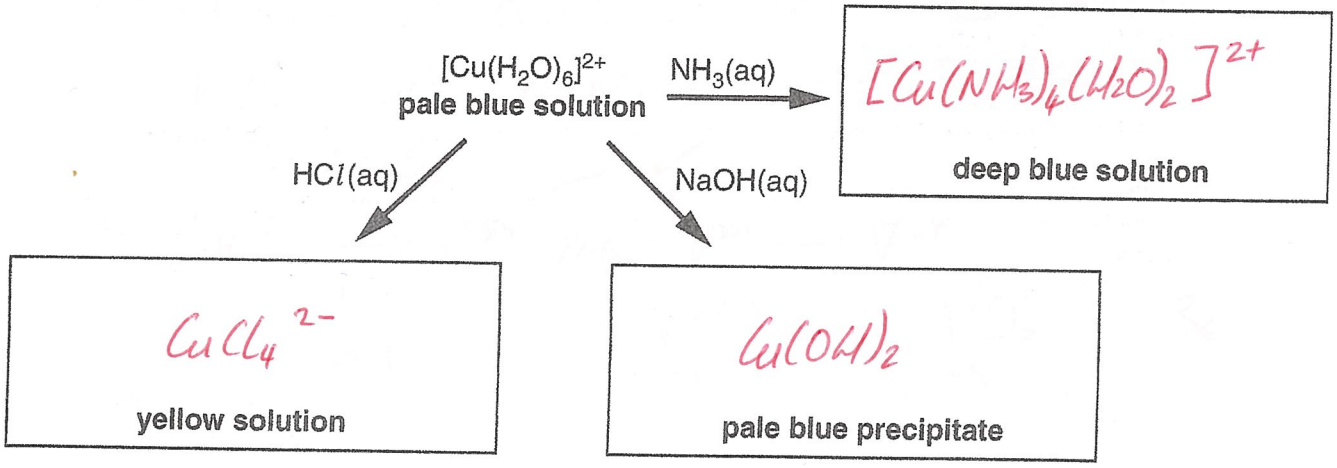
Mn [1]

(v) The element that has atoms with an average mass of 8.64×10^{-23} g.

Cr [1]

(b) The flowchart below shows three reactions of the complex ion $[Cu(H_2O)_6]^{2+}$.

In the boxes below, write down the formulae of the species formed.



[3]

(c) The answers to this question all refer to complex ions of nickel.

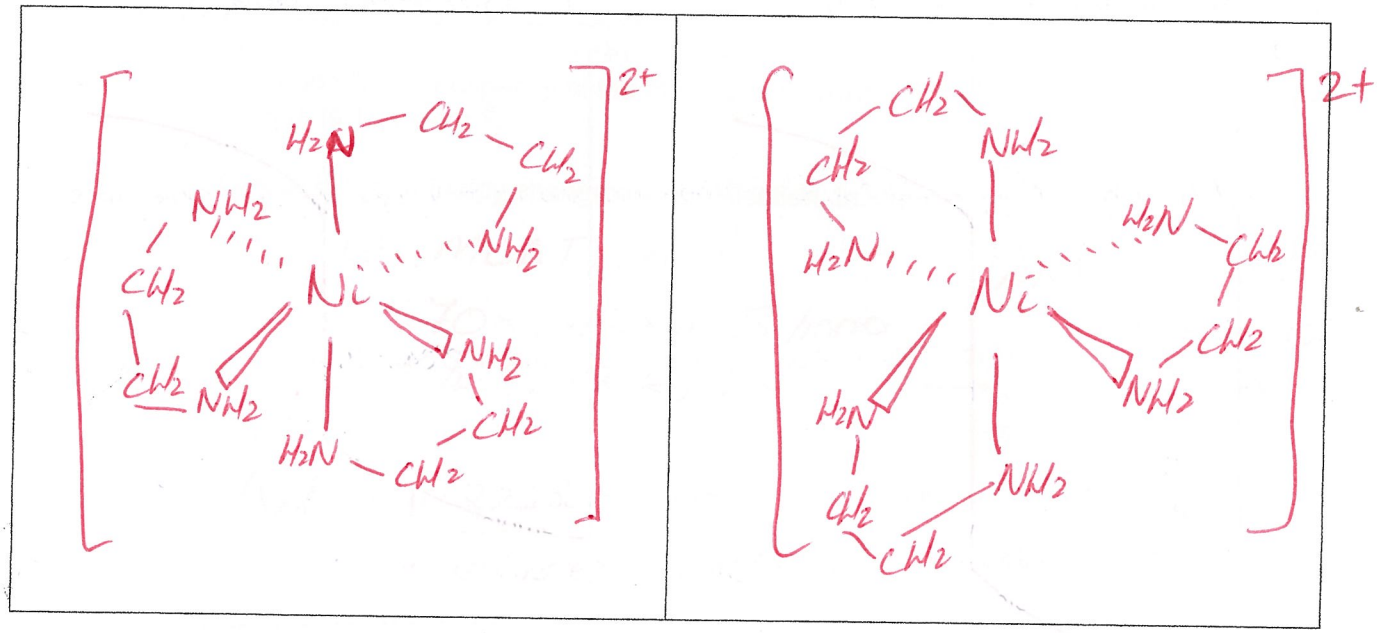
(i) State the shape of the complex ion $[Ni(H_2O)_6]^{2+}$.

OCTAHEDRAL [1]

(ii) What is the formula of the complex ion of Ni^{2+} containing six fluoride ligands?

NiF_6^{4-} [1]

(iii) Show the 3-D shapes of the stereoisomers of the complex ion $[Ni(en)_3]^{2+}$.
(en = $H_2NCH_2CH_2NH_2$)



[2]

[Total: 13]

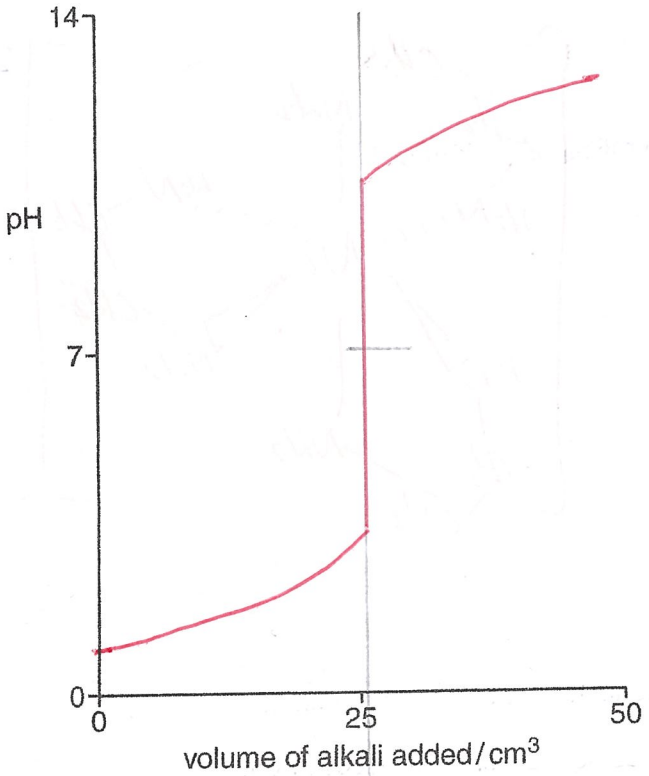
2 This question looks at different aspects of neutralisation.

(a) Acid–base titration pH curves can be used to help choose suitable indicators for the following titrations:

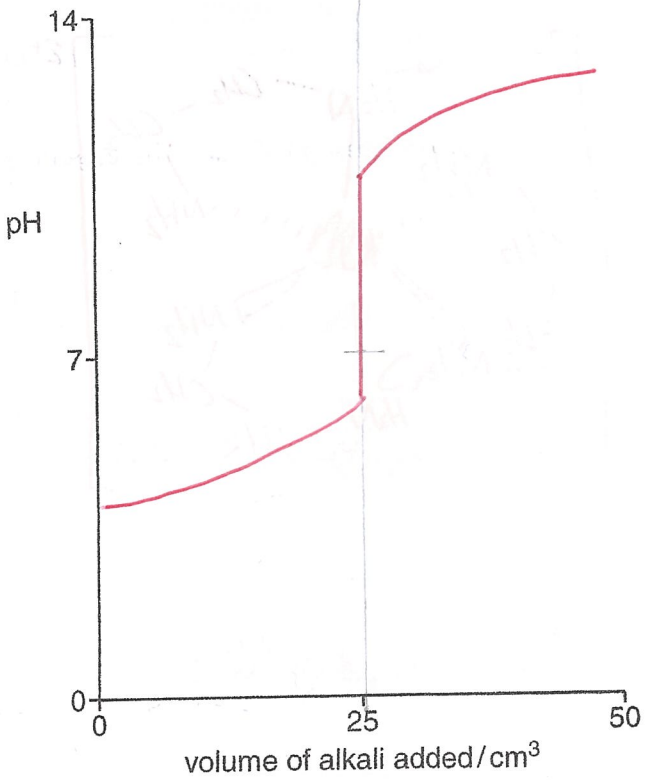
- 25.0 cm^3 of 0.100 mol dm^{-3} HC*l*(aq) with 0.100 mol dm^{-3} NaOH(aq)
- 25.0 cm^3 of 0.100 mol dm^{-3} CH_3COOH(aq) with 0.100 mol dm^{-3} NaOH(aq).

(i) On the axes below, sketch pH acid–base titration curves to show how the pH changes when the alkali is added from a burette until the alkali is in excess.

25.0 cm^3 of 0.100 mol dm^{-3} HC*l*(aq) with 0.100 mol dm^{-3} NaOH(aq)



25.0 cm^3 of 0.100 mol dm^{-3} CH_3COOH(aq) with 0.100 mol dm^{-3} NaOH(aq)



[4]

(ii) Explain how the choice of indicator is linked to the pH curve.

INDICATOR MUST CHANGE COLOUR IN VERTICAL SECTION OF pH CURVE.

.....

.....

.....

[1]

(b) A student carries out an experiment to measure the enthalpy change of neutralisation.

(i) Define the term *enthalpy change of neutralisation*.

FORMATION OF 1 MOLE H_2O FROM
REACTION OF H^+ AND OH^-

..... **[1]**

(ii) The student measures out 35.0 cm^3 of 2.40 mol dm^{-3} NaOH and 35.0 cm^3 of 2.40 mol dm^{-3} HCl. The temperature of each solution is the same.

The student mixes the two solutions. The temperature rises by 16.5 °C.

The specific heat capacity of the mixture is 4.18 J g^{-1} K^{-1}. Assume that the density of the mixture is 1.00 g cm^{-3}.

Calculate the enthalpy change of neutralisation, in kJ mol^{-1}.

$Q = MC\Delta T / 1000$

$= 70 \times 4.18 \times 16.5 / 1000$

$= 4.8279$ kJ mol^{-1}

MOLES $= 2.4 \times 0.035$

$= 0.084$

$\Delta H = \frac{4.8279}{0.084}$

enthalpy change of neutralisation = -57.5 kJ mol^{-1} **[3]**

(iii) The student repeats the experiment using 70.0 cm^3 of 1.20 mol dm^{-3} HCl instead of 35.0 cm^3 of 2.40 mol dm^{-3} HCl.

Explain why the temperature rise is less, and predict what the temperature rise will be.

SAME AMOUNT OF Q DISTRIBUTED
OVER A LARGER VOLUME

$2/3 \times 16.5 = 11$ °C

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

[Total: 11]

3 Energy changes take place when water dissolves compounds and when water changes its physical state.

(a) You are provided with the following information.

Ion	$\Delta H_{hydration}$ /kJ mol^{-1}
Na^+	–405
Mg^{2+}	–1926
OH^-	–460

The enthalpy change of solution of $Mg(OH)_2$ is –152 kJ mol^{-1}.

(i) Define, in words, the terms *enthalpy change of solution* and *enthalpy change of hydration*.

enthalpy change of solution .....

ΔH WHEN 1 MOLE OF COMPOUND FULLY DISSOLVES .....

.....

.....

enthalpy change of hydration .....

ΔH WHEN 1 MOLE GASEOUS IONS FORM .....

1 MOLE OF aq IONS .....

..... [3]

(ii) Explain the difference between the $\Delta H_{hydration}$ values for Na^+ and Mg^{2+}.

Mg^{2+} HAS GREATER CHARGE / SMALLER ION .....

CHARGE DENSITY .....

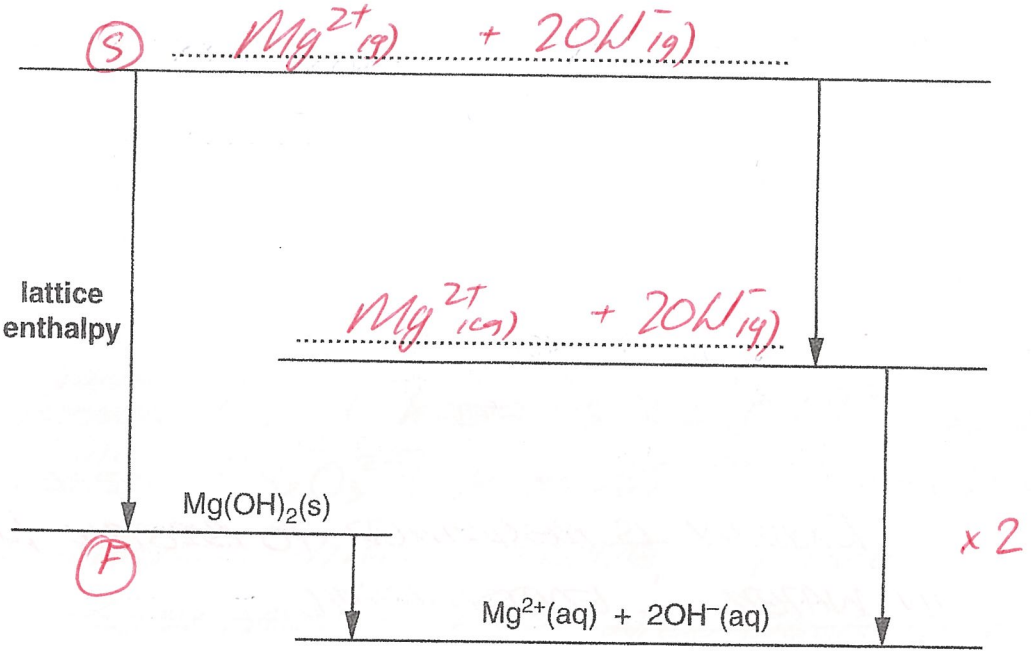
.....

∴ GREATER ATTRACTION BETWEEN .....

Mg^{2+} + H$_2$O ..... [3]

(iii) A Born–Haber cycle can be drawn to link the lattice enthalpy and enthalpy change of solution of $Mg(OH)_2$ with hydration enthalpies.

On the two dotted lines, add the species present, including state symbols.



[2]

(iv) Calculate the lattice enthalpy of $Mg(OH)_2$.

$\Delta H_{LE} = -1926 + (2 \times -460) + (-152)$

$= -2694\ kJ\,mol^{-1}$

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

(b) Energy changes for the melting and boiling of H_2O are shown below.

$H_2O(s) \rightarrow H_2O(l)$ $\quad \Delta H = +6.01\,kJ\,mol^{-1}$
$H_2O(l) \rightarrow H_2O(g)$ $\quad \Delta H = +40.7\,kJ\,mol^{-1}$

Standard entropies of H_2O in its three physical states are given in the table below.

	$H_2O(s)$	$H_2O(l)$	$H_2O(g)$
$S^{\ominus}$ / $JK^{-1}\,mol^{-1}$	+48.0	+70.0	+188.7

(i) Explain the following:

- When water melts or boils, ΔH is positive
- When water melts or boils, $S^{\ominus}$ increases.

In your answer, you should explain why the increase in $S^{\ominus}$ is much greater when water boils than when water melts.

ENERGY IS REQUIRED TO BREAK H-BONDS IN WATER ∴ ENDOTHERMIC

MELTS/BOILS: INCREASE IN DISORDER

S → L → G

→ INCREASE IN DISORDER

[3]

(ii) Using the data in the table above, show that ice melts at 0 °C (at standard pressure).

$\Delta S^{\ominus} = S_P^{\ominus} - S_R^{\ominus}$
$= 70 - 48$
$= 22\ JMol^{-1}$ / $0.022\ kJMol^{-1}K^{-1}$

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

$\Delta G = 6.01 - (273 \times 0.022)$
$= 4 \times 10^{-3} \sim 0$ ∴ FEASIBLE.

$T = \frac{\Delta H}{\Delta S} = \frac{6.01}{0.022} = 273K = 0°C$

[3]

[Total: 16]

4 Iodide ions, I^-, react with $S_2O_8^{2-}$ ions as shown in the equation below.

$$2I^-(aq) + S_2O_8^{2-}(aq) \longrightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

A student investigates the rate of this reaction using the initial rates method.

The student measures the time taken for a certain amount of iodine to be produced.

(a) Outline a series of experiments that the student could have carried out using the initial rates method.

How could the results be used to show that the reaction is first-order with respect to both I^- and $S_2O_8^{2-}$?

In your answer you should make clear how the results are related to the initial rates.

VARY ~~DOUBLE~~ $[I^-]$ KEEPING $[S_2O_8^{2-}]$ CONSTANT

VARY ~~DOUBLE~~ $[S_2O_8^{2-}]$ KEEPING $[I^-]$ CONSTANT

+ COMPARE TIME → RATE = 1/TIME

~~IN BOTH CASES RATE WILL DOUBLE WITH A DOUBLED [ ]~~

PLOT GRAPH OF RATE VS CONC^n = STRAIGHT LINE IE $r \propto [\ ]$

[4]

(b) In one of the experiments, the student reacts together:

- 8.0×10^{-2} mol dm^{-3} $I^-(aq)$
- 4.0×10^{-3} mol dm^{-3} $S_2O_8^{2-}(aq)$.

The initial rate of this reaction is 1.2×10^{-3} mol dm^{-3} s^{-1}.

The reaction is first-order with respect to I^- and first-order with respect to $S_2O_8^{2-}$.

Calculate the rate constant, *k*, for this reaction.
State the units, if any.

$$k = \frac{r}{[I^-][S_2O_8^{2-}]}$$

$$= 3.75 \text{ mol}^{-1} \text{ dm}^{+3} \text{ s}^{-1}$$

k = ... units ..... [3]

(c) This reaction between I^- ions and $S_2O_8^{2-}$ ions can be catalysed by either $Fe^{2+}(aq)$ ions or $Fe^{3+}(aq)$ ions.

Standard electrode potentials are shown below.

$S_2O_8^{2-}(aq) + 2e^-$	$\rightleftharpoons$	$2SO_4^{2-}(aq)$	$E^\ominus = +2.01\,V$
$Fe^{3+}(aq) + e^-$	$\rightleftharpoons$	$Fe^{2+}(aq)$	$E^\ominus = +0.77\,V$
$I_2(aq) + 2e^-$	$\rightleftharpoons$	$2I^-(aq)$	$E^\ominus = +0.54\,V$

(i) Using this information, write two equations to show how the reaction of I^- ions and $S_2O_8^{2-}$ ions can be catalysed by Fe^{2+} ions.

equation 1: $S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$

equation 2: $2Fe^{3+} + 2I^- \rightarrow I_2 + 2Fe^{2+}$ **[2]**

(ii) Suggest why the reaction of I^- ions and $S_2O_8^{2-}$ ions is also catalysed by Fe^{3+} ions.

Fe^{3+} COULD ~~CATALYSE~~ REACT I^- FIRST

Fe^{2+} FORMED WOULD THEN ~~CATALYSE~~ REACT WITH $S_2O_8^{2-}$ **[1]**

[Total: 10]

5 Methanol can be prepared industrially by reacting together carbon monoxide and hydrogen. This is a reversible reaction:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -94\,kJ\,mol^{-1}$$

- A chemist mixes together 0.114 mol CO(g) and 0.152 mol H_2(g) in a container.
- The container is pressurised and then sealed. The total volume is 200 cm^3.
- The mixture is heated to 500 K and left to reach equilibrium.
  The volume of the sealed container is kept at 200 cm^3.
- The chemist analyses the equilibrium mixture and finds that 0.052 mol CH_3OH has formed.

(a) Calculate the value of K_c, including units, for the equilibrium at 500 K.

Give your answer to **three** significant figures.

	CO	+ $2H_2$	$\rightleftharpoons CH_3OH$
MOLES START	0.114	0.152	0
MOLES REACTED	0.052	0.104	
MOLES EQM	0.062 ✓	0.048 ✓	0.052
[ ] EQM ÷ 0.2	0.31	0.24	0.26 ← ✓

$$K_c = \frac{[CH_3OH]}{[CO][H_2]^2} \quad ✓$$

$$= 14.6 \quad mol^{-2}\,dm^{+6} \quad ✓ \quad ✓$$

K_c = ... units ..... **[6]**

(b) The chemist repeats the experiment using the same initial amounts of CO and H_2.
The same procedure is used but the mixture is heated in the 200 cm^3 sealed container to a higher temperature than 500 K.

As the gas volume is kept at 200 cm^3, the increased temperature also increases the pressure.

- Explain why it is difficult to predict how the yield of CH_3OH would change.
- Explain what happens to the value of K_c.

↑T MOVES EQ^M TO LEFT, ENDO SIDE
↑ PRESSURE MOVES EQ^M TO RIGHT, FEWER MOLES OF GAS
T MOVES TO LHS, P MOVES TO RHS
∴ DIFFICULT TO PREDICT YIELD.

K_C ↓ AS TEMP MOVES EQ^M TO LHS (ENDO SIDE) **[4]**

[Total: 10]

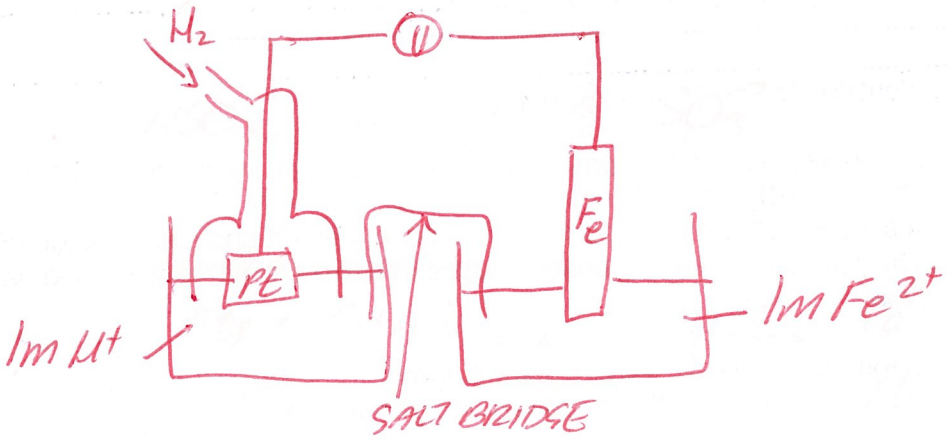
6 Storage cells and fuel cells are types of electrochemical cell used as sources of energy.

Information about five redox systems that could be used in electrochemical cells is shown below. You may need to use this information throughout this question.

redox system					$E^\ominus$ / V
1	$Fe^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Fe(s)$		−0.44
2	$2H_2O(l) + 2e^-$	$\rightleftharpoons$	$2OH^-(aq) + H_2(g)$		−0.83
3	$2H^+(aq) + 2e^-$	$\rightleftharpoons$	$H_2(g)$		0.00
4	$O_2(g) + 2H_2O(l) + 4e^-$	$\rightleftharpoons$	$4OH^-(aq)$		+0.40
5	$O_2(g) + 4H^+(aq) + 4e^-$	$\rightleftharpoons$	$2H_2O(l)$		+1.23

(a) The standard electrode potential of redox system **1** can be measured by constructing an electrochemical cell.

- Draw a diagram below to show how the standard electrode potential could be measured for redox system **1**.
- State the conditions needed to measure this standard electrode potential.



conditions: 298K, 1ATM, 1MOLAR SOLNS

.....[4]

(b) When an **alkaline** hydrogen–oxygen fuel cell is being used to produce electrical energy, chemical changes take place within the cell.

(i) Write half-equations for the changes that take place at each electrode.

oxygen electrode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

hydrogen electrode: $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$ ×2 [2]

(ii) Write the overall equation for the cell reaction.

$2H_2 + O_2 \rightarrow 2H_2O$ [1]

(iii) What is the standard cell potential of this fuel cell?

standard cell potential = 1·23V V [1]

(c) State **one** important difference between a fuel cell and a conventional storage cell.

USES A FUEL (H_2) WITH O_2 TO PRODUCE ELECTRICITY [1]

(d) People often assume that hydrogen–oxygen fuel cells are a source of energy that is carbon neutral, *i.e.* there is no net increase in carbon dioxide from using the fuel cell.

Suggest **one** reason why this assumption may **not** be correct.

FOSSIL FUELS REQUIRED TO MAKE FUEL [1]

(e) A student constructs a cell as follows.

- A half-cell is made from a strip of chromium metal and a solution of aqueous chromium(III) sulfate.
- A second half-cell is made from a strip of a metal **X** and a solution of $XSO_4(aq)$.
- The two half-cells are connected together and a current is allowed to pass for a length of time.

The chromium electrode gains 1.456 g in mass.
The electrode made of metal **X** loses 1.021 g in mass.

Determine the identity of metal **X**.
Show all your working.

$Cr^{3+} + 3e^- \rightarrow Cr$ ×2 (AS IT GAINS MASS)

$M \rightarrow M^{2+} + 2e^-$ ×3 (LOSES MASS)

$\therefore 2Cr^{3+} + 3M \rightarrow 3M^{2+} + 2Cr$

1·456 1·021g 1·456

MASS/Ar = 1·456/52 = 0·028

÷2×3 → 0·042 MOLES

$Ar = \frac{1·021}{0·042} = 24·3$

X = Mg [4]

[Total: 14]

7 This question looks at two weak acids that are used as food additives to preserve food:

- calcium hydrogensulfate(IV), $Ca(HSO_3)_2$
- a carboxylic acid, **HA**.

(a) $Ca(HSO_3)_2$ can be made by reacting an excess of sulfur dioxide gas with a suspension of calcium carbonate in water.

Write the equation for this reaction.

$2SO_2 + CaCO_3 + H_2O \rightarrow Ca(HSO_3)_2 + CO_2$ [1]

(b) Calcium hydrogensulfate(IV), $Ca(HSO_3)_2$, dissolves in water forming an aqueous solution containing $Ca^{2+}(aq)$ and $HSO_3^-(aq)$ ions. This solution is weakly acidic.

(i) What is meant by a *weak acid*?

Write an equation to show why this solution is weakly acidic.

weak acid: PARTIALLY DISSOCIATES

equation: $HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$ [2]

(ii) An aqueous solution of $Ca(HSO_3)_2$ oxidises magnesium forming hydrogen gas.

Construct full and ionic equations for the oxidation of magnesium metal by $Ca(HSO_3)_2(aq)$.

full equation: $Mg + Ca(HSO_3)_2 \rightarrow MgSO_3 + CaSO_3 + H_2$

ionic equation: $Mg + 2H^+ \rightarrow Mg^{2+} + H_2$

[2]

(iii) $HSO_3^-(aq)$ can act as either a Brønsted–Lowry acid or a Brønsted–Lowry base.

Explain this statement.
Include equations for the reaction of $HSO_3^-(aq)$ with $H^+(aq)$ and with $OH^-(aq)$.

$HSO_3^- + H^+ \rightarrow H_2SO_3$

BASE. ACCEPTS H

$HSO_3^- + OH^- \rightarrow SO_3^{2-} + H_2O$

ACID DONATES PROTON

[4]

ACIDS PROTON DONOR

BASE PROTON ACCEPTOR.

(c) A carboxylic acid **HA** is a food additive used as a preservative in cakes.

The K_a value of **HA** is 1.51×10^{-5} mol dm^{-3}.

A student analyses a sample of **HA** using the procedure below.

- A student dissolves 0.7369 g of **HA** in water and makes the solution up to 1.00 dm^3.
- The student measures the pH of the resulting solution as 3.52.

(i) Determine the molar mass of **HA** and suggest a possible formula for **HA**.
HA has one carboxylic acid group and contains C, H and O only.
Show all your working.

$Mr = \frac{\text{MASS}}{\text{MOLES HA}}$ ✓

$[H^+] = [A^-]$

$K_a = \frac{[H^+][A^-]}{[HA]}$ ✓

$10^{-3.52} = 3.02 \times 10^{-4}$ ✓

$[HA] = \frac{[H^+]^2}{K_a}$

$= \frac{(3.02 \times 10^{-4})^2}{1.51 \times 10^{-5}}$

$= 6.04 \times 10^{-3}$ Mol dm^{-3} ∴ MOLES $= C \times V$

$= 6.04 \times 10^{-3} \times 1$

$= 6.04 \times 10^{-3}$

$Mr = \frac{0.7369}{6.04 \times 10^{-3}} = 122$

COOH
= 45
∴ 122 − 45
77 ÷ 12
= 6 r 5

C_6H_5

molar mass of **HA** = ... g mol^{-1}

possible formula for **HA** = C_6H_5COOH ..... **[6]**

(ii) The student had considered analysing the solution of **HA** by carrying out a titration with an alkaline solution of known concentration.

The student rejects this method as being invalid because **HA** is a weak acid and only a small proportion of H^+ ions would be neutralised.

Explain whether the student was correct in rejecting the titration method.

INCORRECT: AS H^+ USED EQM SHIFTS TO RHS UNTIL ALL $C_6H_5COOH \rightarrow C_6H_5COO^-$

..... **[1]**

[Total: 16]

8 Vanadium is a transition element that forms compounds and ions in which vanadium has oxidation states +2, +3, +4 and +5.

(a) Complete the electron configuration of a vanadium ion in the +3 oxidation state:

$1s^2 2s^2 2p^6$ $3s^2 3p^6 3d^2$ [1]

(b) Suggest why vanadium does **not** form ions in which vanadium has an oxidation state greater than +5.

ONLY 5 e's IN $4s^2 3d^3$

6TH e WOULD BE IN 3P SUBSHELL

[1]

(c) A student carries out an investigation into the oxidation states of vanadium as outlined below.

Stage 1 A 0.126 g sample of vanadium metal is completely reacted with acid to form a yellow solution. The solution is made up to 50.0 cm^3 in a volumetric flask. This yellow solution contains VO_3^- ions with vanadium in the +5 oxidation state.

Stage 2 The yellow solution is reduced (GAINED e's) to form a violet solution containing V^{n+} ions. This 50.0 cm^3 violet solution contains vanadium in the $+n$ oxidation state.

Stage 3 10.0 cm^3 of the violet solution is titrated with 2.25×10^{-2} mol dm^{-3} $KMnO_4(aq)$. 13.2 cm^3 of $KMnO_4(aq)$ are required to reach the end-point.

In the titration,

- V^{n+} ions are oxidised (LOST e's.) back to VO_3^- ions.
- MnO_4^- ions are reduced:

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

(i) Why is there no clear colour change at the end-point of this titration?

MnO_4^- PURPLE
V^{n+} – VIOLET
} SIMILAR COLOURS.

[1]

(ii) Analyse the student's results as follows:

- Determine the value of n in the V^{n+} ions formed in **Stage 2**
- Construct an equation for the reaction that takes place during the titration.

Show all your working.

MOLES MnO_4^- = C × V
= $2.25 \times 10^{-2} \times 0.0132$
= 2.97×10^{-4} ✓

MOLES V = $\frac{0.126}{50.4}$
= 2.48×10^{-3}
IN 50cm3
✓ MOLES V = $\frac{2.48 \times 10^{-3}}{5}$
= 4.96×10^{-4}
IN 10cm3 ✓

MOLES V	:	MOLES MnO_4^-
4.96×10^{-4}	:	2.97×10^{-4}
1.67	:	1
5	:	3 ✓

÷ SMALLEST

MnO_4^- ½ EQ^n OCCURS 3 × 5e = 15e GAINED
V ½ EQ^n OCCURS 5 × ne = 15e LOST
∴ n = 3e ✓
∴ $V^{5+} \rightarrow V^{2+}$ THEN $V^{2+} \rightarrow V^{5+}$

$V^{2+} \rightarrow VO_3^- + 3e^-$
+2 +5

n = 2+

equation:

$3H_2O +$ $3MnO_4^- + 5V^{2+} \rightarrow 3Mn^{2+} + 5VO_3^- + 6H^+$ ✓✓

[7]

[Total: 10]

END OF QUESTION PAPER