Name:		Class:	

ST ANDREW'S JUNIOR COLLEGE

JC 2 Preliminary Exam (TUTOR'S COPY)

Chemistry **9647/02**

Higher 2 **1 September 2015**

Paper 2 **2 hours**

Candidates answer in the spaces provided on the question paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in dark blue or black pen.

You may use a soft pencil for any diagrams, graphs or rough working.

Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.

You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use:

Question	Marks
1	
2	
3	
4	
5	
Total (72 marks)	

This document consists of **21** printed pages (including this page) and **1** blank page.

[Turn Over

1. Planning

Calcium hydroxide, $Ca(OH)_2$, is sufficiently insoluble in water such that it forms a saturated $Ca(OH)_2$ solution, as shown in the following equation:

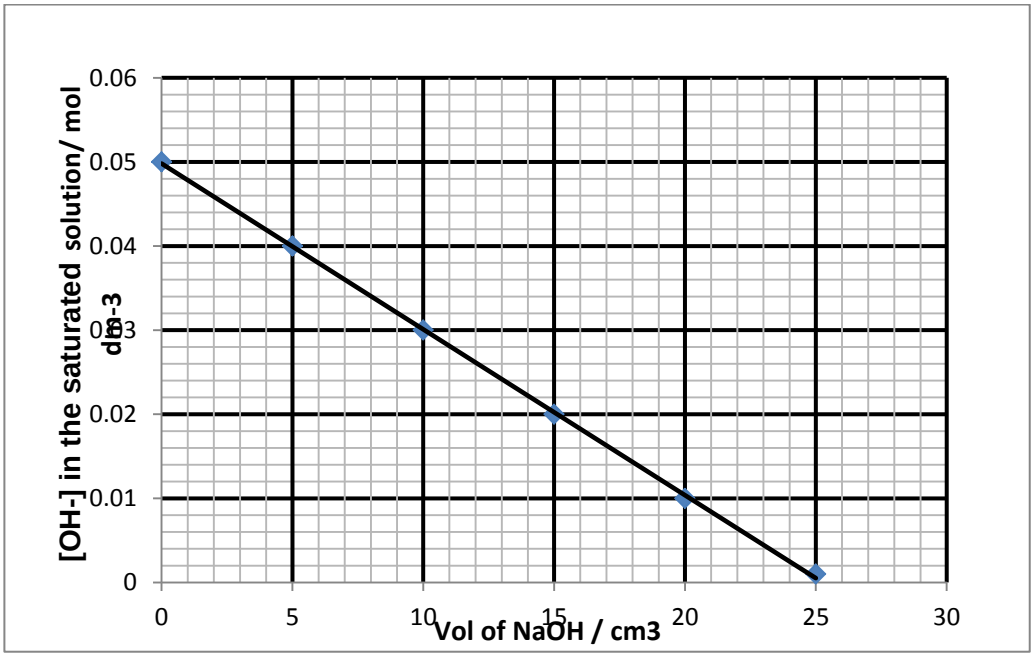
$$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$$

The following experiments were carried out to determine the solubility product of calcium hydroxide. Different volumes of NaOH and water were added separately to different dry conical flasks according to the following table.

Experiment	Vol of NaOH / cm^3	Vol. of water / cm^3	$[OH^-]$ in the saturated solution/ mol dm^{-3}
1	5.00	45.00	0.04
2	10.00	40.00	0.03
3	15.00	35.00	0.02
4	20.00	30.00	0.01
5	25.00	25.00	0.001

Excess solid calcium hydroxide was added to each conical flask before it was stoppered and shaken for a few minutes. The solution was filtered and titrated to determine the concentration of hydroxide ions in the saturated solution.

(a) On the grid provided, plot a graph using the values from the above table. **[1]**



1(b) Explain why the concentration of hydroxide ions in the saturated solution decreases when more sodium hydroxide is added to the conical flask. **[1]**

[OH^-] increases, hence **equilibrium to shift to the left** .

(c) Explain why dry conical flasks needs to be used to prepare the saturated solution. **[1]**

To ensure that the concentration of OH^- used is accurate/ dilution will occur/ affect the [OH^-]

(d) Write the K_{sp} expression for $Ca(OH)_2$, stating its units. **[2]**

$K_{sp} = [Ca^{2+}(aq)] [OH^-(aq)]^2$

Units: $mol^3\ dm^{-9}$

(e) Using the graph plotted, calculate the numerical value of K_{sp} of $Ca(OH)_2$ **[2]**

Extrapolate the line to the y axis to determine the concentration of [OH^-(aq)] when no NaOH(aq) is added.

[OH^-(aq)] = **0.05 mol dm^{-3}**

[Ca^{2+}] = 0.05/2 = 0.025 mol dm^{-3}

$K_{sp} = [Ca^{2+}] [OH^-]^2$

$= 0.025 \times 0.05^2$

$= 6.25 \times 10^{-5}\ mol^3\ dm^{-9}$

(f) Using the information above, you are required to write a plan to

- prepare a saturated solution of calcium hydroxide and
- determine the concentration of hydroxide ions in the saturated solution in experiment **1**.

You may assume that you are provided with:

- solid calcium hydroxide
- 1 mol dm^{-3} aqueous hydrochloric acid;
- the apparatus normally found in the college laboratory

Outline how you would carry out experiment **1**.

Your plan should include details of :

- the apparatus you would use, bearing in mind the levels of precision they offer;
- Indicate the colour change at the end point with your chosen indicator.

[5]

1(f) **Preparation of saturated solution of $Ca(OH)_2$ for titration**

From a **burette**, run 5 cm^3 of NaOH(aq) and 45 cm^3 of distilled water **from a burette** into a 250 cm^3 conical flask.

Add in **excess $Ca(OH)_2$(s) until a white solid of $Ca(OH)_2$ remains**

Stopper the conical flask and shake for a few minutes.

Filter using **filter funnel and filter paper** and

collect the filtrate which contains saturated $Ca(OH)_2$ solution.

Dilution of HC*l* *to 0.04 mol dm^{-3}*

From a **burette**, run **10.00 cm^3 of 1 mol dm^{-3} HC*l*** into a **250 cm^3 volumetric flask**.

Top up to the mark using distilled water.

S**topper and shake well to obtain a homogeneous solution**.

Pour this diluted HC*l* solution into a burette.

Titration

Pipette 25.0 cm^3 of the saturated $Ca(OH)_2$ solution into the conical flask.

Add **1 – 2 drops of phenolphthalein/ methyl orange** to the solution and titrate against the diluted HC*l* in the burette until **pink colour** decolourises.

Repeat the titrations to obtain at least two consistent results within ± 0.10 cm^3.

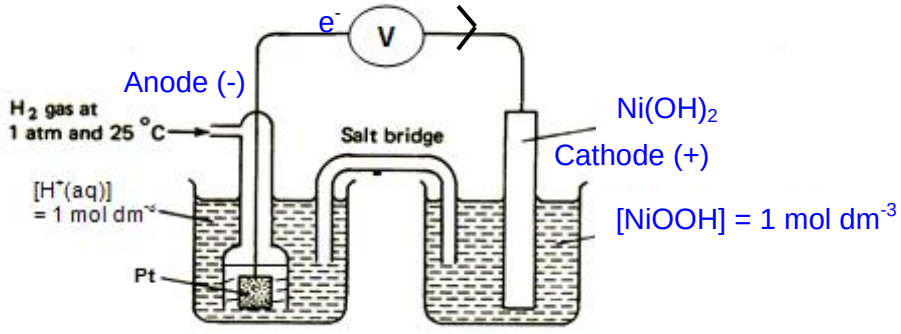
[Total: 12 marks]

2 The Cobasys' NiMH batteries supersede the performance of other rechargeable batteries due to its high performance, lighter weight and longer life cycle. It uses a metal hydride alloy as one of the electrode. Today, NiMH batteries are used pervasively in many applications such as cell phones and hybrid cars.

(a) The standard electrode potential of the NiOOH(aq) / $Ni(OH)_2$(s) system in an alkaline medium is +0.41 V.

Draw a fully labelled diagram of how you would determine the standard electrode potential of the NiOOH(aq) / $Ni(OH)_2$(s) system.

2(a)



(b) The equation at the anode is $MH + OH^- \rightarrow M + H_2O + e^-$

Construct the half equation that occurs at the cathode in an alkaline medium, and the overall equation for the Cobasys' NiMH cell during discharging.

Cathode: ……...

Overall: …….

Cathode: $NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$

Overall: $NiOOH + MH \rightarrow Ni(OH)_2 + M$

[2]

2 **(c)** The table below shows the standard electrode potential of different types of metal hydride, **X**H, **Y**H, **Z**H that could possibly be used as an anode in the Cobasys' NiMH cell.

Metal Hydride, MH	E^θ value/ V
XH	+ 0.37
YH	+ 0.58
ZH	- 0.42

(i) State which metal hydride is the most effective to be used in the Cobasys' NiMH cell.

……

ZH. **[1]**

2 **(c)** **(ii)** Explain your answer in (**c)(i).**

E^{θ} cell = E^{θ} (cathode) - E^{θ} (anode) = + 0.41 - E^{θ} (anode)

As E^{θ}(anode) for ZH is the **least positive/ most negative**, the **E^{θ} cell would be the most positive** or **ZH is most easily oxidized** hence strongest battery.

[1]

(d) Explain the effect, if any, on the e.m.f. of the cell on adding aqueous H_2SO_4 to the anodic half cell during discharging.

$M + H_2O + e^- \rightleftharpoons MH + OH^-$ (1)

The E^{θ}(anode) is **less negative/ more positive or decreasing the extent of oxidation** as the **equilibrium position of (1) shift to the RHS (must come with eqm eqn) [½]**, to replenish the loss of OH^-.

Hence, the **emf is likely to be more negative**.

[2]

(e) The Cobasys' NiMH cell can be recharged when the power is depleted.

(i) Write the overall equation for the reaction upon charging.

$Ni(OH)_2 + M \rightarrow NiOOH + MH$ **[1]**

(ii) To charge the Cobasys' NiMH cell completely, a continuous current of 2.0 A for two hours is required. Calculate the minimum mass of the $Ni(OH)_2$ that would have to be present initially.

$Q = It = 2 \times 2 \times 60 \times 60 = 14400$ C

$Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^-$

No of Faraday = 14400 / 96500 =0.149 F

Since 1F deposit 1 mole of $Ni(OH)_2$,

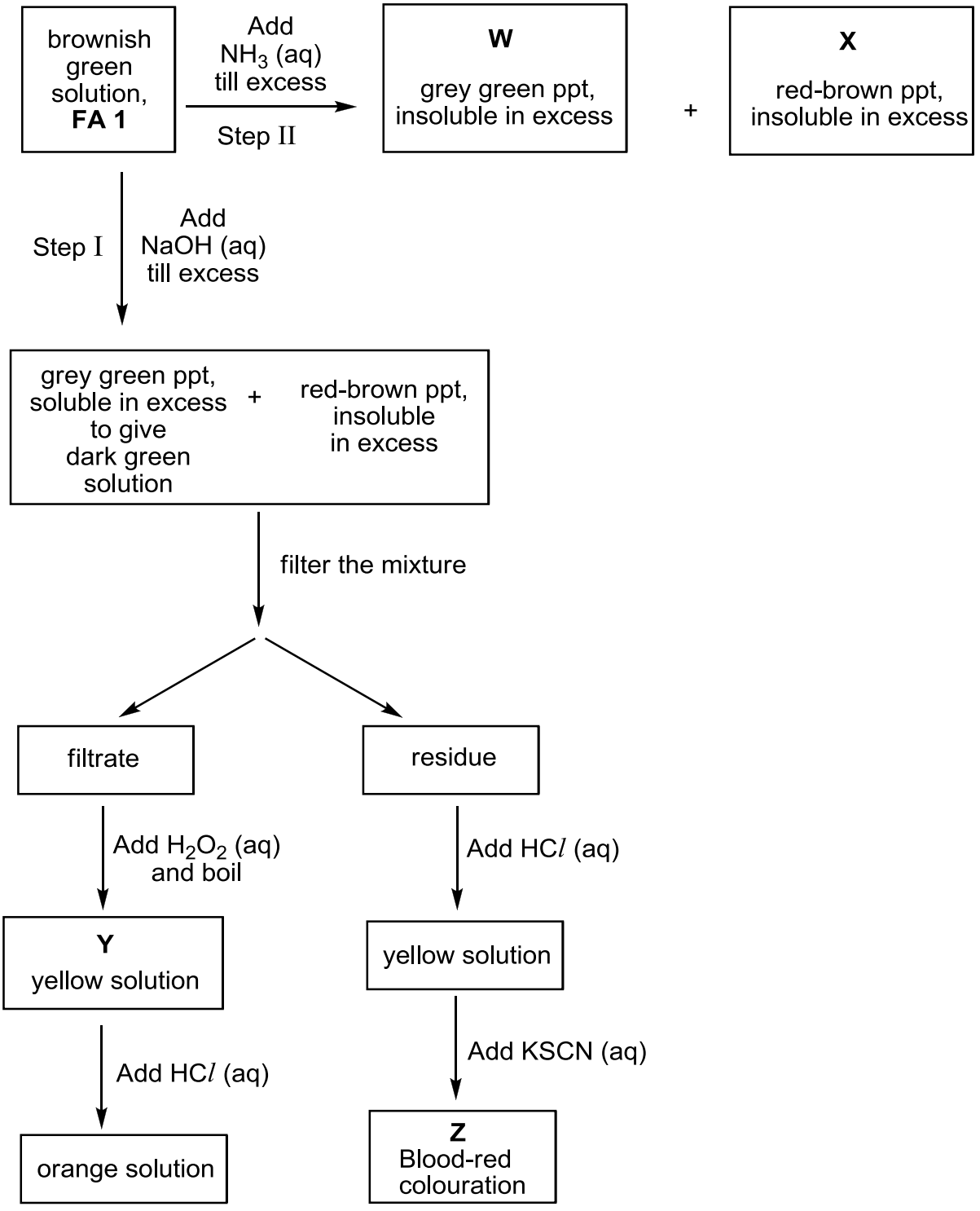
0.149 F will deposit 0.149 mole of $Ni(OH)_2$

Mass of $Ni(OH)_2$ present initially = $0.149 \times 92.7 = 13.8$ g

[3]

[Total: 13 marks]

3 Two cations and one anion are mixed together to form a brownish green solution, **FA 1**. A series of tests is carried out in the reaction scheme as shown.



3 **(a)** **(i)** State the formulae of the two cations present in **FA 1**.

Cation 1: $[Cr(H_2O)_6]^{3+}$ Cation 2: $[Fe(H_2O)_6]^{3+}$ **[2]**

(ii) Write the formulae of the species **W, X, Y** and **Z**.

W: $[Cr(OH)_3(H_2O)_3]$ or $Cr(OH)_3$

X: $[Fe(OH)_3(H_2O)_3]$ or $Fe(OH)_3$

Y: CrO_4^{2-} or Na_2CrO_4

Z: $[Fe(SCN)(H_2O)_5]^{2+}$ **[4]**

(b) The solution of **FA 1** is acidified with HNO_3. $AgNO_3$ (aq) was subsequently added and a white precipitate formed.

State the anion that was present in **FA 1**.

Cl^- **[1]**

(c) **FA 2** contains the same cations but a different anion.

FA 2 undergoes the same reactions as **FA 1** in **(b)** and a cream precipitate was formed instead.

Both precipitates in **(b)** and **(c)** were filtered from the resultant mixtures, washed and separated into two parts. Dilute and concentrated NH_3 was added to each part in separate test tubes.

	Dilute NH_3	Concentrated NH_3
White precipitate in **(b)**	Soluble	Soluble
Cream precipitate in **(c)**	Insoluble	Soluble

With the aid of equation(s), explain fully the difference in the solubility of the precipitates.

[3]

3 **(c)** **K_{SP} of AgC*l* > K_{SP} of AgBr**

$AgX(s) \rightleftharpoons Ag^+(aq) + X^-(aq)$, where X is C*l*, Br ------equilibrium (1)

$Ag^+(aq) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq)$

White precipitate of AgC*l* is soluble in both dilute and concentrated NH_3 and cream ppt of AgBr is soluble in only conc NH_3 to form **silver complex, $[Ag(NH_3)_2]^+$** . $[Ag^+]$ is used up to form complex. The **decrease in $[Ag^+]$ shifts equilibrium (1) to the right** to form $Ag^+(aq)$ ions**.**

Also, the formation of $[Ag(NH_3)_2]^+(aq)$ reduces $[Ag^+]$ such that **I.P. (AgC*l*) < K_{sp} (AgC*l*) [½]**∴ AgC*l* ppt. dissolves.

In dilute NH_3, AgBr does not dissolve because although equilibrium (1) still shifts due to formation of $[Ag(NH_3)_2]^+$, the lowered **I.P. (AgBr) is still greater than K_{sp} (AgBr)**. So AgBr remains insoluble.

In **concentrated NH_3,** there is a larger amount of NH_3 available to form complex, so more Ag^+ can react and the **$[Ag^+]$ is lowered to a greater extent**, resulting in I.P. (AgBr) < K_{sp} (AgBr). ∴AgBr ppt. dissolves**.**

(d) **FA3** is a pink solution that contains Co^{2+}.

A student added NH_3 (aq) to a test tube containing **FA3** and observed a blue precipitate formed. The blue precipitate dissolved when the student added excess NH_3 (aq) to form a yellowish-brown solution.

(i) Explain why aqueous Co^{2+} is pink.

[3]

Co^{2+} has **partially filled d-orbitals**. In the isolated gas phase atoms/ in the absence of ligand, all 5 d orbitals of the metal ion are degenerate. **When ligand approaches Co^{2+}/ forms complexes**, **the d orbitals split into 2 groups with a small energy gap** between them. **When d electron from the lower energy d-orbital is promoted to a higher energy d-orbital, energy from the visible region is absorbed**. The **light energy is not absorbed will be seen (reflected) as the colour of the complex.**

3 (d) (ii) With the aid of equations, explain how the blue precipitate is formed when NH_3 (aq) is added and why the blue precipitate dissolves in excess NH_3 (aq).

[3]

When dilute aqueous NH_3 is gradually added, a **pale blue precipitate of $Co(OH)_2$** is first formed.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$[Co(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Co(OH)_2(H_2O)_4(s) + 2H_2O\ (\boldsymbol{l})$$

pink solution — pale blue precipitate

or

$$[Co(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Co(OH)_2\ (s) + 6H_2O\ (\boldsymbol{l})$$

pink solution — pale blue precipitate

----Eqm 1

Ligand exchange occurs as NH_3 is a stronger ligand.

The formation of $[Co(NH_3)_6]^{2+}$ decreases the $[Co(H_2O)_6]^{2+}$, resulting **a shift of eqm 1 to the left.** Hence the blue precipitate of $Co(OH)_2$ dissolves.

$$[Co(H_2O)_6]^{2+}(aq) + 6NH_3\ (aq) \rightleftharpoons [Co(NH_3)_6]^{2+}\ (aq) + 6H_2O\ (l)$$

pink solution — yellowish brown solution

or

$$Co(OH)_2(H_2O)_4(s) + 6NH_3\ (aq) \rightleftharpoons [Co(NH_3)_6]^{2+}(aq) + 2OH^-\ (aq) + 4H_2O\ (l)$$

Other alternatives of $[Co(NH_3)_6]^{2+}$is not accepted.

[Total: 16 marks]

4 **(a)** Sodium carbonate is a compound with a wide variety of uses, such as regulating the pH in swimming pools, and as a softener in laundry.

Aqueous carbonate ion is a diprotic base as shown in the equation below:

$$CO_3^{2-} \xrightarrow[pK_{b1} = 6.3]{+ H^+} HCO_3^- \xrightarrow[pK_{b2} = 10.3]{+ H^+} CO_2 + H_2O$$

(i) Calculate the pH of a 0.1 mol dm^{-3} solution of sodium carbonate. (You may ignore the effect of pK_{b2})

$[OH^-] \approx \sqrt{Kb\,[Base]} = \sqrt{10^{-6.3}(0.1)} = 2.23 \times 10^{-4}$ mol dm^{-3}

$pOH = -\lg 2.23 \times 10^{-4} = 3.65$

$pH = 14 - 3.65 = 10.35$

[2]

(ii) 20 cm^3 of 0.1 mol dm^{-3} solution of sodium carbonate was titrated against 50 cm^3 of 0.1 mol dm^{-3} hydrochloric acid. Calculate the final pH of the solution.

40 cm^3 of HC*l* is required for complete neutralization. Thus 10cm^3 is in excess.

No. of moles of HC*l* in excess = 0.1 x 0.01 = 0.001 mol

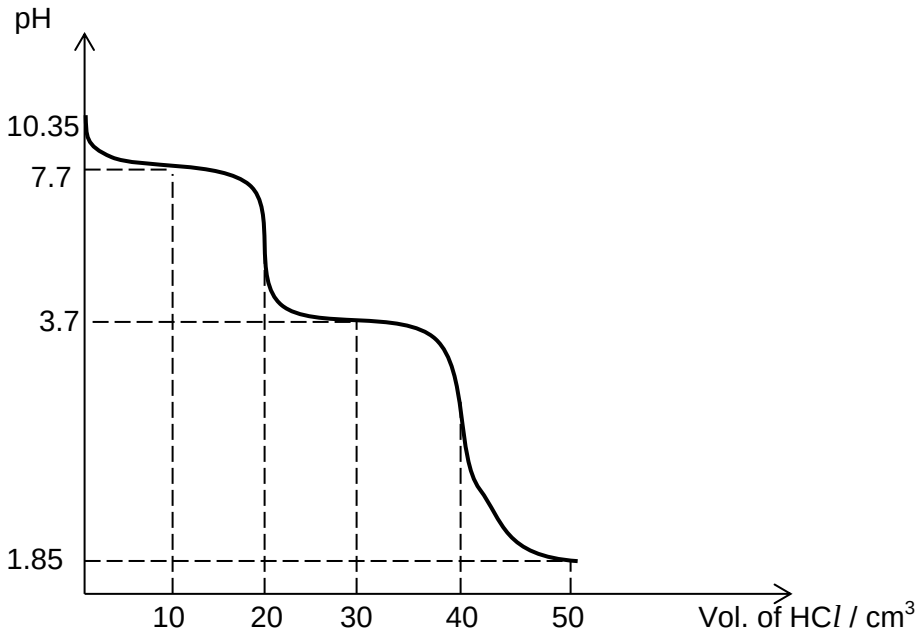
[HC*l*] after titration = 0.001 / 0.07 = 0.014286 mol dm^{-3}

$pH = -\lg[H^+] = 1.845$

[1]

4 **(a)** **(iii)** Sketch a titration curve for the reaction in **(a)(ii)**, labelling clearly any significant pH values and volumes.

[2]



(iv) Two indicators are needed for this titration. The table below shows the working ranges and colours of some common indicators:

Indicator	**Colour**		**pH at which colour changes**
	Acid	**Base**	
Methyl violet	Yellow	Blue-violet	0.0 – 2.0
Methyl yellow	Red	Yellow	2.9 – 4.0
Bromothymol blue	Yellow	Blue	6.0 – 7.6
Cresolphthalein	Colourless	Purple	8.2 – 9.8

State the two suitable indicators for the titration above, as well as the colour change observed for each indicator chosen.

4 **(a)** **(iv)** 1st indicator: **Bromothymol blue**

Colour change: **blue to green**

2nd indicator: **Methyl Yellow**

Colour change: **yellow to orange**

[2]

(b) Sodium hydrogen carbonate is used in baking as a leavening agent. Upon heating, it decomposes, producing sodium carbonate, carbon dioxide and water, causing cakes and other pastries to "rise".

However, the enthalpy change of the decomposition above must be determined indirectly. Several experiments are carried out to determine related enthalpy changes.

In Experiment 1, 2.0 g of solid sodium carbonate was reacted with 30 cm^3 of 2.0 mol dm^{-3} excess hydrochloric acid in a calorimeter. The temperature increased by 5.2°C.

(i) Write an equation for the reaction that occurs in Experiment 1.

[1]

$Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$

(ii) Hence, calculate the enthalpy change of the reaction per mole of sodium carbonate.

Assume that the specific heat capacities of all solutions are 4.2 J g^{-1} K^{-1}.

[2]

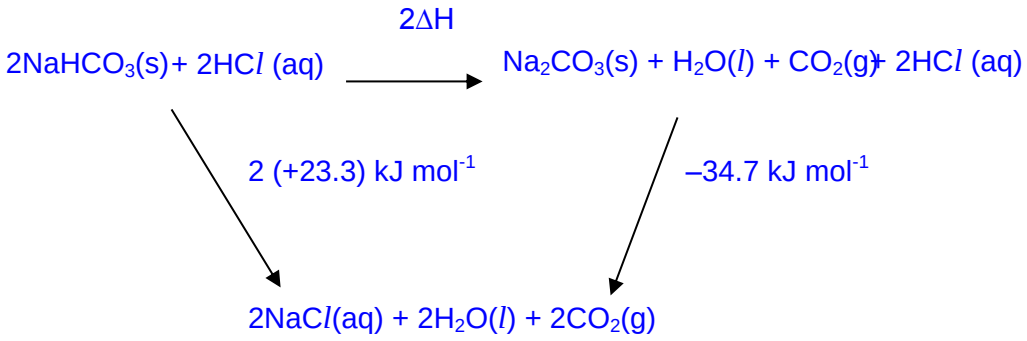
Heat evolved = mcΔT = 30(4.2)(5.2) = 655.2J

$\Delta H = -\frac{0.6552}{2/106}$ = –34.7 kJ mol^{-1} (3sf)

In the second experiment, 2.0 g of sodium hydrogen carbonate was reacted with excess HC*l*, and the enthalpy change for the reaction per mole of hydrogen carbonate was determined to be +23.3 kJ mol^{-1}.

(iii) Using the information above as well as your value in **(b)(ii)**, draw an energy cycle to determine the enthalpy change for the decomposition of one mole of sodium hydrogen carbonate.

4 (b) (iii)



By Hess Law,

$2\Delta H = 2(23.3) - (-34.7)$

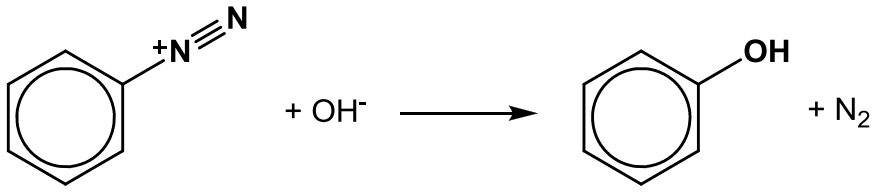
ΔH = + 40.65 kJ mol^{-1}

[2]

[Total: 12m]

5 Benzenediazonium salts are useful compounds in organic synthesis. However, they are unstable.

(a) A simplified equation for the decomposition of benzenediazonium ion, $C_6H_5N_2^+$, is shown below:



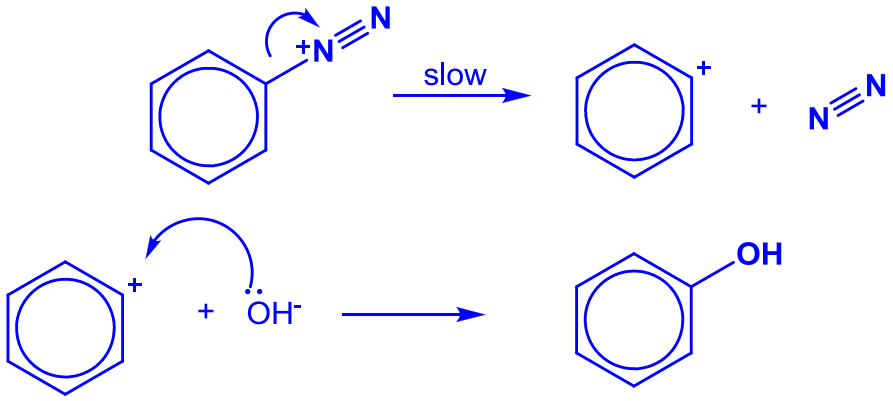
benzenediazonium ion

The reaction is known to proceed via an S_N1 mechanism as follows:

- Heterolytic fission of the C–N bond forms a carbocation intermediate and nitrogen.
- The carbocation intermediate is then attacked by a nucleophile to form the product.

Based on the information above, propose a mechanism for the reaction. You should use curly arrows to represent the movement of electrons.

5 **(a)** Nucleophilic substitution (no marks- as given)



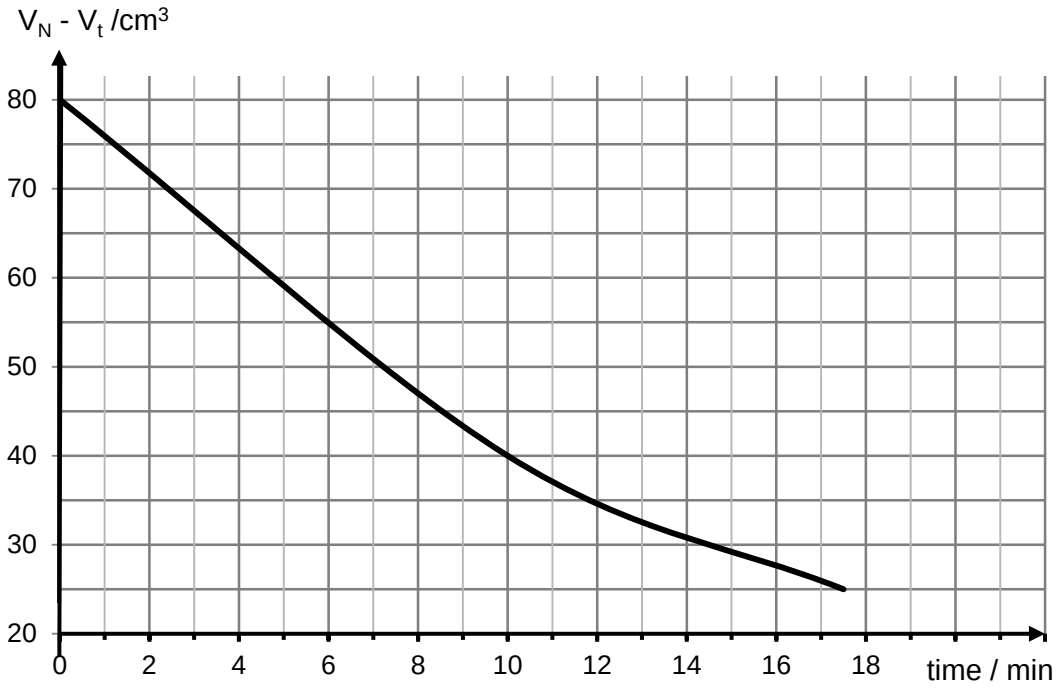
[2]

5 (b) Aqueous benzenediazonium chloride decomposes according to the equation:

$$C_6H_5N_2Cl(aq) + H_2O(l) \rightarrow C_6H_5OH(aq) + N_2(g) + H^+(aq) + Cl^-(aq)$$

The rate of reaction can be followed by measuring V_t, the volume of nitrogen evolved at different time intervals. The following graph was plotted from the results obtained in the experiment.

V_N is the volume of nitrogen evolved at the end of the reaction.



(i) Why should a large volume of water be used in the experiment?

So that water will be in large excess/ concentration of water remains constant and will not affect the rate of reaction. / Pseudo zero-order with respect to concentration of water / Rate of reaction is dependent only on [benzenediazonium chloride]/ [benzenediazonium chloride] is the only variable

[1]

(ii) What is the significance of the term $V_N - V_t$?

It is directly proportional to $[C_6H_5N_2Cl]$ at time *t*.

[1]

[Turn Over

5 **(b)** **(iii)** Using the graph above, deduce the order of reaction with respect to [$C_6H_5N_2Cl$]. Hence, write the rate equation.

From graph, Half-life is constant at **10 min**. (**Accept 9.5 – 10.5 min**)
2 sets of half-life clearly shown on graph / described in words.
Since half-life is constant reaction is **first order** with respect to [$C_6H_5N_2Cl$].
Rate = k [$C_6H_5N_2Cl$]

[3]

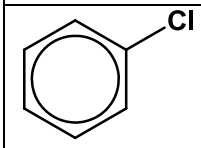
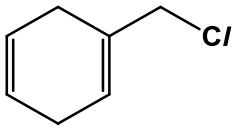
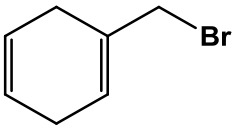
(iv) In an experiment with [$C_6H_5N_2Cl$] = 0.01 mol dm^{-3}, it was observed that 40% of the $C_6H_5N_2Cl$ decomposed in 9 min. What is the time taken for 40% of $C_6H_5N_2Cl$ to decompose when a concentration of 0.02 mol dm^{-3} is used instead?

9 min

[1]

(c) Benzenediazonium ions can also be used to synthesise aryl halides such as chlorobenzene.

A student was tasked to investigate the rate of hydrolysis of chlorobenzene and two other organo-halide compounds.

Chlorobenzene	Compound **B**	Compound **C**
		

State and explain the difference in reactivity of the three compounds to hydrolysis.

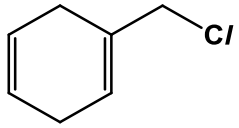
Reactivity: **C > B > Chlorobenzene** (least reactive)

Chlorobenzene is an aryl halide. The **lone pair of electrons on chloride delocalize into the benzene ring**, forming a **partial double bond** with carbon or **strengthening the C-Cl bond**, which is difficult to break . Hence it is unreactive to hydrolysis.

Compound **B** and **C** are both alkyl halides. Compound C is more reactive as the C–Br bond is **weaker** (or quoting Bond Energy data) than C–Cl bond, due to Br atom being **larger** than Cl atom, causing **less effective orbital overlap** and a longer bond, less energy is needed to overcome the C-Br bond.

[4]

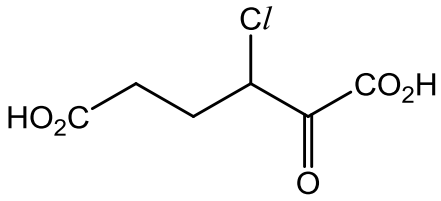
5 (d) Compound **D**, which is a structural isomer of compound **B**, was investigated in two separate reactions.



Compound **B**

Reaction 1: 0.1 mol of **D** was found to react with 10.3 cm^3 of $Br_2(l)$ in the dark. (Density of $Br_2(l)$ = 3.10 g cm^{-3}.)

Reaction 2: Compound **D** was refluxed with acidified potassium manganate, and only one organic product **E,** $C_6H_7O_5Cl$, was obtained.



Compound **E**

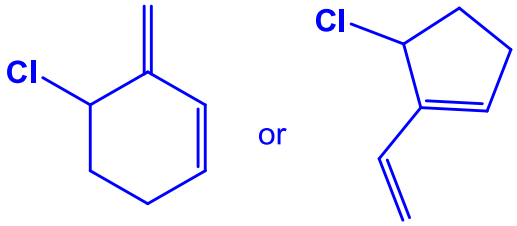
(i) Based on the information above, what can you deduce about the functional groups present in **D**? Explain your reasoning clearly and state the type of reaction that occurs.

	Type of Reaction	Deductions
Reaction 1	Electrophilic addition **[½]**	Mass of bromine = 10.3 x 3.10 = 31.93 g Amt of Br_2 = 31.93 x 2(79.9) = 0.2 mol Since **D** ≡ $2Br_2$, **D** has **2 for working or mole ratio alkene (C=C)** groups.
Reaction 2	Oxidation **[½]**	**E** has 1 less carbon than D (formula of D is C_7H_9Cl) ➔ **D** contains 1 **terminal** alkene. Only 1 organic product formed from C=C cleavage ➔ **D** has a **cyclic** alkene

[3]

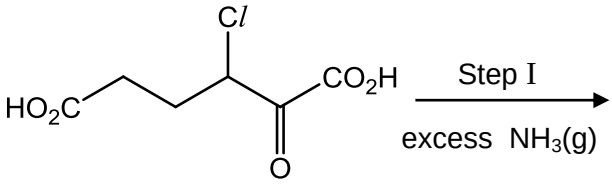
5 (d) (ii) Hence, deduce a possible structure of compound **D**.

D:

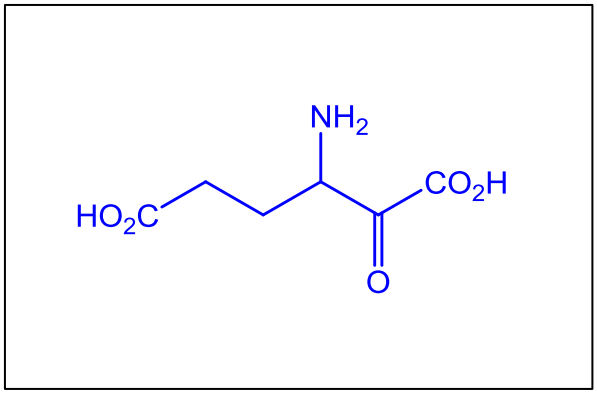


[1]

5 **(e)** Compound **E** can be used to synthesise a cyclic compound **G** according to the following synthetic pathway:

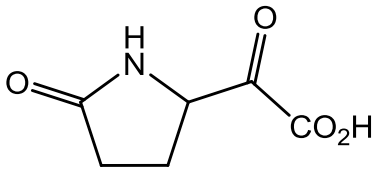


Compound **E**



Intermediate **F**

Step II



Compound **G**

(i) Draw the structure of the Intermediate **F** in the space provided above. **[1]**

(ii) State the type of reaction and the reagents and conditions needed for Step II.

Type of reaction: ……

Reagents and conditions: ……..

5 **(e)** **(ii)** Type of reaction: Nucleophilic substitution OR condensation

R/C: PCl_5 / PCl_3, heat / $SOCl_2$ in pyridine.

[2]

[Total: 19 marks]

End of Paper