Name:		Index Number:		Class:	

DUNMAN HIGH SCHOOL
Preliminary Examinations 2019
Year 6

H2 CHEMISTRY 9729/04

Paper 4 Practical

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this cover page.
2 Give details of the practical shift and laboratory where appropriate, in the boxes provided.
3 Write in dark blue or black pen.
4 You may use an HB pencil for any diagrams or graphs.
5 Do not use staples, paper clips, glue or correction fluid.
6 Protective eye goggles and gloves must be worn at ALL TIMES.

Answer **ALL** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate. You may lose marks if you do not show your working or if you do not use appropriate units.

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

Shift
Laboratory

For Examiner's Use	
Question No.	Marks
1	/17
2	/10
3	/14
4	/14
Total	/55

Answer **all** questions in the spaces provided.

1 Determination of acid concentration and enthalpy change of neutralisation using calorimetry

When an acid is added into an alkali, an exothermic reaction takes place and the temperature of the mixture increases. Maximum heat is given out when stoichiometric amounts of H^+ and OH^- are added together.

FA 1 is an aqueous solution prepared by mixing *equal volumes* of ***y*** mol dm^{-3} hydrochloric acid, HC*l*, and ***y*** mol dm^{-3} sulfuric acid, H_2SO_4
FA 2 is 2.00 mol dm^{-3} sodium hydroxide, NaOH

In this question, you are to follow the neutralisation of known volumes of **FA 2**, NaOH, by measuring the highest temperature obtained as different volumes of **FA 1** are added.

By measuring the maximum temperature rise for different mixtures of the two reagents, you are to determine the following.

- the value of ***y***, concentration of the acids present in **FA 1**
- the enthalpy change of neutralisation, ΔH_{neut}, for the reaction

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

(a) Method

1 Fill the burette with **FA 2**.
2 Support the Styrofoam cup in a 250 cm^3 glass beaker.
3 Run 20.00 cm^3 **FA 2** from the burette into the Styrofoam cup. Stir and measure the temperature of this **FA 2**.
4 Measure 20 cm^3 **FA 1** in a measuring cylinder.
5 Tip the **FA 1** in the measuring cylinder into the **FA 2** cup, stir and record the maximum temperature obtained in the reaction.
6 Rinse and carefully dry the Styrofoam cup.
7 Repeat **steps 1 to 6** three more times, each time using 20.00 cm^3 of **FA 2.** Use 30.0 cm^3, 40.0 cm^3 and 50.0 cm^3 of **FA 1** respectively in these different experiments.

Carry out **two further experiments**.
Choose volumes of **FA 1** which will allow you to investigate more precisely the volume of **FA 1** that produces the highest temperature rise when added to 20.00 cm^3 of **FA 2**.

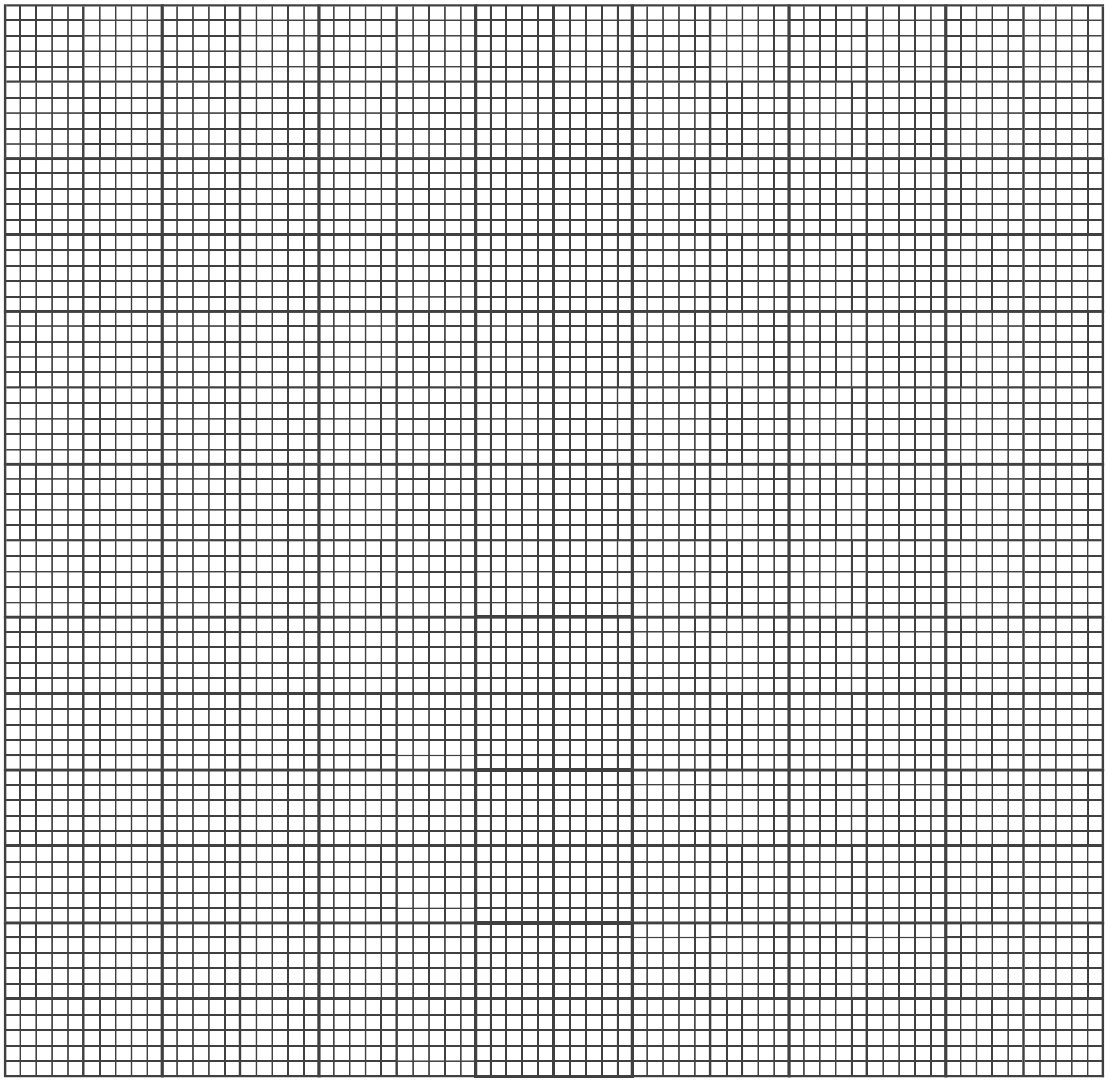
Record your results in an appropriate format in the next page. Record all measurements of volume, temperature and temperature change, ΔT.

(i) Experimental results

Expt No.	Vol of **FA 1**/ cm^3	Vol of **FA 2**/ cm^3	Temperature of **FA 2**/ °C OR initial temperature/ °C	Maximum Temperature / °C	ΔT / °C
1	20.0	20.00			
2	30.0	20.00			
3	40.0	20.00			
4	50.0	20.00			
5	**35**.0	**20.00**			
6	**25**.0	**20.00**			

[5]

(ii) Plot $\Delta \boldsymbol{T}$ (*y–axis*) against volume of **FA 1** (*x–axis*) on the grid below.
Draw a line of best fit through the points where the temperature rise is increasing and another line through the points where the temperature rise is decreasing.



[3]

(iii) Read from the graph the maximum temperature change, ΔT_{max}, and the volume, V_{neut}, of **FA 1** needed to obtain this value. Record these values in the spaces provided below.

maximum temperature change, ΔT_{max} = ……**10.0**……°C

volume of **FA 1** used at ΔT_{max} = V_{neut} = ……**34.0**…….. cm^3

[1]

(b) Use your results from **(a)(iii)** to calculate:

(i) the concentration, in mol dm^{-3}, of the hydrogen ions in **FA 1**.

Moles of OH^- used = 2.0 x $(\frac{20.00}{1000})$ = 0.0400 mol

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

Total moles of H^+ in **FA 1** required for neutralisation = 0.0400 mol

Total concentration of H^+ in **FA 1** = $\frac{0.0400}{0.0340}$ = 1.1764 = 1.18 mol dm^{-3}

concentration of hydrogen ions in **FA 1** = ……**1.18 mol dm^{-3}** ……

[1]

(ii) Hence, the value of ***y***.

Since **FA 1** is an aqueous solution prepared by mixing *equal volumes* of ***y*** mol dm^{-3} hydrochloric acid, HC*l*, and ***y*** mol dm^{-3} sulfuric acid, H_2SO_4;

mol ratio of H^+ from H_2SO_4 : H^+ from HC*l*
2 : 1

concentration of HC*l* in **FA 1** = $\frac{1}{3}$ x (1.1764) = 0.392 mol dm^{-3}

Since ***equal volumes*** of both acids were mixed to obtain **FA 1**

Concentration of HC*l*(aq) before dilution = ***y*** = ***2*** x 0.392 = 0.784 mol dm^{-3}

value of ***y*** is …**0.784**……..

[1]

(iii) the heat change for the reaction and hence the enthalpy change of neutralisation, ΔH_{neut}, for the reaction

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

[Assume that 4.18 J of energy is needed to raise the temperature of 1 g of the solution by 1 K]

Heat released = $mc\Delta T_{max}$ = (20.00 + 34.0)(4.18)(10.0)
= 2257.2 J

$\Delta H_{neut} = -\frac{2257.2}{0.0400}$ = –56430 J mol^{-1} = –56.4 kJ mol^{-1}

[4]

(c) A student suggested using a burette rather than a measuring cylinder to measure the volume of **FA 1** to improve the precision in volume measurement. However, he was advised not to do so by his teacher.

Suggest a disadvantage of using a burette and explain how the calculated ΔH_{neut} would be affected if volume of **FA 1** had been added from a burette.

Disadvantage
Takes **longer** to add **FA 1** into **FA 2**.

Impact on ΔH_{neut}
Since addition of **FA 1** from a burette is a slow process, heat is lost during the slow process. Heat loss reduces ΔT_{max} and would result in a lower value for the heat change and so a lower numerical / less exothermic value for ΔH_{neut}.

[2]
[Total:17]

2 Determination of calcium ion concentration using complexometric titration

The calcium content of milk and tap water and the amount of calcium carbonate in various solid samples can be determined using complexometric titrations.

This method uses ethylenediaminetetraacetic acid, EDTA, which forms a complex with calcium ions in a 1:1 ratio. A blue dye called Patton–Reeder indicator is used to identify the end–point. The dye forms a pink complex with calcium ions. As this complex is less stable than the EDTA complex, the dye is displaced by EDTA as the titration proceeds. The solution turns blue at the end–point due to the uncomplexed dye.

FA 3 is a brand of milk.

In **2(a)**, you perform titrations to determine the calcium content of milk.

You are also provided with
FA 2, 2.00 mol dm^{-3} sodium hydroxide, NaOH
FA 4, 0.0170 mol dm^{-3} EDTA
Patton–Reeder indicator

As EDTA is harmful to the environment, **FA 4** should be disposed in the waste bottle. You should also wear gloves throughout the experiment.

(a) (i) 1. Fill the burette with **FA 4**.

2. Use a pipette to transfer 10.0 cm^3 of **FA 3** into a 250 cm^3 conical flask.

3. Using appropriate measuring cylinders, add 36.0 cm^3 of deionised water then 8.0 cm^3 of **FA 2** into the conical flask. Swirl and allow the solution to stand for about 2 minutes.

4. Add half a spatula of Patton–Reeder indicator into the conical flask and swirl the mixture to dissolve the indicator. The mixture is *pink* at this point.

5. Run **FA 4** from the burette into the conical flask. The end–point is reached when the mixture *loses all trace of purple and turns blue*. As the colour change is gradual, you will find it helpful to compare against the original and / or final colour of another sample.

6. At the end of the experiment, contents of the conical flask should be disposed in the waste bottle.

7. Record your titration results, to an appropriate level of precision, in the space provided.

Titration results

	1	2
Final burette reading / cm^3	14.70	29.50
Initial burette reading / cm^3	0.00	14.70
Volume of **FA 4** used / cm^3	14.70	14.80

[3]

(ii) From your titrations, obtain a suitable volume of **FA 4**, $V_{FA\ 4}$, to be used in your calculations. Show clearly how you obtained this volume.

$$V_{FA\ 4} = \frac{14.70 + 14.80}{2} = 14.75\ cm^3$$

[2]

(b) (i) Calculate the concentration of calcium ions present in **FA 3** using your answer in **(a)(ii)**.

$$Ca^{2+} \equiv EDTA$$
$$\frac{10.00}{1000} \times [Ca^{2+}] = \frac{14.75}{1000} \times 0.0170$$
$$[Ca^{2+}] = 0.0251\ mol\ dm^{-3}$$

[1]

The nutritional label on the packaging states that this brand of milk contains 200 mg of calcium per 200 cm^3 serving.

[1 g = 1000 mg]

(ii) Use your results from **(b)(i)** to comment if your titration results supports the claim on the nutritional label.

[A_r: Ca, 40.1]

$$[Ca^{2+}] = 0.0251\ mol\ dm^{-3}$$
$$no.\ of\ moles\ of\ Ca^{2+}\ in\ 200\ cm^3 = 0.0251 \times \frac{200}{1000} = 5.025 \times 10^{-3}\ mol$$
$$mass\ of\ Ca^{2+}\ in\ 200\ cm^3 = 5.025 \times 10^{-3} \times 40.1 = 0.2015\ g = 201.5\ mg$$

Yes, since the titration results is very close to the value in the nutritional label.

[3]

(c) Trace amounts of magnesium ions present in milk affects the accuracy of this experiment as magnesium ions also readily form a complex with EDTA.

Explain how step 3 of the procedure prevents this error.

Mg^{2+} is removed as $Mg(OH)_2$ ppt.

[1]
[Total: 10]

3 Investigation of some inorganic reactions

FA 5 is an aqueous solution containing two cations.

Carry out the following tests described in Table 3.1 and carefully record your observations.

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured. Test and identify any gases evolved. If there are no observable change, write **no observable change**.

Table 3.1

		tests	observations
(a)	**(i)**	Add 1 cm depth of **FA 5** to a test–tube. Add an equal volume of aqueous sodium nitrite.	**Blue** solution turns **green**
	(ii)	Add 2 cm depth of **FA 5** to a test–tube. Add 2 pieces of zinc into the test–tube. Warm the test–tube gently. Leave to stand until no further change is seen.	**Effervescence** is observed. Colourless gas evolved **extinguishes a lighted splint with a 'pop' sound**. √Gas is **H_2**. Blue solution **decolourises**. **Reddish–brown solid** is deposited on zinc
	While waiting, continue with the next tests		
	(iii)	Add 1 cm depth of **FA 5** to a test–tube. Add **FA 2** slowly, with shaking, until no further change is seen. Filter the mixture. To 1 cm depth of the filtrate, add nitric acid dropwise until no further change is seen.	A **blue ppt** forms, and is **insoluble in excess** NaOH. A **white ppt** forms, and is **soluble in excess** NaOH to form a colourless solution. Residue is a blue solid. **Filtrate is a colourless solution**. **white ppt** reforms, and is **soluble in excess** acid
	(iv)	Add 1 cm depth of **FA 5** to a test–tube. Add aqueous ammonia slowly with shaking, until no further change is seen. Filter the mixture.	A **blue ppt** forms, dissolving in excess ammonia to form a **deep blue solution**. A **white ppt** forms, and is **insoluble in excess** ammonia. Residue is a white solid. Filtrate is a deep blue solution.
	(v)	To 1 cm depth of the filtrate from **(iv)**, add 1 cm depth of aqueous $EDTA^{4-}$ from the small vial with shaking. *The mixture at the end of this test should be disposed in the waste bottle.*	deep blue solution turns (lighter) **blue**.

(vi)	Add 4 cm depth of **FA 5** to a test–tube. Add 2 cm depth of aqueous sodium carbonate. The total depth of the mixture should not exceed half the test–tube. Shake well. Leave to stand for a few minutes. Filter the resultant mixture.	A **pale blue ppt** forms. Blue solution decolourises. **Effervescence** is observed. Colourless gas evolved forms **white ppt with limewater**. Gas is **CO_2**. Residue is pale blue. Filtrate is a colourless solution
(vii)	Transfer the residue from **(vi)** to a boiling tube. Heat gently then strongly until no further change is observed.	Pale blue solid turns **white** and **pale green**. A mixture of white and **black** solid remain. water droplets form on the side of the test tube. Colourless gas evolved forms white ppt with limewater. Gas is CO_2.

[7]

(b) Consider your observations in Table 3.1.

(i) State the identity of the two cations present in **FA 5**.

Cu^{2+} and Al^{3+}

[1]

The wavelengths and corresponding colours of visible light is shown in Figure 3.1.

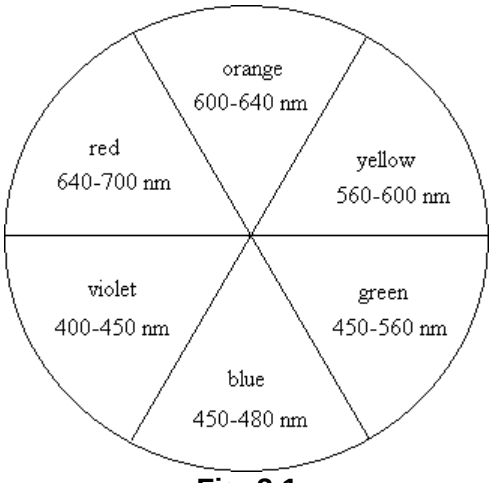


Fig. 3.1

(ii) In terms of the magnitude of d–orbital splitting, account for the colour change observed in **(a)(i)**.

Upon addition of nitrite ligand, a green mixture of the yellow nitrite complex and the original blue $[Cu(H_2O)_6]^{2+}$ complex is obtained. The colour of light absorbed changes from **orange** (600-640nm) to **violet** (400-450nm). Since the light absorbed is of a **shorter wavelength**, nitrite is a stronger field ligand that results in a **larger** magnitude of d–orbital splitting.

OR

The blue $[Cu(H_2O)_6]^{2+}$ complex **absorbs orange light** (600-640nm) while the green nitrite complex **absorbs red light** (640-700nm). Since the **light absorbed is of a longer wavelength**, the magnitude of d–orbital splitting caused by ligand in complex is **smaller**.

[2]

In **(a)(v)**, a ligand exchange occurs with hexadentate $EDTA^{4-}$.

(iii) Write a balanced equation for the ligand exchange reaction in **(a)(v)**.

[1]

$[Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + EDTA^{4-}(aq) \rightarrow [Cu(EDTA)]^{2-}(aq) + 4NH_3(aq) + 2H_2O(l)$

(iv) Each donor atom on $EDTA^{4-}$ binds to the metal centre with similar strength as an ammonia molecule and a water molecule.

Using this information and your answer to **(b)(iii)**, estimate the enthalpy change for the reaction in **(a)(v)** and suggest why it occurs spontaneously.

As each donor atom on $EDTA^{4-}$ binds to the Cu^{2+} centre with similar strength as an ammonia molecule and a water molecule, the strength of bonds broken is similar to the strength of bonds formed. Hence **$\Delta H \approx 0$**.

There is **an increase of aqueous species** (**$\Delta n > 0$**), hence **$\Delta S > 0$**. The **disorder** of the system **increases**. Since $\Delta G = \Delta H - T\Delta S$, **$\Delta G < 0$** and the reaction is spontaneous.

[2]

(v) Write a balanced equation for the reaction occurring in **(a)(vii)**.

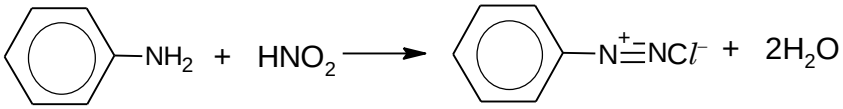
$CuCO_3 \rightarrow CuO + CO_2$ OR $Cu(OH)_2 \rightarrow CuO + H_2O$

[1]

[total: 14]

4 Planning

When an aromatic amine is treated with nitrous acid, a reaction occurs in which *diazonium salt* is formed. This process is known as **diazotisation**. The equation below shows the reaction between phenylamine and nitrous acid to form benzenediazonium chloride, $C_6H_5N_2^+Cl^-$.



Benzenediazonium chloride, $C_6H_5N_2^+Cl^-$, is not stable at temperature above 5 °C.

Nitrous acid is a highly toxic gas. Therefore, it is generally prepared during the reaction itself by reacting $NaNO_2$ with a mineral acid.

A student followed the steps below to prepare benzenediazonium chloride.

1. 3.25 cm^3 of phenylamine was placed in a 500 cm^3 volumetric flask.
2. A mixture of 30 cm^3 of concentrated hydrochloric acid and 30 cm^3 of water was added into the flask containing phenylamine to dissolve it.
3. The solution mixture was stirred and cooled to 1°C.

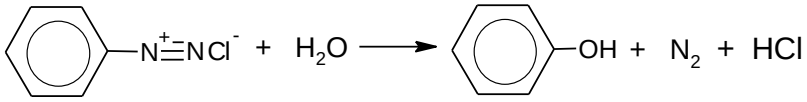
4. Solid $NaNO_2$ was dissolved in 30 cm^3 of water, then *slowly and carefully* added to the solution mixture, with stirring.
5. The resultant solution was made up to 500 cm^3 with water, mixed well and kept cool below 5 °C. This resultant benzenediazonium chloride solution prepared is labelled solution **B**.

(a) Suggest why $NaNO_2$ solution was added *slowly and carefully* in step 4.

[1]

Diazotisation is an exothermic reaction / To prevent temperature from going above 5 °C.

When the temperature is above 5 °C, benzenediazonium chloride hydrolyses to give phenol, nitrogen gas and hydrochloric acid.



The temperature of a portion of 25.0 cm^3 of solution **B** was raised to room temperature at constant pressure.

(b) **(i)** Calculate the theoretical maximum volume of N_2 produced when 25.0 cm^3 of solution **B** is hydrolysed at room temperature and pressure.

[M_r of phenylamine = 93.0; density of phenylamine = 1.02 g cm^{-3}; molar volume of gas at room temperature and pressure = 24.0 dm^3 mol^{-1}]

[3]

Mass of phenylamine used = 1.02 x 3.25 = 3.315 g
Moles of phenylamine used = $\frac{3.315}{93.0}$ = 0.0356 mol

Moles of benzenediazonium chloride prepared in 500 cm^3 = 0.0356 mol
Moles of benzenediazonium chloride prepared in 25 cm^3 portion = $\frac{25}{500}$ x 0.0356
= 0.00178 mol

Moles of N_2 produced = 0.00178 mol
Volume of N_2 produced at r.t.p. = 0.00178 x 24.0 dm^3 = 0.0428 dm^3 = **42.8 cm^3**

Another 25.0 cm^3 portion of solution **B** was transferred to a boiling tube and the hydrolysis of benzenediazonium chloride was carried out at 40 °C.

The progress of the reaction can be monitored by measuring the volume of nitrogen gas produced over time. The volume of gas produced, V after time, t, is proportional to the concentration of benzenediazonium chloride that has been hydrolysed. The final volume of gas produced, V_{final}, is proportional to the original concentration of benzenediazonium chloride.

The order of reaction can be determined from these results.

(ii) Explain the significance of $V_{final} - V$.

[1]

$V_{final} - V$ is proportional to the concentration of benzenediazonium chloride yet to be hydrolysed

(iii) Sketch, on Fig 4.1, the graph of $V_{final} - V$ against time you would expect to obtain if the order of reaction with respect to $[C_6H_5N_2^+Cl^-]$ is one.

[2]

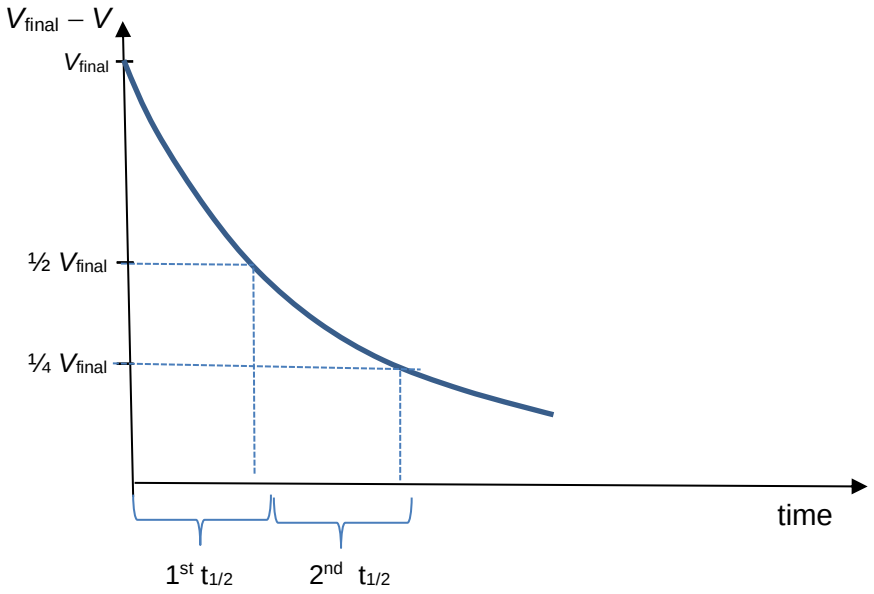


Fig 4.1

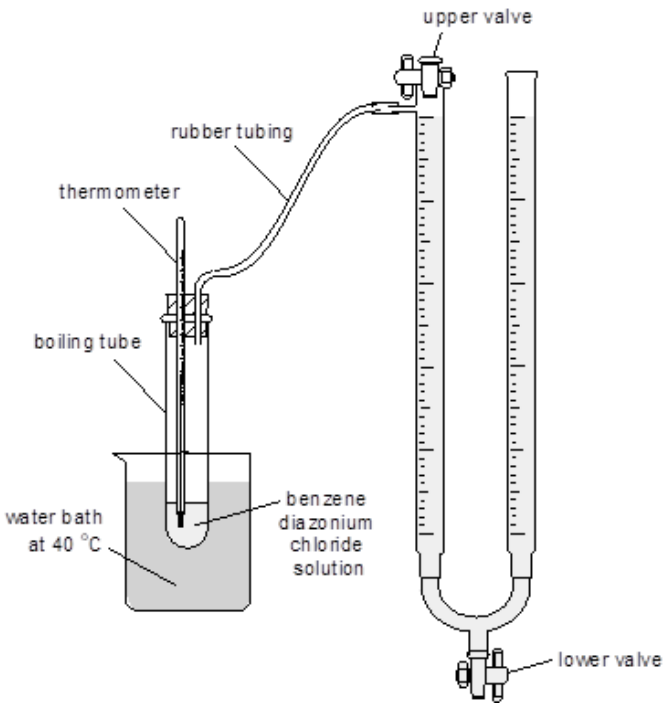


Fig. 4.2

At the start, the lower valve is closed and the upper valve is opened. The two burettes are filled with water and both levelled to 0.00 cm^3. The upper valve is closed once the hydrolysis of benzenediazonium chloride begins. As gas is collected during the experiment, the water level in both burettes will differ slightly. The lower valve is opened and closed carefully from time to time to ensure that the water levels in the two burettes are the same.

(iv) Complete the diagram on Fig 4.2 to show the experimental set–up the student could have used to carry out experiment in **(b)** to measure the volume of nitrogen evolved **at 40 °C**.

Outline the steps involved in carrying out the experiment. You may omit the step to prepare the burettes above for gas collection before the reaction begins.

Your steps should include

- the apparatus you would use
- the reactants and conditions that you would use
- the measurements you would take.

[5]

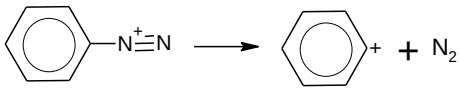
1. **Pipette 25.0 cm^3** of solution **B** in a test–tube. (Place a magnetic stirrer in it.)
2. Stoppered the solution **B** tightly and place it in a **thermostatically-controlled water bath set at 40 °C**.
3. Allow some time (10 minutes?) for the solution **B** to reach **thermal equilibrium**.
4. After 10 min, close the upper valve/stopper the test–tube and **start** the stopwatch.
   (The nitrogen gas evolved will push the water level in the left burette down and the right burette up.)
5. Open the lower valve to drain excess water so that the water level in both burettes are the same.
6. At **every** two minutes **interval** for 30 min, read and record the volume of gas evolved.
7. Continue the volume measurement until **three constant readings** are obtained.

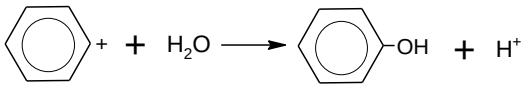
(v) Why is there a need to ensure that the water level in both burettes are the same during the experiment?

[1]

So that gas is collected at constant / atmospheric pressure.

(c) Benzenediazonium chloride hydrolyses in water according to the following steps.

Step 1: 

Step 2: 

Deduce the role of H_2O and suggest the likely type of reaction occurring.

[1]

H_2O acts as nucleophile. Type of reaction is (nucleophilic) substitution or S_N1.

[Total:14]