| Name: | | Centre/Index Number: | | Class: | |
|---|---|---|---|---|---|

# DUNMAN HIGH SCHOOL
## Preliminary Examination
## Year 6

## H2 CHEMISTRY
**9729/04**

Paper 4 Practical

**24 August 2021**

**2 hours 30 minutes**

Candidates answer on the Question Paper.

**READ THESE INSTRUCTIONS FIRST**

Write your centre number, index number, name and class at the top of this page.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

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.
Qualitative Analysis Notes are printed on pages 23 and 24.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

| Shift |
|---|
| |
| Laboratory |
| |

| For Examiner's Use | |
|---|---|
| 1 | 22 |
| 2 | 5 |
| 3 | 15 |
| 4 | 13 |
| Total | 55 |

This question paper consists of **20** printed pages and **4** blank pages.

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

**1 Determination of a value for the enthalpy change of precipitation, $\Delta H_{ppt}$, of barium sulfate**

**FA 1** is 1.00 mol dm$^{-3}$ sodium hydroxide, NaOH.
**FA 2** is a saturated solution of barium hydroxide, $Ba(OH)_2$.
**FA 3** is 1.00 mol dm$^{-3}$ sulfuric acid, $H_2SO_4$.

The addition of **FA 2** to **FA 3** results in neutralisation and precipitation reactions occurring as shown in equations 1 and 2 respectively.

equation 1 $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ $\Delta H_{neut}$

equation 2 $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$ $\Delta H_{ppt}$

In the first experiment, you will determine the maximum temperature change as a result of both reactions occurring in a Styrofoam cup.

In the second experiment, you will measure the temperature of the resulting mixture after each addition of a fixed volume of **FA 1** solution to the remaining $H^+$ ions in the Styrofoam cup. You will analyse your results graphically in order to determine an accurate value for the temperature change of the mixture, caused by the neutralisation reaction shown in equation 1.

You will use this value to calculate the heat change for the second experiment and hence determine a value for the enthalpy change of neutralisation which will then be used to determine a value for the enthalpy change of precipitation for $BaSO_4$.

**(a)** **(i)** **Experiment 1**

1. Use a measuring cylinder to add 20.0 cm$^3$ of **FA 3** into a Styrofoam cup. Place this cup inside a second Styrofoam cup, which is placed in a 250 cm$^3$ glass beaker. Stir and measure the temperature of this solution, $T_{1,initial}$. Record this temperature in Table 1.1.

2. Use another measuring cylinder to add 5.0 cm$^3$ of **FA 2** into the Styrofoam cup. Using the thermometer, stir the mixture and record its maximum temperature, $T_{1,max}$, in Table 1.1. You should expect a small rise in temperature.

**Retain the contents in the Styrofoam cup for experiment 2 in (b)(i).**

Complete Table 1.1 by calculating the value for $\Delta T_{1,max}$.

**Table 1.1**

| | |
|---|---|
| $T_{1,initial}$ / °C | |
| $T_{1,max}$ / °C | |
| $\Delta T_{1,max}$ / °C | |

[1]

**(ii)** Calculate the heat change, $q_1$, for experiment 1.

You should assume that the specific heat capacity of the solution is 4.18 J $g^{-1}$ $K^{-1}$, and that the density of the solution is 1.00 g $cm^{-3}$.

$q_1$ = .............................. [1]

**(iii)** Calculate the percentage error associated with the value of $\Delta T_{1,max}$ and hence comment on the accuracy of the heat change, $q_1$, calculated in **(a)(ii)**.

percentage error = ............................%

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[1]

**(b)** (i) **Experiment 2**

1. Fill a burette with **FA 1**.

2. Record, in Table 1.2, the initial temperature of the mixture in the Styrofoam cup from experiment 1.

3. Run 5.00 $cm^3$ of **FA 1** from the burette into the Styrofoam cup. Using the thermometer, stir the mixture continuously until it reaches its maximum temperature. Record this temperature, $T_{2,max}$, in Table 1.2.

4. Repeat step 3 until a total volume of 50.00 $cm^3$ of **FA 1** is added.

**Table 1.2**

| total volume of **FA 1** added after each addition, $V_{FA 1}$ / $cm^3$ | $T_{2,max}$ / °C |
|---|---|
| 0.00 | |
| 5.00 | |
| 10.00 | |
| 15.00 | |
| 20.00 | |
| 25.00 | |
| 30.00 | |
| 35.00 | |
| 40.00 | |
| 45.00 | |
| 50.00 | |

[2]

**(ii)** Plot a graph of $T_{2,max}$ on the y-axis against $V_{FA\ 1}$ on the x-axis.

Draw two best-fit lines,

- the first is a smooth **curve** taking into account all of the points before,
- the second is a **straight line** taking into account all of the points after

the temperature of the mixture has started to drop.

Extrapolate (extend) both lines until they intersect (cut) each other.

[3]

**(iii)** From your graph, read $V_{FA\,1}$ and $T_{2,max}$ of the intersection point.
Record these values in the spaces provided.
Deduce the maximum temperature change, $\Delta T_{2,max}$.

$V_{FA\,1}$ = ......................... $cm^3$

$T_{2,max}$ = ...........................°C

$\Delta T_{2,max}$ = ...........................°C

[2]

**(iv)** Calculate the heat change, $q_2$, for experiment 2 using the values you deduced in **(b)(iii)**.

You should assume that the specific heat capacity of the solution is 4.18 $J\ g^{-1}\ K^{-1}$, and that the density of the solution is 1.00 $g\ cm^{-3}$.

$q_2$ = .............................. [1]

**(v)** Hence determine a value for the enthalpy change, for the neutralisation reaction shown in equation 1, $\Delta H_{neut}$.

$\Delta H_{neut}$ = .............................. [2]

**(c)** **(i)** The **FA 2** solution was prepared as follows.

An excess of solid $Ba(OH)_2.8H_2O$ was added to 100 $cm^3$ of water and the mixture was allowed to stand. The undissolved solid was then removed by filtration to obtain the saturated solution of barium hydroxide.

Calculate the concentration of barium and hydroxide ions in the **FA 2** solution given that the solubility of $Ba(OH)_2.8H_2O$ in water is 56 g $dm^{-3}$.

[$M_r$: $Ba(OH)_2.8H_2O$, 315.3]

$[Ba^{2+}]$ = ..............................

$[OH^-]$ = ..............................

[1]

**(ii)** Hence calculate the heat evolved from the neutralisation reaction between **FA 2** and **FA 3** in experiment 1.

heat evolved = .............................. [1]

**(iii)** Use your answers in **(a)(ii)** and **(c)(ii)** to determine the heat change due to the precipitation of $BaSO_4$ in experiment 1. Hence determine a value for the enthalpy change for the precipitation reaction shown in equation 2, $\Delta H_{ppt}$.

heat change due to the precipitation of $BaSO_4$ = ...............................

$\Delta H_{ppt}$ = ...............................
[3]

**(iv)** Explain, in terms of the chemistry involved, the sign of $\Delta H_{ppt}$. Hence explain why precipitation of $BaSO_4$ occurs spontaneously under the experimental conditions.

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**(d)** A student performed experiment 2 using 2.00 mol $dm^{-3}$ sodium hydroxide from the bench reagents instead of **FA 1**.

Explain how the volume of 2.00 mol $dm^{-3}$ sodium hydroxide required for complete neutralisation of the mixture in the Styrofoam cup would differ from that of **FA 1**.

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[Total: 22]

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## 2 Investigation of pH of solution

**FA 4** is an organic compound with the molecular formula, $C_2H_4O_2$.

Perform the tests described in Table 2.1. Some of the observations have been completed for you. There is no need to carry out those tests. Record your observations in Table 2.1.

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

**Table 2.1**

| | | test | observations |
|---|---|---|---|
| (a) | (i) | Add 4 cm depth of deionised water to a test-tube and test it using Universal Indicator (UI) paper.<br><br>Add 2 drops of **FA 1** to the test-tube and test the solution using Universal Indicator paper. | UI paper turns light green<br>pH 5<br><br>UI paper turns dark blue<br>pH 12 |
| | (ii) | Add 3 cm depth of **FA 4** to a test-tube.<br><br>Add 1 cm depth of aqueous sodium hydroxide to the test-tube and test the solution using Universal Indicator paper.<br><br>Add 2 drops of **FA 1** to the test-tube and test the solution using Universal Indicator paper. | |
| | (iii) | Add 2 cm depth of **FA 4** to a test-tube.<br><br>Add half a spatula of solid sodium carbonate to the test-tube. | |

[2]

**(b)** **(i)** Suggest the identity of **FA 4**. Give evidence from your observations in **(a)** to support your conclusion.

identity ..........................................................................................................

evidence ..........................................................................................................

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

**(ii)** Explain, in terms of the chemistry involved, the difference in observations made upon the addition of **FA 1** to the test-tubes in **(a)(i)** and **(a)(ii).**

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[Total: 5]

## 3 Determination of amount of $Mg^{2+}$ and $Al^{3+}$ in an antacid tablet

To determine the amount of $Mg^{2+}$ and $Al^{3+}$ in an antacid tablet, a complexometric back titration involving ethylenediaminetetraacetic acid, EDTA, can be used. Both $Mg^{2+}$ and $Al^{3+}$ form a complex with EDTA in a 1:1 mole ratio.

$$Mg^{2+} + EDTA \rightarrow Mg\text{–}EDTA \text{ complex}$$

$$Al^{3+} + EDTA \rightarrow Al\text{–}EDTA \text{ complex}$$

A known amount of excess EDTA is first added to a sample containing $Mg^{2+}$ and $Al^{3+}$. The resultant mixture contains both the complex and unreacted EDTA. This resultant mixture is then titrated with zinc sulfate to determine the amount of unreacted EDTA. $Zn^{2+}$ also reacts with EDTA in a 1:1 mole ratio.

$$Zn^{2+} + EDTA \rightarrow Zn\text{–}EDTA \text{ complex}$$

The dye indicator used in this titration is Eriochrome Black T, which will turn from blue to violet at the end–point.

When the titration is conducted at pH 5, only the Al–EDTA complex forms, while at pH 10, both the Mg–EDTA and Al–EDTA complexes form.

You will only be performing the titrations at pH 10, to determine the total amount of $Mg^{2+}$ and $Al^{3+}$ in a sample.

**FA 5** is a solution prepared containing $Mg^{2+}$ and $Al^{3+}$
**FA 6** is a buffer solution at pH 10, containing $Na_2CO_3$ and $NaHCO_3$
**FA 7** is 0.0100 mol $dm^{-3}$ EDTA
**FA 8** is 0.0100 mol $dm^{-3}$ $ZnSO_4$
**Solution T** is Eriochrome Black T indicator

As EDTA is harmful to the environment, **FA 7** should be disposed in the waste bottle. You should also wear gloves throughout the experiment.

### (a) Pre–titration: Determination of the colour at end-point for titration

1. Using a dropping pipette, add the following solutions into a clean boiling tube:

   - 6 drops of **FA 5**
   - 15 drops of **FA 6**
   - 20 drops of **FA 7**
   - 1 drops of **Solution T**

   The colour of the solution in the test tube should be blue. If the colour of the solution is not blue, add a few more drops of **FA 6** and **FA 7** into the boiling tube.

2. Using a dropping pipette, add **FA 8** dropwise into the test tube, with shaking, until one drop of **FA 8** causes the blue colouration of the solution to fade to yield a violet colour.

3. Keep this solution as a reference for the colour at the end–point of the titration in **(b)**.

**(b) (i) Determination of the amount of $Mg^{2+}$ and $Al^{3+}$ in the sample**

1. Fill a burette with **FA 8**.
2. Using a pipette, transfer 10.0 $cm^3$ of **FA 5** into a 250 $cm^3$ conical flask.
3. Using appropriate measuring cylinders, add 20.0 $cm^3$ of **FA 6**, followed by 35.0 $cm^3$ of **FA 7** into the conical flask.
4. Swirl the conical flask to ensure a homogeneous solution. It is normal for the solution to appear cloudy.
5. Heat the conical flask over the Bunsen burner until the temperature of the solution reaches 65 °C.
6. Remove the conical flask from the flame. If the neck of the flask is too hot to hold safely, use a folded paper towel to hold the flask.
7. Add 5 drops of **Solution T** into the conical flask. The solution should be blue at this point.
8. Run **FA 8** from the burette into the conical flask.
9. The end–point is reached when the blue colour fades to yield the violet colour of the solution in the boiling tube from **(a)**.
10. Record your titration results, to an appropriate level of precision, in Table 3.1.

**Titration results**

**Table 3.1**

| | | |
|---|---|---|
| | | |
| | | |
| | | |
| | | |

[3]

**(ii)** From your titrations, obtain a suitable volume of **FA 8**, $V_{FA\ 8}$, to be used in your calculations. Show clearly how you obtained this volume.

$V_{FA\ 8}$ = ......................... [1]

**(c)** **(i)** Using your answer in **(b)(ii)**, calculate the amount, in moles, of unreacted EDTA present in the conical flask after step 3.

amount of unreacted EDTA = .......................... [1]

**(ii)** Calculate the amount of EDTA that formed a complex with $Mg^{2+}$ and $Al^{3+}$, and hence, determine the total concentration of $Mg^{2+}$ and $Al^{3+}$ in **FA 5**.

amount of EDTA that formed a complex with $Mg^{2+}$ and $Al^{3+}$ = ............................

total concentration of $Mg^{2+}$ and $Al^{3+}$ in **FA 5** = ............................

[3]

**(d)** Briefly outline how you can determine the exact individual amounts of $Mg^{2+}$ and $Al^{3+}$ in **FA 5** by conducting a second titration involving $ZnSO_4$ and EDTA.

You may assume that only $Mg^{2+}$ and $Al^{3+}$ in **FA 5** react with EDTA.

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**(e)** EDTA is better represented as $H_4EDTA$ because it is a weak acid. The $EDTA^{4-}$ anion can be formed from four successive deprotonation of $H_4EDTA$.

$$H_4EDTA(aq) \rightleftharpoons EDTA^{4-}(aq) + 4H^+(aq) \text{ ---- (1)}$$

At high pH, $Zn^{2+}$ readily forms a complex with $EDTA^{4-}$.

$$[Zn(H_2O)_6]^{2+} + EDTA^{4-} \rightleftharpoons [Zn(EDTA)]^{2-} + 6H_2O \text{ ---- (2)}$$

**(i)** Explain the effect of increasing pH on the concentration of the $[Zn(EDTA)]^{2-}$ complex.

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**(ii)** The reaction mixture is kept at high pH due to the $Na_2CO_3$ and $NaHCO_3$ buffer. With the aid of an appropriate chemical equation, explain how this buffer maintains the high pH when a small amount of acid is added.

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

**(iii)** Given that the p$K_a$ of $HCO_3^-$ is 10.3, calculate the $\frac{[CO_3^{2-}]}{[HCO_3^-]}$ ratio in the $Na_2CO_3$/$NaHCO_3$ buffer solution at pH 10.

$\frac{[CO_3^{2-}]}{[HCO_3^-]}$ = .......................... [1]

[Total: 15]

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**4 Planning**

In the presence of glucose, acidified potassium manganate(VII) decolourises. This is because glucose acts as a reducing agent, reducing $MnO_4^-$ to $Mn^{2+}$.

A series of experiments can be carried out at various temperatures to investigate the effect of temperature on the rate constant of the reaction. The time required for the purple reaction mixture to turn colourless will allow for the determination of the rate of reaction.

**(a)** **(i)** State the effect of an increase in temperature on the time taken for the purple reaction mixture to turn colourless.

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

**(ii)** Using the concept of Collision Theory, explain your answer in **(a)(i)**.

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**(b)** To investigate the effect of temperature on the rate constant, a series of experiments at different temperatures can be carried out.

You may assume that you are provided with:

- 0.1 mol $dm^{-3}$ glucose solution
- 0.1 mol $dm^{-3}$ aqueous potassium manganate(VII), $KMnO_4$,
- 2 mol $dm^{-3}$ sulfuric acid, $H_2SO_4$,
- the apparatus normally found in a school laboratory.

Table 4.1 shows the volumes of reactants used for experiment 1.

Once all the reactants have been added to a dry conical flask, the initial temperature of the reaction mixture, $T_i$, was measured and recorded. Immediately after the decolourisation of $KMnO_4$, the final temperature of the mixture, $T_f$, was also measured and recorded. The average temperature of the reaction mixture, $T_{ave}$, was then determined.

Table 4.1 also shows the time required for the decolourisation of purple $KMnO_4$ for experiment 1.

**Table 4.1**

| Experiment | Vol. of glucose solution / $cm^3$ | Vol. of $KMnO_4$ / $cm^3$ | Vol. of $H_2SO_4$ / $cm^3$ | $T_i$ / °C | $T_f$ / °C | $T_{ave}$ /°C | Time taken for decolourisation / s |
|---|---|---|---|---|---|---|---|
| 1 | 5.0 | $x$ | 20.0 | 29.0 | 30.0 | 29.5 | 240 |
| 2 | | | | | | | |

**(i)** Given that glucose and $KMnO_4$ react in a molar ratio of 5 : 24, state an appropriate value for $x$, the volume of $KMnO_4$ used in experiment 1.

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

To investigate the effect of temperature on the rate constant, experiment 2 can be conducted at a different temperature such that the time taken for the decolourisation of purple $KMnO_4$ will be more than 240 s.

**(ii)** Fill Table 4.1 with the volumes of glucose, $KMnO_4$ and $H_2SO_4$ needed for experiment 2.

[1]

**(iii)** Explain your choice of reactant volumes used in **(b)(ii)**.

..................................................................................................................

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

**(iv)** You are required to write a plan, describing how **experiment 2** can be carried out.

In your plan, you should have details of:

- the apparatus you would use,
- the measurements you would take,
- the procedure you would follow.

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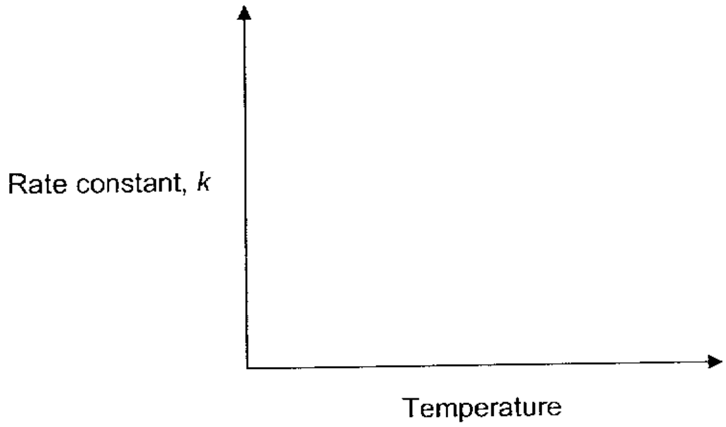
(v) The rate of reaction approximately doubles for every 10 °C increase in temperature.

Using the axes below, sketch a graph to show how the rate constant of the reaction would vary with temperature.




[1]

[Total: 13]

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**Qualitative Analysis Notes**
*[ppt. = precipitate]*

**(a) Reactions of aqueous cations**

| *cation* | *reaction with* | |
|---|---|---|
| | $NaOH(aq)$ | $NH_3(aq)$ |
| aluminium, $Al^{3+}(aq)$ | white ppt.<br>soluble in excess | white ppt.<br>insoluble in excess |
| ammonium, $NH_4^+(aq)$ | ammonia produced on heating | – |
| barium, $Ba^{2+}(aq)$ | no ppt. (if reagents are pure) | no ppt. |
| calcium, $Ca^{2+}(aq)$ | white. ppt. with high [$Ca^{2+}(aq)$] | no ppt. |
| chromium(III), $Cr^{3+}(aq)$ | grey–green ppt.<br>soluble in excess<br>giving dark green solution | grey–green ppt.<br>insoluble in excess |
| copper(II), $Cu^{2+}(aq)$ | pale blue ppt.<br>insoluble in excess | blue ppt.<br>soluble in excess<br>giving dark blue solution |
| iron(II), $Fe^{2+}(aq)$ | green ppt., turning brown on contact with air<br>insoluble in excess | green ppt., turning brown on contact with air<br>insoluble in excess |
| iron(III), $Fe^{3+}(aq)$ | red–brown ppt.<br>insoluble in excess | red–brown ppt.<br>insoluble in excess |
| magnesium, $Mg^{2+}(aq)$ | white ppt.<br>insoluble in excess | white ppt.<br>insoluble in excess |
| manganese(II), $Mn^{2+}(aq)$ | off–white ppt., rapidly turning brown on contact with air<br>insoluble in excess | off–white ppt., rapidly turning brown on contact with air<br>insoluble in excess |
| zinc, $Zn^{2+}(aq)$ | white ppt.<br>soluble in excess | white ppt.<br>soluble in excess |

**(b) Reactions of anions**

| *ion* | *reaction* |
|---|---|
| carbonate, $CO_3^{2-}$ | $CO_2$ liberated by dilute acids |
| chloride, $Cl^-$(aq) | gives white ppt. with $Ag^+$(aq) (soluble in $NH_3$(aq)) |
| bromide, $Br^-$(aq) | gives pale cream ppt. with $Ag^+$(aq) (partially soluble in $NH_3$(aq)) |
| iodide, $I^-$(aq) | gives yellow ppt. with $Ag^+$(aq) (insoluble in $NH_3$(aq)) |
| nitrate, $NO_3^-$ (aq) | $NH_3$ liberated on heating with $OH^-$(aq) and $Al$ foil |
| nitrite, $NO_2^-$ (aq) | $NH_3$ liberated on heating with $OH^-$(aq) and $Al$ foil;<br>NO liberated by dilute acids<br>(colourless NO $\rightarrow$ (pale) brown $NO_2$ in air) |
| sulfate, $SO_4^{2-}$ (aq) | gives white ppt. with $Ba^{2+}$(aq) (insoluble in excess dilute strong acids) |
| sulfite, $SO_3^{2-}$ (aq) | $SO_2$ liberated with dilute acids;<br>gives white ppt. with $Ba^{2+}$(aq) (soluble in dilute strong acids) |

**(c) Tests for gases**

| *gas* | *test and test result* |
|---|---|
| ammonia, $NH_3$ | turns damp red litmus paper blue |
| carbon dioxide, $CO_2$ | gives a white ppt. with limewater<br>(ppt. dissolves with excess $CO_2$) |
| chlorine, $Cl_2$ | bleaches damp litmus paper |
| hydrogen, $H_2$ | "pops" with a lighted splint |
| oxygen, $O_2$ | relights a glowing splint |
| sulfur dioxide, $SO_2$ | turns aqueous acidified potassium manganate(VII) from purple to colourless |

**(d) Colour of halogens**

| *halogen* | *colour of element* | *colour in aqueous solution* | *colour in hexane* |
|---|---|---|---|
| chlorine, $Cl_2$ | greenish yellow gas | pale yellow | pale yellow |
| bromine, $Br_2$ | reddish brown gas / liquid | orange | orange–red |
| iodine, $I_2$ | black solid / purple gas | brown | purple |

| Name: | | Centre/Index Number: | | Class: | |
|---|---|---|---|---|---|

# DUNMAN HIGH SCHOOL
# Preliminary Examination
# Year 6

## H2 CHEMISTRY

**9729/04**

Paper 4 Practical

**24 August 2021**
**2 hours 30 minutes**

Candidates answer on the Question Paper.

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

| Shift |
|---|
| |
| **Laboratory** |
| |

| For Examiner's Use | |
|---|---|
| 1 | 22 |
| 2 | 5 |
| 3 | 15 |
| 4 | 13 |
| Total | 55 |

This question paper consists of **18** printed pages.

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

1 **Determination of a value for the enthalpy change of precipitation, $\Delta H_{ppt}$, of barium sulfate**

**FA 1** is 1.00 mol $dm^{-3}$ sodium hydroxide, NaOH.
**FA 2** is a saturated solution of barium hydroxide, $Ba(OH)_2$.
**FA 3** is 1.00 mol $dm^{-3}$ sulfuric acid, $H_2SO_4$.

The addition of **FA 2** to **FA 3** results in neutralisation and precipitation reactions occurring as shown in equations 1 and 2 respectively.

equation 1 $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ $\Delta H_{neut}$

equation 2 $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$ $\Delta H_{ppt}$

In the first experiment, you will determine the maximum temperature change as a result of both reactions occurring in a Styrofoam cup.

In the second experiment, you will measure the temperature of the resulting mixture after each addition of a fixed volume of **FA 1** solution to the remaining $H^+$ ions in the Styrofoam cup. You will analyse your results graphically in order to determine an accurate value for the temperature change of the mixture, caused by the neutralisation reaction shown in equation 1.

You will use this value to calculate the heat change for the second experiment and hence determine a value for the enthalpy change of neutralisation which will then be used to determine a value for the enthalpy change of precipitation for $BaSO_4$.

**(a)** **(i)** **Experiment 1**

1. Use a measuring cylinder to add 20.0 $cm^3$ of **FA 3** into a Styrofoam cup. Place this cup inside a second Styrofoam cup, which is placed in a 250 $cm^3$ glass beaker. Stir and measure the temperature of this solution, $T_{1,initial}$. Record this temperature in Table 1.1.

2. Use another measuring cylinder to add 5.0 $cm^3$ of **FA 2** into the Styrofoam cup. Using the thermometer, stir the mixture and record its maximum temperature, $T_{1,max}$, in Table 1.1. You should expect a small rise in temperature.

**Retain the contents in the Styrofoam cup for experiment 2 in (b)(i).**

Complete Table 1.1 by calculating the value for $\Delta T_{1,max}$.

**Table 1.1**

| | |
|---|---|
| $T_{1,initial}$ / °C | 30.0 |
| $T_{1,max}$ / °C | 31.0 |
| $\Delta T_{1,max}$ / °C | +1.0 |

[1]

**(ii)** Calculate the heat change, $q_1$, for experiment 1.

You should assume that the specific heat capacity of the solution is 4.18 J $g^{-1}$ $K^{-1}$, and that the density of the solution is 1.00 g $cm^{-3}$.

[1]

$q_1 = mc\Delta T = (25)(4.18)(\Delta T_{1,max})$ = w J (3sf)

$q_1$ = ..............................

**_Marker's Comments_**

This question was answered well by the majority. Some students identified the total volume of solution wrongly.

**(iii)** Calculate the percentage error associated with the value of $\Delta T_{1,max}$ and hence comment on the accuracy of the heat change, $q_1$, calculated in **(a)(ii)**.

[1]

% error = $\pm\frac{0.1 + 0.1}{\Delta T_{1,max}} \times 100 = \pm$ ___ %

Since there is a high percentage error associated with the value of $\Delta T_{1,max}$, the heat change, $q_1$, calculated using $\Delta T_{1,max}$ is not accurate.

**(b)** (i) **Experiment 2**

1. Fill a burette with **FA 1**.
2. Record, in Table 1.2, the initial temperature of the mixture in the Styrofoam cup from experiment 1.
3. Run 5.00 $cm^3$ of **FA 1** from the burette into the Styrofoam cup. Using the thermometer, stir the mixture continuously until it reaches its maximum temperature. Record this temperature, $T_{2,max}$, in Table 1.2.
4. Repeat step 3 until a total volume of 50.00 $cm^3$ of **FA 1** is added.

**Table 1.2**

| total volume of **FA 1** added after each addition, $V_{FA 1}$ / $cm^3$ | $T_{2,max}$ / °C |
|---|---|
| 0.00 | 30.8 |
| 5.00 | 32.8 |
| 10.00 | 34.2 |
| 15.00 | 35.4 |
| 20.00 | 36.2 |
| 25.00 | 37.0 |
| 30.00 | 37.8 |
| 35.00 | 38.4 |
| 40.00 | 38.4 |
| 45.00 | 37.8 |
| 50.00 | 37.2 |

[2]

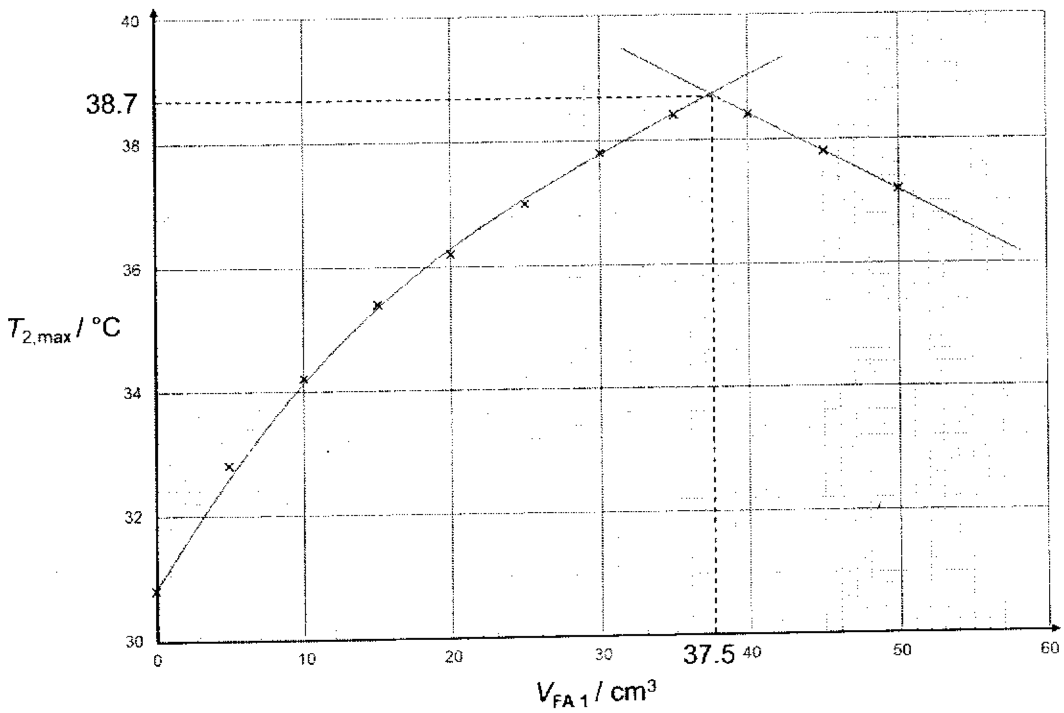
**(ii)** Plot a graph of $T_{2,max}$ on the y-axis against $V_{FA\,1}$ on the x-axis.

Draw two best-fit lines,

- the first is a smooth **curve** taking into account all of the points before,
- the second is a **straight line** taking into account all of the points after

the temperature of the mixture has started to drop.

Extrapolate (extend) both lines until they intersect (cut) each other.




[3]

**(iii)** From your graph, read $V_{FA\,1}$ and $T_{2,max}$ of the intersection point.
Record these values in the spaces provided.
Deduce the maximum temperature change, $\Delta T_{2,max}$.

$V_{FA\,1}$ = .......................... cm³
$T_{2,max}$ = .......................... °C
$\Delta T_{2,max}$ = .......................... °C

$V_{FA\,1}$ = 37.50 cm³
$T_{2,max}$ = 38.7 °C
$\Delta T_{2,max}$ = 38.7 – 30.8 = +7.9 °C

[2]

**(iv)** Calculate the heat change, $q_2$, for experiment 2 using the values you deduced in **(b)(iii)**.

You should assume that the specific heat capacity of the solution is 4.18 J g$^{-1}$ K$^{-1}$, and that the density of the solution is 1.00 g cm$^{-3}$.

$q_2$ = ..............................

$q_2 = mc\Delta T = (25+V_{max})(4.18)(\Delta T_{2,max})$ = x J (3sf)

[1]

**(v)** Hence determine a value for the enthalpy change, for the neutralisation reaction shown in equation 1, $\Delta H_{neut}$.

$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

$NaOH \equiv H_2O$

Moles of $H_2O$ formed = moles of NaOH added = $V_{max} \times 10^{-3} \times 1$ = y mol

$\Delta H_{neut} = -\frac{x}{y} \times 10^{-3}$ = –z kJ mol$^{-1}$

$\Delta H_{neut}$ = ..............................

[2]

**(c)** **(i)** The **FA 2** solution was prepared as follows.

An excess of solid $Ba(OH)_2.8H_2O$ was added to 100 cm$^3$ of water and the mixture was allowed to stand. The undissolved solid was then removed by filtration to obtain the saturated solution of barium hydroxide.

Calculate the concentration of barium and hydroxide ions in the **FA 2** solution given that the solubility of $Ba(OH)_2.8H_2O$ in water is 56 g dm$^{-3}$.

[$M_r$: $Ba(OH)_2.8H_2O$, 315.3]

[1]

solubility of $Ba(OH)_2.8H_2O = \frac{56}{315.3}$ = 0.17761 mol dm$^{-3}$

$[Ba^{2+}]$ in FA 2 = 0.178 mol dm$^{-3}$

$[OH^-]$ in FA 2 = 0.17761 × 2 = 0.355 mol dm$^{-3}$

$[Ba^{2+}]$ = ..............................

$[OH^-]$ = ..............................

**(ii)** Hence calculate the heat evolved from the neutralisation reaction between **FA 2** and **FA 3** in experiment **1**.

[1]

moles of water formed = moles of $OH^-$ neutralised

= 0.35522 × 0.005 = 0.0017761 mol

Heat evolved from neutralisation = 0.0017761 × $|\Delta H_{neut}|$ × $10^3$ = r J

**(iii)** Use your answers in **(a)(ii)** and **(c)(ii)** to determine the heat change due to the precipitation of $BaSO_4$ in experiment 1. Hence determine a value for the enthalpy change for the precipitation reaction shown in equation 2, $\Delta H_{ppt}$.

[3]

Heat evolved from precipitation = $q_1$ – heat evolved from neutralisation = s J
Heat change of solution due to the precipitation of $BaSO_4$ = +s J
moles of $BaSO_4$ = moles of $Ba^{2+}$ = $0.17761 \times 0.005 = 8.8804 \times 10^{-4}$ mol

$$\Delta H_{ppt} = -\frac{\text{heat evolved from precipitation}}{8.8804 \times 10^{-4}} \times 10^{-3} = -\text{p kJ mol}^{-1}$$

Heat change due to the precipitation of $BaSO_4$ = ..............................

$\Delta H_{ppt}$ = ..............................

**(iv)** Explain, in terms of the chemistry involved, the sign of $\Delta H_{ppt}$. Hence explain why precipitation of $BaSO_4$ occurs spontaneously under the experimental conditions.

Energy is released on formation of ionic bonds between the oppositely charged ions, $Ba^{2+}$ and $SO_4^{2-}$, in the solid ionic compound, $BaSO_4$.

$\Delta S < 0$. There is a decrease in disorder of the system as the ions in the solid ionic lattice structure are more orderly than the aqueous ions dispersed in the solution.
$\Delta G_{ppt} = \Delta H_{ppt} - T\Delta S_{ppt}$. Although $-T\Delta S_{ppt} > 0$, magnitude of $T\Delta S_{ppt}$ is smaller than that of $\Delta H_{ppt}$ such that $\Delta G_{ppt} < 0$ and the precipitation occurs spontaneously.

[2]

**(d)** A student performed experiment 2 using 2.00 mol $dm^{-3}$ sodium hydroxide from the bench reagents instead of **FA 1**.

Explain how the volume of 2.00 mol $dm^{-3}$ sodium hydroxide required for complete neutralisation of the mixture in the Styrofoam cup would differ from that of **FA 1**.

[2]

The volume of 2.00 mol $dm^{-3}$ sodium hydroxide required for complete neutralisation will be half that of FA 1.
The $[OH^-]$ in 2.00 mol $dm^{-3}$ sodium hydroxide is twice that of FA 1. Half the volume of 2.00 mol $dm^{-3}$ sodium hydroxide is required to provide the same moles of $OH^-$ for neutralisation of $H^+$ in the mixture.

[Total: 22]

**2 Investigation of pH of solution**

**FA 4** is an organic compound with the molecular formula, $C_2H_4O_2$.

Perform the tests described in Table 2.1. Some of the observations have been completed for you. There is no need to carry out those tests. Record your observations in Table 2.1.

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

**Table 2.1**

| | | test | observations |
|---|---|---|---|
| **(a)** | **(i)** | Add 4 cm depth of deionised water to a test-tube and test it using Universal Indicator (UI) paper.<br><br>Add 2 drops of **FA 1** to the test-tube and test the solution using Universal Indicator paper. | UI paper turns light green<br>pH 5<br><br>UI paper turns dark blue<br>pH 12 |
| | **(ii)** | Add 3 cm depth of **FA 4** to a test-tube.<br><br>Add 1 cm depth of aqueous sodium hydroxide to the test-tube and test the solution using Universal Indicator paper.<br><br>Add 2 drops of **FA 1** to the test-tube and test the solution using Universal Indicator paper. | UI paper turns light orange<br>pH 4<br><br>UI paper turns light orange<br>pH 4 |
| | **(iii)** | Add 2 cm depth of **FA 4** to a test-tube.<br><br>Add half a spatula of solid sodium carbonate to the test-tube. | effervescence observed<br>gas evolved formed white ppt with limewater<br>the gas is carbon dioxide |

[2]

**(b)** **(i)** Suggest the identity of **FA 4**. Give evidence from your observations in **(a)** to support your conclusion.

identity ..........................................................................................

evidence ..........................................................................................

[1]

FA 4 = ethanoic acid

FA 4 contains a carboxylic acid functional group because acid-carbonate reaction occurred in (a)(iii) to produce $CO_2$ gas.

**(ii)** Explain, in terms of the chemistry involved, the difference in observations made upon the addition of **FA 1** to the test-tubes in **(a)(i)** and **(a)(ii)**.

[2]

In **(a)(i)**, addition of FA 1 containing $OH^-$ to water produced a basic solution and thus there was a large increase in pH.

In (a)(ii), addition of NaOH(aq) partially neutralised FA 4 to give an acidic buffer solution containing $CH_3COOH$ and $CH_3COO^-Na^+$ which resisted changes in pH when a small amount of FA 1 containing $OH^-$ was added. The pH of the solution remains relatively constant.

[Total: 5]

**3 Determination of amount of $Mg^{2+}$ and $Al^{3+}$ in an antacid tablet**

To determine the amount of $Mg^{2+}$ and $Al^{3+}$ in an antacid tablet, a complexometric back titration involving ethylenediaminetetraacetic acid, EDTA, can be used. Both $Mg^{2+}$ and $Al^{3+}$ form a complex with EDTA in a 1:1 mole ratio.

$$Mg^{2+} + EDTA \rightarrow Mg\text{–}EDTA \text{ complex}$$

$$Al^{3+} + EDTA \rightarrow Al\text{–}EDTA \text{ complex}$$

A known amount of excess EDTA is first added to a sample containing $Mg^{2+}$ and $Al^{3+}$. The resultant mixture contains both the complex and unreacted EDTA. This resultant mixture is then titrated with zinc sulfate to determine the amount of unreacted EDTA. $Zn^{2+}$ also reacts with EDTA in a 1:1 mole ratio.

$$Zn^{2+} + EDTA \rightarrow Zn\text{–}EDTA \text{ complex}$$

The dye indicator used in this titration is Eriochrome Black T, which will turn from blue to violet at the end–point.

When the titration is conducted at pH 5, only the Al–EDTA complex forms, while at pH 10, both the Mg–EDTA and Al–EDTA complexes form.

You will only be performing the titrations at pH 10, to determine the total amount of $Mg^{2+}$ and $Al^{3+}$ in a sample.

**FA 5** is a solution prepared containing $Mg^{2+}$ and $Al^{3+}$
**FA 6** is a buffer solution at pH 10, containing $Na_2CO_3$ and $NaHCO_3$
**FA 7** is 0.0100 mol $dm^{-3}$ EDTA
**FA 8** is 0.0100 mol $dm^{-3}$ $ZnSO_4$
**Solution T** is Eriochrome Black T indicator

As EDTA is harmful to the environment, **FA 7** should be disposed in the waste bottle. You should also wear gloves throughout the experiment.

**(a) Pre–titration: Determination of the colour at end-point for titration**

1. Using a dropping pipette, add the following solutions into a clean boiling tube:

   - 6 drops of **FA 5**
   - 15 drops of **FA 6**
   - 20 drops of **FA 7**
   - 1 drops of **Solution T**

   The colour of the solution in the test tube should be blue. If the colour of the solution is not blue, add a few more drops of **FA 6** and **FA 7** into the boiling tube.

2. Using a dropping pipette, add **FA 8** dropwise into the test tube, with shaking, until one drop of **FA 8** causes the blue colouration of the solution to fade to yield a violet colour.

3. Keep this solution as a reference for the colour at the end–point of the titration in **(b)**.

**(b) (i) Determination of the amount of $Mg^{2+}$ and $Al^{3+}$ in the sample**

1. Fill a burette with **FA 8**.
2. Using a pipette, transfer 10.0 $cm^3$ of **FA 5** into a 250 $cm^3$ conical flask.
3. Using appropriate measuring cylinders, add 20.0 $cm^3$ of **FA 6**, followed by 35.0 $cm^3$ of **FA 7** into the conical flask.
4. Swirl the conical flask to ensure a homogeneous solution. It is normal for the solution to appear cloudy.
5. Heat the conical flask over the Bunsen burner until the temperature of the solution reaches 65 °C.
6. Remove the conical flask from the flame. If the neck of the flask is too hot to hold safely, use a folded paper towel to hold the flask.
7. Add 5 drops of **Solution T** into the conical flask. The solution should be blue at this point.
8. Run **FA 8** from the burette into the conical flask.
9. The end–point is reached when the blue colour fades to yield the violet colour of the solution in the boiling tube from **(a)**.
10. Record your titration results, to an appropriate level of precision, in Table 3.1.

**Titration results**

**Table 3.1**

| | 1 | 2 |
|---|---|---|
| Final burette reading / $cm^3$ | 14.90 | 29.80 |
| Initial burette reading / $cm^3$ | 0.00 | 15.00 |
| Volume of **FA 8** used / $cm^3$ | 14.90 | 14.80 |

[3]

**(ii)** From your titrations, obtain a suitable volume of **FA 8**, $V_{FA\ 8}$, to be used in your calculations. Show clearly how you obtained this volume. [1]

$$V_{FA\ 8} = \frac{14.90 + 14.80}{2} = 14.85\ cm^3$$

**(c) (i)** Using your answer in **(b)(ii)**, calculate the amount of unreacted EDTA present in the conical flask after step 3. [1]

$Zn^{2+} \equiv EDTA$

No. of moles of unreacted EDTA = $\frac{14.85}{1000} \times 0.0100$

= $1.485 \times 10^{-4}$ mol = $1.49 \times 10^{-4}$ mol (to 3 s.f.)

**(ii)** Calculate the amount of EDTA that formed a complex with $Mg^{2+}$ and $Al^{3+}$, and hence, determine the total concentration of $Mg^{2+}$ and $Al^{3+}$ in **FA 5**.

[3]

Total moles of EDTA added = $\frac{35.00}{1000} \times 0.0100 = 3.50 \times 10^{-4}\ mol$

No. of moles of EDTA reacted = $(3.50 - 1.485) \times 10^{-4}\ mol$ = $2.015 \times 10^{-4}$ mol

Since both $Mg^{2+}$ and $Al^{3+}$ form a complex with EDTA in a 1:1 mole ratio,

Total moles of $Mg^{2+}$ and $Al^{3+}$ = $2.015 \times 10^{-4}\ mol$

Total conc. of $Mg^{2+}$ and $Al^{3+}$ in FA 5 = $2.015 \times 10^{-4} \div \frac{10}{1000}$ = 0.0202 mol $dm^{-3}$(3 sf)

**(d)** Briefly outline how you can determine the exact individual amounts of $Mg^{2+}$ and $Al^{3+}$ in **FA 5** by conducting a second titration involving $ZnSO_4$ and EDTA.

You may assume that only $Mg^{2+}$ and $Al^{3+}$ in **FA 5** react with EDTA.

[2]

Repeat the same procedure but conduct the titration at pH 5. This will allow us to determine the amount of $Al^{3+}$ in FA 5.

Subtract this amount from the total amount calculated in (c)(ii) to obtain the amount of $Mg^{2+}$ in FA 5.

**(e)** EDTA is better represented as $H_4EDTA$ because it is a weak acid. The $EDTA^{4-}$ anion can be formed from four successive deprotonation of $H_4EDTA$.

$$H_4EDTA(aq) \rightleftharpoons EDTA^{4-}(aq) + 4H^+(aq) \text{ ----- (1)}$$

At high pH, $Zn^{2+}$ readily forms a complex with $EDTA^{4-}$.

$$[Zn(H_2O)_6]^{2+} + EDTA^{4-} \rightleftharpoons [Zn(EDTA)]^{2-} + 6H_2O \text{ ----- (2)}$$

**(i)** Explain the effect of increasing pH on the concentration of the $[Zn(EDTA)]^{2-}$ complex.

[2]

As pH increases, the concentration of $H^+$ in solution decreases.
By Le Chatelier's Principle, the position of equilibrium (1) shifts right to increase the concentration of $H^+$. This results in an increase in concentration of $EDTA^{4-}$ present in the solution.

As the concentration of $EDTA^{4-}$ in solution increases, by Le Chatelier's Principle, position of equilibrium (2) shifts right to decrease the concentration of $EDTA^{4-}$. This results in an increase in the concentration of complex formed.

**(ii)** The reaction mixture is kept at high pH due to the $Na_2CO_3$ and $NaHCO_3$ buffer. With the aid of an appropriate chemical equation, explain how this buffer maintains the high pH when a small amount of acid is added.

[2]

$CO_3^{2-} + H^+ \rightarrow HCO_3^-$
The added $H^+$ is removed as $HCO_3^-$. Hence, $[H^+]$ is relatively constant and the pH is maintained at a high pH level.

**(iii)** Given that the p$K_a$ of $HCO_3^-$ is 10.3, calculate the $\frac{[CO_3^{2-}]}{[HCO_3^-]}$ ratio in the $Na_2CO_3$/$NaHCO_3$ buffer solution at pH 10.

$\text{pH} = \text{p}K_a + \log \frac{[CO_3^{2-}]}{[HCO_3^-]}$

$10 = 10.3 + \log \frac{[CO_3^{2-}]}{[HCO_3^-]}$

Hence, $\frac{[CO_3^{2-}]}{[HCO_3^-]} = 10^{-0.3} = 0.501$

[Total: 15]

**4 Planning**

In the presence of glucose, acidified potassium manganate(VII) decolourises. This is because glucose acts as a reducing agent, reducing $MnO_4^-$ to $Mn^{2+}$.

A series of experiments can be carried out at various temperatures to investigate the effect of temperature on the rate constant of the reaction. The time required for the purple reaction mixture to turn colourless will allow for the determination of the rate of reaction.

**(a)** **(i)** State the effect of an increase in temperature on the time taken for the purple reaction mixture to turn colourless.

[1]

An increase in temperature will result in a faster rate, and hence will result in a shorter time for the solution to turn colourless.

**(ii)** Using the concept of Collision Theory, explain your answer in **(a)(i)**.

[2]

The increase in temperature results in an increase in average kinetic energy of all reactant particles. More reactant particles possess energy more than or equal to activation energy, resulting in an increase in the number of effective collisions per unit time. Since rate of reaction is proportional to the frequency of effective collisions, the rate of reaction increases, resulting in a shorter reaction time.

**(b)** To investigate the effect of temperature on the rate constant, a series of experiments at different temperatures can be carried out.

You may assume that you are provided with:

- 0.1 mol $dm^{-3}$ glucose solution
- 0.1 mol $dm^{-3}$ aqueous potassium manganate(VII), $KMnO_4$,
- 2 mol $dm^{-3}$ sulfuric acid, $H_2SO_4$,
- the apparatus normally found in a school laboratory.

Table 4.1 shows the volumes of reactants used for experiment 1.

Once all the reactants have been added to a dry conical flask, the initial temperature of the reaction mixture, $T_i$, was measured and recorded. Immediately after the decolourisation of $KMnO_4$, the final temperature of the mixture, $T_f$, was also measured and recorded. The average temperature of the reaction mixture, $T_{ave}$, was then determined.

Table 4.1 also shows the time required for the decolourisation of purple $KMnO_4$ for experiment 1.

**Table 4.1**

| Experiment | Vol. of glucose solution / $cm^3$ | Vol. of $KMnO_4$ / $cm^3$ | Vol. of $H_2SO_4$ / $cm^3$ | $T_i$ / °C | $T_f$ / °C | $T_{ave}$ /°C | Time taken for decolourisation / s |
|---|---|---|---|---|---|---|---|
| 1 | 5.0 | $x$ | 20.0 | 29.0 | 30.0 | 29.5 | 240 |
| 2 | | | | | | | |

**(i)** Given that glucose and $KMnO_4$ react in a molar ratio of 5 : 24, state an appropriate value for $x$, the volume of $KMnO_4$ used in experiment 1.

[1]

$24\ cm^3$

To investigate the effect of temperature on the rate constant, experiment 2 can be conducted at a different temperature such that the time taken for the decolourisation of purple $KMnO_4$ will be more than 240 s.

**(ii)** Fill Table 4.1 with the volumes of glucose, $KMnO_4$ and $H_2SO_4$ needed for experiment 2. [1]

Use exactly the same volumes as experiment 1

**(iii)** Explain your choice of reactant volumes used in **(b)(ii)**. [1]

By using the same volumes as experiment 1, the concentrations of reactants in the reaction mixture are kept constant. Hence, the only variable that has changed is the temperature.

**(iv)** You are required to write a plan, describing how **experiment 2** can be carried out.

In your plan, you should have details of:

- the apparatus you would use,
- the measurements you would take,
- the procedure you would follow.

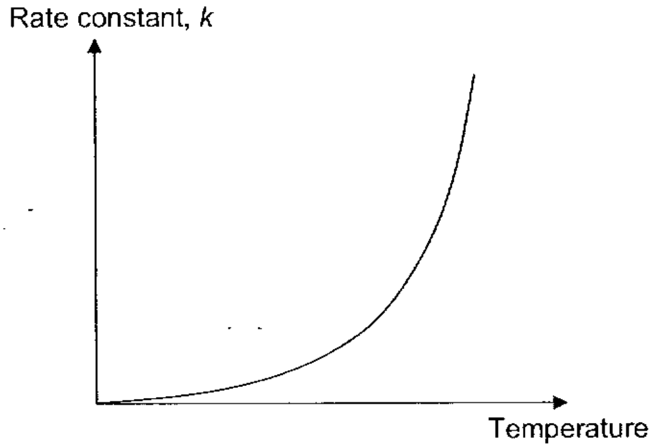
[6]

1. Using a $10\ cm^3$ measuring cylinder, measure out $5.0\ cm^3$ of the glucose solution.
2. Using another burette, add $x\ cm^3$ of aqueous $KMnO_4$ into a dry $100\ cm^3$ conical flask / beaker.
3. Using a $25\ cm^3$ measuring cylinder, add $20.0\ cm^3$ $H_2SO_4$ into the conical flask containing $KMnO_4$ and swirl the solution.
4. Place the conical flask in a thermostatic water bath set at 15 °C (or any temperature below 29.5 °C) and use a thermometer to measure the temperature of the solution in the conical flask.
5. Once the temperature of the solution reaches 15 °C, add the glucose solution from the measuring cylinder into the conical flask and start the stopwatch immediately.
6. Use the thermometer to measure the temperature of the reaction mixture once the stopwatch has been started. This is the initial temperature of the reaction mixture.
7. Stop the stopwatch once the reaction mixture turns colourless.
8. Record the time taken.
9. Use the thermometer to measure the temperature of the reaction mixture once it turns colourless. This is the final temperature of the reaction mixture.

**(v)** The rate of reaction approximately doubles for every 10 °C increase in temperature.

Using the axes below, sketch a graph to show how the rate constant of the reaction would vary with temperature.

[1]




[Total: 13]