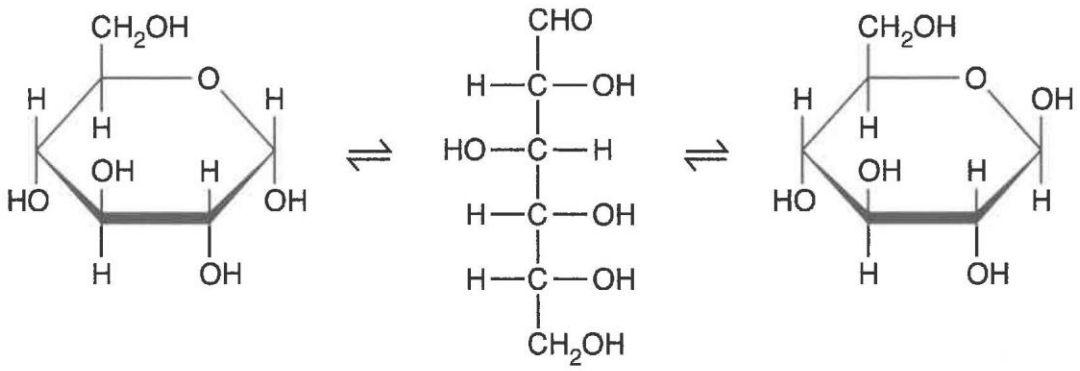
Answer **all** the questions in the spaces provided.

1 Investigation of some reactions of D-glucose

D-glucose is a sugar with molecular formula $C_6H_{12}O_6$. In aqueous solution D-glucose exists in a number of isomeric forms.

In aqueous solution, an equilibrium mixture of these isomers is formed. It is thought that at any one time less than 1% of the D-glucose molecules are present in the linear form, as shown in Fig. 1.1.



α-D-glucopyranose D-glucose β-D-glucopyranose

Fig. 1.1

FA 1 is 0.5 mol dm^{-3} D-glucose, $C_6H_{12}O_6$.

(a) Carry out the following test. Carefully record your observations in Table 1.1.

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured.

Table 1.1

test	observations
Add 2 cm depth of aqueous silver nitrate to a clean dry boiling tube.	
Add 1 cm depth of aqueous sodium hydroxide slowly to the same tube.	Brown ppt formed in colourless solution.
Add aqueous ammonia slowly, with shaking, until the precipitate just dissolves. You may use a clean glass rod to help dissolve the precipitate.	Brown ppt dissolved in $NH_3(aq)$ to give a colourless solution.
Add 2 cm depth of **FA 1** to this mixture and shake the tube.	Brown ppt formed in colourless solution.
Place the boiling tube in the test-tube rack and leave it for 3 minutes.	Silver mirror is formed in the test tube
Important: After about 3 minutes, pour the mixture down the sink and wash out the boiling tube several times with tap water.	

[2]

(b) In **(a)**, the organic product **Z** can be obtained from D-glucose. Product **Z** has a linear structure with molecular formula $C_6H_{12}O_7$.

(i) Name the type of reaction that D-glucose undergoes in **(a)**.

..... [1]

(ii) Draw the structure of **Z**.

[1]

(iii) State and explain the chemical change the **reagent** undergoes during the reaction in **(a)**.

.....

..... [1]

(c) Consider the observations recorded in Table 1.2.

Table 1.2

You should not do the following tests. Observations have been recorded for you.

test	observations
Add 1 cm depth of **FA 1** to a test-tube. Add 5 cm depth of 2,4-dinitrophenylhydrazine (2,4-DNPH) solution to the test-tube. Observe the mixture for a short time.	no observable change
Repeat this test but replace **FA 1** with propanone.	yellow precipitate formed

(i) Name the functional group that can be identified using 2,4-DNPH.

..... [1]

(ii) Consider the information provided on page 2.

Suggest why D-glucose (**FA 1**) does **not** give a positive result with 2,4-DNPH, whereas propanone does.

.....

.....

..... [1]

[Total: 7]

2 Determination of the identity of a salt and a value for its enthalpy change of solution

Solid FA 2 is an anhydrous potassium salt containing one anion.

When added to water, **solid FA 2** quickly dissolves and the temperature of the mixture falls.

You are provided with an aqueous solution of **FA 2**, labelled **FA 2 solution**.

(a) You will devise and perform a series of simple tests, based on the Qualitative Analysis Notes on pages 23–24, to identify the anion present in the **FA 2 solution**.

(i) **FA 2** does **not** contain sulfite ions, SO_3^{2-}, or any nitrogen.

Use the Qualitative Analysis Notes on pages 23–24 to deduce the possible anions present in **solid FA 2**.

CO_3^{2-}, SO_4^{2-}, Cl^-, Br^-, I^-

[2]

(ii) Describe **three different** tests, using only the bench reagents provided, which will allow you to distinguish between the anions you listed in **(a)(i)**.

In each case, state how you will decide if the test result is positive.

test 1 To test for CO_3^{2-}, add HCl(aq) to FA2 solution.

CO_3^{2-} will give effervescence of CO_2 that gives a white ppt with limewater.

test 2 To test for SO_4^{2-}, add $Ba(NO_3)_2$(aq) to FA2 solution, followed by excess HNO_3(aq). SO_4^{2-} will give white ppt that is insoluble in excess HNO_3(aq).

test 3 To test for Cl^-, Br^-, I^-, add $AgNO_3$(aq) to FA2 solution, followed by excess NH_3(aq). Cl^- will give white ppt that is soluble in excess NH_3(aq).

Br^- will give pale cream ppt that is partially soluble in excess NH_3(aq).

I^- will give yellow ppt that is insoluble in excess NH_3(aq).

[3]

(iii) Perform the tests you described in **(a)(ii)** using the **FA 2 solution** provided.

Record your observations and hence deduce the identity of the anion in **solid FA 2**.

Any test requiring heating MUST be performed in a boiling tube.

test 1 ..... No effervescence observed. Solution remains colourless .....

.....

test 2 ..... No ppt formed. Solution remains colourless. .....

.....

test 3 ..... White ppt formed in colourless solution. Upon adding excess $NH_3(aq)$, ...

..... white ppt dissolves to give a colourless solution. .....

identity of anion ..... Cl^- .....

[3]

(b) Determination of the enthalpy change of solution, ΔH_{sol}, of solid FA 2

In this experiment, you will measure the temperature of the contents of a polystyrene cup at timed intervals, both before and after **solid FA 2** is added. You will analyse your results graphically in order to determine an accurate value for the temperature change of the mixture, caused by **solid FA 2** dissolving.

You will use this value to calculate the heat change, q, for the experiment and hence determine a value for the enthalpy change of solution for **solid FA 2**, ΔH_{sol}.

In an appropriate format in the space provided on page 8, prepare tables in which to record results for your experiment in **(b)**:

- all weighings to an appropriate level of precision,
- all values of temperature, T, to an appropriate level of precision,
- all values of time, t, recorded to the nearest 0.5 min.

It is important that you measure each temperature at the specified time.

1. Weigh the capped bottle containing **solid FA 2**.
2. Place one polystyrene cup inside a second polystyrene cup. Place these in a glass beaker to prevent them from tipping over.
3. Use a measuring cylinder to transfer 50 cm^3 of deionised water into the first polystyrene cup.
4. Stir the water in the cup with the thermometer. Read and record its temperature, T (time, t = 0.0 min).
5. Continue to stir the water. Read and record T every minute.

6. At **exactly** three minutes, transfer all the **solid FA 2** to the polystyrene cup. Stir the mixture but do not read *T*.

7. Continue to stir the mixture. Read and record *T* at *t* = 3.5 min.

8. Continue to stir the mixture. Read and record *T* at *t* = 4.0 min and every minute until *t* = 9.0 min.

9. Reweigh the empty bottle and its cap.

(i) Results

Mass of FA 2 + weighing bottle / g	13.846
Mass of residual FA2 + weighing bottle / g	5.888
Mass of FA 2 used / g	7.958

Time/ min	T / °C
0.0	29.8
1.0	29.4
2.0	29.2
3.5	23.4
4.0	22.0
5.0	21.6
6.0	21.6
7.0	21.9
8.0	22.0
9.0	22.4

[4]

(ii) Plot a graph of temperature, T, on the y-axis, against time, t, on the x-axis on the grid in Fig. 2.1.

Draw a best-fit straight line taking into account all of the points before $t = 3.0$ min.

Draw another best-fit straight line taking into account all of the points after the temperature of the mixture has started to rise steadily.

Extrapolate (extend) both lines to $t = 3.0$ min.

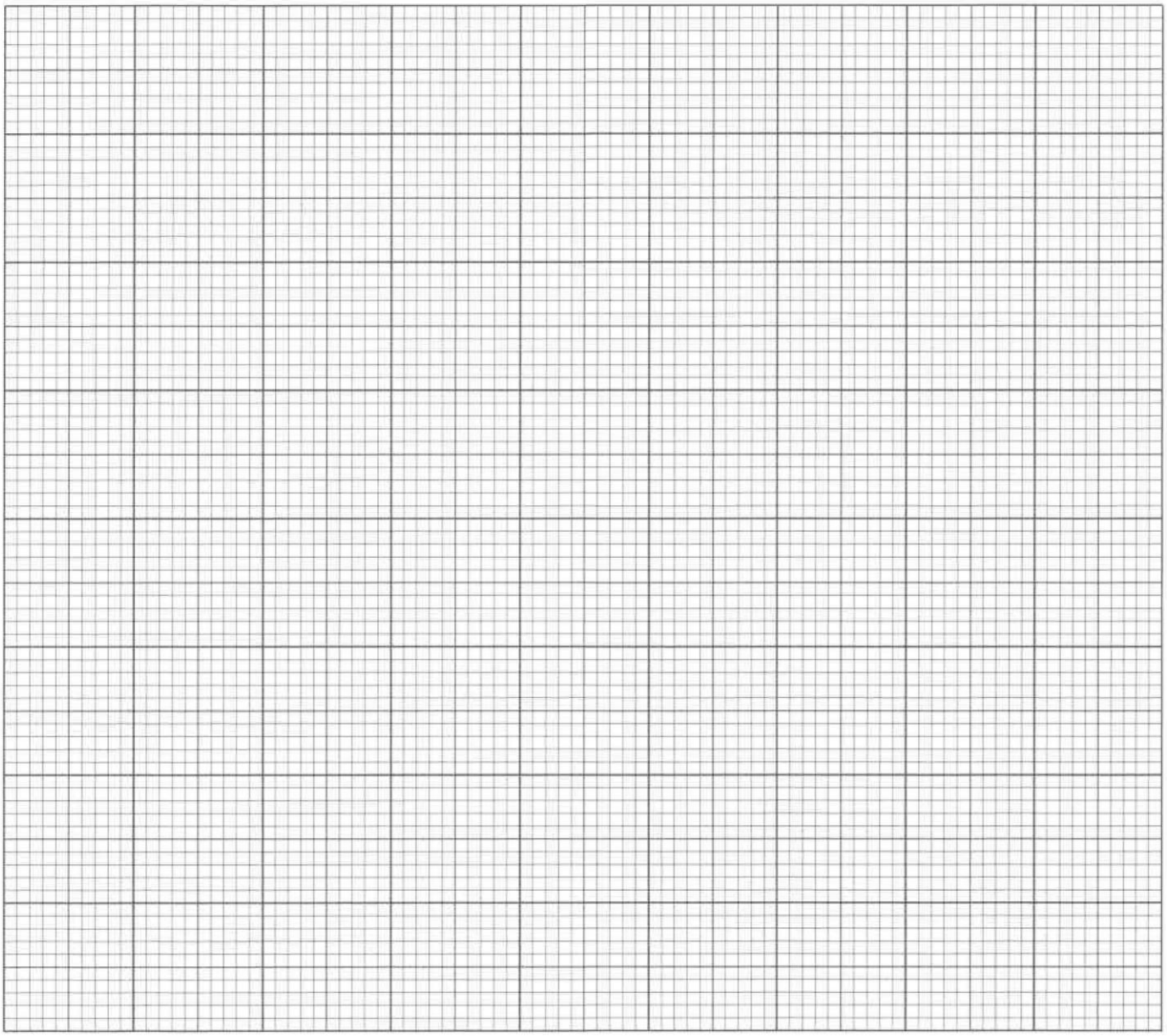


Fig. 2.1

[3]

(iii) From your graph, read the minimum temperature, T_{min}, and the maximum temperature, T_{max}, at $t = 3.0$ min. Record these values in the spaces provided.

Deduce the temperature change, ΔT, at $t = 3.0$ min.

T_{min} = ...

T_{max} = ...

ΔT = ...

[1]

(iv) Calculate the heat change, q, for your experiment using the value 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 = ... [1]

(v) Determine the enthalpy change of solution, ΔH_{sol}, for **solid FA 2**.

Include the sign of ΔH_{sol} in your answer.

[A_r: Br, 79.9; C, 12.0; Cl, 35.5; I, 126.9; K, 39.1; O, 16.0; S, 32.1]

ΔH_{sol} = ... [3]

(vi) Suggest the effect that using $100\,cm^3$, rather than $50\,cm^3$, of water would have on your value for ΔT. Hence, deduce and explain the effect this will have on the value for ΔH_{sol}.

.....

.....

..... [1]

(c) Table 2.1 gives some enthalpy change of hydration, ΔH_{hyd}, values taken from a data book for the ions in **FA 2**.

Table 2.1

ions	ΔH_{hyd} / kJ mol^{-1}
K^+	–322
anion	–364

Use your value for ΔH_{sol} and these data to determine a value for the lattice energy, ΔH_{latt}, for **solid FA 2.**

ΔH_{latt} = ... [3]

[Total: 24]

3 Determination of the concentration of phosphoric acid

Phosphoric acid, H_3PO_4, is used as a rust converter. It reacts with the iron(III) oxide present in rust to form iron(III) phosphate. The concentration of phosphoric acid in a rust converter is too great for it to be titrated directly against sodium hydroxide.

Phosphoric acid, H_3PO_4, is a triprotic weak acid. When it is titrated against sodium hydroxide, it loses its protons one after another. This means that one proton is removed to produce the $H_2PO_4^-$ ion. Once this removal is complete, a second proton is removed. Once this proton is removed, the third proton is removed.

Equations 1 and 2 show the first and second stages in this neutralisation process.

equation 1 $\quad H_3PO_4(aq) + NaOH(aq) \rightarrow NaH_2PO_4(aq) + H_2O(l)$

equation 2 $\quad NaH_2PO_4(aq) + NaOH(aq) \rightarrow Na_2HPO_4(aq) + H_2O(l)$

The pH curve obtained when 25.0 cm^3 of 0.100 mol dm^{-3} H_3PO_4 is titrated against 0.100 mol dm^{-3} NaOH is shown in Fig. 3.1. The pH values shown on Fig. 3.1 represent the pH of the solution when each stage of the neutralisation is completed.

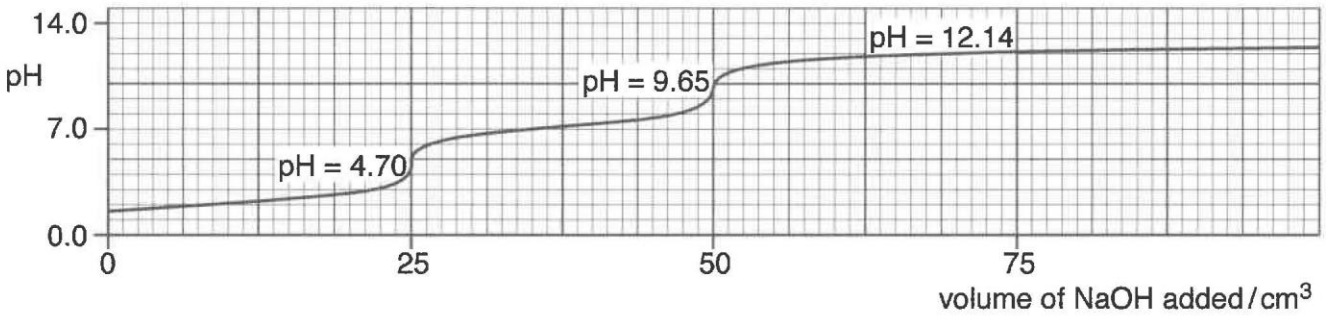


Fig. 3.1

FA 3 is a diluted solution of the rust converter.
FA 4 is 0.100 mol dm^{-3} sodium hydroxide, NaOH.

FA 3 was prepared by diluting 26.75 cm^3 of the rust converter to 1.00 dm^3 in a volumetric flask using deionised water.

Solution S is screened methyl orange indicator.
Solution T is thymolphthalein indicator.

(a) (i) Titration of FA 3 against FA 4 using solution S

1. Fill a burette with **FA 4**.
2. Use a pipette to transfer 10.0 cm^3 of **FA 3** into a 100 cm^3 conical flask.
3. Add about 25 cm^3 of deionised water to the conical flask.
4. Add a few drops of solution S into the conical flask.
5. Run **FA 4** from the burette into the flask. The end-point is reached when the solution changes from violet to grey. If the solution becomes green, you have passed the end-point.
6. Record your titration results in Table 3.1.
7. Repeat points 2 to 6 until consistent titre values are obtained.

Table 3.1

final burette reading / cm^3	10.30	30.30				
initial burette reading / cm^3	0.00	20.00				
volume of **FA 4** added / cm^3	10.30	10.30				

[1]

(ii) From your titration results, obtain a suitable volume of **FA 4**, V_1, to be used in your calculations. Show clearly how you obtained this volume.

V_1 = ...cm^3 [2]

(b) (i) Titration of FA 3 against FA 4 using solution T

Repeat points 1 to 7 in **(a)(i)** but add solution T at point 4 in place of solution S. Using this indicator, the end-point is reached when the solution changes from colourless to a permanent **pale** blue colour. Record your titration results in Table 3.2.

Please cap solution T after use.

Table 3.2

final burette reading / cm^3	44.70	47.80				
initial burette reading / cm^3	20.70	23.80				
volume of **FA 4** added / cm^3	24.00	24.00				

[1]

(ii) From your titrations, obtain a suitable volume of **FA 4**, V_2, to be used in your calculations. Show clearly how you obtained this volume.

V_2 = ... cm^3 [2]

(c) **(i)** Use your value for V_2 from **(b)(ii)** to calculate the concentration of phosphoric acid, $[H_3PO_4]$, in **FA 3**.

$[H_3PO_4]$ = ... $mol\,dm^{-3}$ [2]

(ii) The concentration of phosphoric acid in rust converter is usually expressed as the percentage by mass of phosphoric acid present.

Calculate the concentration of phosphoric acid in the rust converter, $[H_3PO_4]_{RC}$, used to prepare **FA 3**. Hence deduce the percentage by mass of phosphoric acid present in the rust converter.

The density of this rust converter is $1.24\,g\,cm^{-3}$.

[A_r: H, 1.0; P, 31.0; O, 16.0]

$[H_3PO_4]_{RC}$ = ... $mol\,dm^{-3}$

percentage by mass of H_3PO_4 present = ...%
[3]

(d) Both screened methyl orange and thymolphthalein are good, reliable and accurate acid-base indicators.

However, it is likely that your mean titre, V_2, in **(b)(ii)** will be more accurate than your mean titre, V_1, in **(a)(ii)**.

(i) Explain, in terms of the uncertainties associated with the apparatus used, why V_2 is likely to be more accurate than V_1.

.....

.....

..... [1]

(ii) Assuming your value for V_2 to be correct, deduce what you would expect the V_1 value to be. Explain your answer.

expected V_1 value = ... cm^3

explanation .....

.....

.....

[1]

(iii) The difference between your V_1 value from **(a)(ii)** and your answer in **(d)(ii)** provides an estimate of the uncertainty in your V_1 mean titre value.

Calculate this difference and use it to calculate the percentage uncertainty as a percentage of the answer in **(d)(ii)**.

difference = ... cm^3

percentage uncertainty = ...%

[2]

(e) Suggest why the third end-point, for the complete neutralisation of phosphoric acid, cannot be obtained by titration.

.....

.....

..... [1]

[Total: 16]

4 (a) Planning

Under acidic conditions, iodine reacts readily with propanone to form 1-iodopropanone.

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + HI(aq)$$

Without the presence of an acid catalyst, the reaction rate is very slow, as H^+ ions are involved in the rate determining step of the mechanism.

The rate equation for this reaction is

$$\text{rate} = k[CH_3COCH_3][H^+]$$

where k is the rate constant.

The order with respect to $[I_2]$ may be confirmed to be zero order by preparing a reaction mixture containing sulfuric acid, aqueous iodine and a large excess of propanone.

Portions of the reaction mixture are

- removed at timed intervals,
- quenched by adding to an excess of aqueous sodium hydrogencarbonate, $NaHCO_3$,
- titrated against a standard solution of sodium thiosulfate, $Na_2S_2O_3$.

The volume of sodium thiosulfate solution added in each titration (titre) is proportional to $[I_2]$.

$$2Na_2S_2O_3(aq) + I_2(aq) \rightarrow Na_2S_4O_6(aq) + 2NaI(aq)$$

So, in this experiment, there is no need to calculate $[I_2]$.

Plan a procedure to collect sufficient data to allow a graph of *volume of sodium thiosulfate* against *time* to be drawn.

You should plan to make a reaction mixture containing

- 30 cm^3 of aqueous propanone, CH_3COCH_3,
- 30 cm^3 of dilute sulfuric acid, H_2SO_4,
- 30 cm^3 of aqueous iodine, I_2.

This reaction mixture contains a large excess of propanone.

You may assume that you are also provided with:

- a standard solution of sodium thiosulfate, $Na_2S_2O_3$,
- aqueous sodium hydrogencarbonate, $NaHCO_3$,
- starch solution,
- the equipment normally found in a school or college laboratory.

In your plan you should include brief details of:

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

In your plan it is **not** necessary to refer to concentrations or to perform calculations.

.....

.....

[6]

(b) Sketch on Fig. 4.1 the graph you would expect to obtain from your results.

Explain your answer.

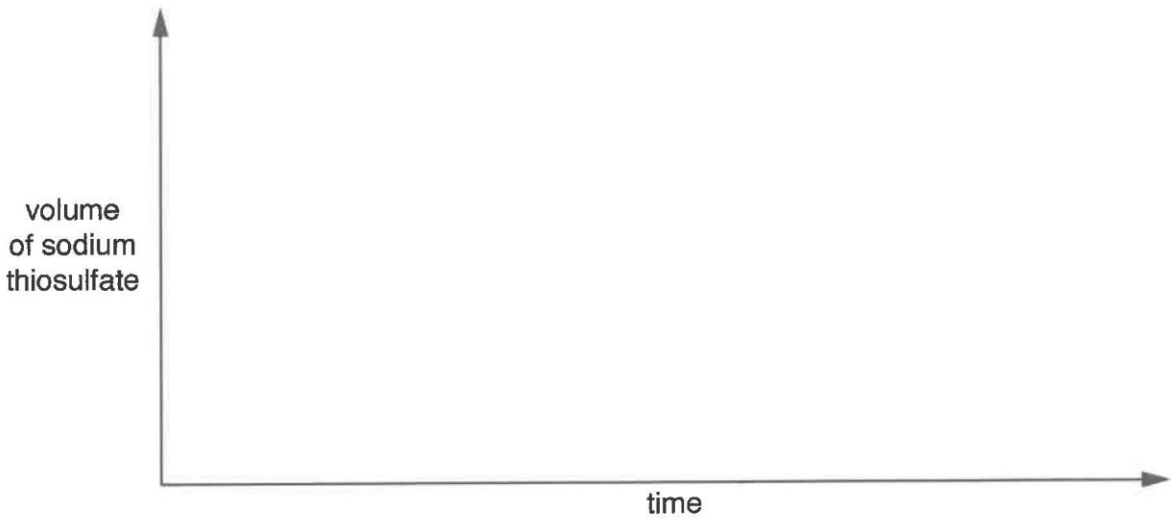


Fig. 4.1

explanation .....

.....

.....

.....

.....

.....

[2]

[Total: 8]

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. 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. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	*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; NO liberated by dilute acids (colourless NO → (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; 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 (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