1 Determination of solubility product, *K*_{sp}, of magnesium carbonate

Magnesium carbonate is basic and sparingly soluble in water, resulting in its use as drying agents in sports and antacids.

You are to carry out a titrimetric analysis to determine the solubility product of magnesium carbonate.

A saturated solution of magnesium carbonate can be prepared by dissolving excess solid magnesium carbonate into a measured volume of water. The mixture will be left to stand for some time before filtering. The filtrate can then be analysed through titration with a standard solution of hydrochloric acid.

The saturated solution of magnesium carbonate, FA 1, has been prepared for you, according to the procedure in (a).

(a) Preparation of FA 1

- 1. Use a measuring cylinder to transfer 50 cm³ of deionised water into a 100 cm³ beaker.
- 2. Use a spatula to add solid magnesium carbonate into the same beaker, a little at a time with stirring until no more can dissolve.
- 3. Leave to stand for five minutes.
- 4. Filter the mixture to obtain the filtrate in a 250 cm³ conical flask. Ensure that the filtrate is clear. Do not wash the residue.
- 5. The filtrate is **FA 1**.

You are provided with:

FA 1 saturated solution of magnesium carbonate **FA 2** 0.0300 mol dm⁻³ hydrochloric acid solution Methyl orange indicator

(b) (i) Dilution of FA 2

The concentration of **FA 2** is too high to be used in the titration. You will dilute **FA 2** before using it in (c).

- 1. Pipette 25.0 cm³ of **FA 2** into a 250 cm³ volumetric flask.
- 2. Top up to the mark with deionised water.
- 3. Stopper and shake thoroughly.

(b) (ii) Calculate the concentration of hydrochloric acid in diluted FA 2.

Conc = $0.025 \times 0.03 / 0.25 = 0.00300 \text{ mol dm}^{-3}$

[HC*l*] in **diluted FA 2** =[1]

(c) (i) Titration of FA 1 against diluted FA 2

- 1. Fill the burette with **diluted FA 2** from (b).
- 2. Use a pipette to transfer 10.0 cm³ of **FA 1** into a 100 cm³ conical flask.
- 3. Add 1 2 drops of methyl orange indicator into the conical flask.
- 4. Run **diluted FA 2** from the burette into this flask until the appropriate colour change is observed.
- 5. Record your titration results, to an appropriate level of precision, in the space provided.
- 6. Repeat steps 1 to 5 until consistent results are obtained.

Results

| Final burette reading / cm ³ | 17.00 | 34.00 | |
|--|-------|-------|--|
| Initial burette reading / cm ³ | 0.00 | 17.00 | |
| Vol of diluted FA 2 used / cm ³ | 17.00 | 17.00 | |

 $(17.00 + 17.00) / 2 = 17.00 \text{ cm}^3$

Volume of **diluted FA 2** =[3]

(d) (i) Calculate the concentration of carbonate ions in FA 1, using your answers in (b)(ii) and (c)(ii).

Amount of H^+ = ans in (b)(ii) x ans in (c)(ii)/1000

Amount of CO_3^{2-} = amount of H⁺ / 2

Concentration of $CO_3^{2^-}$ = Amount of $CO_3^{2^-}$ / 0.0100 = 0.5 [ans in (b)(ii) x ans in (c)(ii)/1000] / 0.0100

[CO₃²⁻] in **FA 1 =**[2]

(ii) Hence, calculate the solubility product of magnesium carbonate. State its units.

 $K_{sp} = [Mg^{2+}][CO_3^{2-}] = [ans from (d)(i)]^2$

Units = mol² dm⁻⁶

*K*_{sp} of magnesium carbonate =

units[1]

(i) State and explain the effect on titre volume if the filtrate was **not** clear.

effect on titre volume **Titre volume will be larger**

explanation The residual carbonate will react with the HCl added

(ii) Explain why the residue should not be washed.

Washing the residue will disturb the equilibrium and cause the solution to be below saturation point (and the titration results will be lower than actual, leading to lower than expected K_{sp}).

(f) The dissociation of magnesium carbonate in water is endothermic.

Sketch a graph to show how the solubility product of magnesium carbonate varies with temperature. Explain your answer.



explanation

As dissociation is endothermic, increase in temperature cause POE of $MgCO_3(s) \leftrightarrow Mg^{2+}(aq) + CO_3^{2-}(aq)$ to shift right to favour reaction that absorbs heat, increasing concentration of ions, increasing K_{sp}

OR

When temperature increases, there is greater kinetic energy for the ions to break away from the ionic lattice, hence increasing concentration of ions, increasing K_{sp}

OR

Since reaction is endothermic, and entropy change is positive, when temperature is higher, reaction is more spontaneous, hence more MgCO₃ dissolves.

[2]

[1]

[1]

(g) Planning

The technique of gravimetry includes all analytical methods in which the analytical property is a measurement of mass or a change in mass. This technique can also be used in determining the solubility product of magnesium carbonate.

One of the possible approaches is to determine the mass of precipitate formed after mixing two solutions of known concentration. After preparing a mixture of saturated solution containing the precipitate, it can be passed through a pre-weighed filter paper that retains the precipitate. Residual moisture can be removed by drying the filter paper and the precipitate. The amount of precipitate can be determined, from which the concentration of ions in the saturated solution and hence solubility product can be determined.

(i) Plan an investigation to determine the solubility product of magnesium carbonate using the approach outlined above.

You are provided with the following:

- 0.400 mol dm⁻³ sodium carbonate solution
- 0.400 mol dm⁻³ magnesium nitrate solution
- apparatus and equipment normally found in a school laboratory

In your plan you should include brief details of:

- the apparatus you would use,
- the quantities you would use,
- the procedure you would follow,
- the measurements you would make to allow for gravimetric analysis.
 - Measure 50.00 cm³ of sodium carbonate solution and 50.00 cm³ magnesium nitrate solution using two separate 50.00 cm³ burettes into a 250 cm³ beaker (and place the beaker in a temperature controlled water bath)
 - Stir the mixture and leave to stand for some time.
 - Filter the mixture using a pre-weighed filter paper (M1 g)
 - Dry precipitated MgCO₃ together with filter paper
 - Weigh the dried precipitated MgCO₃ together with the filter paper (M2 g).

[4]

(ii) Show how the measurements recorded in (g)(i) can be used to calculate the concentration of Mg²⁺ and CO_3^{2-} , in mol dm⁻³, in the saturated solution.

Amount of ppt = (M2-M1)/ Mr of MgCO₃ = amount of Mg²⁺ not dissolved = amount of $CO_3^{2^-}$ not dissolved

Therefore, amount of Mg²⁺ dissolved = $0.4 \times \frac{50/1000}{-(M2-M1)}/Mr$ of MgCO₃ amount of CO₃²⁻ dissolved = $0.4 \times \frac{50/1000}{-(M2-M1)}/Mr$ of MgCO₃

concentration of $Mg^{2+} = [0.4 \times \frac{50}{1000} - (\frac{M2-M1}{M})/Mr$ of $MgCO_3$]/100/1000 concentration of $CO_3^{2-} = [0.4 \times \frac{50}{1000} - (\frac{M2-M1}{M})/Mr$ of $MgCO_3$]/100/1000

*depends on mass and volume used in g(i)

[2]

[Total: 20]

2 Determination of the concentration of NaHCO₃ and the value for the enthalpy change of reaction of NaHCO₃ and NaOH

FA 3 is a solution of sodium hydrogencarbonate, NaHCO₃, of unknown concentration. **FA 4** is 1.50 mol dm⁻³ sodium hydroxide, NaOH.

In this experiment, you will perform a thermometric titration to determine the equivalence point for the reaction of **FA 3** and **FA 4**, where maximum heat is evolved, without the use of an indicator.

You will follow the reaction by measuring the temperature as volumes of **FA 4** are added in regular portions from a burette to a fixed volume of **FA 3** placed in a Styrofoam cup.

The data obtained will allow you to determine the temperature change and then analyse your results graphically in order to determine the equivalence point of the reaction.

In an appropriate format in the space provided on the next page, prepare a table in which you may record the following after each addition of **FA 4**:

- Total volume of **FA 4** added from the burette, starting from 0.00 cm³, up to the point in time
- Total volume of solution in the cup, V_{total}
- Temperature measured, T

In the same table, you also need to calculate the corresponding values of:

- $\Delta T = T T_0$, where T_0 is the initial temperature of **FA 3**
- $(V_{total} \times \Delta T)$ to 3 significant figures

State clearly the units of each parameter on the header of the column.

Procedure

- 1. Fill the burette to the 0.00 cm^3 mark with **FA 4**.
- 2. Place the Styrofoam cup in a 250 cm³ beaker to provide support for the cup.
- 3. Use a measuring cylinder to transfer 40.0 cm³ of **FA 3** into the cup.
- 4. Measure and record the initial temperature of **FA 3**, T₀.
- 5. Run 3.00 cm³ of **FA 4** from the burette into the cup, stir the solution with the thermometer and record the maximum temperature, T.
- 6. Immediately run a further 3.00 cm³ of **FA 4** from the burette into the cup, stir and record the maximum temperature as before.
- 7. Continue the addition of **FA 4** in 3.00 cm³ and record the maximum or minimum temperature reached after each addition. Do this until a total of 45.00 cm³ of solution have been run from the burette.

(a) (i) Results

| Total | Total volume | Temperature | $\Delta T = T - T_0$ | $(V_{total} \times \Delta T)$ |
|------------------------------------|--------------------------------------|-------------|----------------------|-------------------------------|
| volume of | of solution | measured, T | / °C | / cm ³ °C |
| FA 4 added, | in the cup, | / °C | | |
| V _{FA4} / cm ³ | V _{total} / cm ³ | | | |
| 0.00 | 40.0 | | | |
| 3.00 | 43.0 | | | |
| 6.00 | 46.0 | | | |
| 9.00 | 49.0 | | | |
| 12.00 | 52.0 | | | |
| 15.00 | 55.0 | | | |
| 18.00 | 58.0 | | | |
| 21.00 | 61.0 | | | |
| 24.00 | 64.0 | | | |
| 27.00 | 67.0 | | | |
| 30.00 | 70.0 | | | |
| 33.00 | 73.0 | | | |
| 36.00 | 76.0 | | | |
| 39.00 | 79.0 | | | |
| 42.00 | 82.0 | | | |
| 45.00 | 85.0 | | | |

Precision:

- 2 d.p. for V_{FA4}

- 1 d.p. for T and ΔT

- 3 s.f. for (V_{total} × Δ T)

(a) (ii) Plot a graph of $(V_{total} \times \Delta T)$ against total volume of **FA 4** added.

Draw two best-fit straight lines for the ascending and descending points respectively. Extrapolate both lines until they intersect to determine the:

- equivalence point of the reaction, V_{eq}
- maximum value of (V_{total} × Δ T)



V_{eq} =

(b) (i) Write down the chemical equation, with state symbols, for the reaction of $NaHCO_3$ and NaOH.

 $NaHCO_3$ (aq) + NaOH (aq) $\rightarrow Na_2CO_3$ (aq) + H_2O (l)

[1]

(ii) Calculate the concentration of NaHCO₃ in **FA 3**.

 $n_{NaOH} = (V_{eq}/1000 \text{ x } 1.50) \text{ mol}$ $n_{NaHCO3} = n_{NaOH}$ [NaHCO₃] = ($n_{NaHCO3} \div 40.0/1000$) mol dm⁻³

*obtained from the intersection point in (a)(ii)

[NaHCO₃] in **FA 3** =[2]

(iii) Given that the heat capacity of solution is 4.2 J K⁻¹ cm⁻³, calculate the enthalpy change of the reaction of NaHCO₃ and NaOH, Δ H_r.

Heat released, $q = mc\Delta T = 4.2(V_{total} \times \Delta T) J$ $\Delta H_r = (-q/n_{NaHCO3}) J mol^{-1}$

*obtained from the intersection point in (a)(ii)

(c) You plotted a graph of $(V_{total} \times \Delta T)$ against total volume of **FA 4** added in (a)(ii). Suggest, with explanation, whether plotting a graph of ΔT against total volume of **FA 4** instead is likely to yield a more accurate result for the equivalence point.

Doing so is unlikely to yield a more accurate result. As V_{total} is not constant (or increasing) throughout the experiment,

- ∆T will vary less linearly with (or not be directly proportional to) the total volume of FA4 added OR
- curves may be obtained instead since the same amount of heat energy released is distributed over a larger volume

[2]

(d) Performing the same experiment using a burette instead of a measuring cylinder to transfer FA 3 into the Styrofoam cup is not expected to improve the accuracy of the results obtained. Suggest a reason why is this so.

Heat loss to the surroundings throughout the experiment outweighs the improved accuracy of using a burette to transfer FA3.

[1]

(e) You are provided with methyl orange indicator in **Question 1**.

Explain whether methyl orange indicator can be used to determine the end-point of the titration of NaHCO₃ against NaOH instead of performing thermometric titration.

NaHCO₃ acts as a weak acid in the presence of a strong alkali of NaOH, as such the equivalence point (at a relatively high pH) lies outside of the (relatively low) working pH range of methyl orange indicator.

[2]

[Total: 18]

3 Qualitative Analysis and Planning

You are provided with four different compounds labelled **FA 5**, **FA 6**, **FA 7** and **FA 8**. Each of these four bottles contains one of the following:

primary alcohol aldehyde monocarboxylic acid metal halide

You will identify **FA 5**, **FA 6**, **FA 7** and **FA 8** by carrying out the prescribed experiments, as well as planning and conducting your own experiments.

For the prescribed experiments, record your observations in Table 3.1 below carefully. Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured.

You are advised to carry out the experiments in test (a) and (b) on each unknown compound one at a time. You are not required to carry out experiments in test (c) as the results are provided.

| | | Observations | | | |
|-----|--|---|--|---|--|
| | Test | FA 5 | FA 6 | FA 7 | FA 8 |
| (a) | To 1 cm depth of the unknown in a test-tube, add 1 cm depth of sodium nitrite. Test and determine if any gas is evolved. | effervescence pungent brown/ yellow gas evolved blue litmus paper turned red | effervescence pungent brown/ yellow gas evolved blue litmus paper turned red | no gas evolved | no gas evolved |
| (b) | To 1 cm depth of the unknown in a test-tube, add 1 cm depth of dilute sulfuric acid, followed by 5 drops of potassium manganate(VII) solution. Place the test- tube in the hot water bath. | purple KMnO₄ decolourised/ discharged upon standing in hot water bath | purple KMnO ₄ turned brown/ yellow/ formed brown ppt/ decolourised/ discharged upon standing in hot water bath | purple KMnO ₄ decolourise d/ discharged / turned brown / turned colourless upon standing in the hot water bath | purple KMnO ₄ decolourise d/ discharged / turned colourless upon standing in the hot water bath |

Table 3.1

| (c)To 1 cm depth of aqueous iodine, add aqueous sodium hydroxide dropwise until a permanent yellow colour is obtained.No yellow precipitateYellow precipitateYellow precipitateThen add 3 drops of the unknown into the same test-tube.No yellow precipitateNo yellow precipitateYellow precipitateYellow precipitatePlace the test- tube in the hot water bath.Place the test- tube in the hotNo yellow precipitateNo yellow precipitate | | Test and determine if any gas is evolved. | colourless odourless gas evolved blue litmus turned paper red gas produced white ppt with aqueous Ca(OH) ₂ | pungent gas evolved blue litmus turned red and bleached | no gas evolved | no gas evolved |
|---|-----|--|--|---|-----------------------------------|-----------------------------------|
| | (c) | To 1 cm depth of aqueous iodine, add aqueous sodium hydroxide dropwise until a permanent yellow colour is obtained. Then add 3 drops of the unknown into the same test-tube. Place the test- tube in the hot water bath. | No yellow precipitate | No yellow precipitate | Yellow precipitate obtained | Yellow precipitate obtained |

(d) Identifying unknown metal halide

(i) From your observations in Table 3.1, suggest which one of the unknown compounds is the metal halide. [1]

FA<mark>6</mark>....

explanation... It decolourised purple KMnO₄ with the <u>production of a</u> <u>pungent gas which turns blue litmus paper red and then bleaches.</u> ...

(ii) Suggest the reagent and carry out the test to confirm the identity of the halide in the metal halide. [2]

reagent ... silver nitrate ...

observations ... white ppt formed ...

FA ...6...... contains ...chloride/ Cl⁻ ...anion.

(d) (iii) In Table 3.2 below, describe two tests that will allow you to identify the cation in the metal halide. Perform the tests and record the observations in the same table. Use only bench reagents provided. [3]

| Table 3.2 | | | | |
|---|--|--|--|--|
| Tost | Observations | | | |
| Test | FA <mark>6</mark> | | | |
| Add NaOH(aq) dropwise until no further change is observed/ until in excess. | White ppt formed soluble in excess NaOH. | | | |
| Add NH ₃ (aq) dropwise until no further change is observed/ until in excess. | White ppt formed insoluble in excess NH ₃ (aq). | | | |

The cation in metal halide is ... Al³⁺ ...

(iv) The nature of the cation of the metal halide in aqueous solution accounts for its observations in test (a). Describe and explain the nature of the cation by means of an equation.

equation ... $[A/(H_2O)_6]^{3+} + H_2O \rightleftharpoons [A/(H_2O)_5(OH)]^{2+} + H_3O^+$

explanation ... Since Al^{3+} is small and highly charged/ has high charge density, it undergoes hydrolysis with water to produce an acidic solution.

(e) Identifying organic liquids

(i) The three unknown organic compounds are primary alcohol, aldehyde and monocarboxylic acid.

Based on your observations in tests (a) and (b), identify which is the monocarboxylic acid. Suggest the identity of the monocarboxylic acid and support your answer by giving the evidence. [3]

FA ...<mark>5</mark> ...

The identity of monobasic carboxylic acid is ...methanoic acid/ HCOOH ...

evidence ... In test (b) oxidation of methanoic acid by KMnO₄ produced CO₂ which turned blue litmus paper red/ white ppt with limewater.

(ii) Describe how you would conduct a chemical test, using only the bench reagents provided, to distinguish between the remaining two unknown organic compounds.

Carry out the chemical test.

With aid of your observations and results provided in test **(c)**, identify which is the primary alcohol and the aldehyde. [3]

chemical test ... <u>Tollens' reagent</u> (To 1 cm depth of AgNO₃, add NaOH(aq) dropwise till a ppt is formed. Then add NH₃(aq) dropwise till ppt dissolves completely.)

observations ... silver mirror formed with FA8 but not FA7

The primary alcohol is **FA**...**7**...

The identity of the primary alcohol is ...ethanol/ CH₃CH₂OH...

The aldehyde is **FA** ...**8**...

The identity of the aldehyde is ...ethanal/ CH₃CHO ...

[Total: 17]

END OF PAPER

Qualitative Analysis Notes [ppt. = precipitate]

(a) Reactions of aqueous cations

| action | reaction with | | | |
|---|--|--|--|--|
| cation | NaOH(aq) | NH ₃ (aq) | | |
| aluminium, Al ³⁺ (aq) | white ppt. soluble in excess | white ppt. insoluble in excess | | |
| ammonium, NH₄⁺(aq) | ammonia produced on heating | _ | | |
| barium, Ba ²⁺ (aq) | no ppt. (if reagents are pure) | no ppt. | | |
| calcium, Ca²+(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), Cu²+(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, Mg²⁺(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, C <i>l</i> ⁻ (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 NH₃(aq)) |
| nitrate, NO₃ [−] (aq) | NH_3 liberated on heating with $OH^-(aq)$ and Al foil |
| nitrite, NO₂⁻ (aq) | NH ₃ liberated on heating with OH [−] (aq) and A <i>l</i> foil; NO liberated by dilute acids (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 on warming 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, NH₃ | 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, I2 | black solid / purple gas | brown | purple |