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

1 Identification of an unknown organic acid by titration

In this experiment, you will perform titrations to determine the relative molecular mass, M_r , of an unknown monoprotic organic acid, **FA 1**, and use it to identify the acid.

FA 1 is an aqueous solution containing 4.80 g dm^{-3} of an unknown monoprotic organic acid.

You are also provided with: **FA 2** is 0.110 mol dm⁻³ sodium hydroxide, NaOH. thymol blue indicator

Prepare a table in the space provided below to record, to an appropriate level of precision, all your burette readings.

(a) Titration of FA 1 with FA 2

- 1. Fill the burette with FA 2.
- 2. Pipette 25.0 cm^3 of **FA 1** into a conical flask.
- 3. Add 3 to 4 drops of thymol blue indicator into the flask. The solution in the flask should turn pink.
- 4. Titrate **FA 1** in the conical flask with **FA 2**. The end-point is reached when the solution changes from yellow to green.
- 5. Record your burette readings in your table.
- 6. Repeat steps 2 to 5 until consistent results are obtained.

Titration Results

	1	2
final burette reading / cm ³	23.50	47.50
initial burette reading / cm ³	0.00	24.00
volume of FA 2 added / cm ³	23.50	23.50

[5]

From your titrations, obtain a suitable volume of **FA 2**, to be used in your calculations. Show clearly how you obtained this volume.

volume of **FA 2** =[1]

(b) (i) Calculate the amount of sodium hydroxide present in the volume of **FA 2** that you calculated in (a).

amount of NaOH reacted =[1]

(ii) Calculate the concentration of organic acid present, in mol dm⁻³, in **FA 1**.

(iii) Calculate the relative molecular mass, *M_r*, of the organic acid in **FA 1**.

.

(iv) From another experiment, the identity of **FA 1** was narrowed down to these four acids.

CH3COOHHCOOHCH2=CHCO2HCH3CH2CO2HGiven that sodium hydroxide reacts only with the COOH group in the organic acid,
deduce the identity of the organic acid present in FA 1. Explain your answer.[Ar: H, 1.0; C, 12.0; O, 16.0; Cl, 35.5][Ar: H, 1.0; C, 12.0; O, 16.0; Cl, 35.5][1]

(c) This identification method uses the calculated relative molecular mass of the acid.

As the relative molecular masses of $CH_2=CHCO_2H$ and $CH_3CH_2CO_2H$ are so similar, any slight inaccuracy in the titration could lead to an incorrect conclusion.

Describe a chemical test that would enable you to distinguish between CH_2 =CHCO₂H and $CH_3CH_2CO_2H$.

There is **no need** to carry out this test.

(d) Another student was provided a solution of another unknown organic acid. It has the same concentration, in mol dm⁻³, as that used in the titration above. However, this new unknown organic acid is a diprotic acid.

State and explain how the calculated relative molecular mass obtained will differ from that obtained in **b(iii)**.

.....[2]

[Total: 14]

2 Determination of the concentration of NaOH and the enthalpy change of neutralisation, ΔH_{neut}

You are provided with the following solutions:

- **FA 3** is a solution of sodium hydroxide, NaOH
- **FA 4** is a solution of 2.00 mol dm⁻³ hydrochloric acid, HCl

In this question, you are to perform a series of 6 experiments where different volumes of **FA 3** and **FA 4** are mixed together to give a total volume of 50 cm³. The temperature change, ΔT , for each experiment will be determined and a graph of ΔT against the volume of **FA 3** will be plotted.

You will then use the data from your graph to determine the concentration of NaOH in **FA 3**, and the enthalpy change of neutralisation for the reaction between aqueous sodium hydroxide and hydrochloric acid.

 $NaOH + HCl \rightarrow NaCl + H_2O \qquad \Delta H_{neut}$

(a) Procedure

Experiment 1

- Place one polystyrene cup inside a second polystyrene cup. Place these into a 250 cm³ beaker to prevent them from tipping over.
- 2) Use a 50 cm³ measuring cylinder to transfer 10.0 cm³ of **FA 3** into the polystyrene cup.
- 3) Measure the temperature of **FA 3** in the polystyrene cup and record the initial temperature of **FA 3**, T_1 , in Table 2.1 on page 7.
- 4) Use another 50 cm³ measuring cylinder, transfer 40.0 cm³ of **FA 4** into the same polystyrene cup.
- 5) Stir the mixture in the polystyrene cup with the thermometer. Measure and record the highest temperature, T_2 in Table 2.1 on page 7.
- 6) Rinse the polystyrene cup and thermometer with distilled water and dry them with paper towels.
- 7) Repeat steps 2 to 6 using 20.0 cm³, 30.0 cm³ and 40.0 cm³ of FA 3, each time using appropriate volume of FA 4, such that the total volume of the reaction mixture is 50 cm³.
- 8) Record all measurements of volume, temperature (T_1 and T_2) and temperature change, ΔT , in Table 2.1 on page 7.

(b) Results

		experiment				
	1	2	3	4	5	6
volume of FA 3 / cm ³	10.0	20.0	30.0	40.0	25.0	35.0
volume of FA 4 / cm ³	40.0	30.0	20.0	10.0	25.0	15.0
initial temperature, <i>T</i> ₁ / °C	29.0	29.0	29.0	29.0	29.0	29.0
final temperature, $T_2/°C$	33.6	38.0	40.0	34.4	40.0	38.0
temperature change, $\Delta T \sim C$	+4.6	+9.0	+11.0	+5.4	+11.0	+9.0
	•	•	•	•	•	[3]

Table 2.1

(c) (i) Plot a graph of ΔT (y-axis) against volume of **FA 3** used (x-axis) using the four experimental results that you have obtained.

The scales for both axes must be chosen to provide an origin.



By considering your plotted points, perform two additional experiments to identify the volume of **FA 3** needed to produce the maximum temperature change, ΔT_{max} .

In each experiment, ensure that the total volume of the reaction mixture is 50 cm³. You may find it helpful to plot the results from each experiment before choosing the volumes to use in the next experiment.

Record all measurements of volume, temperature (T_1 and T_2) and temperature change, ΔT , in Table 2.1 on page 7. [2]

(ii) Draw two straight lines of best fit. The first best fit line should be drawn using the plotted points where ΔT is increasing and the second best fit line should be drawn using the plotted points where ΔT is decreasing. Extrapolate these two lines until they cross. [1]

8

(d) (i) Use your graph to determine the maximum temperature change, ΔT_{max} , as well as the volume of **FA 3**, V_{FA3}, used to obtain it.

 $\Delta T_{\text{max}} = \dots ^{\circ} C$ $V_{\text{FA3}} = \dots cm^{3} [1]$

(ii) Using your results in (d)(i), calculate the concentration of NaOH in FA 3.

concentration of NaOH in FA 3 =[2]

(iii) Hence, calculate the enthalpy change of neutralisation, ΔH_{neut} .

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

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

- (e) Predict and explain the following:
 - (i) the effect on ΔT_{max} when the volumes of **FA 3** and **FA 4** used in the reaction are doubled.

......[1]

(ii) the effect on ΔH_{neut} if the experiment was repeated with ethanoic acid, CH₃CO₂H, of the same concentration instead of hydrochloric acid.

(f) State one significant source of error in the experiment and suggest an improvement that can be made to reduce this error.

 	 [1]
	[Total: 14]

3 Inorganic Analysis

FA 5 is a solution which contains up to two cations and one anion.

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

Using the observations in Table 3.1, you will then identify the ions present in **FA 5**.

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured. Test and identify any gases evolved.

Table 3.1	Та	ıble	e 3	.1
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test		test	observations
(a)	(i)	Place one drop of FA 5 solution on Universal Indicator paper.	Universal Indicator paper: orange or yellow pH = 3 or pH = 4
	(ii)	Add about 1 cm ³ of dilute nitric acid to 1 cm depth of FA 5 solution.	No effervescence
		Add barium nitrate dropwise until no further change is seen.	White ppt formed.
	(iii)	Add sodium hydroxide to 1 cm depth of FA 5 solution until no further change is seen.	Pale blue ppt forms, insoluble in excess NaOH
		Gently warm the mixture.	Pungent gas forms and turns moist red litmus paper turns blue \Rightarrow Gas is NH ₃ . Blue ppt turns black

(iv)	Add aqueous ammonia to 1 cm depth of FA 5 until no further change is seen.	Blue ppt forms soluble in excess ammonia to give a dark blue solution
(v)	Add I ⁻ (aq) to 1 cm depth of FA 5 solution until no further change is seen. Leave the mixture to stand.	white/off-white/cream ppt in a brown solution.
L	1	[5]

(b)	(i)	Identify the cation(s) and anion present in FA 5 .	
		cation(s) in FA 5	
		anion in FA 5	[3]
	(ii)	Write an equation to explain the observation in test (a)(i).	
			[1]
		[Tc	otal: 9]

4 Determination of oxidising strength of oxidising agents

You are provided with samples of the following four aqueous solutions.

solution that contains bromide ions, $Br^$ solution that contains iron(III) ions, Fe^{3+} solution that contains aqueous iodine, I_2 solution that contains iodide ions, I^-

Carry out the tests in Table 4.1 to investigate possible redox reactions and rank the oxidising strength of the oxidising agents Br_2 , Cl_2 , Fe^{3+} and I_2 .

$$Br_{2} + 2e^{-} \rightleftharpoons 2Br^{-}$$

$$Cl_{2} + 2e^{-} \rightleftharpoons 2Cl^{-}$$

$$Fe^{3+} + e^{-} \rightleftharpoons Fe^{2+}$$

$$I_{2} + 2e^{-} \rightleftharpoons 2I^{-}$$

Your answers should correspond to the given observations/equations/deductions. The results of the first test have been given to you and you should use it as an example.

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Table	4.1
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		test	observations	deductions
(a)	(i)	Transfer 1 cm ³ of Br ⁻ to a test-tube. Add 1 cm ³ of Cl_2 .	Solution turns yellow.	Cl_2 oxidises Br^- to Br_2 $Cl_2 > Br_2$
	(ii)	Transfer 1 cm ³ of Fe ³⁺ to a test-tube. Add 1 cm ³ of Br ⁻ .	Solution remains orange.	
		Add aqueous NaOH dropwise until in excess.	Red brown ppt formed, insoluble in excess NaOH	
	(iii)	Transfer 1 cm ³ of Fe ³⁺ to a test-tube. Add 1 cm ³ of I ⁻ then add 5 drops of starch solution.	Orange solution turns brown. Brown solution turns blue-black with starch	
	(iv)	Transfer 1 cm ³ of I ₂ to a test-tube. Add 1 cm ³ of Br-then add 5 drops of starch solution.	Solution remains brown Solution turns blue-black with starch	

[4]

- (b) Use your information in Table 4.1 to rank the order of oxidising strengths of the species: Br₂, Cl₂, Fe³⁺, I₂.
 - Note: In some of the tests performed in part (a) there will have been no reaction. Such tests can still help you to deduce the relative oxidising powers of the species involved.

.....[1]

(c) Using your observations, explain why aqueous FeI₃ cannot be prepared.

......[1]

[Total: 6]

5 Planning

When a solute is added to two immiscible solvents, **A** and **B**, some of the solute dissolves in each of the solvents and an equilibrium is set up between the two solvents. It has been shown that for dilute solutions, at equilibrium, the ratio of the two concentrations is a constant known as the partition coefficient, $K_{\text{partition}}$.

Trichloromethane, $CHCl_3$, and water separate into two immiscible layers when shaken together and allowed to stand. Ammonia can dissolve in both of these layers. The $K_{partition}$ for ammonia in these two solvents is given by:

 $\mathcal{K}_{\text{partition}} = \frac{[\text{NH}_3]_{\text{water}}}{[\text{NH}_3]_{\text{trichloromethane}}}$

50 cm³ of trichloromethane and 50 cm³ of aqueous ammonia are mixed and left to equilibrate for about an hour. Samples of the aqueous layer are obtained and the amount of ammonia present in the aqueous layer is determined by titration. The concentration of ammonia in the separate layers can be calculated and the value of $K_{\text{partition}}$ can then be determined.

(a) Explain why ammonia is likely to be more soluble in water than in trichloromethane.

.....[1]

(b) You are to plan a procedure that will allow you to obtain the titration results necessary to determine value of $K_{\text{partition}}$ of ammonia between water and trichloromethane at room temperature.

You are provided with the following

- trichloromethane, CHCl₃,
- 1.00 mol dm⁻³ aqueous ammonia,
- 0.500 mol dm⁻³ hydrochloric acid,
- methyl orange indicator,
- 250 cm³ conical flask with stopper,
- 10.0 cm³ pipette,
- the laboratory apparatus normally found in a school.

In your plan you should include the following:

- an outline of how you would prepare the equilibrium mixture,
- practical details of how you would carry out the titration,
- appropriate apparatus and their capacities.

.....

	[7]
(c)	It is unnecessary to titrate both layers of the partition. Explain why the titration is carried out on a sample of the aqueous layer rather than the trichloromethane layer.
	[1]

- (d) A student carried out the experiment and obtained a mean titre of 19.20 cm³.
 - (i) Using this mean titre value, calculate the equilibrium amounts of ammonia
 - 1. in the aqueous layer
 - 2. in the trichloromethane layer

=[1]	amount of ammonia in the aqueous layer
=[1]	amount of ammonia in the trichloromethane layer
	Line and the factor of the mantification of the second states of the sec

(ii) Hence calculate the value of the partition coefficient, $K_{\text{partition}}$.

partition coefficient, $K_{\text{partition}}$ =[1]

[Total: 12]

Answer all the questions in the spaces provided.

1 Identification of an unknown organic acid by titration

In this experiment, you will perform titrations to determine the relative molecular mass, M_r , of an unknown monoprotic organic acid, **FA 1**, and use it to identify the acid.

FA 1 is an aqueous solution containing 4.80 g dm^{-3} of an unknown monoprotic organic acid.

You are also provided with: **FA 2** is 0.110 mol dm⁻³ sodium hydroxide, NaOH. thymol blue indicator

Prepare a table in the space provided below to record, to an appropriate level of precision, all your burette readings.

(a) Titration of FA 1 with FA 2

- 7. Fill the burette with FA 2.
- 8. Pipette 25.0 cm³ of **FA 1** into a conical flask.
- 9. Add 3 to 4 drops of thymol blue indicator into the flask. The solution in the flask should turn pink.
- 10. Titrate **FA 1** in the conical flask with **FA 2**. The end-point is reached when the solution changes from yellow to green.
- 11. Record your burette readings in your table.
- 12. Repeat steps 2 to 5 until consistent results are obtained.

Titration Results

final burette reading / cm ³	23.50	47.50	
initial burette reading / cm ³	0.00	24.00	
volume of FA 2 added / cm ³	23.50	23.50	

[5]

From your titrations, obtain a suitable volume of **FA 2**, to be used in your calculations. Show clearly how you obtained this volume.

average titre = $\frac{1}{2}$ (23.50 + 23.50) = 23.50 cm³

.

volume of **FA 2** =23.50 cm³..... [1]

(b) (i) Calculate the amount of sodium hydroxide present in the volume of FA 2 that you calculated in (a)

amt of NaOH used = $23.50/1000 \times 0.110$ = 2.59×10^{-3} mol

amount of NaOH reacted =2.59 x 10^{-3} mol.....[1]

(ii) Calculate the concentration of organic acid present, in mol dm⁻³ in **FA 1**.

Concentration of organic acid	$= 2.585 \times 10^{-3} \div 25/1000$
-	= 0.103 mol

concentration of organic acid in FA 1 =0.103 mol [1]

(iii) Calculate the relative molecular mass, *M*_r, of the organic acid in **FA 1**.

 $M_{\rm r}$ of organic acid = 4.80 \div 0.1034 = 46.4

*M*_r of the organic acid =46.4..... [1]

(iv) From another experiment, the identity of **FA 1** was narrowed down to these four acids.

CH₃COOH HCOOH CH₂=CHCO₂H CH₃CH₂CO₂H

Given that sodium hydroxide reacts only with the COOH group in the organic acid, deduce the identity of the organic acid present in **FA 1**. Explain your answer.

[A_r: H, 1.0; C, 12.0; O, 16.0; Cl, 35.5]

 $M_{\rm r}$ of HCOOH = 1.0 + 12.0 + 16.0 x 2 + 1.0 = 46.0

HCOOH is the organic acid present in FA 1 as its M_r is the closest to the one calculated in b(iii). [1]

(c) This identification method uses the calculated relative molecular mass of the acid.

As the relative molecular masses of CH_2 =CHCO₂H and $CH_3CH_2CO_2H$ are so similar, any slight inaccuracy in the titration could lead to an incorrect conclusion.

Describe a chemical test that would enable you to distinguish between $CH_2=CHCO_2H$ and $CH_3CH_2CO_2H$.

There is **no need** to carry out this test. [2]

Test: KMnO₄(aq), H₂SO₄(aq), heat Results: <u>purple KMnO₄ decolourises for CH₂=CHCO₂H</u>, CO₂ gas evolved forms white ppt in limewater. <u>Purple colour remains for CH₃CH₂CO₂H</u>

Or

Test: KMnO₄(aq), NaOH(aq), Results: <u>purple KMnO₄ decolourises for CH₂=CHCO₂H and a brown ppt is formed</u>. Purple colour remains for CH₃CH₂CO₂H

Or

Test: $Br_2(aq)/Br_2(I)/Br_2(inert solvent like CCI_4)$ Results: orange (aq)/reddish brown(liquid), orange-red(inert solvent) Br_2 decolourises for CH_2 =CHCO₂H while orange (aq)/reddish brown(liquid), orange-red(inert solvent) colour remains for $CH_3CH_2CO_2H$ (d) Another student was provided a solution of another unknown organic acid. It has the same concentration, in mol dm⁻³, as that used in the titration above. However, this new unknown organic acid is a diprotic acid.

State and explain how the calculated relative molecular mass obtained will differ from that obtained in **b(iii)**. [2]

Since the new acid is diprotic, the volume of FA 2 or NaOH required will be doubled. This causes the calculated amount of acid present to be doubled and in turn, the calculated concentration of FA 1 to be doubled. Hence the calculated M_r will be halved.

[Total: 14]

2 Determination of the concentration of NaOH and the enthalpy change of neutralisation, ΔH_{neut}

You are provided with the following solutions:

- **FA 3** is a solution of sodium hydroxide, NaOH
- FA 4 is a solution of 2.00 mol dm⁻³ hydrochloric acid, HCl

In this question, you are to perform a series of 6 experiments where different volumes of **FA 3** and **FA 4** are mixed together to give a total volume of 50 cm³. The temperature change, ΔT , for each experiment will be determined and a graph of ΔT against the volume of **FA 3** will be plotted.

You will then use the data from your graph to determine the concentration of NaOH in **FA 3**, and the enthalpy change of neutralization for the reaction between aqueous sodium hydroxide and hydrochloric acid.

 $NaOH + HCl \rightarrow NaCl + H_2O \qquad \Delta H_{neut}$

(a) Procedure

Experiment 1

- Place one polystyrene cup inside a second polystyrene cup. Place these into a 250 cm³ beaker to prevent them from tipping over.
- 10) Use a 50 cm³ measuring cylinder to transfer 10.0 cm³ of **FA 3** into the polystyrene cup.
- 11) Measure the temperature of **FA 3** in the polystyrene cup and record the initial temperature of **FA 3**, T_1 , in Table 2.1 on the next page.
- 12) Use another 50 cm³ measuring cylinder, transfer 40.0 cm³ of **FA 4** into the same polystyrene cup.
- 13) Stir the mixture in the polystyrene cup with the thermometer. Measure and record the highest temperature, T_2 in Table 2.1 on the next page.
- 14) Rinse the polystyrene cup and thermometer with distilled water and dry them with paper towels.
- 15) Repeat steps 2 to 6 using 20.0 cm³, 30.0 cm³ and 40.0 cm³ of FA 3, each time using appropriate volume of FA 4, such that the total volume of the reaction mixture is 50 cm³.
- 16) Record all measurements of volume, temperature (T_1 and T_2) and temperature change, ΔT , in Table 2.1 on the next page.

(b) Results

	Experiment					
	1	2	3	4	5	6
Volume of FA 3 / cm ³	10.0	20.0	30.0	40.0	25.0	35.0
Volume of FA 4 / cm ³	40.0	30.0	20.0	10.0	25.0	15.0
Initial temperature, T ₁ / °C	29.0	29.0	29.0	29.0	29.0	29.0
Final temperature, T ₂ / °C	33.6	38.0	40.0	34.4	40.0	38.0
Temperature change, $\Delta T / °C$	+4.6	+9.0	+11.0	+5.4	+11.0	+9.0
						[3

Table 2.1

24

(c) (i) Plot a graph of ΔT (y-axis) against volume of **FA 3** used (x-axis) using the four experimental results that you have obtained.

The scales for both axes must be chosen to provide an origin.



By considering your plotted points, perform two additional experiments to identify the volume of **FA 3** needed to produce the maximum temperature change, ΔT_{max} .

In each experiment, ensure that the total volume of the reaction mixture is 50 cm³. You may find it helpful to plot the results from each experiment before choosing the volumes to use in the next experiment.

Record all measurements of volume, temperature (T_1 and T_2) and temperature change, ΔT , in **Table 2.1.** [2]

[1]

(d) (i) Use your graph to determine the maximum temperature change, ΔT_{max} , as well as the volume of **FA 3**, V_{FA3}, used to obtained it.

 ΔT_{max} =12.6....°C V_{FA3} =28.0....cm³[1]

(ii) Using your results in (d)(i), calculate the concentration of NaOH in FA 3.

volume of HCl reacted = $50.0 - 28.0 = 22.0 \text{ cm}^3$

Amount of HCl reacted = Amount of NaOH reacted = 22.0/1000 x 2.00 = 0.044 mol

Concentration of NaOH = $0.044 / (28.0/1000) = 1.57 \text{ mol dm}^{-3}$

concentration of NaOH in FA 3 =[2]

(iii) Hence, calculate the enthalpy change of neutralisation, ΔH_{neut} .

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

heat released = 50 x 4.18 x 12.6= 2633.4 J

Amount of water produced = amount of NaOH reacted = 0.044 mol

 $\Delta H_{neut} = -2633.4/0.044 = -59850 \text{ J mol}^{-1}$ $= -59.9 \text{ kJmol}^{-1}$

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

- (e) Predict and explain the following:
 - (i) the effect on ΔT_{max} when the volumes of **FA 3** and **FA 4** used in the reaction are doubled [1]

Heat evolved = mc ΔT_{max} = n × $\Delta H_n \Rightarrow \Delta T_{max} = \frac{n \times \Delta H_n}{m \times c}$

When volume of FA1 and FA2 are doubled, <u>both n (amount of water produced)</u> and m (mass of solution)/volume are doubled/increased (ΔH_n and c remain constant). Hence ΔT_{max} is unaffected.

(ii)

lines until they cross.

(ii) the effect on ΔH_{neut} if the experiment was repeated with ethanoic acid, CH_3CO_2H , of the same concentration instead of hydrochloric acid. [1]

 ΔH_{neut} would be <u>less exothermic/smaller/lower</u> as ethanoic acid is a <u>weak acid</u>. <u>Energy is absorbed</u> to <u>ionise/dissociate</u> the weak acid.

(f) State one significant source of error in the experiment and suggest an improvement that can be made to reduce this error. [1]

Heat is lost to the surrounding, hence a cup with lid can be used to minimise heat exchange with the surrounding air. (cannot just say use better insulated cup)

Or

Heat capacity of the styrofoam cup is not accounted for, hence the heat absorbed by the styrofoam cup can be included in the calculation of heat change.

Or

Initial temperature of **FA 4** was not accounted for, hence the weighted initial temperature can be calculated where

 $\textbf{\textit{T}_{weighted initial}} = \frac{(\text{Volume of FA 3 x T_{FA3}}) + (\text{Volume of FA 4 x T_{FA4}})}{\text{Volume of FA 3 + Volume of FA 4}}$

[Total: 14]

3 Inorganic Analysis

FA 5 is a solution which contains up to two cations and one anion.

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

Using the observations in Table 3.1, you will then identify the ions present in **FA 5**.

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured. Test and identify any gases evolved.

		test	observations	
(a)	(i)	Place one drop of FA 5 solution on Universal indicator paper	UI paper: orange or yellow pH = 3 or pH = 4	
	(ii)	Add about 1cm ³ of dilute nitric acid to 1cm depth of FA 5 solution.	No effervescence	
		Add barium nitrate dropwise until no further change is seen.	White ppt formed.	
	(iii) Add sodium hydroxide to 1cm dep of FA 5 until no further change is seen.		Pale blue ppt forms, insoluble in excess NaOH	
		Gently warm the mixture.	Pungent gas forms and turns moist red litmus paper turns blue + Gas is NH ₃ . Blue ppt turns black	

(iv)	Add aqueous ammonia to 1cm depth of FA 5 until no further change is seen.	Blue ppt forms soluble in excess ammonia to give a dark blue solution
(v)	Add I ⁻ (aq) to 1cm depth of FA 5 until no further change. Leave mixture to stand	white/off-white/cream ppt in a brown solution.
		[5]

(b) (i) Identify the cation(s) and anion present in **FA 5**.

cation(s) in FA 5 Cu²⁺, NH₄+

anion in **FA 5**
$$SO_4^{2-}$$
 [3]

(ii) Write an equation to explain the observation in test (a)(i).

 $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

FYI: Test (v) is a redox reaction.

 $2Cu^{2+} + 4I^{-} \rightarrow 2CuI + I_2$

[Total: 9]

4 Determination of oxidising strength of oxidising agents

You are provided with samples of the following four aqueous solutions.

Solution that contains bromide ions, Br^- Solution that contains iron(III) ions, Fe^{3+} Solution that contains iodine water, I_2 Solution that contains iodide ions, I^-

Carry out the tests in Table 4.1 to investigate possible redox reactions and rank the oxidising strength of the oxidising agents Br_2 , Cl_2 , Fe^{3+} and I_2 .

$$\begin{array}{rcl} \mathsf{Br}_2 + 2\mathsf{e}^- &\rightleftharpoons& 2\mathsf{Br}^-\\ \mathsf{C}l_2 + 2\mathsf{e}^- &\rightleftharpoons& 2\mathsf{C}l^-\\ \mathsf{F}\mathsf{e}^{3+} + \mathsf{e}^- &\rightleftharpoons& \mathsf{F}\mathsf{e}^{2+}\\ \mathsf{I}_2 + 2\mathsf{e}^- &\rightleftharpoons& 2\mathsf{I}^- \end{array}$$

Your answers should correspond to the given observations/equations/deductions. The results of the first test has been given to you and you should use it as an example.

Table	4.1
-------	-----

		test	Observations	Deductions
(a)	(i)	Transfer 1 cm ³ of Br ⁻ to a test-tube. Add 1 cm ³ of Cl ₂ .	Solution turns yellow	Cl_2 oxidises Br^- to Br_2 $Cl_2 > Br_2$
	(ii)	Transfer 1 cm ³ of Fe³⁺ to a test-tube. Add 1 cm ³ of Br ⁻ . Add aqueous NaOH dropwise until in excess.	Solution remains orange. Red brown ppt formed, insoluble in excess NaOH	Fe ³⁺ cannot oxidise Br⁻ Br₂ > Fe ³⁺
	(iii)	Transfer 1 cm ³ of Fe³⁺ to a test-tube. Add 1 cm ³ of I [−] then add 5 drops of starch solution.	Solution turns brown. Solution turns blue-black with starch	Fe ³⁺ oxidises I ⁻ to I ₂ Fe ³⁺ > I ₂
	(iv)	Transfer 1 cm ³ of I_2 to a test-tube. Add 1 cm ³ drops of Br ⁻ then add 5 drops of starch solution.	Solution remains brown Solution turns blue-black with starch	I₂ cannot oxidise Br⁻ Br₂ > I₂

- (b) Use your information in the above completed table to rank the order of oxidising strengths of the species: Br_2 , Cl_2 , Fe^{3+} and I_2 .
 - Note: In some of the tests performed in part (a) there will have been no reaction. Such tests can still help you to deduce the relative oxidising powers of the species involved.

.....[1]

 $Cl_2 > Br_2 > Fe^{3+} > I_2 OR$ in any form that clearly shows the correct trend.

(c) Using your observations, explain why aqueous FeI₃ cannot be prepared.

.....[1]

In test (a)(iii), <u>Fe³⁺ oxidises I⁻ to I₂</u>, itself reduced to Fe²⁺.

[Total:6]

5 Planning

When a solute is added to two immiscible solvents, A and B, some of the solute dissolves in each of the solvents and an equilibrium is set up between the two solvents. It has been shown that for dilute solutions, at equilibrium, the ratio of the two concentrations is a constant known as the partition coefficient, $K_{\text{partition}}$.

Trichloromethane, $CHCl_3$, and water separate into two immiscible layers when shaken together and allowed to stand. Ammonia can dissolve in both of these layers. The $K_{partition}$ for ammonia in these two solvents is given by:

 $\mathcal{K}_{\text{partition}} = \frac{[\text{NH}_3]_{\text{water}}}{[\text{NH}_3]_{\text{trichloromethane}}}$

50 cm³ of trichloromethane and 50 cm³ of aqueous ammonia are mixed and left to equilibrate for about an hour. Samples of the aqueous layer are obtained and the amount of ammonia present in the aqueous layer is determined by titration. The concentrations of ammonia in the separate layers can be calculated and the value of $K_{\text{partition}}$ can then be determined.

(a) Explain why ammonia is likely to be more soluble in water than in trichloromethane.

.....[1]

Ammonia can form <u>hydrogen bonds with water</u> molecules while it can only form <u>permanent</u> <u>dipole – permanent dipole interactions with trichloromethane</u>.

(b) You are to plan a procedure that will allow you to obtain the titration results necessary to determine value of $K_{\text{partition}}$ of ammonia between water and trichloromethane at room temperature.

You are provided with the following

- trichloromethane
- 1.00 mol dm⁻³ aqueous ammonia
- 0.500 mol dm⁻³ hydrochloric acid
- methyl orange indicator
- 250 cm³ conical flask with stopper
- 10.0 cm³ pipette
- the laboratory apparatus normally found in a school

In your plan you should include the following:

- an outline of how you would prepare the equilibrium mixture
- practical details of how you would carry out the titration
- appropriate apparatus and their capacities

.....[7]

- 1. Using a 50 cm³ measuring cylinder, add 50 cm³ of aqueous ammonia into a 250 cm³ conical flask.
- 2. Using another 50 cm³ measuring cylinder, add 50 cm³ of trichloromethane into the same conical flask.
- 3. Stopper the conical flask and shake to mix well. Leave the flask at room temperature to equilibrate for 1 hour.

- 4. Using a 10.0 cm³ pipette, transfer 10.0 cm³ of the aqueous layer into another 250 cm³ conical flask.
- 5. Add 2-3 drops of methyl orange.
- 6. Fill a 50.00 cm³ burette with 0.500 mol dm⁻³ HCl
- 7. Titrate the solution against HCl in the burette, taking care to add dropwise near the end. The end point is reached when the solution in the conical flask changes from yellow to orange colour.
- 8. Repeat steps 4 to 7 until at least two consistent results within ± 0.10 cm³ are obtained
- (c) It is unnecessary to titrate both layers of the partition. Explain why the titration is carried out on a sample of the aqueous layer rather than the trichloromethane layer.

.....[1]

The concentration of ammonia is higher in aqueous layer which means the titration reading will be larger. The percentage error associated with the volume used will be lower and hence the determination of its concentration will be more accurate.

Or

Hydrochloric acid is immiscible with trichloromethane layer.

- (d) A student carried out the experiment and obtained a mean titre of 19.20 cm³.
 - (i) Using this mean titre value, calculate the equilibrium amounts of ammonia
 - 3. in the aqueous layer
 - 4. in the trichloromethane layer

amount of HCl reacted = $19.20/1000 \times 0.500$ = 9.60×10^{-3} mol

amount of ammonia in aqueous layer = $9.60 \times 10^{-3} \div 10/1000 \times 50/1000$ = 0.0480 mol

initial amt of ammonia used = $50/1000 \times 1.00 = 0.0500$ mol

amt of ammonia in trichloromethane layer = 0.0500 - 0.0480 = 0.00200 mol

amount of ammonia in the aqueous layer =0.0480 mol[1]

amount of ammonia in the trichloromethane layer =0.00200 mol[1]

(ii) Hence calculate the value of the partition coefficient, $K_{\text{partition}}$.

 $[NH_3]_{water} = 0.0480 \div 50/1000 = 0.960 \text{ mol } dm^{-3}$

 $[\text{NH}_3]_{\text{trichloromethane}} = 0.00200 \, \div \, 50/1000 = 0.0400 \ \text{mol} \ dm^{-3}$

 $K_{\text{partition}} = 0.960 \div 0.0400 = 24.0$

partition coefficient, *K*_{partition} =24.0...[1] [Total: 12]