CANDIDATE NAME	( )	CLASS	24S0		

H

RAFFLES INSTITUTION
2024 YEAR 6 PRELIMINARY EXAMINATION

Higher 2

CHEMISTRY 9729/04

Paper 4 Practical

21 August 2024

2 hours 30 minutes

Do NOT turn over the Question Booklet until you are told to do so.

READ THESE INSTRUCTIONS FIRST.

Write your name and class on the space provided when instructed to do so.
Give details of the practical shift and laboratory where appropriate, in the space provided.
Write in dark blue or black pen.
You may use a 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 number of marks is given in brackets [ ] at the end of each question or part question.

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.

Shift	
Laboratory	
Bench Number	

For Examiner's Use	
Question	**Marks**
1	**/ 15**
2	**/ 13**
3	**/ 14**
4	**/ 13**
Total	**/ 55**

This document consists of **21** printed pages and **3** blank pages.

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

1 Determination of the molar enthalpy change of solution, ΔH_{sol}, of FA 1

FA 1 is solid anhydrous magnesium sulfate, $MgSO_4$.

When added to water, **FA 1** dissolves and the temperature of the solution rises. Some of the heat energy released from the dissolution of **FA 1** is absorbed by the calorimeter. To determine the molar enthalpy change of solution, ΔH_{sol}, of **FA 1**, you will first need to determine the heat capacity of the calorimeter.

The heat capacity of the calorimeter, C_{cal}, is the amount of heat energy required to change its temperature by 1 °C. The calorimeter used in this experiment comprises two polystyrene cups supported by a 250 cm^3 glass beaker.

(a) (i) Determination of the heat capacity of the calorimeter, C_{cal}

When hot water is added to the calorimeter containing room temperature water, heat energy from the hot water is used to raise the temperature of the calorimeter and the room temperature water. To determine the heat capacity of the calorimeter, C_{cal}, you will measure the maximum temperature rise when hot water is added to room temperature water in the calorimeter.

You are to carry out the experiment and record all values of temperature, T, to an appropriate level of precision in Table 1.1.

Procedure

1. Place a polystyrene cup inside a second polystyrene cup and place both cups in a 250 cm^3 glass beaker.

2. Use a 50 cm^3 measuring cylinder to transfer 50 cm^3 of room temperature water into the polystyrene cup.

3. Carefully stir the water in the polystyrene cup with a thermometer. Read and record the temperature of the room temperature water, T_1. Leave the thermometer in the polystyrene cup.

4. Use a 100 cm^3 glass beaker to collect approximately 60 cm^3 of hot water from the hot water dispenser.

   Note: Use a paper towel to hold the hot apparatus. Handle all hot apparatus with care.

5. Use the 50 cm^3 measuring cylinder to measure 50 cm^3 of hot water from the 100 cm^3 glass beaker. Place another thermometer into the measuring cylinder. Read and record the temperature of the hot water, T_2. Remove the thermometer from the hot water.

6. **Immediately** add the hot water from the measuring cylinder to the room temperature water in the polystyrene cup. Carefully stir the combined water using the thermometer and record the maximum temperature reached, T_3.

7. Empty the polystyrene cup and dry it using the paper towel.

Table 1.1

temperature of room temperature water, T_1 / °C	
temperature of hot water, T_2 / °C	
maximum temperature of combined water, T_3 / °C	

(ii) Calculate the heat energy lost by the hot water and the heat energy gained by the room temperature water using the values you obtained in **(a)(i)**.

Assume that the specific heat capacity of water is 4.18 J g^{-1} K^{-1}, and that the density of water is 1.00 g cm^{-3}.

heat energy lost by the hot water = ……

heat energy gained by the room temperature water = ……
[2]

(iii) The heat energy absorbed by the calorimeter during the experiment can be determined from the following equation.

Heat energy absorbed by the calorimeter
= heat energy lost by hot water – heat energy gained by room temp water

Calculate the heat energy absorbed by the calorimeter and hence determine the heat capacity of the calorimeter, C_{cal}.

Use the values you obtained from **(a)(i)** and **(a)(ii)**.

heat energy absorbed by the calorimeter = ……

heat capacity of calorimeter, C_{cal} = ……
[2]

[Turn Over

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(b) (i) Determination of the molar enthalpy change of solution, ΔH_{sol}, of FA 1

In this experiment, you will measure the temperature of the water in a polystyrene cup at regular time intervals, before and after **FA 1** is added. You will analyse your results graphically to obtain an accurate value for the temperature change caused by the dissolution of **FA 1**.

You will use this value to calculate the total heat change, q, of the solution and the calorimeter, and hence determine the molar enthalpy change of solution, ΔH_{sol}, of **FA 1**.

In the space provided on page 6, prepare tables in which to record for your experiment:

- 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 0.5 min.

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

Procedure

1. Weigh the capped container containing solid **FA 1**. Record the mass in your table on page 6.

2. Place a polystyrene cup inside a second polystyrene cup and place both cups in a 250 cm^3 glass beaker.

3. Use a measuring cylinder to transfer 100 cm^3 of room temperature water into the polystyrene cup.

4. Carefully stir the water in the polystyrene cup with the thermometer. Read and record the temperature, T. Start the stopwatch (t = 0.0 min). The stopwatch must be left to run for the rest of the experiment.

5. Continue to stir the water in the polystyrene cup. Read and record T every 0.5 minute for two minutes.

6. At **exactly** 2.5 minutes, transfer all the solid **FA 1** to the polystyrene cup. Stir the solution but do not read T.

7. Continue to stir the solution. Read and record T at t = 3.0 min and every 0.5 min until t = 8.0 min.

8. Reweigh the empty capped container. Record this mass in your table on page 6.

Results

[3]

(ii) Plot a graph of temperature, T, on the y-axis against time, t, on the x-axis, on the grid in Fig. 1.1.

Draw a best-fit straight line taking into account all of the points before t = 2.5 min.

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

Extrapolate (extend) both lines to t = 2.5 min. [3]

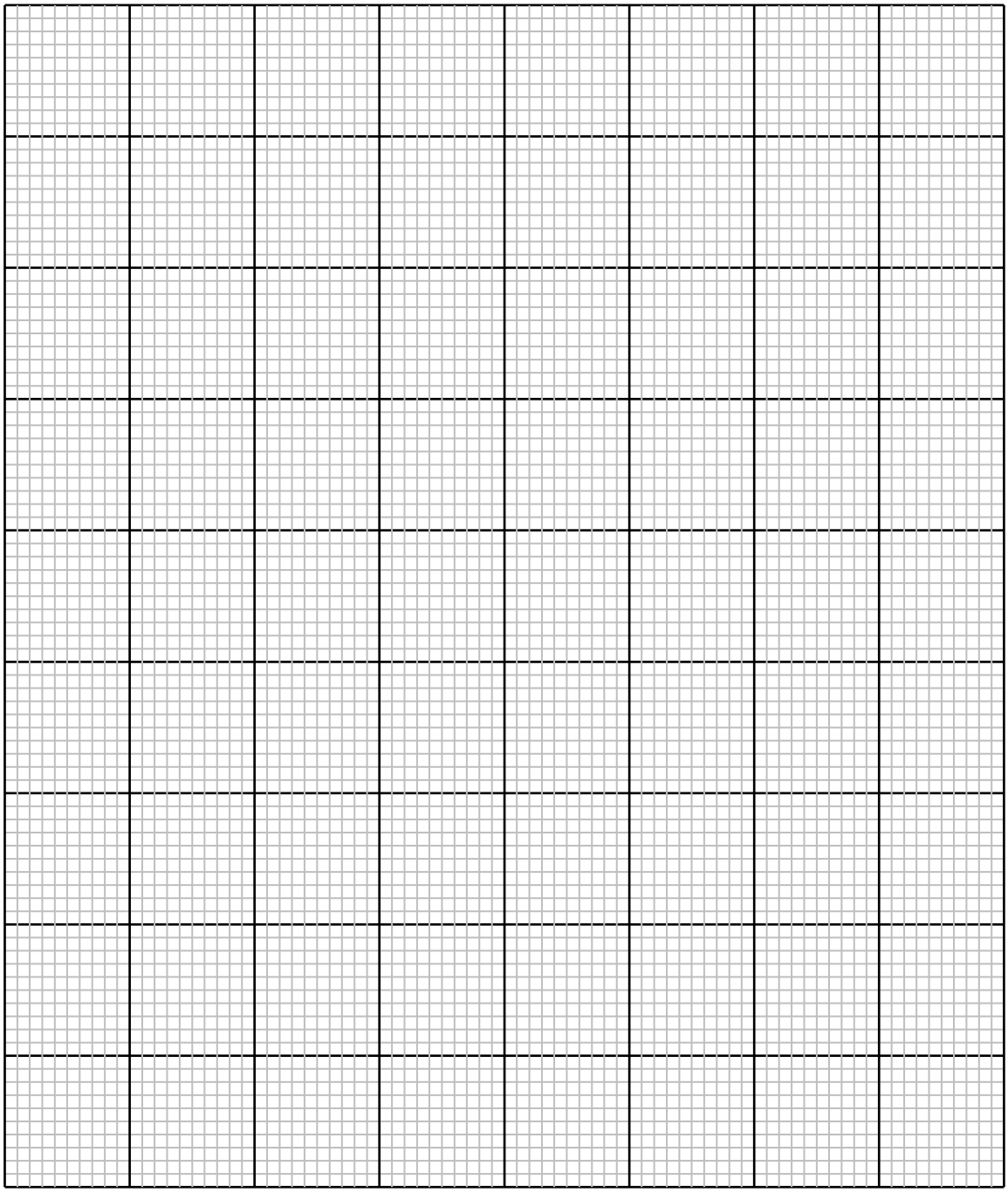

Fig. 1.1

(iii) From your graph, read the minimum temperature, T_{min}, and the maximum temperature, T_{max}, at t = 2.5 min. Record these values in the spaces below.

Calculate the temperature change, ΔT, at t = 2.5 min.

T_{min} = ...

T_{max} = ...

ΔT = ...
[1]

(iv) Calculate the total heat change, q, of the solution and the calorimeter as your sample of **FA 1** dissolved.

Use the values you obtained from **(a)(iii)** and **(b)(iii)**.

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}.

If you were unable to answer **(a)(iii),** you may assume the numerical value of the heat capacity of calorimeter, C_{cal} is 100 (this is not the correct value).

total heat change, q = ... [1]

(v) Determine the molar enthalpy change of solution, ΔH_{sol}, of **FA 1**.

Use the values you obtained from **(b)(i)** and **(b)(iv)**.

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

[A_r: Mg, 24.3 S, 32.1 O, 16.0]

ΔH_{sol} = ... [2]

(c) Heat loss to the surroundings is not accounted for in **(a)(i)**.

Explain how this error affects the ΔH_{sol} of **FA 1** obtained in **(b)(v)**.

……

……

……

…… [1]

[Total: 15]

2 Qualitative Analysis

(a) Organic Chemistry Analysis

FA 2 is an aqueous solution of an organic compound, **W**, which contains two different functional groups.

You will perform tests to identify the functional groups in **W** and hence deduce its possible structure.

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**.

Preparation of hot water bath

Fill a 250 cm^3 glass beaker with about 150 cm^3 of water from the water dispenser. Use this beaker of hot water for tests **1** and **2** in Table 2.1.

(i) Carry out the following tests. Carefully record your observations in Table 2.1.

Table 2.1

tests		observations
1	Add 1 cm depth of **FA 2** into a clean test-tube. To this test-tube add 10 drops of sodium hydroxide followed by iodine solution, dropwise, until a permanent orange colour is present. Warm the test-tube in the beaker of hot water for 2 minutes.	
2	Add 1 cm depth of **FA 2** into a clean test-tube. Add 8 drops of Fehling's solution. Warm the test-tube in the beaker of hot water for 3 minutes.	
3	Test solution **FA 2** with Universal Indicator paper.	

[3]

(ii) The molecular formula of **W** is $C_3H_6O_2$. Using your observations in Table 2.1, draw the displayed formula for **W**.

[1]

(b) Inorganic Chemistry Analysis

FA 3 is an aqueous solution which contains two cations listed in the *Qualitative Analysis Notes*. **FA 3** also contains nitrate ions and another anion listed in the *Qualitative Analysis Notes*.

You will perform tests to identify the two cations and the unknown anion in **FA 3**.

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**.

(i) Carry out the following tests. Carefully record your observations in Table 2.2.

Table 2.2

	tests	observations
1	Using a 10 cm^3 measuring cylinder, add 2 cm^3 of **FA 3** into a clean boiling tube. Using another 10 cm^3 measuring cylinder, measure out 7 cm^3 of aqueous sodium hydroxide. Slowly with shaking, add this completely to **FA 3**. Stir the contents of the boiling tube with a glass rod. Filter the mixture into a clean test-tube. The filtrate will be used for test **4**. While waiting, proceed to tests **2** and **3**.	
2	Add 1 cm depth of **FA 3** into a clean test-tube. Add 2 cm depth of aqueous sodium carbonate.	

tests		observations
3	Add 1 cm depth of **FA 3** into a clean test-tube. Add 1 cm depth of aqueous silver nitrate. Filter the mixture and discard the filtrate. Wash the residue by pouring deionised water through it. Discard the washings. Place the filter funnel containing the residue into a test-tube containing 1 cm depth of dilute nitric acid. Carefully add aqueous ammonia to the filter funnel until it covers the residue. The filtrate will collect in the test-tube containing the dilute nitric acid.	
4	Add 1 cm depth of the filtrate from test 1 into a clean test-tube. Add dilute sulfuric acid drop-wise, until in excess.	

[6]

(ii) Identify the two cations and the unknown anion in **FA 3** and state the evidence for each cation and the anion by completing Table 3.2.

Table 3.2

cation	evidence
anion	evidence

[3]

[Total: 13]

3 The reaction between potassium manganate(VII) and excess acidified potassium iodide is shown.

$$2MnO_4^-(aq) + 10I^-(aq) + 16H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 5I_2(aq) + 8H_2O(l)$$

The iodine liberated reacts with sodium thiosulfate solution.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

In this experiment, you are required to determine the concentration of potassium manganate(VII) in solution **P**. You are **not** provided with solution **P**.

FA 4 is 0.100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$.
FA 5 is 1.00 mol dm^{-3} sulfuric acid, H_2SO_4.
FA 6 is 0.500 mol dm^{-3} potassium iodide, KI.
FA 7 is a diluted solution of **P**.
Starch indicator.

(a) (i) You are to titrate **FA 7** with **FA 4** using starch as indicator.

Titration of FA 7 with FA 4

1. Fill the burette with **FA 4**.
2. Pipette 25.0 cm^3 of **FA 7** into a 250 cm^3 conical flask.
3. Using separate measuring cylinders, transfer to the conical flask
   - 25.0 cm^3 of **FA 5**,
   - 20.0 cm^3 of **FA 6**.
4. Titrate the liberated iodine with **FA 4** until the solution is pale yellow. Then add 6 drops of starch solution and carry on the titration until the deep blue colour is just discharged. **Swirl** the reaction mixture **continuously** during the titration.
5. Record your titration results, to an appropriate level of precision, in the space provided.
6. Repeat the titration until at least two consistent results are obtained.

Titration results

[3]

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

$V_{\mathbf{FA\ 4}}$ = ……..
[3]

(b) Calculations

(i) Calculate the amount of iodine produced in the reaction between 25.0 cm^3 of **FA 7** and 20.0 cm^3 of **FA 6**.

amount of iodine = …… [2]

(ii) Calculate the amount of $KMnO_4$ which reacted to produce the amount of I_2 determined in **(i)**.

amount of $KMnO_4$ = …… [1]

(iii) **FA 7** is a diluted solution of **P**, in which 34.50 cm^3 of **P** was made up to 250 cm^3 with deionised water in a graduated flask.

Calculate the molar concentration of $KMnO_4$ in solution **P**.

molar concentration of $KMnO_4$ = ... [2]

(iv) Calculate the mass of $KMnO_4$ needed to prepare 1.00 dm^3 of **P**.

[A_r: K, 39.1 Mn, 54.9 O, 16.0]

mass of $KMnO_4$ = ... [1]

(c) **(i)** Solution **P** was actually prepared by dissolving 21.0 g of $KMnO_4$ in 1.00 dm^3 of solution.

Calculate the difference between the actual value and your answer to **(b)(iv)** as a percentage of the actual value.

percentage = ... [1]

(ii) A student suggested that the experiment would be more accurate if a burette was used to measure the volume of **FA 6**.

State and explain whether you agree with the student.

.....

.....[1]

[Total: 14]

4 Planning

$[Ni(H_2O)_6]^{2+}(aq)$ reacts with $H_2NCH_2CH_2NH_2(aq)$ to give the purple complex ion, $[Ni(en)_3]^{2+}(aq)$, as shown in equation 4. $H_2NCH_2CH_2NH_2$ is abbreviated as *en*.

equation 4 $[Ni(H_2O)_6]^{2+}(aq) + 3H_2NCH_2CH_2NH_2(aq) \rightleftharpoons [Ni(en)_3]^{2+}(aq) + 6H_2O(l)$ K_c

It is possible to determine the concentration of a solution of $[Ni(en)_3]^{2+}$ using spectrometry.

A series of $[Ni(H_2O)_6]^{2+}$ solutions of known concentrations are prepared and treated with a large excess of $H_2NCH_2CH_2NH_2(aq)$ to form $[Ni(en)_3]^{2+}(aq)$ of different concentrations. For each concentration of $[Ni(en)_3]^{2+}(aq)$, a spectrometer is used to measure the absorbance of light by $[Ni(en)_3]^{2+}(aq)$. Absorbance is directly proportional to the concentration of $[Ni(en)_3]^{2+}(aq)$.

A graph of absorbance against concentration of $[Ni(en)_3]^{2+}(aq)$ is then plotted. This graph is known as a calibration line. By comparing the absorbance of a solution of unknown concentration with the calibration line, the concentration of $[Ni(en)_3]^{2+}(aq)$ in the unknown solution can be determined.

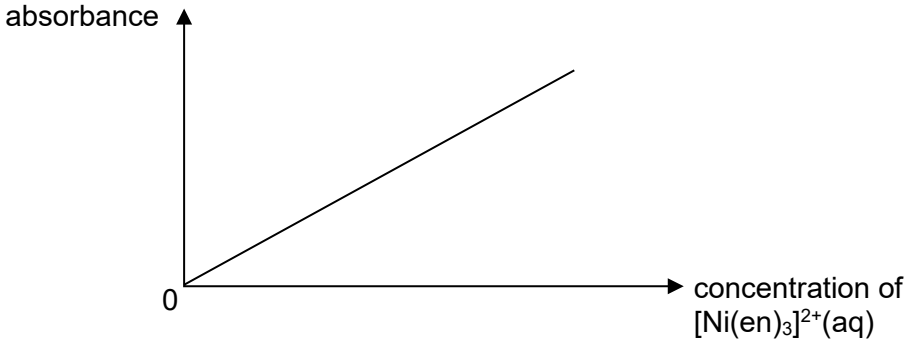

Fig 4.1

(a) Explain why $H_2NCH_2CH_2NH_2(aq)$ must be used in large excess in the preparation of $[Ni(en)_3]^{2+}(aq)$ to obtain the calibration line.

……..……..……..

……..……..……..

……..…..……..[1]

(b) Using the information given above, write a plan to prepare 100 cm^3 each of the following solutions.

solution	$[Ni(H_2O)_6]^{2+}$ / mol dm^{-3}
1	1.00×10^{-3}
2	8.00×10^{-4}
3	6.00×10^{-4}
4	4.00×10^{-4}
5	2.00×10^{-4}

You may assume that you are provided with:

- **FA 8**, 2.00×10^{-3} mol dm^{-3} $[Ni(H_2O)_6]^{2+}(aq)$;
- the apparatus normally found in a school or college laboratory.

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………

……… [2]

To determine a value for K_c, 25.0 cm^3 each of 2.00 x 10^{-3} mol dm^{-3} $[Ni(H_2O)_6]^{2+}(aq)$ and 6.00 x 10^{-3} mol dm^{-3} $H_2NCH_2CH_2NH_2(aq)$ are mixed to produce a solution of $[Ni(en)_3]^{2+}(aq)$. The absorbance of this solution is then measured. Using the calibration line in Fig 4.1, the concentration of $[Ni(en)_3]^{2+}(aq)$ can be determined. This can be used to calculate the concentrations of $[Ni(H_2O)_6]^{2+}(aq)$ and $H_2NCH_2CH_2NH_2(aq)$ in the equilibrium mixture and hence K_c.

The relationship between K_c and temperature in kelvin, T, is represented by the following equation.

$$\ln K_c = -\frac{\Delta H}{R}\left(\frac{1}{T}\right) + \frac{\Delta S}{R}$$

R is the molar gas constant with a value of 8.31 J K^{-1} mol^{-1}.
ΔH is the enthalpy change of reaction.
ΔS is the entropy change of reaction.

A plot of ln K_c against $1/T$ can then be used to graphically determine ΔH and ΔS.

(c) Plan an investigation to determine the effect of temperature, T, on the equilibrium constant, K_c, of the reaction between $[Ni(H_2O)_6]^{2+}(aq)$ and $H_2NCH_2CH_2NH_2(aq)$.

You may assume that you are provided with:
- **FA 8**, 2.00 x 10^{-3} mol dm^{-3} $[Ni(H_2O)_6]^{2+}(aq)$;
- **FA 9**, 6.00 x 10^{-3} mol dm^{-3} $H_2NCH_2CH_2NH_2(aq)$;
- a spectrometer;
- the apparatus normally found in a school or college laboratory.

In your plan you should include:
- an outline of how you would prepare a solution of $[Ni(en)_3]^{2+}(aq)$,
- an outline of how you would determine the concentration of $[Ni(en)_3]^{2+}(aq)$ in the solution at different temperatures,
- brief but specific details of how the concentrations, in mol dm^{-3}, of $[Ni(H_2O)_6]^{2+}(aq)$ and $H_2NCH_2CH_2NH_2(aq)$ in the equilibrium mixture can be determined, and how you would use these concentrations to determine K_c for one of your chosen temperatures.

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....[6]

(d) (i) Given that the reaction between $[Ni(H_2O)_6]^{2+}(aq)$ and $H_2NCH_2CH_2NH_2(aq)$ is exothermic, sketch a graph you would expect to obtain on the axes in Fig 4.2.

Explain your answer.

Fig 4.2.

Explanation

……

……

……[2]

(ii) Describe how you would use your graph in **4(d)(i)** to determine values for ΔH and ΔS.

……

……

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……[2]

[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. 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 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, 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