MATRICULATION AND SECONDARY EDUCATION CERTIFICATE EXAMINATIONS BOARD
UNIVERSITY OF MALTA, MSIDA

MATRICULATION CERTIFICATE EXAMINATION
ADVANCED LEVEL
SEPTEMBER 2012

SUBJECT:	CHEMISTRY
PAPER NUMBER:	I
DATE:	4th September 2012
TIME:	9.00 a.m. to 12.00 noon

Required Data: Relative atomic masses: H=1; N=14; Cl=35.5; Ca=40; Co=59; Ag=108. Self-ionization product for water, $K_w = 1 \times 10^{-14}$ mol^2 dm^{-6}. Gas constant, R = 8.31 J/mol K.

Answer all questions

1. The statements given below refer to the reaction:

$$Q + 2R \rightleftharpoons X + Y \qquad \Delta H = +250 \text{ kJ mol}^{-1}$$

Read each of the following statements and decide whether it is *True* or *False*. Give a reason for each answer. All parts carry equal marks.

(a) The system reaches equilibrium when the concentration of the reactants is equal to the concentration of the products.

_____

_____

_____

(b) When Q and R are mixed together the rate of the forward reaction increases until equilibrium is established.

_____

_____

_____

(c) A high value of the equilibrium constant K_C means that the forward reaction is very fast.

_____

_____

_____

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(d) Since the forward reaction is endothermic, if this system is heated when at equilibrium, the rate of the forward reaction increases but the rate of the reverse reaction decreases.

_____

_____

_____

(e) For this system, since the forward reaction is endothermic, the reverse reaction is exothermic.

_____

_____

_____

(f) When Q is added to the system in equilibrium, the forward reaction will occur to use up all the added material and so restore the equilibrium.

_____

_____

_____

(Total: 9 marks)

2. (a) When titanium(IV) chloride is treated with concentrated hydrochloric acid, it dissolves to give the complex ion $[TiCl_6]^{2-}$.

(i) What is a complex ion?

_____

(ii) Describe the bonding in a complex ion.

_____

_____

_____

(iii) Give the oxidation number of titanium in the complex ion.

_____

(iv) Give the coordination number of the titanium ion in the complex ion.

_____

(v) Suggest a name for $[TiCl_6]^{2-}$.

(iv) Draw a possible structure for this complex ion *(7 marks)*

(b) Cobalt(III) is found in a number of complexes with water and chloride ions. A sample of a compound of formula $CoCl_3(H_2O)_6$, weighing 0.368 g, was dissolved in water and made up to 100 cm^3. Excess silver nitrate solution was added to 10 cm^3 of the solution of the compound. The mass of silver chloride precipitated was 0.0395 g. Determine the formula of the complex ion present. *(5 marks)*

(Total: 12 marks)

3. Buffers are very important components of biological systems.

(a) (i) What is a buffer?

(ii) Describe the components of two types of buffer systems. *(2 marks)*

(b) Human blood is buffered mainly by the following system:

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

(i) Explain how this system can act as a buffer.

_____

_____

_____

(ii) Calculate K_a for H_2CO_3 given that the pH is 6.1 when the concentration of H_2CO_3 is equal to that of HCO_3^-.

_____

_____

_____

_____

(iii) The desired pH of human blood is about 7.4. Calculate the ratio of concentrations of the HCO_3^- and H_2CO_3 in blood at that pH.

_____

_____

_____

_____*(8 marks)*

(c) Suggest a reason why proteins too can act as buffers in biological systems. *(2 marks)*

_____

_____

_____

_____

(Total: 12 marks)

4. A mixture of calcium chloride and sodium chloride was analysed to determine its composition. A sample weighing 1.5 g was dissolved in water and the resulting solution treated with excess sodium ethanedioate in order to precipitate all the calcium ions as calcium ethanedioate (CaC_2O_4). The precipitate was filtered, washed and dissolved in sulfuric acid. The resulting ethanedioic acid ($H_2C_2O_4$) was warmed and titrated with 0.102 mol dm^{-3} potassium manganate(VII). On addition of the first small quantity of potassium manganate(VII), the purple colour of manganate(VII) persisted for some time but after that point any manganate(VII) added was quickly decolourized until the end-point was reached. A titre value of 27.6 cm^3 of potassium manganate(VII) was required for complete reaction. In this reaction the ethanedioic acid was converted to carbon dioxide.

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(a) Write an equation for the precipitation reaction. *(1 mark)*

(b) Write an equation for the reaction between ethanedioic acid and potassium manganate(VII).

(2 marks)

(c) Identify the oxidizing agent and reducing agent in the redox reaction described and give a reason for your answer. *(2 marks)*

(d) Explain why, during the titration, the colour of the first small amount of potassium manganate(VII) persisted in the mixture but after that point further addition of titrant was quickly decolourized. *(2 marks)*

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(e) Calculate the percentage by mass of calcium chloride in the original mixture. *(3 marks)*

(f) What volume of carbon dioxide measured at 26 ^{o}C and 1.01 x 10^{5} Nm^{-2} would one expect to collect as a result of this experiment? *(3 marks)*

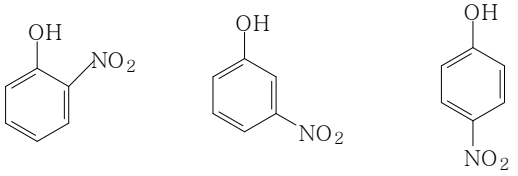
(Total: 13 marks)

5. (a) Explain with reasons which of the following molecules are expected to exhibit hydrogen bonding:

CH_3NH_2 H_2S CH_3F $HOCH_2CH_2OH$ CH_3OOCH_3

(4 marks)

(b) Explain with reasons which of the following substances has the lowest boiling point.



(5 marks)

(Total: 9 marks)

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6. Account for each of the following observations, adding any essential detail as necessary to explain the given statements. Statements of reaction should be supported by chemical equations.

(a) On heating with sodium nitrate, sulfuric acid liberates vapours of nitric acid.

_____

_____

_____ *(2 marks)*

(b) Lead nitrate produces a white precipitate on treatment with an acid. The precipitate dissolves on heating.

_____

_____

_____ *(2 marks)*

(c) Sodium chlorate(I) (hypochlorite) solution releases a gas on treatment with an acid.

_____

_____

_____ *(3 marks)*

(d) Lithium reacts with a gas to produce a white compound having a high melting point; electrolysis of the melt releases hydrogen at the anode.

_____

_____

_____

_____ *(3 marks)*

(e) Aluminium dissolves in potassium hydroxide to form a solution. On treating this solution with a suitable amount of an acid, a double salt can be isolated on crystallisation of the mixture.

_____

_____

_____

_____ *(3 marks)*

(Total: 13 marks)

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7. Fill in the blanks in the following table by providing a suitable example to illustrate the reaction or property described in the column on the left-hand side. Each section carries equal marks.

Reaction/Property	*Example*
(a) Reaction of a primary alcohol and a carboxylic acid to form an organic product and water.	
(b) Alkaline hydrolysis of a halogenoalkane to produce a secondary alcohol.	
(c) Alkaline hydrolysis of a halogenoalkane to produce a ketone.	
(d) An aromatic substance which exhibits *cis-trans* isomerism.	
(e) An aliphatic substance which exhibits keto-enol tautomerism.	

(Total: 10 marks)

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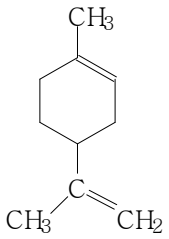
8. Consider the following organic compound called limonene which is found in citrus fruit:



(a) Give the empirical formula of limonene.

_____ *(1 mark)*

(b) Explain why limonene exists in two optical isomers and identify clearly the cause of this isomerism.

_____

_____

_____ *(2 marks)*

(c) Draw the structural formula of the organic product/s which you would expect to form when limonene is treated with each of the following reagents:

(i) excess hydrogen in the presence of Raney nickel:

_____

(ii) excess hydrogen bromide:

_____

(iii) ozone followed by treatment of the product with water in the presence of zinc dust:

_____ *(6 marks)*

(d) Explain how limonene can be obtained from lemon rind in which it is quite abundant using the technique of steam distillation and outline the principle of this technique.

_____

_____

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_____ *(3 marks)*

(Total: 12 marks)

9. Explain each of the following observations as fully as you can, giving chemical equations in support of statements of chemical change.

(a) A liquid substance **X,** of molecular formula $C_4H_{10}O_2$, emits white fumes with phosphorus pentachloride and reacts with acidified dichromate to produce a substance **Y,** with molecular formula $C_4H_8O_2$, which produces a red brown precipitate with Fehling solution. Substance **X** reacts with excess hot concentrated sulfuric acid to produce **Z**, having molecular formula C_4H_8O, which reacts with hydrogen to produce substance **W**. Substance **W** can be prepared by treating ethanol with hot concentrated sulfuric acid.

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_____ *(6 marks)*

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(b) There are four isomers of the aromatic hydrocarbon having molecular formula C_8H_{10}. On treatment with hot alkaline potassium permanganate, one of the isomers produces a substance from which benzoic acid can be obtained on acidification while another isomer produces a substance that can be converted into a product **D.** On heating, **D** readily converts into an acid anhydride.

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_____ *(4 marks)*

(Total: 10 marks)

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MATRICULATION AND SECONDARY EDUCATION CERTIFICATE EXAMINATIONS BOARD
UNIVERSITY OF MALTA, MSIDA

MATRICULATION CERTIFICATE EXAMINATION
ADVANCED LEVEL
SEPTEMBER 2012

SUBJECT:	CHEMISTRY
PAPER NUMBER:	II
DATE:	5th September 2012
TIME:	9.00 a.m. to 12.00 noon

Required Data: Relative atomic masses: C = 12.0; H = 1.0; O = 16.0; Cl = 35.5; Br = 80.0; Ag = 108.0. A Periodic Table is provided.

Answer two questions from each section and any other question.

1. This question is about the three equimolar liquid mixtures shown in the table. Each mixture is made up of two components and all measurements of saturation vapour pressure (SVP) were taken at the same temperature.

Mixture	**SVP of pure component 1 /N m^{-2}**	**SVP of pure component 2 /N m^{-2}**	**SVP of equimolar mixture /N m^{-2}**
1	Liquid **X** SVP = 53.3 x 10^3	Liquid **Y** SVP = 66.7 x 10^3	Mixture of **X**+**Y** = 93.3 x10^3
2	Liquid **A** SVP = 21.6 x 10^3	Liquid **B** SVP = 60.2 x 10^3	Mixture of **A**+**B** = 40.9 x10^3
3	Liquid **Q** SVP = 70.0 x 10^3	Liquid **R** SVP = 80.0 x 10^3	Mixture of **Q**+**R** = 62.7 x 10^3

(a) State Raoult's Law. *(2 marks)*

(b) Use Raoult's Law to determine which mixture is:
(i) an ideal solution;
(ii) a non-ideal solution showing positive deviation from Raoult's law;
(iii) a non-ideal solution showing negative deviation from Raoult's law. *(6 marks)*

(c) Explain, in terms of molecular interactions, the behavior of each type of mixture as shown by the given data. *(6 marks)*

(d) With the help of a boiling point-composition diagram, explain what happens when separation of **the ideal solution** is attempted. *(6 marks)*

(Total: 20 marks)

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2. The data given below are required in order to answer the following questions.

Enthalpy change of atomization $\Delta H^{\ominus}_a$ Mg	+ 150 kJ mol^{-1}	Electron affinity Cl	-364 kJ mol^{-1}
Enthalpy change of atomization $\Delta H^{\ominus}_a$ Cl	+121 kJ mol^{-1}	Enthalpy change of formation $\Delta H^{\ominus}_f$ $MgCl_2$	-642 kJ mol^{-1}
1^{st} ionization energy Mg	+736 kJ mol^{-1}	Enthalpy change of hydration $\Delta H^{\ominus}_{hyd}$ Mg^{2+}	-1920 kJ mol^{-1}
2^{nd} ionization energy Mg	+1450 kJ mol^{-1}	Enthalpy change of hydration $\Delta H^{\ominus}_{hyd}$ Cl^-	-364 kJ mol^{-1}

(a) With the help of a Born-Haber cycle, calculate a value for the lattice enthalpy of magnesium chloride. *(7 marks)*

(b) Use your answer to (a) together with additional data from the table to calculate a value for the enthalpy change of solution of $MgCl_2$. *(6 marks)*

(c) Is $CaCl_2$ expected to have a higher or lower lattice enthalpy than $MgCl_2$? Explain your answer. *(3 marks)*

(d) Describe how dilute sulfuric acid may be used to distinguish between samples of $MgCl_2$, $CaCl_2$ and $BaCl_2$. *(4 marks)*

(Total: 20 marks)

3. The rate of reaction of 2-bromooctane with the hydrogen sulfide ion (HS^-) depends on the concentration of both 2-bromooctane and hydrogen sulfide.

(a) Write the mechanism for this reaction. *(6 marks)*

(b) Give the rate equation for this reaction. *(3 marks)*

(c) With reference to the mechanism of this reaction, explain the meaning of the terms:

(i) molecularity of reaction;

(ii) transition state;

(iii) nucleophile;

(iv) rate-determining step. *(6 marks)*

(d) The reaction occurs more rapidly on increasing the temperature and no reaction occurs at very low temperatures. Use the Maxwell-Boltzmann distribution of molecular energies and the collision theory to explain this statement. *(5 marks)*

(Total: 20 marks)

4. Account for the following observations, identifying all the organic substances mentioned either by name or structural formula and including essential experimental details of the reactions involved. All sections carry equal marks.

   (a) Bromine water reacts with phenylamine to produce an immediate white precipitate. This precipitate can, on suitable treatment, be converted into a product with molecular formula $C_6H_3Br_3$.
   (b) Methanal reacts with hot aqueous potassium hydroxide to produce a mixture of products which, on treatment with excess sulfuric acid and heating transforms into an organic product having the same empirical formula as methanal but double the molecular mass.
   (c) Treatment of propanone with barium hydroxide (as an alkali) forms a product with empirical formula C_3H_6O. This product readily dehydrates to give a substance which, on hydrogenation, converts into a ketone with molecular formula $C_6H_{12}O$.
   (d) There are four isomers of molecular formula C_3H_9N; all the isomers react with hydrogen chloride to produce crystalline compounds but only two of the isomers react with a mixture of cold aqueous hydrochloric acid and sodium nitrite to form an organic substance and an inert gas among the products.

   (20 marks)

Section B

5. Ionization energy, electronegativity and atomic radius are three physical properties that vary from element to element in the Periodic Table.

   (a) Define first ionization energy and electronegativity. *(2 marks)*
   (b) Discuss the factors that determine the atomic radius of an atom. *(2 marks)*
   (c) Describe how these three physical properties vary across Period 2 (Li to Ne) and upon descending a group of the Periodic Table. Explain why these trends occur. Include a sketch of the graph of ionization energy against atomic number for the elements Li to Ne.

   (16 marks)

   (Total: 20 marks)

6. Account as fully as possible for the following observations, giving chemical equations to support statements of reactions mentioned. Each section carries equal marks.

   (a) The reaction of chlorine with aqueous alkali gives different products, depending on the temperature.
   (b) The formation of a yellow precipitate from a solution on treatment with aqueous silver nitrate implies the possible presence of two different anions in the solution. Use of dilute nitric acid can distinguish between these two possibilities.

This question continues on the next page.

(c) Anhydrous aluminium chloride cannot be made by heating to constant mass crystals of aluminium chloride-6-water because a different product will be obtained. The anhydrous chloride can be prepared by a different method.

(d) Addition of dilute sulfuric acid to aqueous sodium thiosulfate generates a yellow precipitate and a gas which on passage through aqueous sodium dichromate produces a green coloured solution.

(20 marks)

7. (a) *(i)* Explain in detail how a small amount of a pure sample of 1-bromobutane can be prepared in the laboratory from butan-1-ol. Assume the source of bromine is potassium bromide.

Your account should include a properly labelled diagram of the apparatus that can be used to prepare the compound and another diagram to illustrate the apparatus required for the purification of the compound.

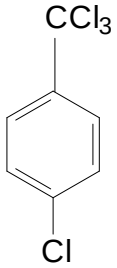
(ii) Explain how one could check if the product so obtained is pure *(experimental details of the technique are not required)*. *(14 marks)*

(b) Calculate the mass of 1-bromobutane that can be obtained from 18.50 g of butan-1-ol assuming that the yield is 85%. *(3 marks)*

(c) Explain how infrared spectrophotometry can be used to check whether a purified sample of 1-bromobutane contains traces of unreacted butan-1-ol. *(3 marks)*

(Total: 20 marks)

8. (a) Outline, but including essential experimental detail, how one could prepare substance **I** starting from benzene and using any aliphatic or inorganic substances as required.



(**I**) *(10 marks)*

(b) Substance (**I**) was heated with hot aqueous sodium hydroxide and the mixture was cooled in an ice bath and then acidified with excess dilute nitric acid. Upon acidification, a white precipitate (**II**) formed which was filtered off. To the filtrate, excess silver nitrate was added and another white precipitate (**III)** formed which was filtered, washed and dried.

(i) Give the name and structural formula of white precipitate (**II**) and explain the changes involved.

(ii) Identify the white precipitate (**III**) and calculate the mass obtained from 5 g of substance **(I)**. *(10 marks)*

(Total: 20 marks)

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UNIVERSITY OF MALTA, MSIDA

MATRICULATION CERTIFICATE EXAMINATION
ADVANCED LEVEL
SEPTEMBER 2012

SUBJECT:	CHEMISTRY
PAPER NUMBER:	III – *Practical*
DATE:	31st August 2012
TIME:	3 hours

Answer all questions.

1. In this experiment you are required to determine the molar concentration of a solution of copper(II) sulfate and the enthalpy change for the reaction between zinc and copper sulfate.

   You are supplied with the following chemicals:

   (i) about 150 cm^3 of a solution of copper(II) sulfate labelled $\mathbf{S_n}$ where n is the candidate laboratory number;

   (ii) a solution of 0.100 mol dm^{-3} sodium thiosulfate labelled **T**;
   (iii) access to a solution of 10% potassium iodide labelled '10% KI';
   (iv) zinc powder in a sachet labelled 'Zn'.

   (a) Enter the value of your laboratory number, n, in the following box.

CANDIDATE LABORATORY NUMBER, n:.....

Determination of the molar concentration of copper(II) in solution $\boldsymbol{S_n}$

(b) Fill the burette with solution **T**.

(c) Using a pipette, transfer 25.0 cm^3 of solution $\mathbf{S_n}$ into a volumetric flask and make up the solution to 250 cm^3 with distilled water. This is solution $\mathbf{S_{ndil}}$. Using a suitably rinsed pipette, transfer 25.0 cm^3 of solution $\mathbf{S_{ndil}}$ into a conical flask, add 20 cm^3 10% potassium iodide and titrate the liberated iodine with solution **T** using starch indicator towards the end of the titration. Repeat the titration for concordant results and enter your results in the table below.

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Results of titration:

Titration number:	1st	2nd	3rd
Final burette reading (cm^3)			
Initial burette reading (cm^3)			
Titre value (cm^3)			

Mean titre value: .....cm^3 of solution **T**

(d) Given that copper(II) reacts with iodide ions according to the equation:

$$2\ Cu^{2+}(aq) + 4\ I^-(aq) \longrightarrow 2\ CuI(s) + I_2(aq)$$

and thiosulfate ions react with the iodine liberated according to the equation:

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

calculate the molar concentration of Cu(II) ions in **solution S_n**.

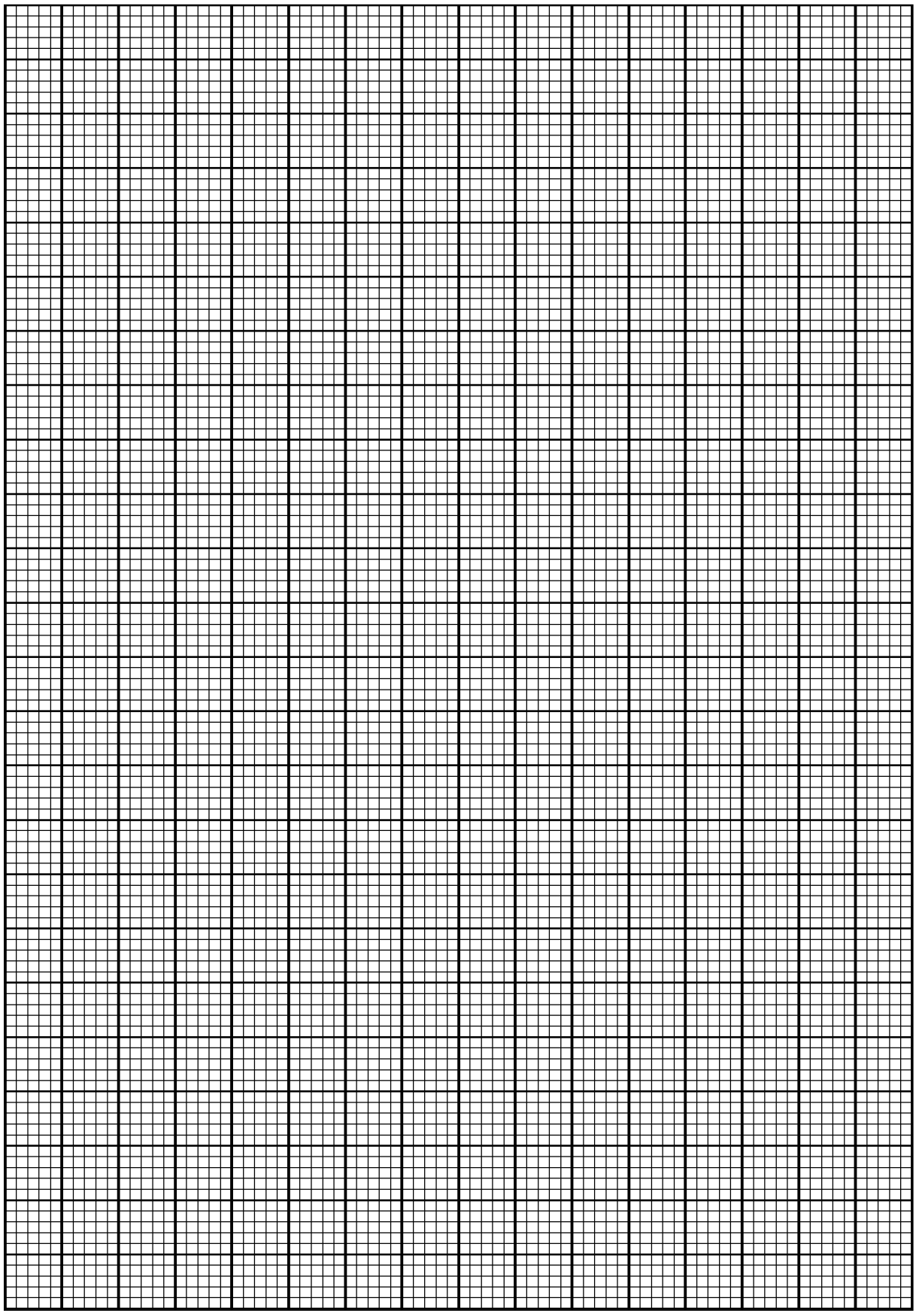
(e) Transfer 50.0 cm^3 of solution $\mathbf{S_n}$ into a polystyrene cup firmly held in a 250 cm^3 beaker. Place the thermometer provided into the solution in the polystyrene cup, stir the solution and record the temperature to the nearest 0.5 ^oC in the table below. Continue to stir the solution, recording its temperature at half minute intervals. At exactly 3 minutes, add all the zinc powder to solution $\mathbf{S_n}$, stirring continuously. Record the temperature of the solution in the polystyrene cup every half minute from 3.5 to 10.0 minutes.

Temperature readings:

Time/min	0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
Temperature/ ^oC											

Time/min	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0
Temperature/ ^oC										

(f) Plot a graph of temperature against time.



(g) Use your graph to determine the temperature change ΔT, for the reaction.

$\Delta T =$ _____

(h) Calculate the number of moles of copper sulfate in 50 cm^3 of $\mathbf{S_n}$.

(i) Calculate the heat evolved in the reaction. (Assume that the final volume of the solution after the zinc powder is added is 50 cm^3. The specific heat capacity of the solution is 4.18 J K^{-1} g^{-1} and its density is 1.00 g cm^{-3}).

(j) Calculate the molar enthalpy change of the reaction:

$$Zn\ (s) + Cu^{2+}\ (aq) \longrightarrow Zn^{2+}\ (aq) + Cu\ (s)$$

(50 marks)

2. You are provided with two solids **A** and **B**, containing the same cation. Carry out the following tests and record your observations and inferences in the spaces provided.

(a) Perform a flame test on solid **A**.

Observation	*Inference*

(b) Perform this test on both **A** and **B** separately.

Add a few drops of dilute sulfuric acid. Test any gases evolved.

Observation	*Inference*

(c) Heat a small amount of solid **A** in a dry boiling tube and test any gas evolved.

Observation	*Inference*

(d) Prepare an aqueous solution of substance **A** and add about 1 cm^3 of aqueous magnesium sulfate. *Keep the mixture for the following test.*

Observation *Inference*

_____ _____

_____ _____

(e) Heat the mixture obtained in (d) and test the gas evolved.

Observation *Inference*

_____ _____

_____ _____

(f) Dissolve a few crystals of substance **B** in about 1 cm^3 water and treat it with drops of calcium chloride solution. Then add dilute hydrochloric acid to the mixture until in excess.

Observation *Inference*

_____ _____

_____ _____

(g) Prepare a solution of substance **B** and add about 2 cm^3 sulfuric acid followed by a few drops of potassium manganate(VII).

Observation *Inference*

_____ _____

_____ _____

Conclusions: **A** is ……..

B is …….. *(25 marks)*

3. You are provided with an organic liquid labelled **C**. Carry out the following tests on **C** and record your observations and inferences.

   (a) Ignite a few drops of **C** on a crucible lid.

Observation	*Inference*

   (b) Add a few drops of **C** to about 1 cm^3 of 2,4-dinitrophenylhydrazine.

Observation	*Inference*

   (c) Add about 1 cm^3 of **C** to an equal volume of a solution of sodium hydrogen carbonate.

Observation	*Inference*

   (d) To about 1 cm^3 of **C**, add an equal volume of a mixture of anhydrous zinc chloride and concentrated hydrochloric acid (**CARE! VERY CORROSIVE)** and allow the mixture to stand.

Observation	*Inference*

   (e) Place about 1 cm^3 of **C** in a boiling tube and add an equal volume of glacial ethanoic acid. Add a few drops of concentrated sulfuric acid **(CARE! VERY CORROSIVE)** and heat the mixture in a water bath for a few minutes. Allow to cool and pour the mixture into a small beaker containing some aqueous sodium carbonate.

Observation	*Inference*

Please turn the page.

(f) Add aqueous sodium hydroxide slowly to about 1 cm^3 of iodine solution until the colour becomes faint yellow. Add two drops of **C.**

Observation	*Inference*
_____	_____
_____	_____

Conclusion: A possible structural formula for **C** is:

(25 marks)