MATRICULATION AND SECONDARY EDUCATION CERTIFICATE EXAMINATIONS BOARD

UNIVERSITY OF MALTA, MSIDA

MATRICULATION EXAMINATION
ADVANCED LEVEL
SEPTEMBER 2013

SUBJECT:	CHEMISTRY
PAPER NUMBER:	I
DATE:	3rd September 2013
TIME:	9.00 a.m. to 12.00 noon

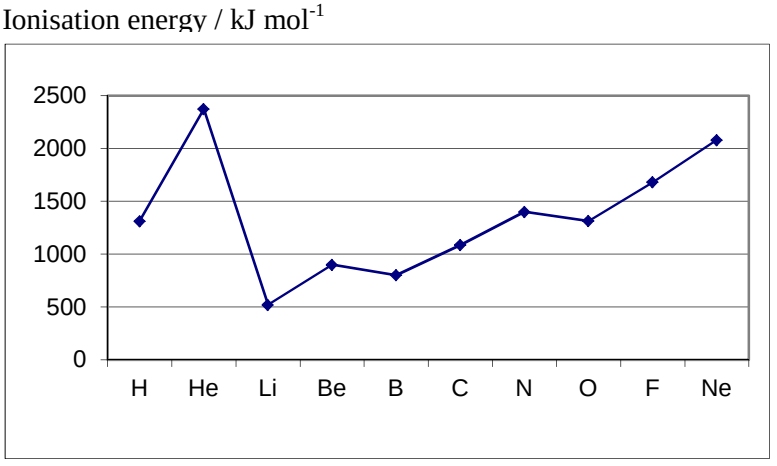
Required Data: Relative atomic masses: H = 1; C = 12; Br = 80; Cl = 35.5; Na = 23

Answer all questions

1. (a) Write an equation for the first ionisation of an element.

(2 marks)

(b) Explain all the trends in the following graph, which shows the first ionization energies of the elements H to Ne.



(4 marks)

(c) (i) Write an equation for the first electron affinity of an element.

(ii) The first electron affinity of oxygen is –142 kJ mol^{-1} and the second electron affinity of the element is +844 kJ mol^{-1}. Explain this large difference in values between the first and second electron affinity.

(4 marks)

(Total = 10 marks)

2. (a) Define the term electronegativity.

(1 mark)

(b) The C=O bonds in carbon dioxide are considered to be *polar*.

(i) Explain the term in italics.

(ii) Explain why, despite polar bonds, carbon dioxide is not a polar molecule.

(4 marks)

(c) Explain the following observations.

(i) The bonds in the carbonate ion are all of the same length.

(ii) Unlike the other alkali metal carbonates, lithium carbonate is thermally unstable.

(6 marks)

(Total = 11 marks)

3. Consider the following data:

(I) $\frac{1}{2}N_2\,(g) + \frac{1}{2}O_2\,(g) \rightleftharpoons NO\,(g)$ $\Delta H^{\ominus} = +90.3 kJ\ mol^{-1}$

(II) $\frac{1}{2}N_2\,(g) + O_2\,(g) \longrightarrow NO_2\,(g)$ $\Delta H^{\ominus} = +33.1\ kJ\ mol^{-1}$

(a) Use Hess' Law to determine the enthalpy change of the following reaction

$$NO\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow NO_2\,(g)$$

(3 marks)

(b) The entropy change in reaction (II) is said to be negative. Explain this statement.

(2 marks)

(c) In light of the given data, explain why reaction (II) can never be spontaneous.

(2 marks)

(d) Write an expression for K_p for reaction (I).

(1 mark)

(e) Calculate the value of K_p for reaction (I) at 2127 °C if the equilibrium pressures of N_2, O_2 and NO are 7.8 atm, 4.8 atm and 0.3 atm respectively.

(2 marks)

(f) Predict, stating your reasons, the direction of the net reaction as a result of:

(i) an increase in temperature at constant pressure.

(ii) an increase in pressure at constant temperature.

(4 marks)

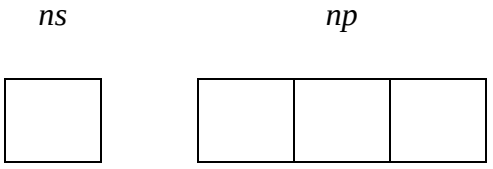
(g) The rate of reaction (I) is found to increase by a factor of four by doubling the concentration of NO whilst keeping that of O_2 constant. However, the rate only doubles when the concentration of O_2 is doubled whilst keeping that of NO constant. Deduce an expression for the rate of the reaction.

(3 marks)

(Total = 17 marks)

4. This question is about two elements of Group IV.

(a) (i) Use the following diagram to represent the electronic configuration of the outermost shell of silicon.



(ii) Using a similar diagram, explain how the carbon exhibits a valency of 4 and why the bonds in methane are equivalent.

(4 marks)

(b) Briefly explain why silicon tetrachloride undergoes hydrolysis but carbon tetrachloride does not.

(2 marks)

(c) Lead forms two chlorides, namely $PbCl_2$ and $PbCl_4$. Explain how the existence of these compounds illustrates the inert pair effect in lead.

(2 marks)

(d) The E^o value of the Sn^{2+}/Sn^{4+} electrode is +0.15 V whilst that of the Fe^{2+}/Fe^{3+} electrode is + 0.77 V. Explain as fully as possible how the electrode potentials can be used to predict whether Sn^{2+} reduces Fe^{3+} or Fe^{2+} reduces Sn^{4+}.

(3 marks)

(Total = 11 marks)

5. Consider the following conversions:

$$Cr^{3+}(aq) \xrightarrow[A]{H_2O_2, OH^-} CrO_4^{2-}(aq) \xrightarrow[B]{} Cr_2O_7^{2-}(aq)$$

(a) Write a balanced ionic equation to represent conversion A.

(4 mark)

(b) State how conversion B may be achieved and how it can be reversed again.

(3 marks)

(c) An aqueous solution of Cr^{3+} (aq) exhibits a pH lower than 7. Explain this observation.

(2 marks)

(d) Chromium(III) forms a complex ion with NH_3 in which the metal has a coordination number of six.

(i) Give the structural formula and describe the bonding present in the complex ion.

(ii) Explain why with the ligand $NH_2CH_2CH_2NH_2$, chromium forms a complex with a ligand : metal ratio is 3:1.

(4 marks)

(Total = 13 marks)

6. (a) Account in terms of structure and bonding for the fact that at room temperature chlorine is a gas while bromine is a liquid and iodine a volatile solid.

(1 mark)

(b) The strength of the X_2 bond varies in the following order:

$F_2 < Cl_2 > Br_2 > I_2$

Explain this variation.

(2 marks)

(c) Concentrated sulfuric(VI) acid is added drop wise over 0.5 g of NaCl until all the salt has disappeared. Calculate the volume of gas is produced at 298 K and 101.33 kPa. The value of the gas constant is 8.314 N m K^{-1} mol^{-1}.

(3marks)

(Total = 6 marks)

7. Give the name and structure of a compound that fits the descriptions given below.
(All parts carry equal marks)

Description	**Name and structure**
A compound which gives ethylamine on treatment with bromine and concentrated alkali.	
A six-carbon hydrocarbon which is unable to form any addition reaction product.	
A hydrocarbon that undergoes an addition reaction with water in the presence of mercury(II) sulfate and dilute sulfuric acid at 60^{o}C to form ethanal.	
A compound containing carbon, hydrogen and oxygen that undergoes a disproportionation reaction when treated with concentrated sodium hydroxide.	
A compound containing carbon, hydrogen, nitrogen and oxygen that may be converted into a zwitterion.	

(10 marks)

8. A compound **K** has the following composition by mass 35.04% carbon; 6.57% hydrogen and 58.39% bromine. The RMM of **K** is 137.

   (a) Determine the molecular formula of compound **K**.

(3 marks)

   (b) Give the structure of four isomers which have this molecular formula and classify these isomers as primary, secondary or tertiary halogenoalkanes.

(4 marks)

   (c) When an isomer of K is treated with ethanolic potassium hydroxide and boiled under reflux, three possible organic molecules may be formed. Identify the isomer of K by giving its systematic name and give the structures of the possible organic products.

(4marks)
(Total = 11 marks)

9. Propanone reacts with the Grignard reagent ethylmagnesium iodide to form a product from which a tertiary alcohol can be prepared.

   (a) Explain how the Grignard reagent can be prepared in the laboratory.

(2 marks)

   (b) Write chemical equations to show the conversion of propanone into the tertiary alcohol.

(2 marks)

   (c) On adding a few drops of the tertiary alcohol to concentrated hydrochloric acid mixed with anhydrous zinc chloride, the clear solution becomes turbid. Explain this observation in terms of the chemical changes involved.

(2 marks)

   (d) Write a mechanism for the reaction of 2-iodo-2-methylbutane with a solution of potassium cyanide.

(5 marks)

(Total = 11 marks)

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MATRICULATION AND SECONDARY EDUCATION CERTIFICATE EXAMINATIONS BOARD

UNIVERSITY OF MALTA, MSIDA

MATRICULATION EXAMINATION
ADVANCED LEVEL
SEPTEMBER 2013

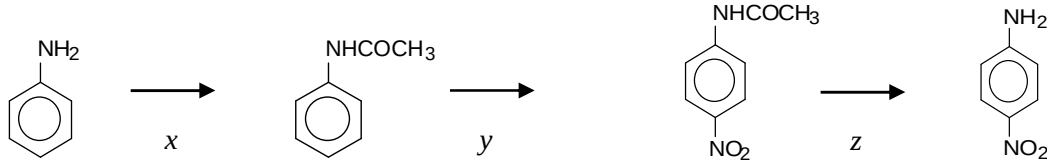
SUBJECT:	CHEMISTRY
PAPER NUMBER:	II
DATE:	4th September 2013
TIME:	9.00 a.m. to 12.00 noon

Required Data: Relative atomic masses: H = 1; C = 12; N = 14; O = 16; S = 32; Cl 35.5
The ionisation constant of water, $K_w = 10^{-14}$ mol^2 dm^{-6}
A Periodic Table is provided.

Answer two questions from each section and any other question.

Section A

1. A series of reactions were carried out to convert a compound **K** into product **N**:

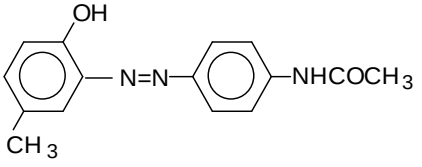


K **L** **M** **N**

(a)
(i) Name compound **N**.
(ii) Give the reagents and conditions required for conversions *x*, *y* and *z*.
(iii) Conversion *y* gives 79% yield. What mass of product **M** is expected when starting with 10.0g of **L**?

(10 marks)

(b) Compound **M** may be converted into the compound **O** via three stages.



O

Describe the three stages giving reactants, reaction conditions, a balanced chemical equation and the name of the type of reaction involved in each stage. You may use both organic and inorganic reactants in order to carry out the conversion.

(10 marks)
(Total = 20 marks)

2. The iodination of propanone follows the following rate law:

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

(a) (i) Describe a series of experiments involving titrimetric analysis that one would use, in order to follow the rate of the reaction. In your answer describe how you would prepare the initial reaction mixture and the reagent(s) you would use for the analysis. Indicate how you would use the data you obtain to determine the rate of the reaction at various times and rate of reaction at different concentrations.

(ii) Sketch separate graphs of the variation of the rate of reaction versus the concentration of H^+ and iodine.

(iii) Suggest why iodine is not present in the rate equation.

(12 marks)

(b) At 298 K and the when initial concentration of propanone is 0.1 mol dm^{-3} and the pH is 1, the rate of the reaction is 1.25×10^{-5} mol dm^{-3} s^{-1}.

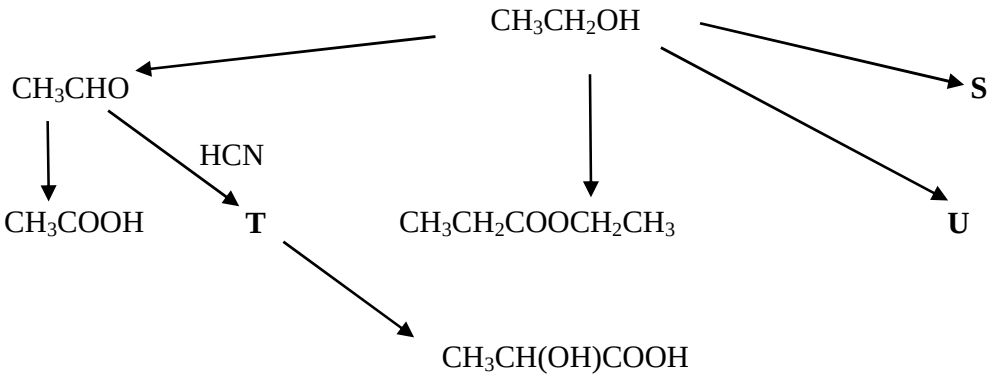
(i) Calculate the rate of reaction when initial pH of the reaction is changed to 2.5.

(ii) Estimate the rate constant of the reaction at 308 K.

(8 marks)

(Total = 20 marks)

3. Ethanol may be converted into a number of other compounds. Some of these conversions are represented by the reaction scheme given below.



(a) Describe how the following conversions may be carried out (using any organic or inorganic reagents):

(i) CH_3CHO to CH_3COOH

(ii) CH_3CH_2OH to $CH_3CH_2COOCH_2CH_3$

(4 marks)

(b) Obtaining a good yield of CH_3CHO via the conversion of CH_3CH_2OH to CH_3CHO requires carefully controlled conditions. Explain why this is necessary and describe how a good yield may be achieved.

(2 marks)

(c) Compound CH_3CH_2OH may be converted into a compound **S** with formula $C_4H_{10}O$ and a compound **U** with empirical formula CH_2. State how these conversions may be achieved by giving reagents, conditions and a chemical equation.

(6 marks)

(d) Compound CH_3CHO may be converted into compound **T** via a nucleophilic addition reaction.

(i) Identify compound **T**.
(ii) Give the mechanism and identify the nucleophile involved in this reaction.

(6 marks)

(e) Compound $CH_3CH(OH)COOH$ exhibits *optical isomerism*.

(i) What are *optical* isomers?
(ii) Identify the feature in compound $CH_3CH(OH)COOH$ that enables it to exhibit optical isomerism.

(2 marks)

(Total = 20 marks)

4. This question is concerned with ammonia and a number of nitrogencompounds.
(All parts carry equal marks.)

(a) Explain briefly how the raw materials for the manufacture of ammonia are produced.

(b) *The industrial production of ammonia revolutionised agricultural food production but this has had negative environmental impacts.* Discuss this statement briefly.

(c) Describe the industrial preparation of nitric(V) acid from ammonia.

(d) Give chemical reactions for the laboratory production NO_2^-, NO_2, N_2O and NH_3 from the nitrate(V) ion.

(e) Discuss why nitrogen is an unreative gas yet hydrazine (N_2H_4) can be used as a rocket fuel.

(Total = 20 marks)

Section B

5. Briefly explain the following statements using chemical principles ***(All parts carry equal marks)***:

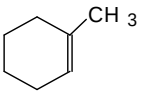
(a) Methylbenzene has carbon atoms in two different forms of hybridization.

(b) The enthalpy of formation of benzene is different from that predicted from the Kekule' structure.

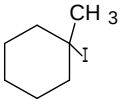
(c) Chloroethene and 3-hydroxybutanoic acid can both form polymers but the types of polymer formed and the processes involved are different.

(d) Steam distillation is suitable for the purification of phenylamine (b.p. 190^oC) whereas distillation is not.

(e) The only product when hydrogen iodide reacts **W**, is **X**.



W



X

(Total = 20 marks)

6. This question is concerned with some aspects of the chemistry of compounds of oxygen and sulfur. (***All parts carry equal marks)***

(a) Describe the allotropy of both oxygen and sulfur and explain why only allotropes of oxygen exhibit different chemical properties, identify the reducing and the oxidizing agent.

(b) Give a chemical equation to describe a laboratory preparation of SO_2 and deduce a redox between iron(III) by SO_2.

(c) Give two sources of SO_2 in the atmosphere and three environmental problems this pollutant causes.

(d) The solubility product of barium sulfate is 1.1×10^{-10} mol^2 dm^{-6}. Calculate the solubility of the salt in g dm^{-3}.

(Total = 20 marks)

7. (a) Codeine ($C_{18}H_{21}NO_3$) is found in many pain relief formulations as a salt with HCl known as codeine hydrochloride. What is the pH of a solution consisting of 5.8 g codeine hydrochloride in a 250 cm^3 of aqueous solution? **(pK_b of codeine is 5.80)**

(8 marks)

(b) (i) Explain why the extraction of codeine by an organic solvent such as dichloromethane is more efficient from alkaline pH environments?

(ii) Extraction of codeine can be carried out using supercritical carbon dioxide. Explain why this is more environmentally friendly than the use of dichloromethane.

(iii) Draw a labeled phase diagram of carbon dioxide indicating clearly the critical point and the region where carbon dioxide is a supercritical fluid.

(12 marks)

(Total = 20 marks)

8. (a) State Raoult's law and explain what is meant by an ideal solution.

(4 marks)

(b) (i) Whilst in the process of conducting an environmental impact assessment a chemist was required to estimate the % by mass of benzene vapour in vapour from petrol. In order to carry out this estimate the chemist modeled petrol as a system of 1 cm^3 of benzene mixed with 99 cm^3 heptane. What would be the fraction of benzene in % by mass of vapour over petrol according to the chemist's model at 293 K?
(Assume the densities of benzene and heptane at this temperature are 0.83 g cm^{-3} and 0.68 g $cm^{-3}$and the vapour pressures are 9.8 kPa and 5.3 kPa respectively.)

(ii) The value obtained experimentally is lower than that calculated by the chemist. Suggest reasons for this observation.

(16 marks)

(Total = 20 marks)

Index No_____ **AM 06/III.13s**

MATRICULATION AND SECONDARY EDUCATION CERTIFICATE EXAMINATIONS BOARD

UNIVERSITY OF MALTA, MSIDA

MATRICULATION EXAMINATION
ADVANCED LEVEL
SEPTEMBER 2013

SUBJECT:	CHEMISTRY
PAPER NUMBER:	III – *Practical*
DATE:	30th August 2013
TIME:	3 hours

Answer all questions.

1. In this experiment you are required to standardize a solution of copper(II) sulfate using an iodometric titration and to determine the enthalpy change of the reaction between aqueous copper(II) sulfate with iron.

   You are supplied with the following chemicals:

   (i) about 200 cm^3 of 0.100M sodium thiosulfate labelled **T ;**
   (ii) about 250 cm^3 of a solution of copper(II) sulfate labelled $\mathbf{S_n}$ where n is the candidate laboratory number;
   (iii) 3 g powdered iron in a sachet labeled **Fe**.

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

CANDIDATE LABORATORY NUMBER, n:.....

Standardisation of the copper(II) sulfate solution $\boldsymbol{S_n}$

(b) Using a burette transfer 100.0 cm^3 of solution $\mathbf{S_n}$ into a 250 cm^3 volumetric flask and dilute to the mark with distilled water. This diluted solution will be referred to as $\mathbf{DS_n}$ and will be used for the iodometric titration.

(c) Pipette 25.0 cm^3 of solution $\mathbf{DS_n}$ into a conical flask, add about 10 cm^3 of 10% potassium iodide solution and 1 cm^3 dilute sulfuric acid. Titrate with solution **T**, using **starch indicator** near the endpoint. Repeat for concordant results and enter your data in the Table below.

(d) Enter your results in the table below:

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**

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

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

calculate (to 3 significant figures) the molar concentration of solution $\mathbf{DS_n}$ and hence deduce the molar concentration of the original copper(II) sulfate $\mathbf{S_n}$.

Determination of the enthalpy change of the reaction of copper(II) with iron

(f) Using a burette, transfer 50.0 cm^3 of solution $\mathbf{S_n}$ into a polystyrene cup placed inside an empty 400 cm^3 beaker. Open the sachet (**Fe**) containing the iron powder and place it next to the cup containing the solution $\mathbf{S_n}$. Place the thermometer provided in solution $\mathbf{S_n}$ and record the temperature at 0.5 minute intervals, stirring continuously with the thermometer. At 2.5 minutes, pour at once the iron powder into solution $\mathbf{S_n}$ and continue to take temperature readings from minute 3 to minute 15 at 1-minute intervals, meanwhile stirring continuously. Enter your results in the following table.

Time (minutes)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	4.0	5.0
Temperature (°C)						x			

6.0	7.0	8.0	9.0	10.0	11.0	12.0	13.0	14.0	15.0

(g) Using the grid below, plot a graph of temperature (y-axis) against time and using the graph deduce the maximum rise in temperature corrected for heat losses.

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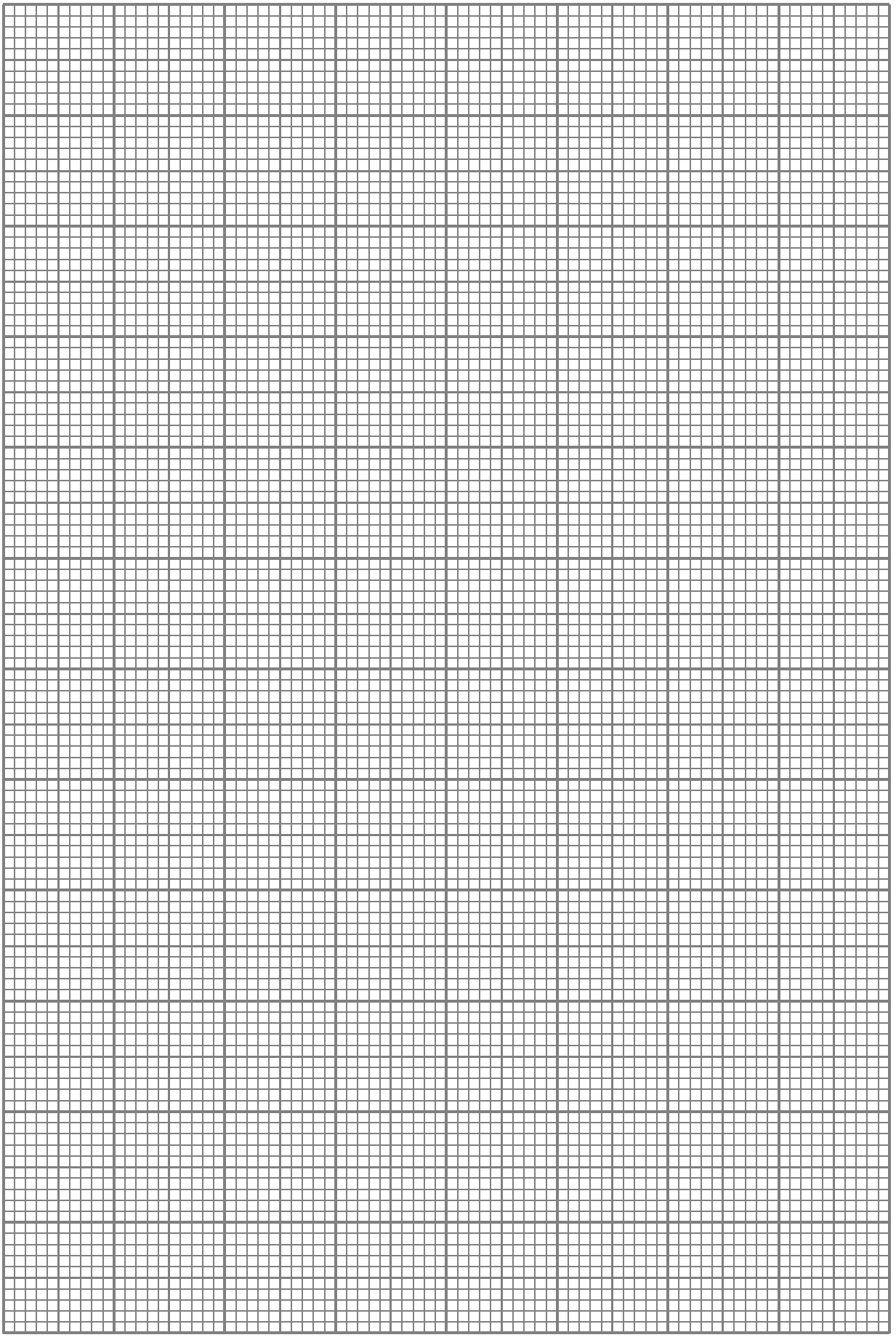

(h) The maximum corrected temperature rise = _____ °C

(i) Assuming that the specific heat capacity of the final solution is 4.18 J cm^{-3} °C^{-1}, and assuming that iron is used in excess, calculate the enthalpy change for the reaction:

$$CuSO_4\ (aq) + Fe\ (s) \longrightarrow FeSO_4\ (aq) + Cu\ (s)$$

(*50 marks)*

2. You are provided with two white inorganic powders labelled **G** and **H**. Carry out the following tests and record your observations and inferences in the spaces provided.

a) Dissolve approximately 1 g of substance **G** in 10 cm^3 of water; **RETAIN THE SOLUTION FOR SUBSEQUENT TESTS**.

Observation	*Inference*

b) Using the pH paper provided, find the pH of the solution.

Observation	*Inference*

c) To 1 cm^3 portions of the solution, add:

(i) sodium hydroxide solution, drop-wise at first, then in excess;

Observation	*Inference*

(ii) aqueous ammonia drop-wise until in excess.

Observation	*Inference*

d) Acidify 2 cm^3 of the solution with 1 cm^3 of dilute hydrochloric acid, and add a few drops of barium chloride solution.

Observation	*Inference*

e) Dissolve approximately 0.5 g of **H** in 5 cm^3 of water. **RETAIN SOLUTION FOR SUBSEQUENT TESTS.**

Observation *Inference*

_____ _____

_____ _____

_____ _____

f) To about 2 cm^3 of the solution add a few drops of barium chloride and then add about 1 cm^3 of hydrochloric acid and test for any gases evolved using lime water.

Observation *Inference*

_____ _____

_____ _____

_____ _____

g) Perform a flame test on the solution from test (f).

Observation *Inference*

_____ _____

_____ _____

_____ _____

Conclusion

Powder **G** is probably : _____

Powder **H** is probably : _____

(25 marks)

3. You are provided with an organic solid substance labelled **I**. Perform the following tests on **I** and record your observations and inferences in the spaces provided.

   a) Burn a few crystals of **I** on a crucible lid and observe any changes.

   Observation *Inference*

   _____ _____

   _____ _____

   _____ _____

   b) Add a few crystals of **I** to about 3 cm^3 of water and shake. Test with litmus paper. Add about 1 cm^3 of sodium carbonate solution.

   Observation *Inference*

   _____ _____

   _____ _____

   _____ _____

   c) Place approximately 0.5 g of **I** in a test tube and add 1 cm^3 of concentrated dilute sulfuric acid. Test for any gases evolved. If no reaction is observed, then heat in a boiling water bath for **2 minutes**.

   Observation *Inference*

   _____ _____

   _____ _____

   _____ _____

   d) Prepare a solution of **I** by dissolving about 0.5 g of the solid in 10 cm^3 of water.

   i) Add 1 cm^3 of aqueous calcium chloride solution to 1 cm^3 of the solution of **I** then add dilute hydrochloric acid.

   Observation *Inference*

   _____ _____

   _____ _____

   _____ _____

ii) Acidify 1 cm^3 of the solution with 1 cm^3 of sulfuric acid and add some drops of aqueous potassium permanganate. Heat gently if no reaction is observed.

Observation	*Inference*

Conclusion

Substance **I** is probably: _____

(25 marks)