

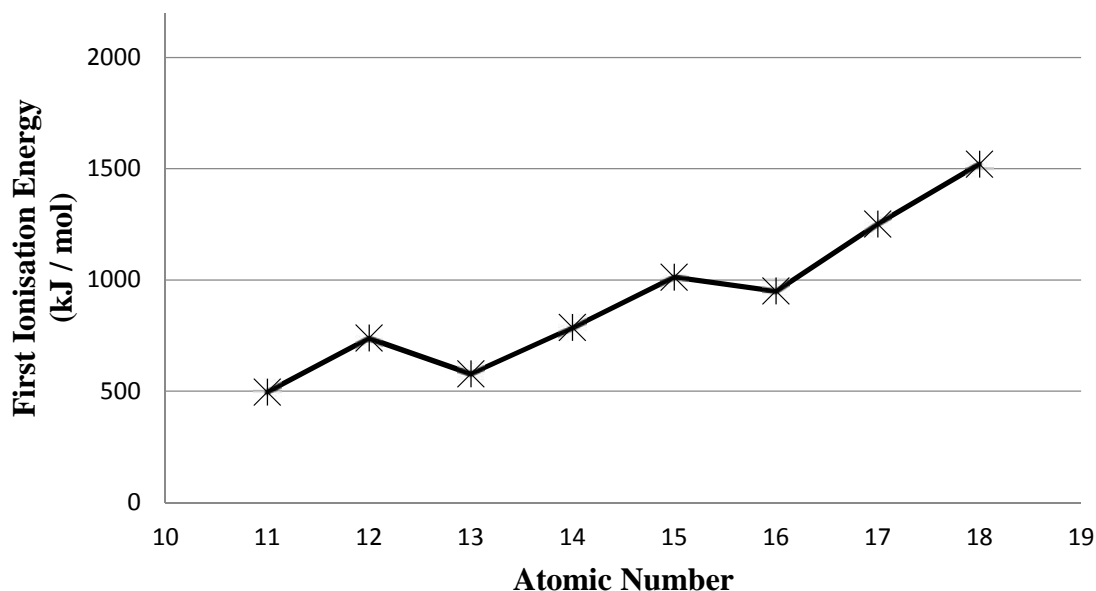
MATRICULATION AND SECONDARY EDUCATION CERTIFICATE EXAMINATIONS BOARD
UNIVERSITY OF MALTA, MSIDA
MATRICULATION EXAMINATION
ADVANCED LEVEL
MAY 2015

SUBJECT: CHEMISTRY
PAPER NUMBER: I
DATE: 28^h April 2015
TIME: 9.00 a.m. to 12.00 noon

Required Data: Molar mass (g mol^{-1}): H = 1 C = 12 O = 16
Chlorine exists as two isotopes: ^{35}Cl and ^{37}Cl
Faraday's Constant = 96 500 C

Answer all questions

1. The graph below shows the variation in the first ionization energies of a number of elements.



- (a) On the graph, plot as accurately as possible, the value of the ionization energy of:
- the element with atomic number 10;
 - the element with atomic number 19.

(2 marks)

- (b) Explain the difference in the first ionisation energies of the elements with atomic numbers 11 and 18.

(2 marks)

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-
- (c) (i) Explain the change in the first ionisation energies of the elements with atomic numbers 12 and 13.

- (ii) Explain the change in the first ionisation energies of the elements with atomic numbers 15 and 16.

(3 marks)

- (d) Explain how the first ionisation energy of elements in a group of the Periodic Table changes down the group?

(2 marks)

(Total = 9 marks)

2. (a) Using the VSEPR theory **draw** and **name** the molecular shapes of the following species:

- (i) PCl_3

Name of molecular shape: _____

- (ii) XeOF_4

Name of molecular shape: _____

(3 marks)

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(b) (i) Draw the arrangement of ions in the unit cell of caesium chloride.

(ii) Give the name of this unit cell.

(iii) Give the coordination numbers for caesium and chloride ions in the unit cell.

(3 marks)

(c) Why do sodium chloride and caesium chloride have a different crystalline structure? Explain.

(2 marks)

(d) (i) Explain the bonding in metallic sodium.

(ii) Mention **one** physical characteristic of sodium that results from the nature of this bonding.

(3 marks)
(Total = 11 marks)

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3. This question concerns Group IV of the Periodic Table.

(a) (i) Using the s, p, d notation, give the electronic configuration of silicon.

(ii) The tetrachlorides of these elements have the same molecular shape. Draw this shape, and give the nature of the bonding present in these molecules.

(2 marks)

(b) (i) CO_2 is a gas at room temperature while SiO_2 is a solid. Explain this difference in terms of bonding.

(ii) Explain why the carbon dioxide molecule does not have a permanent dipole moment.

(4 marks)

(c) (i) Explain why tin(II) compounds show reducing properties while lead(II) compounds do not.

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- (ii) Give a balanced chemical equation for the reaction of lead(IV) oxide and concentrated hydrochloric acid. Identify the oxidising and the reducing agent in the reaction.

(3 marks)

(Total = 9 marks)

4. A colourless gas occupies a volume of 31.3 cm^3 at a pressure of $101,000 \text{ Nm}^{-2}$ and a temperature of $27.0 \text{ }^\circ\text{C}$. Assume that the numerical value of the ideal gas constant is 8.31.

- (a) Deduce the units of the ideal gas constant, showing your reasoning.

(3 marks)

- (b) Calculate the number of moles of gas present.

(2 marks)

- (c) Considering that the mass of gas is 0.0533 g, find its molar mass.

(1 mark)

- (d) (i) If the gas is a hydrocarbon, determine its molecular formula. **Show your reasoning.**

- (ii) Give the structural formula of **two** isomers of this hydrocarbon.

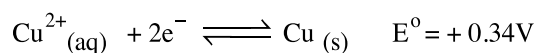
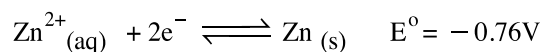
(3 marks)

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- (e) Calculate the mass of oxygen needed for the complete combustion of the quantity of this hydrocarbon calculated in part (b).

*(2 marks)**(Total = 11 marks)*

5. Consider the following two half equations and their respective E° values:



- (a) Give the cell diagram for a galvanic cell made up of zinc and copper electrodes.

(2 marks)

- (b) Find the overall E° value for the cell.

(1 mark)

- (c) Indicate the anode and the cathode of the galvanic cell.

(1 mark)

- (d) Give the redox reaction that would take place if current is allowed to flow in the cell. Indicate clearly which species is being reduced and which is oxidised.

(2 marks)

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-
- (e) Explain the difference between the reaction that takes place in the galvanic cell in part (a) and the same reaction when the chemicals involved are mixed together in a beaker.

(2 marks)

- (f) Show that the redox reaction in part (d) is energetically feasible and spontaneous.

(3 marks)
(Total = 11 marks)

6. (a) Define the terms:

Standard enthalpy of formation;

Standard enthalpy of reaction.

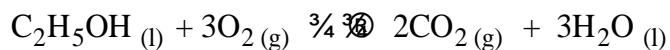
(2 marks)

- (b) (i) What is the value of the standard enthalpy of formation of O₂ (g)?

(1 mark)

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- (ii) Use a Hess diagram to calculate the standard enthalpy change for the reaction:



given that the standard enthalpies of formation of $\text{C}_2\text{H}_5\text{OH}_{(l)}$, $\text{CO}_{2(g)}$ and $\text{H}_2\text{O}_{(l)}$ are -277 , -394 and -286 kJ mol^{-1} respectively.

(3 marks)

- (c) (i) Propose a synthesis, including reagents and conditions where appropriate, for the conversion of ethanol to methylamine.

(4 marks)

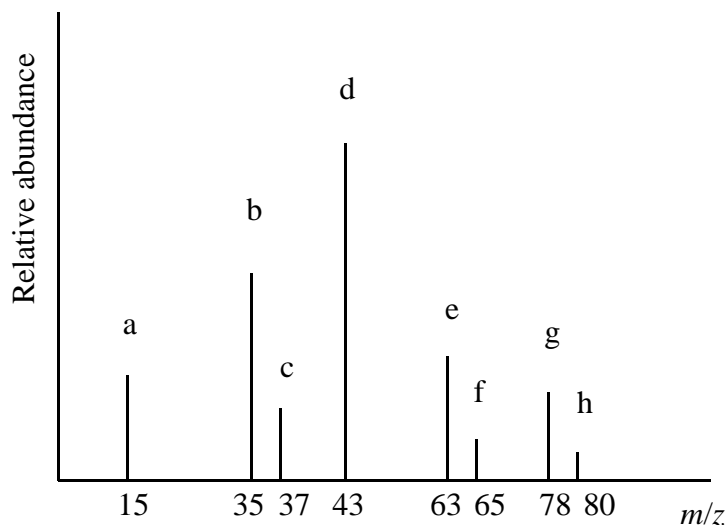
- (ii) Explain why the base dissociation constant, K_b , of propanamide is much lower than that of propylamine.

(2 marks)

(Total = 12 marks)

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7. The reaction of **alcohol X** with reagent **Z**, gives organic compound **Y** and **two inorganic gases** as products. The mass spectrum of a purified sample of compound **Y** is shown below. Note that compound **Y** is composed of carbon, hydrogen and another element.



- (a) Explain why the mass spectrum of compound **Y** has multiple peaks.

(1 mark)

- (b) Identify peaks a, b, d and e in the above mass spectrum.

(2 marks)

- (c) Give the **name** and **structural formula** of compound **Y**. Explain your answer.

(3 marks)

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-
- (d) Using the mass spectrum, calculate the relative molecular mass of compound **Y**, showing your working.

(2 marks)

- (e) Identify reagent **Z**, and hence give an equation for the reaction between **alcohol X** and reagent **Z**.

(2 marks)

(Total = 10 marks)

8. Reductive ozonolysis of alkene **A** yields methanal and ethanal as products.

- (a) Give the **structural formula** and **systematic name** of alkene **A** and hence write a reaction for the reductive ozonolysis of alkene **A**, stating any reagents used.

(3 marks)

- (b) (i) Alkene **A** was reacted with HBr to produce substance **B** as a major product and substance **C** as the minor product. Give the systematic name of substances **B** and **C**.

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- (ii) Give a suitable mechanism for the formation of substance **B**. In your account explain why substance **B** forms in preference to **C**.

(5 marks)

- (c) Substance **B** can be converted into a **primary alcohol** in a synthetic process involving a Grignard reagent. Describe this process and state the reagents and conditions that are required in the synthesis.

(4 marks)

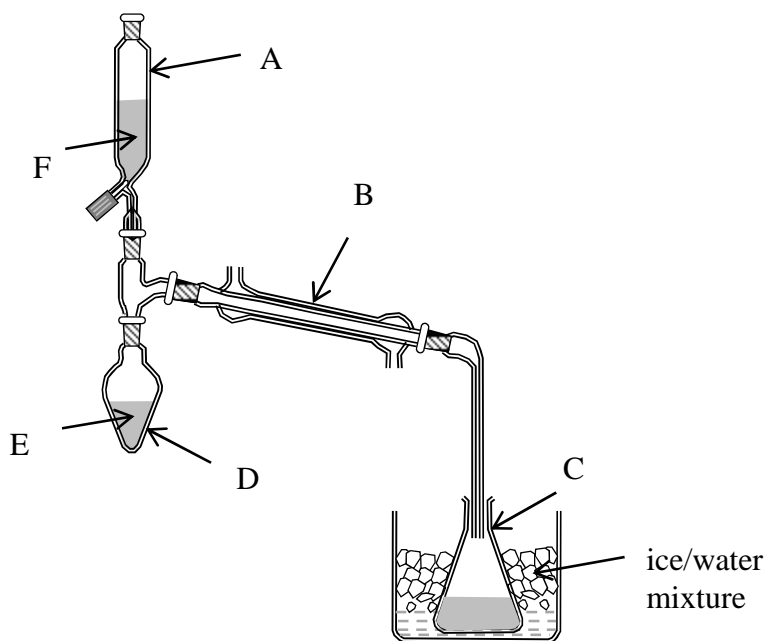
- (d) Propose a synthesis that involves the conversion of substance **B** into a carboxylic acid containing **four** carbon atoms. State the reagents and essential conditions of the reactions in the synthesis.

(2 marks)

(Total = 14 marks)

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9. Ethanal may be produced in the laboratory by the controlled oxidation of ethanol, as shown below.



- (a) Name the apparatus shown as A to D.

A: _____

B: _____

C: _____

D: _____

(2 marks)

- (b) Give the contents found in vessel A and in vessel D.

(2 marks)

- (c) The ethanal collected during the experiment is cooled using ice. Explain.

(1 mark)

- (d) Which reagent should be in excess during this experiment?

(1 mark)

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- (e) Give a test that may be used to show that an aldehyde has been produced. Your answer should include an equation for the reaction.

(2 marks)

- (f) Would ethanal undergo the Cannizzaro reaction on the addition of concentrated sodium hydroxide? Give a reason for your answer.

(2 marks)

- (g) How would you modify the experiment described in part (a), in order to produce ethanoic acid instead of ethanal.

(1 mark)

- (h) Give the reaction of ethanal with PCl_5 and explain any differences between this reaction and that of ethanol with PCl_5 .

(2 marks)

(Total = 13 marks)

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UNIVERSITY OF MALTA, MSIDA
MATRICULATION EXAMINATION
ADVANCED LEVEL
MAY 2015

SUBJECT:	CHEMISTRY
PAPER NUMBER:	II
DATE:	29 th April 2015
TIME:	9.00 a.m. to 12.00 noon

A Periodic Table is provided.

$$K_w = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

Answer two questions from each section and any other question.

Section A

1. (a) White phosphorus is a **volatile solid** (melting point 44 °C) whereas nitrogen is a **gas** (melting point -210 °C). Explain these differences by reference to the structure of the two elements.

(3 marks)

- (b) Briefly describe how you would prepare a sample of **pure** nitrogen monoxide and nitrogen dioxide **from different reagents**.

(6 marks)

- (c) A 1.50 g sample of potassium nitrate(V) was heated strongly in a crucible to produce the nitrate(III) salt.

A titration was carried out to determine the percentage by mass of potassium nitrate(V) that undergoes thermal decomposition. The contents of the crucible were dissolved in distilled water and the solution transferred to a 250 cm³ volumetric flask, which was made up to the mark with more distilled water. This solution was labelled **solution A**.

A sample of 50.0 cm³ cerium(IV) sulfate, Ce(SO₄)₂, solution (**an excess**) of concentration 0.100 mol dm⁻³ was placed in a conical flask together with 10 cm³ of dilute sulfuric acid. To this mixture was added 25.0 cm³ of **solution A**. A redox reaction takes place in which cerium(IV) is reduced to cerium(III) and nitrate(III) oxidised to nitrate(V).

The **unreacted cerium(IV)** in the conical flask was then titrated with 0.150 mol dm⁻³ ammonium iron(II) sulfate of which 19.50 cm³ was required. In this step, cerium(IV) is reduced to cerium(III) by iron(II).

Calculate the percentage by mass of potassium nitrate(V) that undergoes thermal decomposition. Include all the relevant equations in your calculation.

(11 marks)

(Total: 20 marks)

2. This question is about the d-block elements. Give concise explanations for the following. **Include relevant chemical and/or ionic equations where appropriate in your answer.**

(a) Manganese can exist in several oxidation states including +2, +4, +6 and +7, the latter of which being the maximum value.

(4 marks)

(b) When sodium hydroxide solution is added to a blue-violet solution of compound **P** until in excess, a green precipitate forms that dissolves in excess sodium hydroxide forming a green solution **Q**.

Addition of hydrogen peroxide to solution **Q** gives a bright yellow solution **R**, which after boiling turns to an orange solution **S** on addition of dilute sulfuric acid. Identify solutions **P** to **S**.

(5 marks)

(c) Name a **transition metal ion** that is used as a *homogeneous catalyst*. Explain the terms in italics and explain how the ion of your choice functions as such.

(5 marks)

(d) Addition of ethane-1,2-diamine (ethylenediamine) solution to an aqueous solution of hexaaquachromium(III) ions, forms a complex that can exist as two stereoisomers. Further dilution with water does not reform the hexaaquachromium(III) ion. **Include the structures of the stereoisomers in your answer.**

(6 marks)

(Total: 20 marks)

3. Explain in detail the following statements. **Your answers should include all the relevant chemical and or ionic equations.** Each part carries equal marks.

(a) Not all hydrogen halides can be prepared by the reaction of the sodium halide with concentrated sulfuric(V) acid.

(b) When chlorine is added to cold aqueous potassium hydroxide it disproportionates forming a compound that disproportionates further on heating.

(c) Explain why the solution formed by adding sodium chloride to water is neutral while that formed by adding aluminium chloride is acidic.

(d) Sodium hydride is a solid at room temperature that reacts with water while silane, SiH_4 , is a gas at room temperature that is insoluble in water.

(Total: 20 marks)

4. This question is on chemical equilibria.

(a) Water and tetrachloromethane are two immiscible liquids. The value of the partition constant of iodine in these two liquids is 0.0116.

- (i) Explain briefly why the two liquids are immiscible.
- (ii) Iodine is soluble in both liquids, but to different extent. State and explain briefly in which of these two liquids is iodine more soluble.
- (iii) Give the expression for the partition coefficient of iodine in these two liquids, and state its units.
- (iv) Considering that 50 cm³ of tetrachloromethane is used, how many moles of iodine will be extracted into the organic layer if 50 cm³ of a 0.010 mol dm⁻³ aqueous iodine solution is mixed with it?
- (v) Mention the apparatus required for such an extraction.
- (vi) If the 50 cm³ of tetrachloromethane is used in two successive volumes of 25 cm³, find the **total** amount of iodine in moles that will be extracted into the organic layer from the same aqueous solution mentioned in part (a)(iv).

(13 marks)

(b) Consider the following dissociation:



- (i) Give an expression for the equilibrium constant in terms of pressure, K_p. In your answer include the units in Pa.
- (ii) Explain qualitatively what would happen to the degree of dissociation of NOBr when NO gas is added to the reaction mixture at constant volume and temperature.
- (iii) Explain qualitatively what would happen to the position of the equilibrium mixture when helium (an inert) gas is added to the reaction mixture at constant volume and temperature.
- (iv) Explain qualitatively what would happen to K_p when the temperature is increased at constant volume.

(7 marks)

(Total: 20 marks)

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Section B

5. This question is about the ionic equilibria.

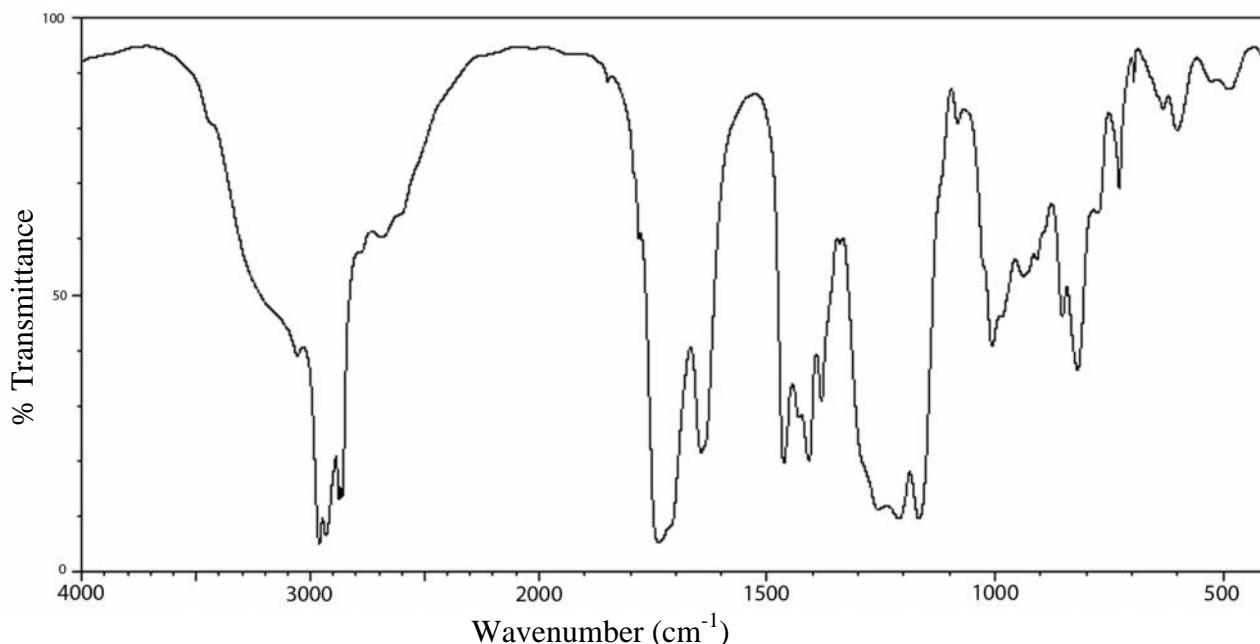
- (a) A solution, labelled **solution B**, was prepared by adding quantitatively 10.0 cm^3 of $0.500 \text{ mol dm}^{-3}$ sodium hydroxide solution to 100 cm^3 of $0.100 \text{ mol dm}^{-3}$ ethanoic acid solution.
- (i) Ethanoic acid is a weak acid. Explain the statement briefly and give an expression for the K_a of ethanoic acid.
- (ii) Explain how **solution B** would behave if a small amount of base is added to it.
- (iii) Calculate the pH of **solution B**. The K_a of ethanoic acid is $1.74 \times 10^{-5} \text{ mol dm}^{-3}$.
(12 marks)

- (b) Silver chloride is a sparingly soluble solid. The **numerical value** of its K_{sp} is 1.80×10^{-10} .
- (i) Explain the terms 'sparingly soluble solid' and ' K_{sp} '.
- (ii) Write the expression for K_{sp} for silver chloride and state its units.
- (iii) Considering the K_{sp} value for silver chloride given above, find the molar solubility of silver chloride.
- (iv) Calculate whether or not a precipitate of silver chloride forms on mixing, at constant temperature, equal volumes of aqueous $1.00 \times 10^{-2} \text{ mol dm}^{-3}$ sodium chloride and $1.00 \times 10^{-5} \text{ mol dm}^{-3}$ silver nitrate solutions.
(8 marks)
(Total: 20 marks)

6. This question is about methylbenzene (compound **A**), chlorobenzene (compound **B**) and nitrobenzene (compound **C**).

- (a) Give an equation for the preparation of **C** starting from benzene, stating the reagents and conditions used. Furthermore, give the mechanism for this reaction.
(5 marks)
- (b) Propose a synthesis for the preparation of **B**, starting from **C**. In your answer include all the relevant reagents and conditions that are required.
(6 marks)
- (c) **A** and **B** can undergo nitration. For each of these compounds, identify the products of nitration, giving the reagents and conditions required.
(3 marks)
- (d) The conditions required to form the mono-nitro compounds from **A**, **B** and **C** respectively are different when compared with those required for benzene. Moreover, the nitro group enters the ring in different positions with respect to the groups already present in **A**, **B** and **C**. Explain these observations in full.
(6 marks)
(Total: 20 marks)

7. Compound **X** is composed of carbon, hydrogen and oxygen. It has **four** carbon atoms and can exist as two stereoisomers, one of which has a melting point of 135 °C and the other has a melting point of 287 °C. An infrared spectrum for one of the stereoisomers of compound **X** is shown below.



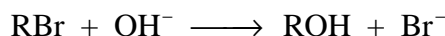
Bond	Wavenumber (cm ⁻¹)	Bond	Wavenumber (cm ⁻¹)
N-H	3500 – 3700	O-H (acids)	2500 – 3300 (broad)
C=O	1700 – 1780	O-H (alcohols)	3200 – 3550 (broad)
C-H	2850 – 2960	C=C	1610 – 1680

- (a) From the above information, and given that compound **X** has an RMM of 116, give the systematic name and structures of the **two stereoisomers** of compound **X**. **Explain your reasoning.**
- (10 marks)
- (b) State how you would prepare compound **X** starting from ethyne. In your answer, state the reagents and conditions used.
- (5 marks)
- (c) The reaction of the two stereoisomers of compound **X** with alkaline potassium manganate(VII) produces three products, two of which are optically active and one which is not. Explain.

(5 marks)
(Total: 20 marks)

Please turn the page.

8. (a) Consider the following chemical reaction for the hydrolysis of a halogenoalkane:



The kinetic data for this reaction, reported in the Table below, were obtained by the method of initial rates.

Experiment	Initial [RBr] (mol dm ⁻³)	pH	Initial rate of formation of ROH (mol dm ⁻³ s ⁻¹) x 10 ⁻³
1	0.20	13.00	1.2
2	0.20	13.47	1.2
3	0.40	13.60	2.4

- Outline the method of initial rates.
- Explain the following terms: **rate of reaction** and **order of reaction with respect to a reagent**.
- Find the order with respect to reactants RBr and OH⁻ respectively, and the overall order of reaction. Show clearly your reasoning.
- From the data, deduce the rate expression for this reaction.
- Suggest a possible structure for RBr and propose a suitable mechanism for the reaction. In your mechanism, identify the rate-determining step.

(14 marks)

- (b) The following table reports the experimental results of the variation of the concentration of RBr (in mol dm⁻³) with time (in seconds) for the reaction in part (a).

Time (s)	Concentration of RBr (mol dm ⁻³)
120	1.00
165	0.80
215	0.60
305	0.34
420	0.18
480	0.13

- Plot a graph** of [RBr] against time and use it to calculate the half-life for this reaction. Show your working.
- Use the graph in part (b) (i) to confirm the rate expression as deduced in part (a).

(6 marks)

(Total: 20 marks)

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

**MATRICULATION EXAMINATION
ADVANCED LEVEL
MAY 2015**

SUBJECT: CHEMISTRY
PAPER NUMBER: III – *Practical*
DATE: 12th June 2015
TIME: 3 hours

There are three questions in this paper. Answer all questions.

1. In this experiment you are required to determine the number of water molecules of crystallisation of disodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot x\text{H}_2\text{O}$.

You are supplied with the following chemicals:

- (i) 125 cm^3 of **20.0 g dm⁻³** hydrated disodium tetraborate labelled **T**.
- (ii) 250 cm^3 of a solution of hydrochloric acid labelled **A_n** where **n** is the candidate laboratory number.
- (iii) 125 cm^3 a solution of sodium hydroxide of concentration **0.110 mol dm⁻³** labelled **S**.
- (iv) Phenolphthalein indicator.
- (v) Methyl red indicator.

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

CANDIDATE LABORATORY NUMBER, n:.....

Standardisation of the hydrochloric acid solution, A_n.

- (b) Pipette 25.0 cm^3 of solution **S** into a conical flask. Add three drops of phenolphthalein indicator and titrate with **A_n** from the burette. Enter your titration results in the table below.

	1 st Titration	2 nd Titration	3 rd Titration
Initial burette reading (cm ³)			
Final burette reading (cm ³)			
Titre (cm ³)			

Mean titre₁ : _____ cm³ of **A_n**

(20 marks)

- (c) Calculate the concentration of the hydrochloric acid solution, A_n .

(3 marks)

Determination of the number of water molecules of crystallisation, x , in disodium tetraborate, $Na_2B_4O_7 \cdot xH_2O$.

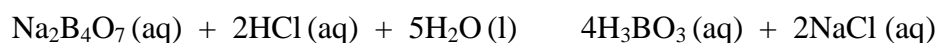
- (d) Pipette 25.0 cm^3 of solution **T** into a conical flask. Add four drops of methyl red indicator and titrate with A_n from the burette to a peach end-point. Enter your titration results in the table below.

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

Mean titre₂ : _____ cm^3 of A_n

(20 marks)

- (e) Given that the neutralisation reaction is:



calculate the molar concentration, to three significant figures, of disodium tetraborate in solution **T**.

(3 marks)

- (f) Given that solution **T** has a concentration of **20.0 g dm⁻³**, calculate the number of water molecules of crystallisation, **x**, in the disodium tetraborate salt, $\text{Na}_2\text{B}_4\text{O}_7 \cdot x\text{H}_2\text{O}$.
(Relative atomic masses: H = 1; B = 10.8, O = 16; Na = 23).

(4 marks)

Please turn the page.

2. You are provided with two inorganic substances, one as a solid labelled **X** and the other as an aqueous solution labelled **Y**. Carry out the tests as described below, record your observations carefully and attempt to identify the compounds.

- (a) Dissolve **approximately HALF** of your sample of substance **X** in approximately 10 cm³ of water. **Retain this solution for tests (b) and (c).**

Observation

Inference

_____	_____
_____	_____
_____	_____
_____	_____

- (b) To about 2 cm³ of the solution from (a), add dilute sodium hydroxide solution slowly until in excess. Add **two pieces of aluminium foil**. Heat the mixture gently.

Observation

Inference

_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____

- (c) To about 1 cm³ of the solution from (a), add an equal amount of dilute sulfuric acid solution.

Observation

Inference

_____	_____
_____	_____
_____	_____
_____	_____

- (d) To about 1 cm³ of substance **Y**, add dilute sodium hydroxide solution slowly until in excess.

Observation

Inference

- (e) To about 1 cm³ of substance **Y**, add dilute ammonia solution slowly until in excess.

Observation

Inference

- (f) Dissolve **the remaining half** of your sample of substance **X** in approximately 5 cm³ of water in a **boiling tube**. Add 4 cm³ dilute sodium hydroxide solution followed by 2 cm³ hydrogen peroxide solution. First warm the mixture **GENTLY** and then boil **carefully** for about one minute. **Retain this solution for test (g).**

Observation

Inference

- (g) To 1 cm³ of the solution from test (f), add 1 cm³ of dilute sulfuric acid. **Retain this solution for test (h).**

Observation

Inference

- (h) To the solution from test (g), add 1 cm³ of **substance Y**. Shake the mixture and add 1 cm³ of starch solution.

Observation

Inference

Conclusion

Substance **X** is probably: _____

Substance **Y** is probably: _____

(30 marks)

3. You are provided with an organic solid, substance **Z**, containing more than one functional group. Perform the following tests on **Z** and record your observations and inferences in the spaces provided.

(a) Burn a **small quantity (tip of a spatula)** of **Z** on a crucible lid. Do not allow the flame to burn longer than you need to make a good observation.

Observation

Inference

_____	_____
_____	_____
_____	_____
_____	_____
_____	_____

(b) Add a **small quantity** of **Z** to about 5 cm³ of sodium carbonate solution. Test for any evolved gas.

Observation

Inference

_____	_____
_____	_____
_____	_____
_____	_____
_____	_____

(c) Dissolve a **small quantity (tip of a spatula)** of **Z** in 5 cm³ of the distilled water. Test the solution with litmus paper. **Retain this solution for test (d).**

Observation

Inference

_____	_____
_____	_____
_____	_____
_____	_____

Please turn the page.

(d) To the solution from test (c), add a few drops of bromine water.

Observation

Inference

_____	_____
_____	_____
_____	_____
_____	_____

(e) To a **small quantity** of **Z** add 3 cm³ of ethanol and three drops of concentrated sulfuric acid (CARE! CORROSIVE) and heat the mixture in a boiling water bath for one minute. Cool and add the mixture to 10 cm³ of sodium carbonate solution.

Observation

Inference

_____	_____
_____	_____
_____	_____
_____	_____

Conclusion: A possible structure for **Z** is: _____

(20 marks)