Index No.:_____ **AM 06/I.15s**

MATRICULATION AND SECONDARY EDUCATION CERTIFICATE EXAMINATIONS BOARD

UNIVERSITY OF MALTA, MSIDA

MATRICULATION EXAMINATION
ADVANCED LEVEL
SEPTEMBER 2015

SUBJECT:	CHEMISTRY
PAPER NUMBER:	I
DATE:	1st September 2015
TIME:	9.00 a.m. to 12.00 noon

Required Data: Molar mass (g mol^{-1}): H = 1 C = 12 O = 16

Answer all questions

1. (a) Explain the following terms.
(i) Atomic number.

_____

_____

(ii) Nucleon number.

_____

_____

(2 marks)

(b) The element chlorine exists as *isotopes.* Define the term *isotopes.*

_____

_____

_____

(1 mark)

(c) The relative atomic mass of chlorine is 35.5. Explain how this fractional value arises.

_____

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_____

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_____

(2 marks)

(d) The analysis of molecular chlorine by mass spectrometry produces a number of peaks. Account for these peaks.

(3 marks)

(e) With the aid of a chemical equation explain how oxygen-18, ^{18}O, is used as a tracer for establishing the mechanisms of esterification reactions.

(2 marks)
(Total = 10 marks)

2. (a) Explain, giving an example in each case, what is meant by:

(i) a dative covalent bond

(ii) a hydrogen bond

(4 marks)

(b) Using Group 6 hydrides, give a physical property that is affected by the occurrence of hydrogen boding and give an example for your answer.

(3 marks)

(c) Using the VSEPR theory **draw** the molecular shapes of the following species, showing the position of any lone pair/s.

BF_3 PCl_3

(2 marks)

(d) Give a reason why the molecular shapes drawn are different.

(2 marks)
(Total = 11 marks)

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

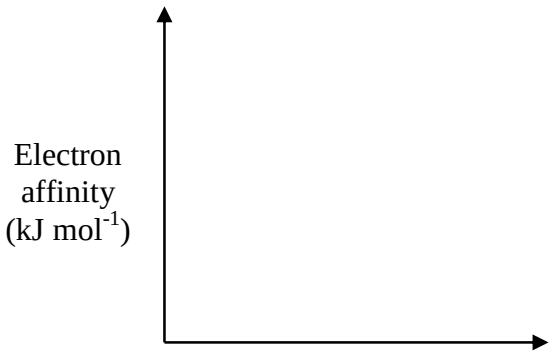
(a) Using one of the halogens as example, define:

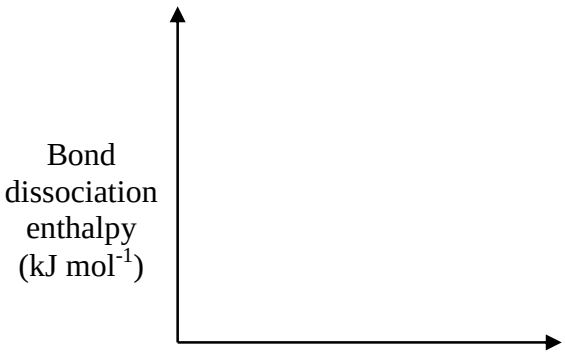
(i) electron affinity

(ii) bond dissociation enthalpy

(2 marks)

(b) On the axes below, sketch the trends in each of the properties mentioned in part (a) for F, Cl, Br and I.





(4 marks)

(c) When sodium chloride is treated with concentrated sulfuric(VI) acid, a colourless gas, X, which fumes in moist air is formed. When sodium iodide is treated in a similar reaction, a coloured vapour Y is produced.

(i) Identify X and Y.

(ii) Explain why the two are different.

(iii) If 90% phosphoric(V) acid is used instead of sulfuric(VI) acid, a colourless gas is produced in each reaction. Give a reason why the two acids react differently.

(3 marks)

(d) A number of oxoanions of chlorine are known: examples include ClO^-, ClO_3^-, and ClO_4^-.

(i) ClO^- is formed when chlorine reacts with cold concentrated alkali. Write an ionic equation for this reaction.

(ii) Write an ionic equation for the reaction that ClO^- (aq) undergoes when heated.

(iii) What is the type of reaction in (ii) called and what is happening to the oxidation state of the species involved?

(3 marks)
(Total = 12 marks)

4. In the paper by Alfred H. Taylor Jr. and R. H. Crist, titled *Rate and Equilibrium Studies on the Thermal Reaction of Hydrogen and Iodine*, it was found that hydrogen iodide is 22.3% dissociated at a temperature of 730.8 K.
The melting point and boiling point of iodine are 113.5 °C and 184.0 °C respectively. The melting and boiling points of hydrogen iodide are −50.80 °C and −35.36 °C respectively.

(a) If one starts with hydrogen iodide, write the equation that represents the chemical equilibrium for the decomposition of hydrogen iodide. Include state symbols.

(2 marks)

(b) Write the expression for the equilibrium constant in terms of concentration for this equilibrium reaction. State its units.

(2 marks)

(c) If one starts with one mole of hydrogen iodide, calculate the value of the equilibrium constant in terms of concentration.

(4 marks)

(d) Explain briefly any shifts in equilibrium that would take place if the pressure on the equilibrium mixture at 730.8 K is increased.

(2 marks)
(Total = 10 marks)

5. Consider the following half equations and their respective E^o values:

$Fe^{2+}_{(aq)} + 2e^- \rightleftharpoons Fe_{(s)}$ $\quad E^o = -0.41$ V

$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2\,(g)}$ $\quad E^o = 0.00$ V

$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$ $\quad E^o = +0.34$ V

(a) Give the cell diagram for a galvanic cell made up of iron and copper electrodes. In your answer indicate the cathode and anode.

(4 marks)

(b) Consider that for a general redox reaction aA + bB $\rightleftharpoons$ cC + dD, carried at 25 °C (298 K), the Nernst equation is:

$$E_{cell} = E^{o}_{cell} - \frac{0.059}{n} \log \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Find the overall E^o value for an iron – copper galvanic cell, if the concentrations of iron and copper ions are 0.80 mol dm^{-3} and 0.40 mol dm^{-3} respectively.

(3 marks)

Please turn the page.

(c) In view of the E^o values given, explain how copper and iron are expected to react with dilute sulfuric(VI) acid.

(4 marks)
(Total = 11 marks)

6. (a) Explain briefly the following statements:

(i) Atomic radii decrease across a period but increase down a group.

(ii) The degree of covalency of $BeCl_2$ and $BaCl_2$ is different.

(6 marks)

(b) Sulfur has a number of allotropes.

(i) Name two allotropes of sulfur.

(ii) How does temperature affect the two allotropes?

(4 marks)

Please turn the page.

(iii) Sulfur is used as a fuel in black powder (gunpowder) which is abundantly used in fireworks. Oxidation of this fuel leads to the formation of two gaseous pollutants. Suggest an identity of these pollutants and their effect on the atmospheric environment.

(3 marks)
(Total = 13 marks)

7. Compound X is a hydrocarbon having an empirical formula C_2H_3 and a molecular mass of 54 g mol^{-1}. One volume of the gaseous sample of X reacts with two volumes of hydrogen and the infrared spectrum shows an absorption band with wavenumber 2400 cm^{-1} which is higher than that associated with C=C double bonds.

(a) What is the molecular formula of compound X, and suggest two possible structures. Explain your reasoning.

(4 marks)

(b) What type of isomerism do the structures given in part (a) show.

(1 mark)

(c) Compound X reacts with an ammoniacal solutions of copper(I) chloride. Give an equation for this reaction stating any observations, and hence identify compound X. Explain.

(3 marks)

(d) Compound X can be hydrated to produce two isomers. Explain, giving the relevant equation and reagents.

(3 marks)
(Total = 11 marks)

8. **A** and **B** are organic compounds composed of hydrogen, carbon and oxygen only. Both **A** and **B** react with PCl_5, where the reaction proceeds without the emission of any vapours. Furthermore, compound **A** reacts with Tollens' reagent whilst compound **B** does not.

(a) If the molecular formula for **A** and **B** is C_3H_6O, give their structural formulae.

(1 mark)

(b) Write equations for the reactions of compound **B** with PCl_5 and compound **A** with Tollens' reagent.

(2 marks)

Please turn the page.

(c) The product of the reaction of compound **B** with $LiAlH_4$, also reacts with PCl_5 giving dense white fumes. Explain giving equations.

_____

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(3 marks)

(d) Compound **A** has a boiling point of 56 °C whilst compound **B** has a boiling point of 46 °C.

(i) What physical method could be used to separate a solution made up of compounds **A** and **B**?

_____

(1 mark)

(ii) Use a properly labelled Temperature-Composition diagram for the two liquids to explain how this method works.

(3 marks)
(Total = 10 marks)

9. (a) Benzene contains six equal carbon-to-carbon bonds in its structure. These bonds are shorter than a single C-C bond but longer than a C=C double bond. Explain.

_____

_____

(1 mark)

(b) Would you expect benzene to be very reactive? Explain, indicating the type of reactions undergone by benzene.

_____

_____

_____

_____

_____

(2 marks)

(c) In industry, benzene is usually obtained from petroleum or coal; nonetheless, it can be made in the laboratory from a number of its derivatives. Give an equation stating reagents and conditions needed to prepare benzene from benzenesulfonic acid.

_____

_____

_____

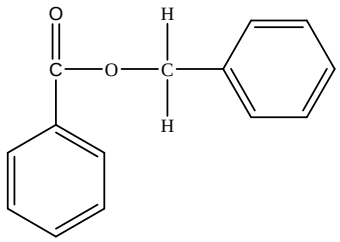
_____

_____

(2 marks)

Please turn the page.

(d) Give a scheme for the preparation of compound **Y** starting from benzene. Note that any aromatic compound used in this scheme must be derived from benzene by giving the appropriate equations.



Compound Y

(7 marks)
(Total = 12 marks)

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UNIVERSITY OF MALTA, MSIDA

MATRICULATION EXAMINATION
ADVANCED LEVEL
SEPTEMBER 2015

SUBJECT:	CHEMISTRY
PAPER NUMBER:	II
DATE:	2nd September 2015
TIME:	9.00 a.m. to 12.00 noon

A Periodic Table is provided.
$K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6} at 25 ^{o}C

Answer two questions from each section and any other question.

Section A

1. (a) (i) The terms transition metal and d block metal are sometimes used as if they mean the same thing but there is a difference between the two terms. Explain this statement.

(ii) The atomic numbers of the elements manganese and iron are 25 and 26 respectively. Taking into account their electronic configurations, explain whether these two elements can be classified as transition elements, d block elements, or both.

(iii) Why is Mn^{2+} more stable to oxidation than Fe^{2+}?

(8 marks)

(b) Consider the following information. The hexaaquamanganese(II) ion readily forms complexes with polydentate ligands, as in the following cases:

$$[Mn(H_2O)_6]^{2+}(aq) + 3en(aq) \rightleftharpoons [Mn(en)_3]^{2+}(aq) + 6H_2O(l)$$
$$[Mn(H_2O)_6]^{2+}(aq) + edta^{4-}(aq) \rightleftharpoons [Mn(edta)]^{2-}(aq) + 6H_2O(l)$$

(i) Explain the term 'ligand'.

(ii) Considering the first reaction, what does 'en' stand for? Give its chemical formula.

(iii) The equilibrium (or stability) constants for the formation of the 'en' complex and the edta complex are 5.0 x 10^5 mol^{-3} dm^9 and 1.0 x 10^{14} mol^{-1} dm^3 respectively. Explain briefly why the ligand exchange occurs, and comment about their relative stabilities of the different types of complexes.

(8 marks)

(c) Iron ions act as a catalyst in the reaction between peroxodisulfate ions and iodide ions. The overall equation for the reaction is:

$$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$$

Discuss and explain the role of Fe^{2+} (or Fe^{3+}) in this reaction.

(4 marks)
(Total: 20 marks)

2. A buffer was prepared containing 0.20 mol dm^{-3} ammonia and 0.10 mol dm^{-3} ammonium chloride. The value of K_b for ammonia at 25 ^oC is 1.8 x 10^{-5} mol dm^{-3}.

   (a) (i) Define the term 'buffer solution'.
   (ii) There are two general types of buffer. Explain briefly, illustrating your answer with an example in each case.
   (iii) Write the equation for K_b for ammonia.
   (iv) Find the pH of the ammonia – ammonium chloride buffer. Explain your reasoning indicating any assumptions made in your calculation.

   (13 marks)

   (b) (i) Explain briefly what would happen to the pH of a 0.20 mol dm^{-3} ammonia solution if the temperature of the ammonia solution were to be increased above 25 ^oC.
   (ii) Explain briefly what would happen if small amounts of acid solution were to be added to the ammonia – ammonium chloride buffer solution.

   (7 marks)
   (Total: 20 marks)

3. (a) Magnesium reacts with aqueous hydrochloric acid to produce hydrogen gas. With the aid of a diagram describe this experiment, and show how this can be used to find the rate of a reaction.

   (5 marks)

   (b) Explain, by means of the Arrhenius equation, $k=Ae^{-E/RT}$, how a change in temperature affects rates of reactions considering that concentrations are kept constant.

   (5 marks)

   (c) Explain the importance of catalytic converters and how they work. *(5 marks)*

   (d) Photochemical reactions use light instead of heat to overcome the activation energy of a reaction. Give an example of a photochemical reaction and explain its mechanism.

   (5 marks)
   (Total: 20 marks)

4. This question is on s-block chemistry.

   (a) Compare the solubility in water of the hydroxides of Group 2. Explain how the solubility affects the alkalinity of the resulting solutions.

   (6 marks)

   (b) (i) Mention **three** chemical similarities between lithium and magnesium and explain why lithium chemically resembles magnesium but differs from other elements of Group 1.
   (ii) Describe a simple method for the removal of small amounts of calcium hydrogencarbonate dissolved in water and give a balanced chemical equation to represent the chemical change

   (9 marks)

   (c) On heating barium in air, a solid **S** forms which reacts with dilute sulfuric acid to form a precipitate **P** and an aqueous solution of substance **Q**. Identify substances **S**, **P** and **Q** and represent the changes by balanced chemical equations.

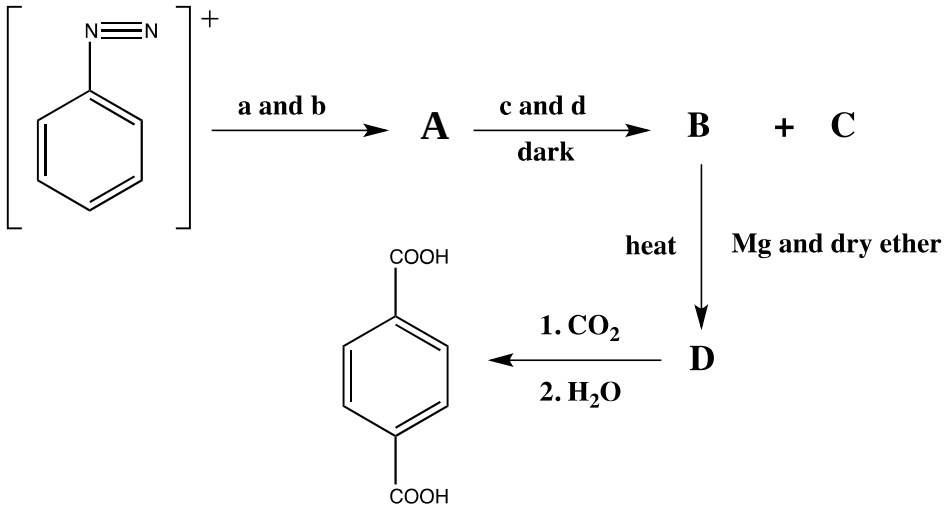
   (5 marks)
   (Total: 20 marks)

Section B

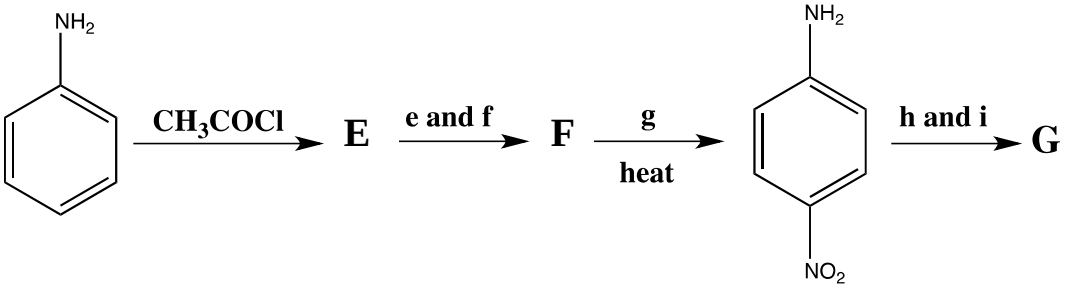
5. Polymers are an important part of modern life. This question is about two polymers, an aromatic polyamide and low density polyethene.

(a) The schemes below result in the formation of an aromatic polyamide. Give the structures of molecules **A** to **H** and substances **a** to **i**.

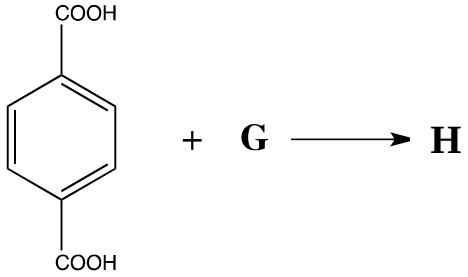
Scheme I: Preparation of benzene-1,4-dioic acid.



Scheme II: Preparation of substance **G**



Scheme III: Preparation of the aromatic polyamide H.



(11 marks)

(b) Give an equation describing the preparation of the diazonium salt given in Scheme I above from phenylamine.

(2 marks)

(c) Give a mechanism for the formation of polyethene, starting from ethene. In your answer you should also state the initial conditions for this polymerization reaction to occur.

(7 marks)

(Total: 20 marks)

6. (a) For each of the following types of reactions, give:

– essential experimental conditions
– the mechanism of the reaction

(i) Nucleophilic addition of HCN to a ketone.
(ii) Friedel-Crafts acylation

(10 marks)

(b) Explain, giving relevant chemical equations how ozonolyis can be used to distinguish between the structural isomers of butene.

(5 marks)

(c) Explain the pKa values for the following compounds:

Compound	pKa
ethanol	15.9
ethanoic acid	4.76
trichloroethanoic acid	0.66

(5 marks)
(Total: 20 marks)

7. (a) (i) State Raoult's law.
(ii) Explain briefly how Dalton's law of partial pressures and Raoult's law can be used to find the saturation vapour pressure of a mixture made up of two miscible liquids A and B. Define all the symbols used in your derivation.
(iii) Raoult's law only works for ideal solutions and real solutions are not always close to behaving as ideal.
Explain the above statement, highlighting what is meant by the term 'ideal solutions' and what actually happens in 'real solutions'. Illustrate your explanation by including vapour pressure-composition diagrams and **one** example in each case.

(14 marks)

(b) Limonene, $C_{10}H_{16}$, distils at 176 ^{o}C but can be distilled at a 97 ^{o}C using steam distillation. At this temperature the saturation vapour pressure of water is 695 mmHg while that of limonene is 65 mmHg. Calculate the amount of water required to distil 5 g limonene and give one essential requirement for steam distillation.

(6 marks)
(Total: 20 marks)

8. W, X, Y and Z are four organic compounds having relative molecular masses of 60, 74, 94 and 46 respectively. W, X and Z react with PCl_5, giving dense white fumes. Addition of dilute NaOH and iodine to compounds W and Z give a pale yellow precipitate, while no visible reaction seems to occur when dilute NaOH and iodine are added to compounds X and Y. When acidified dichromate is added to compounds W and Z, a colour change from orange to green is noted, whilst no reaction occurs when acidified dichromate is added to compound X. Furthermore, the product produced by the reaction of compound Z with acidified dichromate reacts with sodium carbonate, producing carbon dioxide gas in the process. Compound Y also reacts with aqueous sodium carbonate, however no gas is released from this reaction. Reaction of compound Y with $FeCl_3$ yields a purple solution:

   (a) Identify compounds W, X, Y and Z. Explain your reasoning, giving equations where appropriate.

   (10 marks)

   (b) Explain how compound Y reacts with aqueous sodium carbonate.

   (2 marks)

   (c) Compound X and Z can be prepared from their corresponding halogenoalkane. Name and give the mechanism for each of these reactions.

   (8 marks)

(Total: 20 marks)

Index No.:_____ **AM 06/III.15s**

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UNIVERSITY OF MALTA, MSIDA

MATRICULATION EXAMINATION
ADVANCED LEVEL
SEPTEMBER 2015

SUBJECT:	CHEMISTRY
PAPER NUMBER:	III – *Practical*
DATE:	28th August 2015
TIME:	3 hours

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

1. In this experiment you are required to determine the molar concentration of a copper(II) sulfate solution.

You are supplied with the following chemicals:

(i) 150 cm^3 of **0.0200 mol dm^{-3}** potassium iodate labelled **T**;
(ii) 250 cm^3 of a solution of sodium thiosulfate labelled $\mathbf{S_n}$ where **n** is the candidate laboratory number;
(iii) 100 cm^3 of a solution of copper(II) sulfate of concentration labelled **A**;
(iv) 150 cm^3 of a solution of potassium iodide labelled **M.**

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

CANDIDATE LABORATORY NUMBER, n:.....

Standardisation of sodium thiosulfate solution, S_n.

(b) Pipette 25.0 cm^3 of solution **T** into a conical flask followed by 25 cm^3 of solution **M** (an excess) and 5 ml of 1 mol dm^{-3} sulfuric acid (an excess). Titrate with $\mathbf{S_n}$ from the burette and add 1 cm^3 starch indicator close to the end point. Enter your titration results in the table below.

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

Mean titre$_1$: _____ cm^3 of $\mathbf{S_n}$

(18 marks)

(c) Given that the reactions are:

$$IO_3^- (aq) + 5I^- (aq) + 6H^+ (aq) \rightarrow 3I_2 (aq) + 3H_2O (aq)$$

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

calculate the concentration of the sodium thiosulfate solution, $\mathbf{S_n}$.

(3 marks)

Determination of the concentration of copper(II) sulfate solution, A.

(d) Transfer 25.0 cm^3 of solution **A** using a volumetric pipette into a 250 cm^3 volumetric flask. Make the volume to the mark with distilled water and shake the volumetric flask to homogenise the solution. Label the diluted solution **dA**.

Pipette 25.0 cm^3 of solution **dA** into a conical flask followed by 10 cm^3 of solution **M** (an excess). Titrate with $\mathbf{S_n}$ from the burette and add 1 cm^3 starch indicator close to the end point. Enter your titration results in the table below.

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

Mean titre$_2$: _____ cm^3 of $\mathbf{S_n}$

(25 marks)

(e) Given that the reaction between copper(II) ions and iodide is as follows:

$$2Cu^{2+}\,(aq) + 4I^{-}\,(aq) \rightarrow \quad I_2\,(aq) \; + 2CuI\,(s)$$

calculate the molar concentration, to three significant figures, of copper(II) sulfate in solution **A**.

(4 marks)

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

(a) Dissolve your sample of substance **X** in approximately 25 cm^3 of water. ***Retain this solution for tests (b) to (d)***.

Observation	*Inference*

Please turn the page.

(b) To about 1 cm^3 of the solution from (a), add dilute sodium hydroxide solution slowly until in excess. Boil the mixture gently.

Observation *Inference*

(c) To about 2 cm^3 of the solution from (a), add an equal amount of dilute hydrochloric acid solution.

Observation *Inference*

(d) To about 1 cm^3 of the solution from (a), add **three drops** of calcium nitrate solution.

Observation *Inference*

(e) To your sample of substance **Y** add 15 ml of dilute nitric acid. Test for any evolved gases. When the effervescence stops, allow the suspension to stand for 1 minute and filter. ***Retain the filtrate for tests (f) to (h)***.

Observation *Inference*

(f) To 1 cm^3 of the filtrate from test (e), add dilute sodium hydroxide solution slowly until in excess.

Observation *Inference*

(g) To 1 cm^3 of the filtrate from test (e), add an equal amount of potassium chromate(VI) solution and warm for a few seconds. Add 1 cm^3 of glacial ethanoic acid and shake gently.

Observation *Inference*

(h) Carry out a flame test on the filtrate from test (e).

Observation	*Inference*

Conclusion

Substance **X** is probably: _____

Substance **Y** is probably: _____

(30 marks)

3. You are provided with an organic liquid, substance **Z**. Perform the following tests on **Z** and record your observations and inferences in the spaces provided.

(a) Burn a **small quantity (two drops)** 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 cm^3 of sodium carbonate solution.

Observation *Inference*

(c) Test liquid **Z** with litmus paper.

Observation *Inference*

(d) To 1 cm^3 of 2,4-DNPH solution add few drops of **Z**.

Observation *Inference*

Please turn the page.

(e) To 1 cm^3 of **Z** add 1 cm^3 of glacial ethanoic acid and three drops of concentrated sulfuric acid (CARE! CORROSIVE) and heat the mixture in a boiling water bath for 1 minute. Cool and add the mixture to 10 cm^3 of sodium carbonate solution.

Observation	*Inference*

(f) To 1 cm^3 of iodine solution add 5 drops of dilute sodium hydroxide solution. The solution becomes faint yellow in colour. To the resultant solution add 5 drops of **Z** and shake gently.

Observation	*Inference*

Conclusion: Give the structural formula of compound Z given that the mass spectrum of compound **Z** gave a peak having the highest m/z ratio at 74.

(20 marks)