Index No:_____ **AM 06/I.12m**

MATRICULATION AND SECONDARY EDUCATION CERTIFICATE EXAMINATIONS BOARD

UNIVERSITY OF MALTA, MSIDA

MATRICULATION CERTIFICATE EXAMINATION
ADVANCED LEVEL
MAY 2012

SUBJECT:	CHEMISTRY
PAPER NUMBER:	I
DATE:	3rd May 2012
TIME:	9.00 a.m. to 12.00 noon

Required Data: Relative atomic masses: O = 16; Cr = 52; Cl = 35.5. The molar gas constant is 8.314 J mol^{-1} K^{-1}.

Answer all questions

1. (a) Elements in the s-block form a variety of ionic compounds. Define the term *ionic bond*.

_____

_____

_____ *(2 marks)*

(b) The statements given below refer to crystalline sodium chloride. Read each statement and decide whether it is True or False. Give a reason for each answer.

(i) In a sodium chloride crystal, each sodium ion is only bonded to the chloride ion to which it donated its electron.

_____

_____

_____

(ii) A sodium atom can only form one ionic bond, because it has one electron in its outer shell to donate.

_____

_____

_____ *(3 marks)*

(c) Place the ions Li+, Na+ and Cs+ in the order indicated below, giving a reason for each answer:

(i) increasing ionic radius;

_____

_____

_____

(ii) increasing polarizing power;

(iii) increase in covalent character of the iodide.

(6 marks)

(Total: 11 marks)

2. (a) On vaporization, 0.150 g of a red volatile liquid displaced a volume of 30.0 cm^3 measured at 100 ^oC and 100 kPa. Find the molar mass of the red liquid.

(3 marks)

(b) On combustion in excess oxygen, 0.200 g of the red liquid produced 0.0981 g chromium(III) oxide. Calculate the percentage by mass of chromium in the liquid.

(3 marks)

(c) If the red liquid also contains 45.8 % chlorine and the rest is oxygen, determine its empirical and molecular formula.

(3 marks)

(d) Draw a likely molecular structure for the red liquid and explain whether it would be expected to exhibit optical isomerism.

_____

_____

_____

_____ *(2 marks)*

(Total: 11 marks)

3. The rate of reaction of two substances **X** and **Y** was investigated by sampling the reaction mixture and titrating. The reaction taking place may be represented as:

$$\mathbf{X}\,(aq) + \mathbf{Y}\,(aq) \xrightarrow{\text{acid catalyst}} \mathbf{Z}\,(aq) + \mathbf{Q}\,(aq)$$

The procedure is repeated changing the concentration of each substance in turn. The results obtained are shown in the table.

Experiment	***Initial concentrations/ mol dm^{-3}***			***initial rate / mol dm^{-3} s^{-1}***
	[Y]	***[X]***	***[HCl (aq)]***	
I	0.001	0.5	1.25	1.1
II	0.002	0.5	1.25	1.1
III	0.002	1.0	1.25	2.2
IV	0.002	1.0	2.50	4.4

(a) Why is the procedure repeated *changing the concentration of each substance in turn*?

_____

_____

_____ *(1 mark)*

(b) Find:

(i) the order of reaction with respect to **Y**;

_____

_____

(ii) the order of reaction with respect to **X**;

_____

_____

(iii) the order of reaction with respect to hydrochloric acid;

_____

_____ *(3 marks)*

(c) *(i)* Define *overall order* of a reaction.

_____

_____

(ii) Find the overall order of the reaction between **X** and **Y** in the presence of acid catalyst.

_____

_____ *(1 mark)*

(d) Write the rate equation for this reaction and find the value of the rate constant, stating its units.

_____

_____

_____

_____ *(3 marks)*

(e) Explain what the results of this experiment imply with regards to the likely mechanism of the reaction.

_____

_____

_____

_____

_____

_____ *(3 marks)*

(Total: 11 marks)

4. Osmium (symbol Os) is a d-block element with electronic configuration **[Xe]4f^{14}5d^{6}6s^{2}** .

(a) Why can Os be classified as a d-block element?

_____

_____ *(1 mark)*

(b) Os^{3+} is expected to be a stable oxidation state while Os^{2+} is expected to be a reducing agent. Explain this statement with reference to the electronic configurations of these ions.

_____

_____

_____

_____*(2 marks)*

(c) Os and its compounds are used as catalysts.

(i) What is a catalyst?

_____

_____ *(1 mark)*

(ii) Explain why compounds of d-block elements tend to have this property.

_____

_____

_____ *(2 marks)*

(d) Osmium forms the compound with formula $K_2[OsCl_6]$.

(i) State the oxidation number of Os and explain the bonding present in this compound.

_____

_____

_____

_____ *(2 marks)*

(ii) Draw the structure of the anion in this compound. *(2 marks)*

(Total: 10 marks)

5. One mole of nitrogen gas was mixed with 3 moles of hydrogen gas and the reaction is allowed to reach equilibrium at 1000 K. The mole fraction of ammonia in the reaction mixture at equilibrium was 0.15 at a total pressure of 500 atm.

(a) Describe how the following factors change from the start of the experiment until equilibrium is reached:

(i) the rate of the forward and reverse reactions and
(ii) the partial pressures of nitrogen, hydrogen and ammonia.

_____

_____

_____

_____

_____

_____ *(4 marks)*

(b) Calculate the partial pressure of each component in the equilibrium mixture.

_____

_____

_____

_____

_____

_____

_____ *(3 marks)*

(c) Calculate a value for the equilibrium constant K_p for the reaction at 1000 K, stating its units.

_____

_____

_____

_____ *(3 marks)*

(Total: 10 marks)

6. Fill in the blanks in the following table using any of the following chemical substances. Each property may fit one or more substances in which case include all correct answers the table. Each substance may be used once, more than once or not at all.

$NaNO_3$, C_{60}, BaO_2, $CaCO_3$, BeO, $AlCl_3$, $SiCl_4$, PbO

Property	**Chemical species**
An allotrope of graphite.	
A solid with important agricultural uses.	
A white solid which releases an odourless colourless gas on heating.	
A white solid which produces a gas on treatment with dilute acid in the cold.	

A molecular liquid which reacts with water to give a white solid among the products.	
A solid which is insoluble in water but dissolves in both acid and alkali.	
A solid which melts readily on heating to produce a molecular liquid which turns into vapour at higher temperature: the vapour dissociates reversibly on further heating.	
A non-conducting solid which reacts with hot concentrated nitric(V) acid to produce a mixture of gases and no solid residue.	

(11 marks)

7. This question is about the alcohol with the following structural formula.

$$CH_3CH(OH)(CH_2)_3CH_3$$

(a) Name and classify this alcohol as primary, secondary or tertiary and account for your answer.

_____

_____

_____ *(2 marks)*

(b) Explain why the alcohol is more soluble in diethyl ether than in water.

_____

_____

_____

_____

_____ *(1 mark)*

(c) Explain why the alcohol exists in two optically active forms.

_____

_____

_____

_____

_____ *(1 mark)*

(d) On treatment with acidified dichromate, the alcohol produces a substance **R** which reacts with a solution of sodium hydrogensulfite to form a precipitate **P**. Identify **R** and **P** and explain the reactions described.

_____

_____

_____

_____

_____

_____

_____

_____ *(4 marks)*

(e) On treatment with hot concentrated sulfuric acid, the alcohol produces a mixture of two structural isomers, **U** and **V.** The substance **U** is itself a mixture of two stereoisomers. Explain these observations, giving the structural formulae of all the isomers mentioned.

_____

_____

_____

_____

_____

_____

_____

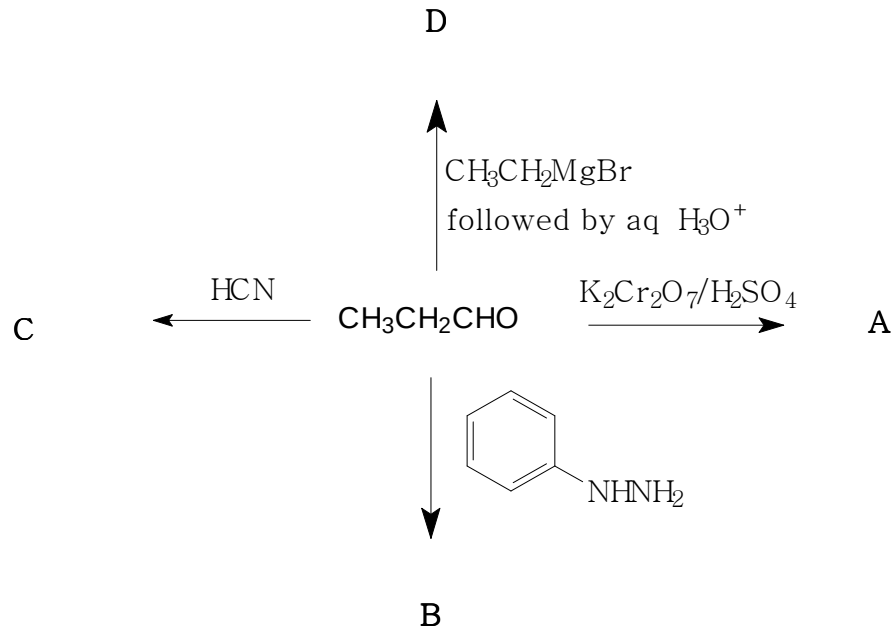
_____

_____ *(4 marks)*

(Total: 12 marks)

This space is deliberately empty.

8. Consider this reaction scheme involving propanal.



(a) Give structural formulae for substances **A, B, C** and **D**.

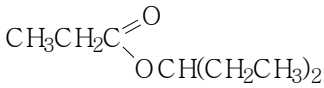
A =

B =

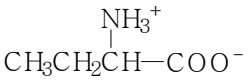
C =

D = *(6 marks)*

(b) Explain how the following two substances **F** and **G** can be prepared using organic products from the reaction scheme in (a) and appropriate inorganic reagents.



F



G

(6 marks)

(Total: 12 marks)

9. Explain the following observations as fully as you can, giving relevant chemical equations or structural formulae as appropriate.

(a) On adding drops of aqueous silver nitrate to liquid (bromomethyl)benzene in a test tube, a cream coloured precipitate forms; no precipitate forms if the organic liquid is 1-bromo-2-methylbenzene.

(3 marks)

(b) When a solution of hexanedioyl dichloride ($ClOC(CH_2)_4COCl$) in hexane is added to an aqueous solution of hexane-1,6-diamine, a white solid forms at the interface of the two liquids from which a fibrous substance can be extracted and rolled onto a glass rod.

_____

_____

_____

_____

_____

_____ *(3 marks)*

(c) On gentle warming, crystals of *cis*-butenedioic acid produce a colourless liquid product which evaporates to leave a white residue; *trans*-butenedioic acid is stable to heat.

_____

_____

_____

_____

_____

_____ *(3 marks)*

(d) When a solution of 4-aminobenzenesulfonic acid in dilute hydrochloric acid is added to an ice-cold solution of sodium nitrite, a colourless product is obtained; on adding this product to an alkaline solution of dimethylaminobenzene, an orange yellow precipitate forms.

_____

_____

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_____

_____

_____ *(3 marks)*

(Total: 12 marks)

MATRICULATION AND SECONDARY EDUCATION CERTIFICATE EXAMINATIONS BOARD

UNIVERSITY OF MALTA, MSIDA

MATRICULATION CERTIFICATE EXAMINATION
ADVANCED LEVEL
MAY 2012

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

Required Data: Relative atomic masses: H = 1; C = 12; N = 14; O = 16; Na = 23; Br = 80. One mole of any gas or vapour occupies 22.4 dm^3 at STP. Self-ionization product for water, $K_w = 1 \times 10^{-14}$ mol^2 dm^{-6}.

A Periodic Table is provided.

Answer two questions from each section and any other question.

Section A

1. (a) A half cell made up of $Co^{3+}(aq)/Co^{2+}(aq)$ is connected to a half cell made up of $Br_2(aq)/Br^-(aq)$. The standard electrode potentials of the half cells at 25 ^oC are:

$$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq) \qquad E^\theta = +1.82\ V$$
$$\tfrac{1}{2}\ Br_2(aq) + e^- \longrightarrow Br^-(aq) \qquad E^\theta = +1.07\ V$$

(i) Give a cell diagram for the reaction using the usual cell notation.
(ii) In which direction will electrons flow in the external circuit? Justify your answer.
(iii) Describe what, if anything, will happen to the colour intensity of the solution of the $Br_2(aq)/Br^-(aq)$ half cell.
(iv) Write a balanced ionic equation for the overall reaction.
(v) Calculate the E.M.F of the cell.
(vi) State, giving a reason in each case, which of the following: Br^-, Br_2, Co^{2+}, Co^{3+} is:
(I) the strongest oxidizing agent
(II) the strongest reducing agent. *(12 marks)*

(b) When a Cr^{3+}/Cr half cell is connected to an Fe^{3+}/Fe half cell, the Fe electrode is positive.
When the Fe^{3+}/Fe half cell is connected to a Cu^+/Cu half cell, the Fe electrode is negative.

(i) Explain this observation.
(ii) Identify the weakest oxidizing agent among these two redox systems giving reasons for your answers. *(4 marks)*

(c) Explain why magnesium alloys are used to protect the hulls of steel ships and other underwater structures from corrosion. *(4 marks)*

2. Cyclohexene (C_6H_{10}) reacts with hydrogen giving cyclohexane (C_6H_{12}). The standard enthalpy changes of formation of cyclohexene and cyclohexane are -38.2 and -156 kJ mol^{-1} respectively.

   (a) Define the term *standard enthalpy change of formation*. *(2 marks)*

   (b) By drawing a suitable enthalpy change cycle, calculate the value of ΔH for the reaction:

   cyclohexene + hydrogen ⟶ cyclohexane

   (5 marks)

   (c) Calculate a second value for ΔH for the reaction using the following average bond enthalpy terms (in kJ mol^{-1}) :

   C-C 347, C-H 413, C=C 612 and H-H 436.

   (5 marks)

   (d) State which of your two answers is more accurate and explain why. *(2 marks)*

   (e) Why is it not correct to estimate the enthalpy of hydrogenation of benzene as three times the value obtained in (b) or (c)? (2 *marks)*

   (f) The enthalpy change of combustion of cyclohexane can be found experimentally and has a value of -3924 kJ mol^{-1}. On the other hand the enthalpy change of formation of cyclohexane cannot be measured directly. How can the enthalpy change of formation of cyclohexane be calculated using the value of the enthalpy change of combustion?
   What other quantities are required? *(4 marks)*

3. This question refers to a number of equilibrium processes.

   (a) Hydrochloric acid of concentration 0.100 mol dm^{-3} is used to titrate 40 cm^3 of ammonia solution, of concentration 0.0500 mol dm^{-3}.

   (i) Sketch a graph to show how the pH of the solution varies with the volume of acid added and on your graph indicate the range over which the solution is behaving as a buffer. In your answer, explain the meaning of *buffer* and how it works.

   (ii) Three common acid-base indicators are:

Indicator	*pH range*
Thymol blue	1.2-2.8
Bromocresol green	3.8-5.4
Phenolphthalein	8.3-10.0

   Which of these three indicators can be used to determine the end-point of the ammonia-hydrochloric acid titration? Explain why this indicator is the most suitable. *(8 marks)*

(b) An aqueous solution of ammonia was shaken with a liquid silicone and the two layers were then allowed to separate (the liquid silicone acts as a solvent which is immiscible with water). On analysis, 20.0 cm^3 of the aqueous layer required 17.0 cm^3 of 1.00 mol dm^{-3} HCl for neutralization while 20.0 cm^3 of the silicone layer required 6.0 cm^3 of 0.0200 mol dm^{-3} HCl.

(i) Calculate the value of the partition constant of ammonia between water and the liquid silicone.

(ii) Explain how the principle behind this experiment may be used to extract and purify the product of a chemical reaction.

(8 marks)

(c) When bromobenzene is extracted by steam distillation at a pressure of 10^5 Pa, the mixture boils at 95.5 ^oC. At that temperature the vapour pressure of pure water is 8.58×10^4 Pa. Calculate the percentage by mass of bromobenzene in the distillate.

(4 marks)

4. A compound **C** has the molecular formula C_3H_6ONBr. It reacts with phosphorus(V) oxide to produce compound **D** (C_3H_4NBr) and with aqueous alkali to form a product which on acidification converts into substance **E** ($C_3H_6O_3$). **E** reacts with thionyl chloride to form **F** ($C_3H_4OCl_2$) and with a mixture of iodine and aqueous sodium hydroxide to form a yellow precipitate **G** and a solution of **H** ($C_2O_4Na_2$) in water.

(a) Deduce the structural formulae of compounds **C, D, E, F, G** and **H** and explain the reactions described including relevant chemical equations. *(12 marks)*

(b) Compound **E** can be converted into the yellow liquid **I** having the following structure:

$$H—C\equiv C—COOH$$

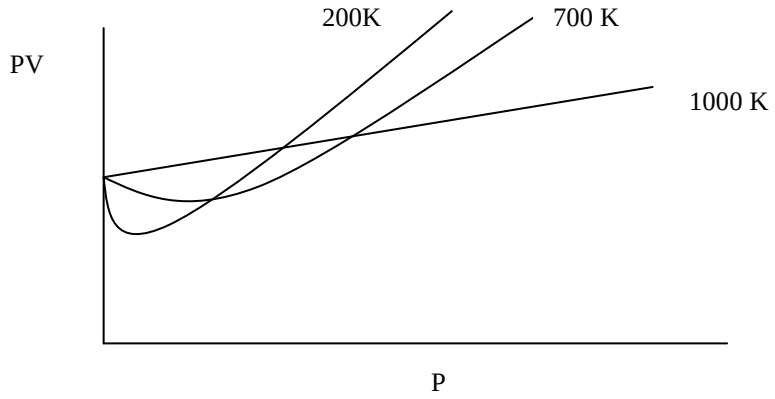
(i) Name substance **I**.
(ii) Suggest a method for converting substance **E** into **I**.
(iii) Compound **I** has delocalized electrons. Draw canonical formulae to represent the delocalization in compound **I**. *(8 marks)*

Please turn the page.

Section B

5. Explain ANY FOUR of the following observations. All parts carry equal marks.

(a) Graphs of PV *versus* P where P is the pressure and V is the volume of a fixed mass of nitrogen gas plotted at different temperatures are as shown in the diagram below.



This behaviour is not the same as that expected of an ideal gas.

(b) The relative molecular mass of ethanoic acid vapour changes with increasing temperature, from a value of about 120 at the lower temperature to about 60 at the higher temperatures.

(c) Even though the molecules BF_3, NF_3 and ClF_3 have the same stoichiometry (XF_3), their molecular structure is different.

(d) The reaction of chlorine with ethene to form 1,2-dichloroethane involves formation of an intermediate carbocation; this explains why 2-chloroethan-1-ol is minor reaction product when the chlorination is performed in the presence of water.

(e) Knowing that the mass spectrum of a ketone contains, as main peaks, those with m/z values 29, 57 and 86 allows one to distinguish between pentan-2-one and pentan-3-one.

(20 marks)

6. Explain the following statements using chemical principles and facts. Provide chemical equations where necessary.

(a) Sodium hydrogencarbonate (baking soda) and ammonium hydrogencarbonate are leavening agents: food additives that produce bubbles in dough or batter, causing baked goods to rise. The leavening effect from a given mass of ammonium hydrogencarbonate is better than that from the same mass of sodium hydrogencarbonate, however the ammonium salt is best used in making flat cookies and pastries but not for baking large cakes. *(4 marks)*

(b) The colour of the flower of the hydrangea is known to depend on the soil pH. Periodic treatment of the soil with aluminium sulfate results in blue hydrangeas.

(3 marks)

(c) When zinc granules were added to a solution of potassium dichromate(VI) in dilute sulfuric acid, the orange solution turned green. When the reaction was repeated in the absence of air, the green solution finally turned sky-blue but the solution became green again when shaken with air. When a solution of potassium dichromate(VI) is treated with alkali, the orange solution turns yellow. *(5 marks)*

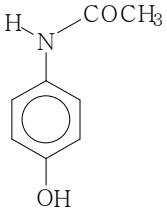
(d) Copper(II) chloride dissolves in water to give a blue solution. When concentrated hydrochloric acid is added, the solution turns green. *(3 marks)*

(e) Magnesium sulfate is more soluble than barium sulfate but barium hydroxide is more soluble than magnesium hydroxide. *(5 marks)*

7. (a) Explain with reasons which of the following species can function as an electrophile, as a nucleophile and which has neither function:

NH_3; CH_3^-; NH_2^-; Br^+; CH_3OH; CH_4; $C_6H_5CH_2^+$; NH_4^+ *(7 marks)*

(b) When 4-aminophenol is treated with ethanoic anhydride, the following product is formed.



Identify the electrophile which is formed from ethanoic anhydride and explain why this species forms a bond with the nitrogen rather than the more electronegative oxygen atom in the aminophenol. *(3 marks)*

(c) Alcohols react with carboxylic acids to form esters but phenols require treatment with carboxylic acid derivatives. *(4 marks)*

(d) Benzoic acid is purified by recrystallisation from water. Write a procedure for carrying out this operation on about 5 g crystals of this acid which a student of chemistry could follow. Briefly explain the principle of this purification technique and also explain how the student could check the purity of the recrystallised acid. *(6 marks)*

8. Give a practical laboratory method of preparation for small amounts of each of the following substances starting from the indicated substance and other readily available materials and including essential details. In your account, include balanced chemical equations for the reactions mentioned. More than one step may be required in certain cases. For (c) and (d), assume deuterium oxide is available. Each section carries equal marks.

(a) anhydrous iron(II) chloride from iron;
(b) sodium thiosulfate-5-water from sodium sulfite;
(c) dideuteroethyne (C_2D_2) from carbon;
(d) lithium tetradeuteridoaluminate ($LiAlD_4$) from lithium and aluminium;
(e) potassium manganate(VI) from manganese(IV) oxide. *(20 marks)*

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MATRICULATION AND SECONDARY EDUCATION CERTIFICATE EXAMINATIONS BOARD

UNIVERSITY OF MALTA, MSIDA

MATRICULATION CERTIFICATE EXAMINATION
ADVANCED LEVEL
MAY 2012

SUBJECT:	CHEMISTRY
PAPER NUMBER:	III – *Practical*
DATE:	14th June 2012
TIME:	3 hours

Answer all questions

1. In this experiment you are required to determine the concentration of a solution of hydrogen peroxide using a solution of potassium permanganate which is first standardized by titration against an iron(II) solution of exactly known concentration.

   You are supplied with the following chemicals:

   i about 200 cm^3 of 0.100 M ammonium iron(II) sulfate labelled **F**;

   ii about 200 cm^3 of a solution of potassium permanganate labelled $\mathbf{P_n}$ where n is the candidate laboratory number and

   iii about 200 cm^3 of a solution of hydrogen peroxide labelled **H** and

   Aqueous sulfuric acid is also provided for this experiment in special containers labelled 'Sulfuric acid'.

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

CANDIDATE LABORATORY NUMBER, n: .....

Please turn the page.

Standardization of the potassium permanganate solution $\mathbf{P_n}$ by titration with iron(II).

(b) Fill the burette with solution $\mathbf{P_n}$.

(c) Pipette 25.0 cm^3 of solution **F** into a conical flask, add 20 cm^3 dilute sulfuric acid and titrate with solution $\mathbf{P_n}$. Repeat the experiment for concordant results. Enter your titration results in the table below.

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

Mean titre value = _____ cm^3 solution $\mathbf{P_n}$

(d) Calculate the molar concentration of potassium permanganate given that the reaction involved in the experiment is the following:

$$MnO_4^-(aq) + 5\,Fe^{2+}(aq) + 8\,H^+(aq) \longrightarrow Mn^{2+}(aq) + 5\,Fe^{3+}(aq) + 4\,H_2O(l)$$

(e) Empty the burette of potassium permanganate solution and after proper cleaning with tap water followed by distilled water, refill it with solution **H.**

(f) Pipette 25.0 cm^3 of solution $\mathbf{P_n}$ into a conical flask, add about 20 cm^3 of dilute sulfuric acid and titrate with solution **H**. Repeat for concordant results. Enter your titration results in the table below.

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

Mean titre value = _____ cm^3 solution **H**

(g) Calculate the molar concentration of hydrogen peroxide in solution **H** given that the reaction between hydrogen peroxide and permanganate ions proceeds according to the equation:

$$2\ MnO_4^-(aq) + 5\ H_2O_2 + 6H^+(aq) \longrightarrow 2\ Mn^{2+}(aq) + 5\ O_2(g) + 8\ H_2O(l)$$

_____

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_____

_____*(50 marks)*

Please turn the page.

2. You are provided with an aqueous solution of an inorganic substance labelled **V** which is a double salt containing a common ion. Carry out the following tests on about 1 cm^3 samples of the solution and record your observations and inferences in the spaces provided.

   (a) Add dilute sodium hydroxide dropwise until in excess. Heat the mixture to boiling (CARE! Sodium hydroxide is caustic) and test for any gases evolved.

   Observation *Inference*

   _____ _____

   _____ _____

   _____ _____

   _____ _____

   (b) Add aqueous ammonia dropwise until in excess.

   Observation *Inference*

   _____ _____

   _____ _____

   _____ _____

   _____ _____

   (c) Add drops of sodium carbonate solution.

   Observation *Inference*

   _____ _____

   _____ _____

   _____ _____

   _____ _____

   (d) Add two drops of dilute nitric acid followed by 5 drops of silver nitrate solution and then add dilute aqueous ammonia until in excess.

   Observation *Inference*

   _____ _____

   _____ _____

   _____ _____

   _____ _____

   Conclusion:

V is probably a solution of the double salt: _____

(25 marks)

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

(a) Burn about 0.2 g of **S** on a crucible lid. Do not allow the flame to burn longer than you need to make a good observation.

Observation *Inference*

_____ _____

_____ _____

_____ _____

(b) Shake a few crystals of **S** with about 1 cm^3 water and warm the mixture; test the solution with litmus paper. *Keep mixture for tests (c) and (d).*

Observation *Inference*

_____ _____

_____ _____

_____ _____

(c) To part of the product from test (b), add drops of bromine water.

Observation *Inference*

_____ _____

_____ _____

_____ _____

Please turn the page

(d) To another part of the product from test (b), add drops of neutral iron(III) chloride solution.

Observation	*Inference*
_____	_____
_____	_____
_____	_____

(e) Add a few crystals of **S** to aqueous sodium carbonate.

Observation	*Inference*
_____	_____
_____	_____
_____	_____

(f) To about 0.3 g **S** add about 3 cm^3 of propan-1-ol, one drop of concentrated sulfuric acid (CARE! CORROSIVE) and heat the mixture in a boiling water bath for a few minutes. Tip the products of this reaction in a solution of sodium carbonate.

Observation	*Inference*
_____	_____
_____	_____
_____	_____

Conclusion:

Substance **S** is possibly:_____ *(25 marks)*

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