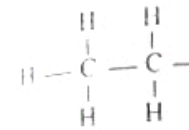
G.C.E. (A/L) Examination
2011 August
Chemistry II / Three hours

Instructions
- Periodic Table is provided.
- Use of calculators is not allowed.
- In answering questions 04 and 10, you may represent alkyl groups in a condensed manner.

Example



may be shown as CH_3CH_2 -

PART A - Structured Essay (Pages 02-08)

Answer all the questions.

Write your answer in the space provided below each question. Please note that the space provided is sufficient for the answer and that extensive answers are not expected.

PART B and PART C - Essay (pages 09-14)

Answer four questions selecting two questions from each part. Use the paper supplied for this purpose.

At the end of the time allotted for this paper, tie the answers to three parts A, B and C together so that Part A is on top and hand them over to the Supervisor.

You are permitted to remove **only** Parts B and C of the question paper from the Examination Hall.

- Universal gas constant, $R = 8.314\ JK^{-1}\ mol^{-1}$
- Avogadro constant $N_A = 6.022 \times 10^{23}\ mol^{-1}$

PART A - STRUCTURED ESSAY

Answer all four questions. Each question carries **10 marks.**

1 (a) You are provided with the following list of compounds.

KIO_3, PCl_5, $CdCl_2$, $CO(NO_3)_2$, $Na_2S_2O_3$

Which one of the above compounds

(i) is used as a primary standard in volumetric analysis?

(ii) gives a pale yellow precipitate when dil. H_2SO_4 is added to its aqueous solution?

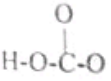
(iii) undergoes hydrolysis to give an acid with a tetrahedral structure?

(iv) gives a dark yellow precipitate when dissolved in dil. HCl and H_2S is passed through the solution?

(v) gives a blue coloured solution on addition of conc. HCl to its aqueous solution?

(2.0 marks)

(b) The following parts (i) - (vi) are based on the bicarbonate ion, HCO_3^-. The skeleton of HCO_3^- is given below.



(i) Draw the **most** acceptable Lewis structure for this ion.

(ii) Draw resonance structures for this ion and comment on their relative stabilities.

(iii) Deduce the shapes around the following atoms using the VSEPR theory.

I. C

II. O attached to H

(iv) Indicate the electron pair geometry (arrangement of electron pairs) around the following atoms.

I. C .....

II. O attached to H .....

(v) Indicate the hybridization of the following atoms.

I. C .....

II. O attached to H .....

(vi) Identify the atomic orbitals/hybrid orbitals involved in the formation of the following σ bonds present in the Lewis structure drawn in (i) above.

I. between C and O attached to H .....

II. between O and H .....

(6.0 marks)

(c) The following table gives the approximate values of melting points and electrical conduction (in relative terms excellent, good, poor, very poor or nil) of five substances, Mg, CO_2, SiO_2, NaCl and MgO. Complete the table by writing the formula of the appropriate substance in the column provided under the heading "Substance."

	Substance	Melting point /K	Electrical conduction in the solid state	Electrical conduction in the molten/liquid state
(1)		3200	poor	good
(2)		1100	poor	good
(3)		920	excellent	excellent
(4)		200	very poor/nil	very poor/nil
(5)		1900	very poor/nil	very poor/nil

(2.0 marks)

2 M is a non-transition element. Some chemical properties of this element are given below.

- It burns in air with a bright white flame to give a mixture of two compounds, A and B.
- It does not react with cold water but reacts slowly with hot water and steam with the evolution of a colourless, flammable gas, C.
- It reacts with conc. HNO_3 to form NO_2.

(i) Identify the element **M** and state one **important** use of it.

(ii) Write the ground state electronic configuration of M.

(iii) Write the chemical formulae of **A**, **B** and **C**.

A .....

B .....

C .....

(iv) **One** of the compounds **A** or **B**, reacts with water with the evolution of a gas. Identify this gas.

(v) Give the balanced chemical equation for the reaction between conc. HNO_3 and **M**.

(vi) Give the balanced chemical equation for the reaction of **M** with hot water.

(vii) Using an acid-base indicator explain how you would demonstrate in the laboratory, the occurence of the reaction of **M** with hot water.

(viii) Giving reasons indicate whether the electron affinity of **M** would be positive or negative.

(ix) State whether the solubi... ...es of oxides and hydroxides of the elements in the group of the Periodic Table to which **M** belongs decrease or increase or increase down the group. (Reasoning not required)

(x) **P** and **Q** are respectively the two elements found immediately before and after **M** in the Periodic Table. Indicate in the table given below with a 'tick' (✓) in the appropriate cage, the nature of the oxides of **P**,**M** and **Q**

element	strongly acidic	weakly acidic	amphoteric	weakly basic	strongly basic
P					
M					
Q					

(10 marks)

3. (a) Consider the chemical reaction.

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

and the thermochemical data given below (at 25°C)

Chemical species	$N_2(g)$	$H_2(g)$	$NH_3(g)$
Standard enthalpy of formation /kJ mol^{-1}	0.00	0.00	-46.1
Standard entropy/ J K^{-1} mol^{-1}	191.5	130.7	192.3

(i) Calculate ΔH^0 for the above reaction at 25°C

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(ii) Calculate ΔS^0 for the above reaction at 25°C.

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(iii) I. Write an expression to relate ΔG of a chemical reaction to its ΔH and ΔS

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II. Calculate ΔG^0 for the above reaction at 25°C

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(5.0 marks)

(b) (i) Non-volatile solute **A** dissolves in solvent **B** forming an ideal solution **C**. At a given temperature, the vapour pressure of the pure solvent and that of solution **C** are p^0 and p respectively. The mole fraction of the solvent in solution **C** is x_B.

I. Write the Raoult's law in the form of an equation for solution **C**, in terms of the symbols given above.

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II. The mole fraction of the solute in solution **C** is x_A. Write an equation for the Raoult's law in terms of p, p^0 and x_A. Hence, derive a mathematical expression for x_A

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(ii) Calculate the mole fraction of the solute in each of the following solutions **P**,**Q** and R.

P : 2.0 mol dm^{-3} aqueous solution of glucose which has a density of 1.26 g cm^{-3}.

Q : Solution containing 180 g of glucose in 162 g of water.

R : Solution containing 171 g of sucrose in 171 cm^3 of water

Consider that hte density of water is 1.0gcm^{-3}

Relative molar masses of water, glucose and sucrose are 18, 180 and 342 respectively.

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(iii) Arrange the solutions P, **Q** and **R** in the order of their **inceasing** vapour pressures, according to Raoult's law

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(iv) Write the Raoult's law as an equation for a mixture consisting of glucose, sucrose and water where the masses of these are known.

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(5.0 marks)

8. (a) (i) State the characteristic type of reaction that benzene undergoes

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(ii) Give the structure of the product and the mechanism, for the reaction between benzene and $(CH_3)_2CHCl$ in the presence of anhydrous $AlCl_3$.

(iii) Explain the stability of the intermediate formed from benzene in the above reaction.

(iv) Draw the structure of the expected major product when benzaldehyde (C_6H_5CHO) is reacted with $(CH_3)_2CHCl$ in the presence of anhydrous $AlCl_3$.

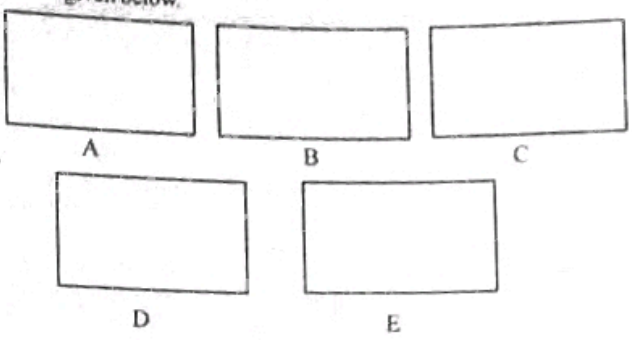
(4.0 marks)

(b) A,B and C are isomeric, optically inactive, monosubstituted aromatic compounds with the molecular formula $C_{10}H_{14}O$

- A reacts readily with conc HCl in the presence of anhydrous $ZnCl_2$ to give the corresponding halide, while B and C do not react with the same reagent at an appreciable rate.
- B and C when reacted with pyridinium chlorochromate give compounds D and E, respectively.

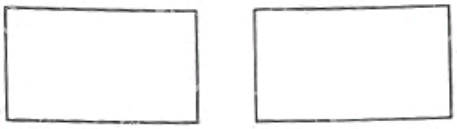
  D undergoes aldol type condensation in the presence of dil. NaOH while E does not

(i) Draw the structures of A,B,C, D and E in the relevant boxes given below.

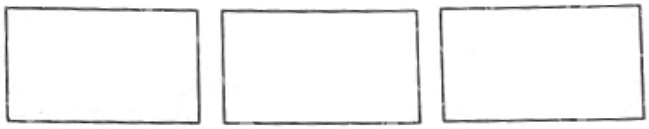


- B when heated with conc. H_2SO_4 gives F
- F when reacted with conc. HBr gives G

(ii) Draw the structures of F and G in the relevant boxes given below.



(iii) Draw the structures of the three products formed. in the boxes given below, when G is reacted with alcoholic KOH.



(iv) State whether G could exist in stereoisomeric forms

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(v) Explain your answer in (iv) above.

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(6.0 marks)

PART B - ESSAY

Answer all four questions. Each question carries 15 marks.

5. (a) At a temperature of 300 K and at a pressure of 1.0×10^5 Pa, a sample of oxygen gas weighing 3.2 g exists in a rigid vessel of volume V. Another rigid vessel of volume V which has been fully evacuated is connected to this vessel, allowing the gas to spread in both vessels. The temperature of the combined vessels is then raised to 400 K. At the same temperature, gas X is then introduced into the combined vessels, until the pressure is raised to 2.0×10^5 Pa. If the mass of the gas X required for this purpose is 8.8 g, calculate the relative molar mass of X. Assume that both these gases behave ideally and that they do not react with each other. (O = 16)

(3.0 marks)

(b) Solute S distributes in solvent A and solvent B in a molar ratio of 1 :9. (S is more soluble in solvent B)
Solute S distributes in solvent A and solvent C in a molar ratio of 1 :4. (S is more soluble in solvent C)
Solute S does not react with A, B or C. Further, A, B and C are inmiscible with each other.

(i) Calculate the partition coefficient of S between A and B.

(ii) Calculate the partition coefficient of S between A and C

(iii) A 25.00 cm^3 sample of 0.10 mol dm^{-3} S in solvent A was thoroughly mixed with 25.00 cm^3 of solvent B and the layers were allowed to separate. Calculate the concentration of S remaining in phase A.

(iv) After equilibrium was reached, a 10.00 cm^3 sample of phase/ from step (iii) above was thoroughly mixed with 20.00 cm^3 of solvent C, and the layers were allowe to separate. Calculate the concentration of S remaining in phase A.

Note : In these calculations, assume that the temperature is constant and that S does **not** undergo polymerization.

(6.0 marks)

(c) A sample of P gas was heated up to 481 K in a rigid container of volume 1.0 dm^3 in order to reach the following equilibrium.

$$2P(g) \rightleftharpoons 2Q(g) + R(g)$$

At equilibrium, it was found that the total pressure of the system was 1.2×10^5 Pa and that the partial pressure of R(g) was 2.0×10^4 Pa.

(i) Calculate the partial pressures of P(g) and Q(g).

(ii) Calculate the concentrations of P(g), Q(g) and R(g) at equilibrium.

(iii) Calculate the equilibrium constant, K_c for the above equilibrium.
($RT = 4.0 \times 10^3$ J mol^{-1} at 481 K)

(6.0 marks)

6. (a) In aqueous medium, the ionization constant, K_a of the monobasic acid HA is 1.0×10^{-5} mol dm^{-3} at 25°C

(i) Calculate the pH of a 0.100 mol dm^{-3} aqueous solution of HA at 25°C.

(ii) Derive a relationship for $\frac{[HA(aq)]}{[A^-(aq)]}$ in terms of $[H_3O^+(aq)]$ and K_a

$[H_3O^+(aq)]$, $[HA(aq)]$ and $[A^-(aq)]$ represent the concentrations of H_3O^+ HA and A^- respectively, at equilibruim in aqueous medium.

(iii) The pH of the HA solution with the initial concentration of 0.100 mol dm^{-3} is maintained at 4.0, by the addition of an appropriate quantity of a suitable base. Calculate [HA(aq)] and $[A^-(aq)]$in this case, using the relationship obtained in (ii) above.

(iv) Using the relationship derived in Part (ii) above, calculate the pH value at which $[HA(aq)] = [A^-(aq)]$ in solution.

(v) Calculate the pH of the solution prepared by mixing 55.00 cm^3 of HA solution of initial concentration 0.0500 mol dm^{-3} with 50.00 cm^3 of NaOH of initial concentration 0.0500 mol dm^{-3}

State the assumptions, if any used in this calculation.

(7.5 marks)

(b) (i) Calculate the concentration of H^+ ions in solution when a sample of 4.00 g of pure $CaCO_3$ is allowed to react with 500.0 cm^3 of 0.30 mol dm^{-3} HCl solution. (Relative molar mass of $CaCO_3$ = 100)

(ii) 250.0 cm^3 of 0.16 mol dm^{-3} NaOH solution is added to 250.0 cm^3 of the solution obtained in step (i) above, maintaining the emperature at 25°C. Show that no precipitation occurs.

Solubility product of $Ca(OH)_2$ at 25°C is 6.5×10^{-6} mol^3dm^{-9}.

(iii) Calculate the minimum mass of solid $Ca(NO_3)_2$ that should be added to the solution obtained in step (ii) above in order to observe a precepitation in it, while maintaining the temperature at 25°C.

(N = 14, O = 16, Ca = 40)

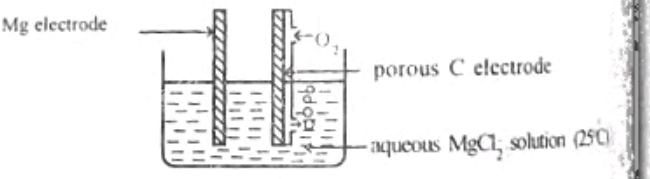
Note : Assume that there are no volume changes during mixing of solutions

(7.5 marks)

7. (a) (i) Sketch a magnesium electrode at its standard stsate. Label all parts.

(ii) Explain briefly why the absolute potential of an electrode cannot be measured.

(iii) Consider the electrochemical cell given below, prepared using a pure magnesium electrode and a porous carbon electrode. Both electrodes are immersed in a $MgCl_2$ electrolyte solution of a known concentration as shown in the diagram.



The equilibrium reactions at the Mg electrode and the C electrode, and their standard electrode potentials are shown below.

$$Mg^{2+}(aq) + 2e \rightleftharpoons Mg(s); \quad E^\ominus = -2.37\ V$$
$$O_2(g) + 2H_2O(l) + 4e \rightleftharpoons 4OH^-; \quad E^\ominus = 0.40\ V$$

I. Identify the cathode of the cell.

II. At standard state, calculate the electromotive force (e.m.f.) of the above cell.

III. Write balanced equations for the anode reaction, the cathode reaction and the overall cell reaction, that occur when the electrodes are externally connected using a conducting wire.

IV. What would you expect to observe if a solution of NaCl of the same concentration was used in place of the solution of $MgCl_2$ as the electrolyte in the cell? Explain briefly your answer

V. When the above cell connected to a circuit, the current produced decreases gradually with time. State **two** methods that could be used to raise the current to a satisfactory level again. Briefly explain the basis of the menthods stated by you.

(6.5 marks)

(b) (i) Define the terms, initial rate and average rate for a given chemical reaction.

(ii) The reactants **A**, **B** and **C** react with each other in an aqueous medium to yield products, as shown below.

$A + B + C \rightarrow$ products

The table below gives the results of four experiments performed at 30°C to investigate the kinetics of this reaction.

Experiment	Initial concentration of A/mol dm^{-3}	Initial concentration of B/mol dm^{-3}	Initial concentration of C/mol dm^{-3}	Initial rate of formation of products / mol $dm^{-3}s^{-1}$
1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

I. Write a mathematical expression to relate the rate of be above reaction to concentrations of **A**, **B** and **C**.

II. Calculate the order with respect to each reactant **A**, **B** and **C**.

III. Write an expression for the rate of the reaction using the orders obtained with respect to **A**, **B** and **C**.

IV. How does the rate of the above reaction change from its initial value the concentration of **C** is tripled keeping the concentrations of each species **A** and **B** unchanged?

(iii) It has been assumed that the above reaction takes place in the following elementary steps.

$A + C \rightleftharpoons X$ (a fast equilibrium step. Equilibrium constant is K_1)

$X + C \rightleftharpoons Y$ (a fast equilibrium step. Equilibrium constant is K_2)

$Y + B \rightarrow Z$ (a slow step)

$Z + nC + nB \rightarrow$ products (a fast step)

Indicate which of these steps will determine the rate of the reaction.

Write a rate expression for the reaction taking place in that step.

Hence, **derive** a rate expression for the reaction in step (b) (ii) above, in terms of [**A**], [**B**] and [**C**].

Note : The order with respect to each reactant of any elementary reaction is the same as the stoichio metric coefficient of that reactant.

(8.5 marks)

PART C - ESSAY

Answer all two questions only. Each question carries 15 marks.

8. (a) **A** and **B** are two water soluble crystalline compounds. When aqueous solutions of **A** and **B** are mixed together, an insoluble compound **C** and a water soluble compound **D** are formed. Given below are some tests carried out to identify **A** and **B**.

Test	Observation
1. Compound **A** was heated.	**A** reddish - brown gas evolved.
2. Aluminium (Al) powder and NaOH were added to an aqueous solution of **A**, the mixture was warmed and the gas evolved was tested with moist litmus.	Red litmus turned blue
3. H_2S was passed into an aqueous solution of **A**.	A black precipitate was formed.
4. Dilute HCl was added to an aqueous solution of **A**.	A white precipitate was formed.
5. The mixture obtained in test (4) above was boiled.	Precipitate dissolved to give a clear solution.
6. The hot solution formed in (5) above was allowed to cool.	White needles precipitated.
7. $BaCl_2$ was added to an aqueous solution of **B**.	A white precipitate insoluble in dil. HCl and dil. HNO_3 was formed.
8. Filtrate from (7) above was divided into two portions and tested as follows. I. NH_4OH was added II. A small amount of conc. HNO_3 was added followed by KSCN	 A dirty green precipitate was formed. The solution turned blood red in colour.

(i) Identify compounds **A** and **B** explaining the above observations.

(ii) Write balanced chemical equations for the reactions taking place in (1), (2), (3) and (4).

(iii) Identify compound **C**

(iv) To identify the cation and the anion present in compound **A**, give **one** chemical test for each, other than those given in the question.

(b) Solution **P** contains SO_4^{2-}, Cu^{2+} and H^+. The following procedures (1-3) were used to determine their concentrations.

Procedure :

(1) Excess $BaCl_2$ solution was added to 25.00 cm^3 of the solution **P**, to precipitate SO_4^{2-} as $BaSO_4$. The precipitate was filtered, washed and dried till a constant mass was observed. The mass of the precipitate was 2.335 g. Determine the concentration of SO_4^{2-} in solution **P** in mol dm^{-3}. (O = 16, S = 32, Ba = 137)

(2) H_2S was bubbled through 25.00 cm^3 of solution P to precipitate Cu^{2+} as CuS. The precipitate was filtered, washed with water, and the filtrate was kept to be used in procedure (3). The precipitate was transferred into a

titration flask containing 30.00 cm^3 of 0.28 mol dm^{-3} acidic $KMnO_4$ to produce Cu^{2+}, Mn^{2+}, and SO_2. The solution was boiled to remnove SO_2, and the excess $KMnO_4$ was titrated with 0.10 mol dm^{-3} Fe^{2+} solution. The burette reading at the end point was 10.50 cm^3. Determine the concentration of Cu^{2+} in solution **P** in mol dm^{-3}.

(3) The filtrate from procedure (2) above was placed in a titration flask, boiled to remove H_2S and cooled to room temperature. To this, both 5% KIO_3 and 5% KI were added in excess. The volume of 0.40 mol dm^{-3} $Na_2S_2O_3$ solution required to titrate the liberated iodine was 25.00 cm^3.

Determine the concentration of H^+ in solution **P** in mol dm^{-3}.

(7.5 marks)

9. (a) Oxidized and reduced forms of nitrogen gas are important chemical species that are involved in environmental pollution.

(i) Give the chemical formulae of **three** nitrogen species with positive oxidation states that contribute to atmospheric pollution.

(ii) Give the chemical formulae of **three** nitrogen species that contribute to ground water pollution.

(iii) Indicate the basic processes by which nitrogen gas is converted to more chemically active forms as given in (i) and (ii) above.

(iv) Explain briefly how the Haber process **indirectly** contributes ot environmental pollution.

(3.0 marks)

(b) Photochemical smog is a major atmospheric pollution problem associated with industrialization and transportation along with specific climatic conditions.

(i) Explain how photochemical smog develops.

(ii) Indicate how you would become aware of the presence of photochemical smog.

(iii) List **four** major toxic products found in photochemical smog. Give chemical reactions to show the formation of one toxic product that does **not** contain carbon.

(iv) Give **three** adverse effects due to photochemical smog.

(v) Suggest a method by which the formation of photodchemical smog can be reduced.

(4.5 marks)

(c) (i) Indicate briefly the steps involved in the production of **C** from copper pyrites.

Note : Balanced chemical equations for the relevant reactions should be given.

(ii) Give one chemical test to identify Cu^{2+} ions in an aqueous solution.

(3.5 marks)

(d) The manufacture of common salt (NaCl) is an important industry in Sri Lanka.

(i) Indicate the factors you would consider to be important in selecting locations to set up salterns.

(ii) Give a brief outline of the steps involved in the production of common salt.

(iii) The mother liquor obtained during [illegible] mon salt in a rish source of chemical [illegible]

List a metal and non metal that are recovered [illegible] mother liquor on a large scale

(4.0 marks)

10. (a) (i) Explain why alkyl halides tend to undergo nucleophilic substitution reactions.

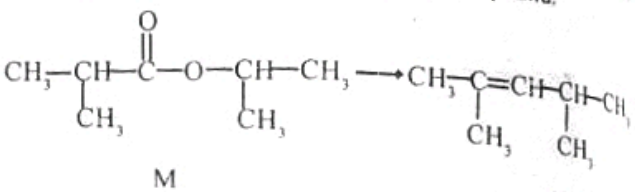
(ii) Explain why chlorobenzene does **not** undergo nucleophilic substitution reactions readily.

(4.0 marks)

(b) Draw the structures of the **three** main products that can be expected from the reaction given below.

(2.0 marks)

(c) Show how you would carry out the following synthesis using **M** as the **only** organic starting compound.

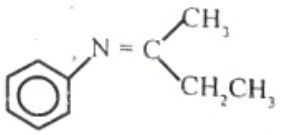


M

(6.0 marks)

(d) (i) Show how you would synthesize 2-butanone using acetylene (C_2H_2) as the **only** organic starting compound.

(ii) Show how you would synthesize the following compound using 2-butanone as one of the starting compounds.



(3.0 marks)