G.C.E. (A/L) Examination
2008 August
Chemistry II / Three hours

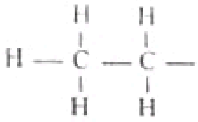
- Periodic Table is provided on page 8.
- Use of calculators is not allowed.

PART A - Structured Essay (Pages 2-7)

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

N.B : INSTRUCTION BOX

- **In answering questions 3 and 4, you may represent alkyl groups in a condensed manner.**

e.g.  may be shown as CH_3CH_2 -

$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-$$

PART B and PART C - Essay (pages 9-12)

Answer **four** questions selecting not more than 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.

$R = 8.314\ JK^{-1}\ mol^{-1}$
$N_A = 6.022 \times 10^{23}\ mol^{-1}$

PART A - STRUCTURED ESSAY

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

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1 (a) The 3d transition element M shows the highest oxidation state of +7.

(i) Identify M ....

(ii) Write the complete electronic configuration of M.

....

(iii) Give the chemical fourmula and the colour of the most stable oxide of M.

....

(2.2 marks)

(b) Fill in the blanks in the following table selecting the most appropriate words/ phrases from **only** those given below the table under categories A,B, C and D for the respective columns.

Material	A Type of material	B Particles occupying lattice positions	C Interactions between particles	D Electrical properties
Diamond				
KF (s)				
Ice				
Li(s)				

A : Ionic lattice, giant covalent lattice, metallic lattice, molecular lattice, amorphous material

B : Atoms, positive ions, negagive ions, positive ions and negative ions, molecules electrons

C : Covalent bonds, van der waals interactions, hydrogen bonds, metallic bonds, electrostatic interactions

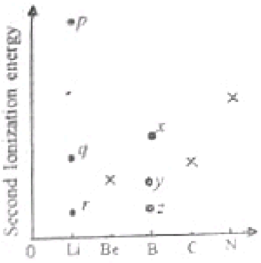
D : Conductor, nonconductor, electrolyte

(4.8 marks)

(c) the points corresponding ot the second ionization energy of Be, C and N are shown by x in the figure given below

(i) Select the most appropriate point corresponding to the second ionization energy of Li out of the points p, q and r, and mark it with a circle (⊙)

(ii) Select the most appropriate point corresponding to the second ionization energy of B out of the points x,y and z and mark it with a square (⊡)



(3.0 marks)

2. (a) A sample of Na_2SO_4 is contaminated with some NaCl. The following procedure was used to determine the percentage of NaCl in the sample.

1.000 g of the sample was dissolved in water in a 250 cm^3 volumetric flask and diluted upto the mark to form the solution A.

The following solutions (1) - (5) were prepared by diluting a 4.0×10^{-4} mol dm^{-3} Cl^- ion solution.

	(1)	(2)	(3)	(4)	(5)
4.0×10^{-4} mol dm^{-3} Cl^- ion solution/cm^3	1.00	2.00	3.00	4.00	5.00
Distilled water/cm^3	9.00	8.00	7.00	6.00	5.00

Into each of the solutions (1)-(5), 1.00 cm^3 of dil. HNO_3 and 1.00 cm^3 of $AgNO_3$ were added. Similarly into 10.00 cm^3 of solution A, 1.00 cm^3 dil. HNO_3 and 1.00 cm^3 $AgNO_3$ were added.

It was observed that the turbidity produced by solution **A** was equal to that of solution (3).

Calculate the mass percentage of NaCl in the sample of Na_2SO_4.
(Na = 23.0, Cl = 35. 5)

(5.0 marks)

(b) **A** and **B** are pure liquids miscible in all proportions forming ideal solutions at temperature T. The boiling point of **A** is higher than that of **B**. Mark/draw the following in Figure l.

(i) P^o_A and P^o_B : Relative points representing vapour pressures of pure **A** and Pure **B** respectively.

(ii) P_A : Line/curve showing the variation of the vapour pressure of **A** with composition.

(iii) P_B : Line/curve showing the variation of the vapour pressure of **B** with composition.

(iv) P_T : Line/curve showing the variation of the total vapour pressure with composition

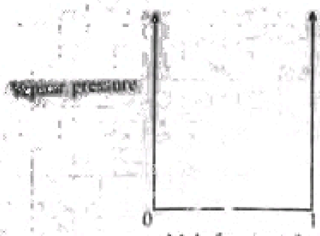


Figure 1

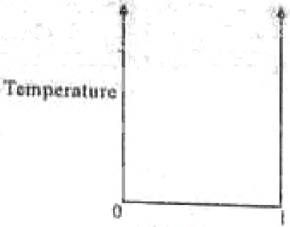


Figure 2

(v) Show that for an equimolar solution of **A** and **B** in equilibrium with its vapour, the mole fraction of A in the vapour phase is,

$$\frac{P^o_A}{P^o_A + P^o_B}$$

....

....

....

....

(vi) Draw the temperature - composition phase diagram for the solutions of A and B in Figure 2. Mark in your diagram,

I. the boiling point, T^v_A, of pure A.

II. the boiling point, T^o_B, of pure B and

III. the regions where the following phases exist. liquid, vapour and liquid + vapour together.

(5.0 marks)

3. Complete the following synthesis, schemes **A** and **B** selecting reagents and solvents only from those given with each scheme.

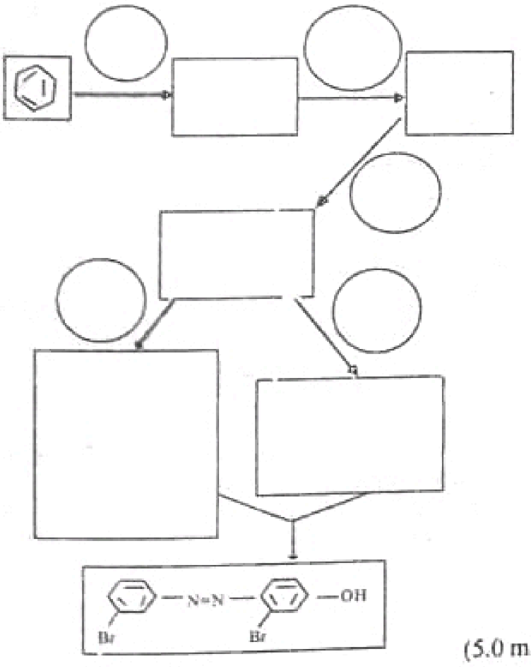
- Write the structure of appropriate compounds in the boxes and the reagents / solvents in the circles.
- Indicate temperature where important.

(i) **Scheme A** :

Reagents and solvents :

dil HCl, conc.HCl, conc.H_2SO_4, conc.HNO_3

aq. NaOH, $NaNO_2$, CuBr, Br_2, $FeBr_3$, Fe, PBr_3, $LiAlH_4$, Sn

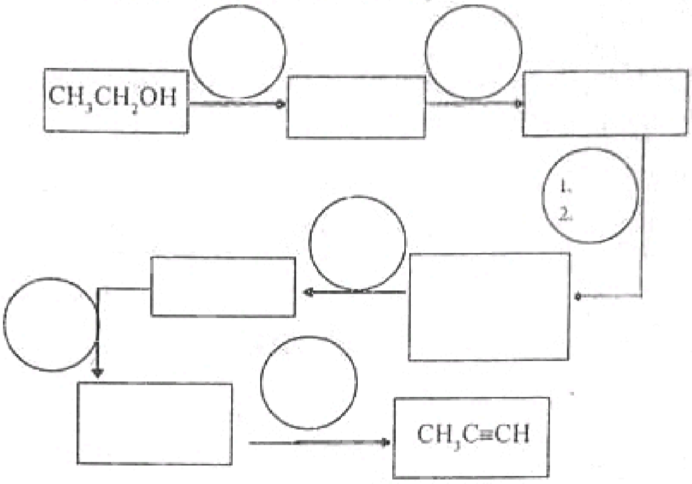


(5.0 marks)

(ii) **Scheme B** :

Reagents and solvents :

conc. H_2SO_4, Br_2, $FeBr_3$, PBr_3, HCHO, alcoholic KOH, CH_3CHO, Mg, Fe, dry ether, H_2O



(5.0 marks)

4 (a) Cinnamaldehyde is the main constituent of cinnamon oil. It has the following structure.

C_6H_5 - CH = CH CHO

(i) Suggest a test, to show that cinnamaldehyde contains a double bond. Give the expected observation/s.

Test	Observation/s
....	....
....	....

(ii) Cinnamaldehyde is reacted with $LiAlH_4$ and reaction mixure is treated with dil. acid.

I. Draw the structure of the final organic product obtained.

....

II. Name the type of reaction occurring between Cinnamaldehyde and $LiAlH_4$.

....

(iii) Cinnamaldehyde reacts with isopropyl magnesium bromide. $(CH_3)_2$ CHMgBr

I. Give the name of a solvent used on this reaction.

....

II. Why is it important to keep the solvent dry?

....

III Write the structural formula of the product obtained when cinnamaldehyde is reacted with $(CH_3)_2$ CHMgBr and the intermediate hydrolysed.

....

IV. Recall the condensation reaction that occurs between two molecules of CH_3CHO in the presence of aqueous NaOH.

Write the structures of the two molecules that would undergo a similar reaction under the same conditions forming cinnamaldehyde.

(5.0 marks)

(b) **The two compounds A and B have the same molecular formula C_3H_6O. Both A and B react with Brady's reagent giving orange coloured precipitates.**

A reacts with HCN forming a single product C.

B reacts with HCN forming a mixture of two stereo-isomers D and E.

(i) Write the structures of A, B, C, D and E in the appropriate cages.

A

B

C

D

E

(ii) State the specific type of isomerism shown by D and E.

....

(iii) State a physical property that can be used to distinguish between **D** and **E**?

....

(iv) What difference is shown by **D** and **E** in respect of the physical property given by you in (iii) above?

....

(5.0 marks)

PART B - ESSAY

- Answer two questions only. (Each question carries **15 marks.**)

$R = 8.314\ JK^{-1}\ mol^{-1}$
$N_A = 6.022 \times 10^{23}\ mol^{-1}$

5 (a) NH_4SH undergoes decomposition at 27 °C as follows:

$$NH_4SH\ (s) \rightleftharpoons NH_3\ (g) + H_2S\ (g)$$

The equilibrium constant, K_c, for this reaction at 27°C is $1.44 \times 10^2\ mol^2\ m^{-6}$

(i) Calculate the equilibrium constant, K_p, for the above reaction at 27°C.

Note : • Derivation of the relevant equations is not necessary.
• Assume that $NH_3(g)$ and $H_2S(g)$ behave ideally
• At 27°C, RT = 2.5 kJ mol^{-1}

(ii) Calculate the minimum mass of NH_4SH that must be placed in an evacuated vessel of volume $1.0 \times 10^{-3} m^3$ to attain the state of equilibrium at 27°C.

(The relative molecular mass of NH_4SH = 51)

(7.5 marks)

(b) Using the descriptions provided for solutions A to G, answer the questions (i) - (vi)

Solution	**Description**
A	Freshly distilled water in a stoppered bottle.
B	An aqueous solution of 0.20 mol dm^{-3} HCl.
C	An aqueous solution of 0.10 mol dm^{-3} CH_3COOH.
D	An aqueous solution of 0.01 mol dm^{-3} CH_3COOH.
E	An aqueous solution which is 0.10 mol dm^{-3} in CH_3COOH and 0.10 mol dm^{-3} in CH_3COONa
F	An aqueous solution which is 0.10 mol dm^{-3} in CH_3COOH and 0.05 mol dm^{-3} in CH_3COONa
G	An aqueous solution which is C_1 mol dm^{-3} in CH_3COOH (dissociation constant K_1) and C_2 mol dm^{-3} in HCOOH dissociation constant K_2)

(i) Arrange solutions **A** to **E** in the order of **increasing** their pH. No explanation is necessary.

(ii) Solution **E** was diluted 10 times. Would the pH change? Explain your answer in brief.

(iii) Which of the solutions E or F would resist more to a change in pH upon addition of a small quantity of an HCl acid solution? Explain your answer in brief.

(iv) Solution **I** was prepared by mixing 50.0 cm^3 of **B** and 50.0 cm^3 of **C**. What is the pH of **I**? State assumptions, if any, you used in this estimation.

(v) What change in pH would you expect when **A** is exposed to air? Explain your answer in brief.

(vi) Derive an expression for the total H^+ ion concentration of solution G in terms of the initial concentrations (C_1, C_2) and the acid dissociation constants (K_1, K_2) of acetic acid and formic acid respectively.

(7.5 marks)

6\. (a) **Calculate the lattice energy of $CaBr_2(s)$ by constructing an appropriate enthalpy level diagram. Necessary thermochemical data are given below.** (Physical states of all chemical species must be given for full marks)

Enthalpy of evaporation of Br_2 (l) = 31 kJ mol^{-1}
Bond dissociation enthalpy of Br_2 (g) = 193 kJ mol^{-1}
Electron affinity of Br (g) = -331 kJ mol^{-1}
Enthalpy of atomization of Ca (s) = 177 kJ mol^{-1}
Sum of first and second ionization energies of Ca(g) = 1740 kJ mol^{-1}
Enthalpy of formation of $CaBr_2$ (s) = -683 kJ mol^{-1}

(6.0 marks)

(b) A 20.0 g sample of dry clay was thoroughly stirred with 100.0 cm^3 of 0.100 mol dm^{-3} KNO_3 solution, and the resulting clay suspension was allowed to settle. The supernatant solution was then separated, and to 50.0 cm^3 of this solution, 100.0 cm^3 of 0.0500 mol dm^{-3} ammonium oxalate solution was added. The resulting solution was filtered, and the precipitate was dried and weighed. The mass of the dry precipitate was 256 mg.

(i) Calculate the concentration of Ca^{2+} in this filtrate.

(ii) Calculate the quantity of Ca in the clay sample in mg/kg. State assumptions, if any, you used in these calculations.
(C = 12. 0 = 16.0, Ca = 40.0)
Solubility product of calcium oxalate (CaC_2O_4) at the relevant temperature = 2.30×10^{-9} mol^2 dm^{-6}

(9.0 marks)

7 (a) Few drops of phenolphthalein were added to a freshly prepared aqueous solution of 0.10 mol dm^{-3} KI. This solution was well stirred, and thereafter, it was electrolysed using carbon electrodes for a specific period of time. The current passed through the solution was kept constant.

(i) What was the colour of the solution before electrolysis?

(ii) Write the balanced chemical equations for

I. the anode reaction
II. the cathode reaction, and
III. the cell reaction

(iii) Indicate the colour changes that would occur around the electrodes with the start of electrolysis.

(iv) Propose a method to determine the fraction of I^- ions left at the end of electrolysis. (No experimental details necessary)

(v) Would the fraction of remaining I^- be different from the value in (iv) if 0.50 mol dm^{-3} KI was used instead of 0.10 mol dm^{-3} KI? Briefly explain your answer.

(vi) In a separate experiment, a solution of $CuSO_4$ was electrolysed using carbon electrodes. What changes would yolu observe.

I. On the electrodes
II. in solution?

Write down the relevant electrode reactions.

(9.0 marks)

(b) (i) "The order of a particular reactant appearing in the rate expression of a given chemical reaction may **not** necessarily be the same as the stoichiometric coefficient of that reactant in the balanced chemical equation." Clarify this statement in brief.

(ii) $FeCl_3$ is reduced by $SnCl_2$ according to the following reaction.

$$2\,FeCl_3\,(aq) + SnCl_2\,(aq) \rightarrow 2FeCl_2(aq) + SnCl_4(aq)$$

A 50.0 cm^3 sample of 0.0360 mol dm^{-3} $FeCl_3$ solution was mixed with a $SnCl_2$ solution of the concentration and of the same volume. It was found that, after 4.00 minutes, 24% of the initial quantity of Fe(III) had been converted to Fe(II). Calculate

I. the rate of reduction of Fe (III)
II. the rate of oxidation of Sn (II).

(6.0 marks)

PART C - ESSAY

* Answer two questions only. (Each question carries **15 marks.**)

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8 (a) $\mathbf{X_2Y}$ and $\mathbf{YZ_2}$ are two gases formed by the element **Y**. **Y** is a solid at room temperature where as $\mathbf{X_2}$ and $\mathbf{Z_2}$ are gases

(A) $\mathbf{X_2Y}$ and $\mathbf{YZ_2}$ dissolve in water giving acidic solutions.

(B) The oxidation state of **Y** in $\mathbf{X_2Y}$ is -2 and in $\mathbf{YZ_2}$ it is +4.

(C) $\mathbf{X_2Y}$ and $\mathbf{YZ_2}$ (moist) react together forming **Y** and $\mathbf{H_2O}$.

(D) When $\mathbf{X_2Y}$ is passed into an acidified $CuSO_4$ solution, a black precipitate is formed.

(E) When $\mathbf{YZ_2}$ is passed into an acidified $\mathbf{CuSO_4}$ solution, the solution turns colourless.

(i) Identify the gases $\mathbf{X_2Y}$ and $\mathbf{YZ_2}$

(ii) Write balanced chemical equations for reactions occuring in **(C)**, **(D)** and **(E)**.

(iii) Give **two** industrial uses of the gas $\mathbf{YZ_2}$

(iv) Describe briefly a chemical method to identify each of these gases when present as a mixture.
Give the relevant balanced chemical equations.

(9.0 marks)

(b) **A** solution **B** contains $C_2O_4^{2-}$ and CO_3^{2-} ions. A 25.00 cm^3 portion of this solution was treated with excess $Ca(NO_3)_2$ solution to completely precipitate $C_2O_4^{2-}$ and CO_3^{2-} ions. The precipitate so obtained after drying had a mass of 0.820 g. This precipitate was then dissolved in dil. H_2SO_4 and titrated with 0.05 mol dm^{-3} $KMnO_4$ solution. The titration required 20.00 cm^3 of the $KMnO_4$ solution.

Calculate the concentrations of $C_2O_4^{2-}$ and CO_3^{2-} ions in the solution **B**.
(Ca = 40. 0 C = 12. 0, O = 16.0)

(6.0 marks)

9\. (a) (i) The density of an aqueous solution prepared using prue Na_2CO_3 was found to be 1.0212 gcm^{-3}. Calculate the concentration of this solution. Assume that the density of water at the very same temperature is 1.000 g cm^{-3} and that there is no change in volume during the dissolution of Na_2CO_3.

(ii) With the solution in (i) above (in the burette) 25.00 cm^3 aliquots of a H_2SO_4 solution were titrated using phenophthalein as the indicator. The average of three appropriate end points obtained was 12.50 cm^3.
Calculate the concentration of the H_2SO_4 solution

(iii) Would it be possible to carry out the above titration in the same way using methyl orange as the indicator?

If yes, what is the end-point you expect? If no, give reasons.

(Na = 23.0, C = 12.0, O = 16.0)

(6.0 marks)

(b) The 3d transition element **M** reacts with dil. H_2SO_4 forming a pale green solution. On addition of NH_4OH this solution gives a light green precipitate. This precipitate turns yellow-brown with time when kept exposed to air.

(i) Identify **M**

(ii) What are the most common (positive) oxidation states of **M**?

(iii) Give **one** test to distinguish between the oxidation states given in (ii).

(iv) Outline a method to determine quantitatively the concentrations of **M** in each of the oxidation states given in (ii) when present together in a sample.

(v) Identify the species responsible for the light green and the yellow-brown precipitates mentioned above.

(vi) Give **one** instance where **M** is used as a catalyst in chemical industry.

(vii) Give the chemical formulae and the names of **two** ores used for the extraction of **M**.

(9.0 marks)

10 (a) (i) I. What is meant by the temporary

II. What chemical species are respo porary hardness?

III. Give **two** domestic problems caused by temporary hardness

IV. Give **two** methods by which temporary can be removed. Write chemical equations appropriate

(ii) Briefly explain the variation of the acids strength following.

HClO, $HClO_2$, $HClO_3$, $HClO_4$

(7.0

(b) Ostwald process is used for the manufacture of HN

(i) What are the starting materials used in this pro

(ii) State the sources/ methods of obtaining these materials.

(iii) Give the chemical steps involved in the Os process together with balanced chemical equatio the necessary conditions (temperature, pre catalyst)

(iv) In the manufacture of HNO_3, rather than oxidizing directly to NO(g), It is first reduced and the pr obtained then oxidized.

Explain the reason for this briefly using the therm chemical data given below.

Values of standard enthalpy of formation, (ΔH_f), of N NH_3(g) and H_2O(g) are respectively +90 kJmol^{-1}, -4 mol^{-1} and -242 kJ mol^{-1}

(8.0 m

The Periodic Table

1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	La- Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	Ac- Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub	113 Uut	....				

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr