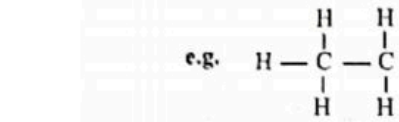
G.C.E. (A/L) Examination
2009 August
Chemistry II / Three hours

- Periodic Table is provided on page 14.
- Use of calculators is not allowed.

PART A - Structured Essay (Pages 2-7)

- Answer all the questions on this paper itself.
- 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.
- **In answering questions 3 and 4, you may represent alkyl groups in a condensed manner.**

e.g.  may be shown as CH_3CH_2 -

PART B and PART C - Essay (pages 8-13)

- 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.
- Take R = 8.314 $JK^{-1} mol^{-1}$ and N_A = 6.022 x 10^{23} mol^{-1}

PART A - STRUCTURED ESSAY

Answer **all four** questions on this paper itself. (Each question carries **10 marks.**)

1. (a) Define "atomic mass unit."

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(1.0 marks)

(b) The element A forms the anions AF_2^- and AF_4^-. AF_2^- is linear and AF_4^- is square plannar in shape.

(i) Sketch the shapes of AF_2^- and AF_4^- indicating the arrangement of lone pairs if any, on the central atom.

AF_2^- AF_4^-

(ii) State the group in the periodic table to which A belongs.

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(4.0 marks)

(c) $^{4}_{2}X + {}^{\cdots}_{4}Be \rightarrow {}^{12}_{6}C + {}^{\cdots}_{\cdots}Y$

(i) Fill in the blanks denoted by dotted lines (...) at **three** places in the above equation.

(ii) Identify X and Y.

X = ... Y = ...

(2.5 marks)

(d) The first ionization energies of five consecutive elements in the periodic table with atomic numbers Z, Z+1, Z+2, Z+3 and Z+4 are given below. Z is less than 16 and one of these elements is a metal. The ionization energy values are not given in any particular order.

Ionization Energies : 495, 1313, 1681, 2081, 1402 kJ mol^{-1}

Write in the table given below, the relevant ionization energy value for each element.

Atomic number	Z	Z+1	Z+2	Z+3	Z+4
Ionization energy /kJ mol^{-1}					

(2.5 marks)

2 (a) $X.H_2$ is a white crystalline salt. The elements present in X and their mass percentages are given below.

Element	C	H	N	O
Mass %	19.4	6.4	22.6	51.6

(C = 12.0, H = 1.0, N = 14.0, O = 16.0)

(i) Deduce the empirical formula of X.

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(ii) On heating, one mole of X produces two moles of NH_3 as the only nitrogen containing product. Write the molecular formula of X.

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(iii) A warm aqueous solution of X decolorizes an acidified $KMnO_4$ solution. Write the chemical name of X.

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(5.0 marks)

(b) (i) What is meant by the standard enthalpy of formation of $CO_2(g)$?

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(ii) When a sample of 72.0 g graphite is burnt in oxygen under standard conditions, the product mixture is found to contain by mass 28% CO(g), 66% $CO_2(g)$ and unburnt C(s).

Standard enthalpy of formation of CO(g) = -111 kJ mol^{-1}

Standard enthalpy of formation of $CO_2(g)$ = -394 kJ mol^{-1}

(C = 12.0, O = 16.0)

1. Calculate the following :

A The mole ratio of C(s), CO(g) and $CO_2(g)$ in the product mixture.

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B. The number of moles of CO(g) released.

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C. The number of moles of CO_2(g) released.

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D. The heat released on burning 1.0 mol of graphite under standard conditions.

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II. Using the above thermochemical data, deduce whether the conversion of CO(g) to CO_2(g), under standard conditions, is endothermic or exothermic.

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(5.0 marks)

3. (a) An industrially important organic compound X, contains carbon, hydrogen and oxygen only.

(i) Write a balanced chemical equation for the complete combustion of **X** taking its molecular formula as $C_xH_yO_z$.

.....

(ii) The combustion of 62 mg of **X** (relative molecular mass. $M_r = 62$) gives 88 mg of CO_2 and 54 mg of H_2O. Deduce values for x, y and z in the molecular formula $C_xH_yO_z$. (C = 12.0, H = 1.0, O = 16.0)

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(iii) The reaction of 62 mg of X with sodium gives 2 mg of hydrogen gas. Deduce the structure of X.

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(4.4 marks)

(b) (i) What is the **main** type of intermolecular force present in each of ethanol ($M_r = 46$), methanoic acid ($M_r = 46$) and propane ($M_r = 44$)?

In ethanol : .....

In methanoic acid : .....

In propane : .....

(ii) Arrange ethanol, methanoic acid and propane in the **increasing** order of their boiling points.

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(iii) Explain your answer in (ii) above.

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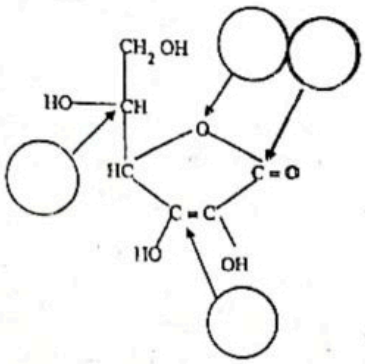
(c) The molecular structure of vitamin C is given below. Write the hybridisation of the carbon and oxygen atoms indicated by arrows as sp, sp^2 or sp^3 in he appropriate circle.

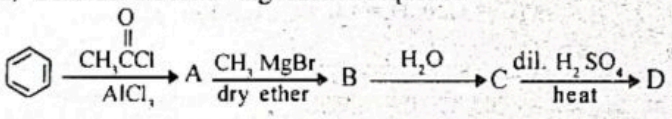


(1.6 marks)

(d) An optically active compound, $C_6H_{12}O$, gives a yellow precipitate with 2,4 - dinitrophenylhdrazine but does not react with ammoniacal silver nitrate. What is the structure of the compound?

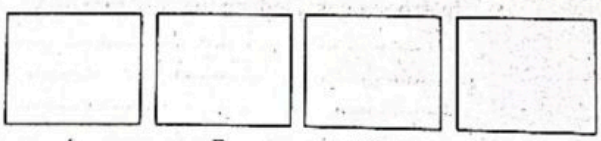
(1.6 marks)

4 (a) Consider the following reaction sequence.



Reaction 1 Reaction 2 Reaction 3 Reaction 4

(i) Write the structures of **A**,**B**,**C** and **D** in the boxes given below.



A B C D

(ii) Classify each of the reactions in the above sequence as addition (Ad), elimination (E), rearrangement (R) or substitution (S) by writing Ad, E, R or S in the appropriate cage.

Reaction	1	2	3	4
Reaction type				

(iii) Write the active species and whether it is an electrophile or a nucleophile, in each of the reactions 1 and 2 in the appropriate cages.

Reaction	Active species	Electrophile/ Nucleophile
1		
2		

(2.4 marks)

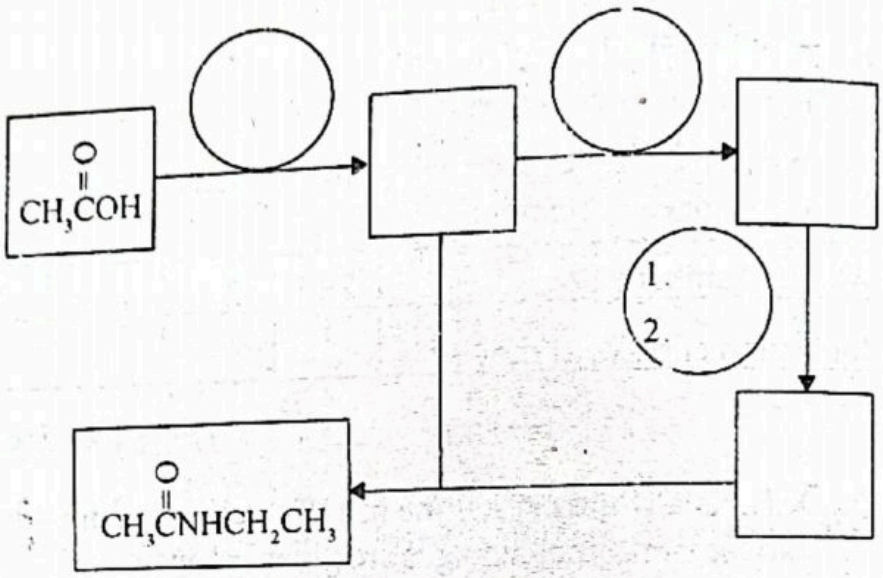
(b) Complete the syntheses in **schemes A** and **B** selecting appropriate reactants/ reagents/ solvents **only** from those given with each scheme.

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

(i) **Scheme A**

Reagents/ solvents

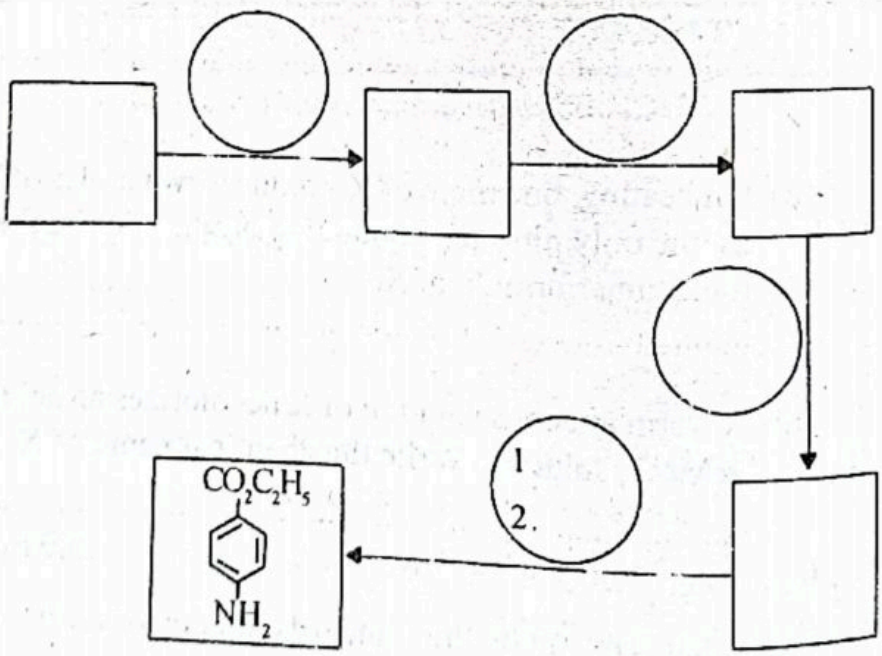
Mg, P_2O_5, PCl_5, $LiAlH_4$, $NaBH_4$, CH_3CHO, conc. NH_3, dil. H_2SO_4, water, dry ether



(i) **Scheme B**

Reactants/ regents / solvents

nitrobenzene, toluene ($C_6H_5CH_3$), CH_3Cl, $AlCl_3$, Zn(Hg), Sn, $KMnO_4$, $NaNO_2$, conc. HNO_3, conc. H_2SO_4, conc. HCl, aq. NaOH, water, ethanol



(7.6 marks)

PART B - ESSAY

* Answer two questions only. (Each question carries **15 marks.**)
* Take $R = 8.314\ JK^{-1}mol^{-1}$ and $N_A = 6.022 \times 10^{23}\ mol^{-1}$

5. (a) (i) 2.0 mol of X(g) was heated upto 450 K in a closed container to establish the equilibrium.

$$X(g) \rightleftharpoons 2Y(g)$$

At this equilibrium, it was found that 25% of the initial amount of **X**(g) was decomposed to produce **Y**(g) and the total pressure was $6.0 \times 10^5\ Nm^{-2}$.

Calculate the following :

I. The mole fractions of **X**(g) and **Y**(g) at equilibrium

II. The equilibrium constant, K_p

(ii) When the temperature of the above system was increased to 600 K, **Y**(g) also underwent decomposition to establish the following equilibrium.

$$X(g) \rightleftharpoons 2Y(g) \rightleftharpoons Z(g)$$

When 2.0 mol of **X**(g) was initially used, it was found that 1.0 mol **X**(g) and 0.50 mol **Z**(g) were present together with **Y**(g) at equilibrium.

I. Calculate the following :

(A) The number of moles of **Y**(g) at equilibrium.

(B) The mole fractions of **X**(g), **Y**(g) and **Z**(g) at equilibrium.

(C) The total pressure of the system at equilibrium.

(D) The equilibrium constant for $X(g) \rightleftharpoons 2Y(g)$

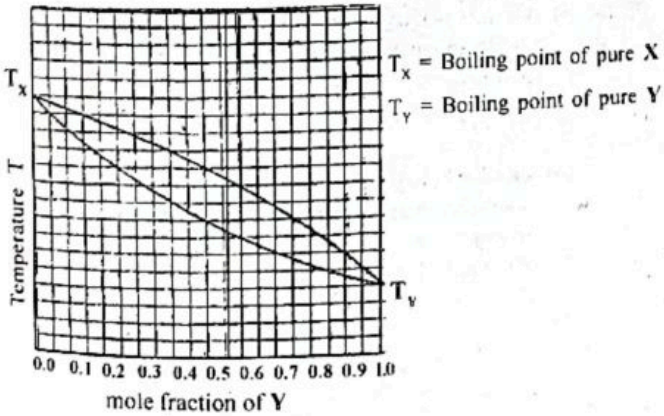
II. (A) State the assumptions, if any, you used in part C above.

(B) Is the reaction $X(g) \rightarrow 2Y(g)$ exothermic or endothermic? Briefly explain your answer.

(9.0 marks)

(b) (i) 75.0 cm^3 of an aqueous solution of solute **E** was shaken well with 50.0 cm^3 of $CHCl_3$ at room temperature, and allowed the two layers to reach equilibrium. Calculate the distribution coefficient, K_D, for the distribution of **E** between $CHCl_3$ and water if 75% of **E** (mol %) was extracted into the organic phase at equilibrium.

(ii) Two **unreactive** liquids X and Y, which are completely miscible in all proportions, are at equilibri with their vapour phase over the temperature range from T_X to T_Y. This equilibrium is shown in following phase diagram.



Use the above phase diagram to answer parts I and II below.

I. If an equimolar solution of **X** and **Y** is in equilibrium with the vapour phase, what is the mole ratio of **X** and **Y (X : Y)** in the vapour phase

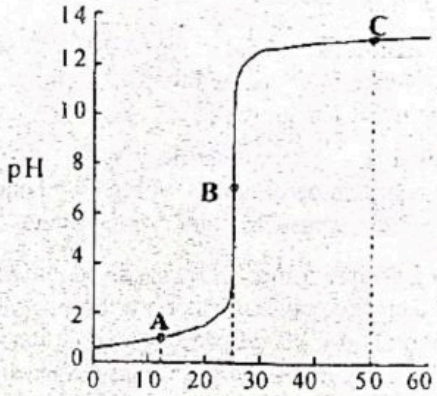
II. Briefly explain how a mixture of **X** and **Y** could be separated into pure components.

(6.0 marks)

6 (a) Four titrations were conducted using different acid and base solutions as shown in the table below.

Titration	Acid solution	Volume of acid solution /cm³	Base solution
I	0.300mol dm⁻³ HCl	25.00	0.300mol dm⁻³ NaOH
II	0.030 mol dm⁻³ HCl	25.00	0.030 mol dm⁻³ NaOH
III	0.300 mol dm⁻³ CH_3COOH	25.00	0.300 mol dm⁻³ NaOH
IV	0.150 mol dm⁻³ CH_3COOH	25.00	0.150 mol dm⁻³ NaOH

(i) The pH - titration curve of titration I is given below.



Points **A,B** and **C** of the curve represent the additions of 12.50 cm³, 25.00 cm³ and 50.00 cm³ volumes of the NaOH solution respectively to the HCl solution. Calculate the pH values corresponding to these three points.

(ii) For each of the titrations II, III and IV, indicate whether the pH values corresponding to the add of 12.50 cm³, 25.00 cm³ and 50.00 cm³ of the NaOH solution, decreased, increased or remain unchanged with respect to the points A,B and C of titration I. Use a table as shown below in your answer script to answer this part of the question.

Titrations	Volume of NaOH added/cm³		
	12. 50	25. 00	50. 00
II			
III			
IV			

(iii) Give reasons for changes in pH values you mentioned in titration III.

(9.0 marks)

(b) Chlorine dioxide (ClO_2) undergoes the following reaction in alkaline medium

$$2ClO_2(aq) + 2OH^-(aq) \rightarrow ClO_3^-(aq) + ClO_2^-(aq) + H_2O(l)$$

The initial rates determined for the above reaction carried out at a constant temperature by changing the initial concentration of ClO_2 and initial pH are given below.

Initial concentration of ClO_2 / mol dm^{-3}	Initial pH	Initial rate mol dm^{-3} s^{-1}
0.060	12	0.022
0.020	12	0.0025
0.020	13	0.024

(i) Calculate the order of the reaction with respect to ClO_2 and with respect to OH^-

(ii) The mechanism of the above reaction does not change when the temperature is increased by 10°C Predict whether.

I. the rate of the reaction

II. the order with respect to each reactant

would increase, decrease or remain unchanged when the temperature is increased by 10°C.

(6.0 marks)

7. (a) (i) At room temperature, 25.0 cm^3 of 4.00×10^{-3} mol dm^{-3} $AgNO_3$ solution were maixed with 75.0 cm^3 of 8.00×10^{-3} mol dm^{-3} NaBr solution.

I. Show that a precipitation occurs.

II. The resulting precipitate was separated and dried. Calculate the mass of the dry precipitate.

(ii) A 0.166 g sample of Ag_2CrO_4 was thoroughly shaken with 50.0 cm^3 of distilled water at room temperature. 50.0 cm^3 of 2.00×10^{-5} mol dm^{-3} NaCl solution were then added to the resulting Ag_2CrO_4 suspension and mixed well. The following changes were then observed.

(A) The reddish-brown precipitate dissolved and a white precipitate was formed.

(B) The colour of the supernatant solution became distinctly yellow.

Explain the above observations using suitable calculations.

Relative molar masses : AgCl = 143.5, AgBr = 188.0, Ag_2CrO_4 = 332.0

At room temperature,

K_{sp} (AgBr) = 5.0×10^{-13} mol^2 dm^{-6}

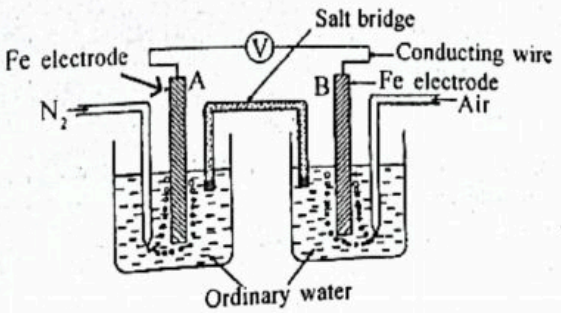
K_{sp} (AgCl) = 1.8×10^{-10} mol^2 dm^{-6}

K_{sp} (Ag_2CrO_4) = 2.4×10^{-12} mol^3 dm^{-9}

Molar solubility of Ag_2CrO_4 = 8.4×10^{-5} mol dm^{-3}

(10.0 marks)

(b) Consider the following electrochemical cell.



(i) Which electrode (A or B) is the cathode?

(ii) Which electrode (A or B) is negatively charged?

(iii) Write a **balanced** equation for the electrode reaction that occurs at A.

(iv) Write a **balanced** equation for the electrode reaction that occurs at B.

(v) Write a **balanced** equation for the overall cell reaction.

(vi) Give one chemical test in each case to show the formation of the ionic species that you have given in (iii) and (iv) above.

(vii) The overall cell reaction you have given in (v) above occurs during a common natural process. Name this process.

(5.0 marks)

PART C - ESSAY

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

8. (a) A solution Y contains dil. H_2SO_4 and oxalic acid.

(i) 25.00 cm^3 of this solution was titrated with a 0.050 mol dm^{-3} $KMnO_4$ solution. The volume of $KMnO_4$ solution required was 24.00 cm^3.

(ii) The solution obtained after completing the titration (i) was further titrated with a 0.040 mol dm^{-3} NaOH solution. The volume of NaOH solution required was 15.00 cm^3.

I. Write balanced chemical equations for the reactions.

II. Calculate the concentrations of

(A) Oxalic acid and

(B) H_2SO_4 acid

in the solution Y.

(8.0 marks)

(b) (ii) Using balanced chemical equations only, suggest one method for the synthesis of each of the following compounds starting from limestone.

I. Bleaching powder

II. A phosphorus fertilizer

III. Acetylene

(ii) During April 2009, a ship containing 6500 tonnes of conc. H_2SO_4 sank off the port of Trincomalee. Predict the possible threats/impacts that could occur due to leaking of conc. H_2SO_4 to the marine environment.

(7.0 marks)

08 (a) (i) Outline briefly how you would identify the following dilute aqueous solutions by mixing them with one another.

KI, $Fe_2(SO_4)_3$, $BaCl_2$, $K_4Fe(CN)_6$

(ii) Outline how you would identify the following aqueous solutions/finely powdered metals by reacting them with one another.

Al, Zn, NH_4Cl, NaOH

(7.0 marks)

(b) A is a coloured inorganic salt containing the metallic element M. On heating, A decomposes giving a green residue B (M_2O_3), a colourless gas C and water vapour. One mole of A gives one mole of residue B. The gas C reacts with heated magnesium forming a white solid D. D reacts with water forming a gas E which turns red litmus blue. Heating A with Na_2CO_3 solution also produces the gas E. The green residue B gives a yellow solution when warmed with an alkaline solution of H_2O_2.

(i) Identify A,B, C, D and E.

(ii) Write **balanced** chemical equations for the relevant reactions.

(8.0 marks)

10 (a) (i) In the determination of dissolved oxygen in a sample of water, 250 cm^3 of the water sample was treated with a solution of $MnSO_4$ and an excess of KI in an alkaline medium. The solution was then acidified and the liberated iodine was titrated with 0.020 mol dm^{-3} $Na_2S_2O_3$ solution. The volume of $Na_2S_2O_3$ solution required was 10.00 cm^3.

(I) Give **balanced** chemical equations for the relevant reactions.

(II) Calculate the concentration of dissolved oxygen in mg dm^{-3} of the water sample. (O = 16.0)

(ii) Hydrogen peroxide is decomposed into H_2O and O_2 on warming.

I. Write **balanced** ionic equations for the two half reactions relevant to this decomposition.

II. Outline one titrimetric method to determine the concentration of an aqueous solution of H_2O_2. (No experimental details are required)

(7.5 marks)

(b) To answer this part of the question, use the page 13 (at the end of PART A) which contains a flow chart.

Consider the production of Na_2CO_3 by Solvay process.

In the flow-chart provided, (page No. 13)

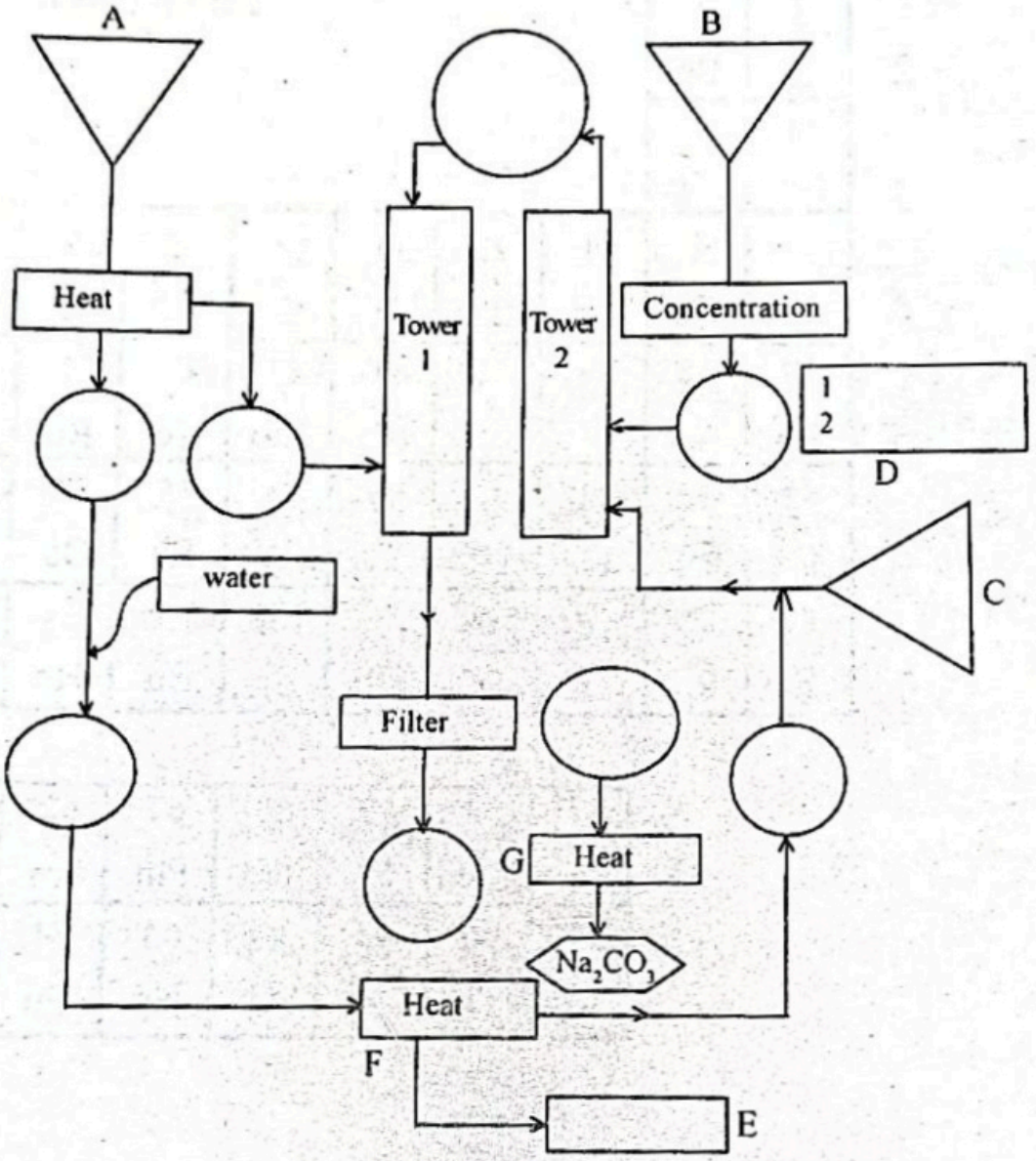
(i) write in the triangles A,B and C, the starting meterials used.

(ii) write in the box D, two by-products formed during the concentration of the starting material in B.

(iii) write in the box E the waste material produced in the process.

(iv) write in the circles the chemical formulae of the appropriate substances involved in the process.

- Only use this page to answer question numbe 10 of PART C. (Question number 10 is not compulsory)



Write in spaces provided below, the **balanced** equations for chemical reactions taking place at F,G and in tower 1.

(v) at F .....

(vi) at G .....

(vii) in tower 1

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