CARIBBEAN EXAMINATIONS COUNCIL

ADVANCED PROFICIENCY EXAMINATION

CHEMISTRY

UNIT 1 – PAPER 02

2 hours 15 minutes

Candidates are advised to use the first 15 minutes for reading through this paper carefully. Writing may begin during this time.

READ THE FOLLOWING INSTRUCTIONS CAREFULLY

1. This paper consists of NINE questions.

2. Section A consists of THREE questions, ONE question from each Module. Answer ALL questions in this section. Answers for this section must be written in this booklet.

3. Section B consists of SIX questions. Answer ONLY THREE questions from this section, ONE question from EACH Module. Answers for this section must be written in the booklet provided.

4. ALL working MUST be CLEARLY shown.

5. The use of non-programmable calculators is permitted.

Materials provided:

- A data booklet
- Graph paper
- Answer booklet

SECTION A

Answer ALL questions in this section.

MODULE 1

1.   In an experiment to determine the empirical and molecular formulae of a hydrocarbon, **A**, the hydrocarbon is completely burnt in excess oxygen and the products collected. **A** gave 3.52 g of carbon dioxide and 1.62 g of water, on complete combustion.

$$[M_r\, CO_2 = 44;\ M_r\, H_2O = 18]$$

(a)   Calculate the mass of

(i)   carbon in 3.52 g of carbon dioxide

_____

_____

[1 mark]

(ii)   hydrogen in 1.62 g of water.

_____

_____

[1 mark]

(b)   Use the answers obtained in (a) (i) and (a) (ii) to calculate the empirical formula of **A**.

_____

_____

_____

_____

_____

_____

[2 marks]

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(c) The molar mass of **A** is 114 g mol^{-1}. Calculate its molecular formula.

_____

_____

_____

[2 marks]

(d) Describe simple tests that could be used to confirm that the products of the combustion of **A** are water and carbon dioxide (You must include in your answer the reagent used and the observation obtained for EACH test).

(i) Water

_____

_____

[2 marks]

(ii) Carbon dioxide

_____

_____

[2 marks]

Total 10 marks

2.   (a)   An organic compound, X, is subjected to chemical analysis and mass spectrometry to determine its structural formula. Some of the results of the chemical analysis are recorded in Table 1 below. Complete the table by writing the observations and inference that have been omitted.

TABLE 1: RESULTS OF TESTS ON COMPOUND X

Test	Observation	Inference
An alkaline solution of silver nitrate is added to a few cm^3 of X. The mixture is warmed.	(i)	Aldehyde
Iodine and X are warmed with some NaOH in a test tube.	(ii)	Methylketone
X is added to a few cm^3 of bromine in tetrachloro-methane.	(iii)	Alkene
X is added to dilute HCl	White crystals are produced.	(iv)

[4 marks]

(v)   Suggest a value for the pH of a solution of X.

_____

[1 mark]

(vi)   The mass spectrum of X reveals that it has a RMM of 203. A prominent peak is also observed in the mass spectrum at m/z 77. Use this information and the results of your chemical analysis as recorded in Table 1 above to draw a displayed structure for X.

[1 mark]

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(b) An organic compound **Y** is also subjected to chemical analysis. Some of the results are presented in Table 2. Complete Table 2 by writing the tests and inference that have been omitted.

TABLE 2: RESULTS OF TESTS ON COMPOUND Y

Test	Observation	Inference
Acidified $KMnO_4$ is added to a few cm^3 of Y, and the mixture is warmed.	Colour changes from purple to colourless.	(i)
(ii)	White precipitate produced.	Phenol present.
(iii)	Gas evolves which forms white fumes with $NH_3(g)$.	Carboxylic acid group

[3 marks]

(iv) The molecular formula for **Y** is found to be $C_9H_{10}O_4$. Suggest a structural formula for **Y**.

[1 mark]

Total 10 marks

3. A student synthesizes a crude organic product in the laboratory. The process of purification is outlined in the flow diagram in Figure 1 below.
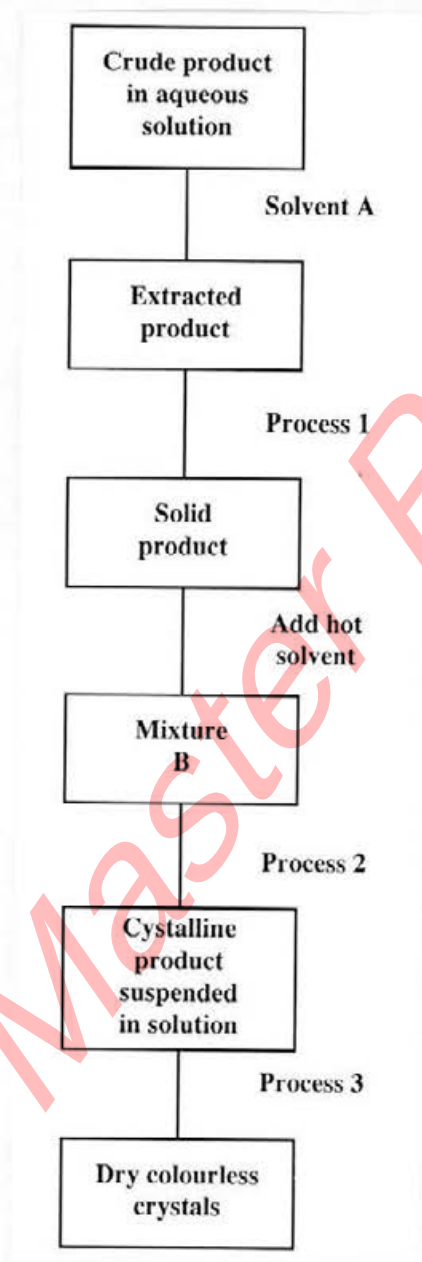
```
         ┌──────────────────┐
         │  Crude product   │
         │   in aqueous     │
         │    solution      │
         └──────────────────┘
                 │ Solvent A
         ┌──────────────────┐
         │    Extracted     │
         │     product      │
         └──────────────────┘
                 │ Process 1
         ┌──────────────────┐
         │      Solid       │
         │    product       │
         └──────────────────┘
                 │ Add hot
                 │ solvent
         ┌──────────────────┐
         │    Mixture       │
         │       B          │
         └──────────────────┘
                 │ Process 2
         ┌──────────────────┐
         │   Cystalline     │
         │    product       │
         │   suspended      │
         │  in solution     │
         └──────────────────┘
                 │ Process 3
         ┌──────────────────┐
         │  Dry colourless  │
         │    crystals      │
         └──────────────────┘
```

Figure 1.

(a) Identify EACH of the processes 1, 2 and 3 in Figure 1.

_____

_____

_____

[3 marks]

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(b)   (i)   Suggest the name of Solvent **A** and explain why the solvent suggested is suitable.

_____

_____

_____

_____

[3 marks]

    (ii)   Describe Mixture **B**

_____

[1 mark]

(c)   Suggest a suitable piece of equipment which could be used to obtain the

    (i)   extracted product

_____

[1 mark]

    (ii)   dry crystals.

_____

[1 mark]

(d)   Mixture **B** shows some discolouration and an additional step is required before Process 2. Name the purifying agent necessary in this step.

_____

_____

[1 mark]

Total 10 marks

SECTION B

Answer THREE questions from this section, ONE question from EACH module.

MODULE 1

Answer EITHER Question 4 OR Question 5.

4. (a) (i) Describe the features of a chemical system in a state of dynamic equilibrium.

[4 marks]

(ii) Define the term 'equilibrium constant'.

[1 mark]

(iii) Iodine gas is purple and hydrogen iodide gas is colourless. Hydrogen and iodine, in the gaseous state, react according to the equation:

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$
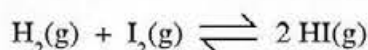
Describe and explain, with reference to changes in colour, the observations made when hydrogen gas is reacted with iodine gas at constant temperature until equilibrium is achieved.

[5 marks]

(iv) Table 3 shows some data for the system given in (iii) above. (Assume that the volume of the vessel is 1 dm^3 and the temperature remains constant.)

TABLE 3: DATA FOR THE SYSTEM ABOVE

Species	H_2	I_2	HI
Initial concentration (mol dm^{-3})	1	2	0
Equilibrium concentration (mol dm^{-3})	.67		

a) Use the information in Table 3 and the equation in (a) (iii) above to calculate the number of moles of hydrogen reacting.

b) Complete the table by inserting the equilibrium concentrations of I_2 and HI.

[3 marks]

(v) Write an equation for K_p for the reaction in (iii) above.

[2 marks]

(b) The terms K_a, pK_a and pH can be used to indicate the relative strength of weak acids. The general equation for the equilibrium of a weak acid is given below:

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$
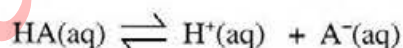
(i) Write an expression for EACH of the following terms:

a) K_a

b) pK_a

c) pH

[3 marks]

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(ii)   Given that K_a for acid HP is 3.0×10^{-5} mol dm^{-3}, predict the relative size of K_a for a stronger acid HQ. Explain your reasoning.   **[2 marks]**
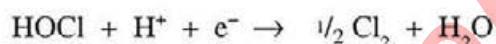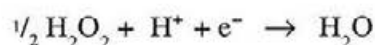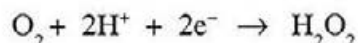
Total 20 marks

5.   (a)   Explain EACH of the terms 'oxidation' and 'reduction', in terms of

       (i)   loss and or gain of electrons   **[2 marks]**

       (ii)   change in oxidation number.   **[2 marks]**

   (b)   Hydrogen peroxide, H_2O_2, can act as both an oxidising agent and a reducing agent, and chloric (I) acid (HOCl) can act as an oxidizing agent.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$

$$\tfrac{1}{2} H_2O_2 + H^+ + e^- \rightarrow H_2O$$

$$HOCl + H^+ + e^- \rightarrow \tfrac{1}{2} Cl_2 + H_2O$$

       (i)   Use the appropriate half equations (from those above) to write a balanced equation to show the reaction between hydrogen peroxide and chloric (I) (hypochlorous) acid.   **[2 marks]**

       (ii)   By making reference to the change in oxidation numbers of the elements in both the hydrogen peroxide AND the chloric (I) acid, determine which reactant is reduced and which is oxidised.   **[6 marks]**

   (c)   In an experiment to determine whether iron or nickel is a better reducing agent, a strip of each metal is placed in an aqueous solution of a salt of the other metal. A reaction occurs in the container in which iron is placed in the aqueous solution of the nickel salt.

       (i)   State what type of chemical reaction occurs and write an ionic equation for the reaction.   **[3 marks]**

       (ii)   Which element has the greater reducing ability? Explain your answer, using a suitable half equation.   **[4 marks]**

       (iii)   Tin shows no reaction with solutions of EITHER iron or nickel salts. Place the elements, tin, iron and nickel in order of INCREASING reducing ability.   **[1 mark]**

Total 20 marks

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MODULE 2

Answer EITHER Question 6 OR Question 7.

6.   (a)   Describe EACH of the following terms, using appropriate examples:

(i)   Homolytic bond fission

(ii)   Inductive effect   [6 marks]

(b)   Citral is an oily liquid which contributes to the flavour and aroma of oranges.

Citral

(i)   State TWO types of reaction mechanisms which citral will undergo, identifying the functional group involved in EACH case.   [4 marks]

(ii)   With the use of simple molecules containing the functional groups identified in (b) (i), explain the steps involved in EACH of the mechanisms mentioned in (b) (i).   [8 marks]

(c)   Oestrone, a female sex hormone, reacts with bromine in the presence of iron (III) bromide via a mechanism not mentioned in (b) (ii).
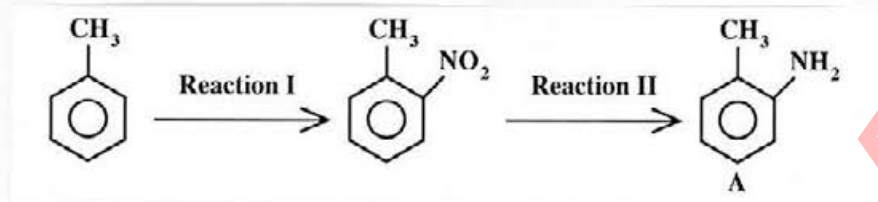

Oestrone
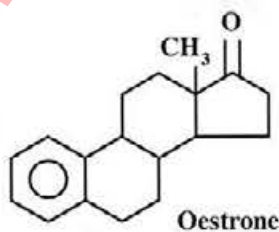
Identify the mechanism and draw the product of this reaction.   [2 marks]

Total 20 marks

7. The reaction sequence below shows the conversion of methylbenzene to A.

(a) (i) For the reaction sequence given above, state the reagents and conditions needed for Reactions I and II. [4 marks]

   (ii) Identify ONE OTHER product that could be obtained in Reaction I by changing the conditions. State the condition(s) needed. [2 marks]

(b) Amphetamine, like A, is an amine. It is a drug that increases the heart rate and causes increased sweating in humans. Its structure is given below:
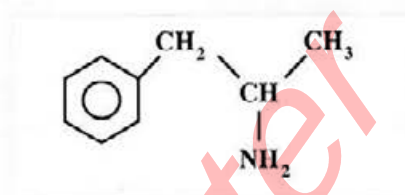
Structure of Amphetamine

   (i) Explain the differences in basic character of A, ammonia and amphetamine. In your explanation make reference to the molecular features of each molecule. State the order of INCREASING basic character of the three molecules.

   [8 marks]

   (ii) Write an equation to show the basic nature of any ONE of the above substances. [1 mark]

   (iii) The pK_b of A is 9.62. Suggest how the pK_b of amphetamine and ammonia should vary relative to that of A. [2 marks]

(c) The pH of ethanoic acid is 4.76 and of dichloroethanoic acid is 1.29.

   (i) Predict pH values for difluoroethanoic acid and dibromoethanoic acid.

   [2 marks]

   (ii) Would benzoic acid be a stronger or weaker acid than ethanoic acid?

   [1 mark]

   Total 20 marks

MODULE 3

Answer EITHER Question 8 OR Question 9.

8.   The enthalpy of solution of sodium chloride is determined in a school laboratory. The results of four trials are presented in Table 4 below.

TABLE 4: EXPERIMENTAL RESULTS OF DETERMINATION OF ΔH_{soln} NaCl

| Trial	1	2	3	4
ΔH_{soln} (KJ mol^{-1})	4.80	4.65	5.25	4.60

The theoretical value is $+5.00$ KJ mol^{-1}.

(a)   (i)   Calculate the mean of ΔH_{soln} NaCl from the data.   **[2 marks]**

(ii)   Comment on the precision and accuracy of the results.   **[3 marks]**

(iii)   Calculate the standard deviation of the data and explain the significance of the value.   **[3 marks]**

(b)   In the above experiment a top loading balance is used to weigh the sodium chloride sample and a 250 cm^3 beaker is used to measure the volume of water. The thermometer readings are measured within ± 0.5 °C.

(i)   Discuss whether each instrument is appropriate for the measurement taken and suggest possible alternatives where necessary.   **[6 marks]**

(ii)   Give TWO reasons for calibrating an instrument such as a thermometer and suggest TWO steps involved.   **[4 marks]**

(c) The volume of water, at room temperature, displaced by a series of standard weights is recorded. The results are given in Table 5 and the calibration curve is plotted in Figure 2.

TABLE 5: VOLUME OF WATER DISPLACED

Mass of standard (g)	Volume of H_2O displaced (cm^3)
2	0.75
4	1.5
8	3.0
12	4.5
16	6.0
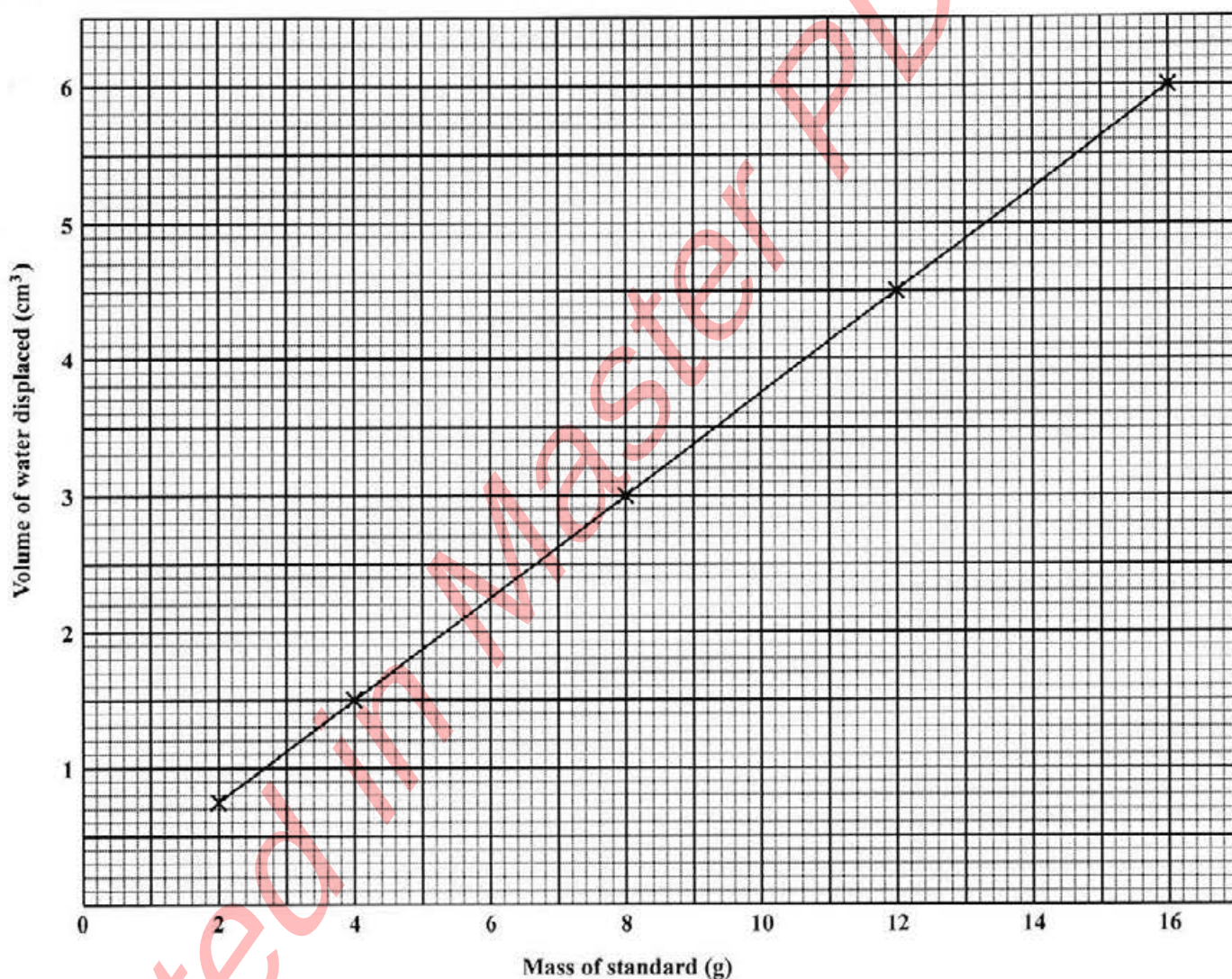
Figure 2.

Use the calibration curve in Figure 2 to determine the density of a block of metal that displaces a volume of 4.0 cm³. [2 marks]

Total 20 marks

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9. Different types of distillation, for example, simple distillation, fractional distillation and steam distillation, are used to separate mixtures. The physical properties of three compounds, W, X and Y are given in Table 6.

TABLE 6: PHYSICAL PROPERTIES OF W, X AND Y

Compound	m.p./ $^{\circ}$C	b.p / $^{\circ}$C	Solubility in water
W	− 97.7	64.5	Soluble
X	− 6.2	84	Immiscible
Y	801	1465	Soluble

(a) State which type of distillation is BEST suited for separating EACH compound from a mixture of the compound in water. **[3 marks]**

(b) A fourth compound, Z, (b.p = 97.2°C) forms a non-ideal mixture with water which boils at 88.1°C at 0.43 mole fraction of Z.

    (i) Construct the b.p / composition curve for the mixture of Z in water. Include in your diagram all data given, and label the two phases present. **[5 marks]**

    (ii) Use the diagram drawn in (b) (i) to explain why this mixture cannot be completely separated using fractional distillation. **[8 marks]**

(c) Steam distillation is used in the extraction of essential oils from plant materials. Suggest

    (i) ONE advantage and ONE disadvantage of carrying out the distillation under increased pressure **[2 marks]**

    (ii) TWO industries that utilize the process. **[2 marks]**

Total 20 marks

END OF TEST