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MAY/JUNE 2005

FORM TP 2005178

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

- This paper consists of NINE questions.
- 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.
- 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.
- ALL working MUST be CLEARLY shown.
- 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. (a)	deter	tances labelled A and B are solids at room temperature (30°C). A studential the melting point (m.p.) of a sample of A, using apparatus that is chool laboratory.	
		cribe FULLY the procedure that the student would follow in order to	o obtain the
			-
			[4 marks]
(b)	Anot	d on the m.p. data obtained, the student concludes that A is a covalent ther student, who has been given a sample of B, decides that B is not pound. Further analysis of A and B reveals that A is soluble in tetrachl that B is not, and that neither A nor B dissolves in water.	ot a covalent
	(i)	Suggest the type of forces of attraction that exist between particles of A how they are formed.	and describe
			[3 marks]
	(ii)	Name and describe the forces of attraction present in B.	
			[3 marks]

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Total 10 marks

MODULE 2

An analyst is given the task of identifying an organic liquid (Z) contained in an unlabelled 2. (a) vial. Table 1 shows the analyst's incomplete record of the tests conducted. Complete the analyst's record by filling in the blank spaces.

TABLE 1: INCOMPLETE RECORD

	Test	Observation	Inference
	Test on separate 1 cm ³ portions of Z.		
(i)	Add 5 cm ³ of distilled water.	A colourless solution formed.	
(ii)	Add 1 cm ³ conc. H ₂ SO ₄ and 1 cm ³ glacial ethanoic acid. Warm this mixture, then pour into cold water.		Ester formed.
(iii)	Warm with 5 cm³ potassium chromate(VI) solution acidified with H ₂ SO ₄ .	The solution turns green.	
(iv)	Add phosphorus penta- chloride (very carefully).	A very vigorous reaction.	

[4 marks
Suggest a displayed formula for Z, given that Z has a relative molecular mass of 46.
[1 mark]
Write the formula of the organic product formed in (a) (ii) in Table 1.
[1 mark]
Suggest a reagent that can be used to identify the gas liberated in (a) (iv) in Table 1 and
state the observations that would be recorded.
[2 marks

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Suggest the reagent and conditions necessary to obtain Z from the product of the reactio in (a) (ii) in Table 1.
[2 marks
Total 10 marks
MODULE 3
lent is given the task of determining the percentage of active agent, salicylic acid, in aspiring. A titrimetric method is suggested to the student.
Salicylic acid is an organic acid. Suggest a suitable titrant (reagent) for this estimation.
[1 mark
Describe the steps involved in preparing the titrant (reagent) suggested in (a) for the practical estimation of the salicylic acid present in each tablet.
[6 marks]

(c) Figure 1 shows the pH change as salicylic acid is titrated with the titrant selected.

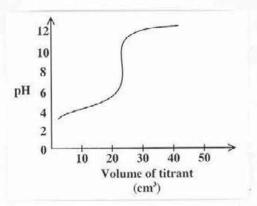


Figure 1. pH change

Table 2 gives a list of indicators and their pH ranges. Select the indicator that would be most suitable for this titrimetric analysis and use the graph to explain your reasoning.

TABLE 2: INDICATORS AND pH RANGES

Indicator	pH range
Methyl orange	2.9 - 4.6
Thymol blue	1.2 - 2.8
Phenolphthalein	8.3 - 10.0
Methyl red	4.2 - 6.3

	[3 marks
Reason:	
Indicator:	

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) Figure 2 shows the concentration of products and reactants for a chemical reaction that achieves a state of dynamic equilibrium.

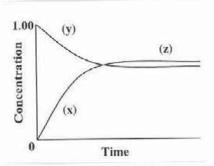


Figure 2. Graph of chemical reaction

Describe the features of a system that exists in a state of dynamic equilibrium and explain which of the features are illustrated by the graph in Figure 2. [5 marks]

- (b) K_c, K_a and K_p are terms that are associated with reactions that achieve a state of dynamic equilibrium, and can be experimentally determined.
 - (i) What is meant by the terms K_c , K_a and K_p ? [3 marks]
 - (ii) The equation below represents an equilibrium system.

$$\mathrm{C_2\,H_5\,OH(l)+\,CH_3\,COOH(l)} \ensuremath{ \Longrightarrow} \ensuremath{ \mathrm{CH_3COOC_2H_5(l)+\,H_2O(l)} }$$

Write an expression for K_c for the reaction.

[2 marks]

(iii) Ethanol and ethanoic acid are reacted together and allowed to achieve a state of equilibrium. The reaction is 'frozen' in order to obtain the equilibrium concentrations. Some data from this practical activity are presented in Table 3. Copy Table 3 in your answer booklet and write in the missing values using the equation in (b) (ii) on page 6.

TABLE 3: DATA FROM PRACTICAL ACTIVITY

	C ₂ H ₅ OH	CH ₃ COOH	CH ₃ COOC ₂ H ₅	H ₂ O
Initial concentration mol/dm ³	1	2		
Equilibrium concentration mol/dm ³			0.70	

[5 marks]

- (iv) Use the data in Table 3 and the expression for K_c in (b) (ii) on page 6 to calculate a value for K_c . [2 marks]
- (c) (i) Write the equilibrium constant expression for the following reaction:

$$2SO_2(g) + O_2(g) \Longrightarrow 2SO_3(g)$$

[1 mark]

(ii) The product of the reaction in (c) (i) above is used in the industrial manufacture of sulphuric acid. However, the value of the equilibrium constant is very small (less than 1).

Explain the meaning of this low value and suggest how the industry can continue to operate and to be viable, in spite of this low value. [2 marks]

Total 20 marks

5. (a) Explain the meaning of the term 'enthalpy (enthalpy change) of a reaction'.

[2 marks]

- (b) With reference to energy profile diagrams and bond energies, explain the difference between exothermic reactions and endothermic reactions. [6 marks]
- (c) Hydrazine (N₂H₄), which is a liquid and is used as a rocket fuel, reacts with chlorine to produce hydrogen chloride and nitrogen.
 - (i) Write a balanced equation for the reaction.

[2 marks]

(ii) Given that ΔH for the reaction in (i) is – 420 kJ mol⁻¹, calculate the enthalpy change when 12.7 g of hydrazine reacts completely with chlorine.

[2 marks]

(iii) Hydrazine also reacts with oxygen as illustrated in the equation below:

$$N_{2}H_{4}(\ell) + O_{2}(g) \rightarrow N_{2}(g) + 2H_{2}O(g) \quad \Delta H = -534 \text{ kJ mol}^{-1}$$

Use the equation and the information given below to calculate the enthalpy of reaction if water is produced in the liquid state.

The molar enthalpy of vaporization is the amount of heat absorbed when 1 mole of liquid at constant pressure changes to a gas.

$$H_2O(\ell) \rightarrow H_2O(g) \quad \Delta H \text{ vap } = 40.7 \text{ kJ mol}^{-1}$$

$$\Delta H_{condensation} = -\Delta H_{vaporization}$$

[4 marks]

- (d) The enthalpy change for the formation of CO: $C(s) + \frac{1}{2} O_2(g) \rightarrow CO(g)$ cannot be obtained experimentally.
 - (i) Suggest a reason for this.

[1 mark]

(ii) Show by means of an energy cycle diagram how knowledge of the standard heat of combustion of carbon and of carbon dioxide could be used to obtain the standard enthalpy of formation for carbon monoxide. [3 marks]

Total 20 marks

- (e) Nylon 6, 6 is formed when the diamine, $H_2N (CH_2)_6 NH_2$ reacts with the dicarboxylic acid, $HO C (CH_2)_4 C OH$.
 - (i) Write the displayed structure of the repeat unit of nylon 6,6.

[3 marks]

(ii) What is the common structural feature exhibited by the natural polymer-proteinsand synthetic nylon 6,6? [1 mark]

Total 20 marks

- 7. (a) Explain EACH of the following terms:
 - (i) Stereoisomerism

[1 mark]

(ii) Structural isomerism

[1 mark]

(b) (i) Label EACH of the following pairs of structures as structural isomers, as geometric isomers, or as the same compound. State reasons for your answer.

a) Br
$$C = C$$
 H H $C = C$ CH_2Br Br H $C = C$

[2 marks]

b)
$$CH_3 - CH_2 - CH_2$$
 $CH_2 - CH_3$ $CH_3 - CH_3$

$$CH_3$$
 $C = C$
 $CH_2 - CH_2 - CH_2 - CH_3$

[2 marks]

c)
$$CI$$
 CI $CH_2 = CH$ CI $CH_2 = CH$ CI $CH_2 = CH$ CI $CH_3 = CH$ CI $CH_3 = CH$

[2 marks]

(ii) Name EACH of the isomers in (b) (i) a) and b) above.

[3 marks]

(c) Two isomeric compounds, A and B, containing only carbon, hydrogen and oxygen are subjected to combustion analysis. One gram (1.0 g) of each compound on complete combustion gives 2.3 g of carbon dioxide and 0.93 g water. The relative molecular mass of each compound is 58.

(i)	Calculate the empirica	and molecular formulae of A and B.	[6 marks]
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(ii) Deduce the structural formulae of A and B. [2 marks]

(iii) State the type of isomerism exhibited by A and B. [1 mark]

Total 20 marks

MODULE 3

Answer EITHER Question 8 OR Question 9.

8. A laboratory technician analyses water samples for degree of hardness, which is expressed in parts per million (ppm) of calcium carbonate. Table 4 gives the results for ten samples.

TABLE 4: DEGREE OF HARDNESS OF WATER SAMPLES

Sample number	CaCO ₃ / ppm
1	250
2	245
3	265
4	300
5	225
6	230
7	248
8	295
9	235
10	220

- (a) Calculate the mean and standard deviation of the values.

 [Relevant formulae must be shown]
- [4 marks]
- (ii) What does the standard deviation value obtained in (a) (i) above indicate about the variability in the degree of hardness? [1 mark]
- (iii) The ten samples of water are taken from ten different sites. How can the reliability of the data obtained from each sample be improved? [1 mark]
- (b) Another laboratory technician analyses Sample 1 and obtains a hardness value of 290 ppm.
 - (i) Compare the TWO results in terms of precision and suggest a reason for the difference. [2 marks]
 - (ii) What additional information would be required to comment on the accuracy of the results at this site? [1 mark]
- (c) In the practical determination of hardness, 100 cm³ samples of water were measured and titrated with EDTA using Erichrome black as the indicator.
 - By reference to apparatus available in the school laboratory, discuss the importance of using appropriate equipment in the quantitative analysis as described above.

[5 marks]

(d) Describe the steps required to determine the accurate volume delivered by a pipette.

[6 marks]

Total 20 marks

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- The quantitative determination of minute quantities of analytical samples can be achieved using ultraviolet/visible spectroscopy.
 - (a) State the principles on which ultraviolet/visible spectroscopy is based. [5 marks]
 - (b) An experiment is carried out to determine the concentration of iron (II) (Fe²⁺) found in water samples taken from a well. A measured volume of the water sample is treated with a buffer and the reducing agent hydroxylamine, followed by the reagent 1,10 phenanthroline, shown below. The resultant solution is then topped up to a volume of 50 cm³. The solution is subsequently analysed in a cuvette, of side 1 cm, at a wavelength of 510 nm in the UV/Vis spectrophotometer.

(i) What would be observed on the addition of the 1,10 - phenanthroline?

[1 mark]

(ii) What properties of the organic reagent make it suitable for this analysis?

[3 marks]

Suggest a reason for selecting a wavelength of 510 nm for analysis.

[1 mark]

(iv) Describe how a calibration curve could be obtained for this analysis.

[3 marks]

- (c) An aqueous solution containing iron (II) (Fe²⁺) at a concentration of 2.5 x 10⁻³ mg cm⁻³ is subjected to the above treatment and measures an absorbance of 0.524. A water sample of unknown iron (II) (Fe²⁺) concentration is similarly treated and measures an absorbance of 0.350.
 - (i) Calculate the concentration of the known iron (II) solution in moles dm⁻³ of iron (II). [3 marks]
 - (ii) Apply the Beer's law to calculate the molar absorptivity of the known iron (II) solution.[3 marks]
 - (iii) Calculate the concentration of iron (II) in the unknown sample in mol dm⁻³.

[1 mark]

Total 20 marks

END OF TEST