CARIBBEAN PAPER

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FORM TP 2008167

MAY/JUNE 2008

CARIBBEAN EXAMINATIONS COUNCIL

ADVANCED PROFICIENCY EXAMINATION

CHEMISTRY

UNIT 1 – PAPER 02

2 hours 30 minutes

READ THE FOLLOWING INSTRUCTIONS CAREFULLY

1. This paper consists of SIX compulsory questions in TWO sections.
2. Section A consists of THREE structured questions, one from each Module. Section B consists of THREE extended response questions, one from each Module.
3. For Section A, write your answers in the spaces provided in this booklet. For Section B, write your answers in the answer booklet provided.
4. ALL working must be shown.
5. The use of non-programmable calculators is permitted.
6. A data booklet is provided.

SECTION A

Answer ALL questions in this section.

Write your answers in the spaces provided in this booklet.

MODULE 1

FUNDAMENTALS IN CHEMISTRY

1. The manganate(VII) ion reacts in an acidic medium according to the following half equation:

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O.$$

(a) (i) Define reduction and oxidation **in terms of oxidation number.**

Reduction: _____

Oxidation: _____

[2 marks]

(ii) Identify the role played by the MnO_4^- ion in the redox reaction above and explain your answer **in terms of oxidation number.**

_____

_____

_____

_____

[2 marks]

(b) An aqueous solution of potassium iodide, KI, reacts with acidified MnO_4^- to form a red-brown solution on completion of the reaction.

(i) Identify the species responsible for the red-brown colour.

_____

[1 mark]

(ii) Given that iodide ions react according to the following half equation,

$$2I^-(aq) \rightarrow I_2(aq) + 2e^-$$

deduce the balanced equation for the redox reaction between MnO_4^- and I^-.

_____

_____

_____

_____

_____

[3 marks]

(c) Compounds X and Y are tested for their reducing and/or oxidizing properties with MnO_4^-(aq) and I^-(aq) separately. The results are shown in Table 1.

TABLE 1: RESULTS OF TESTS ON COMPOUNDS X AND Y

	X	Y
MnO_4^-(aq)	(i) MnO_4^-(aq) decolourized	(i) MnO_4^-(aq) decolourized
I^-(aq)	(ii) Red-brown solution formed	No visible change

Categorise X and Y in terms of their oxidizing and reducing properties based on the above results.

X (i): _____

X (ii): _____

Y (i): _____

[2 marks]

(d) Complete the following table by filling in the missing observations or inferences.

Test	Observation	Inference
MnO_4^-(aq) is added to a solution containing Fe^{2+}(aq).	(i) • (ii) •	(ii) • • Fe^{3+} ions produced
MnO_4^-(aq) is added to a solution containing SO_3^{2-} followed by $BaCl_2$(aq).	(iii) • • White precipitate forms on addition of $BaCl_2$(aq).	• MnO_4^- reduced to Mn^{2+} (iv) •

[5 marks]

Total 15 marks

MODULE 2

KINETICS AND EQUILIBRIA

2. (a) Use the following electrochemical data to construct the labelled cell diagram for the combined half-cells.

$Cu^{2+} / Cu \quad E^0 = +0.34\ V$
$Ag^{+} / Ag \quad E^0 = +0.80\ V$

[4 marks]

(b) Write the relevant half-equations for the change taking place at the

(i) anode

_____

_____

[1 mark]

(ii) cathode.

_____

_____

[1 mark]

(c) Write the equation for the overall cell reaction.

_____

_____

[1 mark]

(d) (i) State at which electrode reduction takes place in the above electrochemical cell.

_____

[1 mark]

(ii) Give ONE reason for your answer to (d) (i).

_____

_____

_____

[1 mark]

(e) Calculate the cell potential.

[1 mark]

(f) (i) Describe THREE changes you would **observe** if you substituted a zinc half-cell for the Ag half-cell in your cell diagram in (a) on page 4.

$Zn^{2+}/Zn \quad E^{\theta} = -0.76\ V$

_____

_____

_____

_____

[3 marks]

(ii) Suggest ONE reason for the changes observed in (f) (i) above.

_____

_____

[1 mark]

(iii) Identify an electrolyte that could be used in the zinc half-cell.

_____

[1 mark]

Total 15 marks

MODULE 3

CHEMISTRY OF THE ELEMENTS

3. (a) (i) Both Al^{3+} and Pb^{2+} give the same results on addition of NaOH(aq) and NH_3(aq). Complete Table 2 by filling in the observations.

TABLE 2: TESTS FOR Al^{3+} AND Pb^{2+}

Test	Observation
NaOH(aq) is added gradually until in excess.	
NH_3(aq) is added gradually until in excess.	

[2 marks]

(ii) Describe a test that could be carried out to distinguish between Al^{3+} and Pb^{2+} ions.

Reagent: _____

Observation: _____

Inference: _____

[3 marks]

(b) An accident occurs at a chemical plant that results in a chemical spill. The team of chemists recruited to do the clean-up takes a sample of the spill for analysis.

The results of the analysis are as follows:

A	–	No characteristic colour change is observed on subjecting the sample to a flame test.
B	–	No precipitate is obtained on treatment with $AgNO_3(aq)$.
C	–	The pH of the sample is found to be 1.2.
D	–	The addition of acidified barium chloride results in the formation of a white precipitate.

(i) What deduction can be made about the sample, based on the observation in A?

_____

[1 mark]

(ii) What does the result in B indicate about the sample?

_____

[1 mark]

(iii) Based on the result in C, what type of compound is present in the sample analysed?

_____

[1 mark]

(iv) Identify the anion present in the sample.

_____

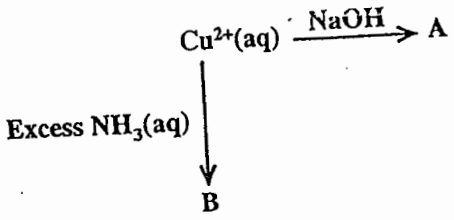
[1 mark]

(v) Suggest the identity of the chemical in the spill as indicated by the results of the analysis.

_____

[1 mark]

(c) (i) Identify the products, A and B, in the reaction scheme below.



A: _____

B: _____ **[2 marks]**

(ii) Write the ionic equation for the formation of B.

[2 marks]

(iii) Name the type of reaction illustrated in the conversion of Cu^{2+} (aq) to B in the reaction scheme in (c) (i) above.

_____

[1 mark]

Total 15 marks

SECTION B

Answer ALL questions in this section.
Write your answers in the answer booklet provided.

MODULE 1

FUNDAMENTALS IN CHEMISTRY

4. (a) The foul odour of dirty socks may be attributed to caproic acid, an organic acid made of carbon, hydrogen and oxygen. The results of combustion of a 0.450 g sample of caproic acid indicate that it contains 0.279 g of C, 0.0467 g of H, and 0.124 g of O.

(i) Distinguish between 'empirical formula' and 'molecular formula,' using suitable examples. **[3 marks]**

(ii) Calculate the empirical formula and the molecular formula of caproic acid, given that its molar mass is 116 g mol^{-1}. **[6 marks]**

(b) In the standardization of sulphuric acid with anhydrous sodium carbonate, a 1.49 g sample of sodium carbonate is dissolved in distilled water to make 250 cm^3 of solution. Three 25.0 cm^3 portions of this solution are pipetted and titrated against a solution of sulphuric acid of unknown concentration using screened methyl orange as the indicator. The average volume of sulphuric acid used for the titration is found to be 24.65 cm^3.

(i) Give THREE precautions that should be taken to ensure that the sodium carbonate, used as a standard in the above titration, is of accurate concentration. **[3 marks]**

(ii) Calculate the number of moles of sodium carbonate used for each titration, if the concentration of the stock solution is 5.65×10^{-2} mol dm^{-3}. **[1 mark]**

(iii) Calculate the accurate concentration of the standardized sulphuric acid in mol dm^{-3}. **[2 marks]**

Total 15 marks

MODULE 2

KINETICS AND EQUILIBRIA

5. The element calcium forms a number of sparingly soluble salts such as $CaCO_3$ found in limestone and CaC_2O_4 found in kidney stones.

(a) (i) Write the equilibrium constant expression for the dissociation of calcium carbonate in an aqueous solution. **[2 marks]**

(ii) Write an expression for the solubility product of $CaCO_3$ and explain its significance as it relates to sparingly soluble salts. **[2 marks]**

(b) A saturated solution of $CaCO_3$, at 25°C, is found to contain Ca^{2+} ions at a concentration of 6.7×10^{-5} mol dm^{-3}.

(i) Calculate K_{sp} (25°C) for $CaCO_3$. **[3 marks]**

(ii) Describe the effect of adding $Ca(NO_3)_2$ and KNO_3 to separate samples of the saturated solution of $CaCO_3$. **[2 marks]**

(c) Kidney stones generally consist of partially soluble salts of calcium such as calcium oxalate, CaC_2O_4. Foods rich in oxalate such as chocolate, spinach or celery can trigger the onset of kidney stones.

(i) Write an equation for the formation of calcium oxalate. **[2 marks]**

(ii) Explain the common ion effect and how it relates to the formation of kidney stones from a diet rich in oxalate, $C_2O_4^{2-}$. **[2 marks]**

(d) What is meant by 'Le Chatelier's principle'? **[2 marks]**

Total 15 marks

MODULE 3

CHEMISTRY OF THE ELEMENTS

6. NaX is a sodium halide which gives the following results on testing:

- Bubbling Cl_2 into an aqueous solution of NaX gives a red-brown solution. On addition of starch a blue-black colour forms.
- Addition of $AgNO_3$ to NaX(aq) gives a yellow precipitate which is insoluble in aqueous ammonia.

(a) Identify Element X and explain the reaction taking place in EACH of the tests above. Include balanced equations in your explanations. **[5 marks]**

(b) Consider the halogens Cl_2, Br_2 and I_2.

(i) State the trend in their colour intensity. **[1 mark]**

(ii) a) State the trend in volatility of the elements.

b) Account for this trend in volatility, in terms of atomic size and inter-molecular bonding. **[3 marks]**

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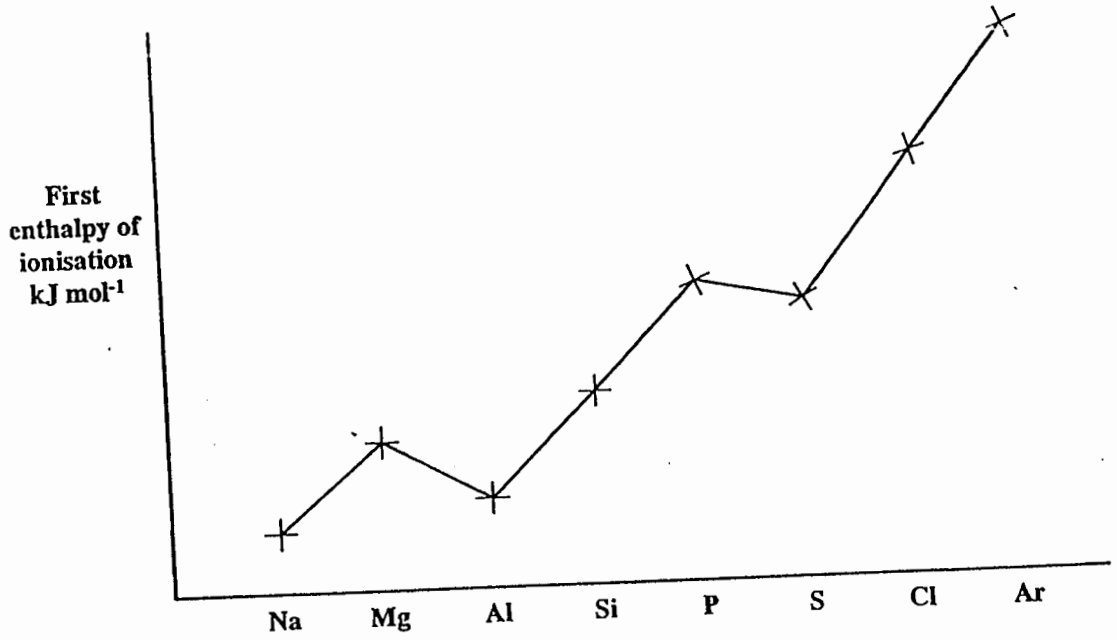
(c) Figure 1 shows the trend in the first enthalpies of ionisation (ionisation energies) in the elements, sodium to argon.



(i) State the general trend in the first enthalpies of ionisation for the elements Na to Ar as shown in Figure 1. **[1 mark]**

(ii) Explain the differences observed in the first enthalpies of ionisation of the following pairs of elements:

a) Mg and Al

b) P and S **[2 marks]**

(iii) Suggest TWO OTHER pairs of elements which should exhibit differences in their first enthalpies of ionisation as those elements given in (c) (ii) above. **[2 marks]**

(iv) Describe the relationship between atomic radius and first enthalpy of ionisation. **[1 mark]**

Total 15 marks

END OF TEST