## FORM TP 2015156

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# CARIBBEAN <br> EXAMINATIONS <br> COUNCIL <br> CARIBBEAN ADVANCED PROFICIENCY EXAMINATION® ${ }^{\circledR}$ <br> CHEMISTRY 

UNIT 1 - Paper 02
2 hours $\mathbf{3 0}$ minutes

## READ THE FOLLOWING INSTRUCTIONS CAREFULLY.

1. This paper consists of SIX questions in TWO sections. Answer ALL questions.
2. Write your answers in the spaces provided in this booklet.
3. Do NOT write in the margins.
4. Where appropriate, ALL WORKING MUST BE SHOWN in this booklet.
5. A data booklet is provided.
6. You may use a silent, non-programmable calculator to answer questions.
7. If you need to rewrite any answer and there is not enough space to do so on the original page, you must use the extra lined page(s) provided at the back of this booklet. Remember to draw a line through your original answer.
8. If you use the extra page(s) you MUST write the question number clearly in the box provided at the top of the extra page(s) and, where relevant, include the question part beside the answer.
dO NOT TURN THIS PAGE UNTIL YOU ARE TOLD TO DO SO.
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## SECTION A

## Answer ALL questions.

MODULE 1
FUNDAMENTALS IN CHEMISTRY

1. (a) (i) Define the term 'bond energy'.
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(ii) The bond lengths and bond energies of carbon-carbon single, double and triple bonds are listed below.

|  | $\mathrm{C}-\mathrm{C}$ | $\mathrm{C}=\mathrm{C}$ | $\mathrm{C}=\mathrm{C}$ |
| :--- | :---: | :---: | :---: |
| Bond Lengths | $1.54 \AA$ | $1.34 \AA$ | $1.20 \AA$ |
| Bond Energy | $348 \mathrm{~kJ} \mathrm{~mol}^{-1}$ | $614 \mathrm{~kJ} \mathrm{~mol}^{-1}$ | $839 \mathrm{~kJ} \mathrm{~mol}^{-1}$ |

State the relationship between the strength of a covalent bond and its length.
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(b) Bond energies can be used to estimate the enthalpies of reactions in which bonds are broken and new bonds are formed. Consider the gas-phase reaction between methane $\left(\mathrm{CH}_{4}\right)$ and chlorine to produce methyl chloride $\left(\mathrm{CH}_{3} \mathrm{Cl}\right)$ and hydrogen chloride.
(i) Write a balanced equation to represent the reaction above.
(ii) Using bond energy values from Table 1, calculate the enthalpy change of reaction, $\Delta H_{r x n}$, for the equation required in (b) (i).

TABLE 1: BOND ENERGY VALUES

| Bond | Energy <br> $\left(\mathbf{k J ~ m o l}^{-1}\right)$ |
| :---: | :---: |
| $\mathrm{H}-\mathrm{H}$ | 436 |
| $\mathrm{~F}-\mathrm{F}$ | 158 |
| $\mathrm{Cl}-\mathrm{Cl}$ | 244 |
| $\mathrm{H}-\mathrm{F}$ | 562 |
| $\mathrm{H}-\mathrm{Cl}$ | 431 |
| $\mathrm{C}-\mathrm{C}$ | 350 |
| $\mathrm{C}-\mathrm{H}$ | 410 |
| $\mathrm{C}-\mathrm{Cl}$ | 340 |
| $\mathrm{C}-\mathrm{O}$ | 360 |
| $\mathrm{~S}-\mathrm{H}$ | 347 |

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(iii) Is the reaction in (b) (i) exothermic or endothermic?
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(iv) On the axes provided below, draw the energy-profile diagram for the reaction in (b) (i).


Progress of reaction
(c) A student is asked to determine the enthalpy of the neutralization reaction between $75 \mathrm{~cm}^{3}$ of 1.00 M hydrochloric acid and $75 \mathrm{~cm}^{3}$ of 1.00 M potassium hydroxide solution. Outline the experimental steps (including calculations) required to obtain an accurate value.
[Assume that the densities of the solutions of acid and base and their heat capacities are equal to the density $\left(1 \mathrm{~g} \mathrm{~cm}^{-3}\right)$ and heat capacity ( $4.18 \mathrm{~J} \mathrm{~g}^{-1}{ }^{\circ} \mathrm{C}^{-1}$ ) of water.]
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Total 15 marks

## MODULE 2

## KINETICS AND EQUILIBRIA

2. (a) Define EACH of the following terms:
(i) Standard electrode potential of a half-cell
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(ii) Standard cell potential of an electrochemical cell
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(b) Consider the following (unbalanced) equation which describes the process that is taking place in an electrochemical cell under standard conditions.

$$
\mathrm{Al}(\mathrm{~s})+\mathrm{Sn}^{2+}(\mathrm{aq}) \rightarrow \mathrm{Al}^{3+}(\mathrm{aq})+\mathrm{Sn}(\mathrm{~s})
$$

(i) Write the ionic half-equation for the reaction taking place at EACH of the electrodes. ANODE:

CATHODE: $\qquad$
(ii) Write the cell diagram.
(iii) Draw a well-labelled diagram of the electrochemical cell. Indicate the direction of electron flow.
(iv) For EACH electrode shown in Table 2, select the $\mathrm{E}^{\boldsymbol{\theta}}$ value to determine the $\mathrm{E}_{\text {cell }}^{\Theta}$.

TABLE 2: ELECTRODE POTENTIALS

| Electrode Reaction | $\mathbf{E}^{\circ} \mathbf{a t ~ 2 9 8 ~ K ~ ( 2 5 ~}$ <br>  <br> (volts) |
| :---: | :---: |
| $\mathrm{Ag}^{+}+e^{-} \rightleftharpoons \mathrm{Ag}$ | +0.80 |
| $\mathrm{Al}^{3+}+3 e^{-} \rightleftharpoons \mathrm{Al}$ | -1.66 |
| $\mathrm{Ba}^{2+}+2 e^{-} \rightleftharpoons \mathrm{Ba}$ | -2.90 |
| $\cdot \mathrm{Sn}^{2+}+2 e^{-} \rightleftharpoons \mathrm{Sn}$ | -0.14 |
| $\mathrm{Sn}^{4+}+2 e^{-} \rightleftharpoons \mathrm{Sn}^{2+}$ | +0.15 |

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## MODULE 3

## CHEMISTRY OF THE ELEMENTS

3. The Group IV elements exhibit oxidation states of +2 and +4 in their compounds.
(a) Complete Table 3 for the oxides of carbon and lead.

TABLE 3: OXIDES OF GROUP IV ELEMENTS

|  | $\mathbf{C O}$ | $\mathbf{C O}_{2}$ | $\mathbf{P b O}$ | $\mathbf{P b O _ { 2 }}$ |
| :--- | :---: | :---: | :---: | :---: |
| Acid/base nature | Neutral |  |  | Amphoteric |
| Thermal stability |  | Stable |  |  |
| Oxidation state of Group IV element |  |  | +2 |  |

[4 marks]
(b) (i) Explain the relative stabilities of the +2 oxidation states of the oxides of carbon and lead.
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[4 marks]
(ii) Use the electrode potential value in the electrode reaction for lead ions, to explain the relative stabilities of the +2 and +4 oxidation states of lead:

$$
\mathrm{Pb}^{4+}+2 e^{-} \longrightarrow \mathrm{Pb}^{2+}, \mathrm{E}^{\mathrm{\theta}}=+1.80 \text { volts }
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(c) Describe what should be observed when
(i) concentrated sodium hydroxide is added to solid lead(IV) oxide
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(ii) concentrated hydrochloric acid is added to solid lead(IV) oxide.
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(d) Describe a test to identify $\mathrm{Pb}^{2+}$ ions in solution.
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## SECTION B

## Answer ALL questions.

## MODULE 1

## FUNDAMENTALS IN CHEMISTRY

4. (a) The atoms of certain elements contain nuclei in which the ratio of neutrons to protons is greater than 1. These nuclei tend to emit radiation in order to bring the ratio closer to 1 .
(i) Describe the THREE types of radiation that an unstable atom may emit. Include in your answer the symbols and penetrating power of EACH type of radiation.
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(ii) Americium-241 (Am-241) decays via alpha particle emission. Write the nuclear equations to show the new element that forms when an atom of 241 Am decays via the emission of 2 alpha particles.
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(b) (i) Draw the diagrams of the atomic orbitals of principal quantum number 2 . Include $x, y$ and $z$ axes in your drawing.
(ii) Comment on the similarity and difference in the electronic configurations of $K$, Sc and $\mathrm{Zn}^{2+}$ given below.

$$
\begin{aligned}
& \mathrm{K}: 1 \mathrm{~s}^{2} 2 s^{2} 2 \mathrm{p}^{6} 3 s^{2} 3 \mathrm{p}^{6} 4 \mathrm{~s}^{1} \\
& \mathrm{Sc}: 1 \mathrm{~s}^{2} 2 \mathrm{~s}^{2} 2 \mathrm{p}^{6} 3 \mathrm{~s}^{2} 3 \mathrm{p}^{6} 3 \mathrm{~d}^{1} 4 \mathrm{~s}^{2} \\
& 2 n^{2+}: 1 s^{2} 2 s^{2} 2 \mathrm{p}^{6} 3 \mathrm{~s}^{2} 3 \mathrm{p}^{6} 3 \mathrm{~d}^{10}
\end{aligned}
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[5 marks]
Total 15 marks

## MODULE 2

## KINETICS AND EQUILIBRIA

5. A buffer consisting of $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}$and $\mathrm{HPO}_{4}{ }^{2-}$ helps control the pH of physiological fluids. Many carbonated soft drinks also use this buffer system.
(a) Using the buffer system mentioned above, describe how the solution maintains an almost constant pH even when small amounts of acid or alkali are added to the solution.
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(b) Calculate the pH of a soft drink in which the major buffer ingredients are 6.5 g of $\mathrm{NaH}_{2} \mathrm{PO}_{4}$ and 8.0 g of $\mathrm{Na}_{2} \mathrm{HPO}_{4}$ per $355 \mathrm{~cm}^{3}$ of solution.
$\left[\mathrm{K}_{\mathrm{a}}\left(\mathrm{H}_{2} \mathrm{PO}_{4}^{-}\right)=6.4 \times 10^{-8} \mathrm{~mol} \mathrm{dm}^{-3}\right]$
[Relative atomic mass: $\mathrm{H}=1, \mathrm{Na}=23, \mathrm{O}=16, \mathrm{P}=31$ ]
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(c) Many chemical reactions occur in living systems such as the human body. Discuss the importance of biological buffers to the maintenance of a healthy body. (Include an example of a chemical reaction of a blood buffer.)
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## MODULE 3

## CHEMISTRY OF THE ELEMENTS

6. (a) The atomic and ionic radii of the Group II elements gradually increase down the group. Outline the reasons for this trend.
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(b) Account for the variation in the melting points of the Group II elements from magnesium to barium.
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(c) Table 4 shows the observations when $0.1 \mathrm{~mol} \mathrm{dm}^{-3}$ solutions of the metal ions are treated with $1 \mathrm{~mol} \mathrm{dm}{ }^{-3} \mathrm{Na}_{2} \mathrm{SO}_{4}$.

TABLE 4: OBSERVATIONS OF REACTIONS

| Solution of Group II Cations <br> $0.1 ~ m o l ~ d m$ | Observations <br> with $\mathbf{1 ~ m o l ~ d m}$ <br>  <br> $\mathbf{3} \mathbf{~ N a} \mathbf{N O}_{\mathbf{2}}$ |
| :---: | :---: |
| $\mathrm{Mg}^{2+}$ | No precipitate |
| $\mathrm{Ca}^{2+}$ | Thin, white precipitate |
| $\mathrm{Sr}^{2+}$ | White precipitate |
| $\mathrm{Ba}^{2+}$ | Thick, white precipitate |

Account for the trend indicated in Table 4.
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(d) Explain the variation in the thermal decomposition of the nitrates of the Group II elements.
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## END OF TEST

