



University of Fort Hare  
Together in Excellence

# UNIVERSITY OF FORT HARE

**CHE511**

**DEGREE/DIPLOMA EXAMINATIONS: JUNE 2014**

**TIME: 3 HOURS**

**SUBJECT: CHEMISTRY**

**PAPER: ANALYTICAL CHEMISTRY**

**MARKS: 100**

## Examiners

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## INSTRUCTIONS

**Answer all the questions**

QUESTION ONE

1.1 With reference to electrochemical methods

1.1.1

What is the significance of  $k^0$ ? [2]

1.1.2

What does HDME stand for? [2]

1.1.3

What is meant by the Electroferogram? [2]

1.1.4

What is described as being Nernstian? [2]

1.2 Distinguish between the following terms:

(i) Linear sweep voltammetry and cyclic voltammetry [4]

(ii) Overvoltage and overpotential [4]

(iii) Voltammogram and Polarogram [4]

(iv) SHE and SCE [4]

(v) Faradaic and Capacitative current [4]

1.3 Describe the modes of mass transport within liquid solution. Also refer to Fick's law of diffusion. Describe all the three modes and label the equation components for each mode. [7]

1.4 The Butler - Volmer equation is given below: [8]

$$i = i_0 \left( \exp \left( \frac{(1-\alpha)nF\eta}{RT} \right) - \exp \left( \frac{-\alpha nF\eta}{RT} \right) \right)$$

(i) State the conditions under which the Butler-Volmer equation holds.

(ii) On a single diagram, sketch current-overpotential curves for anodic, cathodic and total currents, as predicted by the Butler-Volmer equation for the redox reaction:  $O + e^- \rightleftharpoons R$

#### QUESTION 2

2.1 Sketch a Tafel plot that could be obtained from  $i_{total}$  vs.  $\eta$  curves. [5]

2.2 Electrochemical measurements are frequently made in a three electrode cell comprising a working electrode, an auxiliary electrode and a reference electrode connected to a potentiostat. The electrodes are placed in an electrolyte solution containing the electroactive species.

(a) Explain how the system described above can be used to oxidise R and allow the current for the oxidation to be measured [5]

(b) Define the term electrochemically reversible [2]

#### QUESTION THREE

3.1 Capillary electrochromatography (CEC) is a technique that is growing in popularity particularly with the advent of microfluid system and the 'lab on the chip concept'.

Carefully explain the working principals of this technique

and how is it integrated with microfluid system. [6]

3.2 Electrospray ionization (ESI), matrix-assisted laser desorption ionization (MALDI) are relatively new approaches to ionizing large molecules in mass spectrometry. Compare how ions are formed in each process and discuss the similarities. [5]

3.3 List two sources of broadening, explain how it occurs in open tubular capillary columns for gas chromatography [4]

#### QUESTION FOUR

4.1 Draw a fully labelled schematic diagram of a typical gas chromatograph system. [5]

4.2 Consider the Van Deemter equation. Which term is likely to be primary contributor to band broadening in GC? Sketch a van Deemter plot to justify your answer. [7]

#### QUESTION FIVE

5.1 A certain inorganic cation has an electrophoretic mobility of  $4.31 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ . This same ion has a diffusion coefficient of  $9.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ . If this ion is separated from other cations by capillary zone