



KENYATTA UNIVERSITY

UNIVERSITY EXAMINATIONS 2010/2011

INSTITUTIONAL BASED PROGRAMME (IBP) DECEMBER SESSION

EXAMINATION FOR THE DEGREE OF MASTER OF SCIENCE

SCH 556: ANALYTICAL ELECTROCHEMICAL TECHNIQUES

DATE: Wednesday, 27th April, 2011

TIME: 9.00 a.m. – 12.00 p.m.

INSTRUCTIONS:

Answer ALL questions

1. (a) (i) With the aid of an appropriate sketch, describe the Differential Pulse Polarography. (8 marks)
- (ii) Which parameters control the resolution and selectivity in Differential Pulse Polarography? (2 marks)
- (iii) Why does the diffusion current of a particular Polarographic step vary with the applied voltage? (2 marks)
- (b) The concentration of As(III) in water can be determined by differential pulse polarography in 1 M HCl. The initial potential is set to -0.1 V versus SCE, and is scanned towards more negative potential at a rate of 5 mV/s. Reduction of As(III) to As(0) occurs at a potential of approximately -0.44 V versus SCE. The peak currents, corrected for the residual current for a set of standard solutions are shown in the following table.

[As(III)] (M)	i_p (μ A)
1.00×10^{-6}	0.298
3.00×10^{-6}	0.947
6.00×10^{-6}	1.83
9.00×10^{-6}	2.72

What is the concentration of As(III) in a sample of water if the peak current under the same condition is 1.37μ A? (6 marks)

2. (a) (i) What are ion-selective electrodes? **(2 marks)**
 (ii) Describe the construction and working of a solid state membrane electrode. **(6 marks)**
 (iii) Give the important advantages of ion-selective electrodes. **(2 marks)**
- (b) You are responsible for determining the amount of KI in iodized salt and decide to use an I^- ion-selective electrode. Describe how you would perform this analysis using (i) external standards and (ii) the method of standard addition. **(8 marks)**
3. (a) The Saturated Calomel Electrode (SCE) is used as a reference electrode.
 (i) With an aid of a diagram, describe the calomel electrode. **(4 marks)**
 (ii) Write its half-cell presentation and the electrode reaction. **(2 marks)**
 (iii) What are the factors that would affect the effectiveness of this electrode? **(2 marks)**
- (b) Select reference electrode for the following applications, giving reasons for your choice.
 (i) For a combined glass electrode to measure pH. **(2 marks)**
 (ii) For use with Cl^- ise at 298K. **(2 marks)**
 (iii) Fro use with a potassium ise to analyse sea water. **(2 marks)**
 (iv) For use with a F^- to examine drinking water. **(2 marks)**
- (c) Write the Nernst equation in a form that compensates for the effects of the identified ions in (b) on the measured emf. **(2 marks)**
- (d) The selectivity coefficient for K_{H^+/Na^+} for Corning 015 (glass) is approximately 10^{-11} . What error is expected for a solution of 0.05 M NaOH? **(5 marks)**
4. (a) Distinguish between
 (i) Voltammetry and polarography **(2 marks)**
 (ii) a limiting current and a residual current **(2 marks)**
- (b) What do you understand by the term?
 (i) Selectivity coefficient **(2 marks)**
 (ii) Indicator electrode **(2 marks)**
 (iii) liquid-junction potential **(2 marks)**

(c) Explain the following observations

- (i) The behaviour of a glass electrode become non-nernstian at the extremes of pH. **(2 marks)**
- (ii) Mercury electrode is not employed as a reference electrode in electrochemical measurements. **(2 marks)**

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