

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SWAZILAND

C404

ELECTROANALYTICAL CHEMISTRY

MAY 2006 FINAL EXAMINATION

Time Allowed :

Three (3) Hours

Instructions:

1. This examination has six (6) questions and one data sheet. The total number of pages is six (6) including this page.
2. Answer any four (4) questions fully; diagrams should be clear, large and properly labeled. Marks will be deducted for improper units and lack of procedural steps in calculations.
3. Each question is worth 25 marks.

Special Requirements

1. Data sheet.

YOU ARE NOT SUPPOSED TO OPEN THIS PAPER UNTIL PERMISSION TO DO SO HAS BEEN GIVEN BY THE CHIEF INVIGILATOR.

QUESTION 1 [25]

- a) Explain the difference between a “Galvanic” and an “Electrolytic” cell in electroanalytical chemistry. [2]
- b) Explain the difference between “Potentiometry” and “Voltametry” in electroanalytical chemistry. [2]
- c) In a Galvanic cell employing Zn/Zn^{2+} and Cu/Cu^{2+} , explain which is the anode and which is the cathode. [2]
- d) In electroanalytical chemistry, what do the following acronyms stand for? [3]
- i) DME ii) ISE iii) NCE
- e) For the $Cr_2O_7^{2-}/Cr^{3+}$ system in acid,
- i) Write down the balanced redox half cell reaction. [1]
- ii) Write down the Nernst expression. [2]
- iii) Calculate the concentration of $Cr_2O_7^{2-}$ at pH=3 if the potential measured for a 0.0625M Cr^{3+} solution is 0.562V. [3]
- f) What is the role of a reference electrode in potentiometry? [1]
- g) Discuss each of the two (2) main requirements of reference electrodes in potentiometry. [2]
- h) i) With the aid of a diagram, explain how an AgCl/Ag electrode is fabricated, and explain the role of each component in the electrode. [3]
- ii) Write down its half cell reaction and Nernst expression. [1]
- iv) State its standard electrode potential and typical input impedance. [1]
- v) Under what experimental conditions will this electrode not work? [2]

QUESTION 2 [25]

- a) i) With the aid of a diagram, use ion exchange theory to explain how a pH glass membrane electrode works. [3]
- ii) Write the Nernst expression for an ideal pH glass electrode, and show that unit calibrations in the readout are in increments of 59mV. [3]

- b) i) With the aid of a diagram, explain how an SCE electrode is fabricated, and explain the role of each component in the electrode. [3]
- ii) Write down its half cell reaction and Nernst expression. [1]
- iii) State the standard electrode potential for the SCE. [1]
- iv) Under what conditions will the SCE not work. [1]
- c) In the analysis of fluoride ion in tap water using the LaF_3 solid state electrode, TISAB is almost always added to both standards and unknown samples.
- i) What does the acronym "TISAB" stand for? [1]
- iii) List all the components that make up "TISAB" and explain briefly the role of each. [3]
- d) i) Outline the steps involved in calibration of pH glass electrodes. [2]
- ii) List two (2) sources of standards used in the calibration of pH glass electrodes. [2]
- iii) Scratched membranes make electrodes difficult to calibrate. Explain how scratched membranes are regenerated in potentiometry. [2]
- iv) Explain, using diagrams and equations, how the selectivity coefficient and ion exchange principle enable fabrication of a pNa electrode. [3]

QUESTION 3 [25]

- a) In voltammetry, what do the following acronyms stand for? [3]
- i) HMDE ii) NPP iii) RDE
- b) Describe the term "overpotential" in relation to the polarography technique, and explain why overpotential is desirable in this electroanalytical technique. [2]
- c) Draw and label the electrode used in classical polarography, explain how it works, and use chemical equations to explain the shape of the polarogram of Pb^{2+} . [4]
- d) Voltammetry in the upper right quadrant can be complicated by the presence of dissolved oxygen in solution.
- i) Use chemical equations to explain the origin of oxygen waves. [3]
- ii) How are oxygen waves eliminated in voltammetry? [1]
- e) i) Use diagrams to explain the origins of "non-faradaic" current in polarography. [2]

- ii) Use a diagram to illustrate the dependence of “non-faradaic” current on time during the lifetime of mercury drop in polarography. [2]
 - iii) Use a diagram to illustrate the dependence of “faradaic” current on time during the lifetime of mercury drop in polarography. [2]
 - iv) Use a diagram to illustrate the effect of concentration on “non-faradaic” current during the lifetime of a mercury drop in polarography. [2]
- f) Use equations to explain the processes that dictate the useful range of potentials in polarography. [4]

QUESTION 4 [25]

- a) For each of the following modern variants of the polarographic technique, draw the shape of the voltammogram:
- i) Alternating current polarography. [1]
 - ii) Fast linear sweep polarography. [1]
 - iii) Cyclic sweep voltammetry. [1]
- b) For each of the following techniques, indicate, on a voltage-time plot, when sampling of the signal is carried out. Draw the shape of the resultant voltammogram, and indicate the typical resolution (in Volts) and detection limit (in mol/L).
- i) Fast scan polarography. [3]
 - ii) Normal pulse polarography. [3]
- c) i) Draw a schematic diagram of the apparatus used in Anodic Stripping Voltammetry (ASV). [3]
- ii) Assume that ASV is being carried out on an environmental sample containing the toxic element cadmium. Use equations to describe the chemical processes taking place at each of the three steps involved in the ASV of the sample. [3].
 - iii) Explain why ASV is considered superior over most analytical techniques in terms of detection limit. [2]
- d) Cyclic voltammetry is a very useful analytical tool in thermodynamic studies.
- i) Write down the Randles-Sevcik equation for reversible and irreversible systems, and explain the difference between the two. [3]
 - ii) Use diagrams to explain how cyclic voltammograms of reversible systems are different from those obtained for irreversible systems. [3]

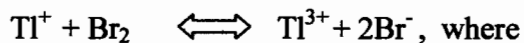
- iii) Explain how you would differentiate between reversible and irreversible systems on the basis of the peak current and peak potentials observed in cyclic voltametry? [2]

QUESTION 5 [25]

- a) In the coulometric titration of Fe^{3+} , describe the role of Ti^{4+} intermediate added at the beginning of the analysis. [2]
- b) i) Use diagrams and equations to describe how an amperometric titration of Pb^{2+} can be carried out with a one-polarized electrode system using SO_4^{2-} as titrant (Pb^{2+} is electroreducible at potentials more negative than -1.0V vs SCE). [3]
- ii) Plot the titration curve expected for an amperometric titration with one polarized electrode for each of the following:
- SO_4^{2-} (non-electroreducible at -1.0V vs SCE) with Pb^{2+} as titrant. [2]
 - Pb^{2+} titrated with a ligand that is also electroreducible at -1.0V vs SCE. [2]
- c) i) Describe how an amperometric titration of Fe^{2+} with Ce^{4+} can be carried out with two indicator electrodes. [2]
- ii) Draw the current-voltage curve for the $\text{Fe}^{2+} / \text{Ce}^{4+}$ system mentioned in c (i) above at the following stages of titration. [4]

$$f = 0; \quad f = 0.5; \quad f = 1.0; \quad f = 1.5$$

- iii) Draw the expected titration curve for the $\text{Fe}^{2+} / \text{Ce}^{4+}$ system described in c (i) and c (ii) above. [2]
- d) Consider the voltametric titration of Tl^+ with electrochemically generated Br_2 according to the reaction



- i) Draw the current-voltage curves of this titration at the following stages of the titration: [4]
- $$f = 0; \quad f = 0.5; \quad f = 1.0; \quad f = 1.5$$
- ii) Plot the titration curve expected for this system using a single indicator electrode. [2]
- iii) Plot the titration curve expected for this system using a two-indicator electrode system. [2]

QUESTION 6 [25]

- a) i) Use diagrams to describe the Rotating Disk Electrode (RDE). [3]
- ii) Use diagrams to describe the hydrodynamic movement of solution in the vicinity of the RDE. [3]
- iii) Describe the two mass transfer phenomena occurring in the RDE. [2]
- iv) Write down the Levich Equation for the RDE and explain all terms appearing in it. [3]
- v) Describe two limitations of the RDE when compared to the dropping mercury electrode. [2]
- vi) What is the advantage of adding a “ring” to the RDE to form what is known as a Rotating Ring Disk Electrode (RRDE)? [1]
- b) Use equations to explain the role of a depolarizer in electrogravimetry. [2]
- c) Use equations to describe the anodic and cathodic reactions taking place during electrodeposition in the measurement of copper in an unknown solution. [3]
- d) A solution of 0.200M Cu^{2+} in 1M H^+ , resistance 0.5 Ω , is to be electrodeposited to 99.995% completion with 1A in an open cell (partial pressure of O_2 in air = 0.2 atm). In the equation $E_{\text{app}} = E_{\text{cathode}} + IR + \dots$ used to ascertain the potential at which electrodeposition will occur:
- i) Calculate E_{cathode} . [1]
- ii) Calculate E_{anode} . [1]
- iii) Calculate the IR drop. [1]
- iv) Describe the term ω , and explain its origins in electrogravimetry using suitable equations. [3]

