UNIVERSITY OF ESWATINI

DEPARTMENT OF CHEMISTRY

MAIN EXAMINATION 2020/2021

TITLE OF PAPER: ANALYTICAL CHEMISTRY II

COURSE NUMBER: CHE 411

TIME ALLOWED: THREE (3) HOURS

INSTRUCTIONS: ANSWER ANY FOUR (4) QUESTIONS

Special Requirements

1. Data sheet.
2. Graph Paper

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

QUESTION 1 **[25]**

a) i) Draw the Standard Hydrogen Electrode (SHE) [5]

ii) Write down the half cell reaction for the SHE [1]

iii) Write down the Nerst expression for the SHE [1]

iv) State the standard electrode potential for the SHE [1]

b) With the aid of a diagram, explain how a Saturated Calomel Electrode is fabricated, and explain the role of each component in the electrode. [6]

c) i) Write down its half cell reaction and Nernst expression for the SCE. [2]

iii) State the standard electrode potential for the SCE. [2]

d) Under what conditions will the SCE not work. [3]

e) List four (4) properties of this electrode that makes it suitable for use as a reference electrode [4]

QUESTION 2 **[25]**

a) For the following indicator electrodes, draw the electrode and write down its Nernst Expression

i) Electrode of the First kind [4]
ii) Electrode of the Second kind [4]
iii) Electrode of the Third kind [4]

b) 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. [6]

ii) Write down its half cell reaction and Nernst expression. [2]

iii) State its standard electrode potential and typical input impendance. [2]

iv) Under what experimental conditions will this electrode not work? [3]

QUESTION 3 **[25]**

a) For the $Cr_2O_7^{2+}$ / Cr^{3+} system in acid, 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 vs the AgCl/Ag electrode. [5]

b) Draw the fluoride ion selective electrode and explain how it works. [4]

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 Fe^{2+} / Ce^{4+} system mentioned in c (i) above at the following stages of titration. [4]

f = 0; f = 0.5; f = 1.0; f = 1.5

iii) Draw the expected titration curve for the Fe^{2+} / 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

$Tl^{+} + Br_2 \Longleftrightarrow Tl^{3+} + 2Br^{-}$, where

$Tl^{3+} + 2e^{-} \Longleftrightarrow Tl^{+}$ $\quad E^0 = -0.78V$ vs SCE

$Br_2 + 2e^{-} \Longleftrightarrow 2Br^{-}$ $\quad E^0 = -1.08V$ vs SCE

i) Draw the current-voltage curves of this titration at the following stages of the titration: [4]

f = 0; f = 0.5; f = 1.0; 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 4 **[25]**

a) Use equations to explain the role of a depolarizer in electrogravimetry. [4]

b) Use equations to describe the anodic and cathodic reactions taking place during electrodeposition in the measurement of copper in an unknown solution. [4]

c) 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 $E_{app} = E_{cathode} + IR + \omega$ used to ascertain the potential at which electrodeposition will occur:

i) Calculate $E_{cathode.}$ [2]
ii) Calculate $E_{anode.}$ [2]
iii) Calculate the IR drop. [1]
iv) Describe the term ω, and explain its origins in electrogravimetry using suitable equations. [5]

d) It takes 9.805 minutes to titrate a sample of Na_2CO_3 coulometrically in an electrolytic cell with electrogenerated hydrogen ions. The generating current is 191.95 mA in a system incorporating Pt electrodes. Assuming that the endpoint occurs when all CO_3^{2-} has been converted to H_2CO_3, calculate the weight of Na_2CO_3 in the sample. [7]

QUESTION 5 **[25]**

a) Describe the term "overpotential" in relation to the polarography technique, and explain why overpotential is desirable in this electroanalytical technique. [3]

b) 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+}. [6]

c) i) Use diagrams to explain the origins of "non-faradaic" current in polaragraphy. [3]

ii) Use a diagram to illustrate the dependence of "non-faradaic" current on time during the lifetime of a mercury drop in polaragraphy. [3]

iii) Use a diagram to illustrate the dependence of "faradaic" current on time during the lifetime of a mercury drop in polaragraphy. [3]

d) Use a diagram to illustrate the effect of concentration on "non-faradiac" current during the lifetime of a mercury drop in polarography. [3]

e) Use equations to explain the processes that dictate the useful range of potentials in polarography. [4]

QUESTION 6 **[25]**

a) 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) Tast polarography. [3]
ii) Normal pulse polarography. [3]
iii) Differential Pulse Polarography [3]

b) i) Draw a schematic diagram of the apparatus used in Anodic Stripping Voltametry (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. [4]

iii) Explain why ASV is considered superior over most analytical techniques in terms of detection limits. [2]

c) 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]

d) Plot the titration curve expected for an amperometric titration with one polarized electrode for each of the following:

i) SO_4^{2-} (non-electroreducible at -1.0V vs SCE) with Pb^{2+} as titrant. [2]

ii) Pb^{2+} titrated with a ligand that is also electroreducible at -1.0V vs SCE. [2]