

**W1-2-60-1-6**

**JOMO KENYATTA UNIVERSITY OF AGRICULTURE AND TECHNOLOGY**

# **UNIVERSITY EXAMINATIONS 2015/2016**

**FOURTH YEAR EXAMINATION FOR THE DEGREE OF BACHELOR OF SCIENCE IN ANALYTICAL CHEMISTRY**

**SCH 2456: ELECTRO ANALYTICAL POTENTIOMETRY AND VOLTAMMETRY**

**DATE: AUGUST 2015 TIME: 2 HOURS**

**INSTRUCTIONS: ANSWER QUESTION ONE AND ANY OTHER TWO QUESTIONS.**

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**DATA:**

**IF=96500Cmol-1**

**E= at 250C**

**QUESTION ONE**

1. Explain using examples where applicable, the following [10 marks]
2. Reference electrodes
3. Polarizable electrodes
4. Voltammetry
5. Coulometry
6. Electrochemical cells
7. For the following cell, write the half-reactions occurring at each electrode and the complete cell reaction and calculate the cell potential [4 marks]

Pt, H2(0.2atm) |HCl(0.5M)| Cl2(0.2atm),Pt

Given

Cl2 + 2e2Cl- E0=1.359V

1. Explain what is the liquid –junction potential and how it can be minimized

[3 marks]

1. (i) What is the selectivity coefficient? [2 marks]

(ii) A potassium ion-selective electrode is used to measure the concentration of potassium ion in a solution that contains 6.0 x 10-3 M. Cesium. The electrodes responds equally to either ion (Kkcs=1). If the potential versus a reference electrode is -18.3 mV for a 5.0x10-1M Kcl solultion and 20.9mV in the sample solution, calculate the activity of K+ in the sample. Assume nernstian response. [6 marks]

1. Consider the titrationof 100ml of 0.1M Fe2+ with 0.1MCe4+in IMHN03. Calculate the potential as a function of titration volume at 50ml of 0.100MCe4+. Fe2++Ce4+ Fe3++ Ce3+ Eø=0.771V
2. The sensitivity of a coulemeter in governed by the delivery of its minimum current for its minimum time. Suppose that 5mA can be delivered for 0.1s
3. Calculate the number of moles of electrons delivered by 5mA for 0.1 seconds. (2 marks]
4. Calculate the milliliters of a 0.01M solution of a two – electron reducing agent required to deliver the same member of electrons. [3 marks]

**QUESTION TWO**

1. A solution of Sn2+ is to be electrolyzed to reduce the Sn2+ to Sn(s). calculate the cathode potential (versus S.H.E) needed to reduce the Sn2+ concentration to 1.0 x10-8 M if no concentration polarization occurs. [3 marks]

(ii) What would be the potential versus S.C.E instead of S.H.E? [2 marks]

 

1. H2S(aq) can be analyzed by titration with coulometrically generated I2.

H2S+I2S(s) +2H+ +2I-

To 50.00ml of sample were added 4g of KI. Electrolysis required 812S at 52.6mA. Calculate the concentration of H2S (g/ml) in the Sample. (H=lg: S=32g) [5 marks]

1. (i) Explain the difference between charging current and faradic current . [4 marks]

(ii) Explain the purpose of waiting 1s after a voltage pulse before measuring current in sampled current voltammetry. [2 marks]

1. (i) Explain what is done in anodic stripping voltammetry. [2 marks]

(ii) Why is stripping the most sensitive polarographic technique?

[2 marks]

**QUESTION THREE**

1. Explain the advantages and disadvantages of using a dropping mercury electrode over solid electrode in voltammetry. [4 marks]
2. With examples, explain the following
3. Decomposition potential [2 marks]
4. Over potential [2 marks]

(c)(i) Calculate the decomposition potential for 0.01M Zn2+ solution at 250C

Zn2++ 2eZn = -0.76V [2 marks]

(ii) At a current of 0.01Acm-2, the overpotential of hydrogen gas on cadmium is -0.04V.Calcualte the concentration of Cd2+ when hydrogen evolutim starts in a solution buffered at PH3. [5 marks]

Cd2++ 2e = -0.40V

(d) A glass electrode was determined to have a potential of 0.395V when measured against the SCE in a standard pH of 7 buffer solution. Calculate the pH of the unknown solution for which 0.467V reading was obtained. [4 marks]

**QUESTION FOUR**

1. (i) Briefly explain the general structure of ion-selective electrodes [4 marks]

(ii) How do ion selective electrodes work? [2 marks]

1. (i) Using a variable potential source, explain how you will separate 99% 0.00Im Zn2+ from 0.01M Cn2+ at 250C on a Pt electrode assuming zero overpotential [5 marks]

Zn2++ 2eZn = -0.76V [2 marks]

Cu2+ + 2+ Cu = -0.34V

1. Explain whether it would be possible to separate lead quantitatively from a solution 0.01M lead. Nitrate at a pH I reducing it to 10-6M.

The hydrogen over potential on lead is -0.40V [5 marks]

Pb2++2e Pb EQ = -0.126V

1. Explain how you can use potentiometry as an analytical tool and the interferences that are excepted. [4 marks]