# **DEPARTMENT OF CHEMISTRY**

# **UNIVERSITY OF SWAZILAND**

#### INTRODUCTION TO ANALYTICAL CHEMISTRY

JULY 2012 SUPPLEMENTARY EXAMINATION

Time Allowed:

Three (3) Hours

#### Instructions:

- 1. This examination has six (6) questions. The total number of pages is five (5), 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.

2. Graph paper.

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

#### C204

#### Question 1[25]

a. (i) Use an example to illustrate the difference between "precision" and "accuracy". (2)

(ii)Use an example to illustrate the difference between "systematic" and "random errors". (2)

- (iii) State the difference between "end point" and "equivalence" point in acid-base titrations.(3)
- b. You are developing a procedure for determining trace Cu in biological samples. A standard reference material (SRM) is taken through the analysis to validate your method, and the analysis is replicated 5 times. The mean of the data obtained is 10.8 ppm with a standard deviation of  $\pm$  0.7 ppm. The SRM has a value of 11.7 ppm. Does your method give a statistically correct value at the 95% confidence interval? (4)
- c. (i) After standardization, a 0.1000M solution of HCl is used to titrate 25.00ml of 0.010M Ba(OH)<sub>2</sub>. Calculate the pH at the following volumes of HCl added during that titration (6)

2.00ml, at equivalence point, 2.00 ml after a equivalence point

- (ii) Plot the titration curve. (2)
- (iii) What is meant by standardization of HCl? And why is this necessary? (3)
- (iv) Use the Henderson equation to suggest a suitable indicator for the titration. (3)

#### **Question 2[25]**

- (a) (i) State the Von Weimarn Ratio, and define all the terms appearing in it. (2)
  - (ii) Using the Von Weimarn Ratio as reference, discuss the effects of relative supersaturation of a solution on the size of the crystalline precipitate formed in the solution concerned during gravimetric analysis. (3)
  - (iii) List and discuss any of four (4) ideal characteristic of a good analytical precipitate? (4)
- (b) (i) Consider the Fajan's titration of 50 ml of 0.0100M KBr with 0.025M AgNO<sub>3</sub> given that  $K_{sp} = AgI: 8.3 \times 10^{-17}$ , AgBr: 5.0 ×10<sup>-13</sup>, AgCl: 1.8 ×10<sup>-10</sup>. Calculate the pAg at the following stage of titration: (6)

5ml added, at equivalence point, at 5ml past equivalence point

- (ii) Draw the titration curve for (i) above. (2)
- (iii)On one graph, sketch three curves that you would expect to get for the system in (iv) above for the following salts:

0.01M KBr, 0.01M KCl, 0.01M KI Clearly label each one. (3)

(c) (i) Name the indicator used for the Fajan's method. (1)

(ii) What is the main disadvantage of the Fajan's method, and how is it overcome? (2)

(iii) Use equations to explain how the end point is detected using this indicator. (2)

## Question 3 [25]

- a. Ammonia, NH<sub>3</sub>, is allowed to distribute between water at pH=5 and carbon tetrachloride, CCl<sub>4</sub>.
  - (i) Write down the equilibrium equation in the aqueous phase. (1)
  - (ii) Write down the distribution ratio expression for this solvent extraction system. (2)
  - (iii) Write down the distribution coefficient expression for this solvent extraction system. (2)
- b. Describe four desirable properties of an ideal choice of solvent in liquid-liquid extraction. (4)
- c. Extractions are enhanced through the use of chelation. Write down the chemical structures of the following chelating agents:
  - (i) Oxime (2)
  - (ii) Dithizone (2)
- d. In the determination of trace nickel by liquid-liquid extraction, several reagents are added prior to the extraction step.
  - (i) Name and write chemical structure of the compound used to form the nickel complex that extracts into chloroform (3)
  - (ii) Explain the role of hydroxylamine hydrochloride in the analysis.(2)
  - (iii) Explain the role of pH 6.5 acetate buffer in this analysis (2)
- e. The distribution ratio of iodine gas (at. Wt.=126.9045) between water and carbon tetrachloride is 85. A 50-mL solution containing 0.35 grams of iodine and 75 ppm of Cd is mixed with 25mL of carbon tetrachloride in order to remove the iodine into the organic phase. Calculate the number of times that the extraction needs to be performed in order to get 99.999% of the iodine into the organic phase.(5)

## Question 4 [25]

- a. The metalchloro complex MCl<sub>3</sub> is extremely soluble in ether, the distribution coefficient for a water/ether system being 50. Calculate the concentration of MCl<sub>3</sub> left in 50 ml of an aqueous 0.01MCl<sub>3</sub> solution after extracting:
  - (i) once with a 10ml portion of ether. (2)
  - (ii) once with 20ml portion of ether. (2)
  - (iii) twice with 10ml portions of ether. (2)
- b. In complexometric titrations,
  - (i) Explain what is meant by "Back Titration". (3)
  - (ii) Draw the chemical structure of the indicator calmagite, and explain how it works in the titration of  $Mg^{2+}$  ions with EDTA. (4)
- c. Suppose a 25.00ml solution of 0.02026M  $\text{Co}^{2+}$  is titrated with 0.03855 EDTA at pH = 6.00. Calculate the pCo at the following volumes of EDTA added: (6)

0.10ml equivalence point volume 14.00ml

and plot the titration curve (2)

- d. (i) Explain the role of an auxiliary complexing reagent in EDTA titrations.(2)
  - (ii) Name a commonly used primary standard for EDTA titrations, and explain why, during the standardization process, the initial buret reading is never set at the "0.00mL" mark. (2)

# Question 5 [25]

- a. For the electrochemical cell:
  - Cd(s) | CdCl<sub>2</sub>(aq,0.0538M) || AgNO<sub>3</sub>(aq,0.0328M) | Ag(s)
  - What component is represented by the symbol "|"? Explain how it works and why the component is used in electrochemical titrations. (3)
  - (ii) Would the cell be Galvanic as written? (3)
- b. In the iodometric determination of copper using thiosulfate as titrant,
  - (i) Name a suitable primary standard. (1)
  - (ii) Name a most widely used specific indicator for the titration. (1)
  - (iii) Explain the role of ammonium bifloride added to the sample prior to titration. (2)
  - (iv) Explain why the indicator named in (ii) above is added just before the end point is reached and not at the beginning of the titration. (2)
  - (v) Use chemical equations to illustrate how this acts as an indicator for this titration. (3)
- c. Suppose a 10ml solution of 0.05M  $Fe^{2+}$  is titrated with 0.100M  $Ce^{4+}$  in 1M HClO<sub>4</sub> and the potential measured relative to the saturated calomel electrode (SCE, E = 0.241V). Calculate the measured potential at the following volumes of 0.100M Ce<sup>4</sup> added: (8)

2.50ml 4.99ml 5.0ml 7.00ml

and plot the titration curve. (2)

## Question 6 [25]

- a. An acid solution of  $Na_2Cr_2O_7$  is mixed with a solution of KBr. A redox reaction occurs, resulting in Br<sub>2</sub> and  $Cr^{3+}$ . Write a balanced equation for the redox reaction. (3)
- b. The calomel electrode is one of the main electrodes against which electrode potentials are referenced.
  - (i) Draw the calomel electrode and label all its components. (3)
  - (ii) Write down the half cell reaction taking place in the calomel electrode, and state the electrode potential.(2)
- c. Write down the structure of ferroin indicator, and use the Nernst equation to derive the criterion used for choosing this indicator for electrochemical titrations. (4)
- d. For the silver-silver chloride reference electrode:
  - (i) Draw and fully label this electrode (3)
  - (ii) Right down its half cell reaction (1)
  - (iii) Use the Nernst equation to explain why it has a constant potential of 0.198V (3)
- d. For the redox system  $Fe^{3+} + e^{-} \iff Fe^{2+}$ , in which 0.58g of  $Fe^{3+}$  is starting material,
  - (i) How much charge should be applied to completely reduce the  $Fe^{3+}$ ? (3)
  - (ii) If the process in (i) above were to take place in 10 minutes, how much constant current should be applied  $(F=9.648 \times 10^4 C)$ ? (3)