

DEPARTMENT OF CHEMISTRY**UNIVERSITY OF SWAZILAND****C204****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.

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Question 3 [25]

- a. Ammonia, NH_3 , is allowed to distribute between water at $\text{pH}=5$ and carbon tetrachloride, CCl_4 .
- Write down the equilibrium equation in the aqueous phase. (1)
 - Write down the distribution ratio expression for this solvent extraction system. (2)
 - 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:
- Oxime (2)
 - Dithizone (2)
- d. In the determination of trace nickel by liquid-liquid extraction, several reagents are added prior to the extraction step.
- Name and write chemical structure of the compound used to form the nickel complex that extracts into chloroform (3)
 - Explain the role of hydroxylamine hydrochloride in the analysis. (2)
 - 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_3 is extremely soluble in ether, the distribution coefficient for a water/ether system being 50. Calculate the concentration of MCl_3 left in 50 ml of an aqueous 0.01 MCl_3 solution after extracting:
- once with a 10ml portion of ether. (2)
 - once with 20ml portion of ether. (2)
 - twice with 10ml portions of ether. (2)
- b. In complexometric titrations,
- Explain what is meant by "Back Titration". (3)
 - 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 Co^{2+} is titrated with 0.03855 EDTA at $\text{pH} = 6.00$. 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:



- (i) 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 bifluoride 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_4 and the potential measured relative to the saturated calomel electrode (SCE, $E = 0.241\text{V}$). Calculate the measured potential at the following volumes of 0.100M Ce^{4+} added: (8)

2.50ml 4.99ml 5.0ml 7.00ml

and plot the titration curve. (2)

Question 6 [25]

a. An acid solution of $\text{Na}_2\text{Cr}_2\text{O}_7$ is mixed with a solution of KBr . A redox reaction occurs, resulting in Br_2 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 $\text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+}$, 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 ($F=9.648 \times 10^4\text{C}$)? (3)