CHUKA   **UNIVERSITY**

UNIVERSITY EXAMINATIONS

FIRST YEAR EXAMINATION FOR BACHELOR OF SCIENCE INDUSTRIAL CHEMISTRY

CHIN 101: QUANTITAVE ANALYSIS

STREAMS: BSc   **TIME: 2 HOURS**

DAY/DATE: THURSDAY 01/04/2021   **8.30 A.M. – 10.30 A.M.**

INSTRUCTIONS
- *Answer question one and any two questions*
- *Do not write on the question paper*

Question one (30 marks) compulsory question

1. a) (i) Distinguish between symmetric equivalence point and asymmetric equivalence

    point.   (1 mark)

    (ii) Discuss three types of indicators used in redox titration.   (6½ marks)

    (iii) Calculate the potential of the solution when 15ml of 0.2M Fe^{3+} solution is added to

    10ml of 0.1m of Sn^{2+} solution.

    $Sn^{4+} + 2e^- \longleftrightarrow Sn^{2+}$ $E_v^O = 0.15V$

    $Fe^{3+} + e^- \longleftrightarrow Fe2+$ $E_v^O = 0.77V$

    (iv) Explain whether the redox indicator given below is suitable in the titration of an

    oxidant analyte with a reductant titrant which has an equivalent point potential of 0.32V

    $In_{ox} + 2e \longrightarrow InRed$ $EIn = 0.4V$ (2 marks)

    b) (i) Explain what you understand by the term back titration.   (2 marks)

(ii) A 0.2g of Pyrolusite is analyzed for manganese content as follows:

Add 50.0ml of a 0.1m solution of ferrous ammonium sulphate to reduce the MnO_2 to Mn^{2+}. After reduction is complete, the excess ferrous ion is titrated in acid solution with 0.02 $MKMnO_4$, requiring 15.0ML. Calculate the percentage of manganese in the sample as Mn3O4. {Mn = 54.938, O = 15.999}   (5 marks)

(iii) 800mg of a sample containing Chromium Ore (Cr_2O_3) was dissolved in a conical flack and Cr was converted to $CrO4^{2-}$ using $Na_2C_2O_4$. 10ml of 0.2M of Ag+ solution was added to the flask and the following reaction took place.

$CrO4^{2-} + 2Ag^+ \longrightarrow Ag_2CrO_4$
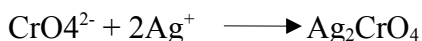
After separating the Ag_2CrO_4 precipitate, the excess Ag^+ in the filtrate was titrated with 0.12m of SCN- solution according to the following equation.

$Ag^+ + SCN^- \longrightarrow AgSCN$

If the volume of SCN^- solution was 14.5ml, calculate the % w/w of Cr_2O_3 {Cr=51.9961 O = 15.999)   (3 marks)

C (i) List five conditions for the selection of adsorption indicators   (2½ marks)

(ii) A sample containing the amino acid alanine CH_3CH (NH_2) COOH, plus inert matter is analyzed by the KJeldahl method. A 2.0g sample is digested, the NH_3 is distilled and collected in 50.0ml of 0.150m H_2SO_4 and a volume of 9.0ml of 0.1m NaOH is required for back-titration. Calculate the percent alanine in the sample.

QUESTION TWO (20 MARKS)

2. a) (i) Describe the principle of the Eriochome Black T used in complexometric titration.
                                                                                    (2 marks)

(ii) State five applications of complexometric titrations.   (3 marks)

(iii) Write short notes on the use of masking and selective demasking agents in complexometric titration   (8 marks)

b) (i) A solution containing 25.0ml of Ni^{2+} in dilute HCl was treated with 25.0ml of 0.05283M Na_2EDTA. The solution was neutralized with NaOH and the pH was adjusted to 5.5 with acetate buffer. The solution turned yellow when a few drops of Xylenol Orange indicator were added. It was then titrated with 17.61ml of 0.002299M Zn^{2+} to reach the end point. Determine the molarity of Ni^{2+} in the unknown. (2 marks)

(ii) Calculate the silver ion concentration in terms of PAg during the titration of 50.0ml of 0.05M NaCl with 0.1M $AgNO_3$ after the addition of the following volumes of the reagent.

   I.   In the preequivalent point region at 10.0ml   (2 marks)
   II. at the equivalent point (25.0ml)   (1 ½marks)
   III. After the equivalent point at 26.0ml. For AgCl, $KSP = 1.82 \times 10^{-10}$ (1 ½marks)

QUESTION THREE (20 MARKS)

3. a) The determination of water hardness of certain borehole water at Chuka town was carried out by year one students. The volume of water sample requiring less than 15ml of titrant which was able to keep the analysis time under 5 minutes was taken and dilutated to 50ml with distilled water. The pH of water sample was adjusted using 1-2 ml of pH buffer containing a small amount of mg^{2+} - EDTA. This was followed by adding 1-2 drops of indicator and titrated with a standard solution of EDTA until the red-t-blue end point was reached.

   (i)   Why was the sample buffered to a pH of 10? and what problems might be expected at a higher pH?   (2 ½marks)
   (ii) Why was a small amount of the Mg2+-EDTA complex added to the buffer?

                                                                              (3 ½marks)
   (iii)   Explain why the procedure had to specify that the titration should not take longer than five minutes.   (1 marks)

b) The concentration of a solution of EDTA was determined by standardizing against a solution of Ca^{2+} prepared using a primary standard of $CaCO_3$. A 0.4071g sample of $CaCO_3$ was transferred to a 500ml volumetric flask, dissolved using a minimum of 6m HCl and diluted to volume. After transferring 50.00ml portion of this solution to a 250ml Erlenmeyer flask, the pH was adjusted by adding 5ml of a pH $10NH_3$. NH_4Cl buffer containing a small amount of $Mg2^+$-EDTA. After adding calmagite as an indicator, the solution was titrated with the EDTA, requiring 42.63ml to reach the end point. Determine the molar concentration of EDTA in the titrant. (1 ½marks)

C) An alloy of chromel containing Ni, Fe and Cr was analyzed by a complexation titration using EDTA as the titrant. A 0.7176g sample of the alloy was dissolved in HNO3 and diluted to a 250ml in a volumetric flask. A 50ml a liquot of the sample, treated with PyroPhospahte to mask the Fe and Cr, required 26.4ml of 0.05831M EDTA to reach the murexide end point. A second 50.0ml a liquot was treated with hexamethylenetetramine to mask the Cr. Titrating with 0.0583M EDITA required 35.43ml to reach the murexide end point. Finally, a third 50.0ml of 0.05831M EDITA, and back titrated to the Murexide end point with 6.21ml of 0.06316M Cu^{2+}. Report the weight percent of NI, Fe and Cr in the alloy. [58.6134, Cu=63.546, Cr = 519961, Fe = 55.845] (5 marks)

d) Discuss with help of a suitable diagram the titration curve of Na_2Co_3 versus Hcl showing the pH range of phenolphthalein, methyl red and methyl orange indicators.

(6 ½marks)

QUESTION FOUR (20 MARKS)

4. a) (i) write short notes on various types of gravimetric analysis. (2 marks)

    (ii) Suggest ways of overcoming many of the possible problems associated with gravimetric analysis. (5 marks)

    (iii) The procedure given below was used by a group of students in order to determine magnesium in water and waste water.

Transfer a sample that contains no more than 60mg of Mg^{2+} into a 600ml. Add 2-3 drops of Methyl red indicator, and if necessary, adjust the volume to 150ml. Acidify the solution with 6M Hcl and add 10ml of 30% w/v $(NH_4)_2HPO_4$. After cooling and with constant stirring add concentrated NH3 drop wise until the methyl red indicator turned yellow (pH > 6.3). After stirring for 5 min, add 5ml of concentrated NH_3 and continue to stir for an additional 10min. Allow the resulting solution and precipitate to stand overnight. Isolate the precipitate by filtering through filter paper, rinsing with 5% v/v NH_3. Dissolve the precipitate in 50ml of 10% v/v HCl and precipitate a second time following the same procedure. After filtering, carefully remove the filter paper by charring. Heat the precipitate at 500^0C until the residue is white and then bring the precipitate to constant weight at 1100^0C.

I. Why does the procedure call for a sample that contains no more than 60mg of $Mg^{2+?}$ (1 ½marks)

II. Why is the solution acidified with HCl before adding the precipitant? (1 ½marks)

III. Why is the acid base indicator Methyl red added to the solution? (2 ½marks)

IV. Explain why forming $Mg(PO_3)_2$ instead of $Mg_2P_2O_7$ increases the precipitates mass? (½marks)

V. Why is the precipitate rinsed with a solution of 5% v/v NH_3? (½marks)

VI. What steps help to improve the precipitates purity? (½marks)

b) 6.4 g of a pure monobasic organic acid is burnt completely in excess of oxygen and CO_2 evolved absorbed completely in one litre of an aqueous solution of NAOH. A 10ml portion of this solution required 14.5ml of a normal HCl solution to reach the phenolphthalein end point. Another 10ml portion of the same solution required 18ml of the same HCl solution to reach the Methyl Orange end point if the organic acid contains 25% oxygen by weight, deduce the empirical formula of this acid and strength of original NaOH [Na = 22.989, O=15.9994, H = 1.0079, C=12.011g]

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