CHUKA  **UNIVERSITY**

UNIVERSITY EXAMINATIONS

FIRST YEAR EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE IN CHEMISTRY/INDUSTRIAL CHEMISTRY

CHIN 101: QUANTITATIVE CHEMICAL ANALYSIS

STREAMS: BSC (CHEM/INDUSTRIAL CHEMISTRY) **TIME: 2 HOURS**

DAY/DATE: WEDNESDAY 15/04/2020 **2.30 P.M. – 4.30 P.M.**

INSTRUCTIONS: Answer question ONE and any TWO other questions

QUESTION ONE (30 MARKS)

(a) (i) Explain how a systematic approach can be used to set up and solve equilibrium problems [5½ marks]

(ii) Write a mass balanced and charge balanced equations for a 0.10 M solution of $NaHCO_3$ [3 marks]

(b) (i) Calculate the ionic strength of a solution consisting of 030 M NaCl and 0.20 M Na_2SO_4 [2½ marks]

(ii) Calculate the activity coefficients for K^+ and SO_4^{2-} in a 0.020 M solution of potassium sulphate $\left(a_{k^+} = 3\text{Å}\ and\ a_{SO_4^{2-}} = 4.0\text{Å}\right)$ at 25°C [3 marks]

(iii) The weak electrolyte AB dissociates to form A^+ and B^- with a thermodynamic equilibrium constant K_{eq} of $2x10^{-8}$ in the presence of a diverse salt of ionic strength 0.1. If the activity coefficient of A^+ and B^- are 0.6 and 0.7 respectively at ionic strength $(\mu) = 0.1$

(I) Calculate the molar equilibrium constant Keq in terms of concentration [2 marks]

(II) Calculate the percent dissociation of a $1.0x10^{-4}M$ solution of AB in water [2½ marks]

(c) (i) Summarize the steps required inagravimetric analysis after the sample has been dissolved [4 marks]

(ii) Explain how the particle size of a precipitate which is influenced in part by experimental variables such as solubility of the precipitate in the medium in which it is being formed, temperature, reactant concentrations and the rate at which reactants are mixed can be accounted for [2½ marks]

(iii) Outline the steps which a chemist should take in order to maintain favourale conditions for precipitation [3 marks]

(d) The amount of protein in a sample of cheese is determined by a Kjeldahl analysis for nitrogen. After digesting a 0.9814 g sample of cheese, the nitrogen is oxidized to NH_4^+ converted to NH_3 with NaoH and distilled into a collection flask containing 50.0 ml of 0.1047 MHCl. The excess Hcl is then back titrated with 0.1183 M NaoH, requiring 22.84 ml to reach the bromothymol blue end point. Report the % w/w protein in the cheese given there is 6.38 g of protein for every gram of nitrogen in most dairy products {*The gravimetric factor for conversion of weight of N to weight of protein is* 6.38} [2 marks]

QUESTION TWO (20 MARKS)

(a) Determination of hardness of water and waste water involves the following steps:

Selecting a volume of sample requiring less than 15 ml of titrant to keep the analysis time under 5 min

Adjusting the pH by adding 1 – 2 ml of a pH 10 buffer containing a small amount of mg^{2+} - EDTA.

Adding 1 -2 drops of calmagite indicator

Titrating with a standard solution of EDTA until the red – to – blue end point is reached

(i) Why is the sample buffered to a pH of 10? [2 marks]

(ii) What problems might be expected at higher or low temperature? [1 mark]

(iii) Why is a small amount of mg^{2+}- EDTA complex added to the buffer? [3 marks]

(iv) Why does the procedure specify that the titration take no longer than 5 min [1 mark]

(b) 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 HNO_3 and diluted to 250 ml in a volumetric flask. A 50.0 ml a liquot of the sample, treated with pyrophosphate to mask the Fe and Cr, required 26.14 ml of 0.05831M EDTA to reach the murexide end point. A second 50.00 ml a liquot was treated with hexamethylenetetramine to mask the Cr. Titrating with 0.05831 M EDTA required 35.43 ml to reach the murexide end point. Finally, a third 50.00 ml aliquot was treated with 50.00 ml of 0.05831 M EDTA, and back titrated to the murexide end point with 6.21 ml of 0.06316 M Cu^{2+} Report the weight percent of Ni Fe and Cr in the alloy [9 marks]

QUESTION THREE (20 MARKS)

(a) The procedure given below was designed to be used for determination of total chlorine residual in public water supply. Study the procedure and answer the questions that follow

Procedure

Select a volume of sample requiring less than 20 ml of $S_2O_3^{2-}$ to reach the end point. Using glacial acetic acid acidifty the sample to a pH in the range of 3 to 4 and add about 1g of KI. Titrate with $Na_2S_2O_3$ until the yellow colour due I_3^- complex disappears. The volume of titrant needed to reach the end point should be corrected for reagent impurities by conducting a blank titration.

(i) Is this an example of a direct or an indirect analysis? Explain [1½ marks]

(ii) Why is the procedure not carried out directly using KI as atitrant [1½ marks]

(iii) Both oxidizing and reducing agents can interfere with this analysis. Explain what effect each of these itnerferents will have on the results of an analysis [1½ marks]

(b) (i) A 25.0 ml sample of a liquid bleach was diluted to 1000 ml in a volumetric flask. A 25 ml portion of the diluted sample was transferred by pipet into an Erlenmeyer flask and treated with excess KI, ixidizing the OCl^- to Cl^-, and producing I_3^-. The liberated I_3^- was determined by titrating with 0.09892 M $Na_2S_2O_3$, requiring 8.96 ml to reach the starch indicator end point. Report the % W/V NaoCl in the sample of bleach. [6 marks]

(ii) A mixture containing only KCl and NaBr is analyzed by the Mohr method. A 0.3172g sample is dissolved in 50 ml of water and tirated to the Ag_2CrO_4 end point, requiring 36.85ml of 0.1120M $AgNO_3$. A blank titration requires 0.17 ml of titrant to reach the same end point. Report the % W/W KCl and NaBr in the sample [4 marks]

(c) (i) A sample containing sodium carbonate, sodium hydrogen carbonate and inert materials is titrated with HCl. The phenaphthalein end point occurs at 15.0ml and the modified methyl orange end point occurs at 50.0 ml. the Hcl was standardized by titrating 0.477g Na_2CO_3, requiring 30.0 ml to reach the modified methyl orange end point. What mixture is present and how many millimeter of each constituent are present. [3 marks]

(ii) Show that CN^- is an appropriate masking agent for Ni^{2+} in, a method in which Nickel's complexation with EDTA is an interference.

$Ni^{2+} + Y^4 \rightarrow NiY^{2-}$ $K_f = 4.2x10^{18}$

$Ni^{2+} + 4CN^4 \rightarrow Ni(CN)_4^{2-}$ $\beta_4 = 1.7x10^{30}$ Y^{4-} is an abbreviation for ethylenediainetetraacetic acid (EDTA) [1½ marks]

QUESTION FOUR (20 MARKS)

(a) Write short notes on the following:

(i) Occlusion and inclusion [3 marks]

(ii) Surface adsorption [1 mark]

(iii) Isomorphous replacement [1½ marks]

(iv) Post-precipitation [½ mark]

(b) A 0.6113 g sample of DOW metal containing aluminum, magnesium and other metals was dissolved and treated to prevent interferences by the other metals. The aluminum and magnesium were precipitated with 8-hyroxyquinoline. After filtering and drying, the mixture of $Al(C_9H_6NO)_3$ and $Mg\ (C_9H_6NO)_2$ was found to weigh 7.8154g. The mixture of dried precipitates was then ignited, converting the precipitate to a mixture of Al_2O_3 and MgO. The weight of this mixed solid was found to be 1.0022g. Calculate the % W/W Al and % W/W Mg in alloy [10 marks]

(c) A 101.3 mg sample of an organic compound known to contain Cl burned in pure O_2 and the combustion gases collected in absorbent tubes. The tube used to trap CO_2 increases in mass by 167.6 mg, and the tube for trapping H_2O shows a 13.7 mg increase. A second sample of 121.8 mg is treated with concentrated HNO_3 producingCl_2, which subsequently reacts with Ag+ forming 262.7mg of $AgCl$. Determine the compounds composition as well as its empirical formula [4 marks]
