THE OPENUNIVERSITY OF SRI LANKA

B.Sc. Degree Programme / Stand alone courses in Chemistry

Level 5 –CMU 3123/CME 5123 –ANALYTICAL CHEMISTRY

FINAL EXAMINATION PAPER 2016/17

Date: 2017.08.08 Duration: Two hours

Time: 9.30 a.m.- 11.30 a.m.

Instructions to students

This question paper consists of six questions. Answer any four questions only.

1. Only $FeCl_3$ and $AlCl_3$ were present in a factory waste. To a sample of this factory waste of 5.00 g, 1.00 M KOH (500.0 mL) was added until the precipitation was completed (not in excess). The resultant precipitates were ignited to form Fe_2O_3 and Al_2O_3 of which the total weight was 3.50 g.
(K_{sp} of $Al(OH)_3$= 2.00×10^{-32} mol^4L^{-4}, K_{sp} of $Fe(OH)_3$= 4.69×10^{-37} mol^4L^{-4}, $FeCl_3$ =162 g, $AlCl_3$= 134 g, Fe_2O_3=160 g, Al_2O_3=102 g, Fe= 56.0 g, Al= 27.0 g)

   (i) Calculate the weight of Al and Fe in the original sample. (25 marks)

   (ii) Give one possible major drawback of this analysis. Suggest a way to improve the accuracy of the results. (15 marks)

   (iii) Calculate the pH of the solution when the first precipitate starts to form. (25 marks)

   (iv) Theoretically is it possible to obtain the two precipitates separately if the amounts of Fe and Al were similar? Justify your answer. (15 marks)

   (v) A student decides to carry out the same analysis without igniting but by getting the weight of the precipitate after adding the hydroxide solution. Do you agree with the decision? Give reasons for your answer. (20 marks)

2. (i) A sample of a factory effluent was analyzed for Ca^{2+} using Flame Atomic absorption spectroscopy with air – acetylene gas. Distilled water was used as the blank solution and the absorbance given by the blank was 0.010. Under the same conditions, a standard solution of 20.0 ppm of Ca^{2+} gave an absorbance of 0.356 while the absorbance resulted by the sample was 0.212. To the standard, blank and the sample 1% $SrCl_2$ was added before taking the measurements.

(a) What change would you expect if 1% $SrCl_2$ was not added? Why? (10 marks)

(b) Calculate the concentration of Ca in the sample. (15 marks)

(c) Describe briefly how you would carry out the above analysis avoiding the error associated with different matrixes of sample and the standard. (10 marks)

(d) Suggest three ways to increase sensitivity in the above analysis. (15 marks)

(ii) X and Y are two species which react with each other to form XY which absorbs at 540 nm with a molar absorptivity coefficient of 440 $cm^{-1}Lmol^{-1}$. Equal volumes of X and Y each having 0.0100 M are mixed with each other. The dissociation constant of XY is 5.00×10^{-5} mol L^{-1}.

(a) What is the significance of molar absorptivity coefficient in an absorbance measurement? (10 marks)

(b) Calculate the expected absorbance value of the resultant solution at 540 nm. (30 marks)

(c) Although the instrument was working well and the sample preparation was done very carefully, the absorbance of the resulted solution was lower than the calculated result. Give possible reasons for getting a lower result. (10 marks)

3. A well water sample was analysed for Z^{2+}using the following procedure.
To a 25.00 mL of sample solution, 5.00 mL of 0.100 M N^{2+} solution was added and titrated with 0.150 M EDTA using Eriochrome Black T as the indicator after adjusting the pH to 10. Both Z^{2+} and N^{2+} react with EDTA. The end point obtained was 30.00 mL. At pH 12, N^{2+} forms a stable hydroxide. ($K_{ZY^{2-}} = 5.00 \times 10^{10}$ $mol^{-1}L$, $K_{NY^{2-}} = 4.00 \times 10^{8}$ mol^{-1})

(i) How do you take a random sample of water from a well? (10 marks)

(ii) Calculate the concentration of Z^{2+} in the sample solution. (15 marks)

(iii) Calculate the pZ^{2+} value at the end point. Write the assumptions clearly. (30 marks)

(iv) If the above titration was carried out at pH= 8, what would you expect for the value of the conditional formation constant of ZY^{2-}? Justify your answer. (15 marks)

(v) Sketch the titration curve for the titration of Z^{2+} with EDTA at pH=8 and pH = 10 in the same graph. (15 marks)

(vi) If you are given a sample having both Z^{2+} and N^{2+}, briefly outline a classical titrimetric method using EDTA to find the concentration of Z^{2+} only. (15 marks)

4. A rock sample was containing the substance Q_2O_5 and 10% (w/w) of H_3QO_4 (a weak acid) in addition to other constituents. To determine the Q_2O_5 amount, 0.500 g of the sample was first dissolved in water. The resultant solution was titrated with 0.200 M NaOH using Methyl red as the indicator. The end point reading was 24.00 mL. (of H_3QO_4 , K_{a_1} =1.1 x 10^{-2} mol L^{-1}, K_{a_2} =1.0 x 10^{-4} mol L^{-1}, K_{a_3} =1.5 x 10^{-9} mol L^{-1}, H_3QO_4= 90 g, Q = 23 g)

$Q_2O_5 + 3H_2O \rightarrow 2H_3QO_4$ The end point was taken at the completion of the following reaction.

$H_3QO_4 + 2NaOH \rightarrow Na_2HQO_4 + 2H_2O$

(i) Sketch and label the titration curve for the above titration between H_3QO_4 and NaOH. Explain the shape of the curve. (20 marks)

(ii) What is the expected pH of the solution when 30.00 mL of NaOH was added? Justify your answer. (20 marks)

(iii) Calculate the percentage of Q_2O_5 in the sample. (35 marks)

(iv) Suggest two adjustments to observe a sharpened end point in the above procedure. (15 marks)

(v) If the end point detection was to be done at the completion of the following reaction, what would be the pH range to be considered when selecting the suitable indicator?

$H_3QO_4 + 3NaOH \rightarrow Na_3QO_4 + 3H_2O$ (10 marks)

5. A 25.0 mL of a solution having an unknown amount of C^+ and 0.01 M A^{2+} was titrated with 0.1 M B^{2+}.

$$C^{3+}(aq) + 2e \rightarrow C^{+}(aq) \quad E^0 = 1.35\,V$$

$$A^{4+}(aq) + 2e \rightarrow A^{2+}(aq) \quad E^0 = 0.74\,V$$

$$B^{2+}(aq) + 2e \rightarrow B_{\downarrow}(s) \quad E^0 = 1.61\,V$$

(i) Sketch and label the potentiometric titration curve and the first derivative curve. Label the end point/s in relation to the analyte ion. (20 marks)

(ii) Do you think that the end point obtained at the completion of the reaction with C^+, can be detected using an indicator? Give reasons for your answer. (10 marks)

(iii) The end point obtained at the completion of the reaction with C^+ was 30.0 mL. Calculate the concentration of C^+. (15 marks)

(iv) If A^{2+}, A^{4+}, C^+, C^{3+} and B^{2+} are having similar molar conductivities, sketch and label the conductometric titration curve for the above titration. Explain the shape of the curve. (20 marks)

(v) The above precipitate B was subjected to Differential Thermal Analysis (DTA). B was vaporized at 300°C.

(a) What is the principle behind Differential Thermal Analysis? (20 marks)

(b) Sketch the DTA curve for the observation of B. (15 marks)

6. (i) Define the terms

(a) Distribution coefficient (K_d)

(b) Distribution ratio (D) (10 marks)

(ii) Dissociation constant (K_a) of an acid HA is 1.00×10^{-5}. Distribution coefficient (K_d) of HA between water and hexane is 3.00. A 50.00 mL sample of 0.025 M aqueous solution of HA with 50.00 mL of hexane.

(a) Write an equation for the dissociation of HA at equilibrium.

(b) Derive an equation for distribution ratio (D) of HA between the two phases, relating K_a and K_d.

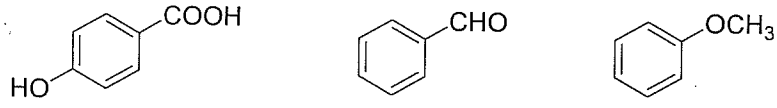
(c) Calculate D for a solution buffered to a pH of 3.

(d) Derive an equation relating D and concentration of HA in both phases at equilibrium and calculate the amount of HA remaining in the aqueous phase.

(e) Explain what would happen to the extraction efficiency if the pH is increased to 5.

(50 marks)

(iii) A plant extract contains the following three compounds as major components. It was subjected to thin layer chromatography (TLC) on silica gel plates using 5% dichloromethane in hexane. R_f values of the compounds were 0.14, 0.43 and 0.76 (not in order).



(a) Assign R_f values to the correct compound giving reasons.

(b) Explain the effect on R_f values if the eluent is changed to 30% dichloromethane in hexane.

(c) Explain the effect on R_f values if the TLC is done using reverse phase silica gel (C18) plates.

(20 marks)

(iv) Metal ions in aqueous solutions can be extracted as chelating complexes.

(a) Give equations for the different equilibria involved in the separation process. (Consider organic chelating ligand as HL and metal as M^{n+})

(b) Indicate two factors that make the extraction process possible.

(20 marks)