THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. Degree Programme / Stand alone courses in Chemistry
Level 5 –CMU 3123/CME 5123 –ANALYTICAL CHEMISTRY
FINAL EXAMINATION PAPER 2011/12

Date: 2012.01.11 Duration: Two hours
Time: 1.00 p.m.- 3.00 p.m.

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

1. (a) State two qualities of a precipitate you would expect in order to carry out a gravimetric analysis. (10 marks)

   (b) A student was given a 50.00 cm^3 solution (expected to have 0.010 mol dm^{-3} chloride ions and 0.010 mol dm^{-3} iodide ions) to find the exact concentration of chloride and iodide ions. He selected gravimetry and to obtain the weight of silver chloride and silver iodide by adding 0.10 mol dm^{-3} $AgNO_3$ solution.

   K_{sp} of AgCl = 1.6 x 10^{-10} mol^2 dm^{-6} K_{sp} of AgI = 8.5 x 10^{-17} mol^2 dm^{-6}

   (i) Which precipitate will be formed first? Give reasons for your answer.
   (ii) Is it possible to precipitate the two precipitates, AgCl and AgI in this solution separately? Explain your answer with proper calculations. (40 marks)

   (c) Write two steps that you should follow in the laboratory in order to get a precipitate with larger particle size and explain how these steps affect the rate of nucleation.(30 marks)

   (d) Explain briefly possible ways contamination of a precipitate at the time of formation. (10 marks)

   (e) The results obtained using gravimetry was less than what was expected. Assuming that there are no personal and instrumental errors involved, suggest one way of improving the accuracy of the results obtained by gravimetry. (10 marks)

2. (a) What do you understand by the term "resonance line" of a given atom? (10 marks)

   (b) In Atomic Absorption Spectroscopy the source used is the Hollow Cathode Lamp but not the tungsten lamp. Why? (16 marks)

   (c) Standard addition technique was used to determine the concentration of manganese ion (Mn^{2+}) in a water sample. The procedure was as follows.
   To a 2.00 cm^3 of water sample in a volumetric flask 2.0 cm^3 of periodate was added and topped up to the 50.0 cm^3 mark with distilled water. The absorbance was measured using UV/Visible spectrophotometer and the absorbance was recorded as 0.180. To another

flask same volume of the sample, periodate and also 1.00 cm^3 of 10 ppm Mn^{2+} was added before topping up to the 50.0 cm^3 mark with distilled water and the absorbance was recorded as 0.540.

(i) What may be the reason for using standard addition technique for the above analysis?
(ii) What is the reason behind addition of periodate in relation to the method of analysis?
(iii) Calculate the concentration of Mn^{2+} in the sample.
(iv) Suggest a method of improving the accuracy of the standard addition technique used here. (50 marks)

(d) Write three differences of Atomic absorption spectroscopy and UV/Visible spectroscopy. (24 marks)

3. (a) List two advantages and two disadvantages of conductometric titrations compared to classical titrations. (20 marks)

(b) Sketch the conductometric titration curve for the titration of 25.0 cm^3 of 0.1 M formic acid with 0.1 M NaOH. (10 marks)

(c) (i) Outline the principle and the methodology of Thermogravimetry (TG) as a qualitative and quantitative method of analysis. (25 marks)
(ii) Comment briefly on the below statement.
"Derivative thermogravimetry (DTG) gives a better accuracy when compared to Thermogravimetry (TG)." (10 marks)
(iii) When 85.0000 g of a sample having calcium carbonate was heated to 100 °C the weight was recorded as 80.0000 g.
(α) What can you deduce from the above data? Give the answer with proper calculations.
(β) Sketch the expected TG curve (showing the stable components) if the sample was subjected to further increase of temperature (Calcium carbonate decomposes at 660◦C). (35 marks)

4. (a) A 10.00 cm^3 of a solution containing an equimolar mixture of A^+ and B^{2+} in 0.1 M H_2SO_4 was titrated with 0.01 M $KMnO_4$ solution.

$E^\circ (MnO_4^-/Mn^{2+}) = 1.51$ V $E^\circ (B^{4+}/B^{2+}) = 0.10$ V $E^\circ (A^{2+}/A^+) = 0.20$ V

(i) Comment on the feasibility of the above titration. (20 marks)
(ii) Sketch and explain the titration curve for the above titration. (20 marks)
(iii) The end point reading was observed at 30.00 cm^3 of 0.02 M $KMnO_4$. Calculate the concentrations of A^+ and B^{2+}. (20 marks)
(iv) Name two methods of detecting the end point of a redox titration. Which is more accurate? Give reasons for your answer. (20 marks)

(b) A 0.02 M solution of a weak acid HX ($K_a = 5.0 \times 10^{-8}$ mol dm^{-3}) and a weak base YOH ($K_b = 6.2 \times 10^{-5}$ mol dm^{-3}) is given to a student. Is it possible to carry out a titration between the two? Explain your answer with proper calculations. (20 marks)

5. (a) Define the following terms in relation to chromatography in brief.
(i). Retention time (ii) Selectivity factor (10 marks)

(b) Of compound **P**, 5g is dissolved in 90 cm^3 of water. Partition coefficient for **P** between water and hexane (K_d) is 5. Calculate and show that extraction with two portions of 45 cm^3 hexane is more efficient than a single extraction with 90 cm^3 hexane. (30 marks)

(c) Give brief explanations for the following statements.
(i) Paper chromatographic separations involve liquid-liquid partitioning mechanism.
(ii) A buffered gel medium has to be used in gel electrophoretic separation of bio molecules.
(iii) In normal phase chromatography, the eluant used first should be a non polar one.
(iv) EDTA –Aluminium complex is less likely to be extracted into an organic solvent.
(60 marks)

6. (a) (i) Write the conditions that must be satisfied for a reaction to be used in a titration.
(ii) What do you mean by "titration error"?
(iii) Selecting appropriate x-, y- axes, draw a suitable graph, to illustrate the titration error. (35 marks)

(b) Ethylenediaminetetraacetic acid (EDTA, H_4Y) is used widely as a complexing agent in titrations for the determination of a variety of metal ions. It has the following dissociation constants (mol dm^{-3}):

$K_1 = 1.0 \times 10^{-2}$; $K_2 = 2.14 \times 10^{-3}$; $K_3 = 6.9 \times 10^{-7}$; $K_4 = 5.5 \times 10^{-11}$

The expression for the fraction $\alpha_{Y^{4-}}$ of EDTA in the form Y^{4-} in terms of H^+ concentration and dissociation constants K_1, K_2, K_3 and K_4 is

$$\frac{1}{\alpha_{Y^{4-}}} = 1 + \frac{[H^+]}{K_4} + \frac{[H^+]^2}{K_3K_4} + \frac{[H^+]^3}{K_2K_3K_4} + \frac{[H^+]^4}{K_1K_2K_3K_4}$$

(i) Calculate $\alpha_{Y^{4-}}$ in a solution of EDTA that is buffered to pH 10.0.

(ii)For the equilibrium, $M^{n+} + Y^{4-} \rightleftharpoons MY^{(n-4)+}$, show that the conditional formation constant K'_{MY} is given by $K'_{MY} = \alpha_{Y^{4-}} K_{MY} = \dfrac{[MY^{(n-4)+}]}{[M^{n+}][Y']}$.

Calculate the conditional formation constant of Ca-EDTA complex at pH 10.0. Formation constant for Ca-EDTA is 5.0×10^{10} mol^{-1} dm^3. (65 marks)