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 2015/16

Date: 2016.07.20 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.

R= gas constant= 8.314 J $K^{-1}mol^{-1}$
T= 25 °C
F= Faraday constant = 96485 C mol^{-1}

1. A sample of factory effluent contains 0.10M of each $X^{3+}$and R^{2+} which forms the precipitates $X(OH)_3$and $R(OH)_2$ respectively with KOH.
(K_{sp} of $X(OH)_3$= 2.0 x $10^{-16}mol^4L^{-4}$, K_{sp} of $R(OH)_2$= 5.5 x $10^{-6}mol^3L^{-3}$

   (i) With the above information given, a student decides to carry out a gravimetric analysis to determine $X^{3+}$and R^{2+}using KOH. Do you agree with the decision? Give reasons for your answer. (20 marks)

   (ii) If the student was to carry out the analysis, how would you advise the student to add KOH? Why? (20 marks)

   (iii) Calculate the pH of the solution when the first precipitate starts to form. (20 marks)

   (iv) What will happen to the solubility of the above precipitate in (iii) if the pH is increased? Explain your answer. (10 marks)

   (v) Theoretically is it possible to obtain the two precipitates separately? Justify your answer with proper calculations. (15 marks)

   (vi) Explain the following in brief.

   "When precipitating AgCl for gravimetric analysis, excess of Cl^- should not be added to Ag^+ solution to ensure completeness of the precipitate." (15 marks)

2. A sample of a factory effluent was analyzed for Pb^{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 ppm gave an absorbance of 0.394 while the absorbance resulted by the sample was 0.250.

(i) Calculate the concentration of Pb^{2+}in the sample. (12 marks)

(ii) What is noise of an instrument? (10 marks)

(iii) Suggest three ways to increase sensitivity in the above analysis. (18 marks)

(iv) Describe briefly how you would carry out the above analysis avoiding the error associated with different matrixes of sample and the standards. (20 marks)

(v) A sample of benzene was analyzed quantitatively using UV-Visible spectrophotometer at the wavelength of 255 nm with a molar absorptivity coefficient of $23 m^2 mol^{-1}$. Comment on the accuracy of the results obtained giving reasons if the analysis was done under the following conditions.
(a) Solution was turbid
(b) Instead of glass cells, quartz cells were used
(c) A tungsten light source was used (15 marks)

(vi) If benzene had been converted to aniline in the above analysis (v), comment on the expected changes in molar absorptivity coefficient and λ_{max}giving reasons. (15 marks)

(vii) How do you analyze a sample accurately when the calibration curve is nonlinear? (10 marks)

3. A 25.00 mL of a sample solution containing metal ions $Z^{2+}$and $M^{3+}$was adjusted to pH 5 with acetate buffer and $Z^{2+}$was titrated with 20.00 mL of 0.150 M EDTA. The pH was then adjusted to 10 and the M^{3+}remaining in the solution were titrated with another 15.00 mL of the same EDTA.

K_{ZY} = 1.3×10^{14}, K_{MY} = 5.2×10^{24}, at pH 5 $\alpha_{Y^{4-}} = 3.5 \times 10^{-7}$ and $\alpha_{Z^{2+}} = 0.875$

(i) What is the significance of having two different pH for the two titrations? (10 marks)

(ii) Calculate the concentration of Z^{2+} in the sample solution. (10 marks)

(iii) Calculate the concentration of EDTA in equilibrium after adding 5.00mL of 0.150 M EDTA to the solution at pH 5. Write the assumptions clearly. (35 marks)

(iv) Give possible reasons with examples for having $\alpha_{Y^{4-}}$ = 3.5 x 10^{-7} and $\alpha_{Z^{2+}}$ = 0.875 at pH=5. (15 marks)

(v) Sketch the titration curve for the titration of $Z^{2+}$with EDTA and show the change in the curve when $\alpha_{Y^{4-}}$ = 3.5 x 10^{-7} and $\alpha_{Y^{4-}}$ = 1 (15 marks)

(vi) If Eriochrome Black T has been used as the indicator for the titration of M^{3+}, briefly explain the reason for the colour change at the end point. State one important theoretical factor to decide the suitability of Eriochrome Black T for this titration. (15 marks)

4. A bottle of $NaNO_3$was contaminated with $NaNO_2$. To determine the NO_2^-amount, 100.0 g of contaminated $NaNO_3$was dissolved in 1.000 L and 25.00 mL of this solution was treated with 50.00 mL of 0.1200 M Ce^{4+}in strong acid and after five minutes the excess $Ce^{4+}$was back titrated with 30.00mL of 0.0200 M Ferrous ammonium sulfate. (N= 14.00, O= 16.00)

$$2Ce^{4+} + NO_2^- + H_2O \rightarrow 2Ce^{3+} + NO_3^- + 2H^+$$

$$Fe^{3+} + e = Fe^{2+} \quad E^0 = 0.771V$$
$$Ce^{4+} + e = Ce^{3+} \quad E^0 = 1.61V$$

(i) Why do you think that the direct titration of NO_2^- was not possible with Ce^{4+}? (05 marks)

(ii) Calculate the percentage of $NaNO_2$present in the sample. (30 marks)

(iii) Calculate the cell potential at the following situations of the titration between excess Ce^{4+} with 0.0200 M Ferrous ammonium sulfate.
(a) Just before adding Ferrous ammonium sulfate
(b) At the end point (30 marks)

(iv) Comment on the following statement.
"For the above calculations the formal potential values should be considered instead of standard potential values." (15 marks)

(v) How do you select a suitable redox indicator for the above titration? (10 marks)

(vi) Sketch and explain the titration curve. (10 marks)

5. (i) The metal ion R^+ was to be determined using gravimetry. The precipitate obtained was RO_3. In order to determine the drying temperature a thermogravimetric analysis was carried out.The thermogravimetric analysis gave the following information. At 120 °C the following endothermic reaction is taking place.

$$RO_3(s) \rightarrow RO_2(s) + \frac{1}{2}O_2(g)$$

(a) What is the main difference with respect to the principle behind in gravimetry and thermogravimetry ? (20 marks)

(b) For 0.1000 g of R, calculate the weight of RO_3, $RO_2$and the weight loss. (R=39.00, O= 16.00) (15 marks)

(c) Do you think that RO_3 can be dried at 100°C? Why? (10 marks)

(d) Draw the Differential Thermal Analysis (DTA) curve for the above reaction. (10 marks)

(ii) A potentiometric titration was carried out to determine the amount of HCl in sample solution of 25.00 mL with 0.1 M Ammonia.

(a) Sketch the titration curve. (10 marks)

(b) The end point of the above titration was not clear. Suggest a method to get the correct end point. (10 marks)

(c) Sketch the conductometric titration curve for the above titration. (10 marks)

(d) The real conductometric titration curve you obtained practically is non- linear. What may be the reason for it? Suggest some practical methods to minimize this error. (15 marks)

6. (i) Define the following terms in relation to solvent-solvent extraction.

(a) Distribution coefficient (K_d)

(b) Extraction efficiency (100q)

Give <u>two</u> factors that affect <u>each</u> of them. (24 marks)

(ii) At 25°C, 0.24 g of an organic acid '**A**' dissolves in 100 mL of water. Amount of **A** that dissolves in 100 mL of ether at the same temperature at equilibrium is 2.70 g.

(a)Calculate the partition coefficient of **A**.

(b) Calculate the amount of **A** extracted in ether (100 mL) if 0.12 g of **A** is left in 100mL of aqueous solution.

(c)Calculate the percentage of extraction for above (ii).

(d) Calculate the volume of ether required to extract 85% of a 3.00 g of **A** in 100 mL of a aqueous solution.

(40 marks)

(iii) (a) List down <u>three</u> applications of planar chromatography.

(b) Describe the following techniques used in planar chromatography stating <u>how they improve the resolution of separation.</u>

A. Descending development
B. 2D development

(c) What are the advantages of planar chromatography over other types of chromatography?

(36 marks)