

**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=  $8.314 \text{ J K}^{-1}\text{mol}^{-1}$

T=  $25 \text{ }^\circ\text{C}$

F= Faraday constant =  $96485 \text{ C mol}^{-1}$

1. A sample of factory effluent contains 0.10M of each  $X^{3+}$  and  $R^{2+}$  which forms the precipitates  $X(\text{OH})_3$  and  $R(\text{OH})_2$  respectively with KOH.  
 $(K_{sp} \text{ of } X(\text{OH})_3 = 2.0 \times 10^{-16} \text{ mol}^4\text{L}^{-4}, K_{sp} \text{ of } R(\text{OH})_2 = 5.5 \times 10^{-6} \text{ mol}^3\text{L}^{-3})$ 
  - (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  $\text{Cl}^-$  should not be added to  $\text{Ag}^+$  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  $23\text{m}^2\text{mol}^{-1}$ . 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  $\lambda_{\text{max}}$  giving reasons. (15 marks)
- (vii) How do you analyze a sample accurately when the calibration curve is nonlinear? (10 marks)

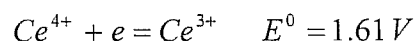
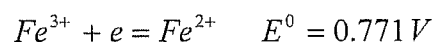
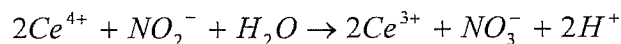
3. A 25.00 mL of a sample solution containing metal ions  $Z^{2+}$  and  $M^{3+}$  was adjusted to pH 5 with acetate buffer and  $Z^{2+}$  was titrated with 20.00 mL of 0.150 M EDTA. The pH was then adjusted to 10 and the  $M^{3+}$  remaining in the solution were titrated with another 15.00 mL of the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

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

- (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 5.00 mL of 0.150 M EDTA to the solution at pH 5. Write the assumptions clearly. (35 marks)

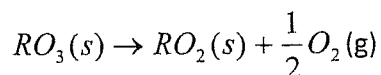
- (iv) Give possible reasons with examples for having  $\alpha_{Y^{4-}} = 3.5 \times 10^{-7}$  and  $\alpha_{Z^{2+}} = 0.875$  at pH=5. (15 marks)
- (v) Sketch the titration curve for the titration of  $Z^{2+}$  with EDTA and show the change in the curve when  $\alpha_{Y^{4-}} = 3.5 \times 10^{-7}$  and  $\alpha_{Y^{2-}} = 1$  (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  $\text{NaNO}_3$  was contaminated with  $\text{NaNO}_2$ . To determine the  $\text{NO}_2^-$  amount, 100.0 g of contaminated  $\text{NaNO}_3$  was dissolved in 1.000 L and 25.00 mL of this solution was treated with 50.00 mL of 0.1200 M  $\text{Ce}^{4+}$  in strong acid and after five minutes the excess  $\text{Ce}^{4+}$  was back titrated with 30.00 mL of 0.0200 M Ferrous ammonium sulfate. (N= 14.00, O= 16.00)



- (i) Why do you think that the direct titration of  $\text{NO}_2^-$  was not possible with  $\text{Ce}^{4+}$ ? (05 marks)
- (ii) Calculate the percentage of  $\text{NaNO}_2$  present in the sample. (30 marks)
- (iii) Calculate the cell potential at the following situations of the titration between excess  $\text{Ce}^{4+}$  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  $120^\circ\text{C}$  the following endothermic reaction is taking place.



- (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  $100^\circ\text{C}$ ? 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 two factors that affect each of them. (24 marks)

- (ii) At  $25^\circ\text{C}$ , 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.