



THE OPEN UNIVERSITY OF SRI LANKA

B.Sc/ B.Ed DEGREE PROGRAMME/ STAND ALONE COURSES IN SCIENCE

FINAL EXAMINATION- LEVEL 4- 2010/2011

CHU 2125/ CHE 4125- ANALYTICAL CHEMISTRY

(2 hours)

*Monday 10<sup>th</sup> January 2011*

*1.00 p.m. - 3.00 p.m.*

ANSWER ANY FOUR QUESTIONS.

IF MORE THAN FOUR QUESTIONS ARE ANSWERED, ONLY THE FIRST FOUR ANSWERS WILL BE MARKED.

1. Water samples of a reservoir taken from one location were checked for the contamination by copper using Atomic Absorption Spectroscopy. The results (in ppm) were as follows.

50, 52, 48, 49, 100, 51

- (a) Why do you think that this analysis was done using an instrumental method and not a classical method like titrimetry? (10 marks)
- (b) What do you understand by the terms "Accuracy" and "Precision"? (20 marks)
- (c) The correct value was found to be 40 ppm. Do you think that there could be a systematic error? Give reasons for your answer. (10 marks)
- (d) Suggest a general way of improving accuracy and write the principle behind the method. (10 marks)
- (e) Why do you reject an outlier from a set of results? Prove your answer by rejecting an outlier from the above set of results (for  $n=6$ ,  $Q_{0.90} = 0.56$ ). (35 marks)
- (f) It was suggested that only the surface layer is contaminated by copper. How should you take samples from the reservoir to prove it? (10 marks)
- (g) How do you advice a person to get a high precision of an analysis? (05 marks)

2. (a)(i) What is meant by a buffer solution?

(ii) Derive an expression for the pH of a buffer that consists of a weak acid HA and its sodium salt NaA in terms of the concentrations of HA and  $A^-$ . Identify the 'buffer ratio' and 'buffer value'. (30 marks)

(b) EDTA ( $H_4Y$ ) is widely used as a complexing agent and it forms complexes with virtually all cations. When direct titration of EDTA with metal ions becomes unsuccessful, back titration is considered.

(i) How do we achieve selectivity in complexometric titration of metal ions with EDTA?

(ii) Explain the role of buffers in EDTA titrations.

(iii) Give three reasons that make direct titrations unsuccessful.

(iv) The pH of a drinking water sample ( $50.00 \text{ cm}^3$ ) was adjusted to 10. Eriochrome Black T (EBT) was added as an indicator. The solution required  $22.00 \text{ cm}^3$  of  $2.5 \times 10^{-3} \text{ mol dm}^{-3}$  EDTA solution to reach the end point. Calculate the hardness of water in terms of  $\text{mg dm}^{-3}$  of  $\text{CaCO}_3$ . (Ca = 40, C = 12, O = 16)

Assume that hardness is totally due to the calcium ions in this water sample.

(50 marks)

(c)(i) Write the expression for the dissociation constant ( $K_{\text{HIn}}$ ) of the indicator  $\text{HIn}$ , in terms of concentrations of  $\text{HIn}$ ,  $\text{H}^+$  and  $\text{In}^-$ .

(ii) The acid base indicator bromocresol green is a weak acid. The yellow acid form and the blue base form of the indicator are present in equal concentrations in a solution when pH is 4.68. What is the  $\text{p}K_a$  for bromocresol green? (20 marks)

3. (a)(i) What is meant by the solubility product of a sparingly soluble compound?

(ii) Write down the expression for the solubility product  $K_{\text{sp}}$  of lanthanum iodate,  $\text{La}(\text{IO}_3)_3$ .

(iii) The solubility product at  $25^\circ\text{C}$  of lanthanum iodate is  $1.20 \times 10^{-11} \text{ mol}^4 \text{ dm}^{-12}$ .

Calculate the molar solubility of lanthanum iodate at  $25^\circ\text{C}$ .

(25 marks)

(b) Briefly explain how each of the following experimental procedures will affect the quality of precipitate for gravimetric analysis.

(i) Carrying out the precipitation reaction at an elevated temperature

(ii) Use of concentrated solutions in the precipitation reaction

(iii) Precipitation from homogeneous solution (PFHS)

(iv) Rapid addition of reagent

(60 marks)

(c) Why is it not desirable to wash the precipitate with water? What is the alternative to this in gravimetry? (15 marks)

4. (a)(i) Define the term 'distillation'.

(ii) Write down the Gibb's phase rule and identify the terms in it. Calculate the number of degree of freedom for the following:

(I) A mixture of liquid and vapour phases of a component

(II) A system in which ice and water are in equilibrium.

(25 marks)

(b)(i) Identifying the terms, write the mathematical expressions for 'volatility' ( $v$ ) of a component and 'relative volatility' ( $\alpha$ ) for a mixture of two components. Write the expression for  $\alpha$  in terms of vapour pressures of components.

- (ii) Defining the terms distribution coefficient  $K_D$  and distribution ratio  $D_C$ , write down expressions for  $K_D$  and  $D_C$  for benzoic acid in a mixture of water and toluene. Assume that in toluene, benzoic acid exists as a dimer. (45 marks)
- (c) 50 cm<sup>3</sup> of aqueous solution containing 0.1 g I<sub>2</sub> is extracted with  
 (i) 50.00 cm<sup>3</sup> of CCl<sub>4</sub>  
 (ii) four portions 12.50 cm<sup>3</sup> of CCl<sub>4</sub>.
- Calculate the percentage of I<sub>2</sub> extracted in each case if  $D_C = 85$ . Hence comment on the efficiency of extraction in (i) and (ii). (30 marks)
5. (a) Write down, using the standard notations, the Nernst equation and the expression for the equilibrium constant for the chemical reaction,  
 $aA + bB \rightleftharpoons cC + dD$  (20 marks)
- (b) The titration of 100 cm<sup>3</sup> of 0.05 mol dm<sup>-3</sup> Fe<sup>2+</sup> solution with a 0.10 mol dm<sup>-3</sup> Ce<sup>4+</sup> solution in 1 mol dm<sup>-3</sup> HClO<sub>4</sub> was monitored potentiometrically. The standard electrode potentials  $E^\circ$  and  $E^\circ$  are +0.767 V and +1.70 V respectively.  
 (i) Write down the balanced equation for the redox titration.  
 (ii) Write down the expression for  $E_{\text{cell}}$ , using the Nernst equation.  
 (iii) The equivalence point of the titration occurs when the volume of Ce<sup>4+</sup> added was 50.00 cm<sup>3</sup>. Explain.  
 (iv) Derive an expression for the potential at equivalence point of the titration.  
 (v) Calculate the cell potential when 36.0 cm<sup>3</sup>, 50.0 cm<sup>3</sup> and 64.0 cm<sup>3</sup> of Ce<sup>4+</sup> is added to the Fe<sup>2+</sup> solution.  
 (vi) Comment on the  $E^\circ_{\text{in}}$  value of a suitable redox indicator that could be used to get an error-free equivalence point. (80 marks)
6. (a) Draw and explain the conductometric titration curves for the following examples:  
 (i) Strong acid (titrant) vs. strong base  
 (ii) Strong base (titrant) vs. weak acid (30 marks)
- (b)(i) Why is atomic absorption spectroscopy (AAS) regarded as both a specific method and a sensitive method?  
 (ii) Briefly describe the important functions of a modulator and a Hollow Cathode lamp (HCL).  
 (iii) Distinguish between spectral interference and chemical interference.  
 (iv) Briefly describe the method of standard addition as used in atomic absorption spectrometry to overcome interferences.  
 (v) Distinguish between standard addition with one added standard and that with a series of added standard. (70 marks)