THE OPEN UNIVERSITY OF SRI LANKA

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

FINAL EXAMINATION- LEVEL 4- 2012/2013

CHU 2125/ CHE 4125- ANALYTICAL CHEMISTRY

(2 hours)

Monday 17th June 2013 ***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. (a) Distinguish between the terms in each of the following pairs:
   (i) Accuracy and precision
   (ii) Random error and systematic error

   Comment on the statement, "Systematic error affects the accuracy but not the precision". (40 marks)

(b) Six samples were randomly taken from a limestone deposit, each was digested with dilute acid and after adding a suitable buffer, 50.00 cm^3 of the digested solution was titrated with 0.02 M EDTA to determine the concentration of Ca^{2+}.

The following results were obtained.

Volume (cm^3) of 0.02 M EDTA	26.05	26.10	26.15	26.05	27.10	26.15

(i) What is a random sample? Suggest a method that would have been followed when taking random samples from this ore.
(ii) If the true concentration of Ca^{2+} in the digested solution was 400 ppm, calculate the equivalence point (Ca = 40).
(iii) Is there a systematic error in the set of results? Explain your answer with proper calculations.
(iv) Check statistically whether there is/are any outlier/s in this set of results at 96% confidence level. (for n = 6, Q=0.64 ; for n = 5, Q=0.73).
(v) Suggest a method to minimize the random error. (60 marks)

2. (a)(i) Write the conditions that must be satisfied by a reaction for it to be used in classical titrimetric methods.

(ii) Write, with an example in each case, a brief description of indirect titration and back titration methods. (35 marks)

(b)(i) Derive the expression for the *pH* of a buffer that consists of a mixture of weak acid HA (dissociation constant K_a) and its conjugate base A^-.

(ii) Calculate the mass of NaA you need to add to 0.5 dm^3 of 0.1 mol dm^{-3} solution of HA to make up a buffer solution of pH 7.5.
For HA, pK_{a1} is 7.1; the relative molecular mass of NaA is 100. (35 marks)

(c)(i) Derive the expression for the dissociation constant (K_{HIn}) of the indicator HIn, in terms of concentrations of HIn, H^+ and 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 pK_a for bromocresol green? (30 marks)

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

(ii) The solubility product (K_{sp}) at 38°C of lead phosphate, $Pb_3(PO_4)_2$ is $3.0x10^{-44}$ mol^5 dm^{-15}. Calculate the molar solubility of lead phosphate at 38 °C.

(iii) Predict whether or not a precipitate will be formed when 10.0 cm^3 of 0.03 mol dm^{-3} $Pb(NO_3)_2$ solution is mixed with 20.0 cm^3 of 0.006 mol dm^{-3} NaCl solution. K_{sp} for $PbCl_2$ is $1.6x10^{-5}$ mol^3 dm^{-9}. (40 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) Precipitation from homogeneous solution (PFHS)

(iii) Rapid addition of reagent (60 marks)

4. (a) 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. (30 marks)

(b)(i) Identifying the terms, write the mathematical expressions for 'volatility' (v) of a component and 'relative volatility' (α) for a mixture of two components. Write the expression for α 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. (50 marks)

(c)(i) When a compound dissolved in the aqueous layer is extracted into an organic layer, the fraction remained in the aqueous layer after n^{th} extraction, f_n is given by

$$f_n = \left[\frac{V_w}{V_w + D_C V_O}\right]^n$$

A compound X dissolved in 50 cm^3 of aqueous layer is extracted four times, using 12.50 cm^3 ether each time for extraction. D_C is given as 50. Calculate the fraction of solute remained after the 4^{th} extraction. (20 marks)

5. (a) Using the standard notations, write down the Nernst equation and the expression for the equilibrium constant for the chemical reaction,

aA + bB == cC + dD (20 marks)

(b) The titration of 100 cm^3 of 0.05 mol dm^{-3} Fe^{2+} solution with a 0.10 mol dm^{-3} Ce^{4+} solution in 1 mol dm^{-3} $HClO_4$ was monitored potentiometrically. The standard electrode potentials for the redox couples Fe^{3+}/Fe^{2+} and Ce^{4+}/Ce^{2+} 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_{cell}, using the Nernst equation.

(iii) The equivalence point of the titration occurs when the volume of Ce^{4+} added was 50.00 cm^3. Derive an expression for the potential at equivalence point of the titration.

(iv) Calculate the cell potential when 36.0 cm^3, 50.0 cm^3 and 64.0 cm^3 of Ce^{4+} is added to the Fe^{2+} solution.

(v) Comment on the E^o_{In} value of a suitable redox indicator that could be used to get an error-free equivalence point. (80 marks)

6. (a)(i) Write down **two** advantages of conductometry as compared with titrimetry.

(ii) The SI unit of conductance is Siemens (S). Express a Siemen in terms basic SI units.

(iii) The resistance of a voltmeter is 3.0×10^{10} Ω; it read 1.5 V, when it was used to measure the potential of a cell. What was the current (in amperes) that passed during the measurement? (30 marks)

(b) Sketch the conductometric titration curve for a titration of weak acid vs. strong base (titrant). Indicate the equivalence point. (20 marks)

(c)(i) Briefly explain why atomic absorption spectroscopy (AAS) is regarded as both a specific method and a sensitive method..

(ii) Briefly describe the important function(s) of atomizer, modulator and Hollow Cathode Lamp (HCL) (50 marks)

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