THE OPEN UNIVERSITY OF SRI LANKA

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

FINAL EXAMINATION- LEVEL 4- 2011/2012

CHU 2125/ CHE 4125- ANALYTICAL CHEMISTRY

(2 hours)

Monday 11th January 2012 *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) Explain the difference between each of the following pairs of terms:
   (i) Accuracy and precision
   (ii) Random errors and systematic errors
   (iii) Population mean and the sample mean (30 marks)

(b) Two chemists A and B have carried out four titrations with 0.01 M HCl to find the concentration of NaOH. The end point readings were as follows.

A (cm^3) – 25.10, 25.20, 25.30, 25.05
B (cm^3) – 24.10, 25.20, 23.30, 25.05

(i) As an analytical chemist, whose results would you accept? Explain your answer with statistical calculations.
(ii) The chemist B rejected the value 23.30 when he calculated the average. Is this rejection statistically accepted? (For 4 observations $Q_{0.90} = 0.76$)
(iii) Suggest one methodological systematic error and one personal systematic error that could have taken place. (40 marks)

(c) (i) Describe how you should carry out the standard addition method and explain how it improves the accuracy of results.
(ii) Comment briefly on the statement given below.
"High accuracy of imprecise results is accidental or rather unlikely."

(30 marks)

2. (a)(i) Define the term, 'buffer capacity', β of a buffer. Write down the mathematical expression for β and identify all the terms in it.

(ii) Write down the 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^-.

(iii) Calculate the mass of NaA you need to add to 1.0 dm^3 of 0.1 mol dm^{-3} solution of HA to make up a buffer solution of pH 7.4.
For HA, pK_{a1} is 7.1; the relative molecular mass of NaA is 100. (60 marks)

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

Calculate the conditional formation constant of Ca-EDTA complex at pH 10.0. Assume that $\alpha_{Ca^{2+}} = 1$. Formation constant for Ca-EDTA is 5.0×10^{10} mol^{-1} dm^3; $\alpha_{Y^{4-}}$ in a solution of EDTA that is buffered to pH 10.0 is 0.35. (40 marks)

3. (a)(i) Write down the expression for the solubility product of lead arsenate, $Pb_3(AsO_4)_2$.

(ii) The solubility product (K_{sp}) of $Pb_3(AsO_4)_2$ at 25 °C is 4.0×10^{-36} mol^5 dm^{-15}. Calculate its molar solubility at 25 °C.

(b) It is often a practice, in gravimetry, to wash the precipitate with a solution containing a common ion. What will be the effect of washing AgCl precipitate with a 0.01 mol dm^{-3} Cl^- solution?

The molar solubility of AgCl at 25 °C is 4.4×10^{-6} mol dm^{-3}. The solubility product K_{sp} of AgCl at 25 °C is 1.8×10^{-10} mol^2 dm^{-6}. (50 marks)

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

(i) Use of dilute solutions in the precipitation reaction

(ii) Precipitation from homogeneous solution (PFHS)

(iii) Slow addition of reagent, with constant stirring (50 marks)

4. (a)(i) 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 ether.

(ii) 1 g of benzoic acid ($K_a = 6.5 \times 10^{-5}$) originally dissolved in 50.0 cm^3 of water is equilibrated with 50.0 cm^3 of ether at pH 6. Distribution coefficient, K_D of benzoic acid between ether and water is 10. Assume that benzoic acid is present in one form in ether.
Calculate the distribution ratio, D_C. (50 marks)

(c) The fraction of a solute remained in the aqueous layer after n^{th} extraction is given by $f_n = \left[\frac{V_w}{V_w + D_C V_o}\right]^n$. 1 g of compound 'X' dissolved in 10.0 cm^3 of water will be recovered by extracting with 10.0 cm^3 portion of organic solvent at a time.

(i) Given that D_C= 9.0, calculate the fraction of solute remained after the 3rd extraction.

(ii) How many times the extraction needs to be carried out with 10.0 cm^3 portion of organic solvent at a time to achieve 99.99% extraction? (50 marks)

5.(a)(i) Write down the electrode reaction for the calomel electrode.

(ii) Show that the potential of the saturated calomel electrode is constant at constant temperature. (30 marks)

(b) Given that

$UO_2^{2+} + 4H^+ + 2e \rightleftharpoons U^{4+} + 2H_2O$ $\quad E° = +0.334$ V

$Ce^{4+} + e \rightleftharpoons Ce^{3+}$ $\quad E° = +1.440$ V

(i) Calculate the $E°_{cell}$ value.

(ii) Comment on the feasibility of the reaction.

(iii) Write the total reaction. (30 marks)

(c) Write down the three types of graphs used to determine the end point in a potentiometric titration. Briefly explain how the end point is obtained from each graph. (20 marks)

(d) Write two advantages and two disadvantages of potentiometry. (20 marks)

6. (a) Draw and explain the conductometric titration curves for the following examples:

(i) Strong acid vs. strong base (titrant)

(ii) Weak acid vs. strong base (titrant) (40 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 an atomizer and a monochromator.

(iii) Briefly describe chemical interference in flame AAS. How can it be eliminated?

(iv) Write two advantages of AAS. (60 marks)

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