THE OPEN UNIVERSITY OF SRI LANKA

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

FINAL EXAMINATION- LEVEL 4- 2013/2014

CHU 2125/ CHE 4125- ANALYTICAL CHEMISTRY

(2 hours)

Thursday 26th June 2014 ***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 following in a set of results.
   (i) Absolute error and relative absolute error
   (ii) Constant systematic errors and proportional systematic errors
   (iii) Repeatability and reproducibility (30 marks)

   (b) One student, Gamini has carried out a redox titration with 0.01 M $K_2Cr_2O_7$ to find the concentration of Fe^{2+} in an industrial effluent tank (25.0 cm^3). He repeated the titration four times and the end point readings (in cm^3) were as follows.

   18.00, 18.10, 15.00, 18.05

   (i) Gamini rejected the value 15.00 cm^3, when he calculated the average. Is this rejection statistically accepted? (For 4 observations $Q_{0.90}$ = 0.76)
   (ii) What is the reason behind rejecting a data from a set of data?
   (iii) Calculate the mean and the standard deviation of the accepted data set.
   (iv) Another student, Sarath did the same analysis using potentiometric titrimetry. He repeated the analysis four times and the average end point was 19.50 cm^3 and the standard deviation of his set of results was ± 0.20 cm^3. Comment on the accuracy and the precision of results of Sarath compared to that of Gamini. Justify your answer.
   (v) Suggest a suitable sampling method that the student should have followed when taking samples from the tank. (70 marks)

2. (a)(i) Write the conditions that must be satisfied by a reaction for it to be used in classical titrimetric methods.
   (ii) Giving an example, write a brief description of back titration method.
   (25 marks)

(b)(i) Give examples of the two types of buffers.

(ii) Write down the expressions for the *pH* of the buffer solutions given in (i) in terms of *pK* values and concentration terms.

(iii)Define the term 'Buffer capacity'of a buffer. Write down thc mathcmatical cxprcssion for it and identify the all the terms in it.

(iv) 25.00 cm^3 of 0.12 M solution of an unknown weak monoprotic acid, HA was titrated with 0.1 M NaOH. After the addition of 17.50 cm^3 NaOH, the *pH* was found to be 8.5. Calculate the dissociation constant K_a of HA. (45 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 HI_n undergoes a colour change when 20% of it is converted to its anionic form. The colour change takes place when the pH is 6.40. Calculate the pK_a of the indicator. (30 marks)

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

(ii) The solubility product (K_{sp}) at 25 °C of lanthanum iodate, $La(IO_3)_3$ is $1.20x10^{-11}$ mol^4 dm^{-12}. Calculate the molar solubility of lanthanum phosphate at 25 °C.

(iii) In a gravimetric analysis where Ba^{2+} is precipitated as $BaSO_4$, 50 cm^3 of 0.1 M H_2SO_4 was used instead of distilled water to wash the precipitate. Comment.
K_{sp} of $BaSO_4$ is $1.08x10^{-10}$ mol^2 dm^{-6}. (40 marks)

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

(i) Rapid addition of concentrated solutions of reagents at low temperature

(ii) Precipitation from homogeneous solution (PFHS) (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 water and steam 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 acetic acid (CH_3COOH) in a mixture of water and toluene. Assume that in toluene, acetic acid exists as a dimer. (50 marks)

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

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

A compound Y dissolved in 50 cm^3 of aqueous layer is extracted four times, using 10.0 cm^3 ether each time for extraction. D_C is given as 5.0. 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 reaction, $A^+_{(aq)} + B^+_{(aq)} \rightleftharpoons A_{(s)} + B^{2+}_{(aq)}$ (20 marks)

(b) Given that

$UO_2^{2+}_{(aq)} + 4H^+_{(aq)} + 2e^- \rightleftharpoons U^{4+}_{(aq)} + 2H_2O_{(l)}$ $\quad E^0 = +0.334$ V

$Ce^{4+}_{(aq)} + e^- \rightleftharpoons Ce^{3+}_{(aq)}$ $\quad E^0 = +1.440$ V

(i) Calculate the E^0_{cell} value.
(ii) Comment on the feasibility of the reaction.
(iii) Write down the cell reaction.
(iv) Write down the expression for the E_{cell} using the Nernst equation.
(v) Calculate the potential at equivalence point in the titration of 0.05 M U^{4+} with 0.01 M Ce^{4+}. Assume both solutions are 1.0 M in H_2SO_4.
(vi) Comment on the E^o_{In} value of a suitable redox indicator that could be used to get an error-free equivalence point. (60 marks)

(c) Briefly explain how redox titration differs from acid base titration. (20 marks)

6. (a)(i) Write down **two** advantages of conductometry as compared to volumetric titrimetry.
(ii) The SI unit of conductance is Siemens (S). Express a Siemen in terms basic SI units.
(iii) Sketch the conductometric titration curves for titration of strong acid vs. weak base (titrant) and strong acid vs. strong base (titrant). Indicate the equivalence point in each case. (50 marks)

(b)(i) Identify the important function(s) of atomizer, modulator and Hollow Cathode Lamp (HCL) in an atomic absorption spectrophotometer (AAS).
(ii) Distinguish between spectral interference and chemical interference.
(iii) Briefly describe the method of standard addition as used in AAS to overcome interferences. (50 marks)

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