THE OPEN UNIVERSITY OF SRI LANKA

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

FINAL EXAMINATION- LEVEL 4- 2009/2010

CHU 2125/ CHE 4125- ANALYTICAL CHEMISTRY

(2 ½ hours)

Thursday 28th January 2010 *1.00 p.m.- 3.30 p.m.*

ANSWER ANY **FOUR** QUESTIONS.

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

1.(a)(i) What is meant by a 'buffer solution'? Write an expression for 'buffer ratio' and identify the terms in it.

(ii) Write down the expression for pH of a buffer solution in terms of pK_a of the weak acid and the concentrations of the weak acid and its conjugate base.

(20 marks)

(b) Ethylenediaminetetraacetic acid (EDTA, H_4Y) is used widely as a complexing agent in titrations for the determination of a variety of metal ions. It has the following dissociation constants (mol dm^{-3}).

$K_1 = 1.0 \times 10^{-2}$; $K_2 = 2.14 \times 10^{-3}$; $K_3 = 6.9 \times 10^{-7}$; $K_4 = 5.5 \times 10^{-11}$

The expression for the fraction $\alpha_{Y^{4-}}$ of EDTA in the form Y^{4-} in terms of H^+ concentration and dissociation constants K_1, K_2, K_3 and K_4 is

$$\frac{1}{\alpha_{Y^{4-}}} = 1 + \frac{[H^+]}{K_4} + \frac{[H^+]^2}{K_3K_4} + \frac{[H^+]^3}{K_2K_3K_4} + \frac{[H^+]^4}{K_1K_2K_3K_4}$$

(i) How will $\alpha_{Y^{4-}}$ vary with increasing pH?

(ii) Calculate $\alpha_{Y^{4-}}$ in a solution of EDTA that is buffered to pH 10.0.

(iii) For the equilibrium, $M^{n+} + Y^{4-} \rightleftharpoons MY^{(n-4)+}$, show that the conditional formation constant K'_{MY} is given by $K'_{MY} = \alpha_{Y^{4-}} K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}][Y']}$. Calculate the conditional formation constant of Ca-EDTA complex at pH 10.0. Formation constant for Ca-EDTA is 5.0×10^{10} mol^{-1} dm^3.

(50 marks)

(c) Titration of Ca^{2+} and Mg^{2+} in a 50.0 cm^3 sample of hard water required 23.50 cm^3 of 0.01 mol dm^{-3} EDTA. A second 50.0 cm^3 aliquot was made strongly basic with NaOH to precipitate Mg^{2+} as $Mg(OH)_2$. After filtration, the supernatant liquid was titrated with EDTA solution; for this titration, 14.50 cm^3 of the EDTA solution was required. Calculate

(i) The total hardness of the water sample expressed as ppm of $CaCO_3$.

(ii) The concentration (ppm) of Ca^{2+} in the sample.

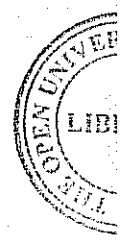
(iii) The concentration (ppm) of Mg^{2+} in the sample.

(C = 12; O = 16; Mg= 24; Ca = 40)

(30 marks)

2. Six random samples were taken from a dolomite ore, digested and 50.00 cm^3 of the digested solutions were titrated with 0.02 M EDTA to determine the concentration of Ca^{2+}. The following results were obtained.

Sample	1	2	3	4	5	6
Volume of EDTA (cm^3)	26.05	26.10	26.15	26.05	27.10	26.15



(a)(i) Outline a procedure that you would have followed in the selection of 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). (Show the calculation steps). (20 marks)

(b)(i) Is there a systematic error in the set of results? Explain your answer with proper calculations.

(ii) Suggest two systematic errors that would have happened during this titration.

(iii) Comment on the following statement. "Systematic error affects accuracy but not the precision".

(30 marks)

(c)(i) Check statistically whether there are any outliers in this set of results at 96% confidence level. (for n = 6, Q=0.64 ; for n = 5, Q=0.73)

(ii) Why do you test for outliers? Explain your answer with proper calculations for the above set of data.

(iii) Assuming that the above set of results is normally distributed, draw schematic diagrams to show the results before and after rejecting the outliers. (40 marks)

(d) One student suggested that repeating the titration with 25.00 cm^3 of the sample solution (instead of 50.00 cm^3) would minimize the error. What do you think of this suggestion? Briefly explain your answer.

(10 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 3.0×10^{-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 1.6×10^{-5} mol^3 dm^{-9}.

(40 marks)

(b) A gravimetric analysis to determine the concentration of Pb^{2+} involved slow generation of SO_4^{2-} in situ by the following reaction:
$HSO_3NH_2 + HNO_3 \rightarrow 2H^+ + SO_4^{2-} + N_2O + H_2O$
to precipitate Pb^{2+} as lead sulphate.

(i) Briefly explain the advantage(s) of this method in terms of the quality and purity of the precipitate.
(ii) Identify the process that takes place above and give another example where this process is used in gravimetry.
(iii) How does this method overcome the problem(s) that you would envisage if you prepared lead sulphate by adding a solution of SO_4^{2-} to a Pb^{2+} solution.

(40 marks)

(c)(i) Write the factors that affect the solubility of a precipitate.
(ii) Write the important steps in gravimetric analysis. (20 marks)

4.(a) Write down the Gibb's phase rule and calculate the number of degrees of freedom:
(i) at the triple point of the water
(ii) for a system in which liquid ethanol is in equilibrium with its vapour.

(20 marks)

(b)(i) Write down the expressions for the terms 'distribution coefficient' K_D and 'distribution ratio' D_C for a substance A present in solvents 1 and 2. Identify the terms in them.
(ii) Write down expressions for the terms K_D and D_C for the system, acetic acid (CH_3COOH) in a mixture of water and benzene. In benzene acetic acid exists as a dimer.
(iii) 1g of benzoic acid originally dissolved in 100 ml of water is to be equilibrated with 100 ml of ether at pH 7. Distribution ratio, $K_D = 100$, $K_a = 6.5 \times 10^{-5}$. Calculate D_C.

(40 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 is dissolved in 50 cm^3 of aqueous layer and it 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.

(ii) Briefly explain the effect of *pH* on solvent extraction of aluminium by 8- hydroxyl quinoline. Draw a typical extraction curve (curve of %E vs. *pH*) for Al^{3+}.

(40 marks)

5.(a) Write down the Nernst equation for the reaction, $A^{+}_{(aq)} + B^{+}_{(aq)} \leftrightarrow A_{(s)} + B^{2+}_{(aq)}$ (10 marks)

(b) For the reaction, $U^{4+} + 2Ce^{4+} + 2H_2O \Leftrightarrow UO_2^{2+} + 2Ce^{3+} + 4H^+$

(i) Comment on the feasibility of the reaction.

(ii) Write down the expression for E_{cell} according to Nernst equation.

(iii) Derive an expression for 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.

$UO_2^{2+} + 4H^+ + 2e \Leftrightarrow U^{4+} + 2H_2O \quad E^0 = 0.334V$

$Ce^{4+} + e \Leftrightarrow Ce^{3+} \quad E^0 = 1.44V$

(iv) In a titration, 25.0 cm^3 of 0.01 M U^{4+}solution required 20.00 cm^3 of Ce^{4+} solution. Calculate the concentration of Ce^{4+} solution. (60 marks)

(c)(i) What is meant by a redox titration? How does it differ from an acid- base titration.

(ii) Write two methods by which the end point in a redox titration can be detected. (30 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 10^{12} 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?

(iv) Sketch the conductometric titration curve for a titration of strong base (titrant) vs. weak acid. Highlight the equivalence point. (40 marks)

(b)(i) A light beam has a wave length of 0.085 microns. What is the energy of a photon in joules? ($c = 3x10^8$ m s^{-1}; $h = 6.63x10^{-34}$ Js)

(ii) In a UV-Visible spectrometer, radiant power of the incident light is 80 and two thirds of it is absorbed by the sample. Calculate the percentage of transmittance.

(iii) A solution having a concentration of 0.002 mol dm^{-3} shows an absorption of 0.36 at 256 nm. (The path length of the cell is 2.00 cm).What is the molar absorptivity (dm^3 mol^{-1} cm^{-1}) of this solution?

(iv) Briefly describe the important function(s) of each of the following units:

(I) Hollow Cathode lamp (HCL)

(II) Atomizer

(III) Photodetector

Write down the disadvantage(s) of an Atomic Absorption Spectrometry (AAS). (60 marks)

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