THE OPEN UNIVERSITY OF SRI LANKA

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

FINAL EXAMINATION- LEVEL 4- 2008/2009

CHU 2125/ CHE 4125- ANALYTICAL CHEMISTRY

(2 ½ hours)

Saturday 24th January 2009 ***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) 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. (30 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 change in *pH* when 0.010 mol of solid NaOH is added to a solution (1.00 L) which is 0.200 mol dm^{-3} with respect to HCO_2H (pK_a= 3.75) and 0.100 mol dm^{-3} with respect to HCO_2^-.

(iii) Write expressions for 'buffer ratio' and 'buffer value' and identify the terms in them. (40 marks)

(c)(i) Write an expression for the conditional formation constant $K_{MY'}$ for the complex NiY^{2-}. Hence calculate K_{NiY2-} at *pH* 3.00. (log K_{NiY2-}= 18.6; at *pH* 3.00, $\alpha_{Y4-}= 2.5\times10^{-11}$).

(ii) Explain the change(s) that take place when a metal ion M^{n+}(analyte) is titrated against EDTA, which is Y^{2-} (titrant), using the indicator HI_n.

(iii) Explain the role of buffers in EDTA titrations. (30 marks)

2. Mr. Silva wanted to identify a suitable laboratory out of the four most reputed laboratories to analyze his new product, a finely powdered fertilizer, on a regular basis. In order to evaluate the laboratories, initially he gave samples with known compositions. Each laboratory was asked to determine the composition of a specific element. The results and some of the calculated parameters are given in the table below.

Laboratory	**L1**	**L2**	**L3**	**L4**
Element analysed	K	Mg	Cu	Fe
Results obtained (ppm)	170 165 180 185	100 61 60 59	0.10 0.19 0.15 0.09	7.0 6.0 6.5 5.9
True value (ppm)	176	60	0.10	5.0
Mean (ppm)	175	70	0.13	
Standard deviation (ppm)	9.13		0.05	0.51
Absolute error (ppm)		10	0.03	1.4

(a) Calculate: (i) Mean of the results of L4
(ii) Standard deviation of the results of L2
(iii) Absolute error of the mean of the results of L1
(Show all the steps in the calculations clearly) (15 marks)

(b) Based on the above results, identify the most reliable laboratory. Justify your answer. (Hint: The composition levels are different). (40 marks)

(c) Show that the precision can be improved by rejecting a result of L2 using a statistically acceptable method (for n= 4, $Q_{0.99} = 0.82$). (10 marks)

(d) Illustrate the improved precision, compared to the precision before, after rejecting the suspected result. (05 marks)

(e) Mr. Silva commented that the results of L4 have a systematic error involved.
(i) Do you agree with Mr. Silva's comment?
(ii) Give reasons for your answer.
(iii) Give one possible systematic error and a random error that may have occurred in this analysis.
(iv) State two general ways of overcoming the random error.
(20 marks)

(f) Briefly outline the method of taking a representative laboratory sample for analysis from a production of one thousand 1 kg packs of the fertilizer.

(10 marks)

3.(a) (i) What factors relating to the concentration of the solutions and /or the solubility of the precipitate should be known to predict whether precipitation of AgCl can occur in a solution of $AgNO_3$ when a solution of NaCl is added?

(ii) Briefly state how these factors are used in the prediction of the precipitate.

(iii)What is the solubility of AgCl at 25^0C in a solution which is ALREADY 0.0100 mol dm^{-3} in chloride ions? K_{sp} for AgCl = 1.77×10^{-10} mol^2 dm^{-6}.

(40 marks)

(b)What is co-precipitation? Explain **one** type of co-precipitation, giving an example.

(20 marks)

(c) A certain barium halide exists as the hydrated salt $BaX_2.2H_2O$, where X is the halogen. In an experiment the barium content of this salt was determined by a gravimetric method. A sample of the halide (0.2650 g) was dissolved in water (200 $cm^{3)}$ and excess sulphuric acid added. The mixture was then heated and kept at boiling for 45 minutes. The precipitate was filtered off, washed and dried. Mass of precipitate obtained was 0.2533 g.

(Ba = 137 ; S = 32 ; O = 16)

(i).Calculate the number of moles of barium in the original sample.
(ii).Determine the identity of X. (40 marks)

4.(a)(i) Define the term 'distillation'.
(ii) Using a labeled diagram of a typical set up for fractional distillation and a temperature- composition diagram for a binary mixture, briefly explain the process(es) that take(s) place in fractional distillation.

(35 marks)

(b)(i) Write down the Gibb's phase rule and identify the terms in it.
(ii) Applying Gibb's phase rule to a system of ethanol vapour above liquid phase of ethanol, calculate the number of independent variables. What are they?

(25 marks)

(c)(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, too.

(iii) Briefly explain the effect of *pH* on solvent extraction of metal by chelating ligand. Draw a typical extraction curve (%E vs. *pH*) for metal ions.

(40 marks)

5.(a) Write down the expression for Nernst equation and the equilibrium constant (using the standard notations) for the following chemical reaction:

$$aA + bB \Leftrightarrow cC + d\,D$$

(20 marks)

(b) Consider the following cell diagram and the standard electrode potentials

$$Cu_{(s)} \mid Cu^{2+}{}_{(aq)}\ (x\ M) \parallel Ag^{+}{}_{(aq)}\ (y\ M) \mid Ag_{(s)}$$

$$E^{o}_{Ag^{+}/Ag} = +0.799\ V \qquad E^{\circ}_{Cu^{2+}/Cu} = 0.337\ V$$

(i) Write down the corresponding electrode (half) reactions and hence, the overall (spontaneous) cell reaction

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

(iii) Derive an expression for the equilibrium constant for this reaction in terms of the standard reduction potentials and hence, determine the value of the equilibrium constant. (45 marks)

(c) An iodometric method to determine the percentage of copper in brass is carried out in the laboratory. In this procedure, 0.24 g of a brass sample was dissolved in acid followed by neutralization with ammonia. This was then treated with excess KI and the liberated iodine was titrated with 0.10 M sodium thiosulphate. The average value of titrant used was reported as 24.50 ml. Calculate the percentage of copper in brass (Write down all relevant equations and steps in obtaining your answer).

(35 marks)

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

(ii) The special name given to the SI unit of conductance is Siemens (S). What is a Siemen (S)? Express a Siemen in terms basic SI units.

(20 marks)

(b) Sketch the conductometric titration curves (highlighting the equivalence point) for the following systems

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

(ii) Weak acid (titrant) vs. strong base (16 marks)

(c)(i) Write down the mathematical expression for Beer Lambert Law using the standard notations.

(ii) Define Absorbance and express the relationship between absorbance and transmittance given that transmittance is the fraction of incident light that passes through the cell without undergoing absorbtion. (14 marks)

(d) The molar absorptivity of the complex ion $Fe(SCN)^{2+}$ at 580 nm (wavelength of its maximum absorption) is 7.00×10^3 dm^3 cm^{-1} mol^{-1}. Calculate

(i) the absorbance of a 2.50×10^{-5} M solution of this complex at 580 nm in a 1.00 cm cell.

(ii) the absorbance of a solution when the concentration of the complex is doubled.

(iii) the transmittance of the solutions described in (i) and (ii) above.

(35marks)

(e) To excite an electron of sodium atom from *3s* state to *4p* state, a photon having an energy of 6.02×10^{-22} kJ is required. Calculate the wavelength (in nm) and the frequency (in s^{-1}) corresponding to this photon.
(Planck's constant, $h = 6.26 \times 10^{-34}$ Js; speed of light, $c = 3.0 \times 10^8$ ms^{-1})

(15 marks)

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