THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. Degree Programme / Stand alone courses in chemistry
Level 4 – FINAL EXAMINATION – 2006/2007

CHU 2125/CHE 4125 – Analytical Chemistry

Duration: Two and half-hours
Date: 30th November 2006 from 1.00 p.m. to 3.30 p.m.

Instructions to candidates

ANSWER ONLY FOUR QUESTIONS. THIS QUESTION PAPER HAS 06 QUESTIONS AND 06 PAGES

Velocity of light = 3.0 x 10^{10} cm s^{-1},
Plank's constant= 6.626 x 10^{-34} Js
Gas constant = 8.314 J K^{-1} mol^{-1}

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1. (i)

$Fe^{3+} + e^- \Leftrightarrow Fe^{2+}$ $\quad E^\circ = +0.771\,V$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \Leftrightarrow 2Cr^{3+} + 7H_2O$ $\quad E^\circ = +1.33\,V$

Write down the balanced equation for the titration of Fe^{2+} with dichromate ion in acidic medium.

(20 marks)

(ii)

Draw a schematic diagram of the potentiometric experimental setup for this titration. Name all important parts of the experimental setup.

(20 marks)

(iii) Derive an expression for the potential at the equivalence point in terms of pH at 30°C. Show your calculations clearly along with the derivation of units.

(60 marks)

2. (i)

To excite an electron of sodium atom from 3s state to 4p state a photon having an energy of 6.02×10^{-19} J is required. Calculate the wavelength of this photon in nanometers. Show your calculations clearly, along with the derivation of units.

(20 marks)

(ii)

What is the atomizer of the atomic absorption spectrometer described in Part V of CHU 2125 book?

(05 marks)

(iii)

Atomic absorption spectroscopy (AAS) is

(a) a **specific** method (b) a **sensitive** method

What do you understand by these terms with respect to AAS?

(20 marks)

(iv)

What is the function of a modulator in AAS?

(20 marks)

(v)

Write down Beer-Lambert's law and clearly state what I_0, I, ϵ, c, and l stand for? Also indicate the units of c, l and ϵ.

(35 marks)

3. (i)

Assume that volume V_1 of an aqueous solution containing m moles of solute S is extracted with an organic solvent having volume V_2. Let q be the fraction of S remaining in aqueous phase at equilibrium. Derive an expression for the partition coefficient K, in terms of q, V_1 and V_2.

(30 marks)

(ii) Draw a diagram of a fractional distillation setup indicating

(a) Distillation flask
(b) Receiving flask
(c) Packed column
(d) Thermometer
(e) Heating device
(f) Inlet and outlet of water to and from the condenser.

(25 marks)

(iii) Define normal boiling point of a liquid in words.

(10 marks)

(iv) Al^{3+} ion can be extracted from the aqueous solution into an organic phase using diethyl ether. Suppose you have 0.2000 g of Al^{3+} dissolved in 150.00 cm^3 of aqueous phase. By calculating percentage extraction in each case prove that

(a) three extractions of ether using 10 cm^3 at a time, is more efficient than
(b) a single extraction using 30 cm^3 of ether.

Suppose Dc = 85.0 and use the following equation

$$W_n = W\left(\frac{V_w}{V_w + D_C\, V_o}\right)^n$$

Show your calculations very clearly.

(35 marks)

4. (i) (a) Write down two(2) features that distinguishes Random Error from Systematic Error.
(b) What is meant by accuracy?
(c) What is meant by precision?

(24 Marks)

(ii) In order to test the applicability of a new method (method **B**) for the determination of calcium in blood, a Chemist carries out replicate measurements using the standard method (method **A**) and the new method. The results are as follows (calcium content is expressed in mg/dL)

Method **A**	Method **B**
25.50	24.90
25.30	25.20
25.60	25.20
24.90	25.30
25.00	25.30
26.40	25.10

The expected value for the calcium content is 25.25 mg/dL
The Chemist, subsequently, makes the (b) and (c) statements:

(a) Write down the expression for percentage absolute error. Identify the symbols used.

(b) Method B is more precise than method A. However, if the value of 26.40 is removed from the rest of the values in method A, then Method A is **more accurate** and **more precise** than Method B

(c) The value of 26.40 reported in method A can be rejected based on Q test at the 90% confidence level. (Q critical values are given below)

(d) Assuming that the value of 26.40 in method A is rejected, calculate the sixth value of the calcium content from method A, that the chemist should get in order to get a mean value of 25.25 mg/dL.

Number of Observations	90% Level of Confidence
5	0.64
6	0.56
7	0.51

Are these statements (b) and (c) correct? Justify your answer with the aid of suitable tabulations where necessary and with reference to the relevant statistical parameters in each case.

$$\text{Standard Deviation, } s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}} = \sqrt{\frac{\sum x_i^2 - \frac{(\sum x_i)^2}{n}}{n-1}}$$

(60 marks

(iii) Given a bowser load of coconut oil, how would you carry out a simple sampling procedure in order to test the quality of oil visually (laboratory tests are not expected). Give your reason/s for adopting the procedure you have outlined.

(16 marks

5.

(i) In a gravimetric experiment where barium ions were precipitated as $BaSO_4$ student X used 0.100 dm^3 of distilled water to wash the precipitate whereas student Y used 0.100 dm^3 of 0.100 mol dm^{-3} H_2SO_4. Which student is more successful in his experiment? Explain your answer by performing necessary calculations.
K_{sp} ($BaSO_4$) = 1.08 x 10^{-10} mol^2 dm^{-6}

(25 marks)

(ii) Explain how the following experimental procedures will affect the gravimetric determination of a crystalline precipitate.

(a) Carrying out the precipitation reaction at an elevated temperature
(b) Generation of the precipitating agent within the solution
(c) Use of concentrated solutions in the precipitation reaction

(30 marks)

(iii) State two problems encountered by a chemist in working with a colloidal precipitate. What remedial action could be taken to overcome them?

(20 marks)

(iv) 0.500 g of a steel sample containing 3.0 % (w/w) Ni was dissolved in 12 M HCl and converted to a red DMG – Nickel complex by adding an alcoholic DMG solution which is 1.0 % (w/w) DMG in alcohol. The density of the alcohol solution is 0.79 g/cm^3.

(a) Calculate the mass of the DMG solution required for a complete precipitation of Nickel.

(b) What will be the volume of the DMG solution if you take twice as much of the DMG required?

$2\ DMG + Ni \rightarrow Ni(DMG)_2$

(molar mass of DMG and the $Ni(DMG)_2$ complex are 116.12 g mol^{-1} and 288.1 g mol^{-1} respectively. Ni = 58.69)

(25 marks)

6. (i)

(a) What is meant by a buffer solution?

(b) Derive an 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^-. Identify the "buffer ratio".

(c) Calculate the change in pH that occurs when 0.01 moles of solid NaOH is added to 1 dm^3 of a solution which is 0.20 mol dm^{-3} in HCOOH and 0.10 mol dm^{-3} in $HCOO^-$. pK_a of HCOOH is 3.75.

(30 marks)

(ii) EDTA (H_4Y) is widely used as a complexing agent and forms complexes with virtually all cations. When direct titrations with metal ions become unsuccessful, back titration is considered.

(a) Draw the structure of the metal chelate formed by Mg^{2+} ion with EDTA.

(b) How do we achieve selectivity in Complexometric titration of metal ions with EDTA?

(c) Give <u>three</u> reasons that make direct titrations unsuccessful.

(d) The pH of a drinking water sample (50.00 cm^3) was adjusted to 10. Calmagite was added as an indicator. The solution required 22.00 cm^3 of 2.5 x 10^{-3} mol dm^{-3} EDTA solution to reach the end point. Calculate the hardness of water in terms of mg dm^{-3} of $CaCO_3$. (Ca = 40, C = 12, O = 16)
Assume that hardness is totally due to the calcium ions in this water sample.

(50 marks)

(iii) Write the expression for the dissociation constant (K_{HIn}) of the indicator HIn, in terms of concentrations of HIn, H^+ and In^-.

P. T. O.

The acid base indicator bromocresol green is a weak acid. The yellow acid and blue base forms of the indicator are present in equal concentrations in a solution when pH is 4.68. What is the pK_a for bromocresol green?

(20 marks)