00102

THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. Degree Programme / Stand alone courses in Chemistry
Level 5 – FINAL EXAMINATION – 2010 / 2011

CHU 3129/CHE 5129 – INSTRUMENTAL METHODS IN CHEMICAL ANALYSIS

Duration: Two and half hours
Date and time: 25th June, 2011 from 1.30 a.m. to 4.00 p.m.

Instructions to students

This question paper consists of six pages and six questions. Answer any four questions only.

1. (a) (i) Write five main differences between photometric titrations with classical titrations.

(ii) Giving reasons explain why the measured absorbance is not suitable to plot against the volume of titrant in photometric titrations. How do you modify the measured absorbance to plot a suitable graph ?

(iii) Sketch the graph expected when only the titrand is absorbing light and both the product and the titrant are non absorbing at a given wave length.

(50 marks)

(b) What is/are,

(i) quantum efficiency in Fluoresence spectroscopy?

(ii) the basic principle behind Raman Spectroscopy?

(iii) the light sources and sample cells used in IR spectroscopy?

(30 marks)

(c) A 2.54 x 10^{-3} M solution of the pure substance Q (molecular weight = 196.00 g) has an absorbance of 0.362 at 284 nm in a 1.00 cm cell. A solution P contains 0.7256 g of Q in one litre and has shown a transmittance of 0.240 in the same cell at the same wave length. Calculate the % of Q in the sample P (give the answer to the correct number of significant figures).

(20 marks)

2. (a) (i) Write five main differences between UV/Visible spectroscopy with Fluorescence spectroscopy.

(ii) Suggest an appropriate procedure to quantify the manganese levels. in a steel sample as permanganate using a spectrophotometer.

(iii) A calibration plot of absorbance against concentration showed negative deviation. Sketch a suitable calibration curve illustrating the negative deviation.

(iv) Give two possible errors/reasons for getting a negatively deviated calibration curve as in 2. (a) (iii). Suggest a suitable method to overcome each of the above error,

(60 marks)

(b) (i) Draw a schematic diagram of a Mass Spectrophotometer.

(ii) Describe briefly how the peaks of relative abundance are resulted by the Mass Spectrophotometer.

(iii) In a mass spectrum account for getting masses which are greater than the parent mass.

(20 marks)

(c) A solution Y is having 1.00 M of NaX and 1.00 M of NaOH. The absorbance of the solution Y in a 1.00 cm cell was (due to the presence of X^- ion only) 0.470 at 273 nm. HX is a weak acid and 1.00 M HX solution shows an absorbance of 0.126 in the same cell at the same wavelength. Calculate the dissociation constant of the acid HX (give the answer to the correct number of significant figures).

(20 marks)

3. (a) Sketch a clearly labeled diagram of the standard hydrogen electrode

(18 marks)

(b) $M|M^{3+} \parallel Cl^-$ (saturated) $|Hg_2Cl_2, Hg|Pt$;

Standard reduction potential of the calomel electrode = 0.27 V

(i) Write down the half-cell reactions at each electrode and hence, the balanced equation for the above cell reaction.

(ii) Given that the standard cell potential of this cell is 1.91 V, determine the standard reduction potential of the $M|M^{3+}$ electrode.

(24 marks)

(c) (i) Consider the half reaction of the form

$A^{3+} + e \rightleftharpoons A^{2+}$

Write down the Nernst equation for this reaction; identify clearly all the symbols used.

(ii) Write the balanced half-equation for the following electrode and hence, calculate its reduction potential. E°(standard electrode potential) = 0.073 V

$Br^- (1.0 \times 10^{-2}\ M) | AgBr(s) | Ag(s)$

(20 marks)

(d) What do you understand by the following terms (i) Buffer (ii) Junction potential

(10 marks)

(e) (i) Compared to metallic electrodes, membrane electrodes work on a different principle. Explain the above statement.

(ii) List the three categories of membranes used to make ion-selective electrodes.

(28 marks)

4. (a) Define the following: (i) Faraday (ii) Overpotential

(12 marks)

(b) (i) Distinguish between (α) Coulometry and Electrogravimetry

(β) Voltammetry and Polarography

(Identify the main difference/s only; details of the techniques **not relevant**)

(ii) Identify clearly (including the units where relevant) all the terms in the Ilkovic equation

$I_D(\max) = 607\ nD^{\frac{1}{2}} m^{\frac{2}{3}} t^{\frac{1}{6}} c$

(28 marks)

(c) (i) Sketch the Current vs Time curve expected in a Constant Potential Coulometric (CPC) experiment; identify the region corresponding to the total charge involved.

(ii) Name the three major components associated with the instrumentation used in the above (CPC) technique. Briefly outline the function of each of these components

(iii) A coulometric titration (constant current) was carried out to determine the amount of dissolved phenol in a certain water sample. The basis of this determination was the stoichiometric and fast reaction between phenol and electrochemically generated bromine to give tribromophenol 100.0 ml of the water sample was acidified and an excess of KBr was added. Coulometric titration was then carried out at a constant current of 25 mA. The end point was reached in 400 seconds. With the aid of the relevant chemical equations, calculate the phenol content in the water sample in **mol m^{-3}.**

(60 marks)

5. (a) Explain the meanings of the following terms used in chromatography.

(i) Authentic sample

(ii) Dead time

(iii) Resolution

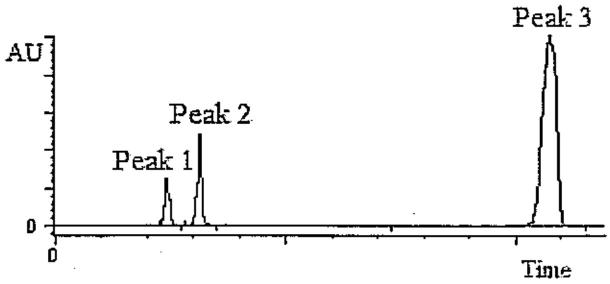
(iv) Diffusion

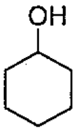
(20 marks)

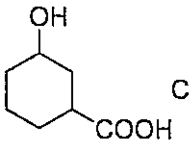
(b) List five different types of partition forces of stationary phases that contribute to the separation of mixtures.

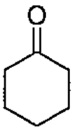
(20 marks)

(c) A chromatogram of a mixture of three compounds A, B and C on isocratic elution on a silica gel column with a non polar solvent is given below.



A =


B =


C =


(i) Giving reasons, assign each peak to the correct compound.

(ii) What information could you obtain from a chromatogram in a chemical analysis?

(iii) Draw the chromatogram that you expect when the above mixture is separated on a reversed phase column using a polar solvent. Assign each peak to the correct compound.

(iv) Explain the difference between the 'isocratic elution' and the 'gradient elution'.

(60 marks)

6. (a) van Deemter equation which relates the height equivalent to the theoretical plate and flow rate is,

$$H = A + \frac{B}{u} + C\,u$$

(i) Identify all the terms in the above equation.

(ii) Describe the significance of the terms A and B in gas liquid chromatography (open tubular column) and in liquid chromatography.

(iii) Indicate the disadvantages if following three factors are reduced individually in order to minimize H.

- thickness of the film of stationary phase
- particle size of the stationary phase
- viscosity of the mobile phase

(60 marks)

(b) List four characteristics of a good detector.

(16 marks)

(c) " GC with a thermal conductivity detector (TCD) can be coupled with a mass spectrometer while that with a flame ionization detector (FID) cannot be." Explain this statement with regard to the detector mechanism.

(12 marks)

(d) State the most convenient action you would take to reduce zone broadening in

i. GC separation

ii. HPLC separation

(12 marks)