



THE OPEN UNIVERSITY OF SRI LANKA  
 B.Sc. Degree Programme / Stand alone courses in Chemistry  
 Level 5 – FINAL EXAMINATION – 2009 / 2010

CHU 3129/CHE 5129 – INSTRUMENTAL METHODS IN CHEMICAL  
 ANALYSIS

Duration: Two and half hours

Date and time: 24<sup>th</sup> June, 2010 from 9.30 a.m. to 12.00 noon

Instructions to students

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

1. (a) What are the information that can get from an IR spectrum for qualitative analysis? (10 marks)
  - (b) (i) Draw and label a schematic diagram of UV/Visible spectrophotometer.  
 (ii) What are the differences in the instrumentation of UV/Visible Spectrophotometer and IR spectrophotometer? (28 marks)
  - (c) (i) When you analyse a compound using a mass spectrophotometer, a mass spectrum is resulted. Account for the signals in a mass spectrum.  
 (ii) In a mass spectrum three important signals are the base peak, molecular ion peak and (M+1) peak. Explain the significance of these peaks and also how these peaks are used to identify the compound. (32 marks)
  - (d) The indicator methyl orange (HI<sub>n</sub>) is a weak acid, with  $K_a = 1.0 \times 10^{-4}$ . At 470 nm, both the dissociated form (I<sub>n</sub><sup>-</sup>) and the undissociated form (HI<sub>n</sub>) have equal molar absorptivities, which is  $10,000 \text{ L mol}^{-1} \text{ cm}^{-1}$ . What is the absorbance of a methyl orange solution in a 1.00 cm cell at pH = 4.5, if the total concentration of both forms is  $3.76 \times 10^{-5} \text{ M}$ ? Show all the steps in calculation and give the answer with the correct number of significant figures. (30 marks)
2. (a) (i) Draw and label a schematic diagram of a fluorimeter.  
 (ii) Briefly discuss the differences in the instrumentation of a fluorimeter compared to the absorption spectrophotometer. (16 marks)

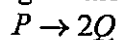
- (b) Explain the following statements.
- Fluorescence spectroscopy is extremely sensitive when compared with atomic absorption spectrophotometry.
  - In atomic fluorescence spectroscopy, the emitted wavelength is equal to absorbed wavelength, but it is not so in molecular fluorescence spectroscopy.

(20 marks)

- (c) Briefly discuss why and how would you carry out method of standard addition in atomic absorption spectrophotometry.

(20 marks)

- (d) The compound P undergoes the following reaction in water.



A 0.100g of P (molecular weight = 100.0 g) was dissolved in 1.00 L of water. The absorbance of this solution was 0.368 at 500 nm at a path length of 1.00 cm. The molar absorptivities of P =  $600 \text{ L mol}^{-1}\text{cm}^{-1}$  and Q =  $10.0 \text{ L mol}^{-1}\text{cm}^{-1}$  at 500 nm. Find the concentrations of P and Q at equilibrium.

Show all the steps in calculation and give the answer with the correct number of significant figures.

(34 marks)

3. (a) Giving reasons identify the most suitable separation/ chromatographic technique that can be applied to separate the following samples
- A mixture of fragments of DNA
  - Volatile components from a mixture of essential oils
  - Metal ions extracted from a soil sample

(27 marks)

- (b) Describe the following terms in brief.

- Dead time
- Zone broadening
- Resolution

(24 marks)

- (c) Calculate the plate height and the plate number for a 1.25 m long column if 10- bromoanthracene has a retention time of 8.32 minutes and a peak width of 31seconds.

(25 marks)

(d) Tabulate the major difference(s) between the following pairs.

- (i) Normal phase liquid chromatography and reversed phase liquid chromatography
- (ii) Isocratic elution and gradient elution
- (iii) Stationary phases in thin layer chromatography and paper chromatography

(24 marks)

4. (a) Identify the changes that you observe in a chromatogram with the increase of the oven temperature of a gas chromatograph.

(15 marks)

(b) What are the basic components of a high pressure liquid chromatographic system?

(25 marks)

(c) List down the advantages and the disadvantages of a UV absorbance detector in a chromatographic system?

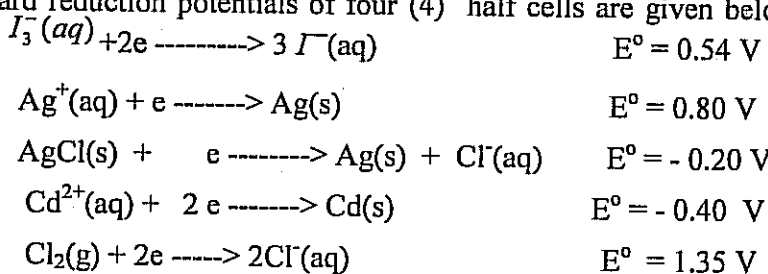
(20 marks)

(d) "Gel permeation chromatography is different from other types of chromatography"

- (i) How does the gel permeation chromatography differ from other chromatographic mechanisms?
- (ii) Explain briefly how the gel (stationary phase) affects the separation.
- (iii) Give three types of gels that can be used as the stationary phases.

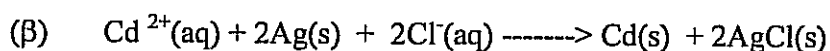
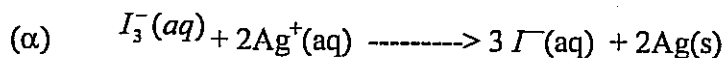
(40 marks)

5. (a) The standard reduction potentials of four (4) half cells are given below



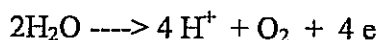
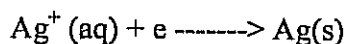
(i) Identify the strongest oxidizing agent amongst them; give the reason for your choice.

- (ii) Explain, giving reasons, whether the following two (2) cell reactions, as written, are feasible or not. If they are incorrect (not feasible), then write down the correct cell reactions and determine their  $E^\circ$  values.



(48 marks)

- (b) The following half cell equations represent the changes taking place at the cathode and anode, respectively.



In an experiment involving electrolysis to determine the concentration of  $Ag^+$  it was found that 1.00 g of Ag (Rel. atomic mass = 108) was deposited on the cathode. Assuming that all the silver ions have been oxidized and that a volume of 50.00 ml of this solution was used for electrolysis,

- (i) Calculate the quantity of electricity that was passed through this solution.
- (ii) Determine the initial concentration of  $Ag^+$
- (iii) Calculate the pH of the solution at the end of the experiment.

(30 marks)

- (c) Sketch and clearly label the diagram corresponding to a calomel electrode and write down its half-cell reaction

(22 marks)

6. (a) A cyanide ion-selective electrode obeys the equation  $E = C - \frac{RT}{F} \ln[CN^-]$  where C is a constant and E is the electrode potential. A  $1.5 \times 10^{-2} \text{ mol dm}^{-3}$   $CN^-$  solution gave a value of -0.300 V for the electrode potential measured under standard conditions ( $T = 25^\circ\text{C}$ ). Calculate the expected value of the potential, measured under the same conditions when the concentration of  $CN^-$  is  $1.5 \text{ mmol dm}^{-3}$

(18 marks)

(b) Concentration polarization is a type of polarization which is useful in electro analytical methods; it occurs when the *transfer* of reacting species from the bulk solution to the electrode surface becomes limiting.

- (i) **Name and outline** the three factors that contribute to the *transfer* mentioned above.
- (ii) **Name and define** the three other types of polarizations other than concentration polarization as a result of which an electrode of an electrolytic cell can become polarized.

(36 marks)

- (c) (i) Sketch a clearly labeled polarogram.
- (ii) What is the primary difference between a polarogram and a voltammogram?
- (iii) A student carried out a polarographic method of analysis to determine the concentration of a metal ion ( $A^{n+}$ ) in an unknown sample present in the form of a solution.  $25.00\text{ cm}^3$  of  $0.5\text{ M KCl}$  (as an inert supporting electrolyte) was added to  $10.00\text{ cm}^3$  of the sample and the total volume made up to  $50.0\text{ cm}^3$  with distilled water. The limiting current (after correcting for residual current) was found to be  $0.75\text{ A}$ . The analysis was then repeated using the same amount of sample and  $\text{KCl}$  and including  $5.00\text{ cm}^3$  of a  $10.0\text{ ppm}$  standard solution of  $A$  ion before diluting to a final volume of  $50.0\text{ cm}^3$ ; the limiting current now was found to be  $0.90\text{ A}$ .

- ( $\alpha$ ) What was the purpose for adding  $\text{KCl}$  solution?
- ( $\beta$ ) Determine the concentration of  $A$  in the original sample in  $\text{ppm}$ .  
[Write down any relevant mathematical expression/s in your calculation and identify the symbols used ]

(46 marks)