RAJARATA UNIVERSITY OF SRI LANKA

FCULTY OF APPLIED SCIENCES

B.Sc. Third year (General / Special) Semester II Examination – April / May 2016

CHE 3311 – Advanced Analytical Chemistry II

Answer any six questions.   Time: 3 hours

The use of non-programmable calculator is permitted.

1) (a) Derive an equation of distribution ratio, D for the solvent extraction of metal chelates, state any assumptions you have made when deriving the equation. Discuss the effect of the pH and of the reagent concentration on the solvent extraction of metal chelates.

(35 marks)

(b) The liquid–liquid extraction of the weak base B is governed by the following equilibrium reactions:

$$B(aq) \rightleftharpoons B(org) ; \quad K_D = 5.00$$
$$B(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HB^+(aq) ; \quad K_b = 1.0 \times 10^{-4}$$
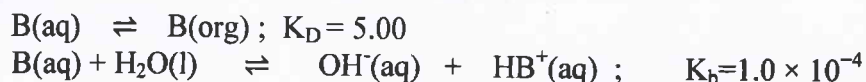
Derive an equation for the distribution ratio, D, and calculate the extraction efficiency if 25.0 mL of a 0.025 M solution of B, buffered to a pH of 9.00, is extracted with 50.0 mL of the organic solvent.

(30 marks)

(c) Calculate the extraction efficiency if we extract 100.0 mL of a 1.0×10^{-6} M aqueous solution of M^{2+}, buffered to a pH of 1.00, with 10.00 mL of an organic solvent that is 0.1 mM in the chelating agent. The partition coefficients for the ligand and for the metal–ligand complex are 1.0×10^4 and 7.0×10^4, respectively. The ligand's acid dissociation constant, is 5.0×10^{-5}, and the formation constant for the metal–ligand complex is 2.5×10^{16}. Repeat the calculation at a pH of 3.00.

(35 marks)

2). (a) (i) Discuss how the pH dependent of distribution ratio, D using log D versus pH graph for a weak acid.

(ii) An acidic solute, HA, has a K_a of 1.00×10^{-5} and a K_D between water and hexane of 3.00. Calculate the extraction efficiency values if 50.00 mL sample of a 0.025 M aqueous solution of HA, is extracted buffered to a pH of 3.00, with 50.00 mL of hexane. Calculate the extraction efficiency values when the extraction is repeated at pH levels of 5.00 and 7.00. Comment your results.

(40 marks)

(b) Discuss the advantages of solid phase extraction (SPE) method and give four types of common sorbents used in SPE.

(25 marks)

(c) Briefly describe the four step procedure used in SPE in order to prepare the sample.

(20 marks)

(d) Give the steps involved in the preparation of sample in solid phase micro extraction (SPME).

(15 marks)

3. (a) Define the following terms:
(i) resolution,
(ii) theoretical plate,
(iii) temperature programming.

(24 marks)

(b) Write down the van Deemter equation and describe the constants in it.

(20 marks)

(c) The following chromatogram was obtained for 500 ng of anthracene in 2.0 m packed column. What is HETP for the column? (w = 1.5 min.)

(17 marks)
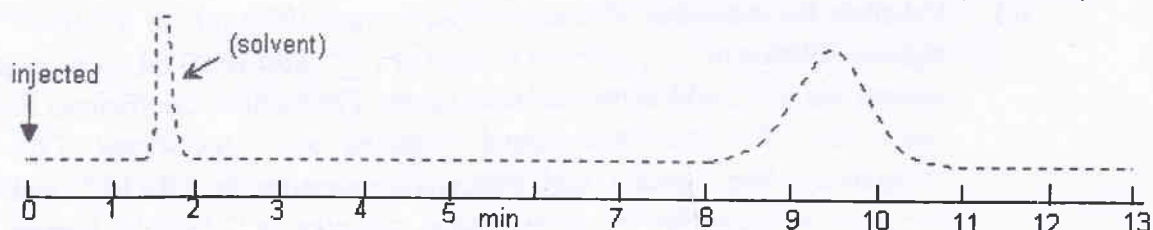
(d) Describe the chromatographic mechanism that allows analytes to separate in the following chromatography methods:
(i) thin layer chromatography,
(i) ion chromatography,
(ii) size exclusion chromatography.

(39 marks)

4). (a) Explain how the electron capture detector (ECD) works and give two advantages and two disadvantages of the electron capture detector (ECD).

(20 marks)

(b) Draw a schematic diagram which identifies the major components of a high performance liquid chromatography (HPLC). Briefly explain how each of the components works and contributes to the overall analytical system.

(30 marks)

(c) Use the following data given for liquid chromatography and answer the questions (i), (ii) and (iii) given below:
The length of column is 35.7 cm, the volumes of the mobile phase and stationary phase are 1.6 mL and 0.134 mL respectively. The column was run at a flow rate of 0.5 ml/min.

A mixture of 4 components (A, B, C and D) provided the following data:

	Retention time (min)	Width of Peak Base (min)
non-retained	2.1	-
A	5.4	0.51
B	10.3	1.03
C	12.1	1.25
D	20.6	1.62

(i) using peak C, calculate the number of plates (N) and the plate height (H) for the column,
(ii) for peak D, calculate the capacity factor (k') and the partition coefficient (K),
(iii) for peak B and C, calculate the resolution (R) and the relative retention (α).

(30 marks)

(d) List four advantages and disadvantages of HPLC.

(20 marks)

5.   (a)   Define the following terms:

                (i)   releasing agent,
                (ii)   pressure broadening,
                (iii)   sputtering,
                (iv)   chemical interference.

                                                                   (20 marks)

       (b)   Compare atomic absorption spectroscopy (AAS) and atomic emission spectroscopy (AES). What are the differences in instrument design and how are the observed signals generated? Describe at least one disadvantage for each technique.

                                                                   (30 marks)

       (c)   A GC analysis of trichloroethylene was conducted with a chlorobenzene internal standard. The 10.5 ppm trichloroethylene solution with 6.80 ppm chlorobenzene gave signals of 1266 and 909 respectively. An unknown solution of trichloroethylene and 7.20 ppm chlorobenzene gave signals of 844 and 954 respectively. What is the concentration of trichloroethylene in that sample?

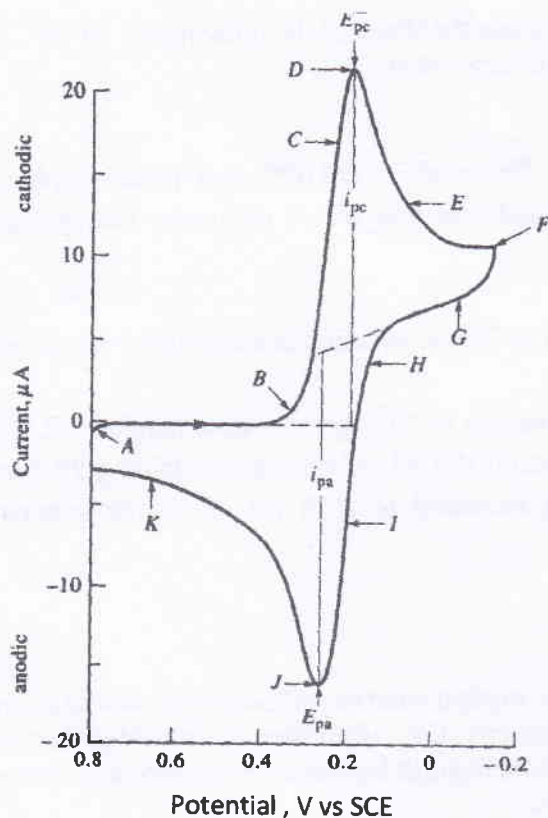   20 marks)

       (d)   Label the transitions of A, B, C, D and E in the following Jablonski Diagram:
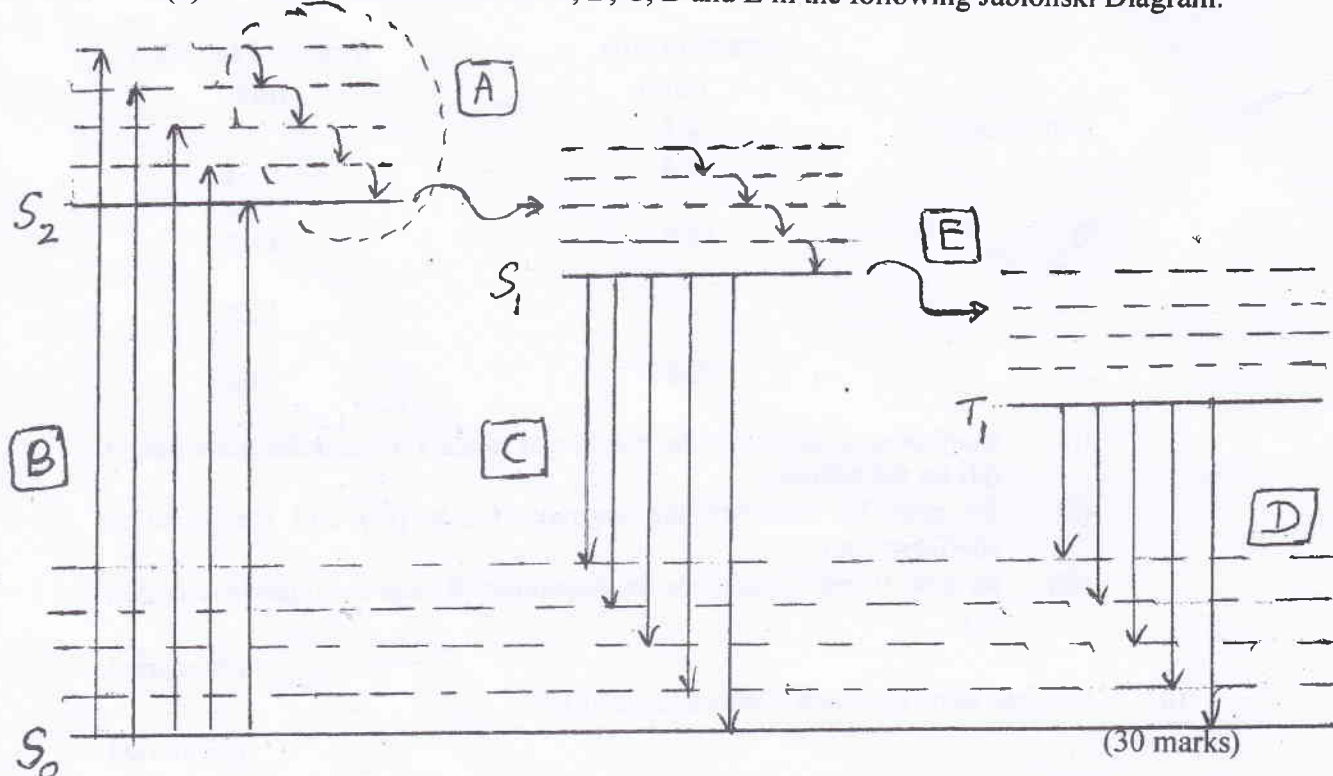
                                                                   (30 marks)

6). (a) Draw and explain the shape of the polarogram of Cd^{2+} / Cd obtained in polorographic experiment.

(30 marks)

(b) Discuss the effect of dissolved oxygen in polarographic experiment using a polarogram and how you would overcome the problem caused by dissolved oxygen.

(25 marks)

(c) Write down the Ilkovic equation and define the terms with units.

(15 marks)

(d) A 25.0 mL sample of Ni^{2+} gave a wave height of 2.36 µA in a polarographic analysis. When 0.500 mL of solution containing 28.7 mM Ni^{2+} was added, the wave height increased to 3.79 µA. Find the concentration of Ni^{2+} in the unknown.

(30 marks)

7). (a) (i) Breifly explain what experiments you would do in cyclic voltammetry, CV what data you would collect, and how to analyze the data to distinguish between a reversible and irreversible electrochemical reaction.

(ii) Describe the features of the CV that you would measure and how would you decide if the reaction is reversible or irreversible?

(30 marks)

(b) The cyclic voltammogram for a solution of 6.0 mM, $K_4[Fe(CN)_6]$ in 1.0 M, KNO_3 is given below. Describe the shape at points A, B, D, H and J. Give the balance reactions taking place at the regions of BCD and HJI.

(20 marks)

Potential , V vs SCE

(c)   Write down the Randles-Sevcik equation for a reversible systems in cyclic voltammetry, and explain the terms. Briefly explain how you would check the reversibility using scan rate.

(20 marks)

(d)   Briefly explain the use of steady state amperometry in chemical analysis.

(20 marks)

(e)   Why is stripping voltammetry is the most sensitive of the polarographic techniques?

(10 marks)