UNIVERSITY OF RUHUNA

BACHELOR OF SCIENCE SPECIAL DEGREE LEVEL I (SEMESTER II) EXAMINATIONS –2021

SUBJECT : CHEMISTRY

COURSE UNIT : CHE 4233 TIME : **Three (03)** hours

Answer **all** questions.

Velocity of light, (c)	$= 2.997 \times 10^{8}$ m s $^{-1}$
Avogadro's number, (N_A)	$= 6.022 \times 10^{23}$ mol $^{-1}$
Universal Gas Constant, (R)	$= 8.314$ x J K^{-1} mol $^{-1}$
Boltzmann constant, (k_B)	$= 1.381 \times 10^{-23}$ J K $^{-1}$
Faraday constant, (F)	$= 9.6485 \times 10^{4}$ C mol $^{-1}$
Plank's constant, (h)	$= 6.626 \times 10^{-34}$ J s
Electron Charge , (e)	$= 1.602 \times 10^{-19}$ C
Proton mass, (m_p)	$= 1.673 \times 10^{-27}$ kg
Electron mass, (m_e)	$= 9.10 \times 10^{-31}$ kg
1 amu	$= 1.661 \times 10^{-27}$ kg
1 eV	$= 1.602 \times 10^{-19}$ J

---

1. Answer **all** parts.

(a) Optical spectroscopic methods are based upon six phenomena including absorption, fluorescence, phosphorescence, scattering, emission, and chemiluminescence.

(i) Using a labelled block diagram of fluorescence spectrophotometer, illustrate the arrangement of **five (05)** major components.

(ii) Discuss the features of photovoltaic cells, phototubes, and photomultiplier tubes which are used as photon transducers in spectroscopic analysis. (Draw the basic structure of each transducer)

(iii) Using a suitable diagram, illustrate how light passes through the following monochromators

(I) Czerney-Turner grating monochromator
(II) Bunsen Prism monochromator

(40 marks)

(b) In mass spectrometry, ions are separated on the basis of their mass to charge ratio.

(i) Draw a labeled block diagram of a mass spectrometer illustrating the five major components.

(ii) List down 4 types of mass analyzers used in mass spectrometers.

(iii) Explain how sample molecules can be ionized by electron impact and chemical ionization methods.

(35 marks)

(c) Briefly discuss the following terms.
(i) Refractive index
(ii) Johnson noise
(iii) Flicker noise
(iv) Boxcar averaging
(v) Calibration sensitivity

(25 marks)

2. Answer **all** parts

(a) The following cell can be used for the determination of $pCrO_4$:

$$SCE||CrO_4^{2-}(xM),\ Ag_2CrO_4\ (sat'd)|Ag$$

(i) Give the half-cell representation and the electrode reaction of SCE.
(ii) Give the electrode reaction of the indicator electrode.
(iii) Calculate $pCrO_4$ if the cell potential is 0.313 V.

$E^{\circ}\ (Ag_2CrO_4/Ag) = 0.447$ V

$E\ (SCE) = 0.244$ V

(30 marks)

(b) A 0.400 g sample of toothpaste was boiled with a 50 mL solution containing a citrate buffer and NaCl to extract the fluoride ions. After cooling, the solution was diluted to 100.00 mL. The potential of an ion selective electrode (ISE) with the Ag/AgCl(sat'd) reference electrode in a 25.0 mL aliquot of the sample was found to be -0.1823 V. Addition of 0.05 mL of a solution containing 0.0107 mg / mL of F^- caused the potential to change to -0.2446 V. Calculate the mass percentage of F^- in the sample.

Hint: neglect the volume change after adding the standard F^- solution.

$E^{\circ}\ (AgCl/Ag) = 0.222$ V
Relative molar mass of F = 19.00

(40 marks)

(c) The water content of a coconut oil sample was determined using the coulometric Karl-Fisher titration. A 10.00 g sample was placed in the coulometric cell along with the anolyte solution consisting of sulphur dioxide, imidazole and KI. Anhydrous methanol was used as the solvent. Electrolysis was carried out at a constant current of 100.0 mA and it took 10 s to reach the end point.

(i) Write the relevant electrode and chemical reactions.
(ii) Calculate the water content in the sample as a percentage (w/w%).

Relative molar mass of H_2O = 18.00

(30 marks)

3. Answer **all** parts

(a) A solution containing 0.1M Cu^{2+} and 0.1 M Sn^{2+} is electrolyzed on a Pt cathode at 25°C.

(i) Calculate the potential values at which Cu^{2+} starts and quantitatively completes deposition.
(ii) Would Sn^{2+} be reduced before the copper is quantitatively deposited?

E° (Cu^{2+}/Cu) = 0.339 V
E° (Sn^{2+}/Sn) = - 0.141 V

(20 marks)

(b) The differential pulse polarographic analysis of a mixture of indium and cadmium in 0.1 M HCl is complicated by the overlap of their respective voltammograms. The peak potential for indium is at –0.557 V and that for cadmium is at –0.597 V. When a 0.600-ppm indium standard is analyzed, ΔIp (in arbitrary units) is 190.5 at –0.557 V and 85 0 at –0.597 V relative to the saturated Ag/AgCl reference electrode. A standard solution of 0.750 ppm cadmium has a ΔI_p of 91.8 at –0.557 V and 130.5 at –0.597 V. What is the concentration of indium and cadmium in a sample if ΔI_p is 180.5 at a potential of –0.557 V and 100.0 at a potential of –0.597V.

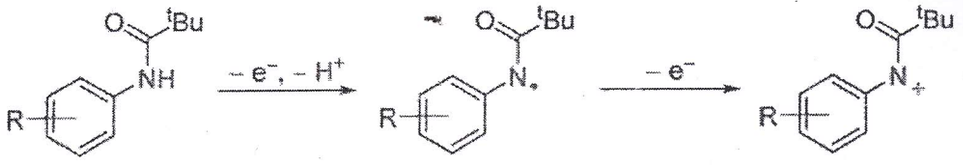
(20 marks)

(c) Giving reasons sketch the expected voltammograms for the experiments described below.

(i) $Fe(CN)_6^{3-}$ /$Fe(CN)_6^{4-}$ system reported anodic and cathodic peak current values as 20.0 mA at a scan rate of 100 V s^{-1}. Then the scan rate was changed to 225 V s^{-1}

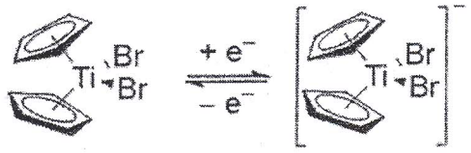
$$Fe(CN)_6^{3-} + e \rightleftharpoons Fe(CN)_6^{4-}$$

(ii) Oxidation and deprotonation of anilide to the amidyl radical and then further oxidation to the corresponding cation.

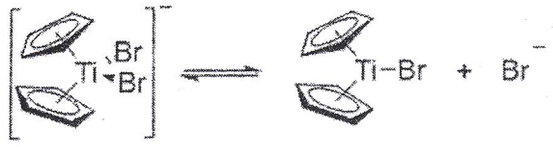


(iii) Studying the system below at different scan rates.

Cp_2TiBr_2 oxidized to $[Cp_2TiBr_2]^-$



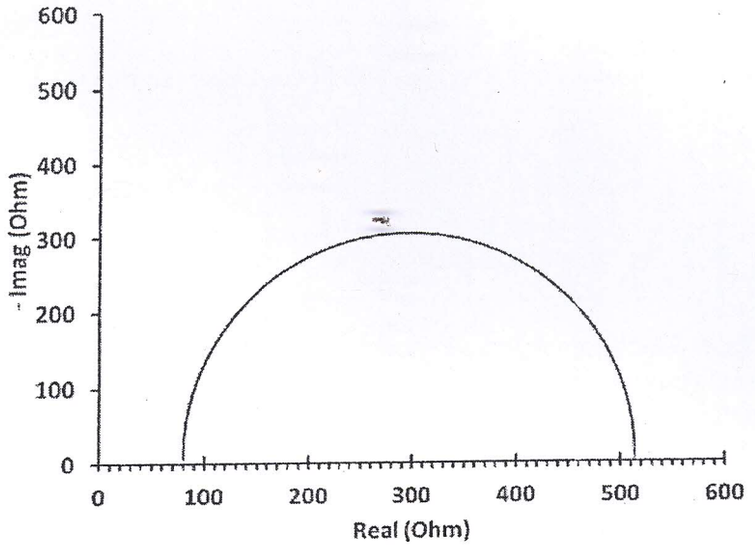
$[Cp_2TiBr_2]^-$ decomposes to Cp_2TiBr and Br^-



(iv) If thiourea is added to the reaction mixture in (iii), it reacts with Br^- forming a stable adduct.

(40 marks)

(d) Given below is the Nyquist Plot for a uniform corrosion process of 1 cm^2 electrode undergoing at a rate of 1 mm/year.



(i) Construct the equivalent circuit for the above corrosion process. Name the circuit elements clearly.
(ii) Find the polarization resistance and solution resistance in the above system.
(iii) How would the above Nyquist plot be changed for a diffusion controlled process?
(iv) Construct the equivalent circuit for the system in iii.

(20 marks)

4. Answer **all** parts

(a) Explain the separation principle behind Thin Layer Chromatography (TLC).

(15 marks)

(b) Explain how each of the following common problems affect TLC and how to avoid the problems.

(i) Large spots
(ii) Streaking
(iii) Uneven advance of the solvent front

(20 marks)

(c) Acid catalyzed esterification of benzoic acid and phenol is given below

X Y Z

(i) Giving reasons sketch the expected pattern of spots of **X**, **Y** and **Z** on TLC when the mobile phase is ethyl acetate: hexanes (1:3) and the stationary phase is silica gel.

(ii) Using suitable sketches show how you would use TLC to monitor the progress of this reaction.

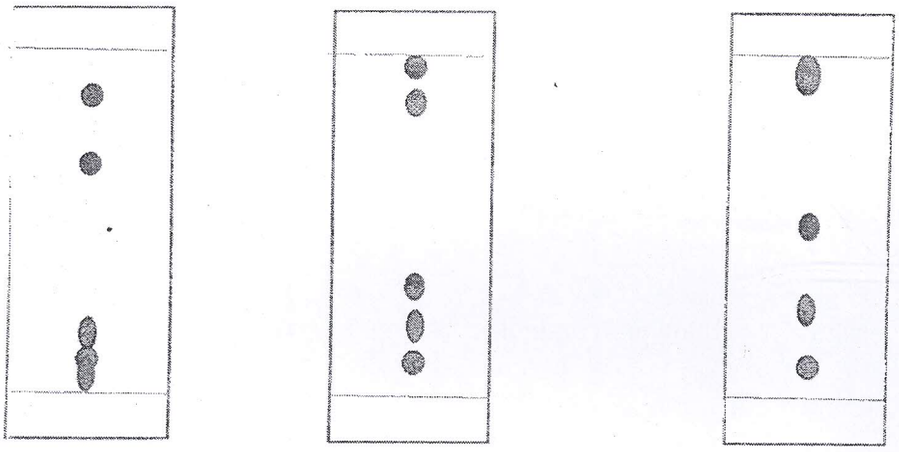
(iii) Propose a suitable detection technique for these TLC analyses and explain the principle behind the visualization.

(30 marks)

(d)

(i) Briefly explain the function of the components of a column chromatography setup.

(ii) As the initial step of a separation of a product mixture, the following TLC result was obtained under the mentioned solvent systems.



2% dichloromethane In hexanes

10 % dichloromethane In hexanes

25% dichloromethane In hexanes

(I) Comment on each TLC observation.

(II) Propose how you would carry out column chromatography to separate the product mixture using dichloromethane/hexane as the mobile phase.

(35 marks)

5. Answer **all** parts

(a) A chromatogram of a mixture of species A,B and C provided following data from a liquid chromatography experiment. The length of the Column packing is 24.7 cm.

	Retention Time/ min	**Width of Peak Base (W)/ min**
Non retained	3.1	-
A	5.4	0.41
B	13.3	1.07
C	14.1	1.16
D	21.6	1.72

(i) What is theoretical plate?

(ii) Calculate the number of theoretical plates for each peak.

(iii) Calculate the average number of theoretical plates and the plate height for the column.

(iv) Calculate the resolution for the peaks of species B and C.

Note : $N = 16\ (t_R/W_B)^2$ $\quad R_s = 2(t_{R(2)}-t_{R(1)})/\ (W_1 + W_2)$ where N is the number of theoretical plates, t_R is retention time , W_B is width of the peak base and R_s is the resolution.

(30 marks)

(b) Briefly explain how to perform the following using gas chromatography

(i) Qualitative Measurements

(ii) Quantitative Measurements

(15 marks)

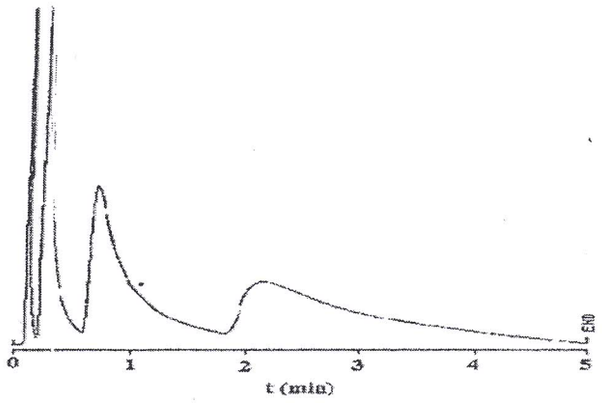
(c) The following data were obtained from a gas chromatogram of a mixture of butyl alcohols.

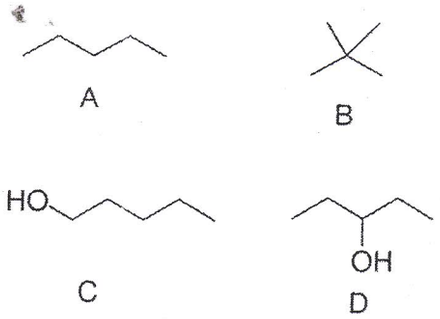
Alcohol	Area of the peak/cm^2
n-butyl	4.54
i- Butyl	14.36
s- butyl	4.78
t- butyl	2.44

Calculate the percentage of each alcohol in the mixture.

(15 marks)

(d) Gas chromatogram of the mixture of A,B, C and D on a CHT ceramic hydroxyapatite column with oven temperature 343 K and nitrogen flow rate 24 cm^3 /min is given below.





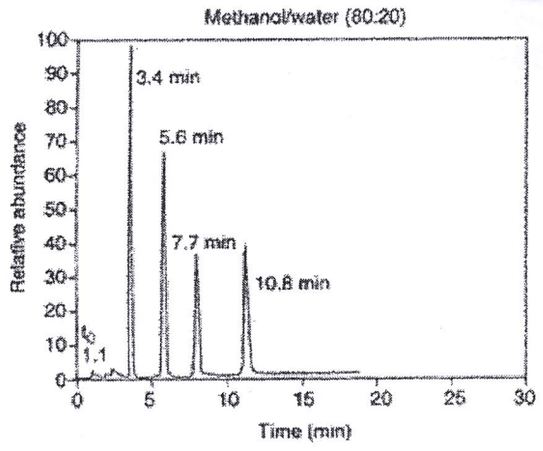
(i) Comment on the resolution of the peaks.
(ii) Giving reasons assign the peaks of the chromatogram to the compounds A,B,C and D.
(iii) Giving reasons explain how you would improve the resolution of peaks without affecting the analysis time considerably

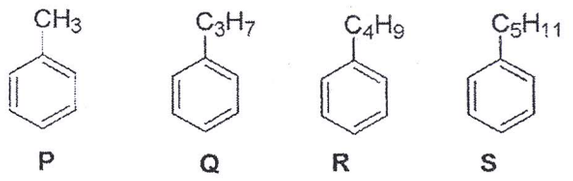
(20 marks)

(e)

(i) Briefly explain the reverse phase separation principle.

(ii) The chromatogram obtained for a series of compounds on a reversed phase high-performance liquid chromatography (HPLC) column (octadecylsilyl (ODS) 4.6 x 150 mm flow rate 1 ml/min) in methanol/water (80:20 v/v) is given below.





Giving reasons assign each of the obtained peaks for the compounds P, Q, R and S.

(20 marks)

@@@@@@@@@@@@@@@@@@@@@@@@@@@