UNIVERSITY OF RUHUNA

BACHELOR OF SCIENCE GENERAL DEGREE LEVEL III (SEMESTER I) EXAMINATION - JULY 2016

SUBJECT: CHEMISTRY

COURSE UNIT: CHE 3114 — TIME: **Three (03)** hours

Answer **six (06)** questions only by selecting **two (02)** from Section **A**, **one (01)** from Section **B** and **three (03)** from Section **C**.

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

Useful Conversion Factors

1 atm = 760 mmHg = 1.01325 bar = 101325 Pa

2.303 (RT/F) = 59.15 mV at 298.15 K

1 eV = 1.6022×10^{-19} J

Section - A

01. Answer **all** parts.

(a) Substitution of CO by PR_3 in $Cr(CO)_6$ is known to proceed *via* a dissociative mechanism as shown below.

$$Cr(CO)_6 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cr(CO)_5 + CO$$

$$Cr(CO)_5 + PR_3 \xrightarrow{k_2} Cr(CO)_5PR_3$$

(i) List four (04) evidences in support of a dissociative mechanism.

(10 marks)

(ii) Using the steady-state approximation for the intermediate present, derive the rate law for the above dissociative reaction.

(30 marks)

(b) Consider the following three reactions.

(I) $[Pt(NH_3)Br_3]^- + NH_3 \longrightarrow$

(II) $[Pt(PR_3)Cl_3]^- + NH_3 \longrightarrow$

(III) $[Pt(CN)Cl_3]^{2-} + NH_3 \longrightarrow$

(i) Predict the products of each reaction. Clearly indicate whether the formed products are *cis* or *trans*.

(15 marks)

(ii) Using energy coordination diagrams, briefly explain the relative ease of formation of products in (b) (II) and (b) (III) compared to $[PtCl_4]^{2-}$.

(25 arks)

(c) Two hypothetical reactions are given below (en = ethylenediamine).

$$[Fe(en)_3]^{2+} + 2H_2O \longrightarrow [Fe(en)_2(H_2O)_2]^{2+} + en$$

$$[Fe(NH_3)_6]^{2+} + 2H_2O \longrightarrow [Fe(NH_3)_4(H_2O)_2]^{2+} + 2\ NH_3$$

Giving reasons, predict which reaction has the higher reaction rate.

(20 marks)

02 Answer **all** parts.

(a) A student was assigned to analyse UV-visible spectra of some titanium complexes. As the first step, he classified them into two groups, based on the molar absorption coefficients of the spectral bands as shown in the following table.

ε : Molar absorption coefficient

Group 1		**Group 2**	
ε ($L\ mol^{-1}cm^{-1}$) < 100		**ε ($L\ mol^{-1}cm^{-1}$) > 10^4**	
Complex	**$\bar{\upsilon}$ / cm^{-1}**	**Complex**	**$\bar{\upsilon}$ / cm^{-1}**
$[TiCl_6]^{3-}$	13,000	TiI_4	19,600
$[Ti(H_2O)_6]^{3+}$	20,300	$TiBr_4$	29,500
$[Ti(CN)_6]^{3-}$	22,300	$TiCl_4$	35,000

(i) What important features should be considered in the interpretation of electronic spectra?

(10 marks)

(ii) Giving reasons identify the types of spectra in the above two groups.

(10 marks)

(iii) Briefly explain the basis of the increase in energy ($\bar{\upsilon}$) of the spectral bands in each group.

(10 marks)

(iv) Complexes in group 1 show only a single peak in their UV-visible spectra. Use the appropriate correlation diagram to explain this observation.

(10 marks)

(v) Determine the crystal field splitting energy of $[TiCl_6]^{3-}$? (10 marks)

(b)

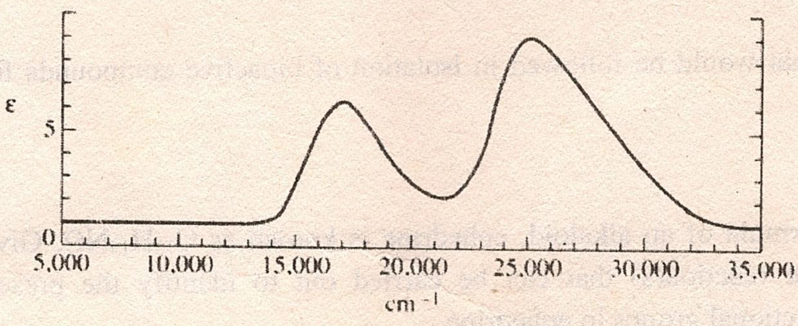
(i) Derive the ground state and the first excited state term symbols for the $[V(H_2O)_6]^{3+}$ complex.

(15 marks)

(ii) Sketch the appropriate Orgel diagram for the above complex and indicate the possible electronic transitions.

(20 marks)

(iii) The observed UV-visible spectrum of $[V(H_2O)_6]^{3+}$ is given below. Explain the peak pattern of this spectrum using the Orgel diagram in part (ii).



(15 marks)

03. Answer **all** parts.

(a) Metals extracted by pyrometallurgy normally contain impurities. Several techniques are used to obtain pure metals based on the properties of the metal and the impurities.

(i) Name five techniques used to obtain pure metals from pyrometallurgically extracted metals.

(20 marks)

(ii) Briefly explain three (03) of these techniques.

(30 marks)

(b) Crystal structures contain different types of defects.

(i) Write a short account on nonstoichiometric compounds.

(20 marks)

(ii) "Ionic compounds such as KCl can be colourerd." Explain using a suitable illustration.

(20 marks)

(iii) Alkali metal halides show different colours. Explain the reasons for this difference.

(10 marks)

Section - B

04. Answer all parts.

(a)

(i) What is meant by "Extraction" of natural products?

(ii) What are the necessities of extraction of Natural Products from their sources?

(iii) List four (04) extraction methods used to extract natural products.

(iv) Explain briefly "Isocratic extraction" and "gradient extraction" used in Natural Product extraction.

(24 marks)

(b) Give the steps that would be followed in isolation of bioactive compounds from a plant source.

(20 marks)

(c)

(i) Molecular formula of an alkaloid, ephedrine is known as $C_{10}H_{15}NO$. Give chemical tests with the reaction(s) that can be carried out to identify the presence of the following functional groups in ephedrine.

(I) Secondary amine group

(II) Hydroxyl group

(III) Benzene ring with side chain

(18 marks)

(ii) Based on the chemical analysis, two structural formulae (I and II) for ephedrine can be proposed.

$C_6H_5CHOHCH_2CH_2NHCH_3$

I

$C_6H_5CHOHCHCH_3$ (with NH CH_3 attached to the second CH)

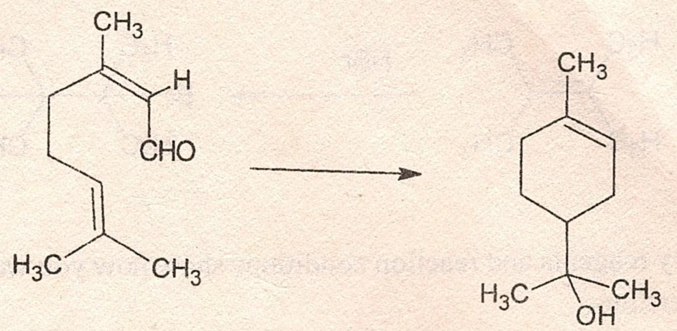
II

But, it has been found that the actual structure of ephedrine is structure –II

Apply Hoffamann exhaustive methylation process to confirm the structure –II as the structure of ephedrine.

(18 marks)

(d) Indicating necessary reagents, reaction conditions and intermediate(s) formed, give the mechanism for the following transformation of terpenoid.



(20 marks)

05. Answer **all** parts

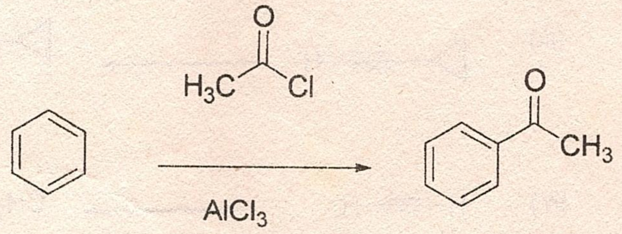
(a)

(i) Briefly discuss the structure, stability and reactivity of carbanions.

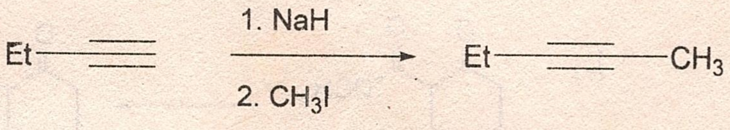
(10 marks)

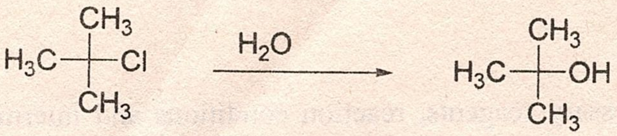
(ii) Give the structure of the reactive intermediate involved in the following conversions.

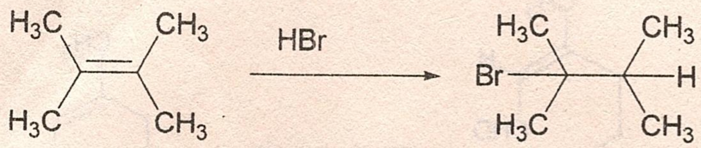
(I)



(II)

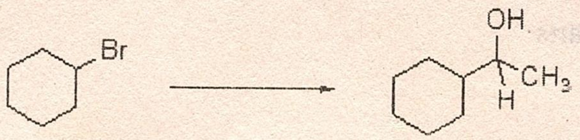


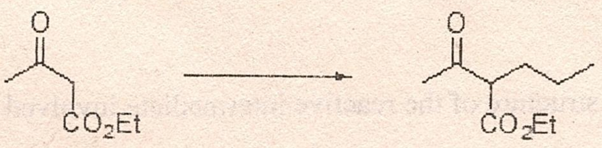
(III) 

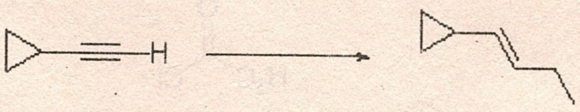
(IV) 

(20 marks)

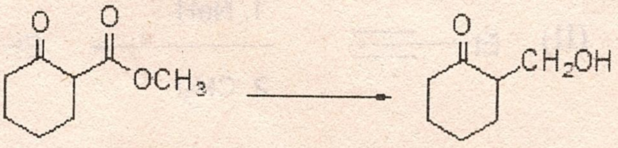
(b) Giving necessary reagents and reaction conditions show how you would carry out following conversions.

(i) 

(ii) 

(iii) 

(iv) $H-C\equiv C-H \longrightarrow CH_3(CH_2)_5OH$

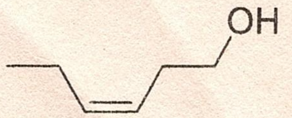
(v) 

(35 marks)

(c)

(i) What is retrosynthetic analysis?

(ii) Assuming acetylene is commercially available give a retrosynthetic analysis for the following component present in violet oil.



(iii) Based on the proposed retrosynthetic analysis in (ii) give synthetic pathway for the target molecule above.

(35 marks)

Section - C

06. Answer **all** parts

(a) Briefly explain what do you understand by the following terms:

(i) Adsorption.
(ii) Adsorbate.
(iii) Adsorbent.
(iv) Adsorption isotherm.

(20 marks)

(b) Discuss the differences between "Chemisorption" and "Physisorption".

(20 marks)

(c)

(i) What are the major assumptions of the Langmuir isotherm?

(ii) Considering a metal – gas interface and assuming that the free gas is in dynamic equilibrium with the adsorbed gas, derive the Langmuir isotherm:

$$\theta = \frac{Kp}{1+Kp}$$

Identify all the terms in this equation.

(iii) Adsorption of N_2 gas on activated charcoal was studied at 273 K. The readings obtained were found to obey the Langmuir isotherm. Calculate the constant K and the volume corresponding to complete coverage using the two experimental observations given below: (V has been appropriately corrected)

p/kPa	26.7	66.7
V/cm^3	18.6	36.9

(60 marks)

07. Answer **all** parts.

(a) The cell SCE $\|$ H^+ (a = x) $|$ glass electrode, is constructed to determine pH of solutions, has a cell potential of 0.2195 V when immersed in the standard pH 4.000 buffer solution at 25 ^0C.

(i) Write cathodic and anodic half reactions of the above cell.

(10 marks)

(ii) Derive an expression to determine the pH of an unknown solution when a standard buffer solution is provided. The cell potential, when the standard buffer solution is used is E_S.

(20 marks)

(iii) Calculate the pH of a solution, if the cell potential is measured to be 0.1307 V at 25 ^0C.

(10 marks)

(iv) Calculate the liquid junction potential of the cell, if the standard electrode potential of the calomel electrode is 0.244 V at 25 ^0C.

(10 marks)

(b) A mixture containing 0.0600 mol dm^{-3} of BiO^+ and 0.0500 mol dm^{-3} of Co^{2+} is to be separated by electrogravimetric method. The pH of the solution was measured as 3.00. What is the concentration of more readily reduced cation, when the other cation initiates its deposition?

$$BiO^+_{(aq)} + 2H^+_{(aq)} + 3e^- \rightleftharpoons Bi_{(s)} + H_2O \qquad E^0 = +0.320\ V$$

$$Co^{2+}_{(aq)} + 2e^- \rightleftharpoons Co_{(s)} \qquad E^0 = -0.277\ V$$

(50 marks)

08. Answer **both** parts

(a)

(i) Name two different types of coulometric methods and discuss their ease of reaching 100% current efficiency.

(20 marks)

(ii) A solution containing 0.25 g of Cu^{2+} requires 20 minutes for complete deposition of copper at 1.25 A.

(I) Calculate the efficiency of the process.

(Relative atomic mass of Cu: 63.54)

(10 marks)

(II) Comment on the efficiency you obtained and suggest a suitable method to improve it.

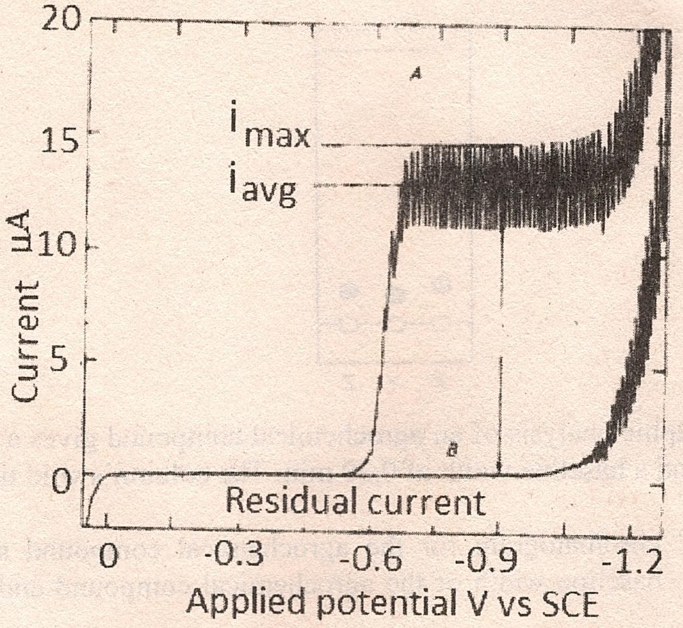
(10 marks)

(iii) A 0.180 g of a purified organic acid sample was titrated coulometrically with hydroxide ions produced in 5 mins by a constant current of 0.514 A. Calculate the molar mass of the acid if the number of electrons exchanged per molecule of organic acid is one.

(20 marks)

(b) Use the graph below to answer the following question.

(i) Explain the shape of the graph.



(20 marks)

(ii) Draw the expected polarograms for oxidation of 1.2 mM Fe^{2+} and 2.4 mM Fe^{2+}. $E^0_{Fe^{3+}/Fe^{2+}} = 0.77\ V$

(20 marks)

09. Answer either Part **X** or Part **Y**.

09. **(X)** Answer **all** parts.

(a) (i) What are the differences between normal and reverse phase liquid chromatography.

(10 marks)

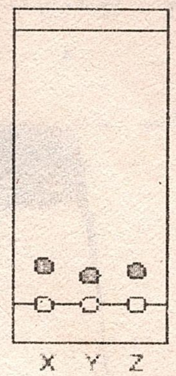
(ii) With reasoning write down the eluting order of benzene, benzoic acid and benzyl alcohol from highest R_f to the lowest R_f in normal phase TLC.

(10 marks)

(iii) List the three basic development methods used in TLC and briefly explain each method with suitable diagrams.

(20 marks)

(iv) The silica gel TLC plate given below shows the relative positions of the compounds X, Y and Z, when developed using hexane/ethyl acetate 9:1. If a mixture containing X, Y and Z is provided, describe how you would improve the separation.



(10 marks)

(b) A GC chromatographic analysis of an agrochemical compound gives a peak with a retention time of 8.68 min and a baseline width of 0.29 min. The column's void time is 0.31 min.

(i) Draw the GC chromatogram for the agrochemical compound and clearly mark the retention time, baseline width of the agrochemical compound and the void time of the column.

(15 marks)

(ii) What does it mean by the retention factor and calculate the retention factor for this GC analysis.

(10 marks)

(iii)Calculate the number of theoretical plates in the GC column used in the analysis.

(15 marks)

(iv)Given that the column is 2.0 m long, what is the height of a theoretical plate in mm?

(10 marks)

9. (Y) Answer <u>**all**</u> parts.

(a) Identify the basic principles to be fulfilled in order to use solvent extraction as a separation technique of components.

(10 marks)

(b) Explain the following terms pertaining to solvent extraction.

(i) Separation and partial separation
(ii) Partition coefficient
(iii) Extraction efficiency
(iv) Limitations in liquid-liquid extractions

(20 marks)

(c) Derive an equation for the distribution ratio to show that when a weak acid is allowed to distribute between two immiscible phases say organic and aqueous, it is possible to control the distribution of weak acid by changing the pH of the aqueous phase. The dissociation constant of the weak acid is 1.00×10^{-5} and the partition coefficient of the weak acid between organic phase and water is 3.

Note that the weak acid dissociates in the aqueous phase, but neither dissociate nor associate in the organic phase.

(i) 50.00 mL of a weak acid having a concentration of 0.25 M is buffered to pH = 3.00 in an aqueous solution. Calculate the distribution ratio when this is extracted with 50.00 mL of an organic phase.

(ii) Later the weak acid solution was buffered to pH = 5.00 and to pH = 7.00 respectively and extracted with 50.00 mL of an organic phase. Compare the distribution ratios.

(iii) What conclusions you can be made based on the obtained results.

(40 marks)

(d) Organic chelating agents are used in metal ion extractions in most cases. Explain why this can be done.

(15 marks)

(e) Explain the principle behind "the solid phase extraction method".

(15 Marks)

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