UNIVERSITY OF RUHUNA

BACHELOR OF SCIENCE GENERAL DEGREE LEVEL III (SEMESTER I)

EXAMINATIONS -JUNE -2015

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**.

Physical Constants

Velocity of light (c)	=	3×10^8 m s^{-1}
Avogadro's number (N_A)	=	6.022×10^{23} mol^{-1}
Universal gas constant (R)	=	8.314 J K^{-1} mol^{-1}
	=	0.0821 dm^3 atm K^{-1} mol^{-1}
Boltzmann constant (k)	=	1.381×10^{-23} J K^{-1}
Faraday constant (F)	=	9.6485×10^4 C mol^{-1}
Electron charge (e)	=	1.602×10^{-19} C
Planck constant (h)	=	6.626×10^{-34} J s
Proton mass (m_p)	=	1.673×10^{-27} kg
Electron mass (m_e)	=	9.10×10^{-31} kg
1 amu	=	1.661×10^{-27} kg
1 eV	=	1.602×10^{-19} J

Section A

01. Answer **all** parts.

(a) (i) The half-lives of some transition metal complexes are given in the following table. Interpret the differences in half-lives given in the table in terms of the electron distribution of the complexes.

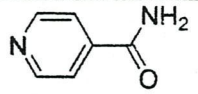
Half-lives less than 1 min.	Half-lives greater than 1 day
$[Cr(H_2O)_6]^{2+}$	$[Cr(CN)_6]^{3-}$
$[Co(H_2O)_6]^{2+}$	$[Co(NH_3)_6]^{3+}$

(25 marks)

(ii) Predict the product(s) expected when 1 mol of $[PtCl_4]^{2-}$ is reacted successively with 2 mol of NH_3 and 2 mol of pyridine (py).

(20 marks)

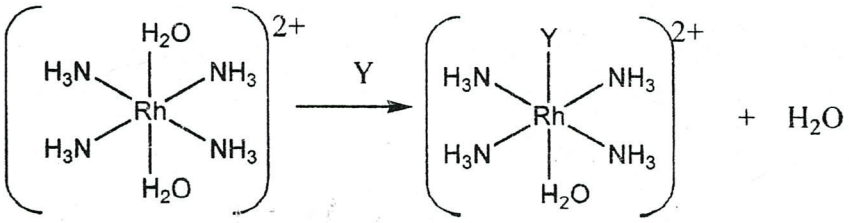
(b) The table below presents rate constants (k_1) and entropy change of activation ($\Delta S^{\ddagger}$) for the reactions of two Ru complexes with different entering ligands.

	$[Ru(EDTA)(H_2O)]^-$		$[Ru(EDTA)(H_2O)]^{2-}$
Entering ligand	$k_1(M^{-1}s^{-1})$	$\Delta S^{\ddagger}$	$k_1(M^{-1}s^{-1})$
	8300 ± 600	-19 ± 3	30 ± 15
SCN^-	270 ± 20	-18 ± 3	12 ± 2
CH_3CN	30 ± 7	-24 ± 4	13 ± 1

Giving reasons suggest the type of mechanism(s) for each of the above reactions.

(30 marks)

(c) A dissociative activated substitution reaction of a Rh(II) complex is given below.



Giving reasons predict the effect(s) of the following conditions on the rate of the above reaction.

(i) Increasing the positive charge on the complex (10 marks)

(ii) Changing the entering group Y from Cl^- to I^- (10 marks)

(iii) Increasing steric crowding of the complex (05 marks)

02. Answer **all** parts.

(a)

(i) Define the term 'microstates'.

(10 marks)

(ii) Derive separately the number of microstates for the p^2 and d^3 electronic configurations.

(10 marks)

(iii) Write <u>five</u> microstates for the p^2 electronic configuration.

(10 marks)

(b) A two-electron system has three types of electronic interactions known as Russell Saunders coupling.

(i) Name and briefly describe the above three types of interactions.

(10 marks)

(ii) Derive the possible terms for the p^2 electronic configuration using the Russell Saunders coupling scheme.

(15 marks)

(iii) Giving reasons identify the ground state term.

(05 marks)

(c) The intensities of the absorption bands of transition metal complexes are governed by two selection rules.

(i) State the two selection rules.

(10 marks)

(ii) Explain the following regarding the colours of the complexes.

(I) $[Co(H_2O)_6]^{2+}$ is pale-red while $[CoCl_4]^{2-}$ is intense blue.

(15 marks)

(II) $[FeF_6]^{3-}$ is colourless whereas $[CoF_6]^{3-}$ is coloured.

(15 marks)

03. Answer **all** parts.

(a) Calcination and roasting are the two main pyrometallurgical processes used to extract metals from their minerals and ores.

(i) How does the term "ore" differ from the term "mineral"? Give an example.

(10 marks)

(ii) In pyrometallurgy; what does the term 'roasting' stand for?

(10 marks)

(iii) How does roasting differ from calcination? Give 2 examples for each process with relevant chemical equations.

(20 marks)

(b) Briefly explain how you would prepare a sample of pure titanium metal starting from ilmenite. Give the relevant chemical equations.

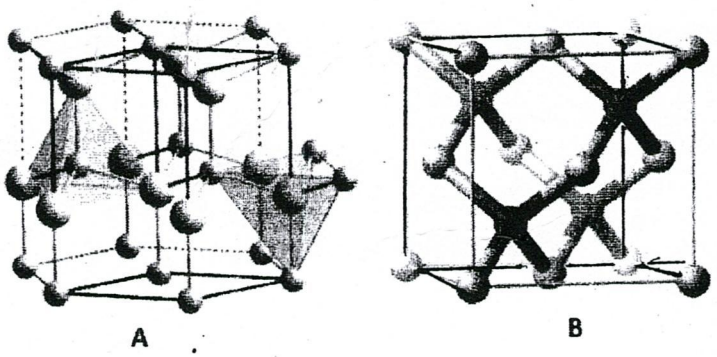
(10 marks)

(c) Solids can be classified into two main categories, amorphous and crystalline.

(i) Write the properties of amorphous and crystalline solids.

(20 marks)

(ii) You have been given the following structures of ZnS. Identify the structures and give a comparative description of both structures.



A B

(30 marks)

Section B

04. Answer **all** parts

(a)

(i) Name four (04) categories of secondary metabolites which are considered as natural products.

(ii) Out of the above four categories indicate the important structural features of the two categories of the compounds.

(14 marks)

(b)

(i) What it meant by "Ethnopharmacology"?

(ii) List five (05) important facts to be considered in collection of plant material for the natural product extraction purpose.

(iii) Briefly explain the steps followed in "maceration" in natural products extraction.

(iv) Name most suitable solvent to be used in extraction of all the compounds from a medicinal plant. (20 marks)

(c)

(i) What are the typical alkaloids and atypical alkaloids? Give an example for each category.

(ii) Briefly explain a procedure that would be followed in extraction of alkaloids from a plant.

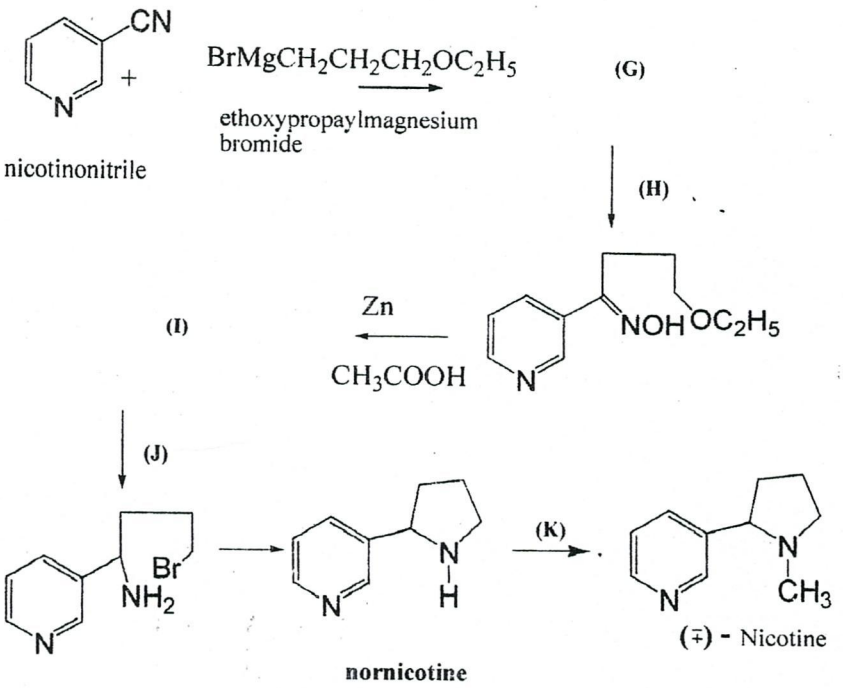
(iii) Give three chemical tests to identify alkaloids from the crude plant extract.

(15 marks)

(d)

(i) Name a plant which contains nicotine.

(ii) A chemical synthesis of nicotine is given below. Fill the gap of the synthesis scheme (G, H, I, J and K) giving missing reagents and intermediates formed.



(25 marks)

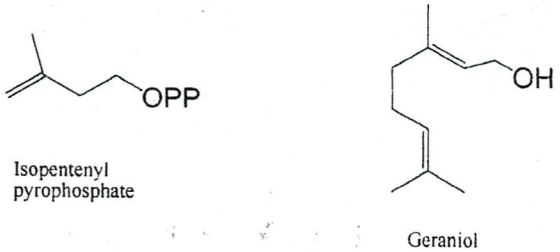
(e)

(i) Categorize the terpenoids according to the number of isoprene units present.

(ii) What are the classes of terpenoids above in (i) present in volatile oil.

(iii) Write down important factors that should be concerned in extraction of volatile oil from volatile oil bearing plants.

(iv) Giving plausible mechanism show how geraniol is biosynthesized from isopentenyl pyrophosphate.



(26 marks)

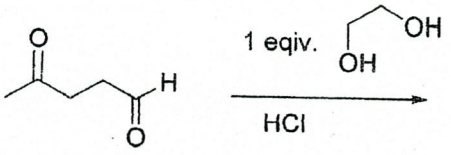
05. Answer **all** parts

(a) Carbocations are very useful reactive intermediates in organic synthesis. Substituted alkyl groups on carbon are able to stabilize the carbocation formed. Account for this statement.

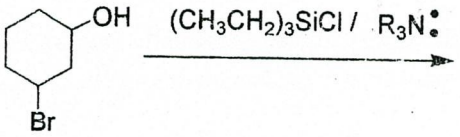
(10 marks)

(b) Write down the product(s) of the following reactions.

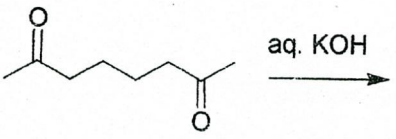
(i)



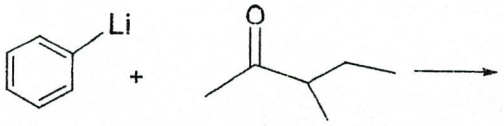
(ii)



(iii)



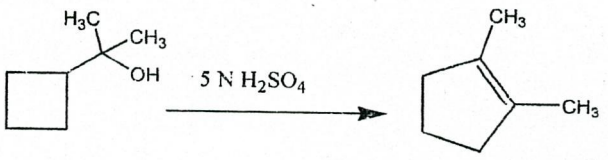
(iv)



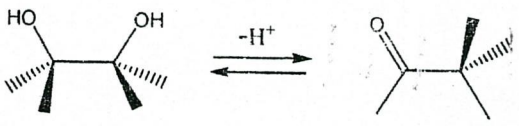
(32 marks)

(c). Give a plausible mechanism for each of the following transformations.

(i)

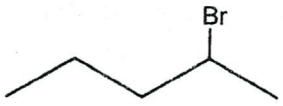


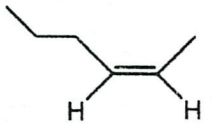
(ii)



(24 marks)

(d) (i) Give a retrosynthetic analysis for the following target molecules assuming that acetylene is commercially available.

(A) 

(B) 

[acetylene : ]

(ii) Giving necessary reaction conditions and relevant reagents show how you would carry out the synthesis of the target molecules using the proposed retrosynthetic analysis.

(34 marks)

Section C

06. Answer **all** parts

(a) Giving properties of solutions and colloids, distinguish between them.

(20 marks)

(b) Temperature dependence of adsorption equilibrium constant, K, can be given by the van't Hoff equation, $\left(\frac{\partial \ln K}{\partial T}\right) = \frac{\Delta_{ad}H^{\emptyset}}{RT^2}$. Data given below show the pressure of CO needed at different temperatures for the adsorption to be 15 mL when 2.0 g of polycrystalline Ni powder was used as the adsorbent. It was also found that the data fit the Langmuir adsorption isotherm.

T/K	273	279	286	293
p/ Torr	1.50	2.25	3.75	6.00

(i) Using the van't Hoff equation and other necessary equation(s), pertaining to the same adsorption process, derive an equation that can be used to determine the enthalpy of adsorption at constant surface coverage (isosteric heat of adsorption).

(20 marks)

(ii) Plot an appropriate graph using the given data and calculate the isosteric enthalpy of adsorption at this surface coverage.

(40 marks)

(iii) Giving reason(s), comment on the type of adsorption and the strength of the bond formed between CO and Ni.

(20 marks)

07. Answer **all** parts.

(a) In potentiometric method, dynamic equilibrium at electrodes is maintained without allowing any oxidation or reduction reaction and the electrode potential measured with respect to a reference electrode is related to the analyte concentration in the electrode.

(i) Compare the equilibrium reaction in redox electrode with the equilibrium reactions in the other two types of metallic electrodes. (20 marks)

(ii) Discuss the equilibrium maintained in the saturated calomel electrode. (10 marks)

(iii) What is the major factor that one must be concerned with when an indicator electrode and a reference electrode are connected? (10 marks)

(b) 25.00 mL of 0.50 M Ce^{4+} solution in an acidic medium was mixed with 25.00 mL of 0.75 M Fe^{2+} solution and a redox electrode was prepared by immersing a Pt metal in the mixture. Then the prepared redox electrode was connected with a saturated calomel electrode and the potential of the cell was measured to be 0.566 V. Calculate the standard electrode potential of the Fe^{3+}, Fe^{2+} redox system. Standard electrode potential of calomel electrode is 0.224 V at 25 °C.

(60 marks)

08. Answer **all** parts

(a) Coulometry is a very versatile dynamic method of electrochemical analysis.

(i) Name two different types of coulometric methods and give an advantage and a disadvantage of each method. (20 marks)

(ii) Nitrobenzene ($C_6H_5NO_2$) in 210 mg of an organic mixture was reduced to phenylhydroxylamine (C_6H_5NHOH) at a constant potential of -0.96 V (vs, SCE) applied to a mercury cathode. The sample was dissolved in 1000.0 mL of methanol and 40.0 mL of this solution was electrolyzed for 30 minutes. An electronic coulometer in series with the cell indicated that the amount of charge required for the reduction was 26.74 C.

Note: Relative atomic weights: C=12.00, H=1.00, N=14.00, O=16.00

(I) Calculate the percentage of $C_6H_5NO_2$ in the sample.

(25 marks)

(II) Suggest a possible method to minimize the time required for the above experiment.

(10 marks)

(b) Polarography is a widely used electroanalytical technique.

(i) State the factors that determine the shape of a voltammogram and draw the current vs potential curves for polarography and hydrodynamic voltammetry.

(20 marks)

(ii) A binary metal alloy solution containing Cu to Zn 1:4 was subjected to linear scan polarography. The resulting polarogram showed a limiting current of 20 μA corresponding to $E_{1/2}$ of 0.34 V. Another binary alloy solution containing the same metals showed a limiting current of 60 μA. The corresponding $E_{1/2}$ was the same as above. Determine the composition of this alloy.

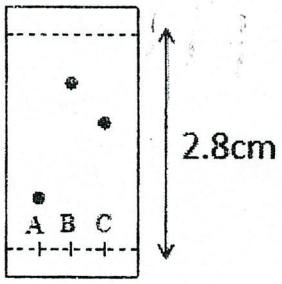
Note: $E^0_{Cu^{2+}/Cu} = 0.34\,V$

(25 marks)

09. Answer **either part X or part Y only.**

X: Answer **all** parts.

(a) Consider the following silica gel TLC plate of compounds A, B and C when hexane is the mobile phase. The distance from base line to the spots are 0.7 cm, 2.1 cm and 1.6 cm respectively.



(i) Write the definition for R_f and determine the R_f value of each spot.

(10 marks)

(ii) Deduce the relative polarities of compounds A, B and C.

(15 marks)

(iii) Giving reasons comment on the expected spot-pattern of the TLC plate if the eluting solvent is changed from hexane to acetone.

(10 marks)

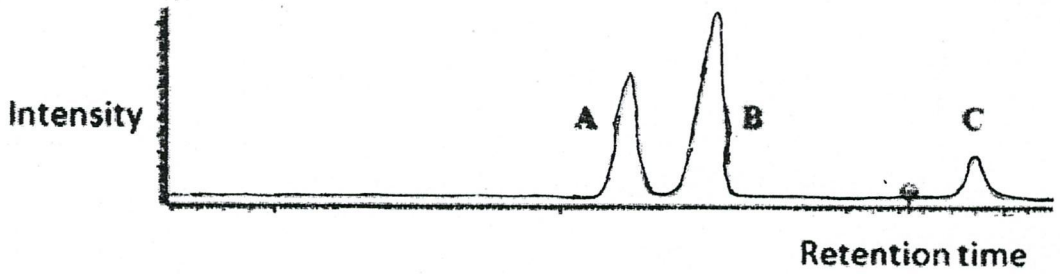
(iv) How would you explain the change in R_f values if eluted with hexane using an alumina TLC plate ?

(10 marks)

(v) Explain how you would determine purity of an aspirin sample using Thin Layer Chromatography.

(20 marks)

(b) A mixture of three liquid hydrocarbons was injected into a GC at 95 ^{0}C. The resulting chromatogram is shown below.



(i) Giving reasons interpret the relative volatilities of A,B and C.

(10 marks)

(ii) Suggest a method to improve the resolution between A and B while maintaining the same flow rate.

(10 marks)

(c) A weak acid HA has a pKa of 6.5. If you are utilizing ion exchange chromatography with an anion exchange resin, giving reasons suggest the lower limit of the pH value which facilitate this acid binding to the stationary phase.

(15 marks)

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

(a). List the fundamental ***solvent*** properties needed to be considered to carry out an extraction efficiently.

(15 marks)

(b). Write two other separation (excluding solvent extraction) methods and the theory behind each of the techniques.

(10 marks)

(c). Graphically illustrate how the amount of solute remaining in the aqueous phase falls off rapidly as the total fixed volume of the organic phase is subdivided into smaller fractions in multiple extractions.

(15 marks)

(d). Draw the structures of three organic chelating agents which can be used in selective separation of divalent metallic cations in a mixture.

(03 x 5 marks)

(e). Using a graphical illustration show "*different chemical equilibrium reactions*" taking place when an organic chelating agent is added into a two phase immiscible (say aqueous/organic) system, where a divalent metal ion (M^{2+}) is distributed.

(15 marks)

(f) 100.00 mL of an aqueous solution contained 10.00 mmol of benzenesulfonic acid. In an extraction process with 20.00 mL of dichloromethane, 4.0 mmol of benzenesulfonic acid remained in the aqueous layer.

(i) Calculate the partition coefficient.

(ii) Calculate how many moles of benzenesulfonic acid would remain in the aqueous layer if you used 10.00 mL of dichloromethane in each extraction and extracted twice.

(30 marks)

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රුහුණ විශ්වවිද්‍යාලය
විද්‍යාවේදී සාමාන්‍ය උපාධි (නෙවන ස්ථල) ප්‍රථම සමාසික පරීක්ෂණය
2015 ජූනි

විෂය : **රසායන විද්‍යාව** කාලය : පැය 03 යි

පාඨමාලා ඒකකය : **CHE3114**

A කොටසින් ප්‍රශ්න **<u>දෙකක් (02)</u>** ද, **B** කොටසින් ප්‍රශ්න **<u>එකක් (01)</u>** ක් ද, **C** කොටසින් ප්‍රශ්න **<u>තුනක් (03)</u>** ක් ද බැගින් තෝරාගෙන ප්‍රශ්න **<u>හයකට (06)</u> පමණක්** පිළිතුරු සපයන්න.

ආලෝකයේ ප්‍රවේගය, c	=	3×10^8 m s^{-1}
ඇවගාඩ්‍රෝ නියතය, N_A	=	6.022×10^{23} mol^{-1}
සර්වත්‍ර වායු නියතය, R	=	8.314 J K^{-1} mol^{-1}
	=	0.0821 dm^3 atm K^{-1} mol^{-1}
බෝල්ට්ස්මාන් නියතය, k	=	1.381×10^{-23} J K^{-1}
ෆැරඩේ නියතය, F	=	9.6485×10^4 C mol^{-1}
ඉලෙක්ට්‍රෝනයේ ආරෝපනය, e	=	1.602×10^{-19} C
ප්ලාන්ක් නියතය, h	=	6.626×10^{-34} J s
ප්‍රෝටෝනයේ ස්කන්ධය, m_p	=	1.673×10^{-27} kg
ඉලෙක්ට්‍රෝනයේ ස්කන්ධය, m_e	=	9.10×10^{-31} kg
1 amu	=	1.661×10^{-27} kg
1 eV	=	1.602×10^{-19} J

A- කොටස

01. **සියලුම** කොටස් වලට පිළිතුරු සපයන්න.

(අ) (i) ආන්තරික ලෝහ සංකීර්ණ කිහිපයක අර්ධ ජීව කාල පහත වගුවේ දී ඇත. සංකීර්ණ වල ඉලෙක්ට්‍රෝන පැතිරීම පදනම් කර ගනිමින් වගුවේ දී ඇති අර්ධ ජීව කාලයන්හි වෙනස පහදන්න.

අර්ධ ජීව කාලය මිනිත්තු 1 කට වඩා අඩු	අර්ධ ජීව කාලය දිනකට වඩා වැඩි
$[Cr(H_2O)_6]^{2+}$	$[Cr(CN)_6]^{3-}$
$[Co(H_2O)_6]^{2+}$	$[Co(NH_3)_6]^{3+}$

(ලකුණු 25 යි)