UNIVERSITY OF RUHUNA

BACHELOR OF SCIENCE GENERAL DEGREE LEVEL II (SEMESTER I) EXAMINATIONS JUNE/JULY 2015

SUBJECT: Chemistry

COURSE UNIT: **CHE 2114** TIME: **Two (03)** hours.

Answer **six (06)** questions only by selecting **two (02)** from each of the sections, **A**, **B**, and **C**.

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}
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's 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
Standard pressure	=	1.01325×10^{5} Pa

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 = 1.602×10^{-19} J

SECTION-A

01. Answer **all** parts.

(a) (i) Draw the structures of the following complexes and identify whether they are optically active or not.

(A) *cis-* and *trans-* isomers of $[Rh(Cl)_2(NH_3)_4]$

(B) *cis-* and *trans-* isomers of $[Co(en)_2Cl_2]$

Note: en - ethylenediamine

(20 marks)

(ii) State the primary and the secondary valencies of $[Co(NH_3)_6]Cl_3$

(05 marks)

(iii) State the coordination number of iron in $K_3[Fe(C_2O_4)_3]$

(05 marks)

(b) (i) Give an example of a hexadentate ligand and draw the structure of a complex formed by it.

(05 marks)

(ii) Giving reasons predict which one in each of the following pairs would be more stable.

(A) $[Cu(en)_2]^{2+}$ and $[Cu(NH_3)_4]^{2+}$

(B) $[Ni(dien)_2]^{2+}$ and $[Ni(en)_3]^{2+}$

Note: dien - diethylenetriamine

(35 marks)

(c) (i) Which one would show a greater ability to form a high spin octahedral complex out of $[FeF_6]^{3-}$ and $[Fe(CN)_6]^{3-}$?

(10 marks)

(ii) Aqueous solutions of the octahedral complex $[Co(NH_3)_6]^{2+}$ and the tetrahedral complex $[CoCl_4]^{2-}$ are coloured. One complex is yellow and the other is green. Giving reasons assign the relevant colour to each of these complexes.

(10 marks)

(iii) Would you expect $[Co(NH_3)_6]^{2+}$ to undergo Jahn Teller distortion ? Give reasons for your answer.

(10 marks)

02. Answer **all** parts.

(a) Briefly discuss the similarities and differences between the non-transition metals and transition metals.

(20 marks)

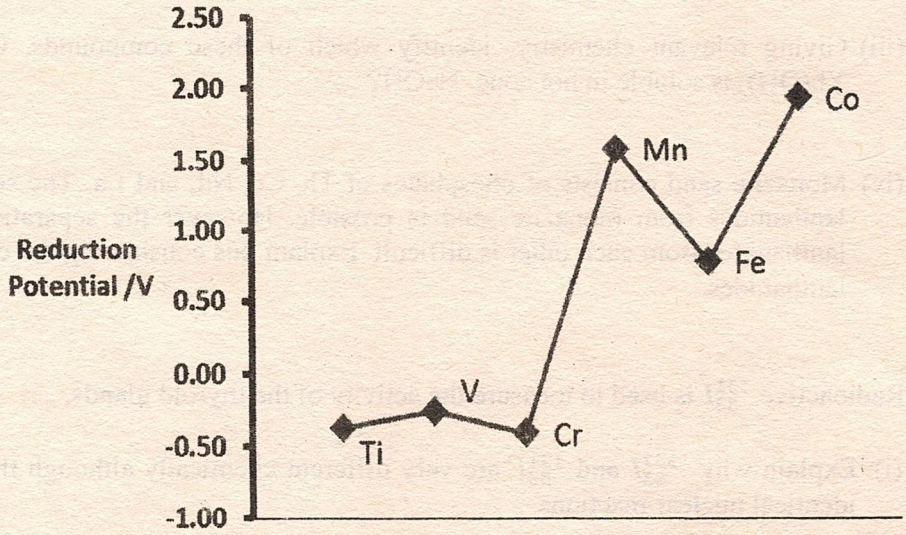
(b) Comment on the following statements.

(i) Elements which give the greatest number of oxidation states are found in or near the middle of the transition metal series.

(ii) Metals in the first transition element series have lower enthalpies of atomization than those of the corresponding metals in the second and third transition series.

(20 marks)

(c) Variation of the standard reduction potentials for M^{3+}/M^{2+} of the first transition metal series is shown in the following figure. Account for this variation.



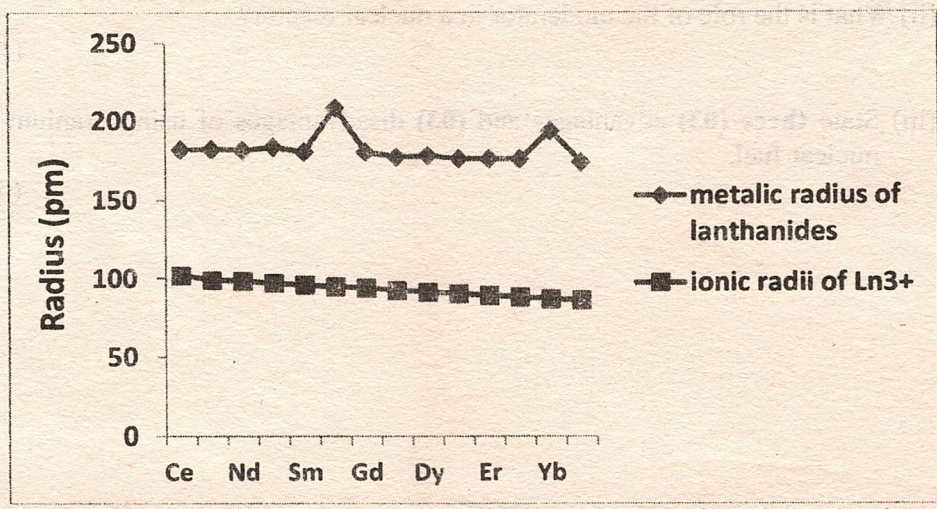
(35 marks)

(d) Calculate the spin only magnetic moment of $[Co(H_2O)_6]^{2+}$. The Experimental magnetic moment of $[Co(H_2O)_6]^{2+}$ is 5.11 BM. Account for the difference between the calculated and the experimental values.

(25 marks)

03. Answer **all** parts

(a) Variation of metallic radii and ionic radii of the +3 oxidation state of lanthanides are shown in the following diagram.



(i) Write the ground state electron configuration of each of the following ions.

(I) La^{3+} (II) Eu^{3+} (III) Gd^{3+} (IV) Lu^{3+}

(12 marks)

(ii) Of Eu^{3+} and Gd^{3+} which ion is more stable? Give reasons for your answer.

(08 marks)

(iii) Giving relevant chemistry, identify which of these compounds, $Ce(OH)_3$ or $Yb(OH)_3$ is soluble in hot conc. NaOH?

(20 marks)

(iv) Monazite sand consists of phosphates of Th, Ce, Nd, and La. The separation of lanthanides from monazite sand is possible. However the separation of these lanthanides from each other is difficult. Explain this considering the chemistry of lanthanides.

(10 marks)

(b) Radioactive $^{131}_{53}I$ is used to measure the activity of the thyroid glands.

(i). Explain why $^{131}_{53}I$ and $^{131}_{53}I^-$ are very different chemically although they undergo identical nuclear reactions.

(10 marks)

(ii).Iodine-131 has a half-iife of 8.07 days. Calculate the percentage of the original Iodine-131 nuclei still present after 7 days.

(15 marks)

(c) In some developed countries, electricity is produced from uranium-235 in nuclear power plants.

(i) Explain how heat is generated in nuclear power plants.

(10 marks)

(ii) What is the role of the moderator in a nuclear reactor?

(10 marks)

(iii) State **three (03)** advantages and **(03)** disadvantages of using uranium-235 as a nuclear fuel.

(05 marks)

SECTION-B

04. Answer **all** parts

(a) A student titrated 50.00 mL of a 0.0500 mol dm^{-3} Zn^{2+} ion solution buffered to pH 10 with 0.0500 mol dm^{-3} EDTA solution in the presence of EBT indicator.

(i) Write balanced chemical equation for the reaction between Zn^{2+} and EDTA.

(05 marks)

(ii) Calculate the Zn^{2+} ion concentration and pZn when 5.00 cm^3 EDTA is added. Write down any assumption you make in the calculation.

(20 marks)

(iii) Briefly explain how you would determine Cr^{3+} ion concentration in a given sample by using the above EDTA and Zn^{2+} solutions.

(15 marks)

(b)

(i) Defining all the terms, write down an expression for relative supersaturation of a substance.

(10 marks)

(ii) What is the relationship between supersaturation and particle size of a precipitate?

(08 marks)

(iii) Explain how you would form a crystalline precipitate by changing experimental variables.

(09 marks)

(c) Write down **three (03)** basic types of coprecipitation processes.

(08 marks)

(d) List different areas of chemistry where Atomic Absorption Spectroscopy (AAS) can be successfully used for analysis.

(05 marks)

(e) Draw rough schematic diagram of a double beam AAS and label the different components.

(10 marks)

(f) Write the **four (04)** major reactions occur inside the hollow-cathode lamp.

(05 marks)

(g) Write the **three (03)** major steps occur in turning ions in a liquid sample into an atomic gas.

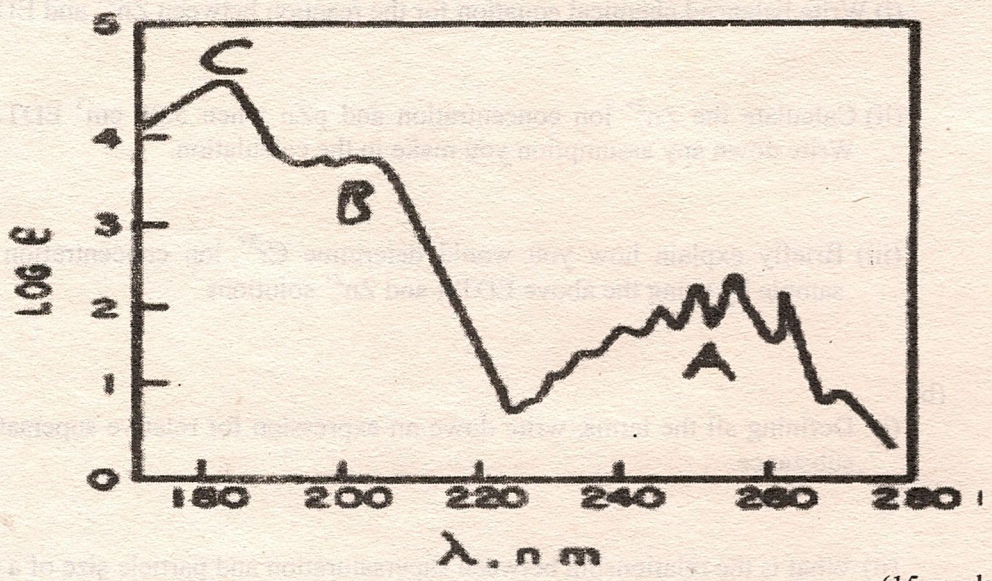
(05 marks)

05. Answer **all** parts.

(a) Common ways of expressing the amount of light absorbed by molecules/ions/atoms are absorbance and percent transmittance. Give the definitions of both.

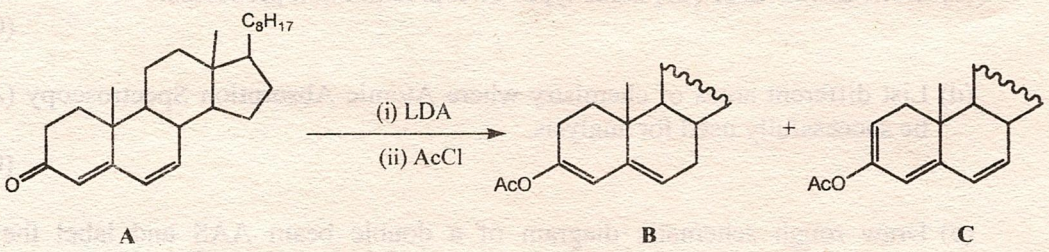
(10 marks)

(b) Estimate λ_{max} and log ε for the UV absorption bands A, B and C of the following spectrum.



(15 marks)

(c) Cholesta-4,6-diene (A) on treatment with lithium diisopropylamide and acetyl chloride gave one of the two possible enol acetate products (**B** and **C**) with λ_{max} of 302 nm, and ε_{max} 12,600 $dm^3\ mol^{-1}\ cm^{-1}$.



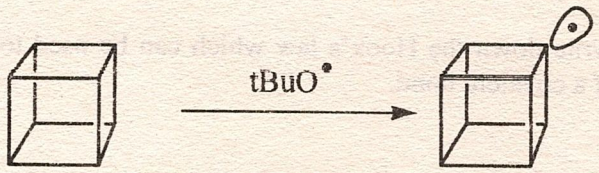
A **B** **C**

(i) Using Woodward-Fieser rules identify the enol acetate formed (**B** or **C**).

(ii) How could you exclude the observed absorption being due to the starting steroid **A**?

(30 marks)

(d) When the hydrocarbon cubane (C_8H_8) is treated with $tBuO^{\bullet}$ radicals, it undergoes a hydrogen abstraction reaction to give the cubyl radical, $C_8H_7^{\bullet}$, which can be observed by ESR spectroscopy.



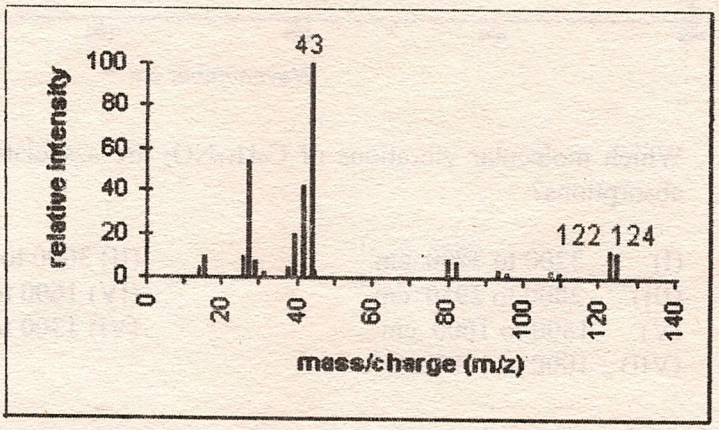
(i) How many different hydrogen environments are there in cubane, and how many in the cubyl radical? How many hydrogens are in each of these environments?

(05 marks)

(ii) What splitting pattern would you expect to see in the ESR spectrum of the cubyl radical? Considering both short and long range hypefine coupling, predict the number of lines expected in the ESR spectrum of it.

(15 marks)

(e) A compound gave the following mass spectrum in which the molecular ion appears as a pair of equal intensity peaks at m/z = 122 and 124. Also large fragment ions are seen at m/z = 43, 41 and 39 and small fragment ion peaks are seen at m/z = 107, 109, 79, 80, 81 and 82.



(i) Suggest a structure for this compound.

(15 marks)

(ii) Write equations for the formation of both molecular ions and the large fragment ions.

(10 marks)

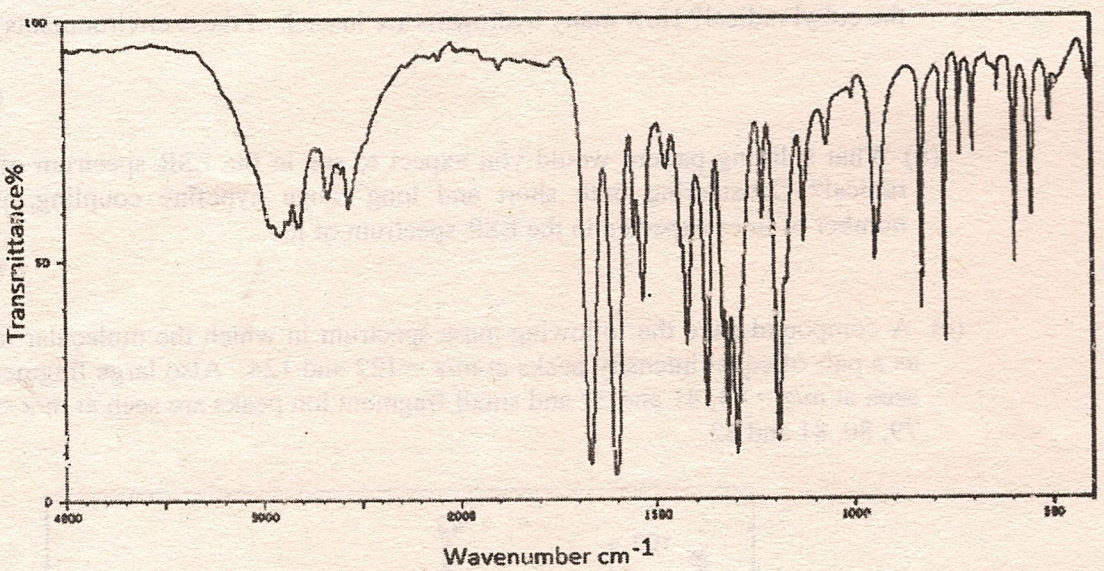
06. Answer **all** parts.

(a) (i) List the factors that determine the wavenumber of an infrared absorption of a bond.

(ii) Defining each term write down the Hook's law which can be used to describe a vibrating frequency of a covalent bond.

(15 marks)

(b) Shown below is the infrared spectrum for a molecule with the molecular formula of $C_9H_{11}NO_2$.



(i) Which molecular vibrations of $C_9H_{11}NO_2$ are associated with the following absorptions?

(I) 3200 to 3700 cm^{-1}
(II) 3000 to 3200 cm^{-1}
(III) 2800 to 2950 cm^{-1}
(IV) 1690 to 1800 cm^{-1}
(V) 1590 to 1600 cm^{-1}
(VI) 1300 to 1500 cm^{-1}
(VII) 1000 to 1300 cm^{-1}

(20 marks)

(ii) Deduce the molecular structure that is most consistent with the infrared spectrum above. (Hint: its ^{1}NMR shows a pair of doublets near 7 ppm)

(15 marks)

(c) (i) Describe briefly the following terms used in NMR spectroscopy.

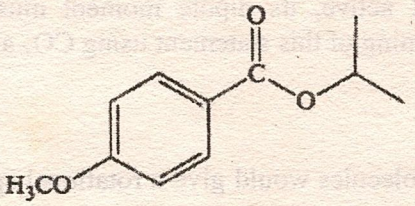
(I) spin spin coupling
(II) signal intensity

(10 marks)

(iii) In which situations would you obtain "a triplet", "a doublet of doublet" in NMR spectroscopy? Explain your answer using suitable stick diagrams.

(20 marks)

(iii) Give a sketch of the ^1H NMR spectrum that you would expect for the following molecule.



(20 marks)

SECTION-C

07. Answer **all** parts.

(a) Discuss the ***symmetry elements***, giving their correct symbols, that a molecule may have and the ***symmetry operations*** associated with these symmetry elements, using appropriate diagrams wherever necessary.

(30 marks)

(b) Consider the **eclipsed** conformation of ethane (C_2H_6):

[Use appropriate diagrams wherever necessary.]

(i) Explain what you understand by the principal axis of a molecule.
(ii) Identify the principal axis for this conformation.
(iii) Show that this molecule possesses a σ_h and a S_3.
(iv) Show that this molecule belongs to D_{3h} point group.

(35 marks)

(c) Consider the **staggered** conformation of ethane:

(i) Using an appropriate diagram(s), show that this conformation possesses a S_6, centre of symmetry, and three (03) σ_d's.

(ii) Show that this molecule belongs to D_{3d} point group.

(35 marks)

8. Answer **both** parts.

(a) (i) Comment on the phrase "*for a molecule to give a **pure rotational spectrum**, it must be **polar***" paying special attention to bold wordings.

(10 marks)

(ii) "For a molecule to be IR active, its dipole moment must change during a vibration". Explain the meaning of this statement using CO_2 as an example.

(15 marks)

(iii) Which of the following molecules would give a rotational spectrum? Give your reasons.

NO, N_2, OCS, $CH_2{=}CH_2$, CH_4,

(10 arks)

(b) The rotational energy levels of a heteronuclear diatomic molecule could be approximated by the rigid rotor model and the rotational energy levels are given by

$$\Sigma_J = \frac{h}{8\pi^2 Ic} J(J+1) = BJ(J+1) \text{ in cm}^{-1}$$

(i) Identify all the terms in the above expression.

If $I = \mu r_e^2$, what is μ and r_e?

(15 marks)

(ii) State the main assumptions of the rigid rotor model.

(10 marks)

(iii) State the specific selection rule for transitions between rotational energy levels of this molecule. Hence show that the rotational spectrum of this molecule consists of a set of absorption lines with a spacing of 2B.

(20 marks)

(iv) The rotational absorption spectrum of nitrogen oxide (NO) showed the first four lines at following wave numbers:

3.405 cm^{-1} 6.810 cm^{-1} 10.215 cm^{-1} 13.620 cm^{-1}

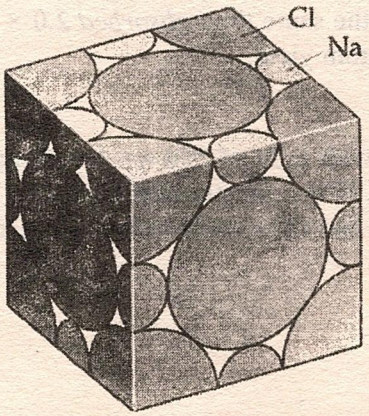
Calculate the bond length.

[RAM: N = 14.007; O = 15.999]

(20 marks)

09. Answer **all** parts.

(a) The diagram below shows a space-filling diagram of a NaCl **cubic unit cell** cut to show only the part of each atom that is inside the unit cell boundaries.



(i) Calculate the net number of Na^+ and Cl^- ions in the above unit cell.

(10 marks)

(ii) Above NaCl crystal gives reflection with radiation of wavelength 137 pm at the glancing angles 10.7°, 17.7°, and 21.9°. The reflection at 17.7° is known to be due to (111) planes.

(I) Calculate the length of the side of the unit cell

(10 marks)

(II) Calculate the $(h^2 + k^2 + l^2)$ values for glancing angles 10.7° and 21.9°.

(20 marks)

(III) What are the possible values for h, k, and l for glancing angles 10.7° and 21.9°.

(10 marks)

(b) State first and second laws of photochemistry.

(04 x 2 marks)

(c) Draw a Jablonski diagram and clearly label the following,

(i) The ground electronic state, S_0
(ii) The first singlet excited state, S_1
(iii) The triplet excited states, T_1
(iv) Internal conversion
(v) Fluorescence
(vi) Phosphorescence

(03 x 6 marks)

(d)

(i) Define the term "quantum yield"

(04 marks)

(ii) When a substance *A* was exposed to light, 0.002 mol of it reacted in 20 minutes and 4 seconds. In the same time *absorbed* 2.0×10^6 photons of light per second. Calculate the quantum yield.

(10 marks)

(iii) When irradiated with light of 500 nm wavelength, 1×10^{-4} mol of a substance was decomposed. If the quantum efficiency is 10.00%, calculate the number of photons that have been absorbed during this reaction?

(10 marks)

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