UNIVERSITY OF RUHUNA
BACHELOR OF SCIENCE GENERAL DEGREE–LEVEL I (SEMESTER I) EXAMINATIONS – JULY 2016

SUBJECT: CHEMISTRY **TIME**: Three **(03)** hours
COURSE UNIT: CHE 1114

Answer **six (06)** questions only by selecting **two (02)** from each sections **A**, **B**, and **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)	$= 8.314$ 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}
Planck'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

Section – A

01. Answer **all** parts.

(a) (i) State Pauli Exclusion Principle. (05 marks)

(ii) Of the following five sets of quantum numbers, I, II, III, IV and V, which ones are incorrect? Give reasons for your answer.

	n	ℓ	m_ℓ	m_s
I	3	2	1	+½
II	3	4	2	+½
III	2	1	2	-½
IV	2	1	0	+½
V	2	1	1	+1

(30 marks)

(b) (i) Give reasons for the following observations.

(I) The boiling point of water (100 °C) is much higher than that of acetone (56 °C).
(II) NaCl is an ionic compound.
(III) The melting point of $SnCl_2$ (227 °C) is much higher than that of and $SnCl_4$ (-34 °C).

(15 marks)

(ii) (I) Give an example for a liquid with molecules having the following features.

- Tetrahedral structure
- Four atoms attached to the central atom are same
- Four bonds are of the same type
- Bonds are polar and symmetrically distributed around the central atom

(05 marks)

(II) Predict whether the above molecule is polar or nonpolar.

(05 marks)

(III) Give two properties of the above liquid.

(05 marks)

(c) (i) Using the Slater's rules, calculate the effective nuclear charge felt by a 2p electron in the potassium atom.

(25 marks)

(ii) The internuclear distance in the I_2 molecule is 2.66 Å. The distance between two iodine molecules in solid iodine is 4.30 Å. Determine the covalent radius of iodine.

(05 marks)

(iii) The standard reduction potentials of **"A"** and **"B"** are -3.05 eV and -2.92 eV respectively. Of these which would be the stronger reducing agent?

(05 marks)

02. Answer **all** parts.

(a) State the Heisenberg's Uncertainty Principle?

(10 marks)

(b) Rydberg Equation is given as

$$E = hcR_H Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right).$$

Here h = Planks' Constant, c = velocity of light, R_H = Rydberg constant

(i) Derive the Rydberg equation in terms of wavelengths using the above equation

(05 marks)

(ii) Considering the first lines of the Lyman, Bahmer, and Paschen series of the hydrogen spectrum, answer the following questions by using the equation derived in (b) (i) and the table given below

(I) n_i and n_f values

(II) the wavelength of light (in nm) generated by each electronic transition

(III) the approximate colour/region of light produced by the emission

Wave length/nm	Colour/Location	Wave length/nm	Colour/Location
400	UV	570-585	Yellow
400-420	Violet	585-620	Orange
420-440	Indigo	620-780	Red
440-490	Blue	>780	IR
490-570	Green		

$$R_H = 1.097 \times 10^{-2}\ nm^{-1}$$

(35 marks)

(c) Consider the application of the Valence Bond Theory to hydrogen cyanide (HCN) molecule. Draw the **hybrid (or atomic) orbitals** involved in the formation of each bond. State the type of **bond** formed and name each hybrid (or atomic) orbital and each bond.

(30 marks)

(d) The hydrogen molecular ion, H_2^+, can be detected spectroscopically. Write the electronic configuration of the H_2^+ ion in molecular orbital terms. What is the bond order of the H_2^+ ion? Compare the bond energies in H_2^+ and H_2.

(20 marks)

03. Answer **all** parts.

(a) (i) State the four types of fundamental forces in the universe.

(10 marks)

(ii) The nucleus of helium atom contains two protons and two neutrons.

(A) State the fundamental force(s) involved in each of the following processes.

(I) repulsion of the above two protons from each other.

(II) holding of these two protons within the helium nucleus.

(III) holding of these two protons and two neutrons together within the helium nucleus.

(IV) holding of quarks together in a proton.

(24 marks)

(B) How many up quarks are present in the nucleus of the helium atom?

(06 marks)

(b) State two differences between hadrons and leptons.

(10 marks)

(c) (i) Briefly explain the following pertaining to nuclear stability.

(I) Odd – even rule

(II) Nuclear binding energy

(20 marks)

(ii) Giving reasons arrange the following nuclei in increasing order of stability.

$^{57}_{26}Fe$, $^{56}_{26}Fe$, $^{14}_{7}N$, $^{19}_{9}F$

(10 marks)

(iii) The observed mass of $^{56}_{26}Fe$ is 55.9375 amu. Calculate the nuclear binding energy in jouls per nucleon.

Note : Mass of a proton and a neutron are 1.007277 amu and 1.008665 amu, respectively. Assume that the mass of electrons can be neglected.

(20 marks)

Section - B

04. Answer **all** parts.

(a) Some characteristics of carbon are given below. Give three examples with structures for each of these characteristics.

(i) ability of forming chain structures
(ii) ability of forming multiple bonds
(iii) ability of forming ring structures

(15 marks)

(b) Briefly explain the importance of orbital hybridization in valence bond theory of bonding using carbon as an example

(10 marks)

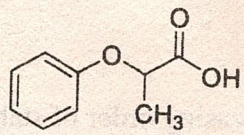
(c) (i) Draw the Lewis structure of ion, $(HCONH)^-$.
(ii) Show the resonance structures of the above ion.
(iii) Out of above structures drawn in (ii), which structure is the most stable? Explain your answer.

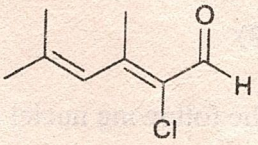
(24 marks)

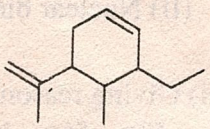
(d) Giving illustrations, explain briefly following
(i) Hyperconjugation
(ii) Inductive effect
(iii) Mesomeric effect

(21 marks)

(e) Name the following compounds according to the IUPAC nomenclature.

(i) 

(ii) 

(iii) 

(15 marks)

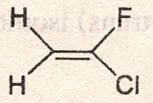
(f) Draw the structures of the following compounds.

(i) 2-ethyl-3-methylpent-2-enoic acid
(ii) 2-chloroethyl but-2-enoate
(iii) bicyclo[4.3.0]nonan-2-one

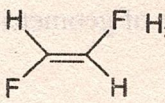
(15 marks)

05. Answer **all** parts.

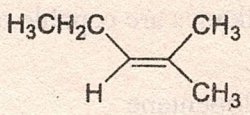
(a) Giving reasons select the following compounds which show geometrical isomerism. Specify (if any) the geometry of the double bonds using E/Z notation.



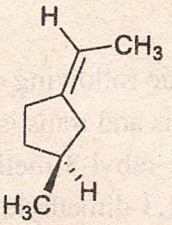
A



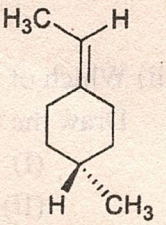
B



C



D



E

(20 marks)

(b) 2,4-heptadiene is a useful diene in organic synthesis.

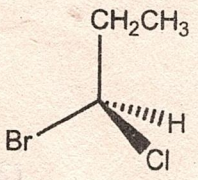
(i) Draw the structure of 2,4-heptadiene.

(ii) How many geometrical isomers are possible for 2,4-heptadiene?

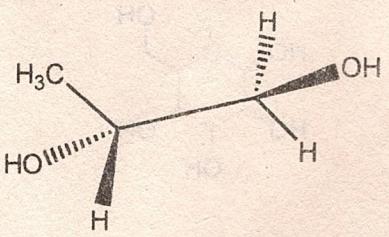
(iii) Draw all possible geometrical isomers and give their IUPAC names including E/Z designations.

(30 marks)

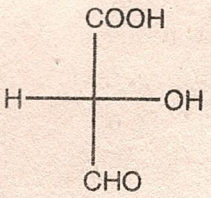
(c) Assign R/S configurations to the following compounds.



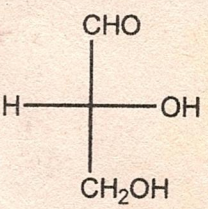
I



II



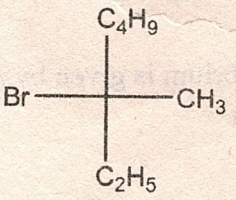
III



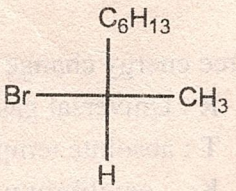
IV

(20 marks)

(d) Two isomers of $C_8H_{17}Br$ are given below.



Isomer I



Isomer II

(i) What is the stereochemical relationship between two isomers?

(ii) Specify the configuration of them as **R** or **S**.

(iii) When these isomers are subjected to substitution reaction with NaOH, **Isomer I** produced racemic mixture and **Isomer II** gave a product with inverted configuration. Draw the structures of the products obtained in each case.

(30 marks)

06. Answer **all** parts.

(a) (i) Draw the 'Eclipsed' and 'staggered' conformation of propane using Newman projection formula. Mark the dihedral angle in each projection.

(10 marks)

(ii) Which of the following cycloalkanes are capable of geometric (cis-trans) isomerism? Draw the cis and trans isomers.

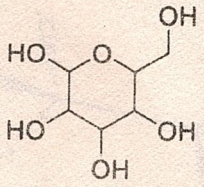
(I) 1-ethyl-3-methylcyclopentane
(II) 1,3-dimethylcyclohexane
(III) 3-ethyl-1,1-dimethylcyclohexane

(15 marks)

(b) (i) Boat conformation of cyclohexane does not have any angle strain. Yet it is unstable. Using suitable structures explain this statement.

(20 marks)

(ii) Below given is the structure of glucose. Giving possible reasons draw the most stable conformation of glucose.



(20 marks)

(c) The axial and equatorial conformers of methylcyclohexane are in equilibrium at room temperature (25 ^{0}C). The 1,3-diaxial interaction between the methyl group and a hydrogen is about 3.8 kJ mol^{-1}. Calculate the axial and equatorial conformers' percentage. Clearly indicate any assumptions you made during the calculations.

Hint: The Gibbs free energy change at equilibrium is given by $\Delta G^{\circ} = -RT \ln K_{eq}$;
where R : Universal gas constant
T : absolute temperature
K_{eq} : equilibrium constant

(35 marks)

Section - C

07. Answer **all** parts.

(a) (i) The force is a derived SI unit which is given in newton and defined as kg m s^{-2}.
What are the derived SI units for energy and pressure?

(10 marks)

(ii) One of the earliest equations of state of a real gas was proposed by Radlich and Kwong (1947) and is given below:

$$p = \frac{nRT}{(V - nb)} - \frac{n^2 a}{T^{1/2} V(V + nb)}$$

What are the SI units of constants **a** and **b**?

(10 marks)

(b) "Generally, a real gas behaves more like an ideal gas at high temperature and low pressure as the potential energy due to intermolecular forces becomes less significant compared with the particles' kinetic energy."
Briefly discuss this sentence paying special attention to underlined phrases.

(30 marks)

(c) (i) Briefly explain what is meant by the critical constants of a substance.
(ii) The first and second derivatives of the van der Waals equation $\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$ are given below.

$$\frac{dp}{dV_m} = -\frac{RT}{(V_m - b)^2} + \frac{2a}{V_m^3}$$

$$\frac{d^2p}{dV_m^2} = \frac{2RT}{(V_m - b)^3} - \frac{6a}{V_m^4}$$

Obtain the critical constants for a van der Waals gas and show that the critical compressibility factor $Z_c = 3/8$.

(iii) The van der Waals coefficient **a** of a particular gas, which obeys the van der Waals equation, is 0.50 m^6 Pa mol^{-2}. Its molar volume was determined to de 5.00 x 10^{-4} m^3 mol^{-1} at 273 K and 3.0 MPa. Calculate the other van deer Waals coefficient **b** and the critical constants of this gas.

(50 marks)

08. Answer **all** parts.

6.3×10^{-3} mol of acetic acid was dissolved in 100 g of cyclohexane after melting to its melting point at 6.4 ^{0}C. This acetic acid lowered the freezing point of cyclohexane by 0.423 K. Cryoscopic constant of cyclohexane is 20.2 K kg mol^{-1}. When the same number of moles of acetic acid was dissolved in 100 g of water, melting point of water was lowered by 0.121 K and its molar conductivity was measured to be 2.461 Ω^{-1} cm^2 mol^{-1}. Cryoscopic constant of water is 1.86 K kg mol^{-1}

(i) Express the relationship between freezing point depression and molality

(10 marks)

(ii) Showing all the necessary calculations, explain the behaviour of acetic acid in cyclohexane solution.

(45 marks)

(iii) Calculate the degree of ionization in water and hence the limiting molar conductivity of acetic acid solution.

(45 marks)

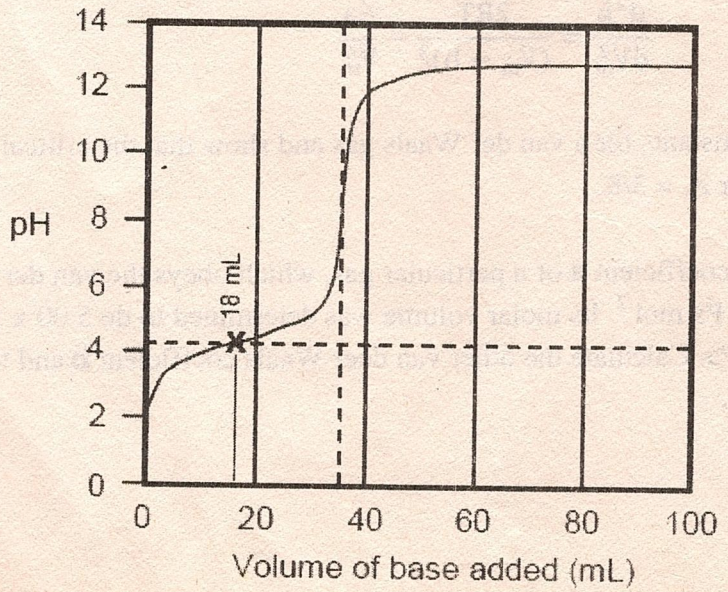
09. Answer **all** parts.

(a) Draw separate titration curves for the titrations between

(i) a weak acid and a strong base
(ii) a weak base and a strong acid
(iii) label the following points on each curve:
  (I) the equivalence point (predict if pH = 7, pH > 7 or pH <7)
  (II) the buffer region
  (III) where pH = pK_a

(30 marks)

(b) A 0.4460-g sample of an unknown monoprotic acid is titrated with 0.1050 mol dm^{-3} KOH. The resulting titration curve is shown below. Determine the molar mass and pK_a of the acid.



(20 marks)

(c) (i) What is the difference between accuracy and precision?

(ii) What are the types of errors (and their characteristics) in a chemical analysis?

(iii) What are the types of errors that affect the accuracy and precision?

(iv) What are the statistical terms used to describe the accuracy and precision?

(08 x 4 marks)

(d) (i) State whether the following volume measurements can be regarded as having a determinate or an indeterminate error:
16.75, 16.47, 16.66, 16.59, 16.77, and 16.55 mL, if the accepted value is 16.97 mL. Explain your answer.

(08 marks)

(e) Giving reasons identify the errors associated with the following as systematic or random or both.

(i) The use of methyl orange for a weak acid- strong base titration.

(ii) When two different solutions are transferred using the same pipette and pipette is not rinsed with distilled water in between.

(iii) Fluctuations of current in a properly calibrated balance.

(10 marks)

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

IUPAC Periodic Table of the Elements

1																	18
1 H hydrogen [1.007, 1.009]	2											13	14	15	16	17	2 He helium 4.003
3 Li lithium [6.938, 6.997]	4 Be beryllium 9.012											5 B boron [10.80, 10.83]	6 C carbon [12.00, 12.02]	7 N nitrogen [14.00, 14.01]	8 O oxygen [15.99, 16.00]	9 F fluorine 19.00	10 Ne neon 20.18
11 Na sodium 22.99	12 Mg magnesium [24.30, 24.31]	3	4	5	6	7	8	9	10	11	12	13 Al aluminium 26.98	14 Si silicon [28.08, 28.09]	15 P phosphorus 30.97	16 S sulfur [32.05, 32.08]	17 Cl chlorine [35.44, 35.46]	18 Ar argon 39.95
19 K potassium 39.10	20 Ca calcium 40.08	21 Sc scandium 44.96	22 Ti titanium 47.87	23 V vanadium 50.94	24 Cr chromium 52.00	25 Mn manganese 54.94	26 Fe iron 55.85	27 Co cobalt 58.93	28 Ni nickel 58.69	29 Cu copper 63.55	30 Zn zinc 65.38(2)	31 Ga gallium 69.72	32 Ge germanium 72.63	33 As arsenic 74.92	34 Se selenium 78.97	35 Br bromine [79.90, 79.91]	36 Kr krypton 83.80
37 Rb rubidium 85.47	38 Sr strontium 87.62	39 Y yttrium 88.91	40 Zr zirconium 91.22	41 Nb niobium 92.91	42 Mo molybdenum 95.95	43 Tc technetium	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs caesium 132.9	56 Ba barium 137.3	57-71 lanthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium [204.3, 204.4]	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium	85 At astatine	86 Rn radon
87 Fr francium	88 Ra radium	89-103 actinoids	104 Rf rutherfordium	105 Db dubnium	106 Sg seaborgium	107 Bh bohrium	108 Hs hassium	109 Mt meitnerium	110 Ds darmstadtium	111 Rg roentgenium	112 Cn copernicium	113 Uut ununtrium	114 Fl flerovium	115 Uup ununpentium	116 Lv livermorium	117 Uus ununseptium	118 Uuo ununoctium

Key:

atomic number
Symbol
name
standard atomic weight

57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.0	71 Lu lutetium 175.0
89 Ac actinium	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium	94 Pu plutonium	95 Am americium	96 Cm curium	97 Bk berkelium	98 Cf californium	99 Es einsteinium	100 Fm fermium	101 Md mendelevium	102 No nobelium	103 Lr lawrencium